

# 12<sup>th</sup> Eastern European Young Water Professionals Conference



Book of Abstracts

## WATER RESEARCH AND INNOVATIONS IN DIGITAL ERA

31 March -2 April 2021, Riga, Latvia

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**12<sup>th</sup> Eastern European Young  
Water Professionals  
Conference**



**Water Research and Innovations in Digital Era**

31 March to 2 April 2021, Riga, Latvia

**BOOK of ABSTRACTS**



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**Editors:**

Maryna Feierabend

Talis Juhna

Sandis Dejus

**Typesetting:**

Liudmyla Odud

Brigita Dalecka

Ronald Zakhar

Zehra Rana Ikizoglu

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## Mathematical Model Used for Microaeration in Sequencing Batch Reactor for H<sub>2</sub>S Removal

M. Andreides\*, L. Pokorná-Krayzelová, E. I. P. Volcke\*\*, and J. Bartáček\*

\* Department of Water Technology and Environmental Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic  
(E-mail: [marketa.andreides@vscht.cz](mailto:marketa.andreides@vscht.cz))

\*\* Department of Biosystems Engineering, Ghent University, Coupure Links 653, 9000 Gent, Belgium

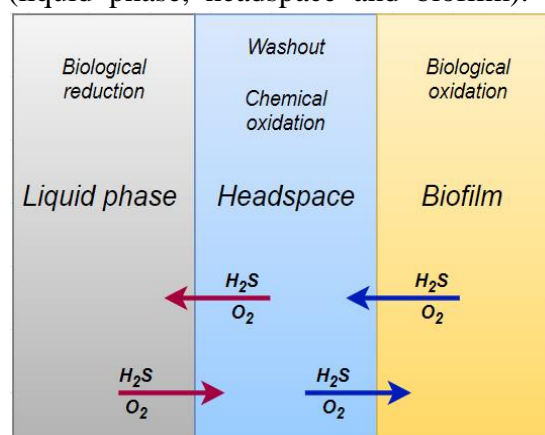
### INTRODUCTION

Microaeration is a simple, non-invasive biological method for the removal of hydrogen sulfide from biogas directly in the fermenter. Nowadays, the control of air/oxygen dosing to the reactor is based on the concentration of hydrogen sulfide in the fermenter. However, during the intermittent mixing of the fermenter, the concentration of hydrogen sulfide in the biogas fluctuates resulting in onerous control. For better understanding of hydrogen sulfide behavior in this type of fermenters, two sequencing batch reactors (control anaerobic, tested microaerobic) were built and operated. The mathematical model describing the hydrogen sulfide concentration in sequencing batch reactor was introduced for the first time. Model was validated with the experimental data obtained from the microaerobic reactor. Based on sensitivity analysis of the model, the mass transfer and the biofilm area were targeted as the most important parameters and for those parameters, scenario analyses was done to see the impact on H<sub>2</sub>S concentration in headspace.

### MATERIALS AND METHODS

To study behavior of hydrogen sulfide in microaerobic fermenter, two reactors were built (tested microaerobic reactor – MR, control anaerobic reactor – CR). The volume of the reactors was 20 L (13 L and 7 L of liquid phase and headspace resp.). Directly into the headspace of MR, 20 mL h<sup>-1</sup> of air was dosed. Both reactors were operated semi-continuously (dosing of substrate/supernatant draining, reaction, sedimentation). The reactors were fed with the synthetic wastewater (chees whey solution 20 g L<sup>-1</sup>) enriched by K<sub>2</sub>SO<sub>4</sub> (0.9 g L<sup>-1</sup>) to increase the amount of H<sub>2</sub>S in biogas.

Mathematical model included three compartments (liquid phase, headspace and biofilm). This Mathematical model was based on well accepted ADM1-S/O (Pokorna-Krayzelova *et al.*, 2017) and extended by chemical oxidation of hydrogen sulfide (Pokorna-Krayzelova *et al.*, 2018) and washout of H<sub>2</sub>S from the reactor with produced biogas. The thermodynamic equilibrium in the liquid was modelled according to Pitter (1999). The equilibrium between adjacent compartments was describe by Henry's law and by mass transfer coefficient ( $k_L a$ ), which was adjusted to fit the experimental data. The gas-biofilm mass transfer was described as a product of biofilm area and mass transfer coefficient  $k_i$  (adjusted). For the modelling, the AQUASIM software (Swiss Federal Institute for Environmental Science and Technology, Dübendorf, Switzerland) was used.



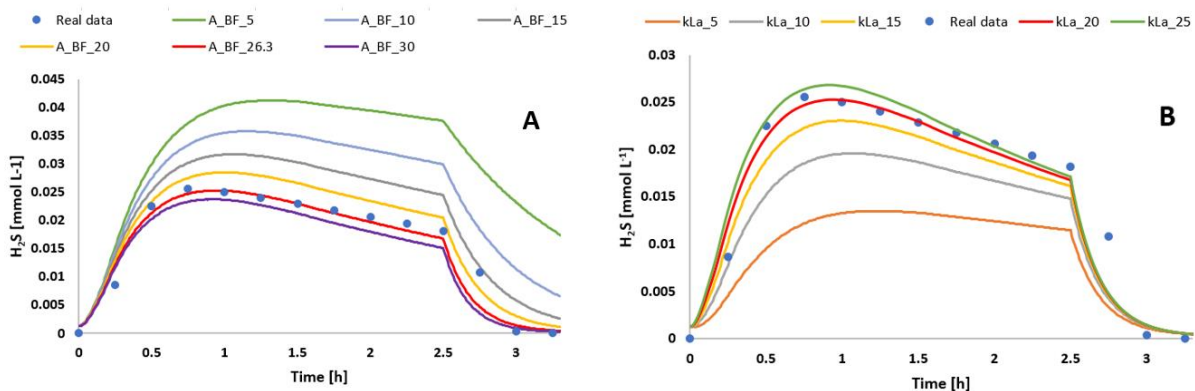
**Figure 1.** Modeled compartments and connected reactions.

## RESULTS AND DISCUSSION

The mathematical model of microaeration in SBR was successfully created and calibrated with experimental data. Based on sensitivity analysis, the biofilm area played an important role in  $H_2S$  removal as well as the gas to liquid mass transfer. Those two parameters can be easily changed in the process (e.g. mixing intensity or providing of support material for biofilm growth) and, therefore, scenario analyses was done for these two parameters.

It is obvious that higher biofilm area facilitates more efficient  $H_2S$  removal. With biofilm area as low as  $5 \text{ dm}^2$ , almost no decrease of  $H_2S$  was observed in the headspace during the reaction period.

Generally, the higher  $k_{La}$ , the higher  $H_2S$  concentration in the headspace and hence higher exposure of SOB to  $H_2S$ . This phenomenon can be controversial, since the higher  $H_2S$  concentration in liquid, the higher risk of toxic shock for methanogens and therefore, the  $k_{La}$  have to be choose wisely. The dependency between the highest  $H_2S$  concentration in the headspace and  $k_{La}$  has a logarithmic trend and its change is especially significant at low  $k_{La}$  values.



**Figure 2.** The influence of biofilm area (A) and mass transfer coefficient (B) on  $H_2S$  concentration in the headspace. The experimental data were measured on day 143.

## CONCLUSION

This study assessed key parameters influencing microaeration in reactors with intermittent stirring. We focused on  $k_{La}$  and biofilm area, since these two parameters can be changed by operators, and, therefore, the microaeration can be enhanced by the change of the stirring intensity and extension of the biofilm area.

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# Use of Cloud-Computing and Predictive Wastewater Analysis

M. Andreides\*, P. Dolejš\*, and J. Bartáček\*

\* Department of Water Technology and Environmental Engineering, UCT Prague, Technická 5, Prague 6 166 28, Czech Republic (E-mail: [marketa.andreides@vscht.cz](mailto:marketa.andreides@vscht.cz))

## INTRODUCTION

Nowadays, more and more emphasis is placed on the protection of watercourses, especially by taking into account the extremely dry years Europe was struggling with in recent years. At the same time, new analytical methods point to hazardous substances – micropollutants, occurring in the effluent of wastewater treatment plants (WWTP). It is therefore clear that the pressure on WWTP operators to comply with strict emission limits is constantly increasing. This entails a hunger for new reliable technologies and innovative systems that can be used to maintain a stable outflow of WWTPs. The effluent from WWTP contains nitrogen and phosphorous compounds which emission must be controlled especially while draining into the river to avoid eutrophication of surface water with fatal consequences for water ecosystems. Effluent from WWTP can be unstable due to the fluctuating inflow which is caused mostly by rainfall or the variable amount of water production (Bartosz *et al.*, 2017). This partially stochastic character of inflow can make the treatment management difficult and not easy to control. When the inflow is predicted, WWTP operation could be adapted to the upcoming situation (i.e. dose adjustment of chemicals, aeration intensity or effective use of rainwater reservoirs). The advantage of WWTP is relatively regular flow change during rainless period (depending on season, day in week and hour in day) and predictable changes in rain flow according to the amount of precipitation fell on the area.

The key role in mathematical modelling and connected prediction is sufficient amount of data used for model calibration. In past, it was difficult to create a reliable predictive system, due to the lack of data. With the fourth industry revolution (Industry 4.0), the digitalization and data collection became to be a new hot topic, because of the knowledge which can be mined from the datasets. On the WWTP, new online sensors were presented and, therefore, preparation of the big datasets for models calibration is easier and the accuracy of the models is higher.

## MATERIALS AND METHODS

In this research, we use the new online sensors (S::CAN) for chemical oxygen demand measurement (COD) installed on the Prague WWTP (1 mil. PE) and the historical data about rain events in Prague. Created predictive system, should be later used even on smaller WWTP, where the investments to expensive online sensors are still off topic.

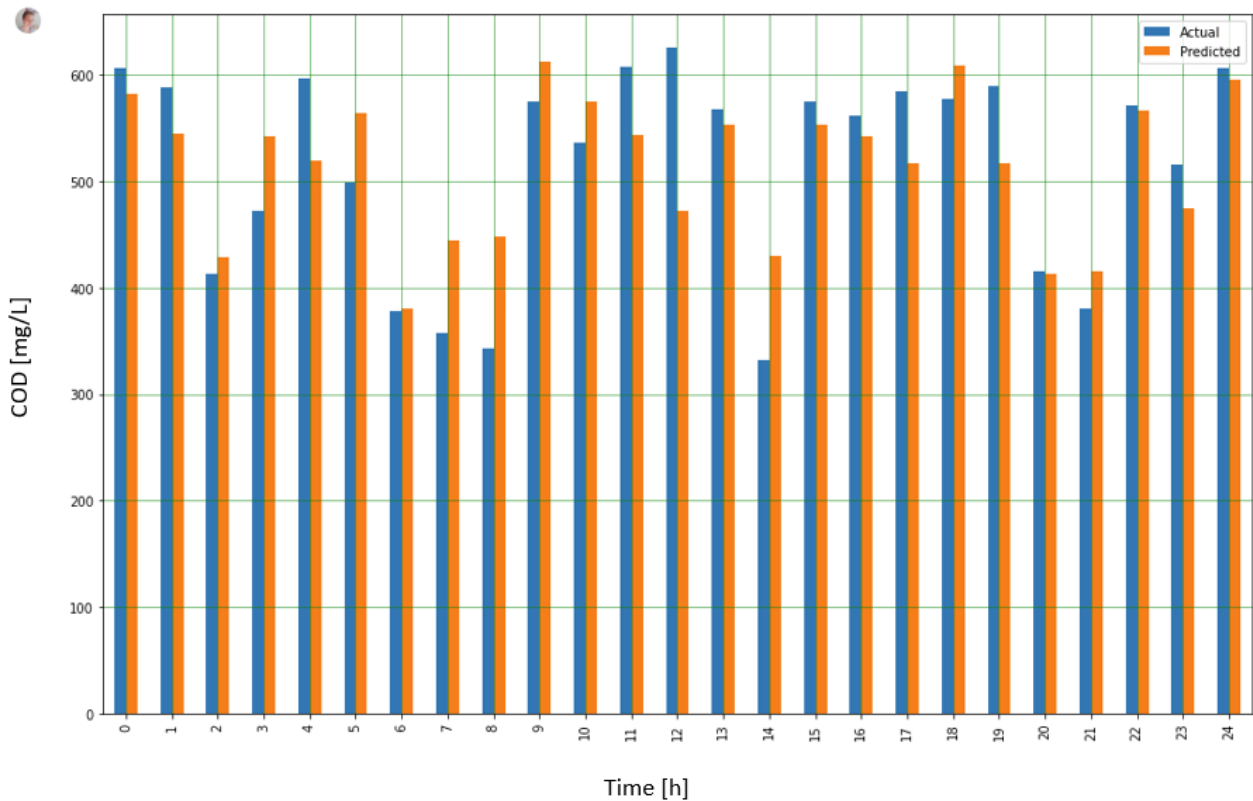
For the data collection Mindsphere by Siemens will be used. MindSphere is an open operating system and cloud solution for the Internet of Things, used to connect various devices to the cloud and to collect data. It connects all sensors, machines, devices, etc.

To demonstrate how the historical data can be used for mathematical modelling and prediction, a simple model based on regression was created and calibrated with two month of data of COD inflowed to the WWTP.

## RESULTS AND DISCUSSION

Based on the results from simple regression model (Fig. 1), it is obvious, that strong database can lead to a great accuracy of chosen model. It is necessary to point out, that data used for this model were mostly from the dry month (January and February) and, therefore, the error caused by rain events was minimal and test mean absolute error of the model was 24.96 mg/L COD.

Prediction of inflow will help to operators react in real-time to upcoming situation on WWTP, which leads to chemicals, energy and costs saving. Moreover, the timely response will keep the WWTP operation more reliable and sustainable, which will help to keep the prescribed discharge limits and protect the recipients and the associated ecosystem.



**Figure 1.** Demonstration of COD prediction by using data from S::CAN and simple linear regression as a mathematical approach.

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# Continuous Microplastic Monitoring to Understand Microplastic Contamination and Its' Seasonal Dynamics in Freshwater Ecosystem

M. Barone\*, M. Robeznieks\*\*, S. Lietina\*\*\*, K. Borg Olesen\*\*\*\*, A. Vianello\*\*\*\*, A. Lanka\*, \*\*\*\*\*, and I. Dimante-Deimantovica\*, \*\*\*\*\*

\* Latvian Institute of Aquatic Ecology, Agency of Daugavpils University, Voleru str. 4, Riga, LV-1007, Latvia (E-mails: *marta.barone@lhei.lv*; *martinsrobez@gmail.com*; *anna.lanka@gmail.com*; *inta.dimante-deimantovica@lhei.lv*)

\*\* Faculty of Geography and Earth Science, University of Latvia, Jelgavas str. 1, Riga, LV-1004, Latvia (E-mail: *martinsrobez@gmail.com*)

\*\*\* Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, LV-1004, Latvia (E-mail: *simonaliatina@gmail.com*)

\*\*\*\* Aalborg University, Section of Water and Environment, Department of the Built Environment, Thomas Manns Vej 23, Aalborg, 9220, Denmark (E-mails: *krbo@civil.aau.dk*; *av@civil.aau.dk*)

\*\*\*\*\* University of Latvia, Faculty of Biology, Jelgavas str. 1, Riga, LV-1004, Latvia (E-mail: *anna.lanka@gmail.com*)

\*\*\*\*\* Norwegian Institute for Nature Research, Gaustadalléen 21, NO-0349 Oslo, Norway (E-mail: *inta.deimantovica@nina.no*)

## INTRODUCTION

The presence of microplastic in water bodies is a global environmental issue. Microplastic is a persistent emerging pollutant which poses a threat to the environment and wildlife, potentially contaminating the food chain and, ultimately, humans (Eerkes-Medrano *et al.*, 2015). It is therefore expected for policy-makers to tackle this issue by requiring regular water monitoring for microplastic occurrence and distribution, but the lack of standardised protocols hampers the comparability between studies. Experimental design is crucial to obtain reliable data; therefore, seasonal monitoring should be preferred to individual surveys, since microplastic amount in surface water may vary depending on specific seasonal conditions. Here we present the preliminary results of a continuous microplastic monitoring in surface freshwaters to better understand the seasonal dynamics involved in microplastic spatial and temporal distribution.

## MATERIALS AND METHODS

Sampling of microplastic (MP) in surface water was carried out from April 2019 to January 2020 (ice-free season) in three lakes (Seksu, Venezers, and Mazais Baltezers) in Latvia. All lakes belong to Daugava catchment basin and are located in urban area representing different levels of potential MP contamination caused by factors such as use of surrounding land, human activities and others.

Seksu and Mazais Baltezers are part of a drinking water supply system that enriches groundwater horizons near Baltezers drinking water pumping station. Therefore, both lakes belong to protected areas. Mazais Baltezers is available for recreation to certain extent and its surrounding area is rather densely populated, while Seksu is located in strict regime protection zone, hence access to lake is limited and it is not a subject of direct anthropogenic effects. Venezers is located in the middle of residential blocks; it is used for recreational purposes and as a treated wastewater discharge place.

Samples were collected from surface waters with a manta net (Hydro-Bios, mesh size 300 µm) that was held to the stern part of the vessel and trawled for 20 minutes (speed varied depending on weather conditions). After trawling, the net was rinsed from the outside to concentrate the sample in

the cod end which was then removed over a metal bowl, inverted and rinsed with distilled water. The sample was moved to a glass tray, covered with a metal lid and stored in the freezer until further treatment. After melting, the samples were pre-oxidized by adding hydrogen peroxide (to maximum 15 %) to digest biological organic matter. If needed, one to several enzymatic treatments were applied to further digest the sample, and thereafter the particles were collected on glass fibre filters (based on Löder *et al.*, 2017). The sorting of potential plastic particles was carried out under light microscope using visual identification. Larger particles were picked out for further analysis, while smaller were counted for total number. Particles were categorized according to their type, size and colour. Larger particles were identified using Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectroscopy (Thermo Scientific, Nicolet iS20).

## PRELIMINARY RESULTS

Preliminary results showed in Table 1. indicated a wide spatial and temporal variability, as the MP amount varied among lakes and within the season. For instance, in April, May and June the amount of particles detected in the surface water varied from 0.93 particles/m<sup>3</sup> in Mazais Baltezers to 8.16 particles/m<sup>3</sup> in Velnezers. In terms of determination of MP polymers, the main limiting factor was particle size. Only approximately 4 % of total amount of particles were suitable for analysis. Most of the identified MP particles consisted of polyethylene or polypropylene, low density polymers (<1 g/cm<sup>3</sup>) which tend to float on the water surface.

**Table 1.** Abundance and most common types of MP particles in Velnezers and Mazais Baltezers.

Lake	Sampling season	Amount of particles per m <sup>3</sup>	Types of particles, % from total amount					
			Fibre	Fragment	Filament	Foil	Foam	Coal
Velnezers	April	1.55	95.18	1.20	1.20	–	2.41	–
	May	8.16	97.38	0.24	0.24	0.71	–	1.43
	June	4.49	95.69	3.92	0.39	–	–	–
Mazais Baltezers	April	1.61	87.64	12.36	–	–	–	–
	May	1.31	90.79	9.21	–	–	–	–
	June	0.93	92.16	7.84	–	–	–	–

Although preliminary, these results clearly show the importance of seasonal monitoring activities to provide a better understanding of the dynamics involved in distribution of MP in surface freshwater.

## FUNDING ACKNOWLEDGEMENTS

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# Short-Term Water Demand Forecast Based on Conv1D Extraction Features

L. Chen\* and T. Tao\*

\* College of Environmental Science and Engineering, Tongji University, 1239, Siping Road, Yangpu District, Shanghai, China (E-mails: [chenleih@tongji.edu.cn](mailto:chenleih@tongji.edu.cn); [taotao@tongji.edu.cn](mailto:taotao@tongji.edu.cn))

## INTRODUCTION

Water is not only an irreplaceable resource for human survival and development, but also the foundation of social sustainable development. Through the forecast of short-term water demand, it can provide the water distribution system scheduling decisions and the real-time detection of abnormalities and real-time location of problems such as pipe burst can be realized (Bennett *et al.*, 2013; Zhou *et al.*, 2019). Previous researches on water demand forecast were mostly based on mathematical statistics theory. With the development of science and technology, deep learning is gradually applied to water demand forecast, but most of the model features are extracted manually, which cannot make full use of the monitoring data. Therefore, a deep learning model is established that automatically extracts feature with Conv1D and automatically learns water demand time series with GRU, which can make full use of the monitoring data and realize real-time forecast of water demand on the basis of improving forecast accuracy.

## METHODOLOGY

### One-Dimensional convolutional neural network (Conv1D)

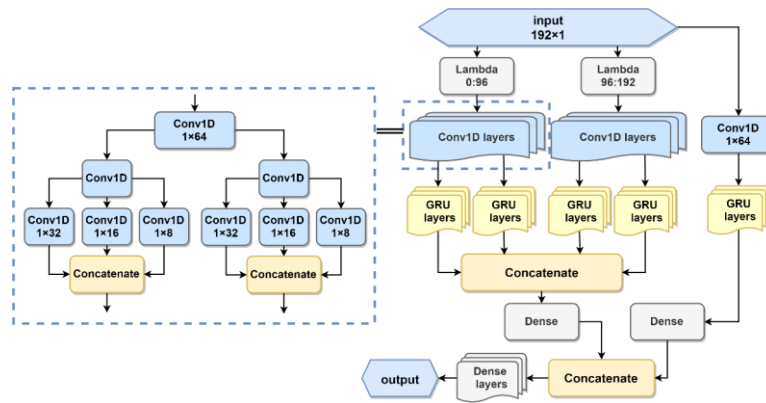
Conv1D is a convolutional neural network that can be applied to time series feature extraction, and it can realize automatic feature extraction of water demand data through local perception, spatial arrangement and parameter sharing (Cheng *et al.*, 2019).

### Gated recurrent neural network (GRU)

GRU is a type of neural network dedicated to processing time series data and the changes in the time dimension of the data are considered during the training process (Cho *et al.*, 2014). GRU not only solves the problems of traditional RNN gradient explosion and gradient vanishing, but also improves the training speed of the network.

## CASE STUDY DESCRIPTION

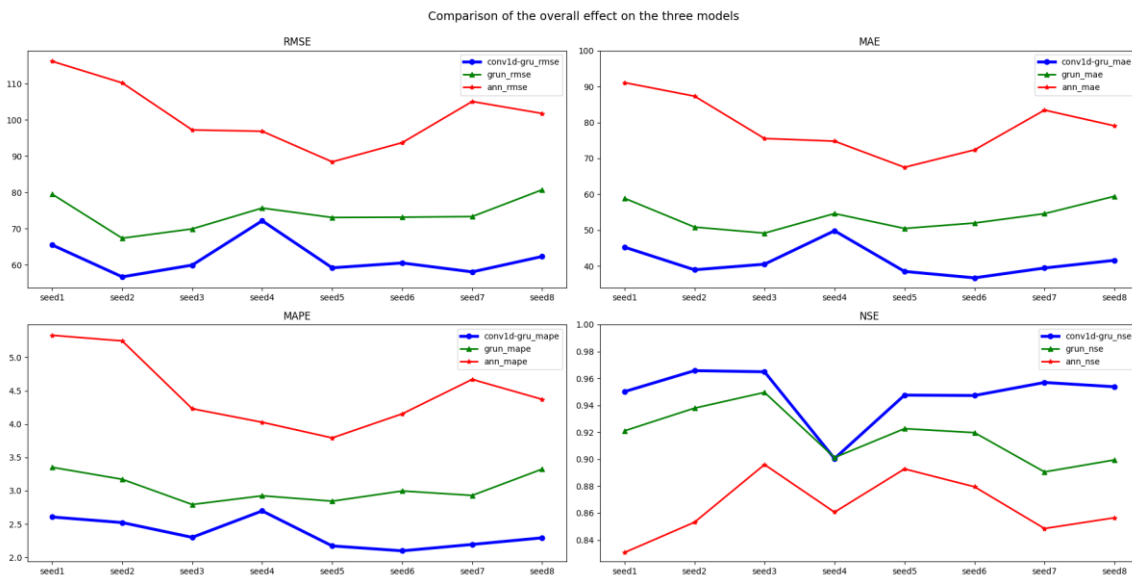
Fig. 1 shows the model structure of the Conv1D-GRU. The model takes two consecutive days of monitoring as input. The model divides the input data into three parts (the first day's data, the second day's data and the overall data), and extracts features by Conv1D on the three parts respectively. Finally, the features extracted by the Conv1D layers are used as the input of the GRU layers; when capturing long-term macroscopic dependencies, the GRU layers with different output space dimensionality are used for feature extraction. In order to make full use of historical data, different training datasets are constructed in the form of random seeds on the total dataset. Each random seed contains seven training dataset lengths (7, 30, 60, 90, 120, 180 and 365 days), and the length of the validation dataset and test dataset is 3 days. The Conv1D-GRU model for automatically extracting features, the GRUN model (Guo *et al.*, 2018) for manually extracting features, and the commonly used ANN model are established respectively. Four indicators are used for model evaluation: RMSE, MAE, MAPE and NSE.



**Figure 1.** The structure of the Conv1D-GRU model.

## RESULTS AND DISCUSSION

Fig. 2 shows the overall training effect of different random seeds on training datasets of seven lengths. It can be seen that no matter what training dataset is used, the prediction of the Conv1D-GRU model with automatic feature extraction is better than that of GRUN model with manual feature extraction and ANN model. In addition, the training success rate of the Conv1D-GRU model (96.25 %) is much higher than that of the GRUN model (70.00 %) and ANN model (81.25 %).



**Figure 2.** Comparison of the overall effect on the three models.

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# Implications of Microorganism Survival in Different Constructed Wetland Environment

H. S. Choi\*, F. K. F. Geronimo\*, M. S. Jeon\*, N. J. Reyes\*, and L. H. Kim\*

\* Department of Civil and Environmental Engineering, Kongju National University, 1223-24 Budaedong, Seobukgu, Cheonan city, Chungnamdo, 31080, Republic of Korea  
(E-mail: [leehyung@kongju.ac.kr](mailto:leehyung@kongju.ac.kr))

## INTRODUCTION

Stormwater from different sources contains considerable amounts of particulates, heavy metals, nutrients, and organic matter which can potentially degrade the quality of receiving water bodies and the aquatic ecosystem as a whole. Generally, the occurrence and characteristics of non-point pollutants are dependent on the land use type, vegetation density, soil type and slope, and rainfall characteristics (i.e. intensity, duration, frequency, and antecedent dry days). Effective NPS pollution management can be accomplished through the implementation of various environmental engineering techniques such as nature-based solutions (NBS), LID, GI, and blue-green networks. Constructed wetlands (CW) can be regarded as LID, GI, and NBS. Due to their diverse functions, CW are increasingly applied to various land-uses (urban, agricultural, livestock, and industrial areas). CW provide ecosystem services through maintaining energy flow and mass circulation in the environment. In order to effectively evaluate overall the sustainability of CW, a comprehensive evaluation method should be established. Moreover, improving the CW ecosystem services entails necessary design techniques that consider the biological factors affecting the facility's performance. An in-depth assessment regarding the physical and biological attributes of a CW is necessary to improve its cultural, environmental education, and landscaping functions. This study was conducted to develop a comprehensive evaluation index and ecological design techniques that consider the various ecosystem services of CW.

## MATERIAL METHODS

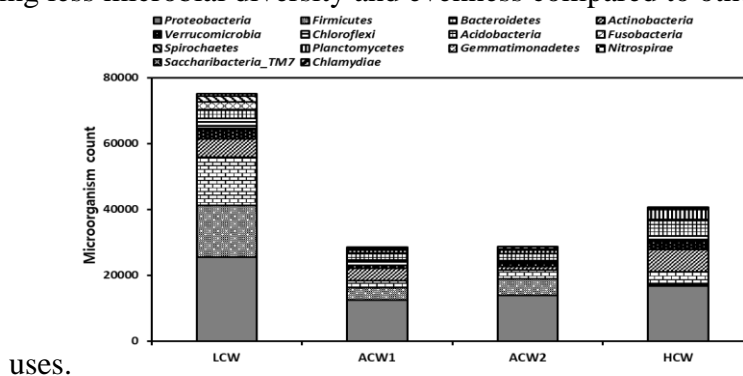
Water quality and quantity were monitored during wet days and dry days to monitor the biological characteristics of the CW environment. Monitoring during rainfall was performed to investigate the occurrence and runoff characteristics of non-point pollutants generated during rainfall events. Livestock constructed wetland (LCW) was monitored from 2010 to 2020. Agriculture constructed wetland1 (ACW1) and Agriculture constructed wetland 2(ACW2) were monitored during rainfall from 2016 to 2020. Urban constructed wetland (HCW) was monitored from 2010 to 2018. Water quality samples were collected from each cell and sections. Soil and water microorganism analysis was performed for soil and water samples collected in different parts of LCW, ACW1, ACW2 and HCW. 16S rRNA gene sequence obtained by the Roche 454 pyro-sequencing technology was used for the microbial analysis of the samples same as the method of analyses summarized in the study conducted by D'Argenio and Francesco, 2015.

## RESULT AND DISCUSSION

Apart from the abundance and diversity of microbial clusters, cluster distribution is an important factor related to microbial activity in the growing environment. Fig. 1 represents the distribution of the top ten soil microorganism species from various CW. LCW was found to have the highest percentage of the dominant soil microorganisms followed by HCW, ACW2 and ACW1, respectively. Soil microorganism count in LCW was found to be three-fold greater than ACW1 and

ACW2 due to the accumulation of nutrients in the soil from LCW.

The TN concentration for LCW was 2500 mg/kg while the TP concentration was 3600 mg/kg. On the other hand, soil TN and TP concentration in ACW1 and ACW2 ranges from 125 mg/kg to 200 mg/kg and 630 mg/kg to 140 mg/kg, respectively. The TN concentration in HCW was 360 mg/kg and the TP concentration was 930 mg/kg, indicating that the TN concentration was higher compared to ACW1 and ACW2. Among the soil and water microorganisms found in the three land uses, five phyla including *Proteobacteria*, *Firmicutes*, *Bacteroides*, *Actinobacteria*, and *Verrucomicrobia* were commonly found in all the land uses. The ten dominant water microorganisms consisted 93.2 %, 97 % and 98.7 % of the total water microorganisms found in LCW, ACW1 and ACW2, and HCW respectively. Similarly, the ten dominant soil microorganisms consisted 94.9 %, 96.4 % to 97.4 %, and 96.4 % of the total water microorganisms found in LCW, ACW1 and ACW2, and HCW, respectively. These finding is attributed to the agricultural areas having less microbial diversity and evenness compared to other land



uses.

**Figure 1.** Comparison of soil microorganism count from different landuse.

## CONCLUSIONS

The microorganism diversity indicated the stability of the microbial community, and environmental and ecological mechanisms affecting the microorganism community. The abundance of microorganism in CW can be the closest indicator to the impact of pollutants. The creation of optimum environment for the growth of microorganisms inside the CW is an important design factor that affects the long-term operation of the CW and the efficiency of reducing pollutants. The CW environment is affected by the characteristics of the catchment basin where the facility is installed, the pollutants, and climate factors thereby also affecting the microbial community and growth in the CW.

## ACKNOWLEDGEMENT

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# Estimation of SSC in Rivers Using ADCP Backscatter Data

N. Cvijanović\*, M. Babić Mladenović\*, and M. Kostić\*

\* Jaroslav Černi Water Institute, Jaroslava Černog 80, 11226 Belgrade, Serbia  
(E-mail: [nevena.cvijanovic@jcermi.rs](mailto:nevena.cvijanovic@jcermi.rs))

## INTRODUCTION

For more than two decades, Acoustic Doppler Current Profilers (ADCPs) have been in common use measuring current profiles. In recent years, the acoustic sensors such as ADCP have become a more widely used in means of estimating suspended solids. Plenty of studies have indicated that there is a strong relation between acoustic backscatter intensity and Suspended Sediment Concentrations (SSC). Conventional measurement techniques for collecting of data on SSC are real challenge considering the time and effort to collect all necessary data. Furthermore, it is often unfeasible to perform measurements during the floods, which leads to a lack of data in this range of flow. For those reasons, there is a need to establish a contemporary and sustainable methods in sediment monitoring systems which will enable continuous data acquisition. Acoustic sensors such as ADCPs offer a lot of advantages over traditional methods in SSC monitoring.

The initial results in utilization of backscatter sensor (Acoustic Doppler Current Profiler – ADCP) for suspended sediment monitoring will be presented in this paper, as well as the reliability assessment relative to the data collected using conventional methods.

## THEORY

ADCPs are primarily developed to measure current velocity profiles. ADCP initiate a Doppler effect by transmitting sound at a fixed frequency and listening to echoes returning from sediment particles in the water. The acoustic signals reflected from suspended sediment particles also provides information about the SSC. This information is measured in the form of reflection intensity, also referred to as backscatter. Using the ADCP backscatter data in purpose of SSC measurements requires the additional processing of acoustic information. In this paper, ADCP backscatter data processing is based on the method described by Deines (Deines, 1999). The idea is to determine the so-called absolute backscatter, that can subsequently be converted to SSC by means of calibration with reference to SSC data from water samples.

## STUDY AREA AND METHODOLOGY

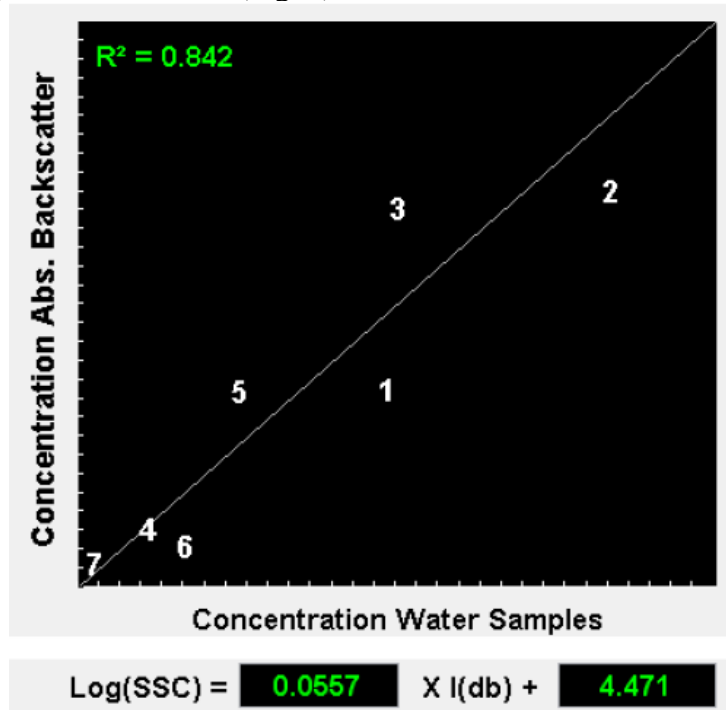
Sediment regime is very significant factor in case of river dams, due to the inevitability of sedimentation process in reservoirs and consequential reduction of its active storage. To provide an assessment of the sediment transport and deposition processes in the Iron Gate Reservoir, located on the Lower Danube in Serbia, a monitoring program has initiated in 1974 by the Jaroslav Černi Water Institute (JCWI) and it is still going on. The annual monitoring program consists in daily observations of suspended sediment concentrations as well as periodic field measurements of water and sediment discharge on certain monitoring sites across the reservoir.

Main advantage of using ADCP is the fact that water samples can only provide information at a specific point of the water column, while ADCP can provide data through the entire cross section. Prior to collecting water samples, at least two ADCP survey lines should be run along the monitoring profile (one in each direction) to collect discharge, average velocity, and acoustic backscatter data.

The method of converting backscatter into SSC can be done by the principle of sonar equation (Deines, 1999). The main goal is to convert the absolute backscatter to SSC. This could be done according to the following equation:

$$\log_{10}(SSC)=A \times I+B \quad (1)$$

In which  $I$  is the absolute backscatter in dB, and  $A$  and  $B$  are constants (conversion coefficients). By assuming that there is a linear relationship between  $I$  and  $\log_{10}(SSC)$ , coefficients  $A$  and  $B$  can be derived from linear regression. This requires the availability of reference concentrations from water samples taken during the measurement (Fig. 1).



**Figure 1.** Correlation plot with water samples and conversion coefficients.

This correlation can be then used to convert all data from ADCP across the entire cross-section into SSC values.

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# Mapping the Water Sector of Latvia

B. Dalecka\*, D. Stebelis\*, T. Juhna\*, G. Daksa\*, and J. Rubulis\*

\* Water Research Laboratory, Riga Technical University, Kipsala 6A–263, Riga, Latvia  
(E-mails: *brigita.dalecka\_1@rtu.lv*; *davids.stebelis@rtu.lv*; *talis.juhna@rtu.lv*;  
*janis.rubulis@rtu.lv*)

## INTRODUCTION

Latvia is rich in surface waters and groundwater resources with the fourth largest water volume of freshwater resources per capita in the European Union. Now, water is used for renewable energy productions, recreation and agriculture, and public water supply. However, the potential of water sectors arguably is not fully engaged in the creation of higher value-added products and services. This is expected within the smart specialisation strategy (RIS3) of Latvia by integrating water sectors within RIS3 areas of advanced materials, technologies, and engineering systems (Cross Sectoral Coordination Centre, 2018; Wehn de Montalvo and Alaerts, 2013).

The Interreg-Europe project *iWatermap* aims to improve cooperation between industry and academia and to address societal challenges in the water sector. For this, the mapping of main research groups and their cooperation in Latvia is needed. The awareness of data might also highlight the latest innovations in the water sector and increase the understanding of science and technology development, including possible education and knowledge transfer from the scientific field to the water sector and industry. Furthermore, these results can present the scientific topics of the water sector where research has not been studied for the last decade. To the best of our knowledge, there is no study where the current data from scientific databases have been collected and analysed for Latvia's water sector.

Thus, the aim of this study was to collect and analyse the bibliometric data in order to assess the current situation in the water sector in Latvia under the scientific field with a focus on 3 keywords: drinking water, wastewater, and groundwater.

## MATERIALS AND METHODS

The data were obtained from Elsevier's Scopus database choosing the time period from 2010 till 2020. The document type was selected "article and review" and the country was limited to Latvia. For data collection was used and searched for 3 keywords: drinking water, wastewater, and groundwater. After data collection, the data were analysed with the *Vosviewer* software tool for constructing and visualizing the network and calibration between water sector researchers (the type of analysis: co-authorship; units of analysis: authors; counting method: full counting; minimums number of documents of an author: 2).

## RESULTS

The results showed that in all selected topics there is a relatively high number of researchers are involved (Fig. 1). Some of the researcher groups (e.g., led by T. Juhna) are represented in all topics whereas others are specialising in more specific areas, for instance, A. Babre and J. Burlakovs are the main authors for scientific papers under the groundwater topic. O. Mutere, V. Bartkevics, M. Klavins have been presented under the wastewater as the most published authors with scientific papers.



# The Efficiency of Suspended Solids Removal in the Open Trays with Different Texture of the Inner Surface

I. S. Dezhina\* and V. A. Orlov\*

\* Moscow State University of Civil Engineering (National Research University), 129337, Yaroslavskoe shosse 26, Moscow, Russia (E-mails: [dejina07@mail.ru](mailto:dejina07@mail.ru); [orlov950@yandex.ru](mailto:orlov950@yandex.ru))

## INTRODUCTION

The effective operation of drainpipes and gravity pipeline systems mostly depends on the improvement of their maintenance (for example, cleaning). Some special situations require repair and renovation work, especially using trenchless technologies (Matthews *et al.*, 2018; Zwierzchowska and Kuliczowska, 2019). The important aspect of the gravity pipeline systems modernization is connected with the improving of their internal surfaces' hydraulic characteristics (Salomeev *et al.*, 2017; Orlov *et al.*, 2017). Currently, a wide range of polymer and composite protective coatings is offered by the construction markets. It allows finding the appropriate material with low hydraulic resistance (Niu and Cheng, 2008). Rational use of such construction materials for trays repair, including trenchless methods, helps to improve the efficiency of wastewater transportation.

## MATERIALS AND METHODS

These studies aim to identify the conditions that ensure the flow vortex formation. It can be achieved even at the low flow rates by improving the geometric shape and location of artificial obstacles at the bottom of the trays.

Studies were carried out on a special testing bench to determine the transporting capacity of the open trays with different texture of the inner surface. The object of studies is a single-phase flow turbulence, as well as two-phase (i. e. containing suspended solids). Studies include an assessment of the transportation efficiency for the differently sized particles of solid fractions. Experiments on the stand aimed to describe the arising of vortex flows, which can appear upon encountering the obstacles. The study can offer options for the optimal texture of the trays and pipes bottom surface, increasing the effect of transporting capacity.

## RESULTS

The analysis of the vortex formation character in single-phase flows, together with the movement of solid fractions in two-phase flows at different fillings, has been carried out. The character of vortex formation was checked by the visual fixation of the shadow line refraction (shadow track) reflected on the water surface by special lamps. During the first stage of experiments, a significant number of artificial obstacles were subject to study.



**Figure 1.** Samples of surfaces with artificial roughness used during the experiments. Left to right: round obstacles; cylindrical bars; cruciform bars arranged in the form of a parallelepiped; the same with a round obstacle in the middle; corners and double obstacles in the form of wedges.

The flow rates in all experiments had approximately the same values: at laminar flow mode (0.20–0.22 m/s), turbulent (0.27–0.29 m/s) and coherent (0.35–0.38 m/s). Thus, the flow velocities were less than self-cleaning (0.7 m/s). The most intensive vorticity shows itself in the case of a two-row arrangement of obstacles in the form of wedges.

The analysis of the experimental results allows us to draw some conclusions on the behavior of the flow, erosion, and removal of sand ridges. Thus, in experiments without obstacles the visual picture can be characterized by the rise (ascent) of a smaller fraction of sand to the water level in the tray. After increasing filling and flow speed the sand is taking the form of the ridge, but no effective flushing of sand is being noticed.

## CONCLUSIONS

The results of the experimental studies on a small-sized hydraulic stand simulating the operation of open gutter trays with a textured surface are presented. The vortex formation was studied. The study was based on the control of shadow line deformation in the textured surface of the tray. The transporting ability of the removal of suspended solids of different compositions in the flow is investigated. Improving the trays texture is possible during repair and renovation works by using the polymeric protective sleeves with the special surface relief.

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## **Adaptive Landscapes: The Aniene River Corridor between Green Areas, Built-Up Space and Resilience**

T. V. Di Giacomo\*

\* Department of Civil, Constructional and Environmental Engineering, Sapienza, University of Rome, 18 Eudossiana Street, 00184 Rome Italy (E-mail: [tulliavaleria.digiacom@uniroma1.it](mailto:tulliavaleria.digiacom@uniroma1.it))

### **THE ANIENE RIVER CORRIDOR**

The Aniene river corridor is a fundamental green & blue resource for the north-east quadrant of the City of Rome and in addition to its aesthetic and recreational functions, it helps mitigating the pollution of the various environmental matrices (air, water, soil), improving the microclimate and maintaining biodiversity. To date, however, these functions and benefits are poorly integrated in local urban planning, especially in the perspective of climate change. The work aims, on the one hand, to carry out an exhaustive review of the margins of the Aniene Valley Nature Reserve and, on the other, to develop reflections and design proposals for the integration of the environmental services that it offers to the city. The river corridor must not be considered only an unbuilt space, but must be understood and managed as a fundamental component of the quality of life and urban sustainability, thanks to the multiple services and benefits – not only environmental – that it provides. The proposed eco-systemic approach is a contribution to a better understanding of the multifunctionality of these urban green areas and their potential. The transversal dimension of the river landscape is investigated with respect to the complex environmental, social and economic issues that together weave the important political-cultural goal of urban sustainability observed from the point of view of risk and resilience to climate change.

The research carries out a clustering activity by classifying the different areas crossed by the river corridor (agricultural areas, infrastructural network, archaeological sites, built-up areas, areas of social marginalization) to collect and evaluate territorial data through which to carry out analyzes of the homogeneous elements and interactions.

The general objective is the environmental protection understood with a broad and holistic vision of the various components that make up these territorial areas towards a design commitment in the virtuous interaction of built space and natural space.

### **THE CONTEXT**

The research is part of a recent trend of adaptation strategies, which recognize the uncertainties of climate change and develop the essential institutional capacity to intervene in the anthropized environment. An example is the strategy of the Bologna Local Urban Environment Adaptation Plan for a resilient city. BLUE AP is a LIFE + project of the Municipality of Bologna which provides for some concrete local measures to be tested, in order to make the city more resilient and able to face the challenges of climate change with the selection of possible actions to be carried out in the public and private sectors and review of the system of monitoring indicators.

At the European level, initiatives have been developed with the aim of combating pollution and improving preparedness for the impacts of climate change related to water resources. The importance of good management has been reiterated by the European Commission since 2011 (European Commission, 2011) with the focus on natural capital and ecosystem services, with close coordination with policies for agriculture, transport and regional development and with control

direct and indirect impacts on land use. For the European Parliament, the reduction of risks associated with natural disasters and hydro geological phenomena is a positive effect of the creation or restoration of green infrastructures such as natural floodplains, forests, wetlands, which can improve resilience to disasters and help adaptation to climate change by significantly reducing the costs of natural disasters to society.

On a global level, the United Nations (UN, 2012) emphasizes the issue of the protection, conservation and improvement of natural resources, inviting governments to intervene to ensure greater attention in decisions on land use with respect to environmental, social and economic impacts.

## THE METHOD

The proposed method has interdisciplinary characteristics, starting from the investigation of the benefits offered by the presence of the reserve to test the models relating to permeability to quantify the added value of open spaces in urban areas in ensuring this surface and underground permeability. We have evaluated the characteristics of the soil and the vegetation cover present, the parameters of permeability of the open areas of the river corridor and how these relate to the built-up fronts that delimit the reserve. Indeed, the relationship between river and aquifer can prove to be crucial in the response to climate change especially in urban areas and for limiting the impacts of hydro geological instability phenomena.



**Figure 1.** The Aniene waterfront.

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# A Comprehensive Approach to Modelling the Transport of Agricultural Pollution from Farm to the Coastal Zone

D. Dybowski\*, M. Janecki\*, and L. Dzierzbicka-Głowacka\*

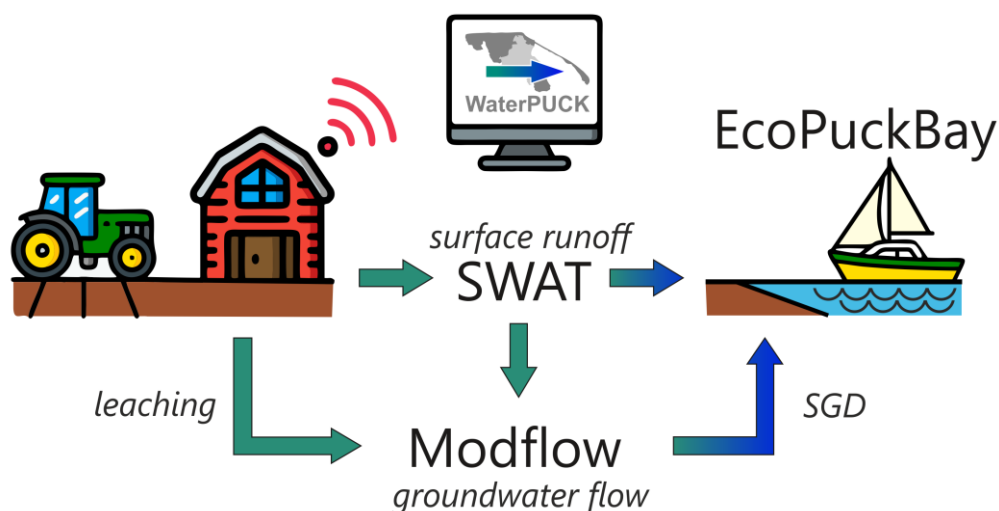
\* Physical Oceanography Department, Institute of Oceanology Polish Academy of Sciences, Powstańców Warszawy 55, Sopot, Poland (E-mails: [dDYBOWSKI@IOPAN.PL](mailto:dDYBOWSKI@IOPAN.PL); [mJANECKI@IOPAN.PL](mailto:mJANECKI@IOPAN.PL); [DZIERZB@IOPAN.PL](mailto:DZIERZB@IOPAN.PL))

## INTRODUCTION

Nowadays the most convenient and effective form of monitoring of the marine environment is the combination of appropriately selected tools based on interdisciplinary models fed by environmental and satellite data. When studying an ecosystem that is changing very dynamically, the rough approximation that applies to large water bodies, for which aggregate trends are more important than local aberrations, should be rejected. Moreover, the set of research tools (models, measurements, simulations) has to be scaled to make these processes noticeable.

## RESULTS

The WaterPUCK toolkit (Fig. 1) has been developed to meet these requirements and to simulate the impact of agricultural pollution from the Puck Commune on the Bay of Puck coastal environment. The novelty of the proposed methods, techniques and outcomes of the WaterPUCK toolkit includes coupling of different models for comprehensive characterisation of nutrients and pesticide transport on land (soil, surface water, groundwater) and in coastal seawater, creation of an extensive database (data originate from monitoring activities, archives, publications, publicly available data and results of numerical model runs), providing to the Puck Commune a tool which allows testing the impact of changes in farming practices, land use and climate on the contamination of the aquatic environment with nutrients and pesticides, development of innovative tools that can be implemented in other Baltic Sea Region areas and therefore increase the competitiveness.



**Figure 1.** Scheme of agricultural pollution transport from farm to the coastal zone.

The construction of the toolkit is based on *in situ* research, surveys, environmental data (physicochemical and hydrological) and numerical modelling. WaterPUCK comprises two calculators for farms in Puck Commune as interactive applications (Dybowski *et al.*, 2020;

Dzierzbicka-Głowacka *et al.*, 2019), a numerical model of groundwater flow based on Modflow (Szymkiewicz *et al.*, 2020), a comprehensive model of surface water runoff based on SWAT (Kalinowska *et al.*, 2020), a three-dimensional ecohydrodynamic numerical model of the Bay of Puck ecosystem (Dybowski *et al.*, 2019; Dybowski *et al.*, 2020).

## SUMMARY

The main goal of the WaterPUCK solution was to provide a practical and professional toolkit for the authorities of the Puck Commune and other users enabling a better understanding of the current environmental situation and planning further activities, while simultaneously increasing the socio-economic development of the region. The WaterPUCK toolkit allows for effective monitoring and supports management of coastal zones. Moreover, the implementation of this toolkit (after necessary calibration) seems to be very desirable for areas where the catchment area has a high share of agriculture.

## FUNDING

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# Inactivation of Pepper Mild Motile Virus by Cold Atmospheric Plasma

A. Filipić\*, \*\*, D. Dobnik\*, I. Gutierrez-Aguirre\*, M. Tušek Žnidarič\*, G. Primc\*\*\*, M. Mozetič\*\*\*, M. Ravnikar\*, \*\*\*\*, and J. Žel\*

\* National Institute of Biology, Večna pot 111, 1000 Ljubljana, Slovenia

(E-mail: [arijana.filipic@nib.si](mailto:arijana.filipic@nib.si))

\*\* The Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia

\*\*\* Jožef Stefan Institute, Jamova cesta 39, Ljubljana, Slovenia

\*\*\*\* University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

## INTRODUCTION

Pepper mild motile virus (PMMoV) is a rod-shaped plant virus from the genus *Tobamovirus*, which infects different pepper species. PMMoV can be found in all water bodies that were exposed to human faecal pollution and it was shown to be a good indicator of water contamination with human enteric viruses. Like many other viruses from the same genus, PMMoV is very resilient as it can withstand even harsh changes in the environmental properties in waters and it stays infective after various water treatments including treatment in wastewater treatment plants (Kitajima *et al.*, 2018). Hence, the decontamination method that would be able to inactivate such a resistant virus would probably be able to inactivate other waterborne human viruses as well. Enteric viruses (e.g. norovirus, rotavirus, hepatitis A) are the most problematic waterborne human viruses as they cause numerous infections, mostly gastrointestinal, that lead to many hospitalizations or even death. Therefore it is very important to inactivate pathogenic viruses in water.

Compared to the already existing methods for water decontamination (such as chlorination and filtrations), cold atmospheric plasma (CAP) is environmentally friendlier, it does not use toxic chemicals, has simple designs and is easy to operate and maintain. Plasma is the fourth state of matter. It is a complex mixture of charged particles (ions and free electrons), reactive species, UV photons and neutral particles (molecules or atoms in their excited or ground state). Plasma can be divided into thermal or equilibrium plasma, where all particles have roughly the same temperature, and non-equilibrium, or cold plasma, where light electrons have much higher temperatures compared to heavy atoms and molecules, which often remain close to room temperature. In other words, cold plasma is at the point of application at room temperature, and as such, it is suitable for treating any biological material, including water (Filipić *et al.*, 2019). Cold plasma can be either low-pressure or atmospheric, which depends on the pressure of the electrical discharge that generates them (Scholtz *et al.*, 2015). CAP has been used for decontamination in different fields like medicine, food processing or agriculture (Hoffmann *et al.*, 2013; Liao *et al.*, 2016) as it has many microbial properties like reactive oxygen and nitrogen species (RONS), charged particles and UV radiation. In our research, we examined the inactivation of PMMoV in water by CAP.

## METHODOLOGY

For inactivating PMMoV in water samples, an atmospheric pressure plasma jet in the single electrode configuration was used. Plasma was created in a mixture of argon and oxygen gas. Each sample (tap water with added plant homogenate with viruses) was treated for a different amount of time, from 60 min to only one minute. Homogenate of pepper plants infected with the virus was used as a virus source. Various methods were applied for characterisation of viral inactivation. Initial virus concentrations were determined with reverse-transcriptase droplet digital polymerase

chain reaction (RT-ddPCR). The most important tests, infectivity assays, were conducted using test plants *Capsicum annum*, followed by the RT-real-time PCR (RT-qPCR). Degradation of the viral RNA was examined with RT-PCR and RT-ddPCR and the integrity of virus particles was studied with transmission electron microscopy. Temperature, pH and concentration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were always measured before and after the treatment.

## RESULTS AND DISCUSSION

We were able to characterize the efficiency of PMMoV inactivation in water by CAP using various methods. We have shown that only 3-minute treatment was enough for virus inactivation using test plants, which is a very short time considering the resistance of the virus and the fact that the virus source was plant homogenate, which besides viruses, contained other organic material derived from the plants. Since chemically reactive plasma particles, such as RONS, react with all organic material, even shorter treatment times would probably be enough to inactivate less polluted samples. We have shown that CAP affects both RNA and coat proteins by using PCR-based methods and TEM.

## CONCLUSIONS

Our results indicate that CAP could be used for inactivation of pathogenic viruses in water, which still pose major problems worldwide since their detection can be problematic and they can be infectious in very low doses. Ultimately, CAP use could lead to reduced human, animal and plant infections, and along with this, lower economic and biological burdens.

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# Investigation on the Factors Affecting the Growth and Survival of Microorganisms in Stormwater Nature-Based Solutions

F. K. F. Geronimo\*, H. B. Guerra\*, H. S. Choi\*, M. S. Jeon\*, N. J. Reyes\*, and L. H. Kim\*

\* Civil and Environmental Engineering Department, Kongju National University, Cheonan City, South Korea 31080 (E-mails: [fkgeronimo@kongju.ac.kr](mailto:fkgeronimo@kongju.ac.kr); [guerraheidib@gmail.com](mailto:guerraheidib@gmail.com); [hyseson27@kongju.ac.kr](mailto:hyseson27@kongju.ac.kr); [minsu91@kongju.ac.kr](mailto:minsu91@kongju.ac.kr); [reyesnashjettdg@gmail.com](mailto:reyesnashjettdg@gmail.com); [leehyung@kongju.ac.kr](mailto:leehyung@kongju.ac.kr))

## INTRODUCTION

Soil microorganisms perform different functions which were is yet not fully understood in ecosystem leading to poor prediction in soil biodiversity affecting ecosystem sustainability (Delgado-Baquerizo *et al.*, 2020). Many studies have already been conducted to assess and fully understand the performance of different LID technologies. However, these LID technologies have been treated as a black box due to fluctuating flow and environmental conditions affecting its operation and treatment performance disregarding the contribution of soil microorganism to its overall performance. As such, this research evaluated the contribution of soil and sediment microorganisms to the overall performance of each LID technologies.

## MATERIALS AND METHODS

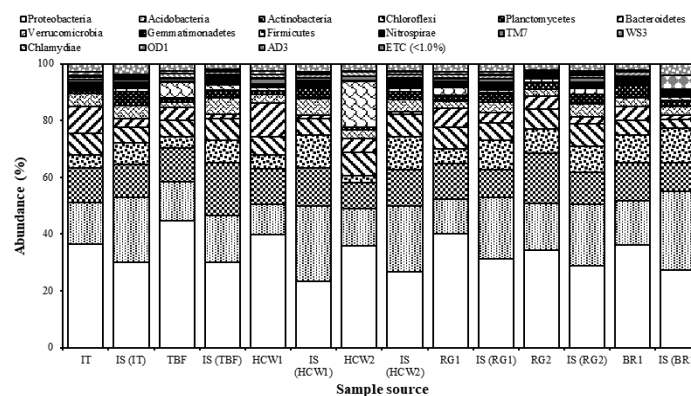
Eight different stormwater low impact development (LID) technologies were monitored from May 2009 to April 2018 with catchment and design characteristics summarized in Table 1. A total of 201 storm events were monitored in the eight LID technologies. These LID technologies were installed inside Kongju National University, Cheonan City, South Korea to manage stormwater runoff from 100 % impervious road, roof, and parking lot areas. Initially, these LID technologies were designed to treat the first flush of storm events.

**Table 1.** Catchment, monitoring and design characteristics of stormwater green infrastructures.

LID Technology	Parameters						
	Runoff source	Catchment area, m <sup>2</sup>	<i>N</i> storm events	Infiltration capability	Filter media	Facility aspect ratio (L:W:H)	Storage volume (SV), m <sup>3</sup>
Infiltration Trench (IT)	Road	371	24	Yes	Sand, woodchip and gravel	1.00:0.20:0.26	3.54
Tree box filter (TBF)	Parking lot	379	26	Yes	Sand, woodchip and gravel	1.00:1.00:0.87	0.71
Hybrid constructed wetland 1 (HCW1)	Road and parking lot	323	21	No	Sand, woodchip and gravel	1.00:0.15:0.10	1.61
Hybrid constructed wetland 2 (HCW2)	Road and parking lot	425	22	No	Sand, bioceramic and gravel	1.00:0.14:0.10	1.56
Rain Garden 1 (RG1)	Roof	161	29	No	Sand, soil, woodchip, and gravel	2.47:1.00	6.26
Rain Garden 2 (RG 2)	Parking lot	481	20	Yes	Sand, woodchip and gravel	5:1:1	2.88
Bioretention 1 (BR1)	Parking lot	139	16	Yes	Sand, soil, bottom ash, and woodchip	2.50:1.08:1.00	2.32

## RESULTS AND DISCUSSION

The comparative analysis of microbial count in LID technologies and in-situ soil (IS) was demonstrated in Fig. 1. *Proteobacteria* remained as the most dominant microorganism for all LID technologies and IS comprising 34 % to 45 % and 23 % to 31 % of the total microorganism count, respectively. Higher abundance of *Proteobacteria* was also observed in LID technologies compared to IS. *Proteobacteria* comprises 40 % of validly published prokaryotic bacteria and encompass a major proportion of traditional gram-negative bacteria since it shows extreme metabolic diversity (Kersters *et al.*, 2006). On the other hand, the abundance of *Acidobacteria* in LID technologies were found to be 2.6 % to 15.8 % less than that of IS. Since LID technologies received stormwater runoff during storm events, more pollutants acting as substrate enter the technologies which obstruct its growth since *Acidobacteria* adapted to low substrate availabilities (Naether *et al.*, 2012). *Actinobacteria* in LID technologies and IS comprised about 9 % to 16 % and 10 % to 17 %, respectively affected by several factors including its ability to resist UV radiation, heat, and desiccation, ability to produce antibiotics excluding other bacteria, and survival in heavy metal contaminated soils.



**Figure 1.** Comparison of microorganism phyla dominance in each stormwater green infrastructure and in situ soil.

## CONCLUSION

Microorganism count in LID technologies exhibited low count compared to those of IS. This finding is attributed to stormwater entering the LID technology during storm events which contained contaminants that might pose stress to the microbial community. However, it was found that more diverse microbial family and genus were observed in LID compared to IS which might have been affected by an intermittent change in pH during storm events. These findings are useful for designing LID technologies considering biological mechanisms.

## ACKNOWLEDGEMENT

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# Comparative Study of Low Impact Development Structures with High and Low Infiltration Soils

H. B. Guerra\*, F. K. F. Geronimo\*, H. S. Choi\*, Y. Kim\*\*, and L. H. Kim\*

\* Department of Civil and Environmental Engineering, Kongju National University, 1223-24 Cheonan-daero Seobuk-gu, Cheonan City, Chungcheongnam Province 31080 Republic of Korea (E-mails: [guerraheidib@gmail.com](mailto:guerraheidib@gmail.com); [fkfgeronimo@kongju.ac.kr](mailto:fkfgeronimo@kongju.ac.kr); [hyeseon27@kongju.ac.kr](mailto:hyeseon27@kongju.ac.kr); [leehyung@kongju.ac.kr](mailto:leehyung@kongju.ac.kr))

\*\* Department of Environmental Engineering, Hanseo University, Hanseo 1-ro, Haemi-myeon, Seosan City, Chungcheongnam Province 31962 Republic of Korea (E-mail: [ykim@hanseo.ac.kr](mailto:ykim@hanseo.ac.kr))

## INTRODUCTION

One of the major goals of low impact development (LID) as a stormwater management solution is runoff volume reduction by allowing the infiltration of treated runoff to the surrounding soil. However, in areas that are experiencing periods of drought or where the in-situ soil infiltration capacity is low, the treated stormwater may be stored for reuse instead. Therefore, the application of stormwater infiltration LID systems may be broadened instead of being limited by in-situ soil or rainfall characteristics. This has also been an interest in Australia which has experienced droughts and where water scarcity is a major challenge (Akram *et al.*, 2014). In this study, a lab-scale infiltration system with gravel and soil media was used to conduct experiments. The runoff capture capacity of high infiltration and low infiltration media were compared and their corresponding effect on pollutant removal with emphasis on suspended solids were analyzed. The study aims to develop basic design provisions for LID applications under different rainfall and soil characteristics.

## METHODOLOGY

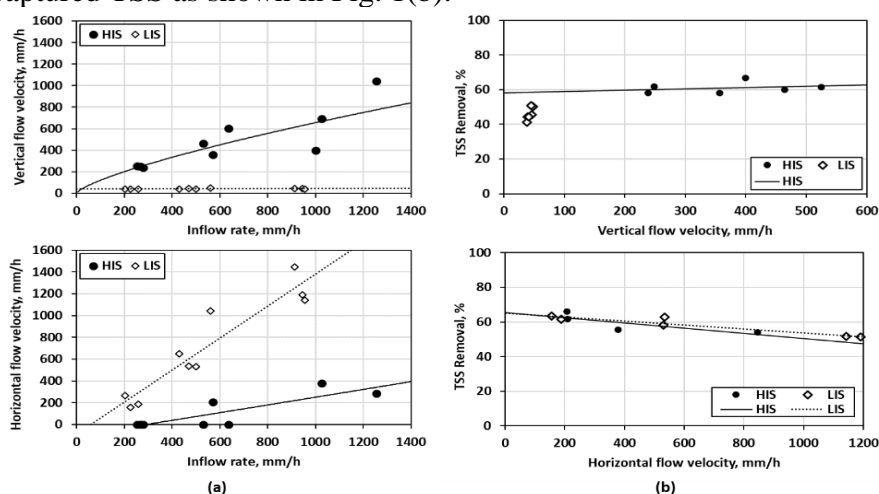
A lab-scale infiltration device with dimensions of 0.7 m × 0.2 m × 0.6 m (L × W × H) was constructed for the experiments. The media were arranged inside the tank such that the bottom layer is 10 cm of soil followed by 30 cm of crushed rock on top. The storage volume is 0.028 m<sup>3</sup> which is equivalent to a 4 mm rainfall assuming a catchment area of 7 m<sup>2</sup> which will create a facility surface area to catchment area of 0.02 according to design guidelines. Two setups were studied; one employs a uniformly-graded sandy soil representing a high infiltration system (HIS) while the other one employs a well-graded clay soil representing a low infiltration system (LIS). A semi-synthetic stormwater was used as inflow and was prepared by mixing highway sediments with municipal tap water. Inflow turbidity was maintained at 100 NTU (equivalent to 1600 mg/L) and was fed to the infiltration device at inflow rates of 250 mm/h, 500 mm/h, and 1000 mm/h. The water levels, inflow, outflow, and overflow rates were measured volumetrically from the start of outflow and every 5 min thereafter. Inflow outflow, and overflow samples were also collected for turbidity measurement and PSD analysis.

## RESULTS AND DISCUSSION

In all the experiments conducted, it was observed that as the water level rose, the infiltration rate increased. The water level above the soil created a positive hydraulic head which pushed the water unto the soil and induced an increase in infiltration rate. Thus, it can be inferred that the available depth for water storage within and above soil media can influence the infiltration rates in stormwater treatment systems. Meanwhile, runoff volume reduction data shows that as the inflow rate increased, the amount of captured runoff also increased in HIS but remained constant in LIS.

This signifies that the rainfall depth and intensity influence the amount of runoff capture more significantly in HIS than in LIS due to the limited infiltration capacity in LIS. Using the rational method, it was estimated that to achieve 100 % capture of the runoff generated by a 10 mm rainfall in Korea, at least 1 m of gavel media depth is required over low infiltration soils. On the other hand, HIS requires only 0.4 m to achieve the same runoff capture. Moreover, a drawdown time of 9 h corresponding to an infiltration rate of 200 mm/h was estimated to be the optimum condition for pollutant removal.

In Fig. 1(a), it can be seen that as the inflow rate increased, the vertical flow in LIS remained constant while the horizontal flow rapidly increased indicating that systems with silty or clay soils are more susceptible to horizontal flow especially during heavy rainfall. This induced an increase in the amount of solids escaping the treatment system through the bypass or overflow thereby decreasing the captured TSS as shown in Fig. 1(b).



**Figure 1.** Variation in vertical and horizontal flows and corresponding TSS removals.

## CONCLUSIONS AND RECOMMENDATIONS

Aside from the rainfall depth and inflow rates, the water depth can influence the infiltration rates in stormwater treatment systems such that the increase in water levels can increase the infiltration rates. High infiltration systems can capture and treat larger volumes of runoff as compared to low infiltration systems but low infiltration systems can capture and treat a consistent amount of runoff that can be infiltrated or released to the storm drains. For optimum runoff capture and pollutant removal, a minimum depth of 0.9 m and maximum infiltration rate of 200 mm/h was found to be ideal to provide enough retention time. Moreover, infiltration systems with or built above silty or clay soils are found to be more susceptible to horizontal flow. Therefore, the length of the media bed is more critical than the depth in this condition and should be considered in the design process.

## ACKNOWLEDGEMENT

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# A Novel Approach to Fault Detection & Isolation in Industrial Water Distribution Systems Using Statistical Method. A Case-Study

H. Hashim\*

\* College of Engineering and Informatics, National University of Ireland, Galway, Ireland H91 TK33 (E-mail: [h.hashim1@nuigalway.ie](mailto:h.hashim1@nuigalway.ie))

## INTRODUCTION

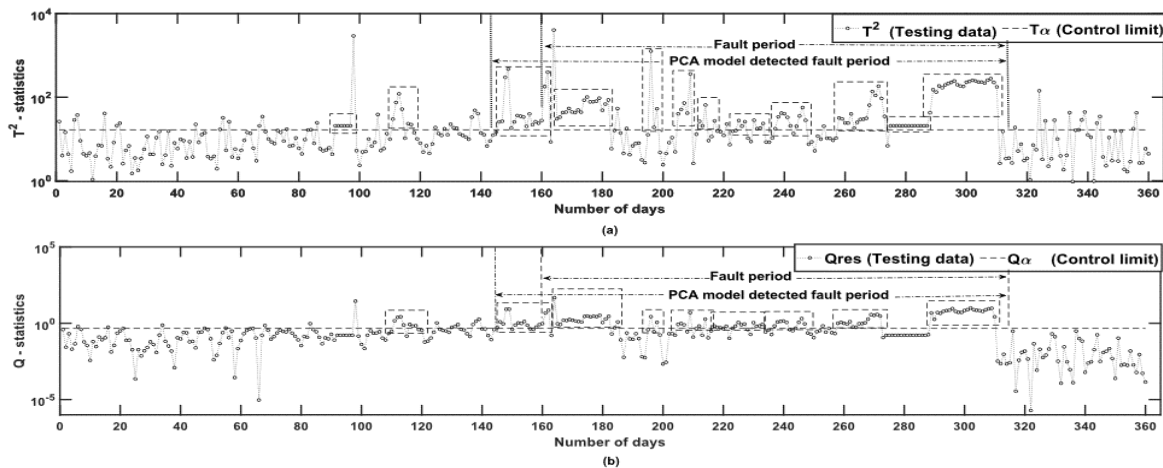
Buildings are estimated to consume 30 % of fresh water and generate approximately 30 % of the world's effluents. Thus, water efficiency in buildings is of significant concern for both water utilities and building managers. Statistical process control approaches have been explored as methods to improve models used to detect and diagnose faults of water distribution systems in buildings. Within industrial buildings water consumption patterns demonstrate significant non-stationarity (i.e. variations in statistical properties over time). Thus, distinguishing normal routine events and system alarms (e.g. non-routine events – NREs or fault alarms) is a challenge. In this study, using case-study data from a food and drinks company, the application of principal component analysis (PCA) to detect and isolate system alarms is presented. Despite the relatively limited training data available, the proposed model performed well in detecting meaningful fault alarms. Such a strategy could provide a robust method that can be applied to buildings to reduce inefficient water use.

## MATERIALS AND METHODS

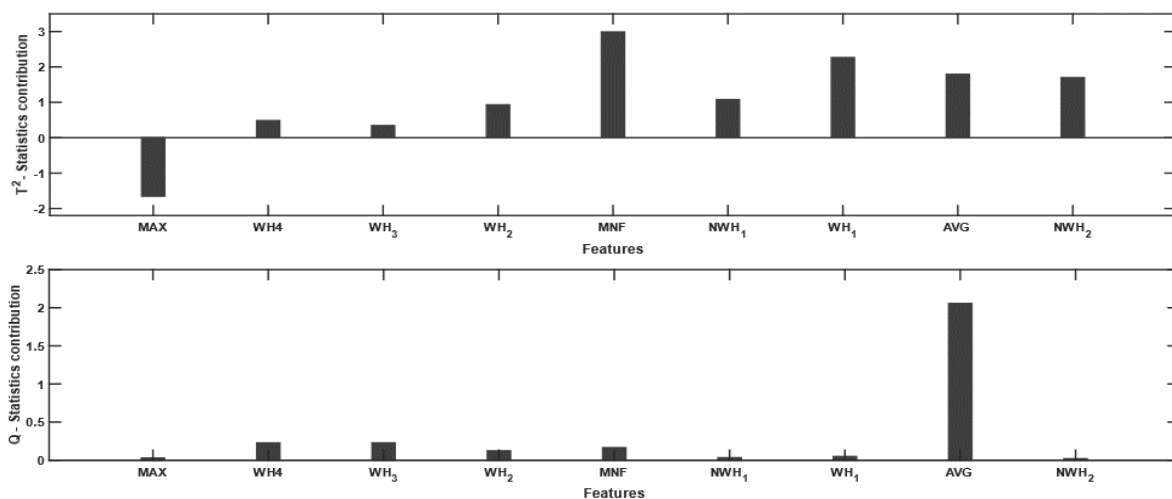
Firstly, the general characteristics of water consumption patterns was analysed within a building using data from water meters. Model training was completed using data from a 6-month period, followed by validation against data from a subsequent 12-month period. Undesired variations in consumption were determined by using a principal component analysis (PCA) model to detect the extent and nature of potential faults. PCA is a well-known technique for unsupervised data analysis which utilises the projection of data in a reduced space, as is often employed in statistical process monitoring and fault detection (Abdi and Williams, 2010; Harrou *et al.*, 2013). Control limits for faults are developed based on the duration of the non-routine event which in turn was based on historical information such as site occupancy and typical events occurring on-site (such as; scheduled cleaning activities, transporting vehicle washing etc.). In the fault isolation stage of FDD, a contribution analysis was performed to identify the feature(s) that caused the system alarm.

## RESULTS AND DISCUSSION

Several data samples were spotted beyond the control limit and can be labelled as system alarms (Fig. 1). Furthermore, analysis of the detected system alarms identified their features – presented as contribution plots (2). Although contribution plots may not be able to provide an unequivocal system alarm diagnosis, they can assist building managers or practitioners in identifying the features or group of features responsible for system alarms. The results of the test exhibited a good performance with a limited amount of data in detecting fault alarms and identifying features which caused system alarms.



**Figure 1.** The time evolution of  $T^2$  – statistics (a) and  $Q$  – statistics on a semi-logarithmic scale for the testing data (b).



**Figure 2.** Hotelling's  $T^2$  – statistics contribution plot for system alarms (a),  $Q$  – statistics contribution plot for system alarms (b).

## CONTRIBUTION OF THE WORK

In this study, a PCA method is applied for detecting and isolating system alarms in WDSs. The proposed methodology can improve performance monitoring of WDS by identifying unusual water consumption at their early stage for building managers, which conventional fault detection method lack in. This will reduce fault identification times, avoiding extra costs and emergency situations. The development of an industrially reliable FDI scheme for WDS in industry settings is a key contribution in helping make such facilities more sustainable.

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# Long-Term Future Impact of Runoff Changes on Hydrotechnical Structures in Low-Land Rivers

D. Jakimavičius\*, J. Kriaučiūnienė\*, and D. Šarauskienė\*

\* Laboratory of Hydrology, Lithuanian Energy Institute, Breslaujos st. 3, LT–444003 Kaunas, Lithuania (E-mails: [darius.jakimavicius@lei.lt](mailto:darius.jakimavicius@lei.lt); [jurate.kriauciuniene@lei.lt](mailto:jurate.kriauciuniene@lei.lt); [diana.sarauskiene@lei.lt](mailto:diana.sarauskiene@lei.lt))

## INTRODUCTION

As energy demand grows, humanity is increasingly turning to alternative energy sources, such as hydropower. Future climate change will affect river runoff and thus the operation and production of hydropower. To identify these changes, five hydropower plants (HPP) (Skuodas, Balskai, Marijampolė II, Akmeniai, and Kavarskas) built on the low-land rivers (Bartuva, Jūra, Šešupė, Lėvuo, and Šventoji) were selected. This research aimed to evaluate a long-term future impact of runoff changes on the operation of hydrotechnical structures in low-land rivers using the hydrometeorological database, regional climate models, RCP scenarios, and hydrological modelling.

## METHODS AND MATERIALS

The primary indicator that determines the operating regime of hydropower plants is the river runoff and its seasonal distribution. To assess the impact of the changed hydrological regime on hydrotechnical structures at the end of the 21<sup>st</sup> century (2081–2100), runoff projections of selected rivers were made. A semi-distributed conceptual HBV model was applied for hydrological modelling. The main HBV equation is (SMHI, 2005):

$$P - E - Q = \frac{d}{dt}[SP + SM + UZ + LZ + V] \quad (1)$$

where  $P$  – precipitation,  $E$  – evapotranspiration,  $Q$  – runoff,  $SP$  – snow pack,  $UZ$  – upper groundwater zone,  $LZ$  – lower groundwater zone,  $V$  – lake or dam volume.

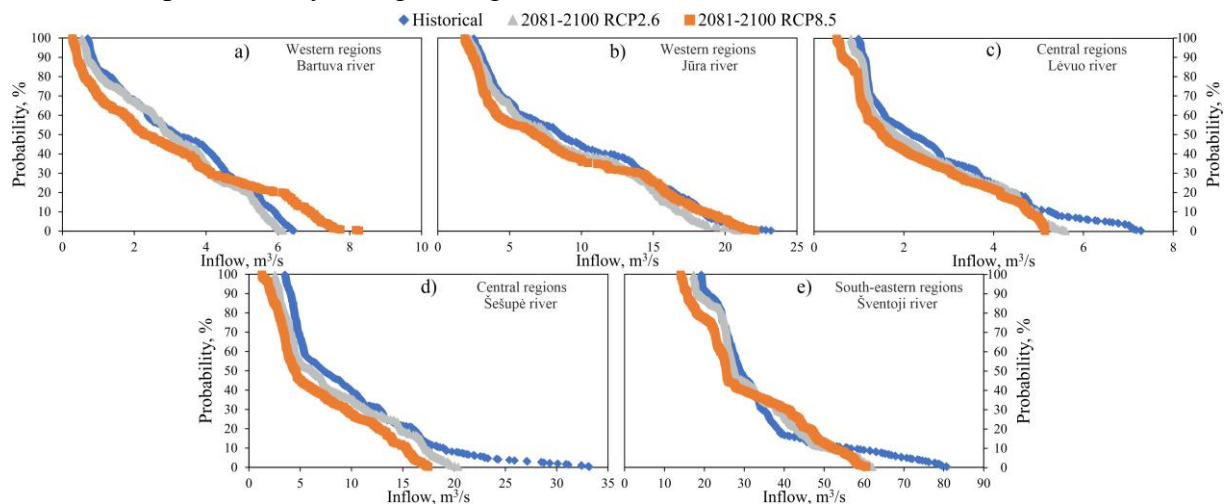
River runoff projections were estimated using meteorological data of ICHEC-EC-EARTH, MOHC-HadGEM2-ES, and MPI-M-MPI-ESM-LR regional models according to optimistic (RCP2.6) and pessimistic (RCP8.5) scenarios. The adaptation of regional climate model data for Lithuanian rivers catchments was performed using the model output statistic method – quantile mapping (QM).

## RESULTS

The runoff projections showed downward trends in river runoff at the end of the century. These trends differed for individual rivers because of the different physical geographical conditions of hydrological regions (western, central and south-eastern) to which they belonged. The future changes in river runoff due to climate change are going to affect the HPP exploitation. In the study of runoff changes, it was decided to analyze how the discharges of different probabilities: 95 % ( $Q_{95\%}$ , frequent), 50 % ( $Q_{50\%}$ , medium) and 5 % ( $Q_{5\%}$ , rare) into HPP reservoirs will change. The projections of the discharges of such probabilities are very relevant to HPP managers. The knowledge on discharges of high probability helps to organize HPP work during the dry season. Knowing the average probability discharge makes it possible to plan the average amount of energy produced by a hydropower plant per year. Meanwhile, the low probability discharge can be used to regulate the HPP operation mode during floods.

Water discharge changes were analysed comparing the historical (reference) and far future (2081–

2100) periods. It was estimated that  $Q_{95\%}$  will decrease from 5.1 % to 52 % in the western region, from 13.3 % to 48.6 % in the central region, and from 8.9 % to 24 % in the south-eastern hydrological region of Lithuania. The biggest negative changes of  $Q_{50\%}$  are expected in the central hydrological region (14.1–37.5 %), slightly negative changes – in the western region (4.3–27.8 %) and the smallest changes - in the south-eastern hydrological region (4.6–12.1 %) compared to the reference period (Fig. 1). Projections of  $Q_{5\%}$  revealed that, in the western hydrological region, this discharge will be from 3.1 % to 17.5 % higher, and in the central and south-eastern hydrological regions from 16.1 % to 30.3 % lower than in the reference period (Fig. 1). The increase of  $Q_{5\%}$  in rivers in the western hydrological region can be explained as the response of physical geographical conditions to climatic factors under the worst-case (RCP8.5) scenario. The projected decline of  $Q_{5\%}$  in the far future depends on the selected climate scenario and the conditions of river runoff formation in a particular hydrological region.



**Figure 1.** Projections of different probability inflow to the reservoirs of: a) Skuodas HPP, b) Balskai HPP, c) Akmeniai HPP, d) Marijampolė II PHH, and e) Kavarskas HPP.

## CONCLUSIONS

1. In all hydrological regions, dry year discharge ( $Q_{95\%}$ ) to HPP reservoirs would decrease the most (up to 52 %). The average discharge ( $Q_{50\%}$ ) may decline to 37.5 % in the far future. The floods of 5 % probability ( $Q_{5\%}$ ) will increase to 17.5 % in the western hydrological region; while in the central and south-eastern hydrological regions they will decrease to 29.4 % and 12.1 %, respectively, compared to the reference period.
2. At the end of the century, due to the decrease in river runoff during distinct seasons, HPP will face energy production challenges. The most difficult operating conditions will be during the dry season when the 95 % probability discharge will decline by almost half. The HPP operation regime will still have to maintain at least the minimum living conditions for aquatic communities. In the future, due to the decrease in river runoff, a shrinkage in electricity production of up to 52 % is projected, depending on the physical and geographical conditions of the river catchments and the selected climate scenario.

## FUNDING

This research has received funding from the Research Council of Lithuania (LMTLT), agreement No. S-SIT-20-3.

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## Analysis of Geo-Ecological Risks of Groundwater Vulnerability within the Pripyat River Basin (Ukraine)

D. V. Kasiyanchuk\*, M. M. Tymkiv\*, and L. I. Davybida\*

\* Department of geotechnical safety and geoinformatics, Ivano-Frankivsk National Technical University of Oil and Gas, Karpatska, 15, Ivano-Frankivsk, Ukraine  
(E-mails: *dima\_kasiyanchuk@ukr.net; maritymkiv@gmail.com; davybida61085@gmail.com*)

### GENERAL CHARACTERISTICS OF THE STUDY AREA

The issue of groundwater contamination within the Pripyat river basin, which is a cross-border area situated in the northern part of Ukraine, is considered in the research.

The study area is characterized by a prolonged spring seasonal flood and short summer drought season. The depth of the groundwater table is less than 1 m to the earth surface due to the predominance of precipitation over evapotranspiration. The territory of the Pripyat basin is composed mainly of marls, chalk and sandstones, which form hilly elevations. A large part of the lowland area was formed under the influence of continental glaciation and therefore composed of water-glacial and river sands. The surface is shallow, flat, but complicated by moraine hills and dunes. The climate is moderately continental, the average annual precipitation is 640–700 mm. The groundwater chemical composition of the basin is dominated by  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{4-}$ , and by  $\text{Cl}^-$ ,  $\text{SO}_4^{4-}$ ,  $\text{Na}^+$  in the central part of the study area. The average mineralization of water is  $1.0 \text{ g/dm}^3$ , pH level – 5.5–9.5.

The significant part of the Pripyat river basin is under state protection, but the environmental situation remains critical. The main reasons are the maintenance of intensive water management, and a significant reduction in the self-reproducing capacity of rivers and depletion of water resources as a consequence, pollution of water bodies by wastewater, large-scale radiation pollution of many river basins within the Chernobyl, Rivne and Khmelnytsky NPP zones, lack of automated permanent hydrogeological monitoring network; illegal amber mining, lack of control over the solid waste landfill locations, lack of control over the observance of sanitary norms at the enterprises within the territory of the basin (Ruban, 2004).

### RISK CALCULATION

Geo-ecological risk should be understood as a quantitative measure of danger. It can be measured in probabilistic quantities or the form of mathematical expectation of damage (Levoniuk, 2018). The degree of impact of landfills for solid waste, amber mining, wetlands, as well as risk assessment of life safety, taking into account the population of the territory of each sub-basin were determined to assess the overall ecological status of the Pripyat river basin.

The population load of the sub-basin can be calculated:

$$r_p = \frac{n / N}{s / S} \quad (1)$$

where  $n$  – population of the sub-basin area,  $N$  – total population of the basin area;  $s$  – the sub-basin area;  $S$  – the basin area.

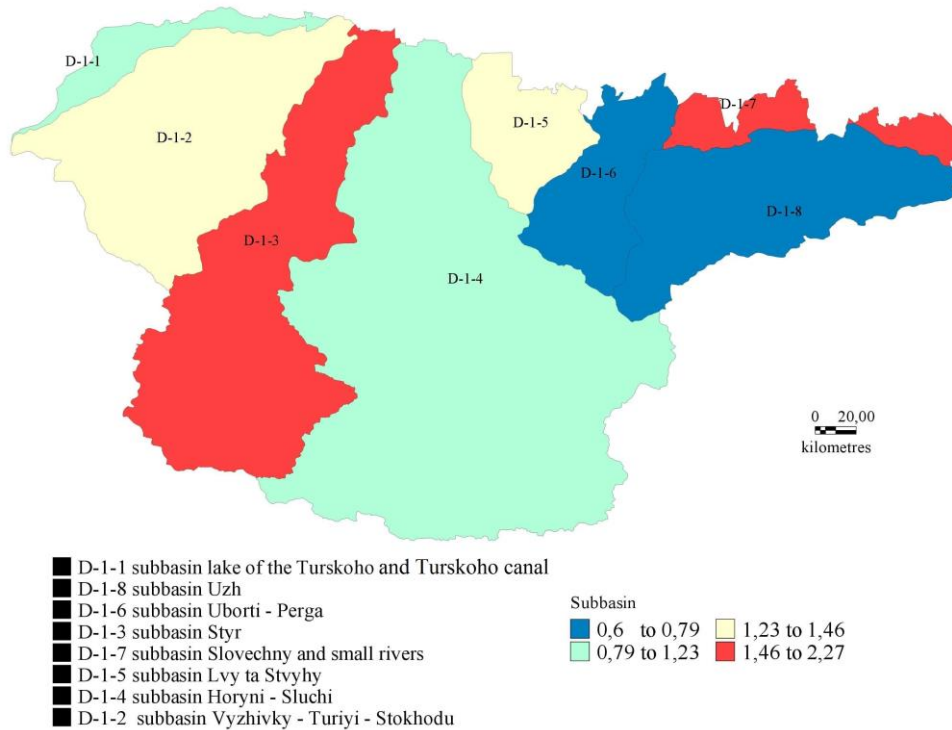
The spatial damage of the sub-basin can be calculated:

$$r = \frac{f_s}{S} \quad (2)$$

$$R_i = \sum_{i=1}^n r_i \quad (3)$$

where  $n$  – the number of factors selected to calculate the risk,  $r_i$  – the risk of a single factor.

The map of geo-ecological risks for the study area was created in the GIS environment based on the calculated values of the spatial damage. (Fig. 1). Obviously, the territory of sub-basins D-1-3 and D-1-7 are the most affected and sub-basins D-1-6 and D-1-8 are the least affected.



**Figure 1.** Map of geo-ecological risks of groundwater vulnerability within the Pripjat River Basin.

## CONCLUSIONS

Systematic analysis of existing methods and algorithms for risk assessment allowed for the first time to offer a spatio-temporal approach to the calculation of the geo-ecological risks because of man-made load on the underground hydrosphere. This approach allows to take into account the spatio-temporal probability of the influence of selected factors (wetlands, amber mining, hazardous man-made structures) on groundwater and determine the part of total pollution area during the study period as an indicator of maximum areal damage.

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# Preliminary Application of Citizen Science for Lake Water Quality Monitoring

E. Kendir Çakmak\*, B. Anbaroğlu\*\*, and A. Uğurlu\*

\* Department of Environmental Engineering, Hacettepe University, Beytepe, Ankara, Turkey  
(E-mails: [ecekendir@hacettepe.edu.tr](mailto:ecekendir@hacettepe.edu.tr); [ugurlu@hacettepe.edu.tr](mailto:ugurlu@hacettepe.edu.tr))

\*\* Department of Geomatics Engineering, Hacettepe University, Beytepe, Ankara, Turkey  
(E-mail: [banbar@hacettepe.edu.tr](mailto:banbar@hacettepe.edu.tr))

## INTRODUCTION

Water quality monitoring is one of the fundamental tools for sustainable management of water sources. For monitoring purposes, various analytical methods are being used which are time consuming, costly and laborious (Becken *et al.*, 2019). In the recent years, ‘citizen science’ approach has emerged as scientific discipline, which is defined as the involvement of citizens to scientific projects as volunteers. Citizen science provides collection of huge data in an easier, faster, and cheaper way. Moreover, raising of environmental awareness among citizens is a favourable outcome of citizen science studies (European Commission, 2013; Cappa *et al.*, 2018).

The present study aimed to perform a citizen science approach to monitor water quality in a lake, Uzungöl, which is located in northern of Turkey. Uzungöl has been a special environmental protection area since 2004 and water quality monitoring is a key factor for sustainable water management in the region. For this purpose, the citizen science-based approach was performed with elementary school students as volunteers to monitor water quality parameters including pH, temperature, and nutrients (phosphate and nitrate) for five months.

## METHODOLOGY

Uzungöl is an open lake with an attitude of 1090 m and surface area of 85 ha. There are fishing and agricultural activities in the lake and the most important activity is identified as tourism (Ministry of Environment and Urbanization, 2013). Water quality of the lake is under pressure due to sewage systems, fish farms, erosion, fertilizers and pesticides (Verep *et al.*, 2002). In this study, citizen science approach was investigated to monitor water quality parameters including pH, temperature and nutrients with contribution of Uzungöl Elementary school students as volunteers. The selection of volunteers was based on their high level of interest and active participation. A one-day training course for volunteers including both theoretical (lake ecosystem, water quality) and practical (sampling and analysis) applications was provided. Then, volunteers were asked to analyse selected water quality parameters between June and December (2018) at four sampling points around the lake. Analysis kit bags were given to volunteers to measure water quality parameters periodically. Some of the water quality parameters were also monitored with a multiparameter device (pH and temperature) in June and October (2018). A mobile application was also developed to provide continuous data flow from citizens and storage of the data.

## RESULTS AND CONCLUSIONS

According to the data collected by volunteers, temperature values ranged from 8.5 °C to 15 °C between October and December. The temperature range was also measured as 13.0 °C to 15.6 °C in October with multiparameter. The values of pH ranges were observed between 2.0 and 8.5 by volunteers, while pH values were measured around 7 in June and October by multiparameter. The

low pH values could be related to subjective errors by volunteers or wastewater discharge. So, pH values should be monitored for a long time to specify the reasons. Another important parameter for water quality in the lake is the amount of nutrients. The nitrate values analysed by citizens were observed below 2.5 ppm. Phosphate values were observed between 0.5–5.0 ppm by citizens and these values can be classified as higher for lake water quality. High phosphate concentrations could be related to sediment dredging operations carried out at the beginning of 2018 and resuspension of phosphate in the water column, intensive tourism and domestic activities or subjective errors during analysis.

In conclusion, this study showed that citizen science approach has potential to be used in water quality monitoring and it is possible to collect data with low cost and labor. The motivation of the volunteers provided continuity of the project and data collection. However, the reliability of the data should be questioned due to low number of collected data and possible measurement errors by volunteers. Involvement of high number of volunteers and more precise measurement methods can increase the reliability of the data. Furthermore, volunteer data should be validated with laboratory analysis. So, future citizen-based water quality monitoring studies should focus on participation of wider volunteer groups with high number and quality of the data.

#### ACKNOWLEDGEMENTS

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# Microbiological Quality, Ecological Status, and Potential Sources of Contamination of the River Water

I. Kljujev\*, J. Jovičić-Petrović\*, B. Lalević\*, V. Karličić\*, I. Todorović\*, M. Prijepoljac\*, and V. Raičević\*

\* Department of Microbial Ecology, Faculty of Agriculture, University in Belgrade, Nemanjina 6, 11080 Zemun-Belgrade, Serbia (E-mail: [ikljujev@agrif.bg.ac.rs](mailto:ikljujev@agrif.bg.ac.rs))

## INTRODUCTION

Surface water contamination becomes a raising problem due to different anthropogenic factors such as agriculture, industry, waste landfills, and wastewater effluents. Microbiological contamination with fecal bacteria is considered as a crucial issue especially in the Danube basin (Páll *et al.*, 2013) representing the sanitary risk when water is used for drinking, recreation, and irrigation. The monitoring of the river water quality in Serbia is performed on the regular basis, but only larger watercourses are included in the monitoring programme (Agency for Environmental Protection, 2019). On the other side, small rivers are also exposed to wastewater influents, pollution from agricultural activities, as well as raising human influence on the river flow (dam building). The differences in the number of pathogenic bacteria in river waters depend on some factors like stream size, year season, water level, degree of eutrophication, water tributaries and geographical area as well as the ability of a watercourse to self-clean (Augustyn *et al.*, 2016). This research aimed to analyze the microbiological quality and ecological status of the water of the small river Ribnica in Western Serbia. Ribnica is a 22 km long tributary of Kolubara. The upper part of the river flow is surrounded by forests, agricultural fields, and small farms. One part of the upstream flow belongs to the Natural monument “Ribnica”, a biodiversity-rich area. Downstream, the river flows through Mionica, a small town where its water quality becomes endangered by communal wastewater, as well as landfills in the river surrounding.

Coliform bacteria, *E. coli*, and intestinal enterococci are commonly used indicators of fecal pollution, and microbiological monitoring of water quality is mainly based on those parameters. The microbiological quality of river water was estimated by the presence of total coliforms, fecal coliforms, and *E. coli*. Additional determination of parameters for water ecological status (a number of oligotrophs and heterotrophs microorganisms and autopurification index) are also included in the present research.

## METHODOLOGY

Sampling was done twice in 2019 and 2020 at four locations.

**Table 1.** Sampling sites.

Sample label	GPS location	Description
1	N 44° 13' 47.712" E 20° 6' 0.575"	After small dam in Pastric village
2	N 44° 12' 19.008" E 20° 5' 34.547"	Natural monument “Ribnica”
3	N 44° 13' 32.196" E 20° 5' 56.4"	Before first farms in Pastric village
4	N 44° 15' 41.148" E 20° 5' 11.4"	Downstream from the Mionica center

Determination of *E. coli* and coliform bacteria was done by Colilert (IDEXX Laboratories, USA). Enterococci were enumerated using Enterolert method (IDEXX Laboratories, USA). The number of oligotrophs and heterotrophs was done by serial dilution method and incubation on selective

nutrient media. The index of autoperification was calculated as oligotrophs/heterotrophs ratio.

## RESULTS

Our results show that the greatest pollution comes in the river after Mionica center, sampling site 4. The reason for this is waste and sewage water pouring into the river without cleaning treatment. The extremely large number of fecal *E. coli* indicates the presence of fecal matter in water which could be a potential risk for human health if this water is used for irrigation of crops or recreation. Also, autoperification index of water in this location indicates very poor self-purification potential which means that this water needs human help for achieving good ecological status. The water on the other three sampling locations (sites 1, 2, 3) also shows fecal pollution.

**Table 2.** The number of coliforms, *E. Coli*, *Enterococcus* and autoperification index in water samples.

	Sampling December 2019				Sampling November 2020			
	1.	2.	3.	4.	1.	2.	3.	4.
Total coliforms (MPN / 100 mL)	396.8	129.2	28.5	>1011.2	285	602	602	>1011.2
Fecal coliforms (MPN / 100 mL)	70	86	3	>1011.2	172	361	249	>1011.2
<i>E. coli</i> (MPN / 100 mL)	70	131.4	20.1	>1011.2	102	54	93	>1011.2
<i>Enterococcus</i> spp. (MPN / 100 mL)	54.5	35	1	>1011.2	5	25	17	>1011.2
AUTOPURIFICATION INDEX	0	0.17	7.43	0.29	0.005	0.000	0.004	0.2

## CONCLUSION

Development of the river water monitoring strategy is one of the main public interests since water quality represents the main concern for human and environmental health. Water quality of small rivers with natural resources and human settlements in their basin, should be monitored in order to estimate the main risk factors causing both local and global pollution. Regular monitoring and analyses of microbiological contamination and ecosystem disturbances should be important input data for public policies and strategic planning in the area of wastewater management, hydraulic engineering, and agricultural management.

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# Hydrological Time-Series Modeling by MLR, MARS, SVR and RF Techniques

P. Kumar\* and A. K. Singh\*

\* Department of Soil and Water Conservation Engineering, GBPUA&T Pantnagar, 263145, India  
(E-mail: [pankaj591@gmail.com](mailto:pankaj591@gmail.com))

\*\* Department of Soil and Water Conservation Engineering, GBPUA&T Pantnagar, 263145, India  
(E-mail: [avi4913@gmail.com](mailto:avi4913@gmail.com))

## INTRODUCTION

Techniques for quantifying evaporation loss need to be strengthened to meet essential needs, such as water requirements for agricultural uses, reservoir operations, domestic use, industrial use, and commercial purposes. An accurate and precise assessment of evaporation is essential for managing, planning of water resources. Evaporation is a process that is nonlinear, unstable, and very complex. (Tezel and Buyukyildiz, 2016). Data processing methods such as random forest (RF), adaptive regression splines(MARS), support vector machines (SVM), have been used widely in hydrology and broader geosciences such as evaporation estimation, streamflow modeling, solar radiation sediment modeling, geoscience, etc. (Bhardwaj *et al.*, 2020; Yaseen *et al.*, 2020).

The paper explores and compares the estimation of pan evaporation of Ranichauri, Uttarakhand, India, using four approaches: (1) Multiple linear regression; (2) Multivariate adaptive regression splines approach (MARS); (3) Random Forest (RF); (4) Support Vector Machine (SVM). The study also examines the association of climatic variables with pan evaporation and selecting the most suitable model for pan evaporation estimation. The adequacy of developed models was examined by statistical indices: root mean square error (RMSE), coefficient of determination ( $R^2$ ), and Nash Sutcliffe coefficient of efficiency (NSE) between observed and estimated pan evaporation values.

## MATERIAL AND METHODS

### Description of the Study Area and Data

The weekly meteorological variables as maximum temperature ( $T_{max}$ ), minimum temperature ( $T_{min}$ ), wind speed ( $W$ ), maximum relative humidity ( $Rh_1$ ), minimum relative humidity ( $Rh_{min}$ ), sunshine hours ( $S_n$ ) and evaporation ( $E$ ) were obtained from the College of Forestry of Uttarakhand University of Horticulture and Forestry from from January 2014 to December 2017. Out of the 4-year total data, 3-year data were used for calibration (2014 to 2016), and 1-year remaining data were used for validation (2017).

### Modeling daily pan evaporation

To avoid the models' overfitting and minimize the complications in the prediction, the Gamma test (GT) used to eliminate the unnecessary input parameters that have an irrelevant role in predicting the output. In the case of the MARS model, for comparison of subsets of the model, the value of generalized cross-validation (GCV) for training and testing was found to be 0.273 and 0.636. In the SVR model, the radial basis kernel function was implemented with kernel parameter gamma of 1.0, moreover, convergence epsilon was 0.001. For RF model, the number of variables randomly sampled as candidates at each split was chosen 3 with 100 numbers of trees. The results of training and testing periods of the MLR, MARS, RF, and SVM models in estimating pan evaporation for the Ranichauri station are shown in Table 1.

**Table 1.** Comparison of the various models by using statistical indices.

Models	Training			Testing		
	RMSE	NSE	$R^2$	RMSE	NSE	$R^2$
MLR	0.53	0.800	0.84	0.67	0.59	0.82
SVR	0.33	0.940	0.94	0.67	0.64	0.88
MARS	0.39	0.971	0.91	0.68	0.52	0.87
RF	0.22	0.972	0.98	0.73	0.47	0.86

It can be apprehended from Table 1 that all model's performance is not consistent in the testing case. The RF model outperformed in the training period, and it could not generalize results for the testing period. However, the MLR model is generally considered the simplest model has done considerably well for the RMSE and NSE statistics during the testing period. Perhaps these uncertainties in the results obtained were due to data division, input uncertainty, and model parameters optimization.

As a final comment, the results obtained suggested that the accuracy of MLR, MARS, SVR and RF techniques was adequate when using maximum temperature ( $T_{\max}$ ), maximum relative humidity ( $Rh_{\max}$ ), maximum relative humidity ( $Rh_{\min}$ ), wind speed ( $W$ ), sunshine hours ( $S$ ) meteorological parameters. In addition, while for Ranichauri station, different machine learning methods' accuracy varies, and SVR output was better than other models examined.

## CONCLUSION

In climatic explanatory variables, in particular, the input combination of the maximum temperature ( $T_{\max}$ ), maximum relative humidity ( $Rh_{\max}$ ), maximum relative humidity ( $Rh_{\min}$ ), wind speed ( $W$ ), sunshine hours ( $S$ ) has significant influence on pan evaporation, thus chosen as inputs for models. All four approaches can estimate pan evaporation accurately ( $R^2 > 0.82$ ). The performance wise ranking of models was done as SVR, MARS, MLR, and RF. Among the four models, the SVR model outperformed in testing periods and also performed good in the training period. Consequently, it can be surmised that the SVR model is delivers the strong potential for estimating pan evaporation at Ranichauri.

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# Deep Learning Identifies Leak in Pipeline System Using Transient Frequency Response

Z. Liao\*, H. Yan\*, Z. Tang\*\*, X. Chu\*\*, and T. Tao\*

\* College of Environmental Science and Engineering, Tongji University, Yangpu District, Shanghai, China (E-mails: [zhqlzy@tongji.edu.cn](mailto:zhqlzy@tongji.edu.cn); [hxyan@tongji.edu.cn](mailto:hxyan@tongji.edu.cn); [taotao@tongji.edu.cn](mailto:taotao@tongji.edu.cn))

\*\* Department of Computer Science, Hong Kong Baptist University, Kowloon, Hong Kong, China (E-mails: [zhtang@comp.hkbu.edu.hk](mailto:zhtang@comp.hkbu.edu.hk); [chxw@comp.hkbu.edu.hk](mailto:chxw@comp.hkbu.edu.hk))

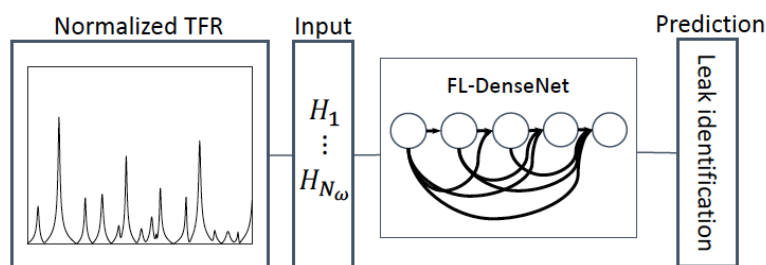
## INTRODUCTION

Transient frequency response (TFR) has been used as a probe to identify leak in pipelines for the past two decades (Lee, 2005; Duan, 2016). However, these techniques require a perfectly calibrated model of the pipelines, which confines their further application. Essentially, the identification of leak via pipeline TFR lies in the field of feature recognition, which is the forte of deep learning (DL). Since DL has shown great success in complex feature extraction, it is promising to achieve leak identification using TFR against model parameter uncertainties.

This work proposed a DL-based framework to identify a leak in a pipeline system and decide the sub-pipe it belongs to. To efficiently generate TRF in the pipeline system, extended version of TFR equations in (Vítkovský, 2010) is derived to take leak in to consideration. The robustness of the proposed framework is confirmed in a hypothetical case study with hydraulic parameter uncertainties.

## METHODOLOGY

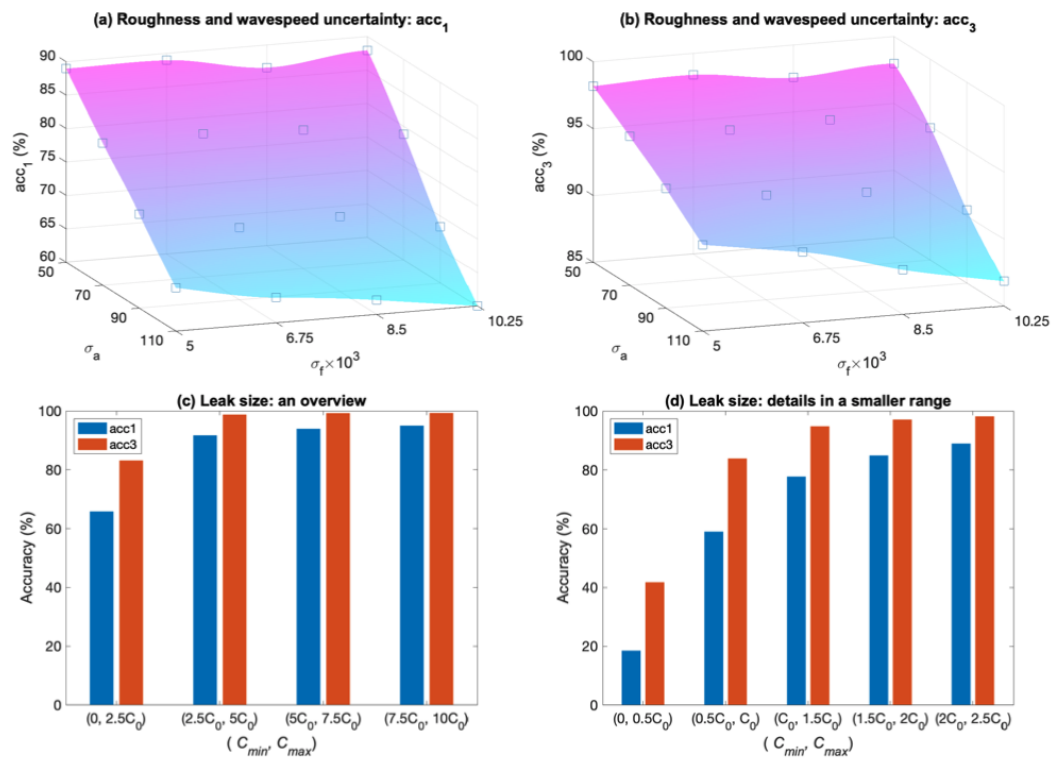
The DL-based leak identification scheme is shown in Fig. 1. Firstly, a transient is injected into the field pipeline system to extract TFR. Then based on the roughly calibrated model, training data is generated through the extended TFR equations and preprocessed. These data are fed to train FL-DenseNet proposed in (Zhou, 2019). Finally, the preprocessed field data is fed for leak identification.



**Figure 1.** Scheme of the leak identification framework.

## CASE STUDY AND RESULTS

The leak identification framework is applied to a hypothetical pipeline system that consists of 12 pipes, 7 junctions, 1 reservoir and 1 downstream valve. The downstream valve is used to inject transients. Both training and testing data set are generated with the extended TFR equations. For each sample in the data set, friction factors and transient wave speeds are disturbed by natural distributed values, and the leak size is randomly determined in certain variation ranges.



**Figure 2.** The performance of the proposed leak identification framework with different parameters: (a, b) joint effect pipe friction and wave speed; (c, d) the effect of leak size.

The performance of the proposed framework is tested under different circumstances as sensitivity analysis. The uncertainties of pipe frictions and wave speeds are considered in a joint manner. While the influence of lead size is separately considered. The results are shown in Fig. 2.  $acc_i$  means the proportion of the test cases that the leak pipe rest in the top  $i$  pipes predicted by FL-DenseNet.

As it is shown in Fig. 2(a) and (b), accuracy decreases as the uncertainties of the pipe friction ( $\sigma_f$ ) and wave speed ( $\sigma_a$ ) increases. In the worst case, the uncertainties of the parameters are considerably large.  $acc_1$  and  $acc_3$  are 60.02 % and 86.85 % respectively and still give valuable predictions. Fig. 2(c) and (d) show that accuracy increases with larger  $(C_{min}, C_{max})$ , i.e. larger leak flow rate. As leak size small as  $(C_0, 1.5C_0)$ , which corresponds to 1.0–1.5 % of the total flow,  $acc_1$  and  $acc_3$  are 77.78 % and 94.81 %. These results show the robustness of the framework against the physical uncertainties.

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# Investigation of Crucial Influencing Factors for Biodegradation of Microplastics by Taguchi Method

M. Miloloža\*, K. Bule\*\*, A. Badurina-Petričević\*, L. Anzulović\*, I. Jazbišek\*, V. Prevarić\*\*, M. Sigurnjak Bureš\*\*\*, M. Cvetnić\*\*, M. Markić\*\*\*\*, T. Bolanča\*\*, Š. Ukić\*\*, V. Ocelić Bulatović\*\*\*\*, and D. Kučić Grgić\*

\* Faculty of Chemical Engineering and Technology, Department of Industrial Ecology, University of Zagreb, 19 Trg Marka Marulića, Zagreb 10000, Croatia (E-mails: [miloloza@fkit.hr](mailto:miloloza@fkit.hr); [dkucic@fkit.hr](mailto:dkucic@fkit.hr))

\*\* Faculty of Chemical Engineering and Technology, Department of Analytical Chemistry, University of Zagreb, 20 Trg Marka Marulića, Zagreb 10000, Croatia (E-mails: [kbule@fkit.hr](mailto:kbule@fkit.hr); [vprevaric@fkit.hr](mailto:vprevaric@fkit.hr); [mcvetnic@fkit.hr](mailto:mcvetnic@fkit.hr); [tbolanca@fkit.hr](mailto:tbolanca@fkit.hr); [sukic@fkit.hr](mailto:sukic@fkit.hr))

\*\*\* Faculty of Chemical Engineering and Technology, Department of General and Inorganic Chemistry, University of Zagreb, 19 Trg Marka Marulića, Zagreb 10000, Croatia (E-mail: [marijas@fkit.hr](mailto:marijas@fkit.hr))

\*\*\*\* Faculty of Chemical Engineering and Technology, Department of Measurement and Automatic Process Control, University of Zagreb, 16 Savska cesta, Zagreb 10000, Croatia (E-mail: [mmarkic@fkit.hr](mailto:mmarkic@fkit.hr))

\*\*\*\*\* Faculty of Metallurgy, Laboratory of Industrial Ecology, University of Zagreb, 3 Aleja narodnih heroja, Sisak 44000, Croatia (E-mail: [vocelicbu@simet.hr](mailto:vocelicbu@simet.hr))

## INTRODUCTION

Microplastics, MP, particles at size lower than 5 mm, represent global environmental problem. They are present and abundant in all environmental systems (Li *et al.*, 2018), even in food intended for human consumption (Liebezeit and Liebezeit, 2013). MPs are cause of concern due to their recalcitrant structure and low biodegradability in the environment; and MPs negative high impact on aquatic organisms through bioaccumulation and biomagnification (Miller *et al.*, 2020). Due to this, further research about impact of MP particles on aquatic organisms is necessary, as well as finding adequate solutions for removal of MPs from the environment. A lot of different processes were investigated in mentioned purposes, and potential solutions are biological processes. Bioremediation, as an economical, efficient and environmentally friendly process (Vidali, 2001), involves the use of microorganisms in the purpose of removing pollutants from the environment. Various microorganisms can be used for MPs removal and the most investigated are bacteria, molds, and yeasts (Kale *et al.*, 2015). A lot of factors are influential in biodegradation processes, abiotic (pH-value, concentration of dissolved oxygen, moisture content, temperature, salinity and presence or absence of UV radiation), biotic factors (type and number of microorganisms, extracellular enzymes, biosurfactants) and properties of MP particles (structure, molecular weight, hydrophobicity, functional groups etc.) (Artham and Doble, 2008).

## MATERIALS AND METHODS

In this study, by bacterium *Bacillus cereus* biodegradation of polystyrene (PS) and polyvinyl chloride (PVC) particles were investigated. According to Taguchi design of experiments, crucial factors that influence on biodegradation process were performed. The experiments were conducted in Erlenmeyer flasks volume of 250 mL, with working volume of 100 mL, during 45 days. It was investigated 7 factors at 2 levels (minimal and maximal value of each factor), that are listed in Table 1: pH-value, temperature, size of MP particles, concentration of MP,  $\gamma_{MP}$ , agitation speed, optical density of bacterial suspension, OD, and addition of glucose,  $\gamma_{GLU}$ . During the experiment, Colony forming units, CFU, total carbon, TC, total organic carbon, TOC, inorganic carbon, IC,

ionic composition by ion chromatography and degradation products in aqueous phase by liquid chromatography were determined.

**Table 1.** Factors and levels evaluated in Taguchi L<sub>8</sub> Orthogonal Array.

	Factor	Level 1	Level 2
A	pH-value / –	6	8
B	<i>T</i> / °C	15	25
C	Size of MP / μm	500–700	<300
D	$\gamma_{MP}$ / mg/L	10	1000
E	Agitation speed / rpm	100	200
F	OD / –	0.1	0.5
G	$\gamma_{GLU}$ / g/L	0.0	0.1

## RESULTS AND DISCUSSION

In this research, changes of pH-value, temperature, size of MP particles,  $\gamma_{MP}$ , agitation speed, OD, and  $\gamma_{GLU}$  were investigated. By Taguchi design of experiments, key process parameters for PS and PVC biodegradation by *Bacillus cereus* were determined using the number of living cells of bacterium, CFU, as response parameter. The influence of each mentioned factor was evaluated by L<sub>8</sub> Orthogonal Array method and the most statistically significant factors were determined. According to the response parameter, CFU in the investigated systems, it can be concluded that biodegradation of PS was higher than PVC. This could be explained by possible toxic effect of PVC due to 57 % of Cl in its structure (Wu *et al.*, 2019).

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# Does Floating Treatment Wetland Can Effectively Treat Agricultural and Urban Runoff Enriched with Nutrients, Heavy Metals, and As Metalloid in the Stormwater Receivers?

N. Nawrot\*, E. Wojciechowska\*, J. Walkusz-Miotk\*\*, and K. Pazdro\*\*

\* Gdansk University of Technology, Faculty of Civil and Environmental Engineering,  
11/12 Narutowicza Street, 80-233 Gdańsk, Poland (E-mail: [nicnawro@pg.edu.pl](mailto:nicnawro@pg.edu.pl))

\*\* Institute of Oceanology of the Polish Academy of Science, Powstancow Warszawy

## INTRODUCTION

Floating treatment wetlands (FTWs) are a relatively new approach in water treatment that consists of emergent wetland plants growing on floating rafts (mats) built of buoyant material (Yeh *et al.*, 2015). FTW has been used primarily for water quality improvement. Wetland plant sections submerged in the water play a major role in FTW treatment processes (Lynch *et al.*, 2015). The main application of FTW includes the treatment of stormwater, sewage, pond water, dairy manure effluent, meat processing industry, and water supply reservoirs (Yeh *et al.*, 2015). Every year, 119 000 km<sup>3</sup> of precipitation is recorded worldwide. Only 61 % (72 000 km<sup>3</sup>) evaporates, and 39 % (47 000 km<sup>3</sup>) continues to flow on the earth's surface. Nowadays, the runoff from paved and soft surfaces is forming as a non-point source of pollution and poses a serious threat for receiving freshwater worldwide. Due to land-use restrictions (plots ownership rights), it is often impossible to make buffer reservoirs or constructed wetlands to reduce the supplied pollution load. FTW offers a solution able to cope with these disadvantages. Biogenic substances (N and P) input leads to water quality impairment and in extreme cases to eutrophication (Jarvie *et al.*, 2018). Heavy metal contamination in the aquatic environment has attracted global attention due to its toxicity, abundance, and persistence (Islam *et al.*, 2015). Another toxic and cancerogenic element that draws the particular attention of researchers in recent years is As metalloid. In the form of arsenate As(V) and arsenite As(III) it prevails in the natural environment and is highly toxic and mobile (Abbas *et al.*, 2018). Notwithstanding, the effect of the vegetation on overall removal performance and As removal by wetland plants is poorly documented (Kumar Rai, 2019). FTW as an emerging "best management practice" should be exhaustively investigated for urban and agricultural runoff in relation to nutrients (N and P), metals (Cu, Cd, Pb), and metalloid (As) removal. A recently published article on the topic of FTW in Water Research (Garcia Chanc *et al.*, 2019) pointed out that "the information regarding the uptake and translocation of nutrients within FTW vegetation are limited" as well as "the knowledge gap is in large part due to the lack of information on two factors: (1) species selection and (2) the rate of nutrient uptake/ release over time". Therefore, the proposed project entitled "Processes and Pathways of Nutrients, Selected Heavy Metal and Arsenic Removal from Surface Runoff from the Agricultural and Urban Catchments in Floating Treatment Wetlands" approved for funding by the National Science Center Poland for 2021–2023 will address this issue. The purpose of the submitted application (which is proposed as a poster presentation) will be to discuss the current research results in the field of FTW as well as the project's intentions.

## MATERIALS AND METHODS

Four native macrophytes (*Phragmites australis* Cav., *Iris pseudacorus* L., *Typha latifolia* L., and *Alisma plantago-aquatica* L.) will be tested in micro- and mesocosm scale in the treatment of urban and agricultural runoff contaminated with N, P, metals (Cd, Cu, Pb), and metalloid (As). The microcosm study will consist of 20 reactors (70 L volume) where plant species will be planted on rafts individually (4 series of 5 reactors with 4 species and 1 control), while in the mesocosm study the reactor with a volume of 1000 L will be equipped with a floating raft with plant species in mixed. The impact of pH and chlorides on treatment results will be analysed. The analysis of

removal efficiency of N, P, Cu, Cd, Pb, and As will be determined.

## RESULTS AND DISCUSSION

The results of this project will help to answer the following research questions:

- What dose of N, P, metals (Cu, Cd, Pb), and metalloid (As) is accumulated by 4 species of wetland plants planted in the hydroponic condition in simulated runoff from agricultural and urban areas?
- How high is the purification efficiency using wetland plants in FTW? What part of the contaminants is bound in sediments?
- How high is the N, P, metals (Cu, Cd, Pb), and metalloid (As) capture performance of the FTW through quantification of biomass production, differential contaminants content of the root, rhizomes, stems, leaves, and flowers of each species?
- What is the composition of microbiomes surrounding the submerged roots and rhizomes, water, sediments, and artificial substrata of FTW?

Described findings can provide necessary information on the appropriability of analysed species into the treatment of the urban or agricultural runoff in dependences from the expected leachate composition. FTW falls within the promoted “best management practice” range. In addition, FTW promotes the green solution and adjusts to the circular economy approach, especially in the case of N and P circulation in the environment.

## CONCLUSIONS

FTWs promote the green solution and adjust to the circular economy approach, especially in the case of N and P circulation in the environment. The project will bring new insights considering removal pathways of N, P, Cu, Cd, Pb, and As by 4 macrophytes in FTW technology for improving the water quality of receivers of agricultural and urban runoff.

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# Effective Microorganisms – an Effective Method to Improve the Wastewater Purification?

K. Pawęska\*, A. Bawiec\*, P. Samborska\*, and K. Marek\*

\* Institute of Environmental Engineering, The Faculty of Environmental Engineering and Geodesy, Wrocław University of Environmental and Life Sciences, Grunwaldzki Square 24, 50-363 Wrocław, Poland (E-mails: [katarzyna.paweska@upwr.edu.pl](mailto:katarzyna.paweska@upwr.edu.pl); [aleksandra.bawiec@upwr.edu.pl](mailto:aleksandra.bawiec@upwr.edu.pl); [samborskapaulina5@gmail.com](mailto:samborskapaulina5@gmail.com); [kinga.marek@gmail.com](mailto:kinga.marek@gmail.com))

## INTRODUCTION

Wastewater treatment, especially on areas without central sewer system, still needs improvement because of insufficient pollutants reduction. Discharge of too high pollutants concentrations into the natural environment without any control, may be harmful for various ecosystems (Dąbrowska *et al.*, 2017). Because of high costs of local wastewater treatment plants modernizations, the possibility of improving the efficiency of wastewater treatment through the dosage of Effective Microorganisms (EM) seems to be a good solution (Abdel-Shafy and Mansour, 2016). The main goal of the use of EM is reduction of organic matter (Higa and Wididana, 1991).

## RESEARCH AIM

The main objective of the research was an attempt to estimate the possibility of using Effective Microorganisms to improve the effects of domestic wastewater treatment in reference to organic matter reduction. The experiment was conducted under laboratory conditions. Measurements were carried out in test cylinders filled with domestic wastewater after preliminary treatment. The impact on treatment processes was referred to changes in selected organic pollution parameters.

## METHODOLOGY

The experiment was planned with different dose of EM (1 g, 2 g, 4 g, 10 g) with comparison to blind sample (0 g). The biochemical oxygen demand (BOD<sub>5</sub>), turbidity, sludge layer thickness, dissolved organic and mineral substance concentrations were determined during measurement cycle. Statistical correlations among the observed parameters were determined on the basis of the nonparametric Kruskal-Wallis test with 3 degrees of freedom, at significance level 0.05. The use of that tests resulted from the lack of normal distribution determined with Shapiro–Wilk *W*-test for a majority of the analysed parameters. The statistical analyses were performed using Statistica software.

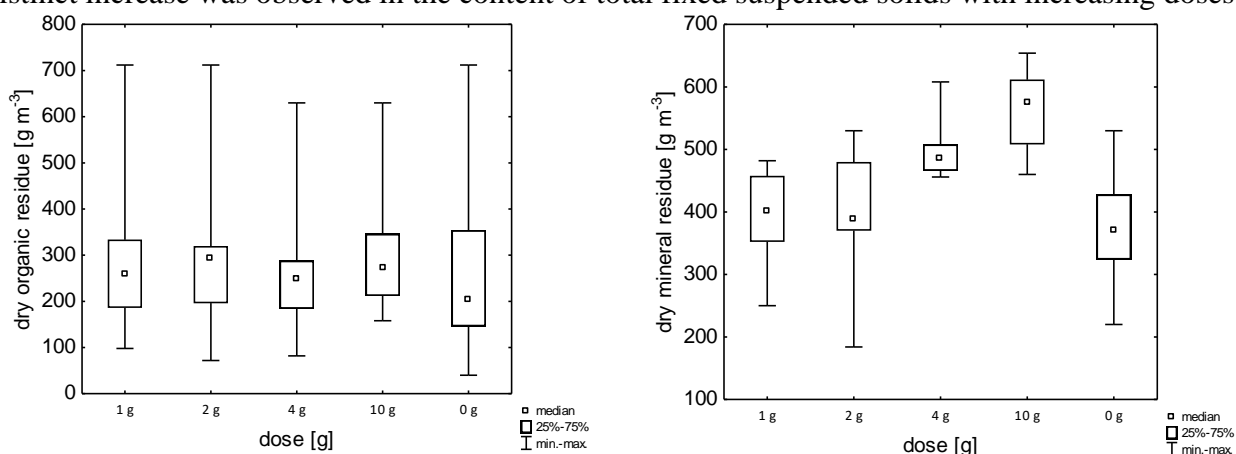
## RESULTS

The application of EM resulted in decrease of the BOD<sub>5</sub> for each of the doses (Table 1). A reduction of organic matter content occurred also in the blind sample (0g). The highest level of organic matter reduction, expressed by the BOD<sub>5</sub> value, was noted at the EM dose of 2 g. The greatest decrease of turbidity was noted at the dose of 4 g (slightly higher than for the dose of 2 g). In the case of total dry residue, lower concentrations were observed after the application of doses of 1 g and 2 g than in the case of the blind sample. Whereas, in the case of the total dissolved substances no significant decrease in that parameter was noted for the doses of 1 g and 2 g, while distinct differences were observed for the doses of 4 g and 10 g. Therefore, it was decided to determine the mineral and organic constituents, and their changes in the total dry residue (Fig. 1).

**Table 1.** Average value of pollution indexes in wastewater after application of EM for doses 1 g, 2 g, 4 g, 10 g and the blind sample (0 g).

Parameter	Unit	Before	Series 1 (1 g, 2 g, 4 g, 10 g)					
		application	–	0 g	1 g	2 g	4 g	10 g
BOD <sub>5</sub>	g m <sup>-3</sup>		610.0	40.0	40.0	10.0	30.0	20.0
Turbidity	NTU		225.0	14.2	7.74	7.35	4.17	26.4
pH	–		8.0	8.1	8.1	8.1	8.4	8.5
Electrolytic conductivity	µS cm <sup>-1</sup>		1429.0	1309.0	1002.0	1235.0	1484.0	1614.0
Total dry residue	g m <sup>-3</sup>		1089.0	1089.0	638.0	636.0	736.0	886.0
Total dissolved substances	g m <sup>-3</sup>		660.0	660.0	628.0	554.0	730.0	858.0
Dissolved oxygen	gO <sub>2</sub> m <sup>-3</sup>		2.44	1.39	1.60	1.60	1.21	1.20
Sludge level	cm		0.0	0.4	0.3	0.3	0.1	0.2
Sample temperature	°C		13.5	20.1	18.7	18.7	20.9	20.9

The content of total volatile suspended solids slightly varied with increase of the dose (F. 1). A distinct increase was observed in the content of total fixed suspended solids with increasing doses.

**Figure 1.** Comparison of the values of total dry organic and mineral residue for biopreparate – nonparametric Kruskal–Wallis test (medians test).

## CONCLUSIONS

The application of EM did not cause degradation of volatile solids but the concentration of fixed suspended solids in the system increased; that could be due to the introduction of mineral substances with the Effective Microorganisms preparations themselves.

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# Increased Tourist Traffic and Problems with Wastewater Treatment in Mountain Protected Areas

K. Pawęska\*, A. Bawiec\*, P. B. Dąbek\*\*, and J. Baran\*

\* Institute of Environmental Engineering, The Faculty of Environmental Engineering and Geodesy, Wrocław University of Environmental and Life Sciences, Grunwaldzki Square 24, 50-363 Wrocław, Poland (E-mails: [katarzyna.paweska@upwr.edu.pl](mailto:katarzyna.paweska@upwr.edu.pl); [aleksandra.bawiec@upwr.edu.pl](mailto:aleksandra.bawiec@upwr.edu.pl); [jeremi.baran@upwr.edu.pl](mailto:jeremi.baran@upwr.edu.pl))

\*\* Institute of Environmental Development and Protection, The Faculty of Environmental Engineering and Geodesy, Wrocław University of Environmental and Life Sciences, Grunwaldzki Square 24, 50-363 Wrocław, Poland (E-mail: [pawel.dabek@upwr.edu.pl](mailto:pawel.dabek@upwr.edu.pl))

## INTRODUCTION

The increasing popularity of mountain tourism and the availability of trails have increased the number of people visiting the mountains National Parks every year. An indispensable element of infrastructure on mountain trails are mountain shelters, which are to provide shelter for tourists but also provide sanitary facilities (Zhao and Li, 2018). Access to water requires sustainable management of water resources, just like the use of toilets requires effective wastewater treatment (Gössling *et al.*, 2012). Both of these issues are currently not sufficiently resolved.

## RESEARCH AIM

The main objective of the research was to assess the impact of increased mountain tourism on the quality of wastewater discharged into the receiver, and thus - on the quality of water in receiving water bodies.

## METHODOLOGY

In the Karkonosze National Park one mountain shelter equipped with local wastewater treatment plant has been chosen. The daily amount of treated sewage flowing into the receiving water body was measured. Samples of treated wastewater were collected at the outflow 5 times a day during 3 days of July (Saturday–Monday). The analyses of wastewater quality included basic measurements (pH, conductivity, turbidity, temperature) as well as nitrogen compounds (NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>) and phosphates concentrations.

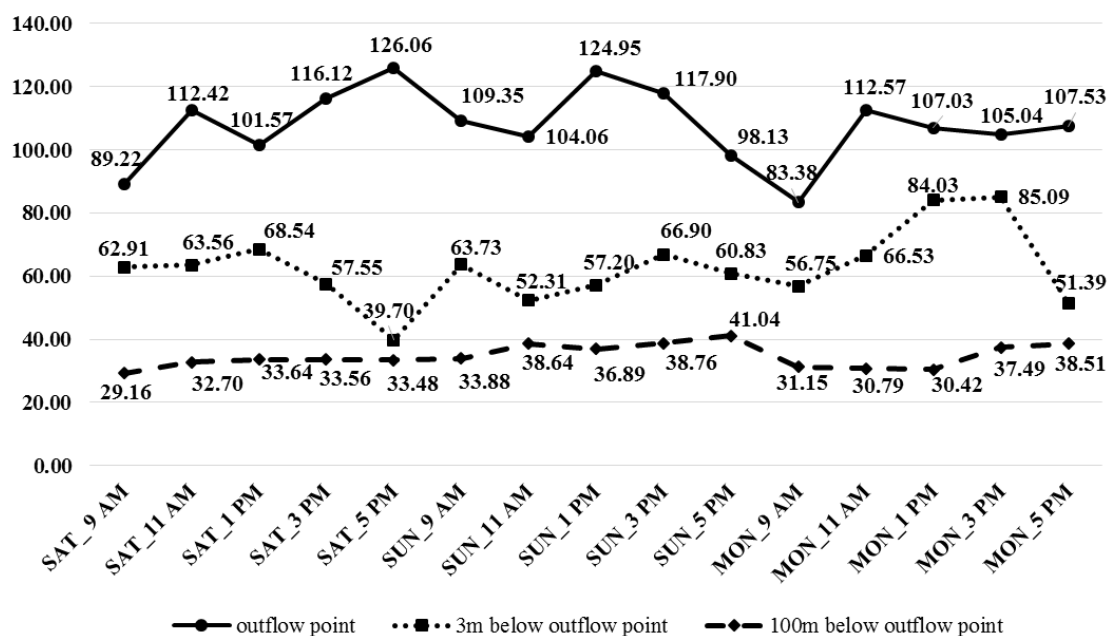
## RESULTS

Analyses of the amount of wastewater discharged from a mountain shelter showed very high unevenness of the outflow. The highest amounts of wastewater were observed on Saturday and Sunday respectively. The average wastewater outflow during the sampling period reached 34.7 m<sup>3</sup>/d. The results of sewage quality measurements are presented in Table 1.

**Table 2.** Average quality of treated wastewater discharged from mountain shelter into the receiving water body.

	pH	Conductivity, S/cm	Temp., °C	Turbidity, NTU	NH <sub>4</sub> , g/m <sup>3</sup>	NO <sub>2</sub> , g/m <sup>3</sup>	NO <sub>3</sub> , g/m <sup>3</sup>	PO <sub>4</sub> , g/m <sup>3</sup>
SATURDAY	8.0	1265.8	15.44	53.392	143.844	3.052	6.094	53.392
SUNDAY	8.2	1333.0	13.02	52.854	142.026	2.226	5.130	52.854
MONDAY	8.3	1289.8	12.70	32.094	182.916	3.058	11.625	32.094

The most characteristic feature of sewage generated in mountain shelters is very high share of ammonium nitrogen comparing to other forms of nitrogen. Such high levels of ammonium nitrogen are associated with the prevailing proportion of urine in the entire wastewater stream. The ratio of ammoniacal nitrogen to nitrite and nitrate clearly indicates a disturbance in biological wastewater treatment process which is based on nitrification. In order to determine changes in the quality of water in the receiver under the influence of discharged sewage, water quality was measured 3 m and 100 m below the discharge point (Fig. 1).



**Figure 1.** Ammonium nitrogen concentration in wastewater flowing out of wastewater treatment and in the receiving water body 3 m and 100 m below the discharge point.

The analyzes show that the reduction of ammonium nitrogen concentration in the water of receiving water body was slow. At the 3 m section, the maximum recorded reduction of  $\text{NH}_4$  concentration was 68.5 % and during the next 97 m the reduction reached average another 35 %.

## CONCLUSIONS

The increase of mountain tourism popularity brings a serious threat to the natural environment associated with discharging anthropogenic pollutants into the environment. Insufficiently treated wastewater containing high concentration of ammonium nitrogen may cause degradation of natural ecosystems of mountain streams due to the use of large amounts of oxygen for the ammonia oxidation. Effective wastewater treatment in mountain areas should be a priority for preserving the rich diversity of natural ecosystems.

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# Water Diversity and Problems in Water Re-Use in Pharmaceutical Enterprises

E. Strade\*, D. Kalnina\*, and J. Kulczycka\*\*

\* Faculty of Materials Science and Applied Chemistry, Institute of General Chemical Engineering, Riga Technical University, Paula Valdena Street 3/7, Riga, LV-1048, Latvia  
(E-mail: [Elina.Strade@rtu.lv](mailto:Elina.Strade@rtu.lv); [Daina.Kalnina@rtu.lv](mailto:Daina.Kalnina@rtu.lv))

\*\* Mineral and Energy Economy Research Institute, J. Wybickiego 7A, Kraków, Poland  
(E-mail: [kulczycka@min-pan.krakow.pl](mailto:kulczycka@min-pan.krakow.pl))

## INTRODUCTION

Water is a critical resource in the pharmaceutical industry. Diverse grades of water are intensively used as raw materials in the synthesis of active pharmaceutical ingredients (APIs), in the preparation of final dosage forms (FDFs), as well as in technological processes such as steam generation and cooling. According to current trends of sustainable water management, water re-use is recognised as a key option to reduce water consumption at the manufacturing facility level. However, implementation of water re-use in practice in the pharmaceutical production is limited, due to the high chemical and microbiological purity requirements for water and stringent good manufacturing practice regulations (European Medicines Agency, 2020).

## RESULTS AND DISCUSSION

The grades of water used in the production of APIs and FDFs depend on the formulation and the route of administration of the pharmaceutical product, as well as on the stage in the manufacturing process at which water is used. Strict quality requirements force pharmaceutical companies to implement novel multi-stage water treatment systems that guarantee water safety and reliable operation (Table 1).

**Table 1.** Diverse application of water in pharmaceutical production.

Water grade	Quality requirements*	Usage
Potable water	World Health Organisation (WHO) guidelines for drinking water quality	- Chemical synthesis of intermediates of APIs - Rinsing/cleaning of manufacturing equipment and facilities - Production of pharmaceutical grade water
Purified water	TOC < 500 µg/L Conductivity ≤ 4.3 µS/cm at 20 °C Nitrate ≤ 0.2 mg/L Heavy metals ≤ 0.1 mg/L as Pb Aerobic bacteria ≤ 100 CFU/mL	- Final isolation and purification of APIs - Preparation of nonsterile FDFs - Final rinse of equipment, containers, and closures in the manufacture of non-parenteral FDFs
Water for injections	TOC < 500 µg/L Conductivity ≤ 1.1 µS/cm at 20 °C Nitrate ≤ 0.2 mg/L Aerobic bacteria ≤ 10 CFU / 100 mL Bacterial endotoxins ≤ 0.25 I.U./mL	- Manufacturing of sterile pharmaceutical products

\*According to European Pharmacopoeia.

Huge amounts of clean water in the pharmaceutical industry are also consumed by cooling systems and steam generators. Pre-treatment of process water depends on feed water quality and usually includes iron removal, softening, the addition of corrosion and scale inhibitors, and treatment with

biocides to prevent biological fouling in the heat exchange systems. Additional treatment of feed water should be performed in the production of pure steam that is used in the production of injectable solutions to ensure that the condensate of pure steam meets WFI requirements for conductivity, TOC, microbial content, and endotoxins.

To avoid product contamination and to decrease patient health risks, pharmaceutical enterprises have to focus on the practical options for closing the water loop in technological processes where water does not come into direct contact with pharmaceutical products (Strade *et al.*, 2020). For example, high water savings can be achieved by replacement of once-through systems by closed closed-loop recirculating cooling systems or by re-use of plant steam condensate. However, re-use of treated wastewater in pharmaceutical production is less feasible. Biological treatment is not sufficient to avoid scale formation, biofouling and product contamination risks. Implementation of zero liquid discharge technologies that would allow re-use of wastewater in technological processes is limited due to the high costs and energy consumption.

Separate collection of individual wastewater streams: containing alkaline or acidic solutions, phosphorus-containing effluents and aluminium containing solutions from the pharmaceutical batch processes may serve as pH controlling agents, nutrient sources for activated sludge microorganisms and even coagulation agents (Table 2).

**Table 2.** Wastewater re-use options in wastewater treatment processes.

Wastewater treatment process	COD removal		Nitrification	Denitrification	Sludge removal	Heavy metal removal
Reusable wastewater streams	Acidic and alkaline solutions	Phosphorus – containing effluents	Alkaline solutions	Recovered solvents	Al <sup>3+</sup> containing wastewater streams	Alkaline streams
Application	pH control	C:N:P ratio balancing	pH control	Carbon source for bacteria	Coagulant	Precipitation agent

## CONCLUSIONS

High quality demands and safety standards for pharmaceutical products limit re-use of water in manufacturing processes where water comes into direct contact with pharmaceutical products. Polluted wastewater streams from pharmaceutical batch processes have different re-use options in wastewater treatment processes.

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# Minimization of Nature-Intensity of Sulphate Pulp Production of Various Products

M. S. Stroganova\* and A. I. Shishkin\*

\* Higher School of Technology and Energy of Saint Petersburg State University of Industrial Technologies and Design, Ivana Chernykh 4, 198095 Saint Petersburg, Russia  
(E-mail: [masha199407@list.ru](mailto:masha199407@list.ru))

## INTRODUCTION

The main aim of the research work is to assessment of reduce the negative impact of sulfate-cellulose production on the aquatic ecosystem of Lake Ladoga, taking into account the effect of nitrification on the oxidative processes of wastewater. Together with the laboratory of the environmental protection department of the pulp mill in the summer-autumn period 2019–2020 the number of laboratory studies of treated wastewater of various products types were carried out in order to implement the procedure for rationing the wastewater of the pulp and paper mill (Shishkin *et al.*, 2019).

## METHODS AND MATERIALS

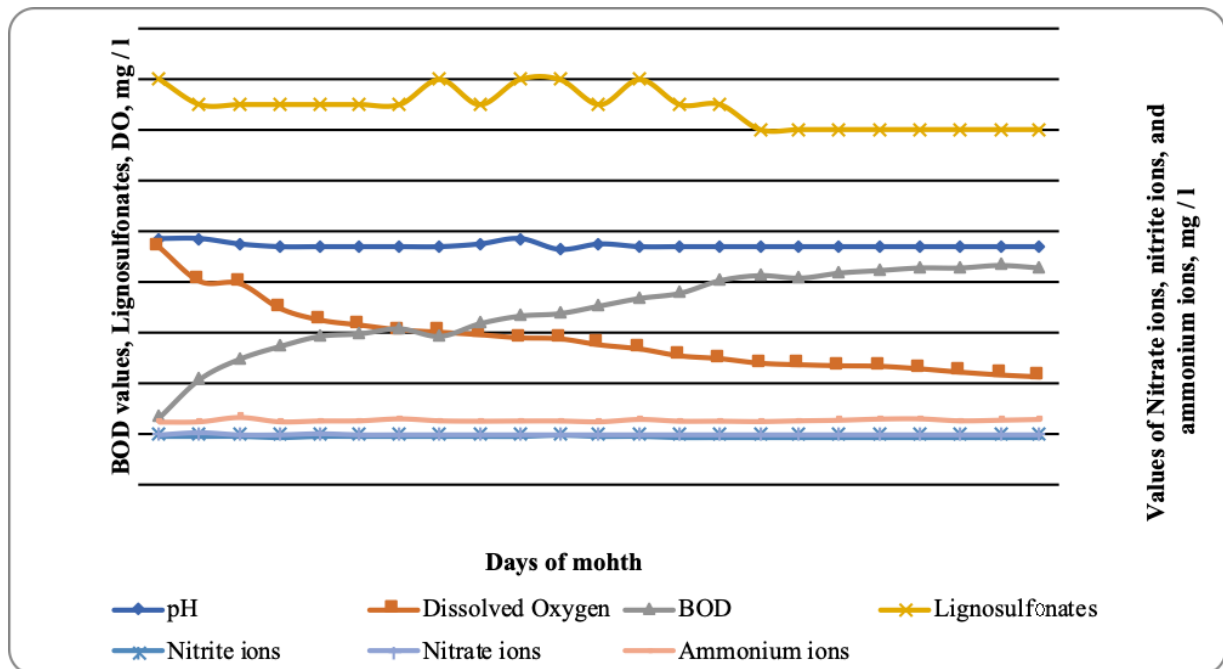
Methods of full-scale and mathematical modelling of biochemical oxidation processes were used. A number of indicators of alkaline-containing wastewater were determined by standard laboratory analysis methods for 30 days: BOD, lignosulfonates, nitrite ions, nitrate ions, ammonium ions, dissolved oxygen, pH and temperature were controlled, and a database was formed for the studied period (Shishkin *et al.*, 2020).

## RESULTS

Were analyzed the effluents on limiting indicators malacostraca wastewater within 30 days with the objective of assessing transformation processes of organic matter in water of lake Ladoga and calculate the coefficients of biochemical oxidation and reaeration of various products types – unbleached sulphate pulp of softwood refined, unbleached Kraft insulating and cellulose for capacitor, cable and transformer paper.

When evaluating treated wastewater of electrical insulating sulfate cellulose for capacitor, cable and transformer paper, the nitrification processes was assessed by concentration of nitrite ions for 30 days, which is almost remained unchanged, and by 18 day the concentration increased, the concentration of nitrate ions for 30 days is increased, than it is decreased.

A rapid increase in the BOD was observed, and the content of lignosulfonates changed by only 2 units – from 14 mg/L to 12 mg/L, it may indicate the end of the biochemical oxidation of easily oxidized organic compounds. The concentration of suspended substances on the first day of sampling was 5.5 mg/L, which does not exceed the norm of maximum permissible values. The COD value on the first day of analysis was 44 mg/l and exceeds the norms of the maximum permissible values by 1.5 times. The BOD index exceeds the norms of permissible values by 2 times after the fifth day. The concentration of lignosulfonates exceeds the norms of maximum permissible values by 2.8 times. The degree of delignification by that cellulose type was 28 %.



**Figure 1.** Change limiting indicators of treated wastewater from electrical insulating sulphate cellulose for capacitor, cable and transformer paper during July 2020.

## CONCLUSIONS

A number of laboratory studies were carried out in 2019–2020, for 30 days each, for treated wastewater of various types of cellulose types produced by the plant in order to assess the wastewater treatment degree and efficiency from organic impurities and differentiate payments for the discharge of suspended substances and organic compounds expressed in terms of BOD<sub>total</sub>, COD and lignosulfonates (Stroganova *et al.*, 2020).

## ACKNOWLEDGEMENTS

The reported study was funded by RFBR, project number 19-35-90128.

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# Model Parameters for Biochemical Oxidation of Pulp Mill Liquor Containing Wastewater

M. S. Stroganova\* and A. I. Shishkin\*

\* Higher School of Technology and Energy of Saint Petersburg State University of Industrial Technologies and Design, Ivana Chernykh 4, 198095 Saint Petersburg, Russia  
(E-mail: *masha199407@list.ru*)

## INTRODUCTION

The research results are given for various degrees of effluent treatment efficiency with the determination of oxidation and reaeration coefficients. The data on the biochemical oxidation coefficients used for a numerical experiment to substantiate the level of permissible wastewater discharge by mass of pollutants are obtained. An analysis of the results of a numerical experiment and laboratory studies allowed us to develop practical recommendations for managing wastewater processes in the system “enterprise – water body”. The study of the oxygen regime of the reservoir, the processes of oxidation of the organic compound was carried out using the tools of mathematical modelling of a mono- and bimolecular model using the example of the north-eastern part of Lake Ladoga from the pulp mill, located in the Republic of Karelia, Russia.

## METHODS AND MATERIALS

The process is described by the system of Phelps-Streeter equations. The system has a limited range of applicability: for large oxygen deficiencies under anaerobic conditions, the oxygen deflection curve constructed using the Phelps-Streeter equations gives a quantitatively implausible picture – a negative value of the oxygen concentration in water, which cannot be. It follows that at such a concentration of BOD, a monomolecular model cannot be used. In this case, you can use the bimolecular model, which is based on two parameters, or the three-molecular model, which also includes the third parameter – the bacterial one.

To determine the dependence of oxygen consumption on the incubation time, the flask method for determining BOD was used.

The change in the value of the BOD is described by the following equation according to the Phelps-Streeter scheme (Streeter and Phelps, 1925):

$$\frac{dc_{BOD}}{dt} = -k_1 c_{BOD} \quad (1)$$

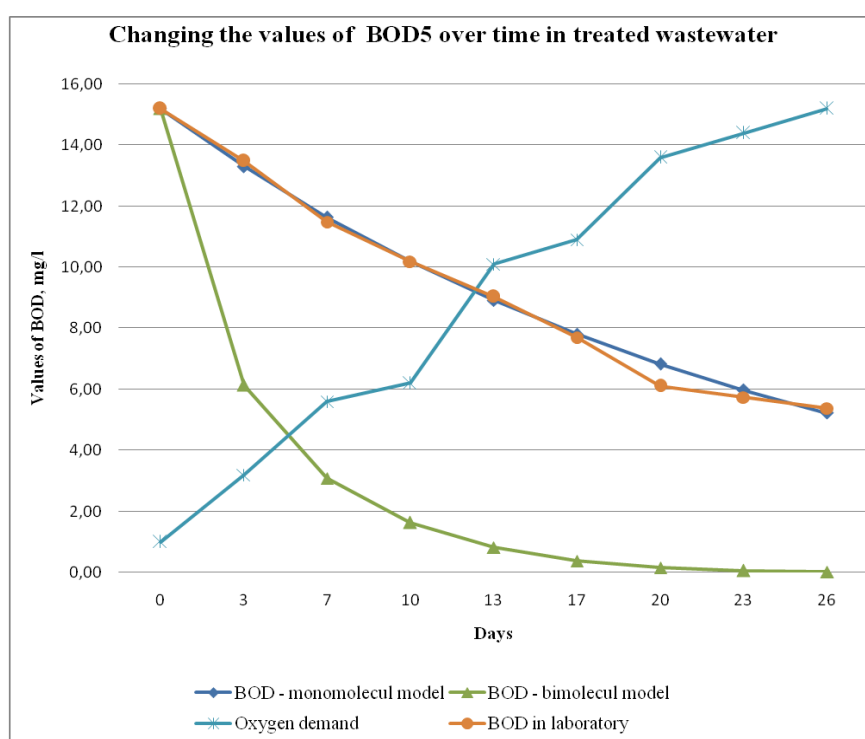
where  $k_1$  is the rate coefficient of biochemical oxidation (mineralization),  $C_{BOD}$  is the value of BOD at the initial time.

An analytical calculation was made of the values of the biochemical oxidation rate coefficient for the oxidation stages for the wastewater entering the wastewater treatment and for the treated wastewater of a pulp mill. The problem of predicting water quality for a specific pulp production was solved at the calculated values of  $k_1$  by numerically solving of mathematical model. For this purpose, the following values were used: BOD values, dissolved oxygen concentration, water temperature at the time of analysis and biochemical oxidation ( $k_1$ ) and reaeration ( $k_2$ ) coefficients.

**Table 1.** Initial data for mathematical modelling of oxidation processes.

Indicator value	BOD, mg/L	O <sub>2</sub> , mg/L	t, °C	$k_1$ , 1/days	$k_2$ , 1/days
Treated wastewater	15.2	7.33	21.0	0.04	0.813

The modelling of the processes of oxidation and transformation of organic matter for wastewater from pulp production was carried out using the MathCAD software (Shishkin *et al.*, 2019). An analytical solution is applied for a laboratory study of the composition of incoming industrial wastewater and treated wastewater with WWTP. The solution is shown in Fig. 1.

**Figure 1.** Changes the values of BOD in time in treated wastewater of pulp industry.

## CONCLUSIONS

The calculation of the coefficient of biochemical oxidation of organic compounds  $k_1$  for wastewater of the pulp industry with varying degrees of purification ( $k_1 = 0.04$ ). A numerical experiment was carried out using monomolecular and bimolecular models to calculate the change in BOD values in time of a specific pulp production at calculated values of  $k_1$ . It can be concluded that the mathematical model is applicable for calculating the change in BOD over time for the treated wastewater of a pulp mill.

## ACKNOWLEDGEMENTS

The reported study was funded by RFBR, project number 19-35-90128.

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# 50 and 100 Year Flood Simulation on Lower Part of Viskan River Floodplain, Sweden

T. Tasmia\* and K. Maryam\*

\* Department of Sustainable Development, Environmental Science and Engineering (SEED),  
KTH Royal Institute of Technology, Teknikringen 10B, 100 44 Stockholm, Sweden  
(E-mails: *tasmia@kth.se*; *maryamka@kth.se*)

## INTRODUCTION

While flood in many countries is interrupting socio-economic development and taking away large number of lives every year, in Sweden the flood hazard has relatively less adverse impact on the society. However, the damages involved by flood hazard in the country can be large as well (Waleed, 2016). According to SMHI (Swedish Meteorological and Hydrological Institute) report, Viskan River drainage basin located in the southwest of Sweden has experienced 35 year return flood in 2006 (SMHI, 2006) and has been reportedly inundated under water during 1943, 2006 and 2011. With blessing of numerical solutions, investigation has been carried out to simulate future flood scenario of the lower part of Viskan River to identify high hazardous area.

## MATERIAL AND METHOD

1D hydrodynamic model for flood mapping has been developed using the Hydrologic Engineering Center River Analysis System (HEC-RAS) in concert with HEC-GeoRAS. Automated GIS processing procedures in HEC-GeoRAS provided a useful and expeditious method for repetitive hydraulic model development of Viskan River floodplain. The geometric data determined in GIS has been imported into HEC-RAS using a data exchange format developed by HEC. The resultant water depth exported from HEC-RAS simulations has been processed by GIS for flood inundation delineation and hazard map generation.

The hydrodynamic model is calibrated with observed water extent width at cross sections along the river reach using Manning's roughness coefficient ( $n$ ). As a source of observed flood extent along the river, Landsat 4-5 TM image was a great help to calibrate the model. The satellite image acquired from United States Geological Survey (USGS) is processed in GIS system to identify the water body with algorithms. Further, investigation has been proceeded to analyze response of the floodplain under 50 and 100 years flood.

## RESULT

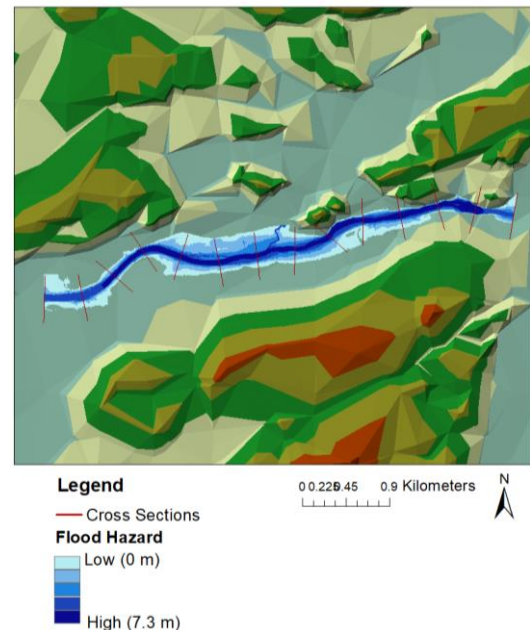
### Calibration of HEC-RAS Model and Future Flood Simulation

Steady state model simulation for the calibration is conducted on 15<sup>th</sup> April, 2007. Essentially, various Manning's roughness coefficients for channel and floodplains are adopted for respective simulation. Finally, Manning's ' $n$ ' value of 0.02 for channel and 0.033 for floodplain resulted in a satisfactory outcome as trend and shape of model simulated flood extent and observed data are almost similar in Fig. 2 and the difference between two them has been minimized as far as possible within the recommended range of ' $n$ ' values. Statistical parameter Mean Absolute Error is found 10.44 for the set input parameters. The result from 50 and 100 year simulation of the model has found that the flood propagates further form the bank of the river and inundates the surrounding about 1.224 km<sup>2</sup> in average (Fig. 1).

Common places of water extent area has been noticed as well from qualitative comparison between model simulated result and observed image. The most hazardous zone assumed to be the zone of high water depth is found along the channel and becomes less severe as distance increases from both of the river bank.

### Uncertainty Analysis

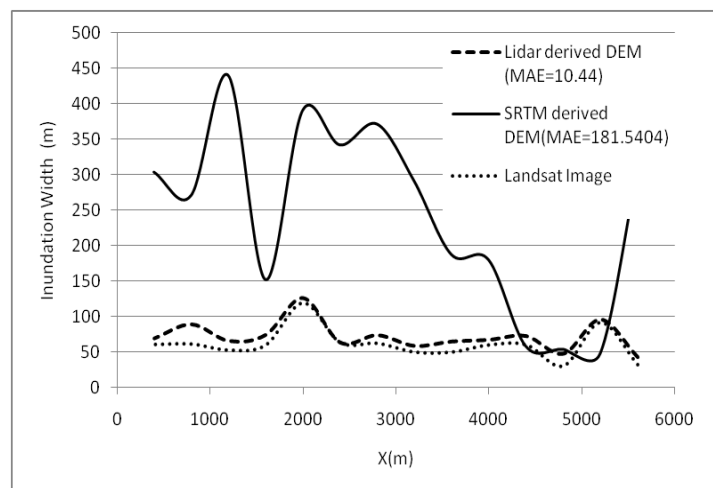
Uncertainty analysis focuses to calculate the output inconsistency of a model due to the unevenness of the input data. Application of Digital Elevation Model (DEM) of Shuttle Radar Topography Mission (SRTM) as an input parameter resulted in an undesirable model performance while keeping the calibrated parameter constant. Water extent width is found to be quite higher along the study river reach; moreover the shape and trend of the model is observed quite disparate compared to the observed value in satellite image (Fig. 2).



**Figure 1.** Flood inundation map of 100 year return period.

### DISCUSSION

Simulation of 1D hydrodynamic model of Viskan River insights the floodplain is susceptible to flooding for higher return period flood. In this circumstance, early effective measures may reduce the potential damages on the studied area. The uncertain analysis of the study has shown that Lidar DEM is more improved than the SRTM DEM with respect to model performance. Generally, the study showed that the methodology for river flood analysis using the 1D hydrodynamic model is generic and can be applied to similar geographical conditions.



**Figure 2.** Comparison between simulated and observed data using SRTM DEM as input.

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## Water Source Protection – Water Circulation

S. Xhafa\* and S. Spahiu\*

\* Regional Water Company Pristina, Pristina, Kalabri, Republic of Kosovo  
(E-mail: [sokol.xhafa@gmail.com](mailto:sokol.xhafa@gmail.com))

### INTRODUCTION

Water resource protection is one of the most important points, in Kosovo, like the most well-known important issue worldwide. Kosovo is a state with scarce of water, based on ground situations, including also national and international studies and reports. From 2010 Government of Kosovo, finalized regulations and rules regarding water zone protection. In this regard Regional Water Company Pristina approached these studies and goals, in order to protect own sources. During 2010 company invested in a design for protection zones and based on this there were construction of RC retaining walls – barriers, screens at the discharge point from the streams, and finally in 2015–2017 construction of Waste Water Treatment Plant (WWTP) at Mramori. WWTP was constructed on 2016, finalized with sewage network on 2017, based on results from the samples taken at the inlet and outlet of the Plant we made calculations on Environmental Impact as well cost savings O&M, methodology is based on an assessment towards main parameters. The treated water discharges directly into Badovc Reservoir, from where it goes to Water Treatment Plant Badovc and after treatment into water supply distribution system for Prishtina and Gračanica.

### MATERIALS AND METHODS

Based on historical measures of the water quality inside the lake, it has been developed a program for source protection, an approach to construct a waste water treatment plant, including sewage collector, in order to protect the stream from the sewage discharge. Referring to the latest studies on water source protection, we used an approach like (Binder *et al.*, 2015). Waste water management involves analysis of elements, their attributes, behavior and parameter estimation, real time optimization and safety (García Einschlag, 2013).

The outlet of the WWTP discharges (Table 1) into reservoir, and then through the pumping station from the reservoir, water goes into WTP Badovc. In this regard the research was titled as a water recirculation (used as a potable water, discharged as a sewage, treated into WWTP, pumped into WTP and then distributed again into water distribution network). Through the installed technology during 2016 we monitored the sewage water quality at the intake of the WWTP and after treatment.

The technology is installed in accordance with CSN 75 6401, and the solution is based and in accordance with Directive 91/271/EC for WWTP with capacity of 2001–10 000 PE, the WWTP's effectiveness in accordance with COD shall above 90 % and in accordance with BOD<sub>5</sub> at least 96 %.

**Table 1.** The pollution- level of the discharged waste water meets the following parameters.

	COD		BOD <sub>5</sub>		Suspended solids		N-NH <sub>4</sub>		P <sub>total</sub> *(mg/L)	
	P	m	p	m	p	m	p	m	p	m
Limit	120	170	25	50	30	60	15	30	2	7

p indicates the average annual values.

m indicates the maximum values in individual sample must not be exceeded.

\* The values of P<sub>total</sub> are specified as mg/L, in comparison with Directive 91/271/EU.

## RESULTS

During the operation time, the company with the laboratory has taken samples in order to see the quality of the treated water. Laboratory devices are in compliance with CSN ISO 5667 Water quality sampling system, including sampling of water, waste water, and sludge and handling all of them. After the process of analyzing it was concluded results as below (Table 2).

**Table 2.** Results at the inlet of WWTP and outlet of the WWTP – after treatment.

Parameters	Methods	Results	Results	According to AO, MESP No 30/2014
Date		26.10.2017.	26.10.2017.	N/A
		Inlet WTP	Outlet WTP	Outlet WTP
BOD <sub>5</sub> 20 °C	Respirometry method	37.332	1.5096	25
Dissolved Oxygen DO	Winkler methods	3.01 mg/ L O <sub>2</sub> or 34.9%	4.41 mg/L O <sub>2</sub> or 51.7%	12.5 mg/L O <sub>2</sub> or 75%
COD	Reactor digestion method	54.9 mg/L	2.22 mg/L	125 mg/L
PO <sub>4</sub> total	Acid persulfate digestion method (also called organic and acid hydrolysable)	7.4 mg/L	0.35 mg/L	2 mg/L
NH <sub>4</sub>	Salicylate method	1.2 mg/L	0.2 mg/L	15 mg/L
TSS	Photometric method	35	3	35–60

## CONCLUSIONS

The overall impact of the constructed and installed WWTP is one of the most important step, this was the first concrete and successful project for water source protection, with a great impact directly in to the lake, not only for the water itself and reduction of the cost for treatment at the WTP, but at the same time with a great impact for the environment and aquaculture as well.

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# Lagrangian Field Experiment of Surface Mixing During a Flood Wave at a River Confluence

M. Zsugyel\* and K. G. Szabó\*\*

\* MTA-BME Water Management Research Group, Műegyetem rkp. 3, Budapest, 1111, Hungary  
(E-mail: [zsugyel.marton@epito.bme.hu](mailto:zsugyel.marton@epito.bme.hu))

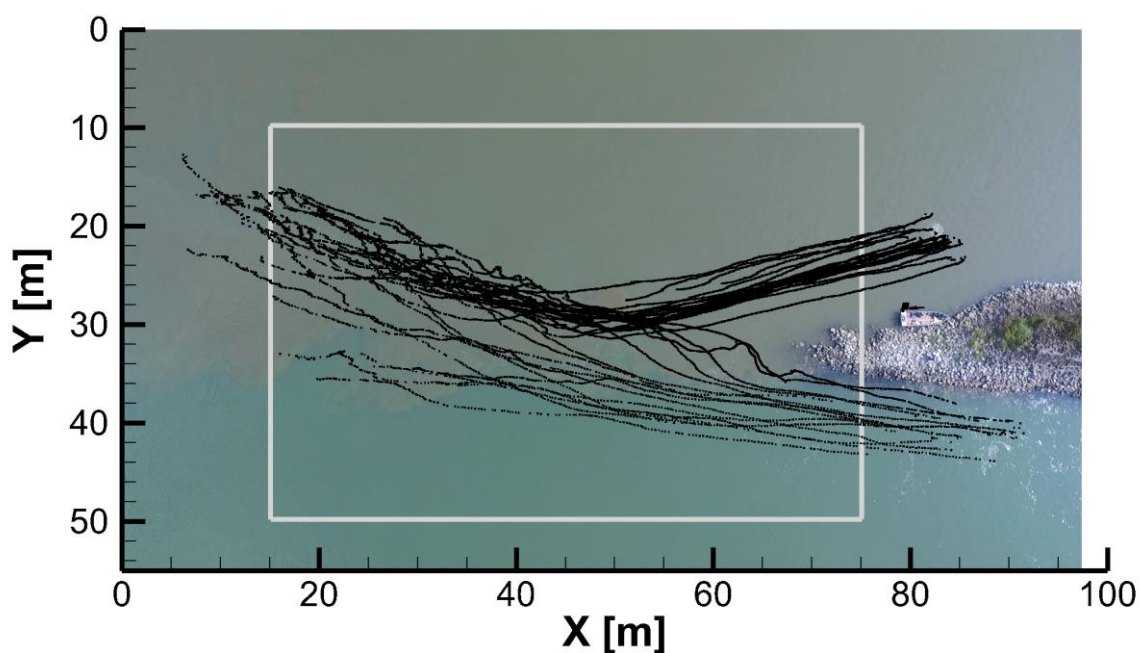
\*\* Budapest University of Technology and Economics, Műegyetem rkp. 3, Budapest, 1111, Hungary

## INTRODUCTION

In recent years as Unmanned Aerial Vehicles (UAV) have become very popular in daily life, their scientific usage is also becoming more widespread. Our Research Group is also using UAVs regularly for observing the surface flow of natural waters. In spite of some obvious disadvantages of this technique (e.g. moving frames, viewing only on the surface processes, limited flight time, etc.), it has great opportunity to observe processes occurring in larger areas at the same time without using any expensive and flow-intrusive instruments.

Confluences of rivers, where water masses meet with different momenta, are typical places where unsteady, complex flow structures develop, such as shear zones, shedding vortices, up- and downwellings. These structures have crucial impact on mixing, since they determine the attracting and repellent characteristics of the flows.

This paper reports on as a follow-up study based on our research (Zsugyel *et al.*, 2019) by including some enhanced technical methods in the image processing and Lagrangian tracking and with more detailed quantitative approach of Lagrangian statistics.



**Figure 1.** The study site and the trajectories of the reconstructed particles. The tributary and the Danube river is in the upper and lower parts of the picture, respectively. The water flows leftward. The rectangle shows the Field of View during the measurement on 29<sup>th</sup> of August.

## METHODS

### Field measurements

In this study we present the analysis of data recorded on two consecutive days, on the 28<sup>th</sup>–29<sup>th</sup> of August, 2018. A small flood wave has passed in the Danube river at this time close to the city Győr, where the field measurements were carried out. Here (Fig. 1.) a smaller tributary, called Mosoni-Danube, flows, containing more suspended sediments (upper part, lighter colour), into the much larger, cleaner and faster Danube (lower part, darker colour) river.

A DJI Phantom3 UAV with a 2.7K resolution camera was used for recording from a fixed point over the river surface in both case. Biodegradable puffed wheat disks were used as surface floating tracers. On the first day the discharge of the Danube reached its peak value, 1400 m<sup>3</sup>/s during a moderate flood wave; this was reduced to 1200 m<sup>3</sup>/s on the second day. The drone hovered at 76 m and 54 m on the second day, thus that the Field of View was almost double on the first day.

### Image processing methods

Scientific grade aerial reconnaissance involves several challenges. In order to overcome these, we improved many steps of our image processing algorithm. For example, the images were undistorted and stabilized before the tracer recognition. In addition, a masking method based on texture recognition was applied to filter out the non-water areas of the field. Image enhancement algorithms were applied for better quality images as well. This allowed us to recognize the floating tracers also from the higher viewpoint. Eventually, we reconstructed about 70 surface particle trajectories in both measurements.

### Lagrangian description

The large number of reconstructed surface particle trajectories allows us to apply the methods of Lagrangian statistics to characterize the flow and mixing properties. In this paper we present the evaluations of some basic measures including single particle statistics (e.g. Probability Density Functions of displacements and velocities) and statistics of multiple particle clusters (LaCasce, 2008).

## CONCLUSION

In our paper we present examples of the quantitative analysis of experimental single trajectory data under non-trivial hydraulic conditions like river confluences and flood waves. We also discuss some image processing methods by which the success rate of the reconstruction of surface floating tracer trajectories can be improved. We show how Lagrangian data analysis offer a new sight into the characterization of surface mixing in natural waters.

## ACKNOWLEDGEMENTS

This research was supported by the Hungarian Academy of Sciences Young International Conference Grant (INKP) and the BME FIKP-VÍZ by EMMI grants.

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## The Results of Comparative Sanitary-Virological Studies of Drinking Water and Water Sources

T. V. Amvrosieva\*, I. V. Belskaya\*, N. V. Paklonskaya\*, S. K. Laziuk\*, and Yu. A. Shilova\*

\* Laboratory of natural reservoir infections, The Republican Research and Practical Center for Epidemiology & Microbiology, 23 Filimonova str., Minsk 220114, Belarus  
(E-mails: [amvrosieva@gmail.com](mailto:amvrosieva@gmail.com); [v.inna.belskaya@gmail.com](mailto:v.inna.belskaya@gmail.com); [labsanvir@gmail.com](mailto:labsanvir@gmail.com))

### INTRODUCTION

The problem of waterborne infectious diseases necessitates an adequate assessment of the quality of water sources and drinking water. In the Republic of Belarus, monitoring of water safety by virological indicators is regulated by current normative document and is based on the detection of enteroviruses (EVs) in it. EVs have high epidemic significance due to their ability to cause large outbreaks involving the waterway of transmission of the infections caused by them. However, the seasonal pattern of circulation among the population is typical for EVs, which does not allow them to reflect reliably the level of viral contamination during periods of decreasing morbidity. Unlike EVs adenoviruses (HAdVs) don't have a pronounced seasonality of their circulation in nature, which makes it possible to consider them as sanitary-indicative agents of viral water pollution. In addition, HAdVs are highly resistant to chemical and physical factors including prolonged UV exposure, as a result of which they are able to remain in water bodies for a long time (Bofill-Mas, 2013). HAdVs are characterized by a pronounced virus carriage among the population, which determines their ubiquitous distribution both at the level of the human population and in the external environment. The indicated advantages of HAdVs over EVs and other intestinal viruses will suggest that their levels of water contamination are not related to seasonal increases in HAdVs morbidity, but are a reflection of fecal pollution of water bodies and violations of water treatment and water use technology.

The aim of this study was to conduct comparative sanitary-virological studies of water sources and drinking water in order to identify EVs and HAdVs in it for getting an experimental confirmation for the selection of the most representative sanitary-indicative agents in analysis and safety assessment of water by virological indicators.

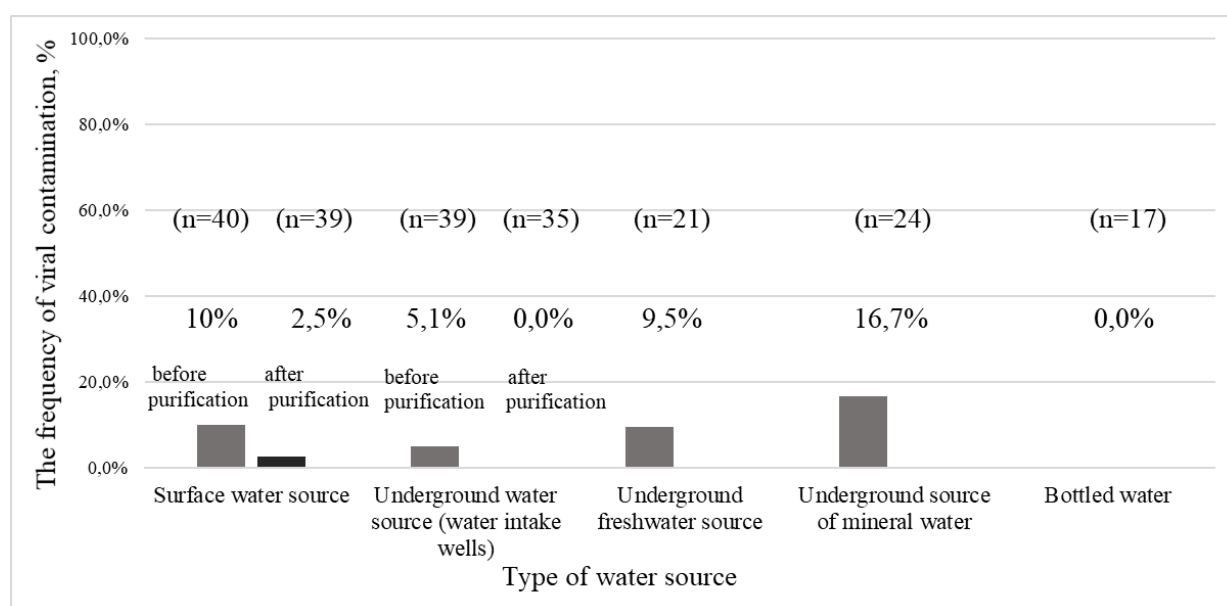
### MATERIALS AND METHODS

Studies of the viral contamination of water from water sources and drinking water were carried out using samples ( $n = 215$ ) collected during 2016–2019 at 34 water intakes of the largest cities of the Republic of Belarus ( $n = 74$ , of which 39 were water samples before treatment and 35 after treatment) and a surface water source ( $n = 79$ , including 39 and 35 samples before and after treatment, respectively); samples obtained from freshwater wells ( $n = 21$ ) and mineral water wells ( $n = 24$ ), as well as bottled water samples ( $n = 17$ ). Viruses were captured from water by the flow-through method based on sorption-elution using Kit for adsorption and concentration of viruses from drinking water using trap device (RRPCEM, Belarus). Viral nucleic acids extraction was carried out with RIBO-prep (AmpliSens, Russia). The genetic material of the studied viruses was detected by the real-time polymerase chain reaction (real time PCR) method using an AIVI-PCR kit (RRPCEM, Belarus) for detecting RNA of EVs, as well as a developed set of primers and probes specific for the conserved region of the HAdVs hexon gene. The pJET1.2-adhex plasmid vector containing the DNA insert corresponding to the target region was used as a positive control for the PCR stage.

## RESULTS

According to the results of the studies, HAdV's DNA was detected in 6 % of the analyzed samples ( $n = 215$ ), while the EVs were not identified in any of them. For the period of 2016, out of 25 samples examined, 16 % positive were found, in 2017 – out of 54 samples, – 9.2 % positive, in 2018 – out of 43 samples, – 2.3 % positive, in 2019 – out of 93 samples, including 3.2 % were positive. A study of the seasonality of the detection of HAdV showed that the levels of viral contamination mainly did not show pronounced differences [in winter – 5 % ( $n = 20$ ), in spring – 4.7 % ( $n = 64$ ), in summer – 4.2 % ( $n = 48$ ) and only during the autumn – 8.4 % ( $n = 83$ )].

Viral contamination of water was most often detected in the study of samples taken from mineral water wells (16.7 %), as well as in water samples before purification from a surface water source (10.0 %). In addition, HAdV's DNA was detected in 2 samples of water before purification obtained from water intakes; in 2 samples from underground freshwater source, as well as in a sample of drinking water from the station of the 2nd rise of the surface water source.



**Figure 1.** The detection frequency of HAdV's DNA in drinking water and water sources.

The presented data indicate the incomplete effectiveness of the existing system that provides the purification of water from a surface water source. In general, the frequency of tap water contamination with viral agents (1.35 % ( $n = 79$ )) was lower than pollution of water from underground mineral water sources.

## CONCLUSIONS

Comparative sanitary-virological studies of water sources and drinking water in relation to EVs and HAdVs revealed significant differences in the results. Thus, the general detection frequency of HAdVs in the analyzed samples amounted to 6 %, while RNA of EVs was not detected in any of water samples. The data presented indicate the need for more extensive research in order to obtain further evidence in favor of the indicator role of HAdVs in monitoring water quality by virological indicators and assessing its safety against human viral infections.

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# Formation of Odorous Aldehydes, Nitriles and *N*-Chloroaldimines from Combined Leucine in Short Oligopeptides during Chlorination

L. Cai\*, S. Yu\*, and L. Li\*

\* Engineering, Tongji University, 1239 Siping Road, Yangpu District, Shanghai 200092, PR China (E-mails: [luyangcai@tongji.edu.cn](mailto:luyangcai@tongji.edu.cn); [ysl@tongji.edu.cn](mailto:ysl@tongji.edu.cn); [lilei@tongji.edu.cn](mailto:lilei@tongji.edu.cn))

## INTRODUCTION

Previous studies have focused on investigating the formation of odorous by-products during the chlorination of free amino acids (AAs) (Cai *et al.*, 2019). However, studies on the formation of odorous by-products during the chlorination of combined AAs, which are much more abundant in natural waters than free AAs (Hureiki *et al.*, 1994), are very limited. In this study, the generation of odorous aldehyde, nitrile and *N*-chloroaldimine from short oligopeptides containing combined Leucine (Leu) (a typical precursor of odorous by-products), including glycylleucine (Gly-Leu), leucylglycine (Leu-Gly), and trileucine (Leu-Leu-Leu), was investigated, hoping to help find the causes of off-flavour problems in drinking water.

## MATERIALS AND METHODS

The evolution of these odorous by-products over time and the effect of chlorine dosage were studied. Mechanisms of odorous by-product formation from chlorination of selected short oligopeptides were then proposed based on Acquity UPLC-qTOF mass spectrometer measurement and kinetic studies modelled with Kintecus.

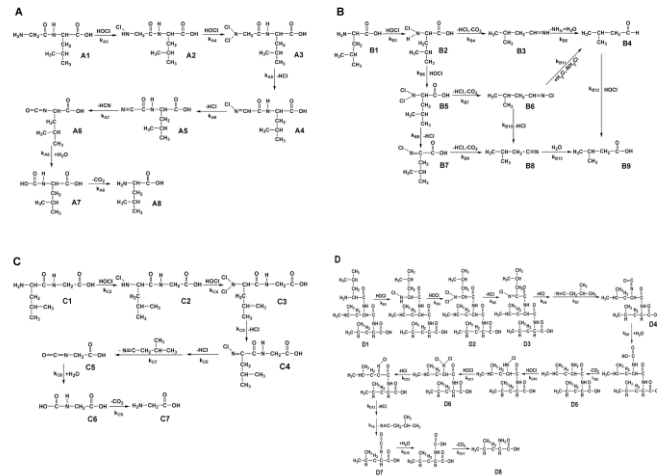
## RESULTS

The results indicated that a series of sequential reactions, including substitution, dehydrohalogenation,  $\beta$ -elimination, hydrolysis and decarboxylation reactions, occurred during the chlorination of short oligopeptides. The chlorination of Gly-Leu and Leu-Leu-Leu formed free Leu, which continued to react with chlorine, producing isovaleraldehyde, isovaleronitrile and *N*-chloroisovaleraldimine. Compared with Gly-Leu, Leu-Leu-Leu produced less free Leu, and therefore, a smaller amount of Leu-derived odorous by-products was generated. Leu-Gly produced free Gly, which was not a precursor of odorous by-products. Thus, neither isovaleraldehyde nor *N*-chloroisovaleraldimine was formed. Notably, isovaleronitriles can be formed directly from a  $\beta$ -elimination reaction during chlorination of Leu-Gly and Leu-Leu-Leu, and thus high yields of isovaleronitriles were observed after chlorination. The yields of odorous by-products during chlorination of short oligopeptides increased with increasing Cl/N ratios (the molar ratio of chlorine to nitrogen in the AAs) and reached their maximum at Cl/N = 2.4, except the yield of isovaleraldehyde formed from Gly-Leu reached its maximum at Cl/N = 1.6. UV and UV/H<sub>2</sub>O<sub>2</sub> pre-treatments decreased odorous by-product formation during subsequent chlorination through non-peptide bond breaking of short oligopeptides.

## CONCLUSIONS

Odorous by-products were not only formed from certain free AAs during chlorination but also from short oligopeptides that contained those free AAs in combined form. The short oligopeptides reacted with chlorine, producing corresponding free AAs, which were subsequently chlorinated to form odorous by-products. In addition, the structure of the short oligopeptide influenced the species and amounts of the odorous by-products formed. UV and UV/H<sub>2</sub>O<sub>2</sub> pre-treatments decreased

odorous by-product formation during subsequent chlorination. This study facilitates the identification of the causes of off-flavour problems in drinking water and the development of ways to control these problems.



**Figure 1.** Proposed mechanism for the chlorination of Gly-Leu (A, B), Leu-Gly (C) and Leu-Leu-Leu (D).

**Table 1.** The proposed reaction rate constants for the reaction pathways (Fig. 1) of the chlorination of Gly-Leu, Leu-Gly and Leu-Leu-Leu.

Reactions numbers	Reaction rate constant	Reactions numbers	Reaction rate constant
$k_1$	$3.20 \times 10^4 \text{ s}^{-1}$	$k_{C3}$	$5.90 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$k_2$	$1.00 \times 10^{12} \text{ s}^{-1}$	$k_{C4}$	$7.93 \text{ M}^{-1} \text{ s}^{-1}$
$k_{A3}$	$6.40 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$k_{C5}$	$8.75 \times 10^{-5} \text{ s}^{-1}$
$k_{A4}$	$8.70 \text{ M}^{-1} \text{ s}^{-1}$	$k_{C6}$	$8.45 \times 10^{-2} \text{ s}^{-1}$
$k_{A5}$	$4.75 \times 10^{-5} \text{ s}^{-1}$	$k_{C7}$	$9.50 \times 10^{-6} \text{ s}^{-1}$
$k_{A6}$	$9.36 \times 10^{-2} \text{ s}^{-1}$	$k_{C8}$	$0.88 \text{ s}^{-1}$
$k_{A7}$	$9.30 \times 10^{-6} \text{ s}^{-1}$	$k_{C9}$	$8.30 \times 10^{-5} \text{ s}^{-1}$
$k_{A8}$	$0.85 \text{ s}^{-1}$	$k_{D3}$	$5.20 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
$k_{A9}$	$8.00 \times 10^{-5} \text{ s}^{-1}$	$k_{D4}$	$5.70 \text{ M}^{-1} \text{ s}^{-1}$
$k_{B3}$	$6.60 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	$k_{D5}$	$6.10 \times 10^{-5} \text{ s}^{-1}$
$k_{B4}$	$9.00 \times 10^{-4} \text{ s}^{-1}$	$k_{D6}$	$5.70 \times 10^{-2} \text{ s}^{-1}$
$k_{B5}$	$6.50 \times 10^4 \text{ s}^{-1}$	$k_{D7}$	$5.60 \times 10^{-6} \text{ s}^{-1}$
$k_{B6}$	$4.85 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	$k_{D8}$	$0.35 \text{ s}^{-1}$
$k_{B7}$	$7.00 \times 10^{-5} \text{ s}^{-1}$	$k_{D9}$	$2.00 \times 10^{-5} \text{ s}^{-1}$
$k_{B8}$	$8.00 \times 10^{-5} \text{ s}^{-1}$	$k_{D10}$	$4.90 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$k_{B9}$	$1.00 \times 10^{-2} \text{ s}^{-1}$	$k_{D11}$	$3.70 \text{ M}^{-1} \text{ s}^{-1}$
$k_{B10}$	$1.00 \times 10^{-6} \text{ s}^{-1}$	$k_{D12}$	$8.33 \times 10^{-5} \text{ s}^{-1}$
$k_{B11}$	$4.00 \times 10^{-6} \text{ s}^{-1}$	$k_{D13}$	$9.06 \times 10^{-2} \text{ s}^{-1}$
$k_{B12}$	$2.00 \times 10^{-5} \text{ s}^{-1}$	$k_{D14}$	$9.73 \times 10^{-6} \text{ s}^{-1}$
$k_{B13}$	$2.00 \times 10^{-6} \text{ s}^{-1}$	$k_{D15}$	$0.65 \text{ s}^{-1}$
		$k_{D16}$	$6.00 \times 10^{-5} \text{ s}^{-1}$

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## ***BIONS* (Business Intelligence of Network Solutions): The Challenge of Integrating AI into Water Business**

A. Campos\*, A. Beivide\*, and F. Zamora\*\*

\* Automation & Control Department, ACCIONA-Water Business, Avda. De Europa 22 Bajo. Parque Empresarial La Moraleja 28108 Alcobendas. Madrid, Spain  
(E-mail: [adrian.campos.gibert@acciona.com](mailto:adrian.campos.gibert@acciona.com))

\*\* IT Department Director, ACCIONA\_Water Business, Avda. De Europa 22 Bajo. Parque Empresarial La Moraleja 28108 Alcobendas. Madrid, Spain

### **CENTRAL MESSAGE**

Over the next few decades, there will be an enormous increase in demand for water due to rising populations in emerging countries, a phenomenon that will be mainly seen in big cities. Sustainable water management is a critical issue for the future of the planet, which is why we need integrated and efficient networks. The rise of smart water cities is a crucial factor in achieving this goal and we at ACCIONA, a world leader in end-to-end water cycle management, are firmly committed to this objective.

### **SUMMARY OF INTERVENTION**

In order to achieve advanced monitoring of our smart water networks, we have developed *BIONS: Business Intelligence of Network Solutions*. This software platform allows us to record of data occurring in real-time, maximize water service quality or detect leakages early. *BIONS* integrates several data sources-smart water meters at household level, DMA sensors, subscriber and incident management systems, tank levels, GIS, weather data or calendar variables (Fig. 1). These databases are cross-referenced thanks to the use of AI, supporting data analysis, prediction and decision-making.



**Figure 1.** *BIONS* data source integration.

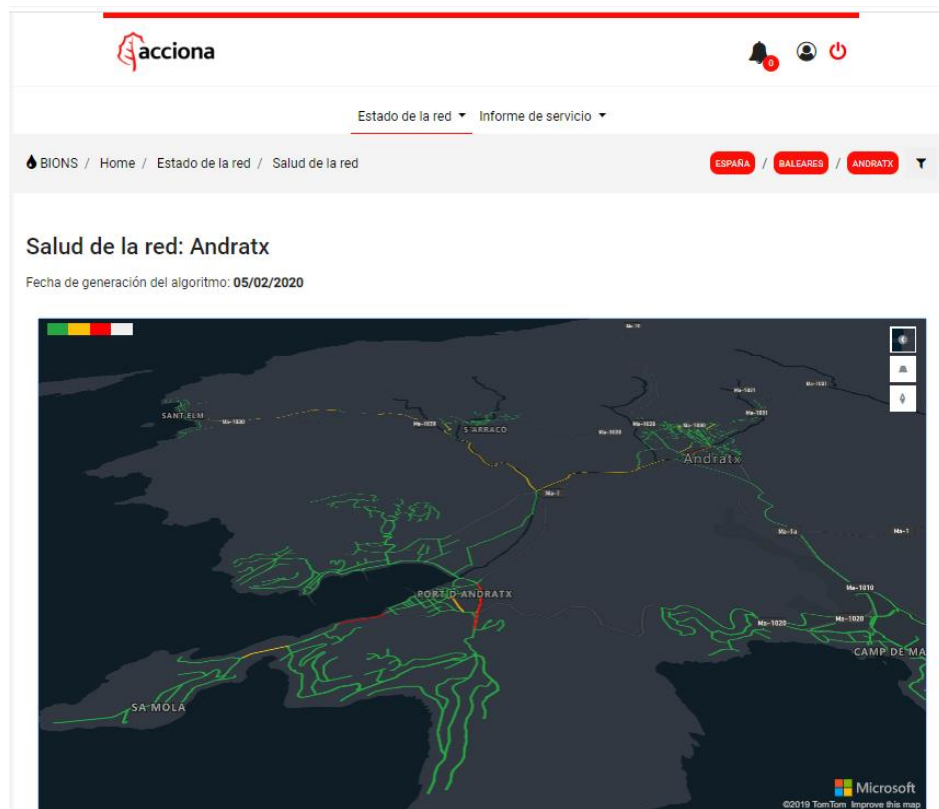
*BIONS* architecture is composed of the following modules: data intake, cloud gateways, data storage, data science and visualization. The different thresholds will generate events and the alarms associated with the algorithms developed to detect leaks online will be activated to warn of possible alerts (also by email). We have built artificial intelligence models, which are running on *BIONS* to predict the flow in different areas within Acciona concessions. The results of using Long-Short

Term Memory neural networks show very good accuracy for 1-week-ahead predictions (Fig. 1 – screenshot).

## CONTRIBUTION OF THE WORK

AI and machine learning augment human-based know-how to improve efficiency and free up resources in the international water sector. In this context, we at ACCIONA are experiencing a digital transformation (or should we say revolution?) and continue to demonstrate that our AI solutions have a brutal impact on the way we run our water services (Fig. 2).

Some key areas that are being worked on further include extracting patterns from flow demand to create predictive models of areas that do not follow a human behaviour-based pattern, where flow changes are difficult to predict since they occur artificially by means of an operator. Also, the relative cost in comparison to the “do-nothing” approach can be higher and there is still the need of opening up human resources at the sites to perform other non-automated functions. However, these are the usual “growing pains” to be encountered when implementing any new technical approach. All in all, we strongly believe that water digitalization is not only a new way of working: it is the only way.



**Figure 2.** BIONS Network health screenshot.

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# The Effect of Chitosan Nanoparticles on *Escherichia Coli* Viability in Drinking Water Disinfection

V. Denisova\* and L. Mezule\*

\* Water Research and Environmental Biotechnology Laboratory, Faculty of Civil Engineering, Riga Technical University, P. Valdena 1–204, Riga, Latvia, LV-1048  
(E-mail: [viktorija.denisova@rtu.lv](mailto:viktorija.denisova@rtu.lv); [linda.mezule@rtu.lv](mailto:linda.mezule@rtu.lv))

## INTRODUCTION

Chlorination is the most often used drinking water disinfection technique in developed countries which has shown to be effective against a wide variety of pathogenic microorganisms, easily applicable and low cost. However, it has several disadvantages, like, unfavourable taste and odour, ineffectiveness against resistant microorganisms, such as *Giardia* and *Cryptosporidium*, and can form potentially toxic disinfection by-products, such as trihalomethanes and haloacetic acids (Xue *et al.*, 2017). Therefore, it is still important to develop effective antimicrobial techniques and agents. Chitosan has been highlighted as a potential compound in drinking water disinfection due to its native antimicrobial properties, and low or no toxicity risk for human health. Chitosan is a linear polysaccharide consisting of randomly distributed  $\beta$ -(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units and is produced by deacetylation of chitin, which is extracted from the exoskeleton of crustaceans such as shrimps and crabs, as well from the cell walls of fungi, insects and yeasts. It is the second most abundant biopolymer with non-toxic, biocompatible, biodegradable, and antimicrobial properties with numerous applications in food, cosmetic, biomedical and agricultural areas (Chung *et al.*, 2003). Due to these properties, in the present study, chitosan nanoparticles (CNs) were investigated as a potential applicable and an alternative antimicrobial agent in drinking water disinfection. The effect of CNs was assessed by determining the inactivation rate of faecal indicator *Escherichia coli* viability.

## EXPERIMENTAL METHODS

### Preparation of chitosan nanoparticles

Chitosan nanoparticles (CNs) were prepared by an ionic gelation method (Yang *et al.*, 2015) from medium molecular weight chitosan (MMWC, 190 000–310 000 Da with 75–85 % degree of deacetylation). 0.25 % (w/v) chitosan solution was prepared in a mixture of 2 % acetic acid (v/v) and 1 % (w/v) Tween®80. The solution was stirred overnight with a constant shaking at 200 rpm until no particles were observed. For cross-linking of chitosan, 2 mL of 10 % of Na<sub>2</sub>SO<sub>4</sub> (w/v) was added to chitosan solution under magnetic stirring until the solution became cloudy. Then, the solution was sonicated for 20 min (60 W, 50 Hz) to decrease its viscosity. The nanoparticle suspension was centrifuged at 8500 rpm at 20 °C for 10 min (OHAUS, Germany). The pellet was re-suspended in sterile distilled water to wash the CN and centrifuged again. Centrifuging and rinsing process was repeated twice before freeze-drying of the pellet.

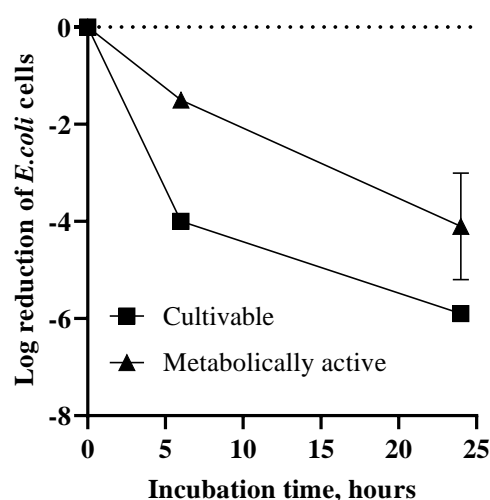
### Evaluation of antimicrobial activity

*Escherichia coli* ATCC®25922 was used as microbial standard to evaluate the inactivation performance and disinfection efficiency. Approximately  $5 \times 10^5$  CFU/mL of *E. coli* were inoculated into 2 mL of pre-filtered tap water (0.2  $\mu$ m pore size filters, pH 7.5) and mixed with CNs to final chitosan concentration of 3.5 mg/mL. Then the samples were incubated for 24 hours at 37 °C with shaking at 200 rpm. Samples were collected after 0 h, 6 h and 24 h. Each experiment was performed

in triplicates. The experiment without chitosan particles was used as a blank control. Antibacterial activity of CN against *E. coli* was evaluated with plate count technique and with *E. coli* cell metabolic activity measurements.

## RESULTS AND DISCUSSION

Within first 6 hours, more than 99.99 % ( $4.00 \pm 0.06$  log) reduction in cultivable *E. coli* count was obtained with the tested CNs (Fig. 1). The metabolic activity of *E. coli* decreased less, showing a decline of only  $1.50 \pm 0.11$  log (97 % inactivation). When the contact time was prolonged to 24 hours of treatment a  $5.90 \pm 0.09$  and  $4.1 \pm 1.1$  log reductions in cultivable and metabolically active *E. coli* were obtained, respectively. At the same time, in control samples  $0.10 \pm 0.01$  and  $2.10 \pm 0.33$  log reduction for metabolically active and cultivable *E. coli* were obtained within 24 h.



**Figure 1.** The effect of 3.5 mg/mL CN concentration on log reduction of cultivable (■) and metabolically active (▲) *E. coli* in tap water.

The results indicated that CNs were able to inhibit the growth of cultivable and metabolically active *E. coli* in tap water and demonstrated the potential use of CNs in drinking water disinfection. Nevertheless, further studies are necessary in order to investigate the optimal treatment conditions (CN concentration, time, etc.) to effectively and more rapidly treat pathogens in drinking water.

## ACKNOWLEDGEMENTS

The research work is supported by ERA-NET EU-LAC Health project Efficient and affordable water treatment technologies to minimize waterborne diseases, Hi-Water (No. ES RTD/2018/26); and Riga Technical University's Doctoral Grant programme (DOK.BIF/20).

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# Groundwater Quality Impacts on Human Health and Internal Consistency of Public Perception: An Exploratory Study

S. M. Didar-UI Islam\* and F. Zhang\*

\* Division of Groundwater and Soil, School of Environment, Tsinghua University, Beijing 100084, China (E-mails: [didar\\_577@yahoo.com](mailto:didar_577@yahoo.com); [fangzhang@tsinghua.edu.cn](mailto:fangzhang@tsinghua.edu.cn))

## BACKGROUND

Assurance of safe drinking water is the primary human needs and essential to a healthy and viable community. It is one of the key agenda of Sustainable Development Goals (SDGs), which is a big challenge for densely populated developing countries due to natural and anthropogenic phenomena. Groundwater is considered as a safe reserve of good quality water, and nearly one-third of the world's population use it for drinking purpose (Bhutiani *et al.*, 2016; Selvam *et al.*, 2017). However, it isn't safe for drinking in many parts of the world, because of contamination by a range of pollutants, which may have serious health effects (Naz *et al.*, 2016; Zhu *et al.*, 2019). Groundwater, which is the main source of drinking water in Bangladesh, is being over-exploited and contaminated by high salinity and arsenic (Dey *et al.*, 2019). This study conducted in Subarnachar of Noakhali district, located at south-eastern coastal region of Bangladesh. It is estimated that, nearly 73.75 % of people use tube wells as a source of potable water, which contains high salinity, arsenic and other contaminants (BBS, 2011). In this background, this study intended to explore the consistency of public perception regarding the impacts of groundwater use on human health.

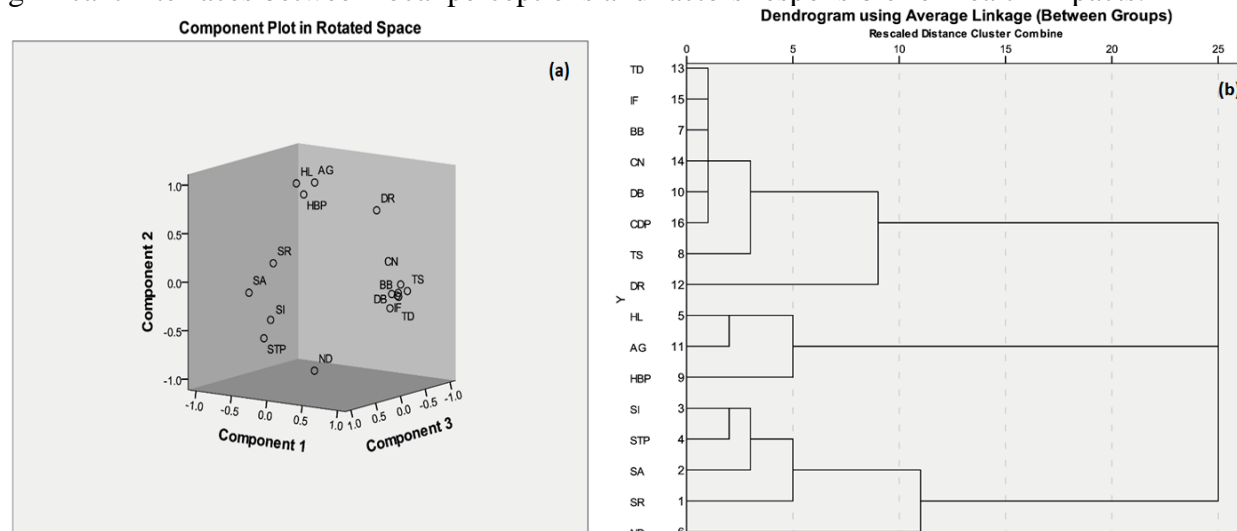
## METHODOLOGY

To investigate the household water use behaviour and impacts of groundwater use on human health both qualitative and quantitative methods were employed; including field observation, household interview and analysis of real field groundwater data. The survey was designed to obtain information regarding the health effects due to use of groundwater, and sample size was determined using a confidence level of 95 % and a confidence interval of  $\pm 7$ . Multivariate statistical techniques i.e., principal component analysis (PCA) and cluster analysis (CA), were used to analyse the surveyed data, by using SPSS (version 22.0) software. To evaluate the consistency of public perception real groundwater data were further analysed, and calculate the health risk via exposure of oral and dermal routes. Both chronic and carcinogenic health risk of groundwater were determined by following the guidelines of USEPA.

## RESULTS

It was found from the study that, local peoples are suffering from several diseases including numerous skin disease i.e., skin rash (SR), skin allergy (SA), skin infection (SI), and skin thickening and pigmentation (STP); hair loss (HL), nail disorder (ND), high blood pressure (HBP), teeth skeletal (TS), brittle of bones (BB), diabetes (DB), diarrhoea (DR), acidity and gastroenteritis (AG), thyroid disorder (TD), infertility (IF) and child development problem (CDP). Most of the respondents indicate that, salinity and arsenic (As) are the main causes of skin disease and ND. Nearly 55.49 % and 77.84 % respondents claimed salinity is the causes of HL, and HBP respectively. Moreover, arsenic along with others contaminants and lifestyle factors may responsible for the occurrence of rest of the diseases. Furthermore, results of PCA and CA revealed

significant interfaces between local perceptions and factors responsible for health impacts.



**Figure 1.** (a) Lading score plot of PCA, and (b) hierarchical cluster of local perception.

However, it was found that, groundwater of the study area is slightly alkaline with high salinity level. The concentration of electrical conductivity,  $\text{Na}^+$  and  $\text{Cl}^-$  ranges from 1649–3380  $\mu\text{S}/\text{cm}$ , 231.6–514.2 mg/L and 435.1–1250 mg/L respectively, which exceed the permissible limit of WHO drinking water quality standards. Moreover, chronic health risk of groundwater As, Fe, Mn and  $\text{F}^-$  exposure via oral and dermal routes were determined by calculating the hazard quotient (HQ) and hazard index (HI), for both adult and children, and found medium to high health risk due to consumption of groundwater without further treatment. Again, carcinogenic risk of As via oral exposure suggests high cancer risk for both adult and children.

## CONCLUSION

Groundwater quality of the study area is poor and affects community health, which is justified from both public perception and health risk assessment of real groundwater. Hence, community based and low cost drinking water treatment should be introduced for safe water supply and to reduce the health hazards.

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# Removal of Cyanobacterial Amino Acids from Water by Activated Carbon: Effect of Temperature

K. Fialova\*, L. Cermakova\*, I. Kopecka\*, and M. Pivokonsky\*

\* Institute of Hydrodynamics of the Czech Academy of Sciences, Pod Pařankou 30/5, 166 12 Prague 6, Czech Republic (E-mails: [fialova@ih.cas.cz](mailto:fialova@ih.cas.cz); [cermakova@ih.cas.cz](mailto:cermakova@ih.cas.cz); [kopecka@ih.cas.cz](mailto:kopecka@ih.cas.cz); [pivo@ih.cas.cz](mailto:pivo@ih.cas.cz))

## INTRODUCTION

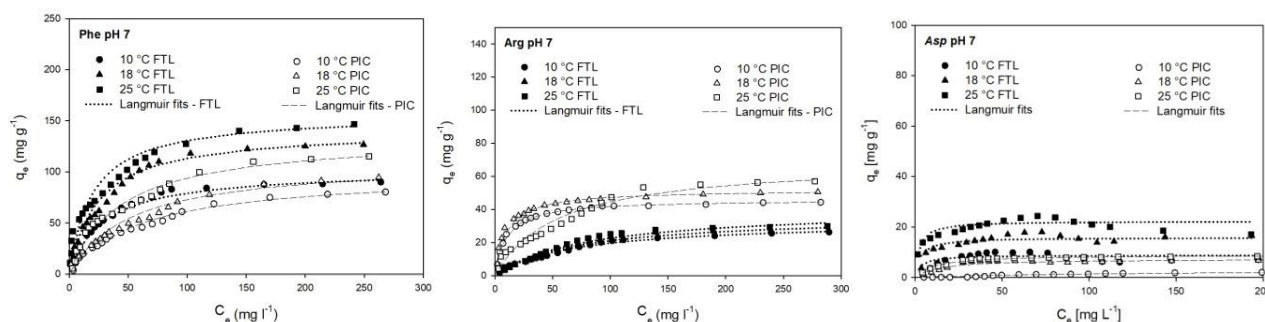
The organic material originating from the production of cyanobacteria and green algae contain a variety of peptides and free and combined amino acids (AAs), which represent together with peptides the dominant part of the low-MW fraction (MW < 10 kDa) (Pivokonsky *et al.*, 2014). It has been reported that the low-MW fraction is removable by the coagulation process with more difficulties than algal products with higher molecular weight (Pivokonsky *et al.*, 2012) and causes many problems in drinking water treatment. Several studies reported that amino acids can interfere with aqueous chlorine during water disinfection and create harmful disinfection by-products, such as trihalomethanes and haloacetic acids (Fang *et al.*, 2010), or cause taste and odour problems (Freuze *et al.*, 2005), or might be a potential source of biodegradable organic carbon for microorganisms in the drinking water network distribution (Hong *et al.*, 2009). Adsorption onto activated carbon (AC) represents a possibility of how to remove these substances. Our previous study revealed that the adsorption efficiency of cyanobacterial AAs fundamentally depends on pH and ionic strength of the solution (Cermakova *et al.*, 2017). In this study, we focused on the effect of the temperature of the solution as another factor that influences the adsorption process.

## MATERIALS AND METHODS

Adsorption experiments were performed with three AAs of different chemical and structural properties: L-phenylalanine (Phe), L-arginine (Arg) and L-aspartic acid (Asp) (Sigma-Aldrich, USA) and two granular activated carbons Filtrasorb TL830 (FTL) (Chemviron Carbon, USA) and Picabiol 12 × 40 (PIC) (Jacobi Carbons, Japan). Adsorption isotherms of AAs were obtained by batch experiments using samples (250 mL of AAs solution with concentration range 5–300 mg L<sup>-1</sup> DOC) shaking for 48 h (pre-determined interval to reach adsorption equilibrium) with 400 mg L<sup>-1</sup> of adsorbent (FTL or PIC) at pH 5, 7 and 9 and temperatures of 10 °C, 18 °C and 25 °C, respectively.

## RESULTS AND CONCLUSIONS

The study showed that the temperature of the solution influences adsorption efficiency according to the character of AAs, the solution pH, and the surface properties of AC. The predominant effect of temperature was observed in adsorption of Phe, on the other hand, there was only a slight effect of solution temperature on the adsorption of Arg. The effect of solution temperature on adsorption is predominant if the dominant adsorption mechanism is not based on interactions controlled by the solution pH. While, Phe is a hydrophilic amino acid and interacts with AC through hydrogen bonds, that are minimally affected by pH, Arg is a basic amino acid and is adsorbed primarily via electrostatic interactions. The uptake in adsorption was higher with increasing solution temperature for all examined AAs. That means the adsorption of amino acids can be promoted as endothermic in nature.



**Figure 1.** Adsorption isotherms for Phe, Arg and Asp at pH 7 under different solution temperature on GAC FTL and PIC.

Adsorption is generally considered as a spontaneous process with exothermic nature and increasing uptake is expected when the adsorption temperature decreases (Moreno-Castilla, 2004). One possible explanation for the endothermic nature of the adsorption process has a connection to hydration. If the compounds want to adsorb to the adsorbent surface they must first lose part of their hydration coating, which is done at the same time as energy consumption (Anastopoulos and Kyzas, 2016). The increase in adsorption efficiency due to the higher temperature can be explained in some cases by the fact that with increasing temperature molecules interact easier with each other. This results in the formation of larger associates that are able to bind to the active centre on the AC surface (Schreiber *et al.*, 2005).

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## SAR Analytical Solutions to Locate Sub-Surface Water

J. Jacobi\* and P. Gagliardo\*\*

\* Utilis, Amal St. 13, Park Afeq, Building A, 1st floor, Rosh Ha'ayin 4809249, Israel  
(E-mail: [Jonathan@utiliscorp.com](mailto:Jonathan@utiliscorp.com))

\*\* Gagliacqua Consulting, 1045 San Dieguito Drive, Encinitas, California, 92024, USA  
(E-mail: [gagliacqua@cox.net](mailto:gagliacqua@cox.net))

### INTRODUCTION

Water scarcity exists in many areas of the European Union and with climate change is likely to become more acute. For many water utilities the amount of water available which is physically lost in the underground pipe network is also very high. These losses are environmentally wasteful, can cause significant service interruptions to customers and result in high economic losses and infrastructure damage for the network operator. A study was performed by Isle Utilities to determine if aerial leak detection technologies could improve the way in which water operators monitor and assess their networks (Isle, 2020). The study was initiated and funded by the European Bank for Reconstruction and Development (EBRD). A satellite solution provided by Utilis was selected for testing and comparison to traditional methods for pinpointing leaks. The testing was performed in cooperation with a Romanian utility, APA Canal 2000, to test the efficacy of the solution, and to enable a comparison with traditional leak detection practices.

The Utilis technology was tested in the field between July and August 2020 by APA Canal 2000 in Pitesti, Romania which is located approximately 120 km from Romania's capital city, Bucharest. APA Canal 2000 is the regional provider of water and wastewater services in the Arges County region. They provide clean water to approximately 250 000 customers through an 850 km water network. A compilation of current system operational data is contained in Table 1. Unaccounted for water (UFW) loss is estimated to be 217 L/s, or 37 % of system delivery based on a simple water balance of plant production versus metered deliveries.

**Table 1.** APA Canal 2000 Operational.

Metric	Value
Distribution System Pipelines	850 km
Number of Water Service Connections	47 500
Average System Delivery	579 L/s
Unaccounted-for Water	217 L/s (37.5 %)

APA Canal 2000 has a team of 5 members of staff (4 field technicians and 1 manager) dedicated to finding leaks in the network. The team uses temporary acoustic loggers, GPRs and correlators to identify and pinpoint leaks that are highlighted by overnight deployment of the acoustic loggers. These tools allow them to find an average of 8 leaks per month. These are unreported leaks that would otherwise be unseen. Additionally, 2300 reported leaks per year are identified by the public across the network.

### METHODS

The process by which Utilis identifies points of interest and likely leaking locations (POI/LLL) starts with the acquisition of a synthetic aperture radar (SAR) satellite image of the area of interest (AOI). SAR can be used regardless of weather conditions. It can penetrate the first few meters

below the surface, therefore detecting underground leaks. The raw image was obtained on 11 March 2020. A single satellite image can cover approximately 3500 km<sup>2</sup> which was adequate to include the entire APA Canal service area. The raw image is prepared for analysis by filtering out of the backscatter signal external objects such as buildings, man-made objects, vegetation and hydrologic features. Utilis then uses its propriety and patented algorithm to analyze the filtered signal to identify the signature of potable water under the ground surface. POI/LLs generated from this analysis were provided to APA Canal in GIS reports including street locations and presented on leak technician's mobile devices. The POI/LLs were made available to the leak crews on 20 March 2020, nine days following the initial satellite image acquisition.

## RESULTS

The results of the trial are presented in Table 2. It shows that a total of 120 POI/LLs were identified following the satellite scan. Of these 120 POIs, 62 POIs were confirmed to have at least 1 leak present, 12 had a suspected leak and 46 were quiet meaning no leak was present. A total of 72 leaks were identified.

It should however be noted that of the total 72 leaks found, only 28 were uniquely highlighted by the satellite data. This is because during the time between the scan being undertaken (March 2020) and the field work actually taking place (July 2020), 44 of the leaks had already been detected by APA Canal 2000's leakage team or by members of the public and was repaired or was in process of being repaired.

**Table 2.** Utilis APA Canal.

<b>Metric</b>	<b>Value</b>
<b>Number of Leaks Found</b>	72
<b>Network Distance Inspected, km</b>	57.6
<b>Leak Inspection Crew Days</b>	15.8
<b>Leaks per Km Inspected</b>	1.2
<b>Leaks per Crew Day</b>	4.7

It is also important to note that of the 72 leaks identified by the satellite survey, 28 (39 %) had not surfaced and are unreported leaks. This is one of the great benefits of the Utilis satellite program, finding unreported, unseen leaks. Additionally, 49 of the 72 leaks were found on the pipe mains (68 %) and 18 (25 %) were found on service lines. These tend to be the largest leaks in a system and contribute the most to non-revenue, real water loss.

## CONCLUSION

The technology has proven to be effective at highlighting the presence of underground leaks that would otherwise remain undetected. Localizing leaks with the Utilis satellite data is simple and the interface is easy to use. This trial demonstrated that more leaks were found using the Utilis satellite program versus the traditional method deployed by APA Canal during a similar period. The Utilis program is a definite improvement over the traditional of searching for and pinpointing leaks in a potable water system.

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# Monitoring Diclofenac Removal by Selected Adsorption Materials

S. Moravčíková\* and R. Biela\*

\* Institute of Municipal Water Management, Faculty of Civil Engineering, Brno University of Technology, Žižkova 17, 602 00, Brno, Czech Republic (E-mails: [moravcikova.s@fce.vutbr.cz](mailto:moravcikova.s@fce.vutbr.cz); [biela.r@fce.vutbr.cz](mailto:biela.r@fce.vutbr.cz))

## INTRODUCTION

Currently, there is extensive use, often overuse of pharmaceuticals. As a result, their occurrence in the environment is becoming increasingly apparent. Pharmaceuticals get into sewage with urine and solid faeces. They may also enter water due to improper disposal of unused medicines, which are often flushed into waste, or, together with municipal waste, exported to landfill sites where they leak into groundwater. Possible negative impact of pharmaceuticals on the environment leads to monitoring of these substances in the aquatic environment (Moravčíková, 2020).

## MATERIALS AND METHODS

An experiment, monitoring diclofenac removal efficiency by selected sorption materials, was performed as a part of a specific research at the Institute of Municipal Water Management, Faculty of Civil Engineering, Brno University of Technology. The aim of the experiment was to compare the selected sorption materials in terms of their effectiveness of removing diclofenac from water.

### Diclofenac

Diclofenac has been selected as a representative of non-steroidal anti-inflammatory pharmaceuticals, which is the most widely used group of pharmaceuticals. Pharmaceuticals included in this group are used to relieve pain, alleviate the symptoms of inflammation and also to lower elevated body temperature. They are mainly used for various inflammatory joint diseases, associated with pain and impaired mobility, and also for various painful soft tissue disorders (Moravčíková, 2020).

### Sorption materials

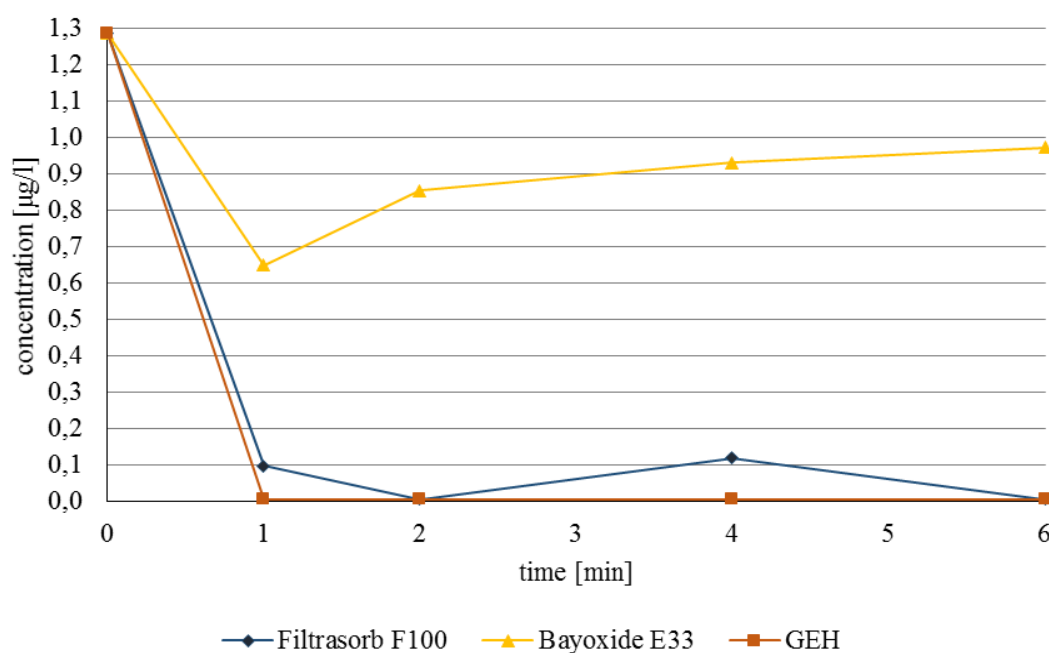
Materials Filtrasorb F100, Bayoxide E33 and GEH were selected for the experimental removal. Granular activated carbon Filtrasorb F100 is able to capture substances dissolved in water, especially of organic character, but also toxic heavy metals such as mercury, cadmium and lead (Moravčíková, 2020). Bayoxide E33 is a dry granular sorbent on the basis of iron hydroxide. The material was designed to remove arsenic, its advantage is elimination of As(III) and As(V) along with the removal of iron and manganese (Biela and Šopíková, 2017). GEH sorption material is based on granulated iron hydroxide and is suitable for efficient and effective removal of arsenic and antimony from water. The adsorption capacity of the material depends on the operating conditions (Barloková *et al.*, 2019).

### Course of the experiment

Filtration was carried out in columns with inner diameter of 4.4 cm. A drainage layer was formed at the bottom of these columns to prevent leakage of sorption materials during filtration. The filtration material itself was then poured over the drainage layer. The height of the filtration layer was chosen based on the recommendations of the material's producer. Model water for filtration was prepared by adding diclofenac to a barrel of water from Brno water supply network. This water was pumped to the top of filtration columns and samples were taken at pre-selected times during the filtration.

Temperature, pH and turbidity were measured, and residual concentrations of diclofenac were analysed in the collected samples.

## RESULTS AND CONCLUSION



**Figure 1.** Diclofenac removal from model water.

Sorption material GEH had the highest efficiency of removing diclofenac, the drug's concentration was below the limit of detection at all observed times. Material Filtrasorb F100 achieved very similar results, with more than 90 % removal efficiency over the entire course of the measurement. For Bayoxide E33, the removal efficiency was significantly lower, with a decreasing tendency. Based on this experiment, only Filtrasorb F100 can be considered suitable material for pharmaceuticals removal. The GEH material, although most effective in removing the pharmaceutical, lowered the pH below the limit for drinking water and therefore does not appear to be a good option for pharmaceuticals removal. Bayoxide E33, very effective in removing metals from water, was found to be inappropriate for removal of the selected pharmaceutical.

## ACKNOWLEDGMENT

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# The Mechanism of Adsorbents Adsorption Affinity in Relation to Geometric Parameters

S. Ntsondwa<sup>\*,\*\*</sup>, V. Msomi<sup>\*,\*\*</sup>, M. Basitere<sup>\*,\*\*</sup>, and Z. Mdletshe<sup>\*,\*\*</sup>

\* Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Cape Peninsula University of Technology, P. O. Box 1906, Bellville, 7535, South Africa (E-mail: [bingon@cput.ac.za](mailto:bingon@cput.ac.za))

\*\* Bioresource Engineering Research Group (BioERG), Cape Peninsula University of Technology, P. O. Box 652, Cape Town, 8000, South Africa (E-mails: [basiterem@cput.ac.za](mailto:basiterem@cput.ac.za); [ntwampes@cput.ac.za](mailto:ntwampes@cput.ac.za))

## INTRODUCTION

In the process of incorporating adsorption with thermal desalination, adsorbents are important because they increase the water vapour uptake rate and this would yield more desalinated water over a short period. they are a solid substance used to collect solute molecules from a liquid or gas. The purpose of adsorbents is to adsorb the water vapor from the saline or brackish source after it has been heated (Rouquerol *et al.*, 2013). Adsorbent determination for evacuation of water contaminants relies upon concentration and type of pollution present in the water, effectiveness and adsorption limit with respect to contamination. In addition, the adsorbents ought to be non-toxic, cost effectively accessible and should be environmentalfriendly (Hübschmann, 2015).

Adsorption and desorption are often used to indicate the direction from which they approached the equilibrium state. Adsorption often used to extract contaminants by allowing adsorbents like activated alumina or silica gel connected to them. Adsorbents are porous solids that tie in their surface liquid or gaseous molecules. The adsorption process mostly includes what referred to as a fixed bed adsorber, where a substance like air passes through a solid adsorbent bed. Adsorbent draws the undesirable particles in the air as the moisture evaporates (Plee and Methivier, 2005). The reaction, at constant temperature, between the amount adsorbed and the equilibrium pressure, or concentration, is known as the adsorption isotherm (Rouquerol *et al.*, 2013).

Selection or synthesis of adsorbents for a target adsorbate molecule is based on the adsorption isotherm. Geometric parameters that are of interest are the pore size diameter, surface area, the affinity to adsorb the vapour, distance between the fin and the material of the fin and the pipe. These geometric parameters will be compared using three different types of adsorbents in a B.E.T machine. The adsorbents used; activated alumina, silica gel and molecular sieve zeolites. It has been shown that surface properties such as surface chemistry and pore size distribution (PSD) of adsorbents play a significant role in the adsorption process and in controlling the adsorptive mechanism of competition for a given size pore, hence the study is conducted (Hübschmann, 2015).

## MATERIALS AND METHODS

An experimental set up designed and built, the system consists of mainly three chambers: adsorbent chamber, (absorber) dosing chamber and evaporator. The chamber connected together throughout a set of valves and tubes. Seawater pumped intermittently into evaporator; pressure monitored and liquid phase change into vapour. Evaporator opens to enable the vapour to escape through valves and adsorbed by the unsaturated adsorbent, which insulated the tube fin heat exchanger inside the reactor bed. The brine occasionally discharged from the evaporator, when the valve between adsorption bed and evaporator open, a continuous vapour uptake achieved. The fluid flowing through heat exchanger will be cold water in order for adsorbent easily trap the vapour and that will happen during adsorption process. Desorption start again saturated vapour escape to condenser.

From condenser the distilled water moves to the storage tank. Due to covid-19 lockdown, lab work had to stop running, therefore there's not much information on results section (results are not yet fully available).

## RESULTS

Table 1 shows the comparison of adsorbents and their geometric parameters

**Table 1.** Table showing the comparison of adsorbents.

Properties	Silica gel	Molecular sieve zeolite	Activated alumina
Desorption temperature	55–140 °C	175–370 °C	120–260 °C
Rate of adsorption	Excellent	Good	Good
Surface area	800 m <sup>2</sup> /g	500–800 m <sup>2</sup> /g	360 m <sup>2</sup> /g
Diameter	2–5 mm	0.5–2.5 mm	2–5 mm
Pore volume	0.4 mL/g	0.35 nm	0.5 mL/g
Bulk density	800 g/L	750 g/L	750 g/L
Capacity for water at 25 °C, 40 % RH	High	High	High

Due to Covid-19 lockdown the experiment is not fully performed, therefore the table above shows the preliminary results. However the experiment will still be going to be continued, and provide clear results.

## CONCLUSION

Key parameters in the selection of adsorbent for an adsorption desalination (AD) cycle are thermo-physical properties, surface characteristics and water vapor uptake capacity. The best adsorbent is used as the adsorbent-refrigerant pair and is driven at 60 °C to 85 °C by low-temperature heat sources, such as solar energy or waste heat from industrial processes and it should have reasonable distance in between fin. The size of the adsorbents relative to the pore size of the adsorbents is important in controlling the adsorptive mechanism of competition for a given size pore. It helps to improve efficiency by placing various layers of these beds (Plee and Methivier, 2005).

As the analysis conducted, all adsorbents show high performance, they are chemically stable and insoluble in solvent. However the silica gel stands out, because it can be easily generated at 85 °C and it is incredibly active in temperatures that are lower than 25 °C. Due to the high desorption temperature of activated alumina and molecular sieve zeolite, both adsorbents will require more energy for desorption to take place whereas silicagel can easily release the vapour. Adsorption and desorption are both triggered by temperature change because the adsorbents are made up of material that has hydrophobic and hydrophilic properties, it adsorbs and desorbs. Therefore it can be concluded that the silica gel has the good qualities of geometric parameters to be used in adsorption desalination.

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## Ozonation and Coagulation of Non-Proteinaceous Algal Organic Matter

M. Prokopova\*, K. Novotna\*, L. Pivokonska\*, and M. Pivokonsky\*

\* Institute of Hydrodynamics of the Czech Academy of Sciences, Pod Patankou 5,  
166 12 Prague 6, Czech Republic (E-mails: [prokopova@ih.cas.cz](mailto:prokopova@ih.cas.cz); [novotna@ih.cas.cz](mailto:novotna@ih.cas.cz);  
[pivokonska@ih.cas.cz](mailto:pivokonska@ih.cas.cz); [pivo@ih.cas.cz](mailto:pivo@ih.cas.cz))

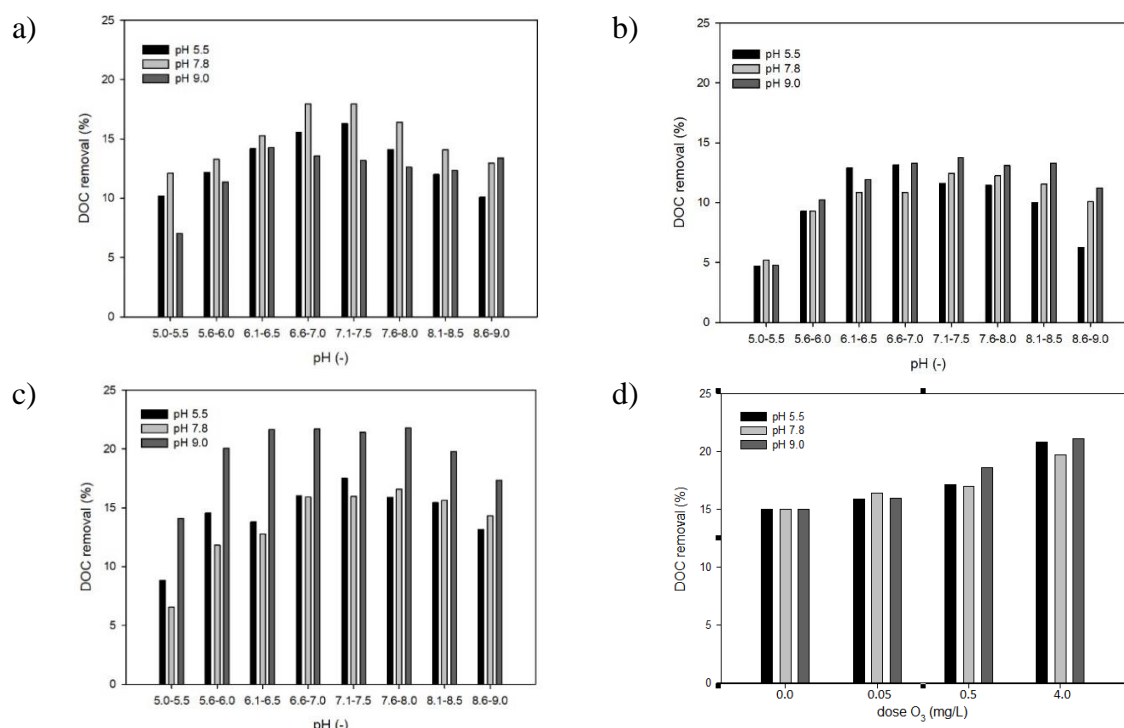
### INTRODUCTION

The presence of algal blooms leads to an increase in the concentration of algal organic matter (AOM) in drinking water sources (Henderson *et al.*, 2008a). Increased content of AOM in drinking water sources may affect the quality of drinking water, but it may also have a harmful effect on human health. Especially, cyanobacterial metabolites and disinfection by-products (DBPs) can be toxic or carcinogenic (Pivokonsky *et al.*, 2015). The composition of AOM is very diverse but most often contains proteinaceous and non-proteinaceous fraction. Depending on the type of microorganism and its growth phase, AOM may contain a higher proportion of non-proteinaceous organic substances (up to 80 %) (Henderson *et al.*, 2008b; Pivokonsky *et al.*, 2006). However, the coagulation efficiency of the non-proteinaceous of AOM is relatively low. The low aggregation efficiency of the non-proteinaceous of AOM is probably caused to the high content of low molecular weight or uncharged organic substances that are difficult to remove by coagulation (Naceradska *et al.*, 2019). The use of a strong oxidizing agent (e. g. ozone) is expected to oxidize natural organic substances present in raw water. It leads to an increase in the carboxylic functional groups, which increase the coagulation efficiency by higher association with metal ions present in the raw water (Bose and Reckhow, 2007). However, pre-oxidation can also harm coagulation. Pre-oxidation can cause cell lysis, the release of toxic or taste and odour substances, but also degradation of AOM to low molecular weight (MW) substances. However, low MW substances formed by the oxidation of AOM may be difficult to remove by the coagulation (Henderson *et al.*, 2008a). This study deals with the effects of coagulation and ozonation on the removal of the non-proteinaceous fraction of AOM during drinking water treatment.

### RESULTS AND CONCLUSION

At first, attention was paid to the influence of ozone on the character of non-proteinaceous AOM of green alga *Chlorella vulgaris*, then to the combining ozonation (pre-ozonation and post-ozonation) with coagulation (aluminum dose 10 mg/L). Different ozone doses (0.05–4.00 mg/L per 5 mg/L dissolved organic carbon – DOC) and various pH values (ozonation pH 5.5; 7.8 and 9.0; coagulation pH 4.5–9.3) were tested. Only a small change (up to 5 %) to the DOC concentration resulted from the application of the ozone itself. However, significant changes in the character of the non-proteinaceous components were observed – the proportion of low MW compounds increased, mostly at the highest ozone dose at pH 9.0. Despite that maximum removal efficiency (15 %) was increased by pre-ozonation up to 22 % depending on the ozone dose and pH value. A possible explanation is that the ozonation affected the charge properties of non-proteinaceous algal organic matter. A similar result was observed in coagulation-ozonation, the removal efficiency of DOC was 21 % at the highest ozone dose at pH 9.0. This was probably due to the degradation of uncoagulated material to carbon dioxide. The removal efficiency of the non-proteinaceous AOM by coagulation can be enhanced by adding an ozonation unit to the drinking water treatment process. However, even after ozonation, the removal efficiency achieved is relatively low. Besides,

improvement occurs only under specific conditions, otherwise, ozonation can deteriorate coagulation (e. g. dose of ozone 0.5 mg/L).



**Figure 1.** Effectiveness of DOC removal of non-proteinaceous AOM at ozone dose a) 0.05 mg/L; b) 0.5 mg/L; c) 4.0 mg/L depending on pH value after ozonation-coagulation; and d) after coagulation-ozonation.

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## Evaluation of the Efficiency of *Escherichia Coli* Inactivation and Water Preservation Using Low Pressure CO<sub>2</sub>

M. N. Saprykina\*, E. S. Bolgova\*, L. O. Melnyk\*, and V. V. Goncharuk\*

\* A. V. Dumansky Institute of Colloid and Water Chemistry, 42, Vernadsky Blvd, Kyiv, Ukraine, 03680 (E-mail: *saprykina\_m@ukr.net*)

### INTRODUCTION

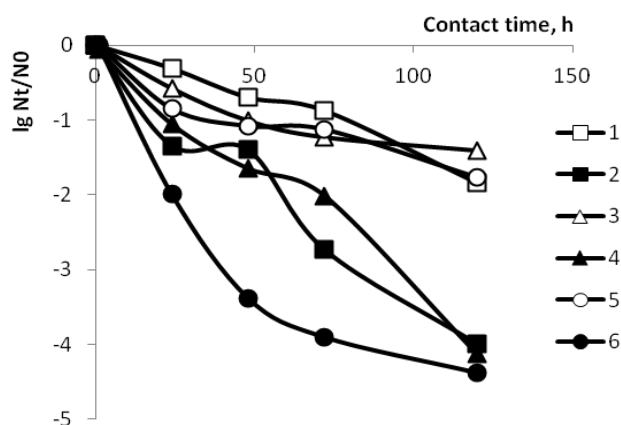
The requirements for the quality of drinking water, which have increased in recent decades, necessitate the search for alternative, environmentally friendly and effective technologies for its preparation, ensuring the receipt of water that is safe for the consumer. In this regard, studies on the possibility of using CO<sub>2</sub> for water disinfection and preservation at low operating pressures are of particular interest (Ribeiro *et al.*, 2020).

### MATERIALS AND METHODS

In the paper in question, the effectiveness of disinfection and preservation of water from *Escherichia coli* (*E. coli*) with CO<sub>2</sub> of low pressure (0.05–0.20 MPa) in the temperature range (14–42 °C) was studied. The processing of model solutions of CO<sub>2</sub> was carried out by short-term supply of the reagent to the bottom of a hermetically sealed mixing vessel through an aerator until the required pressure was established, which was maintained throughout the experiment.

### RESULTS

It has been shown that disinfection of *E. coli* in distilled water reaches 4.0–5.5 orders of magnitude (the initial culture load is  $1.3 \times 10^4$  CFU/cm<sup>3</sup> to  $9.0 \times 10^5$  CFU/cm<sup>3</sup>) in 5 days after the start of treatment at all studied pressure values and temperature (14–37 °C) (Fig. 1). Moreover, higher rates of disinfection were observed at maximum temperature and pressure. Inactivation of *E. coli* in control experiments (without CO<sub>2</sub>) was only ~1.5 orders of magnitude under similar conditions. It was found that a change in the shape of the kinetic curve of *E. coli* inactivation with CO<sub>2</sub> is observed with an increase in temperature, which indicates a significant contribution to the disinfection process of the rate of CO<sub>2</sub> diffusion through the cell membrane.

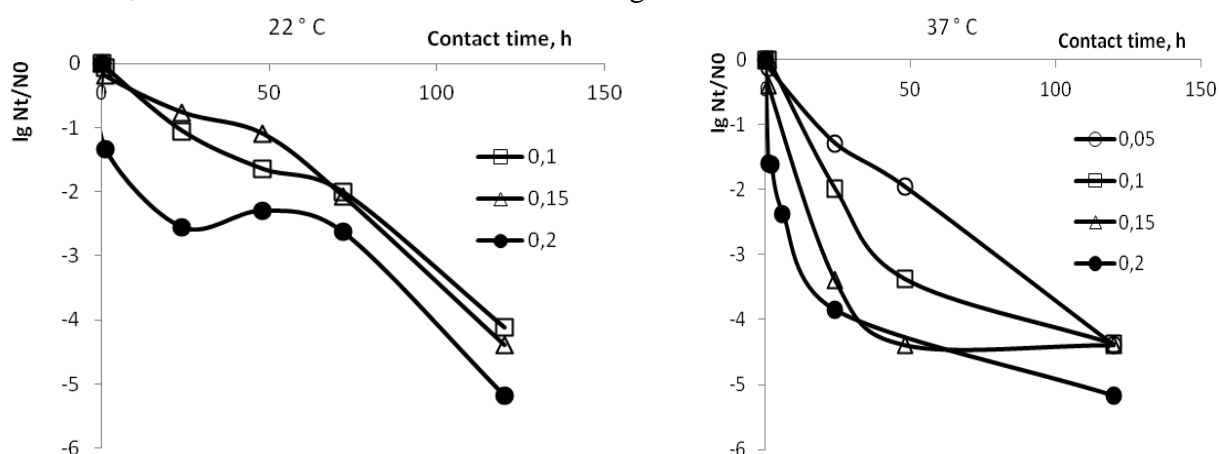


**Figure 1.** Kinetics of *E. coli* inactivation in distilled water (1, 3, 5) and water saturated with CO<sub>2</sub> at a pressure of 0.1 MPa (2, 4, 6). Temperature: 14 °C (1, 2); 22 °C (3, 4) and 37 °C (5, 6).

A high preservative ability of CO<sub>2</sub> was established at a saturation pressure of 0.1 MPa and temperatures of 14–42 °C. The process of water preservation was investigated under conditions of

possible secondary growth of microorganisms in treated water, namely in the presence of nutrients. It was found that *E. coli* did not grow in a CO<sub>2</sub>-treated solution containing nutrient broth in the entire studied temperature range within 6 days. Whereas in control experiments (without CO<sub>2</sub>) the growth of the culture was observed over the same period: 3.2; 3.0 and 0.5 orders at temperatures respectively of 22 °C, 37 °C and 42 °C.

The results of studying the influence of CO<sub>2</sub> pressure within the range of 0.05–0.20 MPa on the level of disinfection of *E. coli* in distilled water at temperatures of 22 °C and 37 °C are shown in Fig. 2. An increase in CO<sub>2</sub> pressure during processing leads to an increase in the degree of inactivation of microorganisms, which is due to an increase in the concentration of carbon dioxide in the solution and a decrease in the pH of the latter, and an increase in temperature, as already mentioned, accelerates the diffusion of CO<sub>2</sub> through the cell membrane.



**Figure 2.** Kinetics of *E. coli* inactivation in distilled water using CO<sub>2</sub> at various pressures (the respective pressure values (MPa) are indicated next to the curve types in the figures) and temperatures.

## CONCLUSIONS

Thus, in this paper, for the first time, the fundamental possibility of water disinfection from *E. coli* with CO<sub>2</sub> at a pressure of 0.1–0.2 MPa is shown. An increase in temperature to 37–42 °C significantly intensifies the process and reduces the time required to achieve a given degree of inactivation. At the specified temperature, even in the presence of nutrients, the level of disinfection of *E. coli* reaches 6 orders of magnitude at  $P = 0.1$  MPa within 6 days.

Despite the need of a long-term contact of CO<sub>2</sub> with the disinfected object for the purpose of effective inactivation, treatment with CO<sub>2</sub> of low pressure can be considered as an alternative to traditional methods of disinfection. This is due the environmental friendliness of the process and the possibility of obtaining safe drinking water that does not contain toxic by-products for human consumption, as well as low costs of the process and the simplicity of the equipment used for its implementation. The results obtained in this work can be used in the development of new strategies for guaranteeing high quality and safety of drinking water.

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# Modeling of the Adsorptive Removal of Pentavalent Arsenic from Drinking Water

R. Zakhar\*, J. Derco\*, F. Čacho\*\*, and M. Pavlík\*\*\*

\* Department of Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava 812 37, Slovakia (E-mails: [ronald.zakhar@stuba.sk](mailto:ronald.zakhar@stuba.sk); [jan.derco@stuba.sk](mailto:jan.derco@stuba.sk))

\*\* Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava 812 37, Slovakia (E-mail: [frantisek.cacho@stuba.sk](mailto:frantisek.cacho@stuba.sk))

\*\*\* Institute of Production Technologies, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava, Jána Bottu 2781/25, Trnava 917 24, Slovakia (E-mail: [xpavlikm2@stuba.sk](mailto:xpavlikm2@stuba.sk))

## INTRODUCTION

Arsenic contamination is a widespread and serious problem all over the world. Strong epidemiological evidence of arsenic carcinogenicity and genotoxicity has forced the World Health Organization (WHO) to lower the Maximum Contaminant Level (MCL) in drinking water to  $10 \mu\text{g L}^{-1}$  (Pal, 2015). In this paper, the possibility of using granular ferric oxide (GFO) to remove pentavalent arsenic As(V) was investigated by batch adsorption studies. The equilibrium data were analyzed to see whether the isotherm obeyed the nonlinear Langmuir (LI), Freundlich (FI), Dubinin-Radushkevich (D-R), Redlich-Peterson (R-PI) or Sips (SI) isotherm models equations. Kinetic parameters were evaluated by nonlinear pseudo-first and pseudo-second order kinetic model. In addition, the reversibility of As(V) sorption onto GFO was studied by different desorbing agents.

## MATERIALS AND METHODS

### Reagents

As(V) stock solution was prepared by dissolving an accurately weighed amount of sodium arsenate hydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) in distilled water to achieve a concentration of  $1 \text{ g L}^{-1}$ . Concentrated HCl solution was used for samples storage. 0.1 M acetic acid ( $\text{CH}_3\text{COOH}$ ), sodium hydroxide (NaOH), sodium chloride (NaCl) solutions and distilled water were used as a desorbing agents.

### Analytical determination

Determination of As(V) was done by flow-through chronopotentiometry with using triple-electrode flow-through measuring cell (type 353c) with work electrode (type E-T/Au), platinum auxiliary electrode and argentochloride reference electrode (Beinrohr *et al.*, 2010).

### Adsorbent preparation

The granular ferric oxide (GFO) was obtained from Severn Trent (United Kingdom) and was used without further purification. It was just rinsed with distilled water to remove dirties and then oven-dried at  $105 \text{ }^\circ\text{C}$  for 24 h.

### Adsorption and desorption studies

Adsorption experiments were carried out by batch method at room temperature ( $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ ). The time dependent behavior of arsenic adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 0–180 min. The 0.1 L solution of As(V) was taken in each

Erlenmeyer flask of volume 0.20 L separately. The initial concentration of arsenic was kept at  $1000 \mu\text{g L}^{-1}$ , while the dose of GFO was 0.2 g. When the adsorption equilibrium contact time was found, so the equilibrium sorption of arsenic ions onto GFO was carried out by contacting 0.2 g of the GFO with 0.1 L of different As(V) concentrations from 100–1000  $\mu\text{g L}^{-1}$  in 0.20 L Erlenmeyer flask on orbital shaker. The obtained As(V)-loaded GFO was then brought in contact with 0.1 L of different desorption agents for 2 h in orbital shaker at 150 rpm. Then, the adsorbent with desorbing agent was placed in a water bath at 70–80 °C for 2 h.

## RESULTS

**Table 1.** Isotherm data for adsorption of As(V) by GFO.

Adsorption isotherm	Parameter, unit	Value	$R_{xy}$
Langmuir	$a_{\max}, \mu\text{g g}^{-1}$	1900.00	0.9400
	$K_L, \text{L } \mu\text{g}^{-1}$	$6.18 \times 10^{-3}$	
	$R_L$	0.14–1.00	
Freundlich	$K_F, \mu\text{g}^{(1-1/n)} \text{g}^{-1} \text{L}^{1/n}$	20.80	0.9300
	$n$	1.27	
Dubinin–Radushkevich	$a_{\max}, \mu\text{g g}^{-1}$	794.00	0.8576
	$\beta, \text{mol}^2 \text{kJ}^2$	$1.83 \times 10^{-4}$	
	$E_V, \text{kJ mol}^{-1}$	0.05	
Redlich–Peterson	$K_{RP}, \text{L g}^{-1}$	40.96	0.9556
	$a, (\text{L } \mu\text{g}^{-1})^b$	3.27	
	$b$	$5.10 \times 10^{-14}$	
Sips	$K_S, \mu\text{g}^{(1-\beta_S)} \text{L}^{\beta_S} \text{g}^{-1}$	6.99	0.9602
	$a_S, (\text{L } \mu\text{g}^{-1})^{\beta_S}$	1.13	
	$\beta_S$	$9.09 \times 10^{-16}$	

## CONCLUSIONS

From the results it follows that correlation coefficient ( $R_{xy}$ ) of R-PI and SI models were the highest ( $R_{xy} = 0.96$ ). The maximum monolayer coverage ( $a_{\max}$ ) from LI model was determined to be  $1900 \mu\text{g g}^{-1}$  and the separation factor ( $R_L$ ) indicating a favorable sorption experiment. The calculated maximum monolayer coverage is in good agreement with the experimentally determined maximum monolayer coverage of GFO, which was determined to be  $2007 \mu\text{g g}^{-1}$ . Also from FI model, the sorption intensity ( $n$ ) indicates favorable sorption process. The mean free energy of D-RI ( $E_V$ ) was estimated to be  $0.05 \text{ kJ mol}^{-1}$  which vividly proved that As(V) adsorption experiment followed a physical process. The kinetic data was the best described using the pseudo–first order kinetic model ( $R_{xy} = 0.99$ ). The basic NaOH desorbing solution showed the best desorption efficiency (95.17 %).

## ACKNOWLEDGEMENT

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# Removal of Acid Dye from Aqueous Solutions Using Orange and Lemon Peel as Bio-Sorbents

A. E. Ahmed\* and K. M. Majewska-Nowak\*\*

\*Faculty of Environmental Engineering, Wrocław University of Science and Technology,  
Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland  
(E-mail: [arif.eftekar.ahmed@pwr.edu.pl](mailto:arif.eftekar.ahmed@pwr.edu.pl))

\*\* Faculty of Environmental Engineering, Wrocław University of Science and Technology,  
Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland  
(E-mail: [katarzyna.majewska-nowak@pwr.edu.pl](mailto:katarzyna.majewska-nowak@pwr.edu.pl))

## INTRODUCTION

Acid dyes are widely used to dye nylon fabric wool, nylon and nylon blend fabric. The colour of aqueous solution containing various acid dyes usually ranges from 200 to 400 Hazen units. Direct discharge of acid dyes is responsible for harmful effect on human and aquatic life and may cause cancer, skin disease etc. (Azis, 2018; Lellis, 2019). Conventional methods such as coagulation, electrocoagulation, and adsorption on activated carbon are commonly used for treatment of wastewater containing acid dyes (Karaca, 2004; Mohammed, 2004). However, these methods do not show enough effectiveness or economic profitability to remove acid dye stuffs. Adsorption technology using low cost adsorbents as wood, China clay, shells of almond, and fly ash could also be an effective method for treatment of acid dye solutions (Aydin, 2004; Bharathi and Ramesh, 2013), but the efficiency of this technique depends on proper selection of adsorbents. In this study orange and lemon peel powders were used for removal of acid dye from aqueous solution. The process efficiency was evaluated taking into consideration the following process parameters: initial dye concentration, adsorbent dosage, solution temperature and pH, contact time, as well as agitation speed. Single and combined adsorbent dosage was applied in a batch adsorption mode. The experimental data were analyzed using Freundlich and Langmuir isotherm models and the adsorption mechanism was identified.

## MATERIALS AND METHOD

### Preparation of adsorbent powder and acid dye solution

10 kg of orange and lemon fruits were washed properly by distilled water and their peels were taken out carefully. Those peels were cut in to small pieces and dried under sunlight for 15 days (orange) and 22 days (lemon). After drying the dried peels were crushed and sieved by sieve No. 100 (US sieve size) which has size of 150  $\mu\text{m}$ , thus that the surface area of peel particles become 150  $\mu\text{m}$ . After making orange and lemon peel powders the weight of the powder samples was 250 g (each). Finally, the powders was collected and kept inside an airtight jar.

The Everacid Yellow Acid dye (Acid Yellow 49, C.I.18640) was obtained from a local dye house of Bangladesh. This dye is widely used for dyeing wool, nylon and nylon blend fabric. The solution of acid dye was prepared by taking appropriate amount of dye into beaker and then adding required volume of distilled water with further agitation of dye solution.

### Adsorption experiments and process parameters

Adsorption experiments were carried out in a batch mode at variable process parameters: contact time (45–120 min), initial dye concentration (25–100 mg/dm<sup>3</sup>), adsorbent dosage (0.2–2.0 g/dm<sup>3</sup>), speed of shaker (140–240 rpm), temperature (25–55 °C), and pH (2–12). Orange and lemon peel powders were dosed individually into dye solutions, as well as combined adsorption with simultaneous dosage of both adsorbents (at a weight ratio of 1:1) was performed.

Dye concentration was determined before and after adsorption with the use of spectrophotometer at a wavelength of 560 nm. The bio-sorbent powder was separated before spectrophotometric analysis by simple sedimentation (20 min) and filtration through Whatman filter paper.

In the course of experiments dye removal efficiency, dye uptake after a given time, as well as sorption capacity at equilibrium state were determined. Langmuir and Freundlich models were fitted to the experimental data with the use of appropriate model formulae.

### RESULTS AND CONCLUSIONS

Agricultural waste such as unmodified orange and lemon peels can be effectively used for the removal of acid dye (Everacid Yellow Acid dye) by adsorption. The maximal dye removal efficiency amounted to 78 % (for orange peel powder), 83 % (for lemon peel powder), and 88 % (for the mixture of both adsorbents). It was found that optimum process parameters for adsorption of Everacid Yellow Acid dye on both orange and lemon peels were as follows: contact time – 60 min, adsorbent dosage – 1 g/dm<sup>3</sup>, speed of shaker – 160 rpm, temperature – 25 °C, optimum pH – 7. The maximum adsorption capacities were equal to 12.5 mg/g, 14.2 mg/g and 22.72 mg/g for orange and lemon peel powder and mixture of adsorbents, respectively. The Langmuir isotherm model was found to fit the adsorption of Everacid Yellow Acid dye on orange and lemon peel powders. An unmodified orange and lemon peels, as a low cost and easily available waste material, are interesting alternative for more expensive adsorbents used for dye removal from water solutions.

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# Potential Methane Production for Wild Salt-Tolerant Biomass Based on Anaerobic Respirometer Tests

T. Amen\*, M. Sun\*, M. Terashima\*, and H. Yasui\*

\* Faculty of Environmental Engineering, the University of Kitakyushu, 1-1, Hibikino, Wakamatsu, Kitakyushu, 808-0135, Japan (E-mail: [t-amen@kitakyu-u.ac.jp](mailto:t-amen@kitakyu-u.ac.jp))

## INTRODUCTION

Since decades, salinity became one of the most important environmental stresses that have greatly reduced the area of arable land. Therefore, employing salt-tolerant crops is an important strategy to mitigate the loss of land available for crop cultivation. Salt-tolerant plants that can grow under high salinity stress is a fundamental approach to overcome the soil salinity. Applying the anaerobic digestion (AD) to decompose the salt-tolerance plants not only has the advantage of controlling of accumulation of salts but also offers the benefit of biogas recovery (Ras *et al.*, 2011). For decades, the Aral Sea area in Uzbekistan classified as a salt-affected area. The crop productivity of the agricultural area was decreased or mostly lost. Unlike an ordinary plant, the salt-tolerant plants have a good yield in saline-affected lands. The aim of this study is to investigate the performance of AD for the biodegradation of wild salt-tolerant plants harvested from the Aral Sea area. To accomplish this, biochemical methane potential was carried out with several salt-tolerant species harvested from a saline contaminated site in Uzbekistan. As indicator for evaluating the anaerobic process, fiber compositions were analysed, and methane yield was monitored. For comparison, the biochemical methane potential test was also carried out with the addition of ordinary fodder plant.

## MATERIAL AND METHODS

### Respirometer test

Wild salt-tolerant species were harvested from Aral Sea area in Uzbekistan. The species used for the tests were *Alhagi pseudoalhagi*, *Sorghum bicolor* and *Sorghum bicolor* mixed with its grains. The ordinary fodder plant – *Panicum coloratum* – was used for comparison. Glass bottles with a working volume of 500 mL were utilized as a batch reactors and each reactor has inoculum volume of 450 mL. The salt-tolerant plant was mixed with municipal inoculum and then the tests were anaerobically incubated at 35 °C after tightly capped the reactors with a perforated cap to allow to collect the generated methane. All reactors were continuously stirred over the course of the tests duration to ensure mixing of the reactors content. The biodegradability of the salt-tolerant biomass was calculated in terms of the percentage between the methane yield and the methane potential.

### Characterization and analytical methods

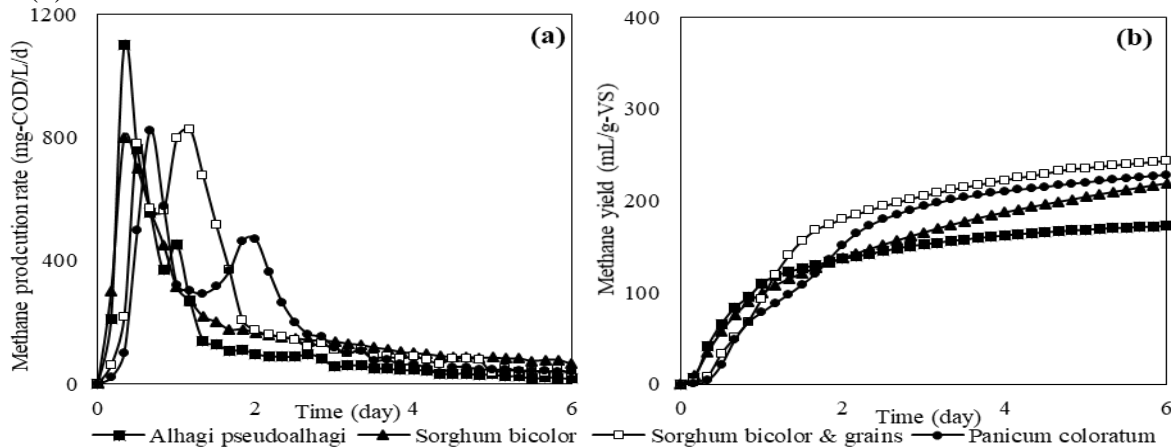
To quantify the fiber contents, detergent analysis of the neutral detergent fiber (NDF = hemicellulose, cellulose, and lignin), acid detergent fiber (ADF = cellulose, and lignin) and acid detergent lignin (ADL) were performed according to the Association of Official Analytical Chemists (AOAC) official method, (Segura-Campos *et al.*, 2014).

## RESULTS AND DISCUSSION

### Methane potential and degradation trends

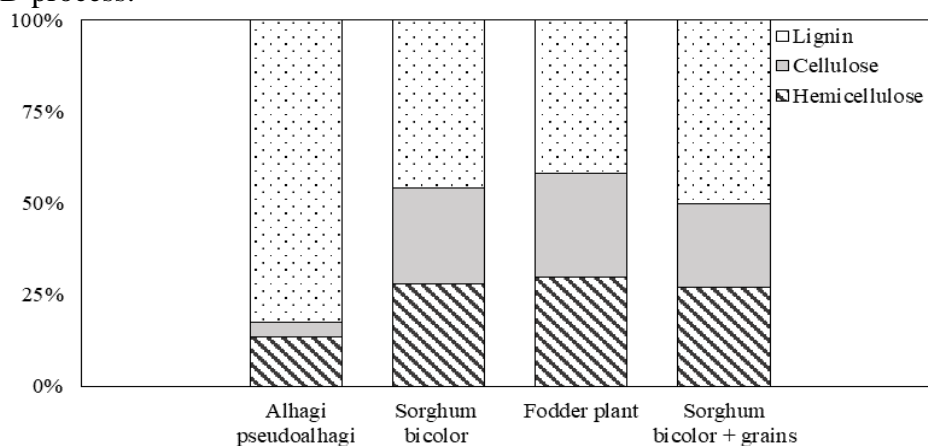
As shown in Fig. 1(a), the generated methane for all tests were started immediately and kept increasing until reaching the peak within the first day of the test, another peak also was appeared

and then the methane production was steeply decreased, after 6 days of digestion, almost 90 % of the experimental methane yield was obtained. Excepting the *Sorghum bicolor*, the batch respirometer tests resulted in a unique double-peak methane production rate curves. The first appeared peak was due to the degradation of readily degradable materials of the salt-tolerant biomass. Whereas the second peak was attributed to slowly biodegradable organics where it required the disintegration period as a main phase of AD process. Additionally, the specific methane yield ranged from 206.51 mL/gvs to 259.59 mL/gvs for the salt-tolerant biomass as Fig. 1(b).



**Figure 1.** The specific methane production rate (a), and methane potential profiles (b) for different salt-tolerant plants.

The remaining fiber contents at the end of the batch respirometer tests were shown in Fig. 2, the lignin was the main component in the remaining biomass. The results displayed that the methane potential of cellulose was higher than that of hemicellulose, while the lignin was so difficult to be utilized by AD process.



**Figure 2.** Lignocellulosic composition at the end of the experiments.

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# Performance of Syngas Biomethanation in Thermophilic Anaerobic Sludge Digestion

D. Andreides\* and J. Zábranská\*

\*Department of Water Technology and Environmental Engineering, University of Chemistry and Technology Prague, Technická 1905, 166 28 Prague, Czech Republic  
(E-mail: [dominik.andreides@vscht.cz](mailto:dominik.andreides@vscht.cz))

## INTRODUCTION

Thermochemical processes (e.g. gasification and pyrolysis) are well-known technologies for converting of hardly- or non-biodegradable biomass waste into value-added products such as synthetic gas (syngas), bio-oil and biochar (Giwa *et al.*, 2019). According to thermochemical processes conditions, syngas contains H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in a different ratio. Although syngas can be used for bio-fuels production or converted via catalytic methanation (Molino *et al.*, 2016; Watson *et al.*, 2018), these processes face to extensive investment and operation costs. Therefore, novel strategies for the syngas conversion have been proposed in recent years. As a promising alternative, the biological conversion of syngas to CH<sub>4</sub> mediated via the anaerobic culture has been successfully demonstrated (Li *et al.*, 2020; Wang *et al.*, 2013). This novel approach offers simplicity and no additional technology for the syngas utilisation. Nevertheless, the effect of syngas dosage to anaerobic sludge digestion remains unclear.

Accordingly, the aims of this study were: a) to perform syngas biomethanation in the lab-scale anaerobic sludge digestion and to study the performance of the system; b) to set the maximum syngas loading rate for the anaerobic sludge digestion.

## MATERIALS AND METHODS

### Inoculum and Substrate

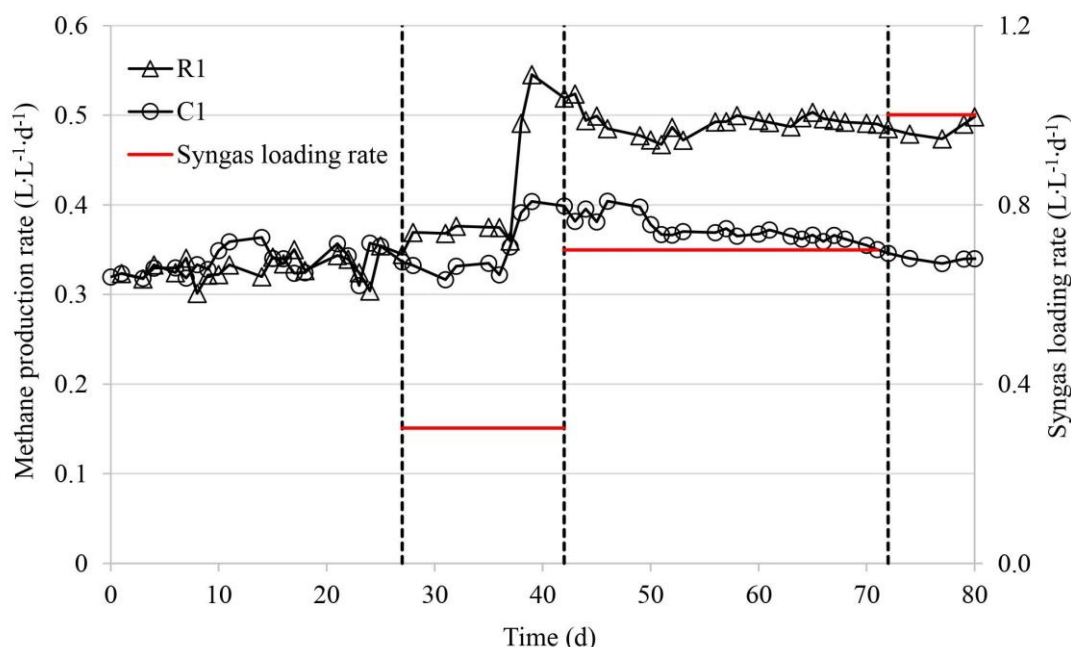
The inoculum was obtained from a thermophilic anaerobic fermenter located on Prague Central Wastewater Treatment Plant (Prague, Czech Republic). A mixture of primary and thickened-disintegrated secondary sewage sludge was used as a substrate. The substrate was collected weekly from the aforementioned wastewater treatment plant (TS 64.2 g L<sup>-1</sup> ± 10.1 g L<sup>-1</sup>, VSS 40.0 g L<sup>-1</sup> ± 4.5 g L<sup>-1</sup>).

### Experimental setup

The experiment was performed in two continuously stirred-tank reactors (CSTR) operated under thermophilic conditions (55 °C ± 1 °C). One reactor was operated as conventional anaerobic sludge digestion, denoted as control reactor (C1). The second reactor was operated as anaerobic sludge digestion with the syngas injection (R1). The total working volume of reactors was 10.5 L. The hydraulic retention time (HRT) of reactors was 18 days. Organic loading rate (OLR) varied since the real substrate was used. During the experiment, an average OLR was 4.5 g ± 0.5 g COD per litre of reactor volume (VR) per day (g L<sub>VR</sub><sup>-1</sup> d<sup>-1</sup>) in both reactors. At the bottom of R1, a fine-bubble disc diffuser was installed. Syngas containing H<sub>2</sub> and CO (ratio H<sub>2</sub>:CO of 1.3:1.0) was continuously injected into the R1 through the diffuser at different loading rates (0.3–1.0 L L<sub>VR</sub><sup>-1</sup> d<sup>-1</sup>). To measure biogas volume; a gas counter was used (MGC-1 PMMA, Ritter, Germany). Biogas composition was determined as described in Andreides *et al.* (2021).

## RESULTS AND CONCLUSIONS

Preliminary results showed as the syngas loading rate increased, the syngas addition improved CH<sub>4</sub> production in R1 compared to C1. The fluctuations in CH<sub>4</sub> production in both reactors resulted from real substrate usage. However, an increase in pH (7.5 to 7.8) was observed in R1 due to the CO<sub>2</sub> consumption by hydrogenotrophic methanogens. The maximum syngas loading rate was set on 1.0 L L<sub>V</sub>R<sup>-1</sup> d<sup>-1</sup> since no VFA accumulation was observed at this rate in R1. Therefore, the system's capacity was not reached, and still higher syngas loading rate could be applicable. Nevertheless, at the maximum applied syngas loading rate, the CH<sub>4</sub> content in R1 and C1 was 43.1 % ± 1.3 % and 64.9 % ± 0.5 %, respectively. This phenomenon was due to the high H<sub>2</sub> and CO content in produced biogas in R1 (up to 17 % and 15 %, respectively). Thus, the gas-liquid mass transfer must be improved.



**Figure 1.** The methane production rate in R1 (anaerobic sludge digestion with syngas injection) and C1 (control reactor) and the applied syngas loading rate.

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# Nitrates-Polluted Water Remediation by Functional Polyurethane-Based Foams

S. Barroso-Solares\*, B. Merillas\*\*, P. Cimavilla-Roman\*\*, M. A. Rodriguez-Perez\*, and J. Pinto\*

\* Cellular Materials Laboratory (CellMat), Condensed Matter Physics Department  
BioecoUVA Research Institute, University of Valladolid, 47011, Valladolid, Spain  
(E-mails: sbarroso@fmc.uva.es; marrod@fmc.uva.es; jpinto@fmc.uva.es)

\*\* Cellular Materials Laboratory (CellMat), Condensed Matter Physics Department, University of Valladolid, 47011, Spain (E-mails: b.merillas@fmc.uva.es; paulacimavilla@fmc.uva.es)

## MOTIVATION

Nowadays, about 11 % of the world's population does not have access to drinking water, a situation which is not expected to improve soon due to the several current threats to water reservoirs and drinking water supply throughout the world. In fact, the United Nations (UN) forecasts about half of the entire world population living in water-stressed areas by 2025 (WHO, 2019). One of these threats, directly linked to human activity, is the rise of nitrates concentration in open water over the safety thresholds. The presence of high concentrations of nitrates is related to a reduction of the oxygen transport to the tissues (e.g., methemoglobinemia), which is particularly dangerous for infants under 3 months of age (WHO, 1995).

The European Union (EU), well-aware of this threat, developed and applied a Nitrates Directive which has achieved promising results facing this problem. However, the nitrates pollution remains as a severe risk in many Member States of the EU, mainly related to the intensive use of nitrogenate fertilizers and the use of manure and slurry from livestock as fertilizers (European Commission, 2018). Accordingly, the development of new technologies and materials capable of safely removing nitrates from polluted water is a pressing need. A promising approach is the use of nanoparticles with the capability of adsorbing nitrates selectively, being possible to highlight the use of sepiolite, a natural, low-cost, and widely available nanomaterial. Several works have shown that both the control of the pH of the nitrates solution or the chemical functionalization of the sepiolite can enhance the nitrates adsorption capacity (Bhatnagar and Sillanpää, 2011).

However, the need of controlling the pH to achieve good nitrates-adsorption performance is a drawback for their application in natural water resources. Moreover, the recovery of the nanoparticles from the water after the nitrates adsorption requires of additional filtration steps, while their accidental release or incomplete recovery could cause additional damage to the environment. Herein, a new approach is proposed, combining the enhancing of sepiolite by chemical modification with their incorporation in a porous polymeric substrate. This approach allows reaching a high nitrates adsorption performance without requiring controlling the pH and overcomes the difficulties to manipulate and recover the sepiolite, avoiding any accidental release of the sepiolite to the environment (Barroso-Solares *et al.*, 2020).

## RESULTS

### Sepiolite modification and characterization

Pristine and modified sepiolite with quaternary salts of ammonium, were first characterized by BET and FTIR. Then, their nitrates adsorption isotherms were determined, using UV-Vis spectroscopy to measure the initial and remaining nitrates concentration in the solutions before and after being in contact with the sepiolite. It was found that the natural sepiolite showed a negligible nitrates

adsorption capacity at pH about 6.3 to 6.6, whereas the modified sepiolite reached adsorption capacities over 20 mg/g at RT (comparable to the highest previously reported in the literature). Accordingly, the modified sepiolite were selected for further characterization and their incorporation into a porous polymeric substrate. Among other results, it was found that their adsorption capacity rises to 40 mg/g when the water temperature decreases down to 15 °C, while decreases down to 13 mg/g at 45 °C. The higher adsorption performance when decreasing the temperature is a relevant feature, as most of the nitrates polluted water in the EU present temperatures below RT most of the year. Moreover, a negative value of the Gibbs free energy change of the process was found, proving the spontaneous character of the adsorption process, while also its exothermic character and the negative entropy change (corresponding to the reduction of the degree of freedom of the nitrates due to their adsorption) were confirmed. Also, it was determined that these modified sepiolite provide a proper nitrates adsorption performance in a broad pH range from 2.50 to 8.18.

### **Nanocomposite polymer foam production and characterization**

Pristine and nanocomposite polyurethane (PU) foams were produced by chemical foaming. Different sepiolite concentrations were incorporated to the nanocomposite PU foams (from 1 wt. % to 10 wt. %), finding that 8 wt. % was the maximum concentration admissible by the foams (i.e., without inducing the foam collapse and therefore keeping high porosities up to 0.90 and 100 % open-cell structure). A key feature of the developed nanocomposites was the proper chemistry selection of the PU foam with the aim to achieve a hydrophilic behaviour. It was found that the polymeric matrix swells in presence of water (i.e., the water molecules can diffuse between the polymer chains). Moreover, X-ray tomography results showed that the sepiolite were homogeneously distributed, whereas FTIR analysis proved that the sepiolite did not affect the polymerization of the PU. Therefore, the nanocomposite PU foams presented optimal features to ensure the proper interaction among the modified sepiolite and the nitrates-polluted water.

As expected, the nanocomposite PU foams shown the same nitrates adsorption capacity than the corresponding modified sepiolite, while pristine PU foams shown no nitrates adsorption. Moreover, no sepiolite release or nitrates release after the adsorption process were detected independently of the time that the nanocomposite PU foams remained immersed in water (even under shaking). Finally, the produced nanocomposite PU foams were tested on actual polluted waters collected from nearby streams, finding that they keep their nitrates adsorption capabilities at these circumstances (i.e., no control of the pH, filtration, or treatment of any kind was performed on the collected water). Accordingly, the proposed materials fully achieved the objectives of this work, being a feasible candidate for nitrates removal of actual polluted waters.

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# Trinal Simulator Stages for Modelling a Pilot Scale Poultry Slaughterhouse Wastewater Treatment Plant Using Sumo

M. N. Bingo<sup>\*. \*\*</sup>, M. Basitere<sup>\*. \*\*</sup>, S. K. O. Seteno<sup>\*\*\*</sup>, and D. N. Dlamini<sup>\*. \*\*</sup>

\* Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Cape Peninsula University of Technology, P. O. Box 1906, Bellville, 7535, South Africa (E-mail: [bingon@cput.ac.za](mailto:bingon@cput.ac.za))

\*\* Bioresource Engineering Research Group (BioERG), Cape Peninsula University of Technology, P. O. Box 652, Cape Town, 8000, South Africa (E-mail: [basiterem@cput.ac.za](mailto:basiterem@cput.ac.za))

\*\*\* School of Chemical and Minerals Engineering, Faculty of Engineering, North West University, Private Bag X1290, Potchestroom, 2520, South Africa (E-mail: [Karabo.Ntwampe@nwu.ac.za](mailto:Karabo.Ntwampe@nwu.ac.za))

## INTRODUCTION

Abattoir waste is considered to be the most challenging food type waste to handle with poultry slaughterhouse wastewater (PSW) being the largest contributor at 43 % of the total abattoir waste generated in the Western Cape (WC), SA, during the 2015/2016 period (Western Cape Government, 2016). Due to its hazardous nature and potential impact on human health and the environment extensive research has been carried out to improve on the PSW treatment technologies available. The treatment methods applied to PSW are considered to be dynamic because of the fluctuations of influent flow rate and composition, thus they are a combination of physico-chemical, biological and biochemical processes (Gazsó *et al.*, 2017). Mathematical modelling of biological treatment processes permits for a comprehensive design of the operating parameters, attainable effluent quality and prediction of systems reactions. Therefore, to have a better understanding of how wastewater treatment plants (WWTPs) perform under several operating conditions, mathematical modelling is applied. SUMO is a wastewater process multipurpose simulator software that was developed by Dynamita Incorporate for environmental models, specifically for municipal and industrial wastewater treatment plant modelling (Ndeba-Nganongo *et al.*, 2018). Kolovos *et al.* (2016) recommend the application of SUMO because of its user-friendly interface and Excel-based open-source process code language called SumoSlang (Sumo Simulation language), making the calculations behind the simulation model used easily understandable. SUMO contains internally researched and developed whole plant and focused models such as the activated sludge models (ASM1, ASM2d and ASM3) for nitrogen and phosphate removal, and is capable of simulating bio-kinetic, mixed equilibrium-kinetic and direct algebraic models in steady-state, subject to the outputs of the intended process (Gazsó *et al.*, 2017).

The main purpose for this study was to use data from an existing working pilot-scale biological treatment plant to develop a model that would simulate the performance of the treatment plant with respect to the removal efficiency of chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), phosphate and fats, oil and grease (FOG). The obtained simulation results were compared to the experimental results of the pilot plant to assess whether the developed model actually was capable of predicting the performance of the treatment plant. Finally, the quality of the treated PSW was compared to the industrial effluent discharge standards as stipulated by the City of Cape Town (CCT) by-laws.

## MATERIALS AND METHODS

The raw wastewater used in this study was collected in 25 L polypropylene containers from a

sampling point prior to being discharged into a collection pond of a poultry slaughterhouse located in the WC, SA. The wastewater stream was a combination of water used for cleaning and washing carcasses and meat products, and the sanitation and disinfection of equipment as well as processing areas of the slaughterhouse. The raw PSW was stored in a refrigerator at 4 °C until it was fed into the pilot-scale biological treatment plant.

The treatment plant consisted of 1) a 25 L aerobic pre-treatment tank in which Eco-flush, a bioremediation agent, was added to hydrolyse FOG and reduce odour; 2) screens; 3) a 2 L expanded granular sludge bed (EGSB) bioreactor; and 4) a membrane bioreactor (MBR). The pre-treatment tank was operated as a batch reactor in order to allow for the breaking down of the FOG and the resulting product was screened using 1.18 mm and 53 µm screens prior to being fed into a feeding tank. The remaining units in the plant were operated continuously with the temperature of the EGSB being maintained between 35–37 °C by means of a water bath.

The development of the simulation model involved the 1) building and plant configuration, 2) using measured and parameters of the pilot plant as well as operating conditions to set up the model, 3) specifying the variables and the format in which they should be presented and saved during simulation, and 4) running the simulation.

## RESULTS AND DISCUSSION

The pilot-scale treatment plant was successful in treating the PSW and the quality of the effluent was within the by-laws prescribed by CCT. The appearance of the effluent was clearer and the smell was reduced drastically. When comparing the results obtained by the treatment plant to those obtained by the simulation, the COD removal efficiencies fell within the same range therefore, it can be said that the performance of the treatment plant was successfully predicted with regards to COD removal. However, there were discrepancies observed with the removal efficiencies of FOG, TSS, TDS and FOG. Even though a slight increase in the concentration of phosphate was observed, the effluent quality of the simulation also met the discharge standards of the CCT.

## CONCLUSION

The model developed using SUMO was successful in predicting the performance of the proposed pilot-scale biological treatment plant with regards to COD removal however, and the quality of the effluent was compliant with the discharge standards.

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# Degradational Behaviour of 2- and 4-Methoxyanilines by the Application of Laterite Soil in Fenton-Like Oxidation: A Rational Analysis

N. K. Chaturvedi\*<sup>\*,\*\*</sup> and S. Singh Katoch\*

\* Department of Civil Engineering, National Institute of Technology Hamirpur, Hamirpur, Himachal Pradesh, India, 177005

\*\* Department of Civil Engineering, Anurag University, Venkatapur, Ghatkesar, Hyderabad, Telangana, India, 500088 (E-mail: [naveenk@nith.ac.in](mailto:naveenk@nith.ac.in); [sskatoch@nith.ac.in](mailto:sskatoch@nith.ac.in))

## INTRODUCTION

Pharmaceutical and Dye industries utilize a huge amount of freshwater in the preparation of their products, which led to large quantity of toxic and harmful wastewater to be disposed of in the environment (Nguyen *et al.*, 2020). 2-Methoxyaniline (2MA) and 4-Methoxyaniline (4MA) are some important pharmaceutical and dye industries intermediate present in their wastewater (Chaturvedi and Katoch, 2020a). They are extremely toxic, carcinogenic and have severe adverse health effects on humans and other living organisms. Fenton-oxidation is one of the methods, which is being utilized for the treatment of wastewater containing harmful and toxic pharmaceuticals and dye compounds. Fenton-oxidation involves the use of Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and Ferrous ion (Fe<sup>2+</sup>) for the generation Hydroxyl ions (HO•) in aqueous medium (Eq. (1)).



The Fe<sup>2+</sup> used is generally obtained commercially and several researchers have shown that it can be substituted by other chemical species in Fenton-like oxidation to produce similar results. Laterite soil, abundantly available in India, can be a great source of iron in the form of Ferric ions (Fe<sup>3+</sup>) to be used alternatively to commercially procured iron in Fenton-like oxidation. Therefore, in this study, iron leached from laterite soil is used to treat 2MA and 4MA during fenton-like oxidations. The effect of various key reaction parameters such as pH, H<sub>2</sub>O<sub>2</sub>, Fe<sup>3+</sup> and initial concentration of 2MA and 4MA are explained rationally to justify the literature. Also, ring cleavage test is conducted to determine the initial position of bond breaking in the Benzene ring of the Methoxyanilines.

## MATERIAL AND METHODOLOGY

### Experimental Methods

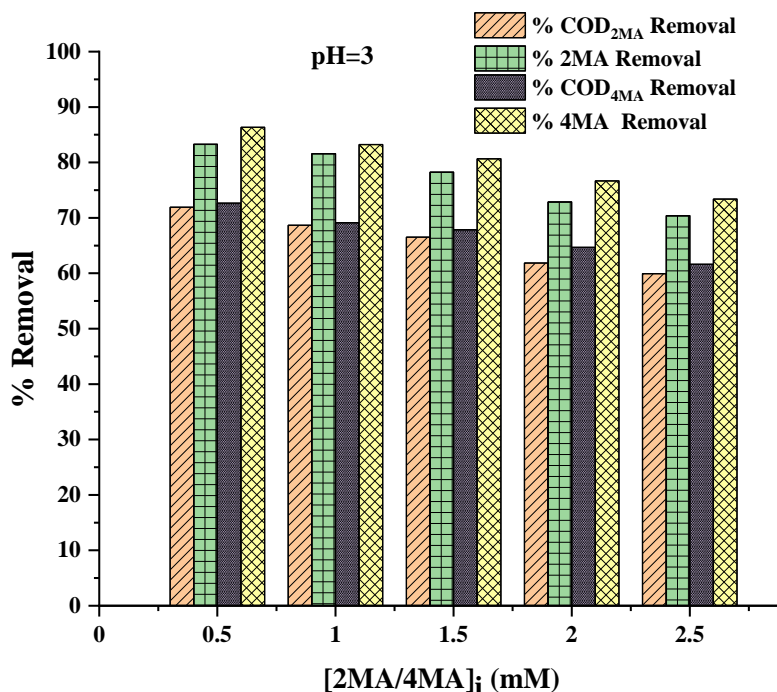
Experiments is conducted batch mode in five Erlenmeyer flasks of 2L capacity. Each time 1L of synthetic samples of Methoxyanilines was taken in each 2L flask. All samples are tested initially for COD and initial concentration check by UV Vis Spectrophotometer. pH of the solution was set to 3.0 and 2.5 with the help of NaOH and H<sub>2</sub>SO<sub>4</sub> as suggested by previous studies (Chaturvedi and Katoch, 2020b). After mixing of reagents solutions were kept for rapid mixing for two hours by magnetic stirrers and after 24 hours, aliquots of the solution were taken for testing of final COD and final Methoxyanilines concentrations.

## RESULTS

### Degradation Behaviour of 2MA and 4MA during Fenton-like oxidation

Both the Methoxyanilines showed similar behavior during Fenton-like oxidations using Fe<sup>3+</sup> from

laterite soil. Initially reaction mixtures form a dark grey color and after 24 hours of reaction duration a clear solution is formed in the Erlenmeyer flask. The supernatant of the solution was taken for COD and initial drug analysis. The maximum COD removals and maximum Methoxyanilines removals were found to be 71.91 % and 72.64 % and, 83.28 % and 86.34 % respectively for 2MA and 4MA at optimize dosages of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$ . The degradation trend for 2MA and 4MA is shown in Fig. 1.



**Figure 1.** Degradation behaviour of 2MA and 4MA during Fenton-like oxidation with  $\text{Fe}^{3+}$ .

## CONCLUSIONS

The Fenton-like oxidation showed that  $\text{Fe}^{3+}$  was efficient in the treatment of 2MA and 4MA with a maximum removal of 83 % and 86 % respectively. Also, when the results of 2MA and 4MA were analysed, it is found that 4MA showed slightly more degradation than 2MA in both type of oxidation processes. From ring cleavage test it was confirmed that for both the compound, ring cleavage was taking place at the ortho position and due to the presence of the amino group at this position in 2MA structure, the breaking of the bond will possibly be more challenging. Overall, it can be inferred that iron extracted from laterite soil can be applied as substitute for commercial iron source in Fenton's Oxidation of harmful and toxic pharmaceuticals compounds.

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# Selection of the Most Efficient Textile Wastewater Pretreatment for Treatment with Membrane Separation Processes

I. Ćurić\* and D. Dolar\*

\* University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, HR-10000 Zagreb, Croatia (E-mail: [iva.curic03@gmail.com](mailto:iva.curic03@gmail.com))

## INTRODUCTION

The textile industry, as one of the largest industries worldwide, generates significant amount of wastewater through production processes such as dyeing, washing, and bleaching (Li *et al.*, 2016). This wastewater contains a considerable amount of organic and inorganic components which makes wastewater treatment more complicated (Hassanzadeh *et al.*, 2017). There are various treatment techniques to reduce textile wastewater (TWW) pollution. For instance, physico-chemical methods, such as chlorination, adsorption and advanced oxidation processes, such as, ozonation, Fenton treatments. These methods suffer from certain serious disabilities in terms of high initial capital cost, adjunction of non-reusable chemicals, sludge generation, etc. (Lafi *et al.*, 2018). Using membrane separation processes (MSPs) can overcome most of these drawbacks due to the ability to remove organic and inorganic components in one step (Hassanzadeh *et al.*, 2017). The problem with MSPs can be if the wastewater stream is released directly to the membranes, for example, ultrafiltration (UF), nanofiltration, and reverse osmosis. It can cause irreversible fouling which leads to higher operating costs and energy consumption and shorter membrane life. Therefore, providing a pre-treatment process prior to MSPs appears to be necessary to mitigate membrane fouling and to achieve high removal quality (Riera-Torres *et al.*, 2010; Hassanzadeh *et al.*, 2017). The aim of this study was to examine coagulation, coagulation/flocculation, sand filtration, and a UF hollow fiber membrane in order to select the most efficient pre-treatment of TWW for treatment with MSPs according to turbidity, total organic carbon (TOC), and colour.

## MATERIAL AND METHODS

### Sampling and analytical methods

The untreated TWW samples required for this study were supplied from the discharge effluent of a textile factory (Galeb d.d. Croatia). Hollow fiber membrane was ZeeWeed 1 (ZW-1, GE Water and Process Technologies, Hungary).

Total organic carbon was determined on Carbon Analyzer Shimadzu TOC-V<sub>ws</sub> (Japan) and turbidity was measured with turbidimeter WTW Turb 430 (Germany). Colour was determined using Hach Lange DR3900 spectrophotometer (Germany) and expressed by Spectral absorption coefficient (DFZ, *Durchsichtsfarbzahl*), determined based on absorbance measurements by the spectrophotometric method at three wavelengths ( $\lambda = 436$  nm, 525 nm, and 620 nm), according to the DIN-38404/1. Optimal concentration of coagulant and flocculant, and pH were determined with Response surface methodology (RSM).

### Lab scale TWW pretreatments

Coagulation process was investigated by running a series of jar tests using the coagulant, ferric chloride (FeCl<sub>3</sub>) 40 % solution. The experiment was carried out using 500 mL TWW by applying 12 different coagulant concentration ranging from 0.35 to 4.48 mM of FeCl<sub>3</sub> at different pH (3.5, 4.5, 5.5, 7.3, and 8.5). Coagulation – flocculation process involves adding of optimal concentration

(2.07 mM) of coagulant ( $\text{FeCl}_3$ ) at pH 5.95 and six concentration of an anionic flocculant MagnaFloc LT25 (0.1–1.0 mg/L). Optimal conditions were calculated by the coefficient of determination or regression coefficient  $R$  – square ( $R^2$ ) and analysis of variance (ANOVA). Sand filtration was performed through a column (55 cm high with a diameter of 5.5 cm) filled with sand (the grain size ranged from 0.18 mm to 1.85 mm). UF with Hollow fiber ZW-1 module was performed in a laboratory setup operating in continues mode at transmembrane pressure around – 0.035 bar, permeate flux of 18 L/(m<sup>2</sup> h), and air supply rate 15 L/min.

## RESULTS AND DISSCUSION

**Table 1.** Turbidity, TOC, and colour (DFZ) values for TWW and effluents after treatment.

	Turbidity		TOC		Colour (DFZ, m <sup>-1</sup> )					
	NTU		mg/L		436 nm		525 nm		620 nm	
	TWW	Effluent	TWW	Effluent	TWW	Effluent	TWW	Effluent	TWW	Effluent
SF	140	82.3	363.4	242.3	101	103	61	64	46	48
Coagulation	202	28.0	528.3	312.3	653	118	436	64	313	52
Coagulation–floculation	202	34.1	528.3	294.1	653	119	436	61	313	48
ZW-1	196	12.4	322.6	229.0	98	19	52	5	40	3

ZW1 membrane efficiently reduced turbidity (~93 %), TOC (~29 %), and the colour expressed by DFZ (~80 % DFZ<sub>436 nm</sub>, ~90 % DFZ<sub>436 nm</sub>, ~92 % DFZ<sub>436 nm</sub>). Other examined pretreatment processes did not sufficiently remove turbidity (the highest, 86 %, was for coagulation), which is crucial in TWW treatments with MSPs. Turbidity causes membrane blockage and interfere with permeate flux. Further, an increase in the colour of the effluent after coagulation mean that the chemicals present in the TWW dissolved part of the sand and additionally coloured the water resulting in higher DFZ values. Findings from coagulation and coagulation–floculation tests reveal that due to high dose of coagulant  $\text{FeCl}_3$  (2.07 mM) requirement, coagulation is not effective because leads to increase in treatment costs and also large volumes of sludge to be handled.

## CONCLUSION

The obtained results showed the use of a hollow fiber membrane as the best pretreatment for processing with MSPs. With such pretreatment, less membrane fouling and reduced permeate flux drop is expected, which is crucial for efficient MSPs.

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# Surveillance of SARS-CoV-2 in Extensive Monitoring of Municipal Wastewater: Key Issues to Yield Reliable Results

F. Cutrupi\*, M. Cadonna\*\*, S. Manara\*\*\*, and P. Foladori\*

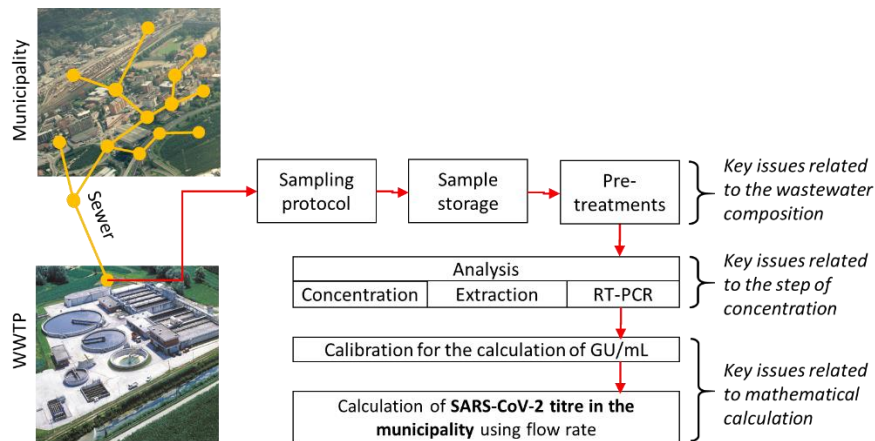
\* Department of Civil, Environmental and Mechanical Engineering (DICAM) – University of Trento, via Mesiano, n. 77, 38123 Trento, Italy (E-mails: [francesca.cutrupi@unitn.it](mailto:francesca.cutrupi@unitn.it); [paola.foladori@unitn.it](mailto:paola.foladori@unitn.it))

\*\* ADEP – Agenzia per la Depurazione, Autonomous Province of Trento, via Gilli, n. 3, 38121 Trento, Italy (E-mail: [maria.cadonna@provincia.tn](mailto:maria.cadonna@provincia.tn))

\*\*\* Department of Cellular Computational and Integrative Biology (CIBIO) – University of Trento, via Sommarive, n. 9, 38123 Trento, Italy (E-mail: [serena.manara@unitn.it](mailto:serena.manara@unitn.it))

## INTRODUCTION

Several studies have shown that gastrointestinal problems, like diarrhoea, nausea, vomiting, and abdominal pain, may be an early symptom of COVID-19 disease. Most of these mild diseased people are positive to the SARS-CoV-2 virus in faeces. Furthermore, 18–40 % of infected people appear asymptomatic while their stools may remain positive to SARS-CoV-2 for long periods, from days to weeks. The viral load of SARS-CoV-2 measured in the stool of infected people can vary largely in the range of  $10^3$ – $10^7$  genomic unit/g faeces (GU/g). When faeces are transported to the sewage network, the viral titre undergoes an important dilution (about  $10^3$  times) due to the presence of drinking water, rainwater or infiltrations. As a result, the viral load of SARS-CoV-2 in municipal wastewater drops to the range of 1– $10^3$  GU/mL, also taking into account that only a small fraction of the community is infected. The quantification of SARS-CoV-2 in wastewater appears today as a powerful tool that can help in the Wastewater-based epidemiology (WBE). The goal is to improve the prediction or to anticipate new waves of COVID-19 outbreaks. This approach can provide an early warning of the evolution of the infection in a population in order to better define mitigation strategies.



**Figure 1.** Flow chart that shows the main steps used to calculate the viral titre of SARS-CoV-2 in raw wastewater and in a municipality.

However, the success of WBE depends on the ability to accurately quantify the SARS-CoV-2 titres in wastewater. At present, despite the efforts made in many countries, this quantification in wastewater remains an open issue and some critical aspects still exist. In this research we highlighted some practical and scientific aspects that emerged during an extensive ongoing monitoring campaign carried out on a huge number of wastewater treatment plants (31 WWTPs) located in the province of Trento (North Italy) and aimed at the detection of SARS-CoV-2 in raw municipal wastewater (Fig. 1). In order to carry out the monitoring of a large number of WWTPs in

a territory, sampling, storage and analysis of samples should be fast enough to be feasible in a laboratory with moderate efforts in terms of personnel, equipment and costs but at the same time ensuring reliable results to be used efficiently in epidemiological surveillance. This study provides some insights that can be exploited into the implementation of surveillance plans in other regions.

## RESULTS

### Issues related to the wastewater matrix

**Sampling protocol.** Samples of raw municipal wastewater were collected at the inlet of 60 WWTPs in the period October–December 2020 during a peak of the outbreak in Italy. One aspect to be considered is the sampling protocol that can be based on the use of 24 h composite or instantaneous samples. If grab samples may be sufficient to detect the SARS-CoV-2 presence, composite sampling are advised to minimize potential bias in WBE applications. **Sample storage.** Samples were transported to the laboratory and stored at 4 °C. The storage temperature and duration are also key factors to preserve correctly the number of the virus copies, but at the moment there is not full international agreement. However, in our extensive monitoring campaign, the storage at –80 °C, although recommended by some authors in the literature, was not feasible due to the large number of WWTPs sampled (31) and the relatively large volumes of samples (3 × 250 mL) used in the subsequent analyses (this leads to the need to store tens of litres per week).

**Pre-treatments.** Pasteurization of raw wastewater has been proposed in some protocols (La Rosa *et al.*, 2020) to avoid any possible risks for the operators involved in the analysis. However, some research showed a loss of RNA integrity with thermal inactivation step.

### Issues related to the molecular analysis

**Concentration.** The low concentration of SARS-CoV-2 in raw wastewater (3– 600 GU/mL in the samples taken from 31 WWTPs monitored in this research) imposes an initial high-efficiency viral enrichment step. We applied two enrichment methods (La Rosa *et al.*, 2020; Wu *et al.*, 2020): (i) biphasic system (PEG-dextran) adapted from the WHO procedure for Poliovirus surveillance; (ii) centrifugation with the addition of PEG. These two methods were compared in this paper with regards to the time of application and the influence of PCR-inhibitory substances like organic solids that can prevent the correct amplification of viral RNA. Finally, the same protocol of RT-PCR was used to obtain CT values.

### Issues related to the mathematical calculation

**Calibration curve to obtain GU/mL.** The results provided by RT-PCR were converted into GU/mL of SARS-CoV-2 on the basis of a standard curve prepared through serial dilutions of a positive reference material with sequences from SARS-CoV-2 genome. **Flow rate measurements.** Finally, the viral load in a municipality can be calculated using the flow rate measured directly in the WWTP during the time interval of sampling. The flow rate for WBE cannot be calculated using the population equivalent and the average daily water consumption per capita ( $L PE^{-1} d^{-1}$ ).

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# Sewer and Rainwater Drainage Networks' Design: The Use of Modelling Software

G. Dakša<sup>\*,\*\*</sup>, V. Urbanovičs<sup>\*</sup>, M. Zemīte<sup>\*</sup>, M. Kaļinka<sup>\*</sup>, and J. Rubulis<sup>\*</sup>

<sup>\*</sup> Faculty of Civil Engineering, Riga Technical University, Kalku Street 1, Riga, LV-1050, Latvia  
(E-mails: *Gints.Daksa@rtu.lv*; *Valts.Urbanovics@rtu.lv*; *Marta.Zemite@rtu.lv*;  
*Maris.Kalinka@rtu.lv*; *Janis.Rubulis@rtu.lv*)

<sup>\*\*</sup> Jūrmalas Ūdens Ltd., Promenādes Street 1a, Jūrmala, LV-2015, Latvia

## INTRODUCTION

The design of sewer and rainwater drainage networks is guided by countries' legislation, in Latvia must be followed building code 223-15 "Sewerage structures" (RLC, 2015).

During the design phase of both sanitary sewers and rainwater collection networks, dimensioning is performed for main collectors of the system. If modelling approach is used during the planning phase, more efficient and cost-effective sewer systems can be created.

## MATERIALS AND METHODS

Bentley SewerGEMS and EPA's Stormwater Management Model (SWMM) (Rossman, 2010) software was used for modelling purposes. Sanitary sewers and rainwater drainage were modelled separately.

In case of sanitary sewers, to bring the hydraulic model closer to an existing network and obtain a clear image of hydraulic behaviour for a given system, during modelling phase sanitary inflows were assigned to their respective manholes. To account for changes in water demand, all inflows were assigned demand patterns depending on consumer type (e.g. household, school, carwash, etc.). Modelling and system performance evaluation was conducted in three steps. Initially, hydraulic simulations were performed for a network based on manual calculations in accordance with existing legislation. Subsequently, analysis of wastewater flow rates and pipeline H/D ratios was carried out. Pipeline sections with disproportionately large diameters were identified. Finally, repeated simulations were carried out for a network in which the dimensions of pipelines were adjusted.

In case of rainwater drainage, information about the system was collected from all available sources to create a layout of the catchment. Using land-use and elevation information about the catchment territory, a model was created.

## RESULTS AND DISCUSSION

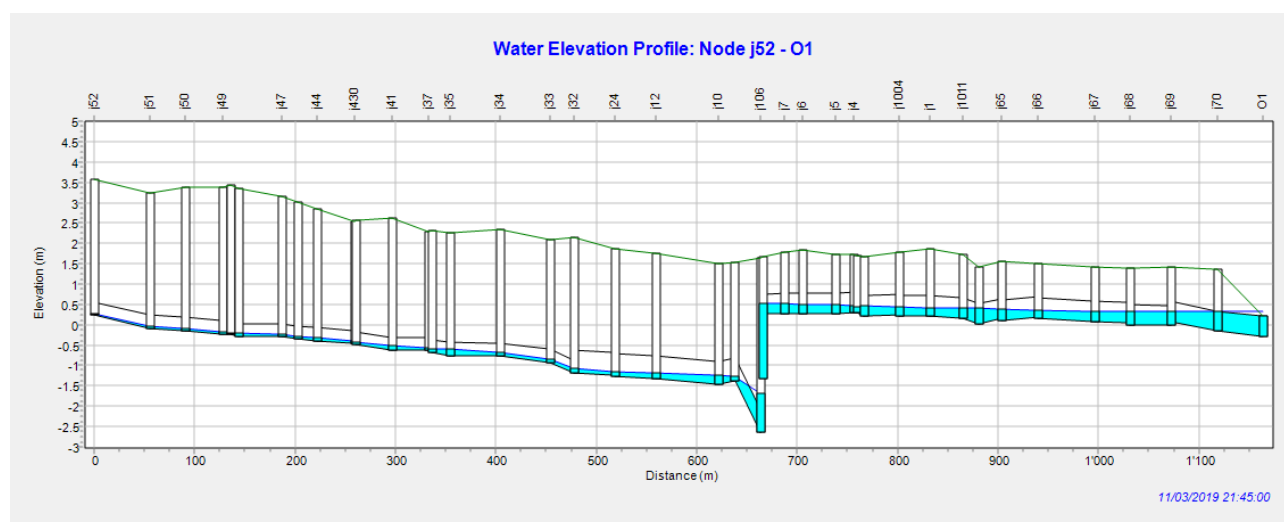
Results acquired by manual pipeline dimensioning and hydraulic simulation optimization are compared in Table 1. Discrepancies in manual calculations and hydraulic simulations are evident in downstream sections of sewage collection networks. This can be explained by the fact that the wastewater does not reach the main collector immediately – there is a time lag that depends on existing demand patterns.

Results acquired from hydraulic modelling of rainwater drainage system are shown in Fig. 1. The rainwater drainage system model can be used for different applications, such as identification of problematic locations in the drainage system, solving problems related to the catchment, making the

system more efficient by carefully locating pumping stations, floodgates etc., and potentially saving money when it is used during system design phase.

**Table 1.** Comparison of optimal pipeline diameters acquired by manual hydraulic calculations and hydraulic simulations.

Pipeline section No.	Diameter (legislation), mm	Diameter (modelling), mm
0–3	400.00	400.00
3–5	450.00	450.00
5, 6	500.00	500.00
6, 7	600.00	600.00
7, 8	700.00	<b>600.00</b>
8–10	800.00	<b>600.00</b>



**Figure 1.** Tebras Street (Liepaja) catchment hydraulic model profile.

## CONCLUSIONS

Hydraulic models are beneficial during the wastewater or rainwater drainage network design phase. The use of modelling can ease the burden of planning, whether for new pipelines or existing system expansion. Over-sizing of collection structures can be evaded, and bottlenecks of the current system can be quickly pinpointed. Different modelling ways are used based on the application and the scale of the catchment.

## ACKNOWLEDGEMENTS

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# Incidents of Industrial Wastewater Discharge to Municipal Sewerage System in Baltic Sea Region Countries

S. Dejus\*, J. Zviedris\*, K. Tihomirova\*, and T. Juhna\*

\* Water Research Laboratory, Riga Technical University, Kipsala 6A–263, Riga, LV-1048, Latvia  
(E-mail: [sandis.dejus@rtu.lv](mailto:sandis.dejus@rtu.lv))

## INTRODUCTION

Industrial organisations are a potential source of highly polluted wastewater that must be managed accordingly. Correspondingly, to legislation in European Union, the industrial wastewater must be treated before discharge to nature or pre-treated before discharge to municipal wastewater collection systems and treatment plants (MWWTP) to reduce the potential impacts to nature (European Commission, 1991). Overall in the Baltic Sea region (BSR) countries discharge (flow and quality) of industrial wastewater to MWWTP is the subject of the contract between the industrial organisation and water utility operating the MWWTP. Based on the quality and flow parameters of industrial wastewater at industrial organisation and that are set in contracts, the industrial organisations are responsible for pre-treatment of industrial wastewater if needed and discharge of industrial wastewater with adequate quality. However, due to technological failures at industrial wastewater pre-treatment plants, fluctuations of production amount and wastewater flow, power outages (Ashwini *et al.*, 2018) the untreated or partly treated industrial wastewater is discharged to MWWTP. These discharges can be classified as an incidents of industrial wastewater discharges to MWWTP.

The aim of this study is to assess the situation of highly polluted industrial wastewater discharges to MWWTP in BSR and measures taken by water utilities in such a case.

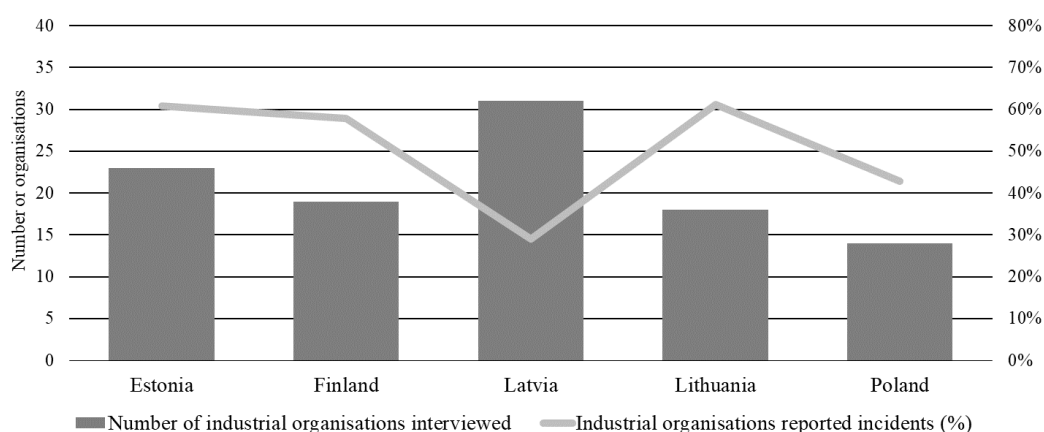
## MATERIALS AND METHODS

In order to assess the situation on discharging industrial wastewater to MWWTP and reported incidents, the main polluting industrial sectors were clarified in five BSR countries (Estonia, Finland, Latvia, Lithuania, Poland). The division of industrial sectors is based on Statistical classification of economic activities in European Community NACE Rev.2.0 (Eurostat European Commission, 2008). The industrial sectors that are in scope of the research are C10.1 – Processing and preserving of meat and production of meat products, C10.5 – Manufacture of dairy products, C11 – Manufacture of beverages, C16 – Manufacture of wood and of products, C20 – Manufacture of chemicals and chemical products, C25 – Manufacture of fabricated metal products, except machinery and equipment, C27 – Manufacture and repairing of electrical equipment, E38 – Waste collection, treatment, and disposal activities; materials recovery (Dejus *et al.*, 2019). In terms of the industrial sectors, the interviews by implementing questions on reported incidents of industrial wastewater discharge with industrial organisations and corresponding water utilities were collected. The results of the interviews were summarized and unified to find the number of industrial organisations that have faced incidents.

## RESULTS

In total 163 interviews in 5 BSR countries were conducted. In total 103 interviews with industrial organisations and 58 interviews with water utilities were conducted. The number of interviews carried out in each country and industrial organisations reported the incidents on industrial

wastewater discharges are summarized in Fig. 1. On average 49 % of industrial organisations have addressed incidents regarding industrial wastewater discharge to MWWTP. The highest number of incidents in 61 % of industrial organisations in scope have been reported in Estonia and Lithuania, while the lowest number of incidents 29 % of cases have been reported in Latvia.



**Figure 1.** The number of industrial organisations interviewed and reported incidents on industrial wastewater discharged.

In most of the cases when highly polluted industrial wastewater has been discharged to MWWTP, the water utilities have fined the industrial organisations based on the methodology set in the contract. There has been 1 case reported when the industrial organisation has been temporally shut down till the proper operation industrial wastewater pre-treatment process and facilities were established.

## CONCLUSIONS

In terms of the research, it has been found that at least 49 % of industrial organisation have reported incidents on industrial wastewater discharged to municipal wastewater treatment plants meaning that there is a huge potential of improvement of wastewater processing at industrial organisations. The high number of reported incidents shows that the fining of industrial organisations in a case of incidents is not reaching objectives.

## ACKNOWLEDGEMENT

This work has been supported by the INTERREG Baltic Sea region program project BEST (Better Efficiency for Industrial Sewage Treatment, #R054).

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## Performance of a Biological Pre-Treatment System Coupled with Static Granular Bed Reactor (SGBR) for Poultry Slaughterhouse Wastewater Treatment

D. N. Dlamini\*, M. Basitere\*\*, and S. K. O. Ntwampe\*\*\*

\* Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Cape Peninsula University of Technology, P. O. Box 1906, Bellville, 7535, South Africa (E-mail: [dlaminid@cput.ac.za](mailto:dlaminid@cput.ac.za))

\*\* Bioresource Engineering Research Group (BioERG), Cape Peninsula University of Technology, P. O. Box 652, Cape Town, 8000, South Africa (E-mail: [basiterem@cput.ac.za](mailto:basiterem@cput.ac.za))

\*\*\* School of Chemical and Minerals Engineering, Faculty of Engineering, North West University, Private Bag X1290, Potchestroom, 2520, South Africa (E-mail: [Karabo.Ntwampe@nwu.ac.za](mailto:Karabo.Ntwampe@nwu.ac.za))

### INTRODUCTION

Water is an important aspect to human existence, and as well as to all other living things on earth. The meat processing industry is one of the largest consumers of freshwater in the world (Bustillo-Lecompte and Mehrvar, 2017). Poultry slaughterhouse factories use high volumes of water during processing and thus yielding high volumes of poultry slaughterhouse wastewater (Yaakob *et al.*, 2018). The rising demand of poultry produce requires an increase in poultry processing facilities which would result in high volumes of PSW to be treated (Valta *et al.*, 2015). Poultry slaughterhouse wastewater effluent is stubborn in nature, and it needs significant treatment before it is safely discharged to the environment, due to the high amounts of organics and nutrients contained (Barrera *et al.*, 2012). The poultry slaughterhouse process involves a series of processing steps, from processing a live bird to converting it to edible meat fit for human consumption. The latter processing steps require large volumes of freshwater during processing, and this also contributes to the pollution of the freshwater as well. The high volume amounts of water usage emanates from the fact that these steps require numerous sanitization (Meneses *et al.*, 2017). A high volume of clean water usage translates to a high generation of polluted wastewater.

There is a need of developing plants that are highly efficient in the treatment of high poultry slaughterhouse wastewater volumes. This study seeks to present current innovation strategies that have been developed in the poultry processing sphere in order to maintain high efficiencies and through-puts. Poultry slaughterhouse wastewater has proven to be a challenge when it comes to environmental pollution in general. Therefore, there is a need to develop new processing plants which would keep up with the treatment of poultry wastewater generated. Poultry industries have been growing rapidly due to the high demand in poultry meat consumption.

This paper focuses and highlights an innovative development that has been used in the treatment of poultry slaughterhouse wastewater.

### MATERIALS AND METHODS

Sampling of poultry slaughterhouse wastewater (PSW) is done from poultry waste pond. The PSW samples are collected in 25 L plastic drums. To avoid any further reaction, the samples are kept in cold rooms maintained at 10 °C.

Analysis of the following parameters is performed: chemical oxygen demand (COD), biological oxygen demand (BOD), fats, oil and grease (FOG), pH, total suspended solids (TSS), total dissolved solids (TDS).

The second step involves pre-treatment of the raw PSW effluent. This process entails the addition of bacterium strains, into the PSW effluent, which survive under aerobic conditions. The addition ratio is 20 mL (bacterium strains): 20 L of raw PSW effluent. Aeration happens over a period of 24 h after which the samples are screened and kept in the feed holding tank.

The third step entails treatment of the effluent discharged from the pre-treatment step by using anaerobic bio-digesters called the expanded bed granular reactor (EGSB) and static granular bed reactor (SGBR) at 2 L holding capacity each. Brewery activated bacteria sludge is added on the pretreated PSW effluent.

## RESULTS AND DISCUSSION

Removal efficiency on the pretreatment and anaerobic digester sections:

$$= \frac{\text{COD}_{\text{input}} - \text{COD}_{\text{output}}}{\text{COD}_{\text{input}}} \times 100.$$

**Table 1.** This is an average COD average of results obtained in the first month.

	Pre-treatment process		SGBR process	
	Input	Output	Input	Output
COD, mg/L	2977	1190	1190	450

Currently, with the data obtained so far it can be said that raw PSW effluent comes in at high chemical oxygen demand (COD) content and leaves at lower value. This shows an improved removal efficiency, and while noting that there may be a need of cultivating microbes that would adapt speedily. The process is still in its startup phase where we are still trying to find stable conditions.

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# Are Side-Stream Loads of Pharmaceutical Compounds Important for the Large-Scale Wastewater Treatment Plants?

T. Dolu\* and B. Nas\*

\* Department of Environmental Engineering, Konya Technical University, Konya, Turkey  
(E-mails: [tdolu@ktun.edu.tr](mailto:tdolu@ktun.edu.tr); [bnas@ktun.edu.tr](mailto:bnas@ktun.edu.tr))

## INTRODUCTION

The presence of pharmaceutical compounds in the environment has become a serious global concern since they pose a direct or indirect threat for almost all aquatic species, animals and even people (Lee *et al.*, 2019). Wastewater treatment plants (WWTPs) are considered as the one of the most important point sources with regard to the discharge of pharmaceutical compounds into receiving environments. Since most of the existing conventional WWTPs cannot completely remove pharmaceuticals (Tran *et al.*, 2018), determining the individual and total pharmaceutical loads discharged from WWTPs into receiving environments is crucial for evaluating their potential adverse effects on all living creatures.

Although there are numerous studies performed about occurrence, distribution and removal of pharmaceuticals in WWTPs found in different geographical regions, there are very few researches investigating the side-stream contribution of these compounds to total loads in WWTPs. In this study, the effect of side-streams of three pharmaceutical compounds belonging to different therapeutic groups on total loads were investigated in order to determine their behavior patterns both in sludge thickener and sludge dewatering units found in an advanced biological WWTP. Within this scope, diclofenac (DCF) from the group of nonsteroidal anti-inflammatory drugs, carbamazepine (CBZ) from the group of anticonvulsants and ciprofloxacin (CIP) from the group of antibiotics were investigated. Besides, the increase and decrease in the concentration values of the each investigated pharmaceutical compounds in the side streams returning to the beginning of the plant were evaluated based on the concentration values determined in the raw wastewater. Finally, within the scope of the findings, it was evaluated whether the side streams were a serious problem for a large-scale WWTP by calculating the extra pharmaceutical load percentages caused by the side-streams originating from both in sludge thickening and the sludge dewatering (decanter) units.

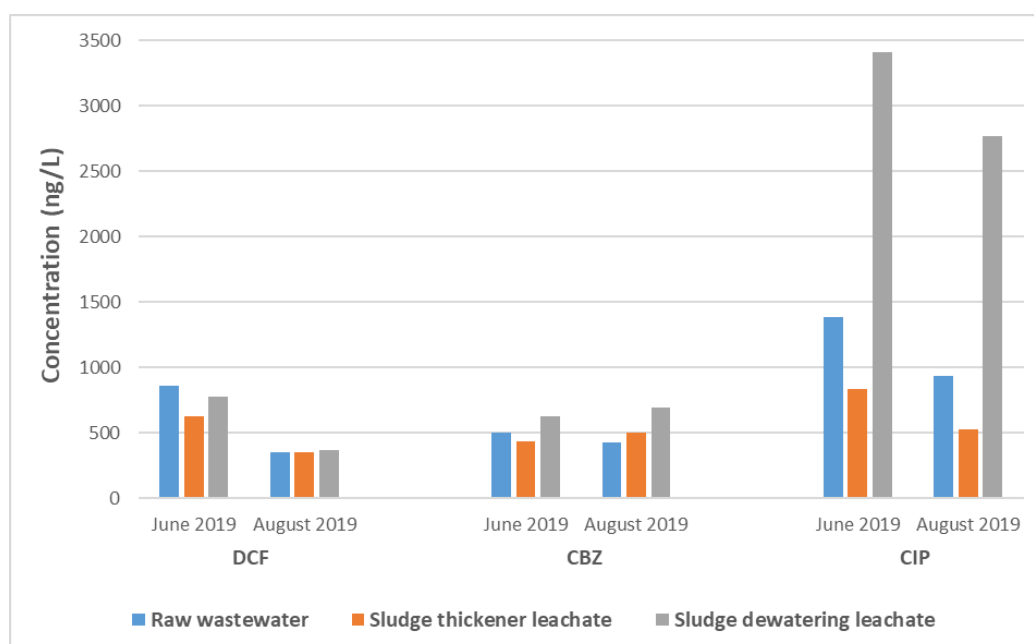
## MATERIALS AND METHODS

Sampling campaigns were performed in the months of June and August of the summer season of the year of 2019. The study was performed in a large-scale urban WWTP which is operated as biological 4 stage Bardenpho process found in the city of Konya, Turkey. Wastewater samples were collected from the raw wastewater, sludge thickening and sludge dewatering units. Although the capacity of the WWTP is 200 000 m<sup>3</sup>/d, an average of 165 000 m<sup>3</sup> of wastewater was treated daily at the WWTP during the sampling months. Besides, flows of side-stream originated from the sludge thickening and sludge dewatering units were measured as about 5500 m<sup>3</sup>/d and 1500 m<sup>3</sup>/d, respectively in the sampling campaigns. Hydraulic retention times of wastewater treatment processes were also taken into consideration in the sampling campaigns while sampling.

Collected wastewater samples were firstly filtered through 0.45 µm polytetrafluoroethylene (PTFE) filters. After solid-phase extraction (SPE) method was performed, wastewater samples were analyzed by liquid chromatography mass spectrometry / mass spectrometry (LC-MS/MS).

## RESULTS AND CONCLUSION

Concentrations of three pharmaceutical in raw wastewater and side-streams originated from both sludge thickener and sludge dewatering units in the sampling campaigns are given in Fig. 1. While very similar behaviors were determined for CIP in the side-streams for the different sampling months, small behavioral differences were found for DCF and CBZ. In general, the concentrations determined in the side streams for both DCF and CBZ were found to be very close to the raw wastewater concentrations. In addition, the highest concentration values for CBZ were detected in sludge dewatering leachate in both sampling months. However, the behavior of CIP was found to be quite different from other investigated compounds. While the concentration of CIP detected in raw wastewater decreased by about half in sludge thickening leachate, it increased considerably in the sludge dewatering unit leachate up to 3 times of the concentration values in raw wastewater.



**Figure 1.** Concentrations of pharmaceutical compounds in raw wastewater and side-streams.

Considering the flows of side-stream that occurred during the sampling campaigns, contribution of the side-stream loads caused by the sludge thickener and sludge dewatering units to total pharmaceutical loads ranged between 1.87–3.91 % and 0.82–2.69 %, respectively. The total side-stream contributions to total load were calculated in the ranges of 3.25–4.26 %, 4.01–5.40 % and 4.27–4.56 % for DCF, CBZ and CIP, respectively. As a result, it has been determined that the extra pharmaceutical loads caused by side-streams in WWTPs can be roughly calculated over the raw wastewater concentrations of pharmaceutical compounds and the generated side-stream flows in WWTPs. Therefore, it can be said that extra pharmaceutical loads caused by side streams are a greater drawback for WWTPs than estimated.

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# Removal and Yearly Variability of Selected Non-Steroidal Anti-Inflammatory Drugs and Antibiotics in a Large-Scale Municipal Wastewater Treatment Plant

T. Dolu\* and B. Nas \*

\* Department of Environmental Engineering, Konya Technical University, Konya, Turkey  
(E-mails: [tdolu@ktun.edu.tr](mailto:tdolu@ktun.edu.tr); [bnas@ktun.edu.tr](mailto:bnas@ktun.edu.tr))

## INTRODUCTION

Due to their extremely consumption all over the world, pharmaceuticals are frequently detected in different water bodies, sediments, agricultural lands, plants, vegetables and even aquatic species (Ben *et al.*, 2019; Tran *et al.*, 2018). Presence of these emerging compounds with threatening concentrations almost in all different environmental matrices are mainly associated with wastewater treatment plants (WWTPs). Because, existing conventional WWTPs cannot act as a full barrier for complete elimination of pharmaceuticals similar to other micropollutant groups. Consequently, many of these pharmaceuticals pass into receiving water bodies along with discharged treated wastewaters with their known or unknown adverse effects both for ecosystems and human.

Nonsteroidal anti-inflammatory drugs (NSAIDs) and antibiotics are the most consumed two important sub-groups of pharmaceuticals for the different purposes both in the field of human and veterinary medicine (Moreno-González *et al.*, 2014). Primary objective of this study was to determine the occurrence levels and fate of six pharmaceuticals belong to the groups of NSAID and antibiotic in a conventional urban WWTP in consecutive years. Within this scope, acetaminophen and diclofenac in the group of NSAID and ciprofloxacin, sulfamethoxazole, trimethoprim and erythromycin in the antibiotic group were investigated. Secondly, the annual changes of each studied pharmaceuticals in the same WWTP were compared in terms of both occurrence concentrations and removal efficiencies. Finally, the possible reasons of significant differences observed yearly regarding to the total removals of certain compounds were evaluated.

## MATERIALS AND METHODS

The study was performed in Konya WWTP which was designed to treat approximately 200 000 m<sup>3</sup>/d wastewater. Has an activated sludge treatment system involving biological 4 stage Bardenpho process, Konya WWTP serves approximately 1.3 million population in the city. All domestic, industrial and hospital wastewater of the city are directed to Konya WWTP through the combined sewerage system.

Sampling campaigns were carried out in the September months of 2018 and 2019 years. Wastewater samples were collected as 2 h composite samples from the raw wastewater before the screens and effluents of both primary and secondary clarifiers by a 1 L amber bottles with teflon-lined caps. Hydraulic retention times of the treatment units were also taken into account during the sampling campaigns. In both sampling years, collected wastewater samples were filtered through 0.45 µm polytetrafluoroethylene (PTFE) filters. While direct injection method was used in the first sampling year, a solid-phase extraction (SPE) method was applied in the second sampling year. All analyses were performed by liquid chromatography mass spectrometry/mass spectrometry (LC-MS/MS) in both sampling campaigns.

## RESULTS AND CONCLUSION

Occurrence concentrations and behaviors of two NSAIDs and four antibiotics in the wastewater line of Konya WWTP were determined in the same months of consecutive years. Within this scope, it was aimed to minimize the seasonal effects to evaluate the fate of selected compounds. The results obtained in two sampling campaigns were given in Table 1.

**Table 1.** Fate and removal of pharmaceuticals throughout the wastewater line of Konya WWTP.

Pharmaceuticals ng/L	September of 2018				September of 2019			
	R. W.	P. C.	S. C.	Removal, %	R. W.	P. C.	S. C.	Removal, %
<b>NSAIDs</b>								
Acetaminophen	2324.5	932.3	<LOQ	>95.7	25842	364	<LOQ	>99.9
Diclofenac	827.6	744.6	528.1	36.2	36	172	75	-108.3
<b>Antibiotics</b>								
Ciprofloxacin	895.4	1258.8	<LOQ	>88.8	2639	3461	153	>94.2
Sulfamethoxazole	95.8	162.9	223.6	-133.4	313	197	146	53.4
Trimethoprim	<LOQ	<LOQ	<LOQ	-	20	<LOQ	37	-85.0
Erythromycin	<LOQ	<LOQ	<LOQ	-	<LOQ	<LOQ	<LOQ	-

\* R. W. (raw wastewater); P. C. (primary clarifier); S. C. (secondary clarifier); LOQ (limit of quantification).

\* While LOQ was 50 ppt for the first sampling campaign, the value of LOQ was 10 ppt for the second sampling campaign.

In general, occurrence concentrations of all pharmaceuticals in raw wastewater increased except the diclofenac in the year of 2019 compared to 2018. Substantial increase was observed especially for acetaminophen. Erythromycin was not detected in any of the sampling points during both sampling campaigns. Besides the occurrence concentrations, significant differences were detected in the behavior patterns of some compounds within two years. While diclofenac was treated to some extent as positive in 2018, serious negative removal rate was seen in 2019. Another example was that while negative removal efficiency was obtained for sulfamethoxazole in 2018, moderate positive removal was achieved in 2019. Although the removal rates between the treatment units were different between the sampling campaigns, both behavior patterns and total removal efficiencies of acetaminophen and ciprofloxacin were found as quite similar for the year of 2018 and 2019. As a result, although the studies were conducted in the same WWTP in the same period, it was found out that it is very difficult to make accurate predictions and generalizations about the fate and removal of pharmaceuticals.

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# Poultry Slaughterhouse Wastewater Treatment Using a Down-Flow Expanded Granular Bed Reactor Coupled with Single Stage Nitrification-Denitrification System, Submerged Membrane, and Ultraviolet System

P. A. Dyosile<sup>\*,\*\*</sup>, M. Basitere<sup>\*,\*\*</sup>, and S. K. O. Ntwampe<sup>\*\*\*</sup>

\* Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Cape Peninsula University of Technology, P. O. Box 1906, Bellville, 7535, South Africa (E-mail: [phumezadyosile@gmail.com](mailto:phumezadyosile@gmail.com))

\*\* Bioresource Engineering Research Group (BioERG), Cape Peninsula University of Technology, P. O. Box 652, Cape Town, 8000, South Africa (E-mail: [basiterem@cput.ac.za](mailto:basiterem@cput.ac.za))

\*\*\* School of Chemical and Minerals Engineering, Faculty of Engineering, North West University, Private Bag X1290, Potchestroom, 2520, South Africa (E-mail: [Karabo.Ntwampe@nwu.ac.za](mailto:Karabo.Ntwampe@nwu.ac.za))

## INTRODUCTION

Though the poultry industry has become the confidant in the South African agricultural industry due to growing demand from its affordable prices compared to other animal protein, the water requirements for the poultry slaughtering and the preparation process (including cleaning) are extensive. Governed by the South African Meat Safety Act no. 40 of 2000 and Abattoir Hygiene Act no. 121 of 1992 simultaneously, operating abattoirs both high and low volume (quantified by the number of birds slaughtered per day) are committed to providing clean and wholesome products which are safe for consumption (Molapo, 2009). To achieve this, they are required to use at least 15 litres of high pressured, filtered and chlorinated water per bird (Molapo, 2009).

A typical high-volume abattoir that slaughters over ten thousand birds per day produces more than one hundred and fifty thousand litres of poultry slaughterhouse wastewater (PSW) that contains a high level of organics, overload nutrients, solids, fat, oil and grease (FOG) and pathogenic microorganisms due to the presence of blood, faecal matter, traces of urine, skin trimmings, feathers and cleaning products (Rinquest *et al.*, 2019).

The excessive level of nutrients ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ), organics (COD, BOD, TOC), solids (TDS, TSS, VSS) and change in physical properties in the untreated PSW is detrimental to the environment, municipal sewer systems and poses as a human health hazard (Njoya *et al.*, 2019; Basitere, 2017).

There have been numerous treatment technologies used for high strength PSW treatment, both aerobic and anaerobic. The use of aerobic digestion requires a large volume of oxygen thus making it an expensive treatment method. In the case of this study, the down-flow expanded granular bed reactor (DEGBR) was used for its anaerobic function, cost efficiency, high organic removal rate, ability to produce effluent that has minimal suspended solids additional recycle stream which activates the sludge and reduce clogging (Njoya *et al.*, 2019).

The train also includes a nitrification-denitrification system coupled with submerged membranes and an ultraviolet system to assist the reactor in organic, nutrient, solid and pathogen removal.

## MATERIALS AND METHODS

Granular sludge collected from a brewery located in Cape Town, South Africa, and filtered PSW was also fed into the reactor. To facilitate the growth of microorganisms inside the reactor, infant formula solution is fed into the reactor along with eco-flush which serves as a fat resucing agent which pre-treats the wastewater and works as an anti-clogging mechanism.

Due to the complexity of PSW, pH, TDS, TSS, BOD, COD, VSS, FOG,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are analysed prior, during and post treatment to note the effectiveness of the plant.

## RESULTS AND DISCUSSION

The SGBR has been associated with clogging. The present study looks at the Hybrid-SGBR which contains a recirculatory recycle that will alleviate solid build up in the reactor granules. Along with the added pre-treatment and based on past studies, the reactor performance is expected to achieve a COD removal higher than 90 %.

The single-stage nitrification-denitrification, membranes and ultraviolet system will eradicate present particulates and coliforms and further reduce COD and solid removal.

## CONCLUSION

The proposed Treatment train which includes an eco-flush driven pre-treatment, Hybrid-SGBR, Single stage nitrification-denitrification, membranes and ultraviolet system will treat solids, nutrients, organics and physical properties to produce water quality which far exceeds the set general limit.

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# Characterization of the Wastewater Discharged from a Latvian Dairy Industry

B. Ekka\* and T. Juhna\*

\* Faculty of Civil Engineering, Riga Technical University, Latvia (E-mails: *basanti.ekka\_1@rtu.lv*; *Talis.Juhna@rtu.lv*)

## INTRODUCTION

The European dairy industry is the largest milk producer in the world accounting for approximately 160 million tonnes of milk (22 % of the world's total milk production) and this industry plays a dynamic role in the agri-food sector of the European Union (EU). Apart from the dairy industry is generally considered to be the largest source of food processing wastewater in many countries as it consumes countless amounts of water and generates huge quantities of wastewater. The dairy industry due to the nature of the raw material used and the processing technology affects primarily the quality of water, and a lesser amount of the air and soil (Raghunath *et al.*, 2016). The dairy wastewaters consist of fractions of milk, detergents and sanitizing agents, mainly from cleaning and washing operations. It is characterized by great diversity of pollutant concentrations over time. Dairy wastewaters have a high polluting potential as they are typically characterized by high concentrations of biological oxygen demand (BOD) (40–8240 mg L<sup>-1</sup>), chemical oxygen demand (COD) (430–18045 mg L<sup>-1</sup>), nutrients (total nitrogen, TN: 14–830 mg L<sup>-1</sup>, total phosphorus, TP: 9–280 mg L<sup>-1</sup>) and suspended solids (SS) (24–4500 mg L<sup>-1</sup>) (Hemalatha *et al.*, 2019).

Currently, there is lack of data in the scientific literature on the composition of the dairy waste stream which is obstacle to optimize its valorization process and sustainable management. In order to meet the discharge effluent quality, the dairy processing sector needs to achieve BOD: 16 mg L<sup>-1</sup>, COD: 125 mg L<sup>-1</sup>, SS: 30 mg L<sup>-1</sup>, TN: 5–25 mg L<sup>-1</sup>, TP: 2–5 mg L<sup>-1</sup> and total ammonia (NH<sub>4</sub>-N): 10 mg L<sup>-1</sup> in the treated effluents (Gil-Pulido *et al.*, 2018). In the past two decades, organic matter characterization, through identification of biochemical families, has become decisive in several topics of environmental treatment processes. Initially, quantification of organic matter was done by few conventional variables such as chemical oxygen demand (COD), biological oxygen demand (BOD) or volatile solids (VS). Later, with the growing necessity to optimize and to model treatment process performance, a more accurate characterization of the organic matter was required. In this context, detailed organic matter quantification methods have been developed and used. The present study focuses on the detail characterization of organic matter by using different instrumental techniques.

## EXPERIMENT

### Reagents

Analytical grade copper sulfate, Lipid standards: triglyceride mixtures,  $\alpha$ -Lactose were purchased from Sigma-Aldrich. Analytical solutions were prepared with ultrapure water (Millipore Milli-Q, resistivity > 18.2 M $\Omega$  cm), whereas reagents and organic solvents such as toluene, methanol, chloroform, and diethyl ether were of HPLC or analytical grade supplied by Merk.

### Dairy wastewater sample collection

The raw dairy wastewater was obtained from Latvijas Piensaimnieks dairy industry Jelgava, Latvia.

Samples were collected in polyethylene bottles and stored at 4 °C before analysis of contaminants present in it.

### Analysis of physicochemical parameters of the dairy effluents

The physicochemical parameters such as pH, temperature, salinity, conductivity, COD (chemical oxygen demand), Total Nitrogen, Nitrogen Ammonia, Reactive Phosphate, Nitrite, Total Iron were analyzed by HACH water analyzer kit.

### Biochemical analysis of dairy effluents

The biochemical parameters such as lipids, protein (amino acids) and carbohydrates are analyzed by different instrumental techniques such as UV-vis, FTIR, NMR, HPLC, GC-FID as required.

## RESULTS AND DISCUSSIONS

The physicochemical parameters (Table 1) were characterized by HACH water analyzer kit.

**Table 1.** Physicochemical parameters of dairy wastewater collected from Latvijas Piensaimnieks dairy industry Jelgava.

Analysis	Amount
COD	1650 mg/L
Total Nitrogen	36 mg/L
Nitrogen Ammonia	22 mg/L
Reactive Phosphate	5.5 mg/L
Nitrite	0.145 mg/L
pH	6.2
Total Iron	0.61 mg/L

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# Chemical Deposition of Iron Nanoparticles (Fe<sup>0</sup>) on Titanium Nanowires for Efficient Adsorption of Ciprofloxacin from Water

O. Falyouna\*, I. Maamoun\*, K. Bensaida\*, R. Mokete\*, A. Tahara\*\*, Y. Sugihara\*, and O. Eljamal\*

\* Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka, Japan, 816-8580 (E-mails: [omar.falyouna@kyudai.jp](mailto:omar.falyouna@kyudai.jp); [ibrahim-maamoun@kyudai.jp](mailto:ibrahim-maamoun@kyudai.jp); [bensaida.khaoula.227@s.kyushu-u.ac.jp](mailto:bensaida.khaoula.227@s.kyushu-u.ac.jp); [lelemokete@gmail.com](mailto:lelemokete@gmail.com); [sugihara@esst.kyushu-u.ac.jp](mailto:sugihara@esst.kyushu-u.ac.jp); [osama-eljamal@kyudai.jp](mailto:osama-eljamal@kyudai.jp))

\*\* Institute of Advanced Material Chemistry, Kyushu University, 6-1 Kasuga-Koen Kasuga, Fukuoka, Japan, 816-8580 (E-mail: [tahara.a.aa@cm.kyushu-u.ac.jp](mailto:tahara.a.aa@cm.kyushu-u.ac.jp))

## INTRODUCTION

Over the years, pharmaceutical scientists have designed a broad spectrum of antibiotics to cure several bacterial infections in human and animals. Ciprofloxacin (CIP) is an extensively prescribed antibiotic worldwide to treat various infections (Mao *et al.*, 2019). The unwise application of CIP in human and veterinary medicine and the poor performance of traditional treatment plants resulted in frequent detection of CIP in several water mediums across the universe. The persistent occurrence of CIP in water is linked to the accelerated growth of antimicrobial resistance genes (AMRs) (Rahdar *et al.*, 2019). These genes are famous in developing irremediable disease. Thus, this research is proposing a unique nanocomposite material, composed of nanoscale zerovalent iron (nZVI) supported on titanium nanowires (TNWs), to efficiently remove the residues of CIP from water.

## MATERIALS AND METHODS

### Materials

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, JUNSEI, Japan), sodium borohydride (H<sub>4</sub>BNa, Sigma Aldrich, USA), sodium hydroxide (NaOH, FUJIFILM Wako Pure Chemicals, Japan), and Titanium (IV) oxide (TiO<sub>2</sub>, FUJIFILM Wako Pure Chemicals, Japan) were utilized to synthesis nZVI, TNW and (nZVI/TNW) nanocomposite. Ciprofloxacin hydrochloride monohydrate (C<sub>17</sub>H<sub>18</sub>FN<sub>3</sub>O<sub>3</sub>·HCl·H<sub>2</sub>O, Tokyo Chemical Industry CO., LTD, Japan) was dissolved in deionized water to prepare CIP solutions.

### Synthesis of nZVI and TNW

Nanoscale zerovalent iron particles were produced by a chemical reduction process. Separately, titanium nanowires (TNWs) were synthesised through a hydrothermal procedure (Wang *et al.*, 2018). (nZVI/TNW) nanocomposites were synthesised in a chemical reduction process similar to that of nZVI with some modifications. More detailed information about these methods will be provided in the full paper.

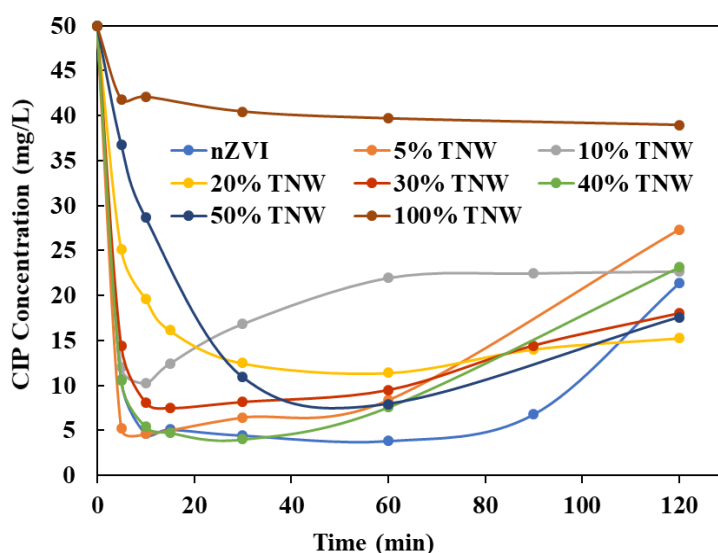
### Batch experiments

Batch experiments were conducted in 300 mL conical flasks. The conditions of the experiments were designed to be as follows: CIP initial concentration – 50 mg L<sup>-1</sup>, volume of CIP solution – 200 mL, dosage of nZVI, TNWs or (nZVI/TNW) – 0.5 g L<sup>-1</sup>, temperature – 25 °C, initial pH – 6 and contact time – 120 min. The reaction was started by placing the flask on a magnetic stirrer at

1000 rpm. At specific time intervals (i.e. 0 min, 5 min, 10 min, 15 min, 30 min, 60 min, 90 min, and 120 min), 2 mL samples were taken by syringes and filtered by 0.22  $\mu\text{m}$  filters and kept in 2 mL sampling tubes for UV-Vis analysis.

## RESULTS AND DISCUSSION

The removal efficiency of ciprofloxacin by 0.5 g L<sup>-1</sup> of nZVI within the first 60 min was promising because it achieved 89.49 % as shown in Fig. 1. However, at 90 min of reaction, the concentration of CIP in the aqueous solution started to increase which proves the desorption of CIP molecules from the surface of nZVI to the solution. Afterwards, the performance of nZVI towards the removal of CIP severely deteriorated until eventually reached 55.54 % after 120 min of reaction. On the other hand, TNWs showed poor but stable performance in removing CIP from water as they could only remove 21.48 % of ciprofloxacin. Synthesis of (nZVI/TNW) nanocomposite with different mass ratios of TNWs (i.e. 5 %, 10 %, 20 %, 30 %, 40 %, and 50 %) was carried out in order to define the optimum mass ratio of TNWs that would overcome the limitations of nZVI, initiate the photodegradation of CIP, and attain a better CIP removal efficiency. It is clear from Fig. 1 that the uptake behaviours of (nZVI/TNW) nanocomposites with different percentages of TNWs and nZVI are the same as the (nZVI/TNW) nanocomposites succeeded to remove significant proportion of CIP in the beginning of the reaction, nevertheless, desorption of CIP took place in the later stage of reaction.



**Figure 1.** Performance of nZVI and (nZVI/TNW) nanocomposite with different ratios of TNWs.

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# Hydrochar Derived Adsorbent for Pollutants Removal from Wastewater

R. Ferrentino\*, L. Fiori \*, and G. Andreottola\*

\* Department of Civil, Environmental and Mechanical Engineering, University of Trento, 77 Mesiano Street, Trento 38123, Italy (E-mails: [roberta.ferrentino@unitn.it](mailto:roberta.ferrentino@unitn.it); [luca.fiori@unitn.it](mailto:luca.fiori@unitn.it); [gianni.andreottola@unitn.it](mailto:gianni.andreottola@unitn.it))

## INTRODUCTION

Organics and inorganics pollutants, largely present in wastewater, need to be safely removed in order to avoid environmental and health problems. Among all the treatment methods, adsorption technology is rather cheap, easily scalable and relatively environmental-friendly (Dong *et al.*, 2019). Generally, the wastewater adsorption treatment is performed by using activated carbon as adsorbent material; however, in last years, the utilization of hydrochar as adsorbent has received increasing attention due to its sustainability, economy and availability (Liu *et al.*, 2021). Hydrochar is a solid carbon-rich product from wet biomasses thought the hydrothermal carbonization (HTC). Hydrochar has been tested for adsorbing a large number of pollutants such as heavy metals, nutrients, dyes and emerging contaminants. However, the adsorption capacity of the hydrochar depends on several aspects such as the feedstocks, the operative parameters of the HTC process and the activation treatment of the hydrochar. As far as we know, a literature study specifically focused on hydrochar, usable as adsorbent, is missing. Thus, this work aims to fill this gap reporting the state of the art about hydrochar characterization and pollutant removal in wastewater.

## CHARACTERIZATION OF HYDROCHAR

### Feedstock

The physicochemical properties of the hydrochar are largely related to the biomass used as feedstock for the HTC process. Different from pyrolysis carbonization, HTC allows the direct conversion of wet biomass into hydrochar without drying. Thus, HTC could be carried out with a large variety of raw substrates such as agro-industrial residues, animal manures, organic fraction of municipal solid waste, sewage sludge, aqua culture and algal residues.

### HTC operative parameters

The main operative parameters of the HTC process are the temperature and the reaction time. Hydrothermal carbonization could be carried out applying mild temperature (180–260 °C), under saturated vapor pressure and with a certain retention time, generally higher than 30 minutes.

### Activation treatment

The activation of hydrochar is performed to increase the surface area and pore volume than the original feedstock. The hydrochar can be chemically or physically activated. The chemical activation of hydrochar can be performed within the HTC reactor, thus operating simultaneously the HTC and the activation treatment, or post-treating the hydrochar after the HTC. The physical activation is performed by first carbonizing the feedstock in an inert atmosphere and then activating with a mild oxidizing gas such as CO<sub>2</sub> or steam at temperature above 800 °C. This latter activation method is more effective than the chemical activation but less performed due to high energy requirement.

## POLLUTANTS REMOVAL

As reported above, the hydrochar could be used as adsorbent for a large variety of pollutants comprising heavy metals and organic pollutants. Hydrochar shows a high value of maximum adsorption capacity for several heavy metals such as chromium, lead and mercury accounting up to  $976 \text{ mg g}^{-1}$ ,  $241 \text{ mg g}^{-1}$  and  $167 \text{ mg g}^{-1}$  (Lei *et al.*, 2018; Wang *et al.*, 2018; Zhou *et al.*, 2017). Moreover, high values of sorption capacity were reported also for the adsorption of phenol, dyes and pharmaceuticals products accounting, respectively, up to  $137 \text{ mg g}^{-1}$  (Tran *et al.*, 2017),  $68 \text{ mg g}^{-1}$  (Leng *et al.*, 2015) and  $11 \text{ mg g}^{-1}$  (Delgado-Moreno *et al.*, 2021).

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## Biocorrosion in Concrete Sewers: Status and Treatment

G. Fytianos\*, V. Baltikas\*\*, D. Loukovitis\*\*\*, A. Sfikas\*\*, E. Papastergiadis\*, and P. Samaras\*

\* Department of Food Science and Technology, International Hellenic University, Sindos, GR-57400 Thessaloniki, Greece (E-mail: [gfytianos@gmail.com](mailto:gfytianos@gmail.com))

\*\* Decus Consultants and Engineers, Ethnikis Antistaseos 4, 55133 Kalamaria, Thessaloniki, Greece

\*\*\* Department of Agriculture, International Hellenic University, Sindos, GR-57400 Thessaloniki, Greece

### BACKGROUND

The deterioration of concrete pipes in sewage collection systems has a major impact on environmental health and safety. Microorganisms that produce sulfuric acid accelerate the deterioration of concrete sewer pipes in a process termed Microbially Induced Corrosion (MIC) or biocorrosion. In concrete sewer systems, when H<sub>2</sub>S emitted from sewage meeting condensing moisture, it results in the formation of H<sub>2</sub>SO<sub>4</sub> which rapidly corrodes the concrete in sewer tunnel (U.S. EPA, 1991). MIC can damage the concrete in sewer tunnels via a gradual loss of concrete, which significantly reduces the service life of concrete structures in sewer systems and may lead to structural failures such as collapse, threatening public safety while increasing the maintenance cost of the system dramatically (Wu *et al.*, 2017). Sulphur-oxidising bacteria, combined with the bacteria of the Acidiphilium genus, are the main agents of concrete biocorrosion in sanitary sewers (Yamanaka *et al.*, 2002). If the pH is lowered to approximately 4, acidophilic bacteria such as *T. thiooxidans* and *T. ferrooxidans* can grow, resulting in acceleration of the corrosion of the concrete (Mori *et al.*, 1992).

### METHODOLOGY

The authors conducted a national survey for identifying and understanding the nature of concrete corrosion in Greece with the help of local Hellenic associations of municipal water and sewerage companies. The overall condition of the sewerage network, the maintenance frequency and the corrosion prevention techniques used in Greece are described. Moreover, results from field measurements of different cities will be presented. Moreover, a semi-solid sample of sludge, coming from a pipe (slime layer) of the sewage network, was used for bacterial community analysis. A detailed molecular genetic analysis was performed on the bacteria slime which exists at the interlayer between the concrete wall and the sewage. Finally, different techniques for the application of a resistant protective coating based on magnesium oxide will be described.

### RESULTS

Survey results showed that MIC is present in Greece's sewage networks and has even caused the destruction of sewage pipe sections made of concrete. From the field measurements and observations, the most characteristic examples of MIC were found in the city of Kozani. In addition, gas analyses result from field measurements showed hydrogen sulfide (H<sub>2</sub>S) gas presence in the gaseous phase of the sewage system while corroded concrete samples were examined stereoscopically. The microbial diversity analysis of the DNA sample revealed a wide spectrum of bacterial species that were present in the slime layer. The resolution of the microbial profiling was, in most cases, feasible down to family/genus level and in some cases down to species level. Bacteria belonging to various phyla were identified, i.e., *Acidobacteria*, *Actinobacteria*,

*Bacteroidetes*, *Chlamydiae*, *Chloroflexi*, *Cyanobacteria*, *Firmicutes*, *Gemmatimonadetes*, *Ignavibacteriae*, *Nitrospirae*, *Planctomycetes*, and *Proteobacteria*. Among the bacterial families detected was also the *Acidithiobacillaceae* family (order: *Acidithiobacillales*, class: *Gammaproteobacteria*, phylum: *Proteobacteria*). The specific family contains a single genus, *Acidithiobacillus*, with *Acidithiobacillus thiooxidans* as the type species. Four other species of this genus are currently recognized: *At. ferrooxidans*, *At. caldus*, *At. albertensis*, and *At. ferrivorans*.

The *Acidithiobacillus* genus is of special interest because its species include some of the most extremely acidophilic bacteria known, which tolerate extraordinarily high concentrations of some toxic metals. *Acidithiobacillus thiooxidans* oxidizes sulfur and produces sulfuric acid, and it has also been observed, causing biogenic sulfide corrosion of concrete sewer pipes by altering hydrogen sulfide in sewage gas into sulfuric acid.

## CONCLUSIONS

Corrosion of sewer pipes is a widespread phenomenon in Greece. According to the responses of the wastewater and sewerage companies, the sewer pipes are corroded mechanically due to the flow of sewage and waste materials, as well as biochemically. The type of corrosion that occurs each time depends on the material of the drainage pipe construction, while both MIC and mechanical corrosion can act simultaneously. Some recommendations to mitigate biocorrosion in concrete sewers (Fytianos *et al.*, 2020) could be i) the regular measurement and recording of H<sub>2</sub>S concentrations, pH, COD, sewage temperatures, effluents properties, and flow rates. These are all parameters that, together with the geometrical characteristics of the network, can be used for calculations of hydrogen sulfide production and risk; ii) the use of mobile units equipped with cameras for regular inspections; iii) treatment of the concrete surface so as to be less susceptible to corrosion (this can be done by using spray-on coatings, e.g., Mg(OH)<sub>2</sub> based coatings); iv) inhibition of the biological activity, e.g., with biocides.

## ACKNOWLEDGEMENTS

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# Gravimetric Selection of Activated Sludge for Settling Properties Improvement and Granular Sludge Formation – Full Scale Case Study

N. Gemza\*, \*\* and M. Kuśnierz\*\*\*

\* Wrocław Municipal Water and Sewage Company, Na Grobli 19 50-421 Wrocław, Poland  
(E-mail: [natalia.gemza@mpwik.wroc.pl](mailto:natalia.gemza@mpwik.wroc.pl))

\*\* Faculty of Environmental Engineering, Wrocław University of Science and Technology,  
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

\*\*\* Faculty of Environmental Engineering and Geodesy, Wrocław University of Environmental  
and Life Sciences, Norwida 25, 50-375 Wrocław, Poland  
(E-mail: [magdalena.kusnierz@upwr.edu.pl](mailto:magdalena.kusnierz@upwr.edu.pl))

## INTRODUCTION

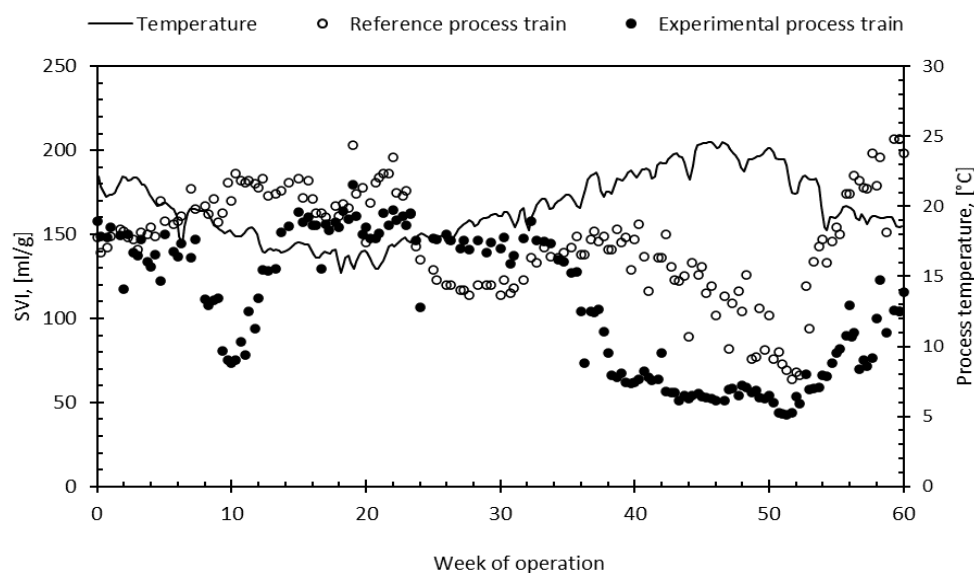
One of the main hydraulic bottlenecks of activated sludge systems is efficiency of solid-liquid separation in secondary settling tanks (SSTs). In the event of wet weather inflow, SSTs with poor settling sludge are prone to sludge blanket build-up and biomass washout. As the number of factors influencing sludge settleability and compressibility is high (Jin *et al.*, 2003) and some of them are beyond operators control, novel solutions that help improve SST performance such as granular sludge technology are in demand. Classical granular sludge is successfully cultivated in SBR systems and currently efforts are being made to achieve sludge granulation in continuous flow systems (Devlin and Oleszkiewicz, 2018). The objective of this study was to evaluate full scale gravimetric selection technology conducted in hydrocyclones as a way for activated sludge (AS) settling characteristic improvement in continuous flow BNR with a long SRT and assess its ability to form granular sludge.

## MATERIAL AND METHODS

System under study is a mechanical-biological WWTP with enhanced biological nutrient removal coupled with chemical phosphorus precipitation. It treats on average 140 000 m<sup>3</sup>/d with a load of 1 050 000 P.E. Biological treatment consists of three independent process trains where one – experimental train – was equipped with gravimetric selection installation placed on the recirculated activated sludge (RAS) line. Approximately 2 % of RAS was pumped through the installation. SVI value was monitored and used as a simplest indicator of sludge settling characteristic throughout the whole trial period. Floc size distribution was monitored using automated image analysis with Malvern Morphologi® G3.

## RESULTS AND DISCUSSION

Long term operational data and sludge morphology monitoring data were analysed. A significant drop in SVI (to values under 50 mL/g) and increase in RAS solids concentration (values above 40 g/L) was observed. Stable separation and first quantifiable results of its performance were visible when time period equal to two SRT had passed. Fig. 1 presents changes in SVI where distinctive drop is visible at 8 week and then again at 35 week. Settling parameters improvement was not stable and a gradual rise in SVI started at 10 and 52 week. It is hypothesised that the reason behind this is seasonal filamentous outgrowth since filamentous index (FI) increased from 1.5 to 3.5 during that period. AS poor settling period lasted till late spring when second rapid decrease in SVI occurred.



**Figure 1.** SVI variations in experimental and reference train.

During that period flocs size distribution changed. Flocs median diameter increased from 200  $\mu\text{m}$  in week 25 to 400  $\mu\text{m}$  in week 40 when SVI dropped to 50 mL/g. Aggregates larger than 500  $\mu\text{m}$  constituted in early spring only 5 % of all flocs volume whereas in mid-summer and early autumn 30 % and 25 % accordingly. Additionally this shift in sludge morphology is confirmed by more frequent occurrence of granule-like aggregates with diameter exceeding 1000  $\mu\text{m}$ .

Results of AS gravimetric selection implementation presented in this study contradict findings of a lab-scale experiment from Xu *et al.* (2019) where hydrocyclone operation decreased average floc size and no granules occurred. Reasons behind that might be different operation condition such as overflow/feed ratio or lack of mineral precipitates that in full scale demonstration might have acted as a granule seed. All of the above prove that exact effect hydrocyclone might have on AS floc is not yet clear and its implementation in different AS systems might have unknown outcomes.

## CONCLUSIONS

A full-scale implementation of AS gravimetric selection technology was demonstrated. The evaluation of the effects of the technology led to the following conclusions:

- Start-up phase lasted approx. two SRT when after initial phase quick improvement in settling characteristic occurred with an average SVI decrease in SVI of 14 mL/g every week.
- Good settling properties couldn't be maintained during winter season probably due to filamentous outgrowth. SVI values were maintained at the level of 160 mL/g until late spring.
- Long term hydrocyclone operation resulted in a clear change in sludge morphology. Sludge in experimental train had a significantly higher frequency in granule occurrence.

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## Removal of Heavy Metals from Wastewater by Electrocoagulation

O. R. Govedarica\*, V. N. Rajaković-Ognjenović\*, A. R. Đukić\*, and B. B. Babić\*

\* Institute for Hydraulic and Environmental Engineering, Faculty of Civil Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, Belgrade, Serbia (E-mail: [ogovedarica@grf.bg.ac.rs](mailto:ogovedarica@grf.bg.ac.rs))

### INTRODUCTION

Removal of heavy metals from wastewater and selection of the optimal method for efficient and environmentally acceptable technology remains scientific challenge in many aspects. Electrocoagulation (EC), method which has been tested and applied within this research is based on the separation of solid phase from the solution of wastewater. In this research, the object of the analysis was removal of the zinc ions ( $Zn^{2+}$ ) from a sample of real wastewater from galvanizing industry. EC is one of the electrochemical methods that can be applied for the treatment of wastewater. The EC process starts with the formation of a metal ion which is initiated by a direct current, which is passed through the electrodes. Ions that are released depend on the type of metal electrode. Typically, metal electrodes may be made of aluminum, iron or scrap materials containing these metals (Djukić *et al.* 2016; Xu *et al.* 2017; Chen *et al.* 2018).

### ELECTROCOAGULATION – BASIC DESCRIPTION

Removal of the metal ions by EC is achieved through combination of various processes:

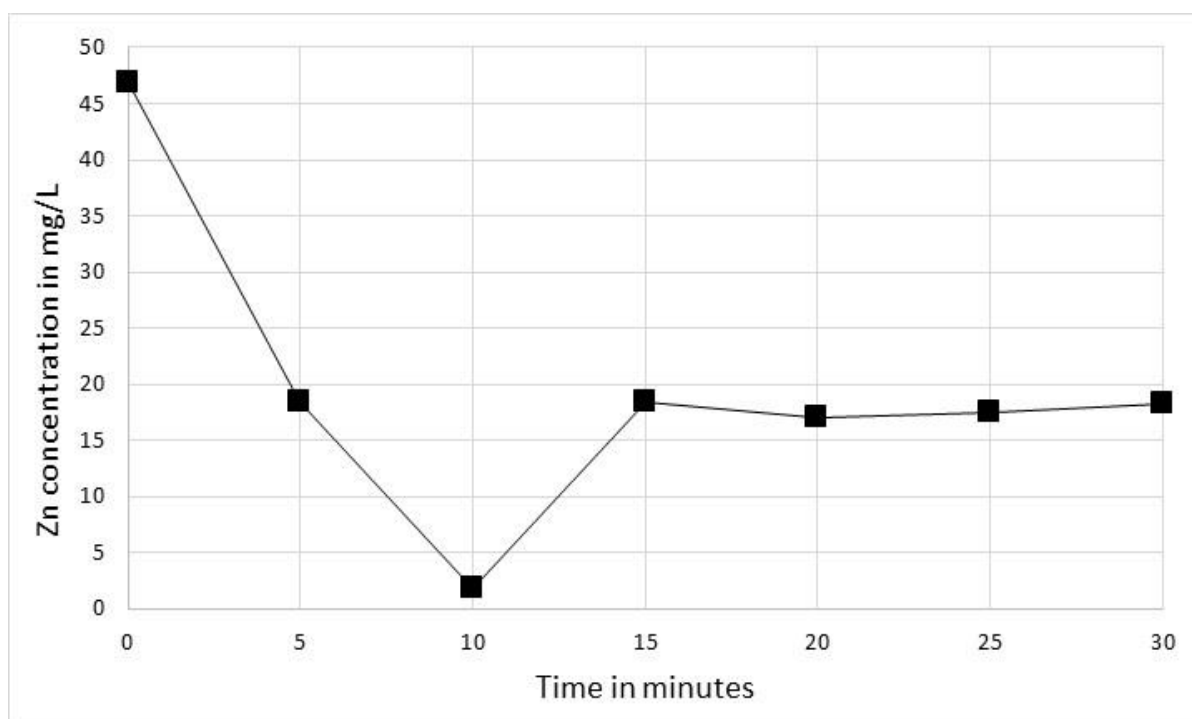
- precipitation – chemical precipitation, in the form of hydroxide, due to release of ions and oxidation of the metal electrodes, which initiate the coagulation,
- adsorption – with the formation of hydroxide, in the form of flocs of aluminium or iron (in the system with electrodes of iron and/or aluminium),
- co-precipitation (followed by precipitation) – taking place due to deposition allocated by all the coarse particles in the solution,
- floatation – production of hydrogen by cathodic reduction (Chen *et al.* 2018).

### RESULTS AND DISCUSSION

In this research the aim was the removal of zinc ions ( $Zn^{2+}$ ) from a sample of real wastewater. The chemical reaction at the anode, and the process of dissolution of the anode depends on the quality of wastewater (pH value, conductivity, turbidity, the concentration of other ions, etc.) The concentration of  $Zn^{2+}$  ions was reduced from 50.12 mg/L to 0.12 mg/L, within time period of 10 min. In Fig. 1, and in Table 1 the change of  $Zn^{2+}$  concentration with the time is presented.

**Table 1.** Water quality analysis.

n	Analysed parameters								
	Time, min	Voltage, V	Amperage, A	Temperature, °C	pH	Conductivity, $\mu$ S/cm	$Zn^{2+}$ , mg/L	$Fe^{3+}$ , mg/L	$Al^{3+}$ , mg/L
0	0	–	–	–	7.92	1641	46.9	37.94	0.023
1	5	28.3	1.15	22	7.83	1233	18.5	40.48	1.30
2	10	11.3	1.13	23	7.78	1222	1.89	38.72	19.30
3	15	11.8	1.13	24	7.73	1203	18.50	42.88	11.15
4	20	12.3	1.13	24	7.70	1192	17.10	36.32	27.0
5	25	12.8	1.13	25	7.62	1178	17.50	35.04	25.80
6	30	13.4	1.13	25	7.60	1166	18.20	46.88	30.40



**Figure 1.** Change of  $Zn^{2+}$  concentration with time.

### CONCLUDING REMARKS

It has been proven that EC is an effective process for removing heavy metals from wastewater. The process can be achieved on a lab scale with relatively simple equipment and by simple process control. The tested EC process in laboratory showed a great efficiency in removing zinc ions from wastewater. The obtained value, after EC treatment was in accordance with legislation and values proscribed for  $Zn^{2+}$  in effluent.

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# Oxidative Degradation of Black Azo Printing Dye with Homogeneous Fenton Treatment and Its Optimization by Definitive Screening Design

V. Gvoić\*, M. Prica\*, Đ. Kerkez\*\*, M. Petrović\*\*\*, A. Kulić Mandić\*\*, M. Bečelić-Tomin\*\*, and B. Dalmacija\*\*

\* Department of Graphic Engineering and Design, University of Novi Sad, Trg Dositeja Obradovića 6, Novi Sad 21000, Serbia (E-mails: [kecic@uns.ac.rs](mailto:kecic@uns.ac.rs); [miljana@uns.ac.rs](mailto:miljana@uns.ac.rs))

\*\* Department of Chemistry, Biochemistry and Environmental Protection, University of Novi Sad, Trg Dositeja Obradovića 3, Novi Sad 21000, Serbia (E-mails: [djurdja.kerkez@dh.uns.ac.rs](mailto:djurdja.kerkez@dh.uns.ac.rs); [aleksandra.kulic@dh.uns.ac.rs](mailto:aleksandra.kulic@dh.uns.ac.rs); [milena.becelic-tomin@dh.uns.ac.rs](mailto:milena.becelic-tomin@dh.uns.ac.rs); [bozo.dalmacija@dh.uns.ac.rs](mailto:bozo.dalmacija@dh.uns.ac.rs))

\*\*\* Department of Environmental Engineering, University of Novi Sad, Trg Dositeja Obradovića 6, Novi Sad 21000, Serbia (E-mail: [majadjogo@uns.ac.rs](mailto:majadjogo@uns.ac.rs))

## INTRODUCTION

One of the primary environmental problems in printing industry is a release of generated dyed effluents into the recipients. Due to their complex structure, high molecular mass and the presence of one or more chromophore groups, printing dyes are classified as a group of difficult biodegradable compounds with a tendency to exhibit teratogenic, mutagenic or carcinogenic effects (Kecić *et al.*, 2018). The homogeneous Fenton process has gained considerable application within the wastewater treatment for the removal of organic contaminants, with pronounced application based on its simplicity, easy manipulation, ability to use conventional equipment and operation at ambient pressure and temperature (Bensalah *et al.*, 2019). The aim of this study was to investigate the possibility of synthetic dye solution decolorization using a homogeneous Fenton treatment, in order to optimize the process and to apply it in the treatment of real printing effluent.

## MATERIALS AND METHODS

The experiment was performed on a sample of synthetic dye solution and real printing effluent collected from flexographic printing facility in Novi Sad, Serbia. Decolorization efficiency of synthetic solution and real printing effluent was calculated according to Eq. (1).

$$E(\%) = (A_0 - A) / A_0 * 100 \quad (1)$$

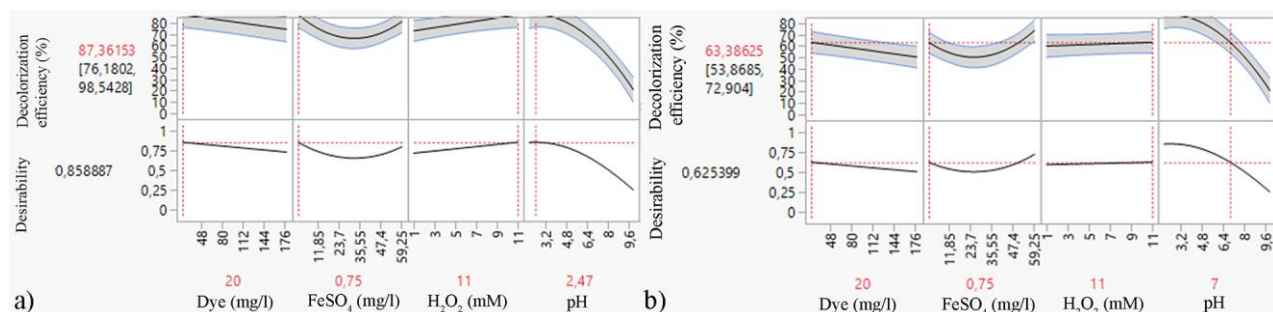
where  $A_0$  is the initial absorbance of the aqueous solution sample before Fenton treatment and  $A$  is the absorbance of the aqueous solution sample after Fenton treatment.

Statistical analysis, definitive screening design (DSD), was used to examine the influence of four process parameters: initial dye concentration (20–180 mg L<sup>-1</sup>), iron concentration as a catalyst in a homogeneous Fenton process (0.75–60.00 mg L<sup>-1</sup>), pH values (2–10) and a hydrogen peroxide concentration (1–11 mM), as well as to optimize the process.

The physico-chemical characterization of printing effluent before and after Fenton treatment included measurement of pH, electrical conductivity, temperature and turbidity. Mineralization degree is determined by measuring the total organic carbon (TOC) content and the chemical oxygen demand (COD).

## RESULTS AND DISCUSSIONS

The optimization diagram (Fig. 1) evaluates the best dye removal under optimal process conditions. Statistical software suggests a decolorization efficiency of 87.36 % (Fig. 1a) in a highly acidic medium at pH 2.47 under the lowest concentration of dye and catalyst and the highest concentration of hydrogen peroxide. However, with the pH increase from 3 to 5, 6 and 7, the Fenton process efficiency decreases to 79.87 %, 72.79 % and 63.38 % (Fig. 1b), which certainly represents a satisfactory percentage of dye removal in a slightly acidic or neutral environment. Nevertheless, the limitation of homogeneous Fenton process application is reflected through the sludge formation. Therefore, the FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> Fenton treatment of real printing effluent at the optimum values of the process parameters was carried out at pH 2.47 over a reaction time of 180 minutes.



**Figure 1.** Optimisation diagram of homogeneous Fenton treatment in a) acid; b) neutral environment.

The highest decolorization efficiency of real printing effluent of 67.96 % was achieved in the 120<sup>th</sup> minute of the reaction. Results of physico-chemical characterization indicated conductivity increment after Fenton treatment, which may be in accordance with the formation of numerous degradation products and the release of certain inorganic ions. Also, a fragmentation of highly complex structure of dye molecule into smaller fragments and mineralization of treated effluent was confirmed with TOC and COD reduction.

## CONCLUSION

The obtained results indicated that the applied treatment efficiency depends mostly on reaction medium pH. The homogeneous Fenton process is optimized in the narrow pH range 2–3, with a maximum decolorization efficiency of synthetic dye solution of 87 %. However, treatment of real printing effluent resulted in lower but significant decolorization efficiency of 68 %, confirming the assumption that homogeneous Fenton process may be applied in treatment of organic contaminants such as printing dyes.

## ACKNOWLEDGEMENTS

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# Facilitating the Granulation of Halophilic Activated Sludge Inoculated with Estuarine Sediments by Divalent Cation Addition

J.-L. Huang\* and Y.-W. Cui\*

\* National Engineering Laboratory for Advanced Municipal Wastewater Treatment and Reuse Technology, Beijing University of Technology, No.100, Pingleyuan, Chaoyang District, Beijing, China (E-mails: [jilin1435@163.com](mailto:jilin1435@163.com); [cyw@bjut.edu.cn](mailto:cyw@bjut.edu.cn))

## INTRODUCTION

The effective treatment of saline wastewater poses a technical problem in the field of wastewater treatment. As the most widely used and eco-friendly technology, biological treatment is applied to the treatment of saline wastewater. However, the current study shows that high concentration of salt would lead to the inhibitions of microbial activities even microbial cells plasmolysis in common wastewater treatment. Otherwise, it takes a long time to domesticate the salt tolerance of freshwater activated sludge. Halophiles were found to be the potential microorganisms that can degrade the pollutant in saline wastewater. Researchers began to develop halophilic microbes for saline wastewater treatment. However, high buoyancy and smaller biofloc make solid-liquid separation difficult thus causing high turbidity in the effluent (Uygur, 2006), which restricted the application development of halophilic activated sludge.

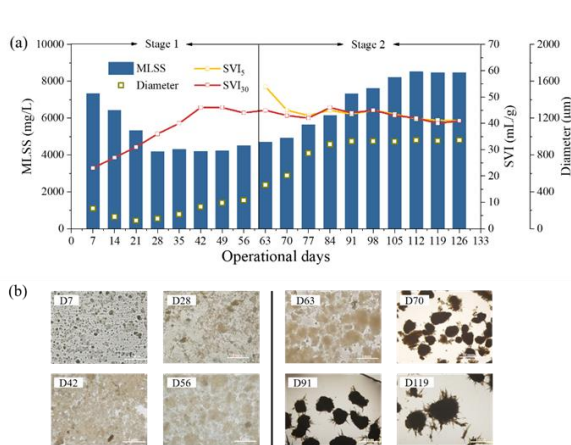
Aerobic granular sludge can be a promising solution to the problem of halophilic activated sludge mentioned above due to its good sedimentation and increases biomass retention. However, granulation process generally needs to be completed under high organic loading rates (OLR) conditions while granules couldn't form in low-strength condition (Huang *et al.*, 2019). Divalent cation is the main inorganic component in saline wastewater as well as demonstrated to facilitate the granulation process. In this study, extra divalent cations were added during granulation in low-strength saline wastewater and aerobic halophilic granular sludge was enriched successfully. Granulation of halophilic activated sludge in low-strength saline wastewater provides an effective solution to solve the sludge loss problem, which is an advance to realize the biological treatment of saline wastewater by halophiles.

## RESULTS AND DISCUSSION

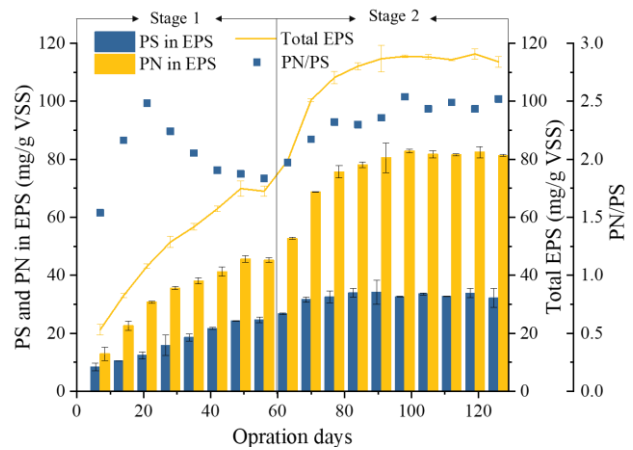
The experiment was separated into two stages, the first 60 days were stage one and the last 60 days with the addition of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were stage two. It can be seen that granulation was not achieved in stage one with the average  $\text{SVI}_{30}$  and  $\text{MLSS}$  remained at activated sludge level steadily (Fig. 1a). Otherwise, no granules can be observed by microscope (Fig. 1b). Granulation process occurred when dosed  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in stage two. The values of  $\text{SVI}_{30}$  and  $\text{SVI}_5$  gradually converged and the ratio of  $\text{SVI}_{30}$  and  $\text{SVI}_5$  tend to be 1 on day 77 which indicated that halophilic granular sludge was cultured completely. According to the image captured by microscope, granules with compact structure was found in the view.

Fig. 2 shows the concentration of PN, PS, total EPS and the ratio of PN to PS. Lower OLR (400  $\text{mg}_{\text{COD}}/\text{L}$ ) in stage one is not enough to provide nutrients for extracellular polymeric substances (EPS) secretion and microbial growth (the most important factors for granulation) of activated sludge which would weaken the microbial attachment and lead to the failure of

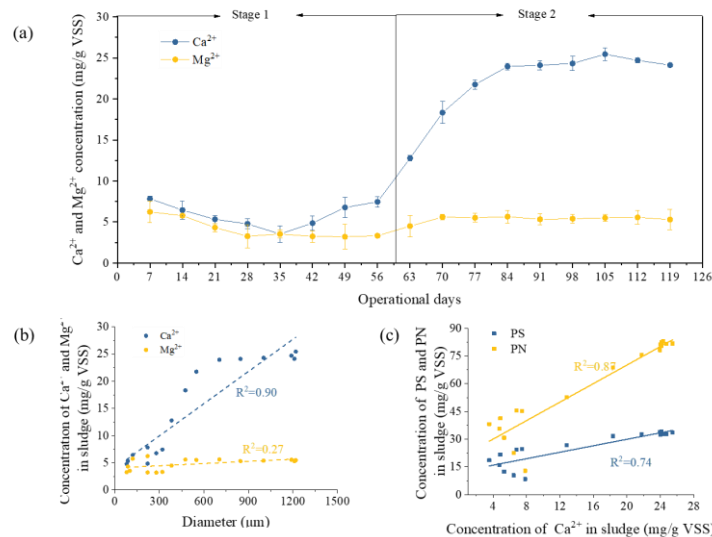
granulation. However, the contents of EPS increased with the formation of halophilic granular sludge when extra  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were dosed in stage two. Quantitative analysis of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the sludge shown that the increase of  $\text{Ca}^{2+}$  was more significant (Fig. 3a). The relative analysis between divalent cation and particle size shown that  $\text{Ca}^{2+}$  was the main element that promoted the granulation of halophilic activated sludge (Fig. 3b).  $\text{Ca}^{2+}$  in wastewater was the key to form the EPS network by linking the PN fraction and microorganisms with negative surface together while PN was the dominating content in EPS. Otherwise, the relative analysis between  $\text{Ca}^{2+}$  and EPS content shown that  $\text{Ca}^{2+}$  stimulated the secretion of EPS thus enhance the granulation (Fig. 3c). Therefore,  $\text{Ca}^{2+}$  addition is a feasible strategy to cultivate halophilic granular sludge in low-strength condition.



**Figure 1.** Changes of particle size and sedimentation performance in the granulation process.



**Figure 2.** Quantitative analysis of EPS in the halophilic sludge.



**Figure 3.** Quantitative analysis of divalent cation in halophilic sludge and the relativity analyses.

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# Removal of Phosphate from Aqueous Solutions Using Supported Engineered Nanoparticles

C. Hür\* and E. Erdim\*

\* Marmara University, Environmental Engineering Department, Istanbul, Turkey  
(E-mails: [esra.erdem@marmara.edu.tr](mailto:esra.erdem@marmara.edu.tr); [cernhr@gmail.com](mailto:cernhr@gmail.com))

## INTRODUCTION

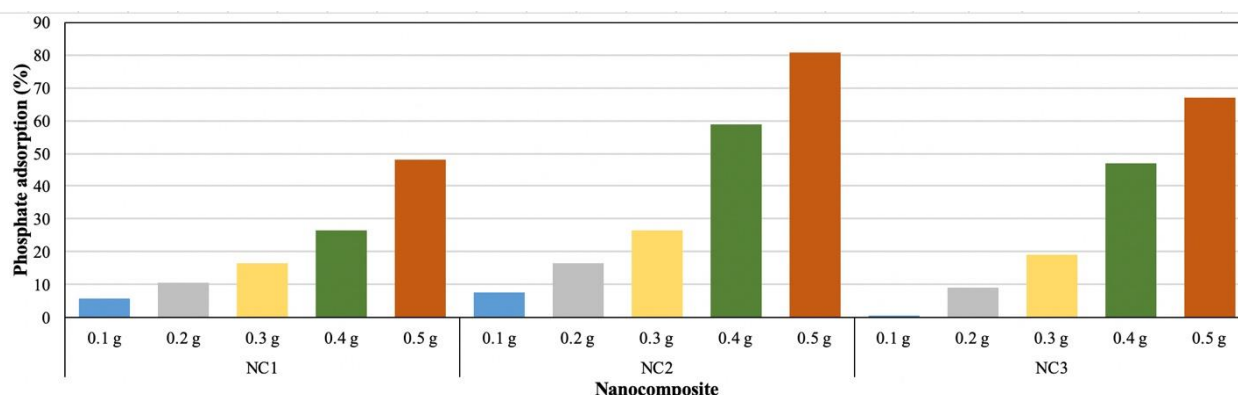
Phosphorous is one of the pollutants which degrades water quality and is a concern for eutrophication of water. On the other hand, phosphorus is a non-renewable resource necessary to support global food production. Therefore, it is crucial to develop and improve phosphorus recovery technologies from phosphorus-containing waste streams such as agricultural runoff, animal manures, food and food-processing wastes, sewage sludge and municipal wastewater. Phosphorus in wastewater, if economically recovered, can partly overcome the future scarcity of phosphorus resulting from exhaustion of natural phosphate rock reserves (Soliemanzadeh and Fekri, 2017).

Adsorption is a well-recognized technique to remove and recover phosphorus because of ease of operation, simplicity of design, and economics, provided low-cost sorbents are used. Cost effectiveness is identified as the key criterion in the selection of a sorption technology whether it uses synthetic or natural sorbents. Phosphate can be removed from water using sorbents such as iron oxides, calcite, goethite, active red mud, and activated carbon (Loganathan *et al.*, 2014). However, these sorbents have very low sorption capacities. Nanoscale zero-valent iron (nZVI) particles have received much attention because of their unique reactive and sorptive characteristics in the last decades. nZVI particles show good sorptive characteristics due to their high surface to volume ratio. Iron nanoparticles have a high affinity to aggregate into agglomerates as a result of van der Waals and magnetic forces which in turn decreases the reactivity of the particles. Moreover, agglomeration of iron particles in fixed bed column or any other dynamic flow system results in high-pressure drop, thus restricting the direct use of nZVI for field scale application. Hence, nZVI should be supported on certain materials to overcome clumping aggregation of nanoparticles and to enhance their separation and hydraulic conductivity (Tandon *et al.*, 2013).

Clay mineral has unique characteristics such as large specific surface area, high cation exchange capacity (CEC), low-cost, and wide-spread availability, which makes it suitable for hosting nZVI. Various physical and chemical processes are currently used to synthesize nZVI nanoparticles, which allow tuning the particles with the desired characteristics. However, these production methods are usually expensive, labor-intensive, and are potentially hazardous to the environment. Thus, there is an obvious need for an alternative, cost-effective, safe and environmentally sound method of nanoparticle production. Recently, a greener bottom-up method that involves the use of extracts from natural products (usually leaves or peels) has gained great attention. These extracts have high reduction capabilities and assure the reduction of the iron(III)/iron(II), producing nZVI (Ozkan *et al.*, 2017). This green method also provides stabilization of the nZVIs through the capping action of the polyphenols present in the extract, which delays the agglomeration process and increases the reactivity and efficiency of the remediation. It is well known that synthesis of the iron nanoparticles involves various parameters and each parameter has an effect on the resultant nanoparticle suspension.

The aim of the study is to synthesize clay supported iron nanoparticles following a green route and evaluate the effectiveness of the composite material in the removal and recovery of phosphate from a synthetic wastewater stream. Synthesis variables include different clay/Iron mass ratios (2 g /2 g; 2 g / 1 g; 2 g / 0.56 g), Iron/Plant extract volumetric ratios (1/1, 1.0/0.5) and pH (2–5). Clay is supplied from a local company located in the west part of Turkey.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is used as the iron precursor, green synthesis protocol involves use of green tea leaves as the polyphenol source to act as the reducing and stabilizing agent. The dried leaves are brewed at 80 °C for 20 min. The brewed solution is filtered through 0.45  $\mu\text{m}$  PVDF filter once cooled to room temperature. Adsorption and desorption experiments are run at constant temperature (22 °C) and at constant rpm. Desorption studies are conducted with 0.1 N NaOH considering the phosphorus species and  $\text{pK}_a$  relationships. Preliminary results show that highest (81 %) phosphate adsorption is achieved with one of the nanocomposites at all masses after a 6 h equilibration period (Fig. 1).

Similar to adsorption results, the nanocomposite shows the highest desorption percentage (78 %). Further studies are planned to include the determination of adsorption isotherms, kinetic modelling of the best nanocomposite, characterization of the nanocomposite using BET, XRD, FTIR and SEM before and after phosphate adsorption/desorption to understand the underlying mechanism of phosphate removal and recovery. Also, the desorbed phosphate will be mixed with a calcium salt to obtain a product similar to a commercial fertilizer.



**Figure 1.** Phosphate adsorption efficiencies of nanocomposites.

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## **Case: Data Analytics Provide Tools for Faster Reactions and More Accurate Predictions – a Startup’s Journey**

J. Kariniemi\*

\* Neuroflux , Vilhonvuorenkatu 12, 00500 Helsinki, Finland  
(E-mail: [julia.kariniemi@neuroflux.fi](mailto:julia.kariniemi@neuroflux.fi))

### **INTRODUCTION**

It all started in 2016 when Helsinki Region Environmental Services Authority HSY organized a hackathon, bringing together computer scientists and water engineers. Our idea developed further into a tool that has now been adopted by a number of water utilities in Finland and Sweden.

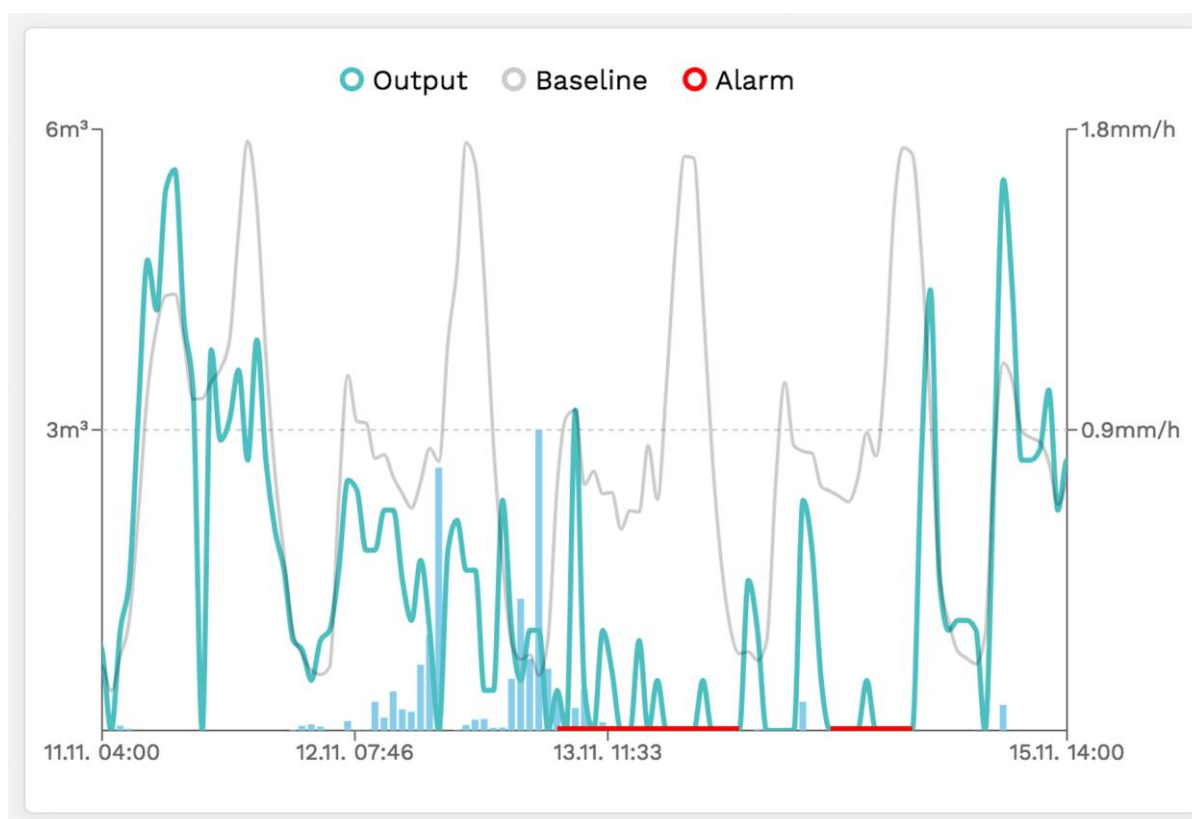
### **COMMON CHALLENGES IN THE NORDICS**

Even smaller cities in the Nordics have hundreds of kilometres of sewer network. There are many kinds of issues in the complicated system: pumping stations get blocked, excess water leaks into the sewers and machines can break. Monitoring and repairing the network is a time-consuming process that requires a lot of work: often problems are discovered by going through the data manually or by somebody reporting an issue from the field. What kind of tools could help with this work?

With new digital tools, water utilities can control the circulation of water from nature to built environment and out of there more efficiently than before and with fewer risks to the environment. At first, digitalisation could mean that water utilities begin to utilize the data they have collected when assessing the status of their network. And the first step for adopting new tools is to begin a systematic collection of network data. When the right kind of data analysis is applied to the collected data, visibility into the underground network increases significantly.

### **DIGITAL TOOLS AND DATA ANALYTICS**

What kind of visibility can new digital tools provide? The first benefit is the ability to react to acute changes faster than before. High-quality data visualization reveals if water flow suddenly drops at a specific location. This usually points to a blockage in a pumping station or elsewhere in the network. And what does it mean if the pumping station’s electricity consumption drastically increases? It could point to a machine failure. Unauthorized connections, stuck kickbacks and other sources of excess water become visible when water flow suddenly increases. Together and separately these measurements provide concrete information about the network. A new kind of visibility is created when the water utility’s measurements are combined with other data sources. By combining different sets of data it is possible to create a machine learning model that can be used to automatically detect different anomalies, highlighting the relevant bits of information from the mass. The idea is that any problems are recognized well in time before they cause harm to the environment.



**Figure 1.** Changes in pumping station data reveal anomalies in the network. (Neuroflux Solutions, 2021).

### PREDICTIVE MAINTENANCE

In addition to speeding up reaction times to acute problems, data-based tools also make predictive maintenance easier. In the Neuroflux environment, for example, it is possible to see how catchment areas fare in different conditions and how much of their capacity is already in use. For example, if heavy rain causes the pumping stations to run at full capacity, the risk of an overflow increases sharply. Recognizing such vulnerabilities beforehand helps allocate maintenance resources efficiently. When measurements and related predictions can be viewed for months or years at a time, long-term trends become visible and problems that have been present for a long time can be located. The rewards are often clearly visible as well: repairs often lead to lower energy consumption or other improvements in efficiency.

One key feature of the new tools is the ability to flexibly utilize information and automatically sort it to highlight the important pieces. When the number of work-intensive routine tasks decreases, resources can be targeted more efficiently at preventative maintenance. If a water utility was interested in recognizing and locating problems in the water network with data, one good way to approach the question is to select a tool they would like to try and find out what kind of information it would require. Usually water utilities' existing meters provide sufficiently accurate data and the biggest benefits are gained with the right kind of data analysis.

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# Phenol Remediation of Oily Wastewater Using a Novel Ozonized Electro-Membrane Reactor

O. M. Khalifa\*, F. Banat\*, C. Srinivasakannan\*, and S. W. Hasan\*

\* Center for Membranes and Advanced Water Technology (CMAT), Department of Chemical Engineering, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates (E-mails: [omar.khalifa@ku.ac.ae](mailto:omar.khalifa@ku.ac.ae); [fawzi.banat@ku.ac.ae](mailto:fawzi.banat@ku.ac.ae); [shadi.hasan@ku.ac.ae](mailto:shadi.hasan@ku.ac.ae))

## INTRODUCTION

Recently, industrial practices have bloomed, and the consumption of resources has drastically increased. The oil and gas industries are large consumers and producers of water, yielding a huge amount of oily wastewater with every oil barrel produced. Such samples contain a variety of contaminants that ought to be removed before discharging or reutilization. Phenol compounds are amongst the most occurring contaminants in petroleum-based oily wastewater and they pose a great risk on the aquatic life. Oily wastewater has proven to be recalcitrant and persistent to the conventional treatment methods. Advanced treatments are sought to remove the small-sized oil emulsions and meet environmental regulations or limits for reutilization practices. Even advanced processes would suffer from some drawbacks pertaining to the high energy consumption, technical issues that risk the integrity of the technology, and lack of applicability. A proposed solution is to hybridize technologies into a single treatment system to achieve the desired treatment. In this work, an electrochemical cell (mainly electrocoagulation – EC), ceramic microfiltration membrane, and ozonation have been combined in a one-pot reactor (Khalifa, 2020a). Different parameters have been studied on the effect of phenol removal, including the hydraulic residence time (HRT), aeration, frequency of power supply, current density (CD), initial pH, and ozonation. Several experiments have been conducted using the hybrid reactor, which is designed with a continuous-flow mode of operation. Some experiments were conducted with aeration and other with ozonation. Part of the foam, sludge, and electrodes were characterized using scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS).

## MAIN FINDINGS

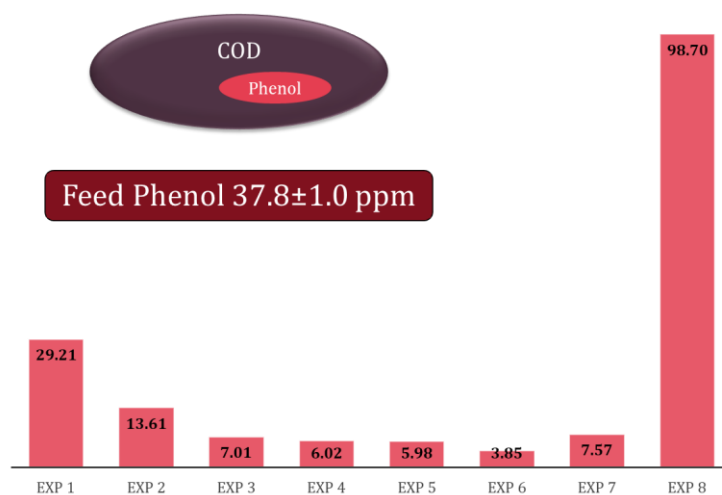
The removal of phenol using the ozonized electro-membrane reactor reached 98.7 % topping the best performing air-based electro-membrane reactor by 3.4 folds (Fig. 1). The inclusion of ozone to the electro-membrane reactor has imposed synergies and positive interactions with the other technologies. The electrocoagulation was enhanced by producing larger flocs and the submerged ceramic microfiltration membrane was able to reject more contaminants through the enhanced size-exclusion process. Ozonation also played a role in degrading organic compounds, especially phenol, through the formation of radicals in the basic media of the oily wastewater sample.

### Effect of HRT, CD, and other variables

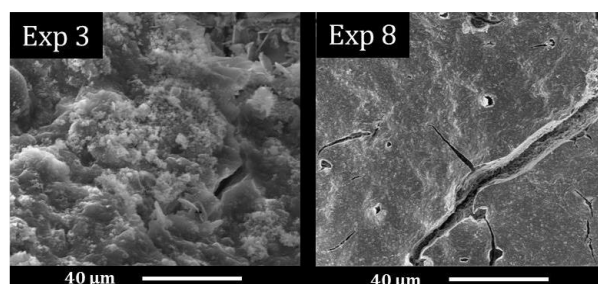
Experiments 1, 2, and 3 were conducted at different HRT values. The lowest value of 12 h (EXP 1) performed the best in terms of phenol removal efficiency as of the higher flow rate and increased mixing. Exp 4, 5, 6, and 7 tested aeration (OFF/ON), CD, power supply (intermittent or continuous), and initial pH/CD, respectively. As such, the reactor better performed with aeration, elevated CD, intermittent power, and acidic feed. Yet, the removal of phenol did not show an increase. Experiment 8 (incorporating ozone) boosted the efficiency of the reactor.

### Surface morphology

Generally, aeration imposes different effects on the electrodes' and sludge's morphology in an EC cell (Khalifa, 2020b). Ozonation also exhibited noticeable changes to the structure of the formed foam and sludge of the EC. Fig. 2 shows SEM images of two sludge samples from air- and ozone-based experiments. The ozone-based sludge appears to more compact and denser than the air-based sludge, which was loose and fragile. The characteristics of the sludge would dictate the performance of the membrane, having more rejection in the case of ozone. Consequently, ozonation has proved to be linker between electrocoagulation and membrane filtration when employed in a hybrid fashion for the treatment of oily wastewater, and particularly phenol remediation.



**Figure 1.** Phenol removal percentages for all experiments. The ozonized electro-membrane experiment is the last one, while the rest are air-based with different variables.



**Figure 2.** SEM images air-based (Exp 3) and ozone-based (Exp 8) sludge.

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# Pollution Minimization of Biodiesel Processing Wastewater by Means of Optimization

M. N. Kiliçarslan\* and M. E. Argun\*

\* Department of Environmental Engineering, Faculty of Engineering and Natural Science, Konya Technical University, Konya, Turkey (E-mails: [mnkilicarslan@ktun.edu.tr](mailto:mnkilicarslan@ktun.edu.tr); [meargun@ktun.edu.tr](mailto:meargun@ktun.edu.tr))

## INTRODUCTION

Biodiesel could be produced from waste oils that are harmful to the environment and human health. However, some wastes of biodiesel process have also been generated such as wastewater and glycerine (De Gisi *et al.*, 2013). While many studies have focused on biodiesel production (Kiliçarslan and Argun, 2019), there are limited studies on environmental assessment of biodiesel production wastes especially for wastewaters (Veljković *et al.*, 2014). For this reason, characterization study has been conducted for washing water of biodiesel produced from waste oils.

## MATERIALS AND METHODS

In this study, waste frying oil mixture, methanol and KOH were used to produce biodiesel. Pure water was used for washing processes. The effect of four experimental variables including alcohol and catalyst ratios, reaction temperature and time on to biodiesel and wastewater quality were optimized. The values of these variables are shown in Table 1. ANOVA analysis were conducted to obtain the relationship between the independent variables and experimental results for 30 experiments (Design Expert 11).

**Table 1.** Ranges of independent variables in the experiments.

Independent Variables	Min value	-1	Midpoint	+1	Max value
A: Catalyst ratio, w/w %	0.32	0.5	0.75	1	1.18
B: Alcohol ratio, v/v %	2.8	10	20	30	37.2
C: Temperature, °C	42.8	50	60	70	77.2
D: Reaction time, min	34.2	45	60	75	85.8

Chemical oxygen demand (COD), phosphate (PO<sub>4</sub>), total nitrogen (TN), conductivity, pH measurements and absorbance scans were carried out according to standard methods. As an important contribution to the literature, fatty acids passing from biodiesel into wastewater were determined by gas chromatography and their relation to COD were analyzed.

## RESULTS AND DISCUSSION

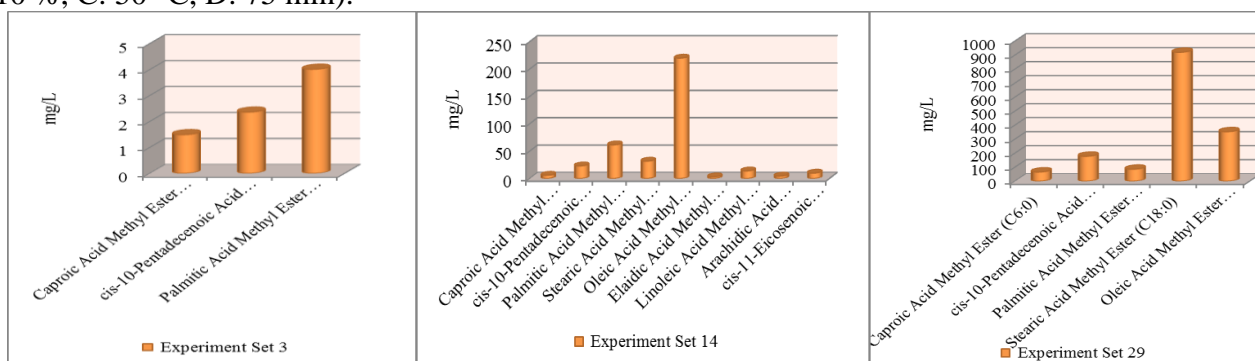
It was concluded that the experimental conditions of biodiesel production were very important on the biodiesel quality and wastewater pollution. Most pollutant parameters were determined in higher values for the lower alcohol ratio (2.8 % and 10 %). Phosphate concentrations were similar to each other and were in trace amounts. The organic content of the waste washing waters in terms of COD was obtained as very high ranged from 5 g/L to above 1000 g/L. In experimental sets with high alcohol ratio, average COD and conductivity values decreased about 30–100 times compared to those with low alcohol ratio (Table 2). The experiment with the lowest TN concentration was found to be the midpoint experiment (A: 0.75 %, B: 20 %, C: 60 °C, D: 60 min). The pH values increased from 6 to 10 with the decreasing of alcohol ratio. The statistical relationships of COD (p: 0.0003), PO<sub>4</sub> (p: 0.0032), TN (p: 0.0233) and conductivity (p: 0.0196) with experimental variables were found to be significant. The obtained models for COD, PO<sub>4</sub> and TN were linear

while 2FI for conductivity.

**Table 2.** Some obtained parameters of washing water for different experimental conditions.

Catalyst % (w/w)	Alcohol % (v/v)	Temp. °C	Time min	COD g/L	PO <sub>4</sub> mg/L	TN mg/L	pH	EC		Absorbance values			
								μS/cm	254 nm	436 nm	525 nm	620 nm	
0.75	20.0	60	60	5	1.46	2.1	7.3	445	0.031	0.059	0.047	0.041	
1.00	30.0	70	45	10	1.61	9.4	7.8	40	0.000	0.009	0.008	0.007	
0.75	2.8	60	60	234	1.14	7.8	10.3	450	0.145	0.372	0.274	0.213	
0.50	10.0	70	75	522	152	583	9.4	15	0.145	2.539	2.075	1.981	

In addition, colour formation was significantly fitted to linear model for absorbance values at the 436, 525, 620 nm. The most effective independent variable on the results was obtained as alcohol ratio. It has been observed that higher concentrations of long-chain fatty acids were determined in wastewaters with relation to COD concentration. The concentrations of fatty acids passing into the washing water have generally increased for the case of lower alcohol ratio (Fig. 1). The lowest fatty acid number and concentration were obtained in experiment set 3 (catalyst (A): 1 %, alcohol (B): 30 %, temperature (C): 70 °C, and time (D): 45 min) while higher values were obtained for lower catalyst (set 14; A: 0.32 %, B: 20 %, C: 60 °C, D: 60 min) and alcohol ratios (set 29; A: 1 %, B: 10 %, C: 50 °C, D: 75 min).



**Figure 1.** Long-chain fatty acid concentrations (mg/L) of some wastewaters.

## CONCLUSION

Among the four variables, it was observed that alcohol and catalyst ratio were more effective variables on biodiesel and wastewater quality. In experiments with low alcohol ratio, biodiesel could not meet the standards. Therefore, the pollution parameters of washing water have increased. In general, the optimum alcohol ratio was found to be 30 % and the catalyst ratio was 1 %. If the alcohol ratio was over 20 %, the optimum time and temperature values were detected as 75 minutes and 70 °C, respectively. It was also determined that there was a correlation between fatty acids passing into washing water and COD values.

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## Upgrading Small Wastewater Treatment Plant

A. A. Kulakov\*

\* Department of Environmental and Industrial Safety, MIREA – Russian Technological University, 86 Vernadsky Avenue, Moscow, Russia (E-mail: [artem.a.kulakov@gmail.com](mailto:artem.a.kulakov@gmail.com))

### INTRODUCTION

Small Wastewater Treatment Plant (WWTP) is a significant quantitative group of sewer facilities. An individual approach to upgrading and operation is necessary due to their specific features. This will ensure reliable and efficient operation and reduce the negative impact on the environment.

Features of small WWTP: Technological factor (high load fluctuation, non-adaptability of standard technologies); Economic factor (high unit cost of WWTP and operation); Organizational factor (lack of qualified personnel) (Kulakov, 2015).

### MATERIALS AND METHODS

Small (package) WWTP for domestic wastewater treatment considered in this abstract. Capacity is 40 m<sup>3</sup>/d; the actual flow of wastewater is 7 m<sup>3</sup>/day. The WWTP consists of a bioreactor, a secondary settling tank (SST), a UV disinfection, a bag dehydrator (Kulakov, 2017).

The bioreactor (volume 6.5 m<sup>3</sup>) contains four sections with polyethylene biofilm carriers (media), which are separated by partitions with holes: 1<sup>st</sup>, 4<sup>th</sup> – MBBR (moving bed biological reactor), 2<sup>nd</sup>, 3<sup>rd</sup> – FBBR (fixing bed biological reactor). Oxygen (technological) zones not divided; a constantly working aeration system is located in all.

After the bioreactor, the treated wastewater separated from the biofilm in a thin-layer settling tank and disinfected. Sludge periodically pumped out for dehydration.

### RESULTS

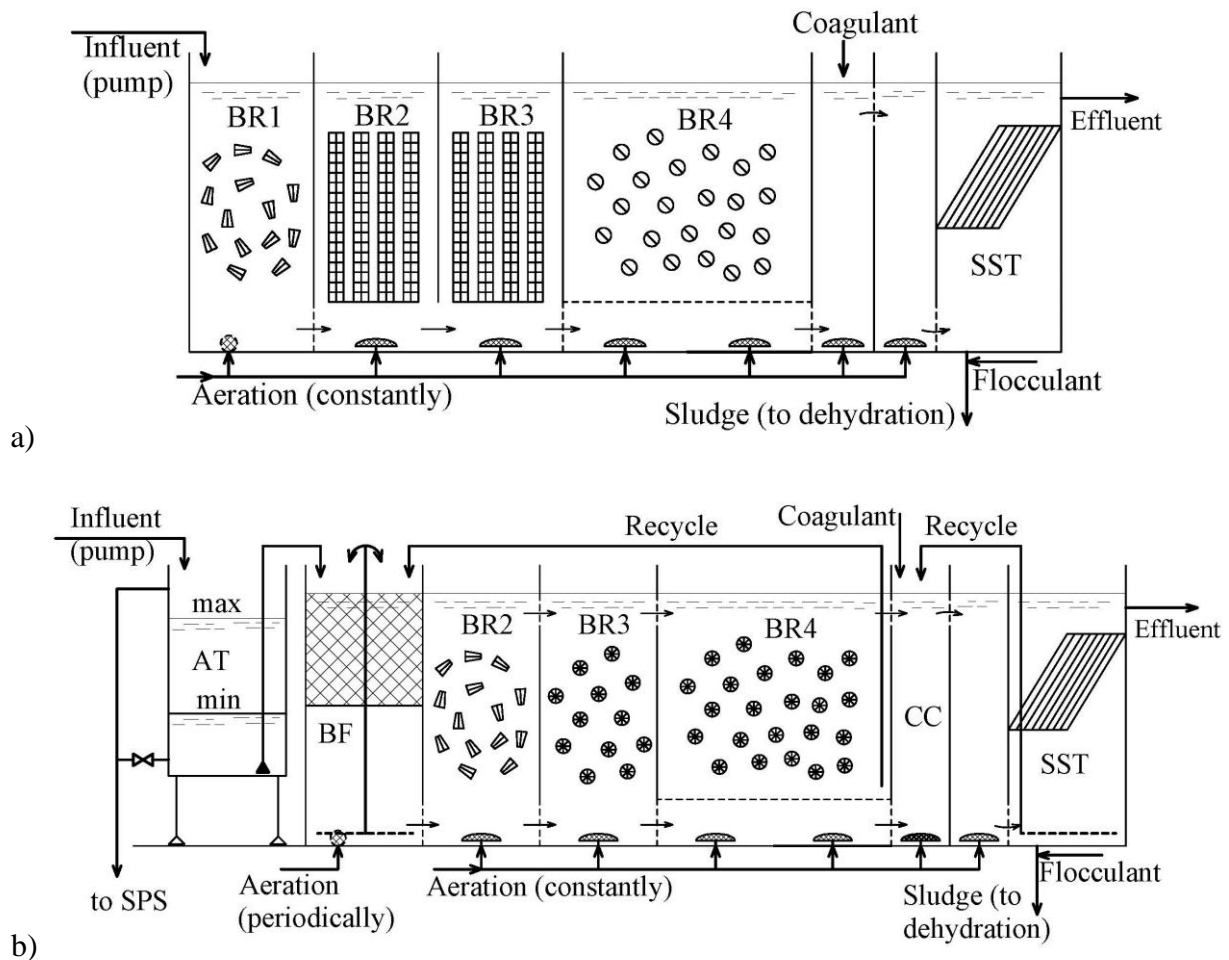
Research WWTP had several disadvantages: not screening; volley feed from the pump (peak load, removal of biofilm and bio-media from SST); no recirculation; siltation and fouling of fixed media; crushing of moving media. All this led to a significant excess of standards, even with significant underloading (Table 1). Technological schemes before and after upgrading presented on Fig. 1.

**Table 1.** Results of operation.

Parameter	Standard	Before upgrading		After upgrading	
	Effluent	Influent	Effluent	Influent	Effluent
TSS, mg/L	3	70–90	12–22	49–77	5.9–11.0
BOD <sub>5</sub> , mg/L	2	55–121	3–7	70–106	1.5–6.0
N-NH <sub>4</sub> , mg/L	0.4	23.4–57.7	2.3–8.6	27.3–88.9	0.10–0.65
N-NO <sub>2</sub> , mg/L	0.02	<0.03	0.03–0.44	<0.03	0.003–0.060
N-NO <sub>3</sub> , mg/L	9	0.12–0.25	11.0–23.9	0.12–0.18	7.4–14.3
P-PO <sub>4</sub> , mg/L	0.2	1.5–3.5	0.05–1.30	1.2–3.0	0.04–0.50

Completed improvements: installation of grid, replacement of crumbling and silt media, wastewater averaging, providing a uniform wastewater flow, recycling, selection of nitrification and denitrification zones, tuning of aeration and the oxygen regime.

After these works, the reliability and stability of the equipment increased, the removal of biofilm and bio-media from settling tank stopped. Treatment efficiency increased by BOD (from 94 % to 96 %), ammonia nitrogen (from 87 % to 99 %) and phosphorus (from 73 % to 87 %).



**Figure 1.** Technological scheme before (a) and after (b) upgrading: BR – bioreactors; BF – biofilter; SST – thin-layer secondary settling tank; AT – averager tank; SPS – sewage pumping station; CC – contact camera.

## CONCLUSIONS

Works complex (analysis of the initial data, upgrading, commissioning of the technology, staff training) allowed improving the treatment efficiency in all parameters.

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# Microbial Fuel Cell Based Biosensor for the Determination of Biochemical Oxygen Demand of Wastewater Samples

B. Lóránt\*, G. M. Tardy\*, M. Gyalai-Korpos\*\*, V. Bakos\*, D. Simpson\*\*\*, and I. Goryanin\*\*\*

\* Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Szt. Gellért tér 4, Budapest 1111, Hungary (E-mails: [lorant.balint@edu.bme.hu](mailto:lorant.balint@edu.bme.hu); [gtardy@mail.bme.hu](mailto:gtardy@mail.bme.hu); [vbakos@mail.bme.hu](mailto:vbakos@mail.bme.hu))

\*\* Pannon Pro Innovations Ltd., P.O.B 41, Budapest 1400, Hungary  
(E-mail: [miklos.gyalai@ppis.hu](mailto:miklos.gyalai@ppis.hu))

\*\*\* Okinawa Institute of Science and Technology, 1919-1 Tancha, Onna-Son, Kunigami-gun, Okinawa 904-0495, Japan (E-mails: [djwsimpson00@googlemail.com](mailto:djwsimpson00@googlemail.com); [goryanin@gmail.com](mailto:goryanin@gmail.com))

## INTRODUCTION

Microbial fuel cells (MFCs) are special bioreactors that can convert the chemical energy of biodegradable organics directly to electricity through the metabolism of exoelectrogenic bacteria. This novel technology might be used as biosensors for the detection and measurement of biodegradable organics and/or toxic materials in water or wastewater (Lóránt *et al.*, 2019; Yang *et al.*, 2015). Biochemical oxygen demand (BOD) is one of the most important parameters for the characterization of polluted water/wastewater samples, thus our goal was to test an MFC-based BOD measurement method: voltage was measured on the external circuits of the cells, than the total charge ( $Q$ ) gained by the elimination of organics in MFCs was calculated within the timeframe of biodegradation. The relationship between  $Q$  and  $BOD_5$  was determined for various artificial samples, furthermore, the accuracy and reliability of the developed method was verified by the investigation of real wastewater samples.

## MATERIALS AND METHODS

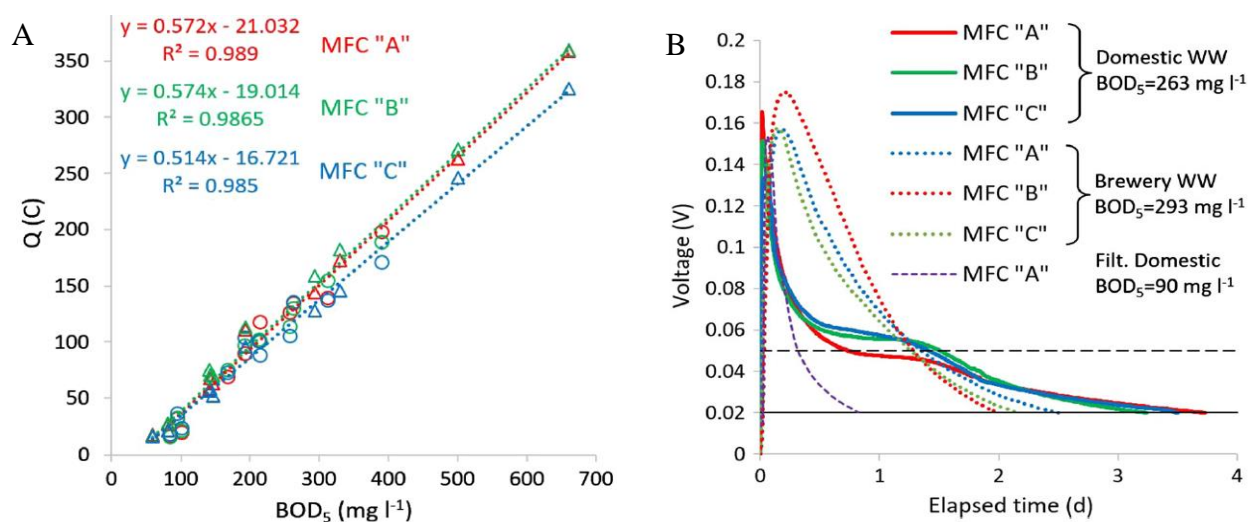
Three identical, single-chamber air cathode MFCs with a working volume of 230 cm<sup>3</sup> each were applied as biosensors. The MFCs were inoculated with diluted primary settled sludge from a domestic wastewater treatment plant, and 1 month of startup period was carried out using acetate substrate to reach stable operation prior to experiments.

In order to investigate and adapt the measurement method with MFC biosensors to real wastewaters, series of artificial samples containing substrates with different complexity and solubility were investigated: Acetate and Peptone (soluble substrates), Corn starch (partly suspended polysaccharide) & Milk (soluble and colloidal organic content). Finally, real domestic and brewery wastewater samples were investigated, some of which were diluted with tap water to cover a wider  $BOD_5$  concentration range (59–660 mg<sub>BOD</sub> L<sup>-1</sup>). Basic sample quality measurements ( $BOD_5$ , COD) were carried out according to international standards. Dissolved COD concentrations were also determined as described by Mamais and Jenkins (1993). Samples were injected into the cells by automatic pipette.

## RESULTS AND DISCUSSION

Artificial sample series provided linear correlations with  $R^2 > 0.97$  for  $Q$  vs. injected  $BOD_5$ , proving that not only soluble readily biodegradable substrates, but suspended and colloidal substrate content can be measured as well with the applied measurement method. Although the two types of wastewaters (domestic, brewery) had significantly different composition, results suggest that they can be measured using the same linear  $Q$  vs.  $BOD_5$  calibration (Fig. 1A,  $R^2 > 0.985$ ). The relative error of BOD values determined with the MFCs related to the  $BOD_5$  concentrations measured by

standard respirometry method was less than 10 %. As most single chamber air cathode MFC designs require little maintenance and the applied method can be easily automated, it can be suggested that this technology is a promising candidate for on-site automatic BOD sensors.



**Figure 1.** (A) Combined correlation for brewery and domestic wastewaters (circles: domestic ww; triangles: brewery ww). (B) Typical shape of the voltage vs. time curve for domestic and brewery wastewaters obtained from the measurement of two representative samples. Solid black line 0.02 V cutoff potential applied for real wastewater samples. Purple dashed line stands for the result obtained in MFC "A" for a filtrated domestic ww sample.

As it is observable on Fig. 1B, characteristics of the voltage vs. time curves obtained for domestic wastewater contains a higher voltage peak supposedly related to the biodegradation of readily biodegradable soluble substrates, and a lower voltage ( $\approx 0.05\ V$ ) "shoulder" presumably belonging to the hydrolysis and consequent biodegradation of suspended slowly biodegradable organics. Thus, not only quantitative analysis of domestic wastewaters can be carried out with the developed method, but possibly the determination of soluble readily biodegradable and suspended slowly biodegradable substrate ratio as well. Further research is required in this matter.

## ACKNOWLEDGEMENTS

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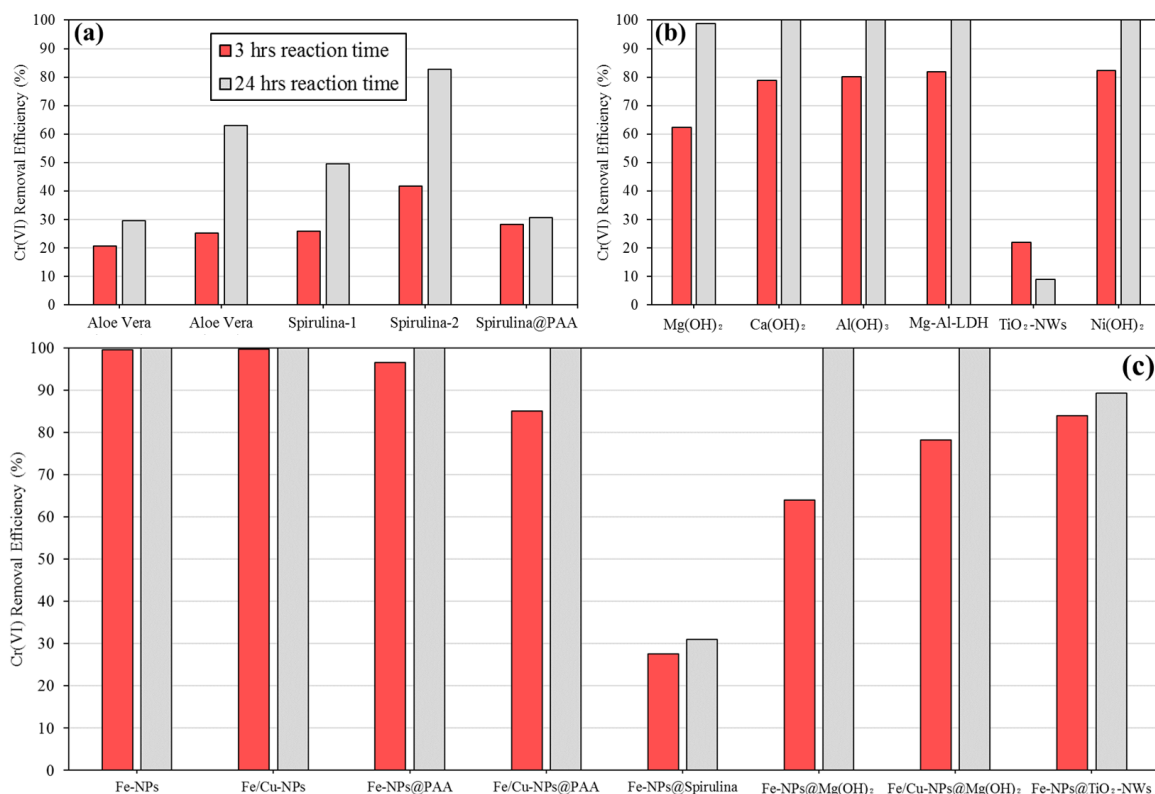
# Comparative Study on Cr(VI) Removal from Aquatic Systems by Different Bio-Sorbents, Nano Powders, and Iron-Based Nanomaterials

I. Maamoun\*, K. Bensaida\*, R. Eljamal\*, O. Falyouna\*, R. Mokete\*, and O. Eljamal\*

\* Water and Environmental Engineering Laboratory, Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka, Japan (E-mails: [ibrahim-maamoun@kyudai.jp](mailto:ibrahim-maamoun@kyudai.jp); [khaoulabensaida@gmail.com](mailto:khaoulabensaida@gmail.com); [ramadaneljamal54@gmail.com](mailto:ramadaneljamal54@gmail.com); [omarail92@hotmail.com](mailto:omarail92@hotmail.com); [lelemokete@gmail.com](mailto:lelemokete@gmail.com); [osama-eljamal@kyudai.jp](mailto:osama-eljamal@kyudai.jp))

## SUMMARY

Chromium (Cr) is one of the highly toxic heavy metals which has attracted great attention of the researchers recently because of the spread of water contamination with it (Li *et al.*, 2020). The continuous discharge of industrial wastewater into water bodies, especially in the developing countries, is one of the main reasons for the occurrence of the primary hexavalent form (VI) of Cr in the environment and aquatic systems (Maamoun *et al.*, 2020). Cr(VI) is much higher toxic than the unstable trivalent form Cr(III), and the exposure to Cr(VI) can cause harmful health effects and lethal diseases to humans (Jiang *et al.*, 2018). Hence, it is urgently needed to find suitable sorbents within an effective removal performance towards Cr(VI) as well as improved characteristics for better applicability in the real water treatment applications. In this study, a critical comparison is introduced based on a real experimental work, considering different bio- and metal-based materials for the removal of Cr(VI) from aqueous solutions.



**Figure 1.** Cr(VI) removal performance of (a) bio-sorbents, (b) nano powders, and (c) iron-based nanomaterials (initial Cr(VI): 20 mg/L, sorbent dosage: 1 g/L, pH: 5.5, at room temperature).

## FINDINGS & CONCLUSIONS

### Removal Performance

*Bio-sorbents.* Results shown in Fig. 1(a) indicated that extracted microalgae powder of spirulina-2 (food grade with less processing) had higher Cr(VI) removal efficiency than the other type (spirulina-1 / higher food processing), with around 83 % and 50 % after 24 h of reaction time, for the former and the latter, respectively. Moreover, the dried powder of aloe vera-stem was better than the leaves' one with around 5 % and 34 % enhancement after 3 h and 24 h reaction time, respectively. Combining algae powder with polyacrylamide polymer (PAA) was not favourable for Cr(VI) removal.

*Nano powders.* Using metal nano powders was significantly effective for Cr(VI) removal, as shown in Fig. 1(b). Among all the considered powders, nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ) had the highest kinetics of sorption rate corresponding to the highest removal efficiency of 82.275 % after 3 h. Magnesium (Mg), calcium (Ca), aluminium (Al) hydroxides, as well as layered double hydroxide (LDH) of Mg-Al approached to the full removal efficiency after 24 h of adsorption, owing to the low/moderate solubility of such powders. Whereas titanium oxide nanowires ( $\text{TiO}_2$ -NWs) reached maximum removal efficiency of 51 % after just 1 h (not shown data), while desorption kept occurring after that during the whole time, which could be related to the photocatalytic effect of the  $\text{TiO}_2$ -NWs which cause the instability of the sorption.

*Iron-based nanomaterials.* Combining iron nanoparticles (Fe-NPs) with different materials to enhance their characteristics did not affect its efficient removal of Cr(VI), as shown in Fig. 1(c). Modifying the surface of Fe-NPs with copper (Cu) or PAA stabilizer high removal of Cr(VI) (very close to full) after 3 h. The physical combination of spirulina with Fe-NPs resulted in undesirable removal performance, hence chemical synthesis of the composite should be considered. The non-magnetic coating of  $\text{Mg}(\text{OH})_2$  resulted a remarkable anti-aggregation effect on Fe-NPs and achieved a novel controlled release of reactivity over 24 h to achieve 100 % Cr(VI) removal efficiency.

## CONCLUSIONS

Bio-sorbents showed a promising potential towards Cr(VI) removal from aqueous media, especially spirulina microalgae and aloe vera-stem powders. The use of metal nano powders was efficient in achieving 100 % removal efficiency of 20 mg/L Cr(VI). Fe-NPs have proven their remarkable abilities for Cr(VI) removal despite surface modifications. The low-soluble  $\text{Mg}(\text{OH})_2$  coating achieved a controlled release of Fe-NPs reactivity over 1 day reaction time, associated with enhanced characteristics, which can be very promising for real groundwater treatment applications.

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# GPS-X Based Simulation and Validation Study for Simultaneous Nitri-Denitrification (SND) Process in Biofloc MBBR

S. S. Magdum\* and V. Kalyanraman\*\*

\* Chemical and Biotechnology Board, Department of Technology, Savitribai Phule Pune University, Pune, India (E-mail: [sandipmagdum@gmx.com](mailto:sandipmagdum@gmx.com))

\*\* COE Biotechnology, R. D. Aga Research, Tecnology and Innovation Centre, Thermax Limited, Pune, India (E-mail: [kalyanraman.v@thermaxglobal.com](mailto:kalyanraman.v@thermaxglobal.com))

## INTRODUCTION

The application of simulation models provides us the fastest mode to analyze and get a design understanding of variable parameters such as incoming contaminant load, flow, and temperature on biological wastewater treatment for the new or retrofitting facility. Overall modelling methods used for wastewater treatment plant engineering design assistance, troubleshooting, optimization, planning, operator training, and education purpose. Operational difficulties and new processes such as nutrient removal led to increased use of the models, and this in turn to the need for the creation of mathematical models incorporating all the involved mechanisms (Liwarska-Bizukojc *et al.*, 2013). GPS-X simulation software (v7.0, Hydromantis Environmental Software Solutions, Inc., Hamilton, Ontario, Canada) can be utilized for MBBR (moving bed bio-reactor) based system with minimum complexity. The developed biofloc MBBR removes ammoniacal nitrogen from wastewater by using SND (simultaneous nitri-denitrification) process. The purpose of this study is to validate the process design parameters required to achieve optimum SND in biofloc MBBR by using GPS-X simulating software.

## MATERIALS AND METHODS

To increase the quality and reliability, this study referred to the guideline for simulation studies of wastewater treatment plants (Langergraber *et al.*, 2004). In order to conduct the simulation, a wastewater treatment system with MBBR based process flow layout (Fig. 1) created by means of GPS-X software.

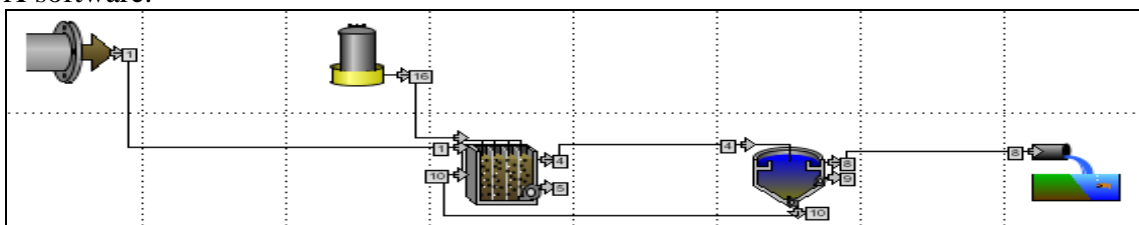


Figure 1. MBBR based process flow layout in GPS-X.

Table 1. Simulation strategy for constant and variable parameters.

Parameters	Set 1 Simulation	Set 2 Simulation	Set 3 Simulation
Influent BOD, mg/L	90	31, 90, 156, 234, 313	31, 90, 190, 290
Vol. Org. Loading, $gm_{BOD5}/(m^3 d)$	72, 144, 216, 289, 361, 433	97, 289, 503, 751, 1002	289
Flow, $m^3/d$	160, 360, 560, 760, 960, 1160	760	2360, 760, 339, 208

The kinetic coefficient and other constants could be considered as per the “mantis2” model library available in GPS-X software. In this study, the simulation strategies applied as per Table 1. Parameters referred to the previous pilot study, such as DO setpoint of 1.5 mg/L, temperature of 20 °C, influent NH<sub>3</sub>-N of 35 mg/L, active biofilm layer on biofloc carrier of 2 mm and 30 % (v/v) carrier filling kept same for all simulation runs. Applied PU foam based biofloc MBBR carriers having characteristics such as pore size of 45 PPI, physical dimensions of 5 mm (L) × 4 mm (W) × 4 mm (H), the specific surface area of 448 m<sup>2</sup>/m<sup>3</sup> with a true material density of 1.17 gm/cm<sup>3</sup>.

## RESULTS & DISCUSSIONS

The comparative analyses carried to examine the performance of the integrated model and its impact on SND based nitrogen removal when exposed to various influent organic concentrations, organic loading rates, and increasing the flow rates (or decreasing HRT). Set 1 simulation evaluated the effect of different HRT and OLR, as previous MBBR study have shown the non-linear relationship between OLR and treatment efficiency (Magdum and Kalyanraman, 2019a). The biofloc MBBR simulation run 3 and 4 shown the higher SND based nitrogen removal with OLR of 216.6 mg<sub>BOD</sub>/(m<sup>3</sup> d) and 288.8 mg<sub>BOD</sub>/(m<sup>3</sup> d). Set 2 simulation evaluate the effect of different influent BOD concentrations and OLR. Simulation run 2 with BOD of 90 mg/L and OLR of 288.8 mg<sub>BOD</sub>/(m<sup>3</sup> d) with C/N ratio of 5 showed the 71 % NH<sub>3</sub>-N removal by SND reactions in biofloc based MBBR reactor. A similar study of aerobic MBBR containing PU foam-based carrier media showed the doubled nitrogen removal through the SND process (Magdum and Kalyanraman, 2019b). This overall result analysis showed that without optimized OLR, only consideration of C/N ratio >5 would not end with effective SND process. Set 3 Simulation run 2, 3, and 4 with HRT of >7.09 h showed higher SND based nitrogen removal at constant OLR of 288.8 mg<sub>BOD</sub>/(m<sup>3</sup> d). Results also showed that at lower influent organic (COD-BOD) concentrations do not support the SND reactions, whereas SND also occurs on a given OLR of 288.8 mg<sub>BOD</sub>/(m<sup>3</sup> d) with higher influent organic concentrations.

## CONCLUSIONS

The biofloc based carrier media showed promising results of SND-based nitrogen removal performance on optimum OLR with GPS-X simulation software. The results indicated the biofloc MBBR based process design parameters such as OLR of 216.6–288.8 mg<sub>BOD</sub>/(m<sup>3</sup> d) with C/N > 5 and DO control at 1.5 mg/L need to be considered to achieve optimum SND. This biofloc MBBR simulation study provides the validation of experimental biofloc based pilot plant results.

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# Energy and Material Recovery from Beach-Cast Seagrass: The Case Study of High-Adriatic Coast

M. Mainardis\*, S. Prapotnich\*, G. Misson\*\*, A. Peressotti\*\*, and D. Goi\*

\* Department Polytechnic of Engineering and Architecture, University of Udine, Via del Cottonificio 108, 33100 Udine, Italy (E-mails: [matia.mainardis@uniud.it](mailto:matia.mainardis@uniud.it); [prapotnich.sara@spes.uniud.it](mailto:prapotnich.sara@spes.uniud.it); [daniele.goi@uniud.it](mailto:daniele.goi@uniud.it))

\*\* Department of Agricultural, Food, Environmental and Animal Sciences, University of Udine, Via delle Scienze 208, 33100 Udine, Italy (E-mails: [gloria.misson@phd.units.it](mailto:gloria.misson@phd.units.it); [alessandro.peressotti@uniud.it](mailto:alessandro.peressotti@uniud.it))

## INTRODUCTION

Anaerobic digestion is a widely diffused technology for renewable and sustainable biogas production from a pool of organic substrates (Mainardis *et al.*, 2020); anaerobic co-digestion, rather than mono digestion, can lead to smoother and more continuous operations, enhancing methane yields and improving the economic balance (Cabbai *et al.*, 2016). Composting is another meaningful technology to stabilize different organic wastes, producing high-quality fertilizer that can sold and reused in agriculture (Cocozza *et al.*, 2011).

Beach-cast seagrass, produced by marine meadows, significantly accumulates on the shoreline in the analysed high-Adriatic coastline (Friuli-Venezia Giulia Region, Italy), depending on seaside and weather conditions, as well as on the season (Boudouresque *et al.*, 2016). Due to the possibility of odour nuisance generation, in touristic areas (such as that analysed in the present study) the material is typically transported to dedicated plants (Parente *et al.*, 2013), with huge economic and environmental downsides, particularly if the material is sent to landfill. Previous literature studies demonstrated the technical feasibility of biogas and biodiesel production from macro- and micro-algae (Sumprasit *et al.*, 2017).

In this work, seagrass wrack from the High-Adriatic basin (Italy) was thoroughly analysed from the physicochemical point of view and the potential methane production from seagrass in the anaerobic digestion process was investigated in the laboratory. In addition, the environmental methane emission from the beached material (and the subsequent contribution to green-house gases) was assessed, to properly evaluate alternative managing routes. Also composting was investigated and compared to landfill and ecological restoration management approaches through a life cycle analysis.

## MATERIALS AND METHODS

Biochemical methane production (BMP) tests were conducted using AMPTS II (Bioprocess) equipment, applying a mesophilic temperature of 35 °C and using a discontinuous mixing regime. Different inoculum to substrate (I/S) ratios were tested. Physicochemical characterization of seagrass wrack was done following Standard Methods (APHA, 2012). Heavy metal analysis was conducted on different substrate mixtures after the end of BMP tests. Seagrass production data and disposal costs were given by beach managing company, considering a beach length of about 1.6 km. The different managing alternatives were evaluated considering the environmental and economic impacts of the investigated processes through a life cycle assessment (LCA) approach.

## RESULTS AND DISCUSSION

Seagrass was composed of a mixture of *Cymodocea nodosa* (45 %), *Zostera Marina* (39 %) and *Zostera Noltii* (16 %). N content of seagrass wrack was 2.4–3.1 %, while H was 4.1–5.2 % and C mean content was 35.7 %; mean calculated C/N and C/H ratios were respectively 12.8 and 7.4. Seagrass was characterized by a moisture content of 33 % and VS concentration of 11.1 %; cellulose, hemicellulose and lignin were respectively 24.1 %, 16.0 % and 2.4 %. The amount of produced seagrass in the analysed shoreline varied consistently throughout the years, with a mean value of 3470 t per year, corresponding to a mean seasonal disposal cost of about 280 000 EUR per year. The produced methane yield from seagrass significantly depended on the applied I/S ratio and salinity levels, showing maximum values of about 250 NmL<sub>CH<sub>4</sub></sub>/g<sub>VS</sub>.

Heavy metal analysis on the digestate showed that Cd, Cr, Hg and Ni presence was more consistent at low I/S ratios, suggesting that these elements were more concentrated in phanerogams rather than in the sludge used as inoculum. Pb, Cu and Zn, instead, were more abundant in the high I/S tests, due to the higher sludge concentration. Anyway, all the obtained heavy metal concentration was lower than the limit legislative value for agricultural reutilisation of the digestate. Anaerobic co-digestion with sewage sludge in local wastewater treatment plants (WWTPs) was shown to be the most feasible solution, leading to an improved biogas generation. Similarly, regarding the composting scenario, the most realizable perspective was to co-compost the produced seagrass with other organic substrates (such as the organic fraction of municipal solid waste, OFMSW) in existing plants. The ecological restoration scenario was shown to be important to reduce the overall amount of material to be handled, even if some emissions of CO<sub>2</sub> and CH<sub>4</sub> (contributing to green-house gases generation) were measured in the laboratory and in-field tests. The natural CH<sub>4</sub> emission from seagrass was shown to be enhanced at higher temperatures and moderate salinity levels (9–18 ‰). Finally, landfill was the scenario which gave the highest environmental impact and the worst economic indices, also due to the long distance to be covered for material transportation.

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# Electrooxidation of Fish Meal Industry Wastewater in Batch Stirred Reactor Using Ti/RuO<sub>2</sub> Anode

R. Meganathan\* and R. Varadarajan\*

\* Department of civil engineering, University College of Engineering (BIT campus) Anna University, Tiruchirappalli-620024, India (E-mail: *sabarriraju95@gmail.com*)

## INTRODUCTION

The direct electro oxidation process has been used to treat effluent coming out of the fish meal industry. The anode used is Titanium coated with ruthenium oxide. Cathode used here is stainless steel. In addition to organic pollutant removal we have also studied color removal using electro oxidation process. We took current density as a varying parameter to see the effect of pollutant removal. The different current densities used here are 10 mA/cm<sup>2</sup>, 20 mA/cm<sup>2</sup>, 27 mA/cm<sup>2</sup>, 34 mA/cm<sup>2</sup>. We have also discussed the effect of mechanical agitator and inter electrode distance on pollutant removal.

**Table 1.** Raw effluent characteristics.

Parameter	Unit	Value
pH	–	7.23
TOC(Total organic carbon)	mg/L	1150
Color	Pt/co	100

## EXPERIMENTAL SETUP

The electro oxidation process was carried out in a cylindrical batch reactor of height 350 mm and diameter 160 mm. The reactor was made up of Borosilicate glass and it has a capacity of about five liters. Earlier the RuO<sub>2</sub> was synthesized in the laboratory using thermal decomposition method. Six numbers of anodes and six numbers of cathodes were used in the process. The size of the electrodes was 6.35 mm in diameter and 300 mm in height. The cathodes and anodes were connected in series using copper wire.

## RESULTS AND DISCUSSION

### Effect of current densities on pollutant removal

Current densities is one of the important factors for organic pollutants removal during electrochemical process (Silveira *et al.*, 2015). To know the effect of current densities in removing pollutants, the current density in the batch reactor was increased from 10 mA/cm<sup>2</sup> to 34 mA/cm<sup>2</sup>. The result shows that as we increase the current density the TOC removal also increases with respect to time. The time for each run was optimized to 4 hours. The highest removal was 72 % without using a mechanical Agitator. Whereas while using a mechanical agitator the removal percentage increased for all current densities supplied and the highest was achieved at 34 mA/cm<sup>2</sup> which was 82 %.

**Table 2.** TOC removal percentage with and without MA.

	Without Mechanical agitator				With Mechanical agitator			
	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h
<b>10 mA/cm<sup>2</sup></b>	5	10	24	26	6	21	28	31
<b>20 mA/cm<sup>2</sup></b>	12	23	38	46	17	32	43	56
<b>27 mA/cm<sup>2</sup></b>	16	37	47	55	25	40	55	59
<b>34 mA/cm<sup>2</sup></b>	25	47	63	72	34	56	70	82

### Effect of spacing

In study conducted by Zhang *et al.* (2011) the lower inter electrode gap will increase the pollution removal efficiency. To verify this we have varied the spacing between the cathode and anode. We started the spacing from 1.5 cm as 1 cm spacing was too close between the electrodes. As the spacing increased from 1.5 cm to 2 cm then to 2.5 cm the TOC removal decreased. At 1.5 cm spacing the highest TOC removal was 82 % which was decreased to 76 % and 75 % at 2.0 cm spacing and 2.5 cm spacing respectively

### Effect of pH

Some of the research work reports that the acidic nature during the EO process is effective in removing the pollutants. While some others report that higher pH range is more effective. Elaoud *et al.* (2011) reported that the pollutants removal is unaffected by pH. To know the effect of pH on pollution removal the pH of the solution was altered to acidic (pH = 2, 4) and alkaline (pH = 8, 11) and corresponding effect in TOC removal was studied. The result shows that the original sample (pH = 7.23) itself gives the highest TOC removal compared to the other pH ranges after four hour of treatment.

### Energy consumption (EC)

As we increase the current densities the EC also increased. Using the mechanical agitator the EC decreased. Also EC decreased when the spacing between the electrodes was less.

## CONCLUSION

In this study, Electro Oxidation Process using Ti/RuO<sub>2</sub> electrode is found to be effective in treating fish meal industry wastewater. 82 % of TOC, 82 % of color removal was achieved by Electro oxidation process for a retention time of about four hours at 34 mA/cm<sup>2</sup>. In the EO process as we increase the current density the pollutant removal also increases and in this study optimum results were achieved at 34mA/cm<sup>2</sup>. The spacing between the cathode and anode should be kept as minimum as possible in case of direct oxidation. There is no need to alter the pH of the wastewater during the treatment.

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# Treatment of Poultry Slaughterhouse Wastewater Using an Expanded Granular Sludge Bed Reactor Coupled with a Membrane Bioreactor

H. B. Meyo<sup>\*,\*\*</sup>, M. Basitere<sup>\*,\*\*</sup>, S. K. O. Ntwampe<sup>\*\*\*</sup>, and C. T. Mdladla<sup>\*\*</sup>

\* Bioresource Engineering Research Group (*BioERG*), Department of Biotechnology, Cape Peninsula University of Technology, Cape Town, South Africa  
(Email: [oneil\\_meyo@hotmail.com](mailto:oneil_meyo@hotmail.com))

\*\* Department of Chemical Engineering, Cape Peninsula University of Technology, Cape Town, South Africa (Emails: [BasitereM@cput.ac.za](mailto:BasitereM@cput.ac.za); [mdladlacebisa44@gmail.com](mailto:mdladlacebisa44@gmail.com))

\*\*\* Faculty of Engineering, School of Chemical and Minerals Engineering, North-West University, Private Bag X1290, Potchefstroom, 2520, South Africa  
(Emails: [Karabo.Ntwampe@nwu.ac.za](mailto:Karabo.Ntwampe@nwu.ac.za); [karabosntwampe@gmail.com](mailto:karabosntwampe@gmail.com))

## INTRODUCTION

The poultry product producers uses tremendous amounts of clean water to process chickens/birds, clean their facilities and in return produces large amounts of high strength wastewater (Njoya *et al.*, 2019). This wastewater contains high organic matter, suspended solids, and high nutrients in the liquefied form/particulate which discharge to the environment can cause serious illness to human, animals and plants (Bustillo-Lecompte and Mehrvar, 2017). South Africa is also facing the issue of water shortage due to the growth of populations that are increasing the potable water demand in urban areas (Basitere *et al.*, 2016). So, the development of anaerobic bioreactors will make it less expensive to treat the wastewater, and improve the generation of bio methane, which is an alternative source of energy (Rinquest, 2017). This kind of systems will benefit industries to reuse their wastewater and utilize less potable water (Williams, 2017). Therefore, the necessity to design a pilot plant (lab scale) to treat poultry slaughterhouse wastewater to meet City of Cape Town (CoCT) discharge was required.

## MATERIALS AND METHODS

The Poultry Slaughterhouse Wastewater (PSW) pilot plant used in this study consist of a Pre-treatment tank, an Expanded Granular Sludge Bed reactor (EGSB) and a Membrane Bioreactor (MBR). The pre-treatment tank has a cocktail solution inside the tank which is composed of Eco-Flush solution and raw PSW to reduce the fats, oil & grease (FOG), the Eco-Flush is a bacterial solution that is used to hydrolyse the raw PSW, the EGSB reactor is used to reduce the organic matter in the effluent and at the same time lead to the formation of bio-methane which is an alternative source of energy. The membrane bioreactor is composed of Simultaneous Nitrification and Denitrification (SND) which is used to remove total nitrogen in the wastewater and Ultrafiltration (UF) Submerged Membrane was used as a final treatment stage for the reduction of residual organic matter and suspended solids in the PSW.

## RESULTS AND DISCUSSION

In a research conducted by Basitere *et al.*, (2016) on the performance of an EGSB digester Coupled with Anoxic and Aerobic Bioreactor for the treatment of PSW resulted to a tCOD removal of 65 %. But, the average efficiency of EGSB digester for COD removal was 51 % which was caused by FOG and suspended solids (SS) in the wastewater. Therefore, the need of using a biological pre-treatment system before the influent goes to the anaerobic bioreactor to ensure better efficiency of

the reactor and less clogging. Furthermore, Núñez & Martínez, (1999) reported that the averaged COD removal were 67 % for total organic loading rates up to  $15 \text{ kgCOD m}^{-3} \text{ d}^{-1}$  and a HRT of 5 h. TSS were 90 % removed for total solids loads of  $6 \text{ kgTSS m}^{-3} \text{ d}^{-1}$ , fats were 85 % removed. Sheldon and Erdogan, (2016) conducted a study that investigated a combination of EGSB-MBR for the treatment of soft drink industrial wastewater, which resulted in a total COD removal of 95 %. Also, Aslan *et al.*, (2013) on the treatment of Slaughterhouse Wastewaters by Anaerobic Submerged Membrane Bioreactor reported that COD removal was 95 %, total nitrogen (TN) and total phosphorous (TP) removal were found to be 30 % and 70 % respectively and that FOG removal were found to be 97 % in the membrane.

## CONCLUSION

Based on these previous studies stated earlier, it is recommended that a treatment system consisting of a biological pre-treatment process, an EGSB coupled with a MBR be investigated with regards to its capability of treating PSW and meeting the CoCT discharge standards limits.

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# Pharmaceuticals Degradation in Surface Water: Occurrence and Purification by Solar Photocatalysis

K. Miklec\*, J. Loborec\*, and I. Grčić\*

\* Department of Environmental Engineering, Faculty of Geotechnical Engineering, University of Zagreb, Hallerova aleja 7, 42000 Varazdin, Croatia (E-mail: [kristina.simunkovic@gfv.unizg.hr](mailto:kristina.simunkovic@gfv.unizg.hr))

## INTRODUCTION

### Substances in surface waters

Pharmaceuticals and their related metabolites are subjected to natural transformation/removal processes in the environment, based on their hydrophobicity, biodegradability, and the environmental conditions, which explains their presence at trace levels in water sources and drinking water (Stefanakis and Becker, 2016). In this paper, the current concentrations of certain substances in the surface waters of Croatia are investigated. The emphasis is on pollutants from the Second Watch list of contaminants of emerging concern (WL) under the Water Framework Directive (WFD). The purification efficiency was tested in laboratory conditions and results were demonstrated.

### Chemical condition of surface waters in Croatia

In this work we were based on the latest assessment of Croatian Waters Report which shows that 92 % of surface water bodies has good chemical condition, and 8 % have not achieved good chemical condition (Commission staff working document, 2019).

## RESULTS

Samples were tested and the results were compared with the available data from Croatian waters. Samples were collected at different sites in NW Croatia and subjected to purification by the means of solar photocatalysis. Acceptable concentration, average detected concentration and expected outcome after purification were shown in Table 1.

## CONCLUSION

Pollutants from the Second Watch list are widely present in the aquatic environment, due to their use in agriculture, industry, and products for human consumption. Although they advance development of modern technologies, their harmful effects on humans and the environment has yet to be determined. Pharmaceuticals have significant effects on humans and development in general but their retention in aquatic ecosystems already shows negative impacts on human health and on other species. Pesticides have also improved agricultural development but have degraded surface water quality. It is necessary to improve conventional methods of wastewater treatment to reduce the concentration of new pollutants in wastewater. Systematic monitoring and analysis of these substances in the environment is certainly needed to accurately determine their occurrence and possible negative impact on the environment and to prohibit their use. Finally, it is worth to mention the risk value of using these substances regardless their influence on environment. Solar photocatalysis presents the alternative technology for complete degradation of pharmaceuticals in situ in surface waters, minimizing the possible risk.

**Table 1.** Main groups and substances from Second Watch list, their maximum acceptable detection limit and monitoring results in Croatia (Report of Croatian Waters, 2020).

Groups	Substances	Maximum acceptable detection limit	Monitoring results of substances	Expected results after solar photocatalysis
		µg/L	µg/L	µg/L
Hormones	17-β-Estradiol (E2)	0.0004	<0.000 053 to 0.000 093	0
	Estrone (E1)	0.0004	<0.000 995	0
	17-α-Ethinyl Estradiol (EE2)	0.000035	<0.000 012 to 0.000 099	0
Pesticides	Methiocarb	0.002	<0.002 39 to 0.003 118	0
	Imidacloprid	0.0083	<0.001 79	0
	Thiacloprid	0.0083	<0.0009	0
	Thiamethoxam	0.0083	<0.001 88 to 0.004 701	0
	Clothianidin	0.0083	<0.001 81	0
	Acetamiprid	0.0083	<0.000 56	0
Macrolide antibiotics	Erythromycin	0.019	<0.003 23	0
	Clarithromycin	0.019	<0.002 59 to <0.009 31	0
	Azithromycin	0.019	<0.003 09 to <0.006 23	0
Insecticides	Metaflumizone	0.065	<0.001 18	0
Antibiotics	Amoxicillin	0.078	<0.004 42 to 0.004 729	0
	Ciprofloxacin	0.089	0.0345 925 to 0.141 6513	0

## ACKNOWLEDGEMENTS

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## Sonozone Process to Recover Wastewater for Fertigation

A. Moretti\* and D. Goi\*

\* Polytechnic Department of Engineering and Architecture, University of Udine, Via del Cotonificio 108, 33100 Udine, Italy (E-mails: [moretti.alessandro@spes.uniud.it](mailto:moretti.alessandro@spes.uniud.it); [daniele.goi@uniud.it](mailto:daniele.goi@uniud.it))

### INTRODUCTION

Many experiments have been carried out in recent years to test the most appropriate technologies to recover and reuse water coming from wastewater treatment plants (WWTPs). In this study, ultrasonic pre-treatment and ozonation were used to treat a primary effluent coming from a municipal wastewater treatment plant (200 000 population equivalent). All the conducted experiments aimed to test different operating conditions, evaluating the system efficiency. The final purpose was to obtain a treated effluent with good physiochemical characteristics, suitable for agricultural reuse. Many experiments have been carried out in recent years to test the most appropriate technologies for wastewater recovery and reuse coming from WWTPs, focusing in particular on nutrient recovery for agricultural applications (Farhadkhani *et al.*, 2018; Li *et al.*, 2019). Nutrient preservation during the processes, was a basic parameter to measure during the sonozone process.

Primary effluents (prEFFs) from WWTPs have a good agricultural reuse potential because most of the nutrients are preserved throughout primary treatment, while only high-density particulate matter is removed (Abdessemed and Nezzal, 2003). Ozone disinfection could be applied to reduce the pathogenic risk and microbial toxicity of these effluents, downgrading organics but largely maintaining total nitrogen and phosphorus amount.

A series of experimental trials were conducted using a bench-top system, composed by a continuous ultrasonic reactor and an ozonation vessel. Different specific ultrasonic energies and ozone doses were tested throughout the tests.

### MATERIALS AND METHODS

The bench-top work was divided into two initial passages. Firstly, the calibration of the ultrasound system, composed by a generator and a probe, followed by the ozone generator production rate. These two initial steps were developed separately.

The combined total process was composed by the sonication apparatus followed in series by the ozonation one, creating this whole new laboratory system. Ozone consumption was measured with and without ultrasound pre-treatment. Three sonication pre-treatments were performed, 5 s, 10 s and 30 s of contact time between the wastewater and the probe. As the main body of the treatment, the ozone supply was monitored after three application times: 120 s, 300 s and 600 s.

Additional tests were conducted to measure all the physiochemical and microbiological parameters before and after the execution of all the various treatment passages.

The whole experimental campaign was performed following the manual “Standard Methods for the Examination of Water and Wastewater” (APHA, 2017).

## RESULTS AND DISCUSSION

At the beginning the laboratory instruments were calibrated, in order to understand if the behaviour of both the generators (ultrasonic and ozone ones) could be trustworthy, obtaining a linear trendline ( $R^2 > 0.95$ ). The two processes then were connected, assembling them into one. Specific attention was paid to the ultrasonic pre-treatment action on the enhancing of ozone consumption. Ozone consumption of no-sonicated wastewater was used as a reference point (only ozonated wastewater). After the ultrasound pre-treatment, it was found that the ozone consumption rate could reach a 98 % increase compared to the previous one, this percentage refers to the strongest oxidation process performed. All the compounds and the contaminants contained inside the not treated wastewater were measured at the beginning, using these data as initial reference for the post-treatment removal efficiency comparison. The reduction of organics and pollutants resulted strong, in almost every type of parameter evaluated.

The total suspended solids value in untouched wastewater set around 70 mg/L, after the strongest sonozone treatment only less than 10 mg/L left. Comparing the previous TSS measures, 48 mg/L were found after the only ozone process. Anionic surfactants initial content was high, set around 1.8 mg/L; the sonozone treatment could reduce it to 0.325 mg/L. Nevertheless, sonozone could not deeply decrease the organic compounds quantity. Pure wastewater organic levels were low and, mostly, the ultrasonic pre-treatment destroyed a certain amount of solids, freeing a partial amount of these compounds (previously this released organic content was attached to the solid surface). Consequently, with the current ozone supply we could not reduce sufficiently the organic part. With regards to the microbiological organisms, the sonozone process has the capability to strongly attack these hazardous enemies. The most powerful process, composed by the longest pre-treatment contact time and ozone supply, could reduce the measured faecal coliform parameter (*E. coli*) from  $3 \times 10^3$  CFU/mL to less than 1 CFU/mL. An important aspect was the recovery of the nutrients (nitrogen, phosphorus) contained inside the wastewater, for a possible reuse in agriculture. Ozone and ultrasound processes could not act in order to reduce these compounds. From the test results is possible to understand that, after every step, the nitrogen and phosphorus total levels remained quite the same as before.

All the achieved results demonstrated the enhancing effect of ultrasound pre-treatment on the ozone consumption rate. Further analyses have to be done for better know about the agriculture reuse. It could be meaningful to better understand which irrigation technique may be suitable for this recover and control the life cycle of a specific plant type, watered with the post treated effluent. Moreover, energy-efficiency and economic analyses are planned as the following steps.

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# Capability Analysis of a Multi-Stage Process Design in Poultry Slaughterhouse Wastewater Treatment Systems

N. Nsanzimana\*, S. K. O. Ntwampe\*\*, M. Basitere\*\*\*, and M. T. Dewa\*\*\*\*

\* Department of Industrial and Systems Engineering, Faculty of Engineering and the Built Environment, Cape Peninsula University of Technology, Cape Town, South Africa (E-mails: 209154128@mycput.ac.za; nsanzimanan@cput.ac.za)

\*\* School of Chemical and Mining Engineering, North-West University, Private Bag X1290 Potchefstroom 2520, South Africa (E-mails: Karabo.Ntwampe@nwu.ac.za; Karabosntwampe@gmail.com)

\*\*\* Bioresource Engineering Research Group (BioERG), Department of Biotechnology, Cape Peninsula University of Technology, P.O. Box 652, Cape Town 8000, South Africa (E-mail: Basiterem@cput.ac.za)

\*\*\*\* School of Mechanical, Industrial and Aeronautical Engineering, University of the Witwatersrand, South West Engineering, 1st Floor, Room (TBA), Braamfontein Campus East, Jorissen Street, Braamfontein, Johannesburg, South Africa (E-mail: mncedisi.dewa@wits.ac.za)

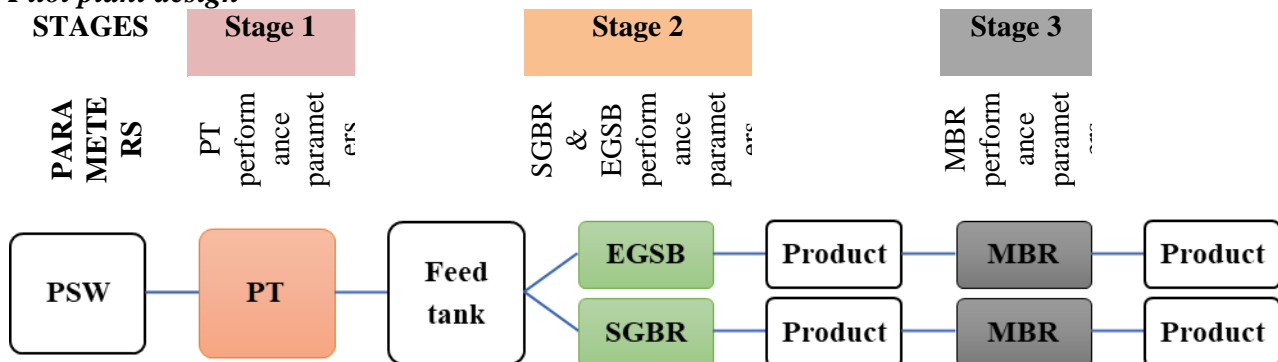
## INTRODUCTION

Wastewater treatment plays a critical role in water resource repossession, although the existing literature focuses on poultry slaughterhouses that generate significant volumes of wastewater (Aziz *et al.*, 2018). The quality of poultry wastewater is measured by organics, nutrients, and solids. In most recent studies, Static Granular Bed Reactor (SGBR) and Expanded granular sludge bed found to be one of the most widely used reactors and have been extensively used for treating different types of wastewaters including PSW. Prior research has analyzed EGSB and SGBR independently, and there is still a need for treated PSW, to meet the requirements. The current study aimed to develop and evaluated the applicability of the capability of a case study on the multi-variate-stages (PT-SGBR/EGSB-MBR) of PSW treatment processes. It was then predicted that the same approach will be applied to the targeted process illustrated in Fig. 1, using the secondary experimental data and QI macros software designed in excels.

## MATERIALS AND METHODS

The literature discusses on use of Process capability indices ( $C_{pk}$  and  $C_p$ ) in the different industries (Aslam *et al.*, 2019) and describes the multi-stage processes (Sarkar, 2019). Hence these methods were preferred to measure the performance of the designed plant.

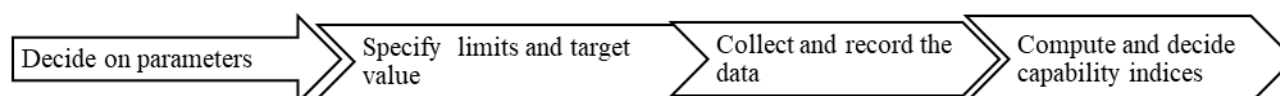
### Pilot plant design



**Figure 1.** Illustrated targeted design of multi-variate and stage process for a pilot PSW treatment plant.

### Data collection and analysis

In the designed process illustrated in Fig. 1, the quality of poultry wastewater parameters like Alkalinity, COD, Fats, Suspended Solids (SS), Total Dissolved Solids (TDS) was measured. These parameters were randomly extracted and recorded in a designed excel spreadsheet, and then analyzed. Fig. 2 sketches the working out of  $C_p$  and  $C_{pk}$ , for the overall process. Furthermore, it was assumed that the data were normally distributed.



**Figure 2.** Framework Compute  $C_p$  and  $C_{pk}$  indices in a designed excel spreadsheet.

## RESULTS AND DISCUSSION

Table 4 illustrates sample sizes ( $n = 15$ ), respective means (35.745; 37.548), and SD (34.106; 33.367) the potential and capability of the overall process were significant, where through SGBR, the  $C_{pk}$  (1.40) and  $C_p$  (1.40) is greater than 1.3. Similarly,  $C_{pk}$  (1.54) and  $C_p$  (1.54) in EGSB are also tabled.

**Table 4.** Process capability indices estimation.

	Process through EGSB	Process through SGBR
$n$	15	15
Mean	35.745	37.548
SD	34.106	33.367
$C_{pk}$	1.54	1.40
$C_p$	1.54	1.40

## CONCLUSION

The capability of a Multi-stage process design in poultry slaughterhouse wastewater treatment systems was intended, the capability was analyzed for both performance and potential into the removal of Alkalinity, COD, Fats, SS, TDS from the multistage process (PT-SGBR/EGSB-MBR). The finding on the overall performance indicated its capability to meet the requirements. Further research to determine the effectiveness of (PT-SGBR/EGSB-MBR) coupled with and UF, and more parameters is then recommended.

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# Propagation and Spread of Antibiotic Resistance during Greywater Recycling – a Preliminary Study

B. Ojobe\*, B. Šátková\*, D. Vejmelková\*, and J. Bartáček\*

\* Department of Water Technology and Environmental Engineering, University of Chemistry and Technology, Prague, Technická 5, Prague 6 166 28, Czech Republic (E-mails: [ojobeb@vscht.cz](mailto:ojobeb@vscht.cz); [satkovab@vscht.cz](mailto:satkovab@vscht.cz); [vejmelkd@vscht.cz](mailto:vejmelkd@vscht.cz); [bartacej@vscht.cz](mailto:bartacej@vscht.cz))

## INTRODUCTION

Decentralised wastewater treatment, including the in-situ recycling of greywater, has been considered as a more suitable alternative to centralised wastewater treatment (Singh *et al.*, 2014). In the last decades, greywater was mainly reused for toilet flushing and irrigation (Troiano *et al.*, 2018). Although these applications provided little or no contact to humans, they pose potential health risks (Troiano *et al.*, 2018). In situations when the expanded use of treated greywater is considered, Troiano *et al.* (2018) expresses concerns about the spread and propagation of Antibiotic-Resistance (AR) during close contact reuse (laundry, car washing, etc.).

Considering micropollutants and pathogens have been confirmed as consistent components of raw greywater and treated greywater effluent. It is correct to assume that greywater could be another means of Antibiotic-Resistant Bacteria (ARB) and Antibiotic-Resistant Genes (ARGs) propagation and dissemination (Etchepare and van der Hoek, 2015; Ottoson and Stenström, 2003).

## METHODOLOGY

Samples were collected from one full-sized and one pilot greywater treatment plant (GWTP), both located in Prague, the Czech Republic. The full-scale and pilot GWTPs incorporate the Membrane Bioreactor (MBR) and the biofilter technology, respectively. A total of 10 samples (7 and 3 from the full-scale and the pilot GWTP, respectively), differences in sample size were due to differences in setup and sampling points. One sample collected from the tap water line was examined to assess the proliferation of ARB and ARGs into GWTPs from tap water sources. The samples collected were transported in less than 2 h in sample boxes kept at 4 °C.

Analysis commenced immediately to preserve the integrity of the samples and their constituents. As our interest was on the cell-associated DNA fraction, the samples' filtration was carried out, and the retentate on the 0.22 µm nitrocellulose filter was used. DNA extraction was achieved using the DNeasy PowerSoil Kit (QIAGEN, Germany) according to manufacturer instructions. The samples' DNA concentration and purity were measured using the Qubit fluorometer (Invitrogen, US) and nano spectrophotometer (BioDrop µLITE, Biodrop, UK), respectively. Isolates were subjected to multiplex PCR targeting resistance to sulfonamides and beta-lactamases, according to Blahna *et al.*, (2006) and Monstein *et al.* (2007), respectively.

## RESULTS

Antibiotic target replacement linked to sulfonamides and antibiotic inactivation by β-lactamases were accessed to detect genes encoding AR. All samples except from Filtration Tank 2 in the full-scale GWTP were positive for *sul1* (known to be linked to other resistance genes in class 1 integrons) and *sul2* genes (known to be located on nonconjugative plasmids), the presence of these genes suggest acquisition of resistance to sulphonamides in samples analysed. In the pilot GWTP, all samples were positive for *sul1*; however, all samples but the accumulation tank were positive for

*sul2*.

One sample (Raw greywater from the full-scale GWTP) was positive for *bla<sub>SHV</sub>*, a class A extended-spectrum  $\beta$ -lactamase (ESBLs), encoded by self-transmissible plasmids that carry resistance genes to other drug classes encoded by self-transmissible plasmids spreading resistance to other drug classes.

**Table 1.** Results of cell-associated DNA screening of sulfonamides and beta-lactamases assessed.

Sample/ARG	Assessed ARGs									
	Full-Scale					Pilot				
	Sulfonamides		$\beta$ -lactamases			Sulfonamides		$\beta$ -lactamases		
	<i>Sul1</i>	<i>Sul2</i>	<i>bla<sub>CTX-M</sub></i>	<i>bla<sub>TEM</sub></i>	<i>bla<sub>SHV</sub></i>	<i>Sul1</i>	<i>Sul2</i>	<i>bla<sub>CTX-M</sub></i>	<i>bla<sub>TEM</sub></i>	<i>bla<sub>SHV</sub></i>
Raw greywater	+	+	–	–	+	+	+	NA	NA	NA
Sedimentation tank	+	+	–	–	–	NA	NA	NA	NA	NA
Aeration Tank	+	+	–	–	–	NA	NA	NA	NA	NA
Filtration Tank 1	+	+	–	–	–	NA	NA	–	–	–
Filtration Tank 2	–	–	–	–	–	NA	NA	–	–	–
Accumulation Tank	+	+	–	–	–	+	–	–	–	–
Effluent	+	+	–	–	–	+	+	–	–	–
Tap Water	+	+	–	–	–	–	–	–	–	–

NA – Not applicable treatment processes based on technological differences of both plants.

## CONCLUSION

Greywater harbours ARGs and ARB, and advanced treatment technologies like the MBR is not well equipped to eliminate them, releasing them into the greywater effluent. In some cases, tap water can be a source of ARGs' infiltration, as seen in the results. Therefore, it is recommended to conduct further monitoring cycles to assess ARB and ARGs and their concentrations in greywater in order to optimize treatment processes geared at eliminating ARB and ARGs from greywater effluent.

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# Brewery Waste By-Product *Saccharomyces Cerevisiae* as an Adsorbent for Remazol Dye Removal

E. Rápó\*, Sz. Tonk\*, K. Posta\*\*, M. Tamás\*\*\*, and M. Suci\*\*\*\*

\* Environmental Science Department, Sapientia Hungarian University of Transylvania, 400193 Cluj-Napoca, Calea Turzii no. 4, Cluj County, Romania (E-mails: *rapoeszter@gmail.com*; *tonk.szende@sapientia.ro*)

\*\* Department of Genetics, Microbiology and Biotechnology, Szent István University, H-2100 Gödöllő, Páter Károly no. 1, Hungary

\*\*\* Department of Food Science, Sapientia Hungarian University of Transylvania, 530104 Miercurea-Ciuc, Piața Libertății no.1, Harghita County, Rmania

\*\*\*\* Electron Microscopy Integrated Laboratory, National Institute for Research and Development of Isotopic and Molecular Technologies, 400293 Cluj-Napoca, Donath no. 67-103, Cluj County, Romania

## INTRODUCTION

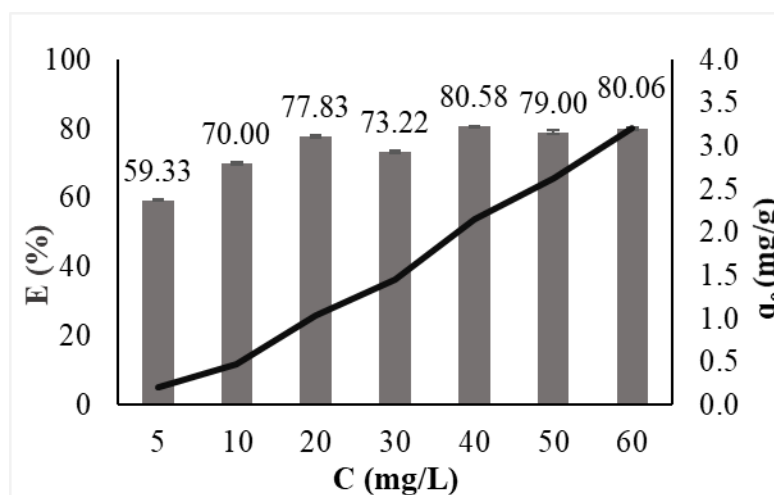
As a result of population growth, economic development, and changing consumption patterns, production has increased in many areas of industry, requiring more and more water consumption. It is estimated that the global water use has increased by a factor of six in the last 100 years and continues to rise at a rate of 1 % per year, as stated by the United Nations World Water Development Report from 2020 (UN Water and UNESCO, 2020). In this research, two water-intensive industries, the garment, and textile industry and the beverage industry (brewing) were combined through their by-products, with the help of the bioremediation process. The textile industry with an estimated 4 % of global freshwater withdrawal (annually 93 billion m<sup>3</sup>), is one of the most water-intensive industries in the world (The Conscious Club, 2019). In addition to large amounts of water, the textile industry is estimated to use the most dyes worldwide, at around 10 000 t per year, which could result in around 100 t of dye solution wastewater, which is particularly dangerous to aquatic ecosystems and human health (Katheresan *et al.*, 2018). The beer industry is said to be the third most consumed beverage after water and tea and requires up to 75 L of clean water to make a pint of beer, making it extremely dependent on one of the most endangered resources on the planet, with an annual production of 1.91 billion hectoliters (Conway, 2020; smarter business, 2020). Its by-product is brewer's yeast, which is generated during fermentation processes and remains in large quantities as waste.

## METHODOLOGY & RESEARCH

The current research aims to design an optimized biosorption process of Remazol Red F3B (RR) on lyophilized, brewery's yeast, moreover, tends to prove that brewery's yeast as a waste product can be used in bioremediation as an adsorbent. Batch adsorption experiments were carried out for optimization of different initial parameters such as initial dye concentration (5–60 mg/L), amount of yeast (0.5–2.5 g), pH (3–11), and temperature (20–40 °C) (Rápó *et al.*, 2020; Rápó *et al.*, 2020; Rápó *et al.*, 2018). Furthermore, the structure and elemental composition of the adsorbent was analysed with SEM and EDS before and after biosorption. Mathematical isotherm, kinetic, and diffusion empirical models were calculated after equilibrium was reached to evaluate the differences between biosorption rates and uptakes of RR textile dye. These models help to describe the performance and interaction between the yeast and the dye, moreover, to study the nature and possible mechanism of the adsorption process by determining the properties of the adsorbents surface and its affinity to the adsorbate.

## RESULTS

After the optimization the adsorption efficiency and quantity in equilibrium was calculated and graphically presented (the effect of initial concentration change). Elemental analyses (EDS) of RR dye showed that it contains S and Cu (0.56 wt. %  $\pm$  0.34 wt. %) in traces, moreover, after adsorption due to dye uptake, the yeast sample contained Cu. Based on the result of the enrichment factors, the amount of C and S increased in the sample.



**Figure 1.** Effect of concentration on adsorption with initial parameters:  $C_i = 20\text{--}60$  mg/L, 1.5 g biomass, 700 rpm,  $\text{pH} = 7.0 \pm 0.2$ ,  $T = 20$  °C  $\pm$  0.5 °C.

As it was the aim of this study, the obtained results proved that the lyophilized brewery yeast is a successful adsorbing agent for Remazol Red F3B textile dye as it can reduce the concentration of RR from aqueous solution with high efficiency.

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# Optimization of the COD Removal Efficiency for a Static Granular Bed Reactor Treating Poultry Slaughterhouse Wastewater

Z. Rinquest\*, M. Basitere\*\*\*, M. M. Ngongang\*, M. Njoya\*\*, and S. K. O. Ntwampe\*\*\*

\* Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Cape Peninsula University of Technology, P. O. Box 1906, Bellville, 7535, South Africa (E-mail: [bingon@cput.ac.za](mailto:bingon@cput.ac.za))

\*\* Bioresource Engineering Research Group (BioERG), Department of Biotechnology, Cape Peninsula University of Technology, P. O. Box 652, Cape Town 8000, South Africa (E-mails: [zainab.rinquest@gmail.com](mailto:zainab.rinquest@gmail.com); [Basiterem@cput.ac.za](mailto:Basiterem@cput.ac.za); [mewamaxwell@gmail.com](mailto:mewamaxwell@gmail.com); [mahomet.njoya@hotmail.com](mailto:mahomet.njoya@hotmail.com))

\*\*\* School of Chemical and Mining Engineering, North-West University, Private Bag X1290 Potchefstroom 2520, South Africa (E-mail: [Karabo.Ntwampe@nwu.ac.za](mailto:Karabo.Ntwampe@nwu.ac.za))

## INTRODUCTION

The poultry industry is one of the largest industries within the South African (SA) agricultural sector (Davids and Meyer, 2017). During bird slaughtering and processing operations, SA poultry industries consume a substantial quantity of potable water in order to maintain the high hygienic standards required for the production of poultry products (DARD, 2009). The treatment of the large quantities of high-strength poultry slaughterhouse wastewater (PSW) generated has proven to be a challenge for SA poultry industries due to the wastewaters' high chemical oxygen demand (COD), suspended solids, colloidal matter (i.e. fats, carbohydrates and proteins), nutrients (i.e. nitrogen and phosphorous), and the prevalence of pathogenic organisms (Debik and Coskun, 2009). The treatment of PSW prior to discharge is therefore crucial in order for poultry industries to achieve compliance with municipal discharge standards and to avoid discharge penalties as per the "polluter pays" principle implemented by local authorities. A static granular bed reactor (SGBR) is a high-rate anaerobic technology proven to be suitable for treating wastewater with COD concentrations exceeding 9000 mg/L (Basitere *et al.*, 2017). In this study, response surface methodology (RSM) was used for the optimization of the SGBR operating conditions, i.e. the hydraulic retention time (HRT) and organic loading rate (OLR), through the development of a quadratic model used to predict the COD removal efficiency (RE) for the SGBR when treating PSW.

## MATERIALS AND METHODS

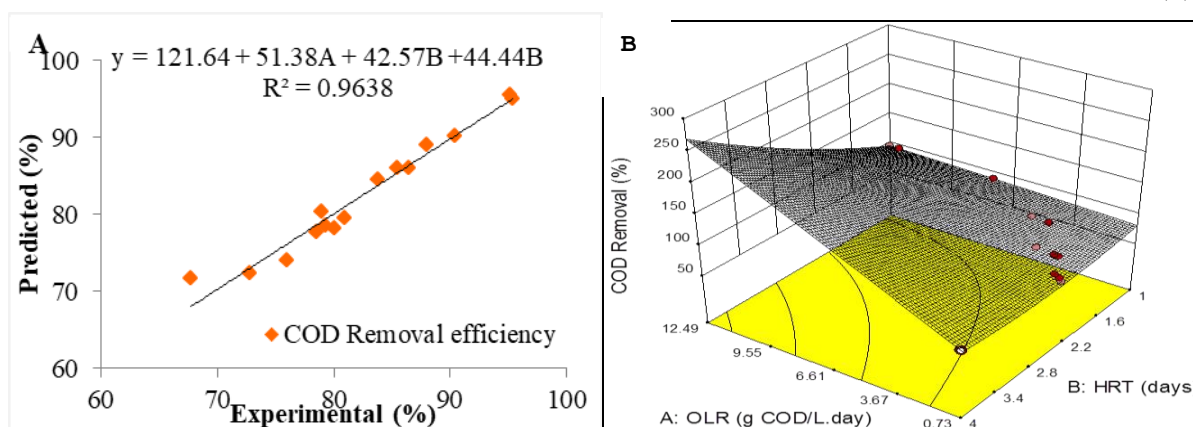
The SGBR was made from a cylindrical glass column with a working volume of 2.0 L (height and inner diameter of 0.62 m and 0.065 m, respectively). The SGBR was inoculated with anaerobic granules (0.4 L) from an up-flow anaerobic sludge blanket (UASB) reactor operated at a local brewery plant (Newlands, SA) and PSW (1.6 L) from a local poultry slaughterhouse (Western Cape, SA). The mesophilic (i.e. 35–37 °C) SGBR was operated for 138 days. The raw PSW was filtered (2 mm) to remove particulate matter. The filtered PSW was diluted [50 % (v/v) and 25 % (v/v)] with potable water to prevent overloading the SGBR during the start-up period. A central composite design (CCD) was used to determine the optimum HRT and OLR, and the interaction between these independent variables, with the COD RE (%) being the response variable. Design Expert® 10.0.3 statistical software (Stat-Ease, Inc., USA) was used for the experimental design. A two-factor, two-level CCD was applied, with 15 experimental runs generated. Feed and effluent samples were collected at 24 h intervals and analysed in triplicate. The COD samples were prepared using Merck COD solutions (solution A: Cat. No. 1.14538.0065 and 1.14679.049; solution B: Cat. No.

1.14539.0495 and 1.14680.1495), digested in a preheated Spectroquant TR420 Thermoreactor, with the concentration being measured using the Merck Spectroquant Nova60.

## RESULTS AND DISCUSSION

The SGBR consistently reduced the COD of the PSW, resulting in an average COD RE of 80.4 % for HRTs of between 1 to 4 days and an average OLR of 2.75 g<sub>COD</sub>/(L d). The predicted results from the CCD indicated that an OLR (A) of 12.49 g<sub>COD</sub>/(L d) and a HRT (B) of 1 day (24 h) were the optimum conditions for attaining a maximum COD RE of 95.5 % (Fig. 1B). Overall, the COD RE increased as the organic strength of the PSW increased and the HRT was decreased. Thus, a balance between the HRT and OLR must be maintained in order to ensure a stable and efficient operation of the SGBR as well as to prevent reactor failure. The interaction between the HRT and the OLR, and their effect on the COD RE were determined using polynomial regression. The adequacy of the proposed model was determined based on the determination coefficient ( $R^2$ ),  $F$ -value and  $p$ -value obtained from the analysis of variance (ANOVA). The model  $R^2$ ,  $F$ -value and  $p$ -value of 0.9638, 47.93 and <0.0001, respectively, indicated that the model was suitable to predict the COD RE. The similarity between the experimental values and the proposed model, was deemed sufficient, with the model describing the performance of the SGBR for PSW treatment (Fig. 1A). Eq. (1) represents the resultant quadratic model which best fit the regression results.

$$\text{COD RE} = 121.64 + 51.38A + 42.57B + 44.44AB \quad (1)$$



**Figure 1.** (A) Predicted vs. experimental COD RE based on the CCD and (B) Three-dimensional (3-D) response surface for COD RE as a function of the OLR and HRT.

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# Adsorption of Phenol from Aqueous Solutions Using Aluminum Oxide Nanoparticles: Kinetics, Equilibrium, and Thermodynamics

S. M. Safwat\* and N. Y. Mohamed\*\*

\* Sanitary & Environmental Engineering Division, Faculty of Engineering, Cairo University, Giza, Egypt (E-mail: [safwat@eng.cu.edu.eg](mailto:safwat@eng.cu.edu.eg))

\*\* Housing & Building National Research Center, Giza, Egypt  
(E-mail: [chem.nouran@gmail.com](mailto:chem.nouran@gmail.com))

## INTRODUCTION

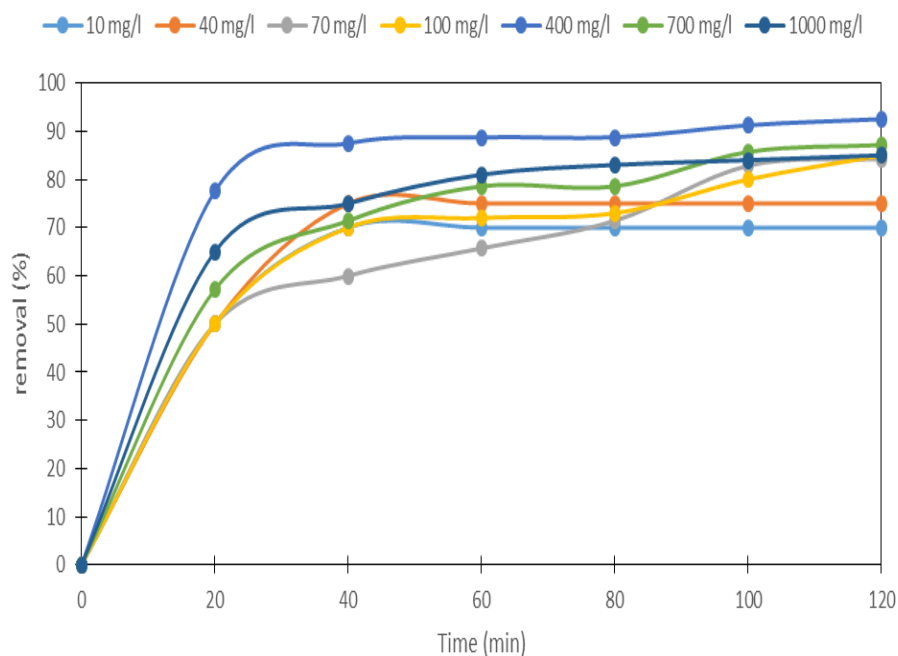
Phenol is a common aromatic hydrocarbon, which is toxic and very soluble in water. It exists in high concentrations in various types of wastewater, such as pesticide, pulp, textile, coke manufacturing, and resin manufacturing effluents (Almasi *et al.*, 2014). Several technologies can be used to reduce the concentration of phenol in wastewater, such as chemical oxidation, electrochemical techniques, membranes, and biological treatment methods. Adsorption is one of the technologies that can uptake phenol from wastewater by transferring it from the liquid phase to a solid surface. It is a simple technology, its cost is low compared to other technologies, and it does not produce by-products. It has proved to be successful in the removal of both inorganic and organic pollutants from wastewater (Lin and Juang, 2009). Aluminum oxide nanoparticles are among the first inorganic nanoparticles to be examined as an adsorbent material. Aluminum oxide as powder has been examined before to remove phenol from aqueous solution, and showed good results (Safwat *et al.*, 2019). Previous researches stated that using the material in a nanoscale in the adsorption process will improve its efficiency in the removal of the pollutants, thus it is important to examine the ability of aluminium oxide in the form of nanoparticles as an adsorbent to remove phenol from aqueous solution.

## MATERIALS AND METHODS

The preparation of aluminum oxide nanoparticles was done using the co-precipitation technique with aluminum sulfate and sodium hydroxide precursors. Batch experiments of adsorption were conducted at 30 °C. Several initial concentrations of phenol ranging from 10 mg/L to 1000 mg/L and various doses of aluminum oxide nanoparticles were examined. Adsorption experiments were conducted at different contact times to perform kinetic studies. Equilibrium studies were performed at the equilibrium contact time, and the thermodynamic experiments were performed at different temperatures.

## RESULTS

The effects of the initial concentration of phenol and the contact time were examined, as shown in Fig. 1. The results showed that the removal efficiencies increased rapidly in the first 20 min, and more than 50 % of the removal was achieved for all concentrations. After that, the removal efficiencies increased slowly until reaching equilibrium after 2 h. The adsorption of phenol onto aluminum oxide nanoparticles demonstrated the best fit with the pseudo second order model. The equilibrium data were best represented by the Langmuir isotherm. The results indicate that the process of adsorption is endothermic.



**Figure 1.** Removal efficiency of phenol at various initial concentrations at dose = 0.5 g, pH = 6, contact time = 2 h.

## CONCLUSIONS

Aluminum oxide nanoparticles were able to remove phenol from an aqueous solution. At higher pH values, the removal efficiencies were lower than those obtained at low pH values. The efficiency of the removal increased with increasing the adsorbent's dose. At low temperatures, the phenol uptake is nonspontaneous, while at high concentrations and high temperatures, the phenol uptake was spontaneous.

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## Analysis of Wastewater Treatment Efficiency

J. Šarko\* and A. Mažeikienė\*

\* Department of Environmental Protection and Water Engineering, Vilnius Gediminas Technical University, Saulėtekio al. 11, Vilnius 10221, Lithuania (E-mails: [julita.starenko@vilniustech.lt](mailto:julita.starenko@vilniustech.lt); [ausra.mazeikiene@vilniustech.lt](mailto:ausra.mazeikiene@vilniustech.lt))

### INTRODUCTION

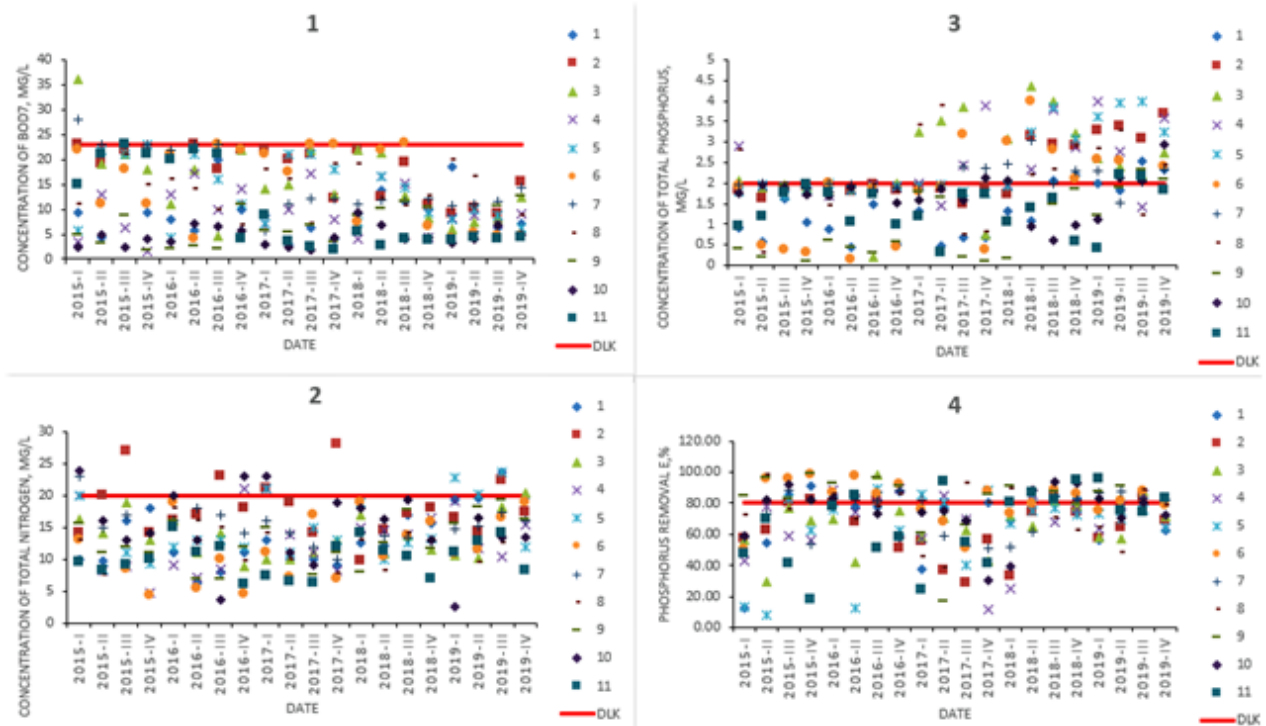
The effective treatment of wastewater from anthropogenic activity is one of prior tool for development of sustainable environment (Hu *et al.*, 2012; Omosa *et al.*, 2012). Wastewater treatment plants (WWTPs), which operate with conventional technology, do not always meet the stricter requirements for the quality of treated wastewater (Crini and Lichtfouse, 2019). Due to inefficient operation of WWTPs concentrations of phosphorus and nitrogen is higher than normal in surface water body (Powley *et al.*, 2016). The release of inefficient treated wastewater into natural water bodies has short and long-term effects on the environment. In order to find out which wastewater pollutants are not treated efficiently; 11 wastewater treatment plants were analysed for their efficiency.

### METHODS

Data of wastewater quality before and after wastewater treatment were collected from 11 municipal wastewater treatment plants in Lithuania. Small and medium size WWTPs with a flow rate more than 5 m<sup>3</sup> per day but with a population equivalent (PE) less than 10 000 were selected. Chemical analysis average data of wastewater samples was collected and evaluated for each quarter of 5 years (2015–2019), in total 20 wastewater samples per WWTP. Selected data were processed statistically applying confidence interval of 95 % and values of arithmetical average, maximum, minimum, median, standard deviation were calculated. The data of wastewater quality from real wastewater treatment systems and calculations results were compared to the requirements for the quality of treated wastewater (Ministry of Environment of the Republic of Lithuania, 2006). An analysis has been carried out to evaluate how much of these requirements are met.

### RESULTS

The results are shown in Fig. 1. Requirements for the quality of treated wastewater from WWTPs with a flow rate more than 5 m<sup>3</sup> per day but with a population equivalent (PE) less than 10 000 are as follows: an instantaneous maximum permitted concentration is 23 mg/L for BOD<sub>7</sub>; an instantaneous maximum permitted concentration is 2 mg/L for TP; an instantaneous maximum permitted concentration is 20 mg/L for TN (Ministry of Environment of the Republic of Lithuania, 2006). BOD<sub>7</sub>, TP and TN removal efficiency from wastewater must reach 70–90 %, 80 % and 70–80 %, respectively. In the figure can be seen, that according to the BOD<sub>7</sub> indicator almost all the WWTPs meet the requirements. Only 3 unallowable concentrations of BOD<sub>7</sub> were detected (1.15 % of total samples). 17 unallowable concentrations of TN were detected (6.54 % of total samples) and 74 unallowable concentrations of TP were detected (28.46 % of total samples). It should be noted that the maximum permitted concentrations were exceeded by the quarterly average concentrations. Therefore, instantaneous concentrations could have been even higher.



**Figure 1.** (1) BOD<sub>7</sub>, (2) TN, (3) TP, (4) TP removal efficiency compliance with the requirements (DLK) for the quality of real treated wastewater from 11 WWTPs.

The efficiency of TP removal was less likely to meet the requirements for the quality of treated wastewater: only 42 % met the requirements and 58 % did not.

## CONCLUSIONS

The results showed that 28.46 % of the analysed samples did not meet the requirements for treated wastewater quality according to the residual total phosphorus concentration. 1.15 % and 6.54 % of all samples, respectively, were below BOD<sub>7</sub> and total nitrogen standards. The efficiency of total phosphorus removal did not meet the requirements for the quality of treated wastewater in 58 % of cases. The results justified the need for tertiary treatment of wastewater, especially to remove phosphorus compounds from the wastewater.

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# Performance and Kinetic Evaluation of Starch Degradation by Thermophilic Anaerobic Moving Bed Bioreactor

H. M. A. Shahzad\*, S. J. Khan\*, and Z. Habib\*

\* Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Sector H-12, Islamabad, Pakistan (E-mails: *ashahzad.phdiase@student.nust.edu.pk*; *s.jamal@iese.nust.edu.pk*; *zunaira.habib@yahoo.com*)

## INTRODUCTION

Textile industries are major water consumers and generate a surplus amount of wastewater. In general, wastewater generated from textile industry contains a wide variety of pollutants (organic matter, dyes and other chemicals) (Yaseen and Scholz, 2019). In this wastewater, the main contributor to chemical oxygen demand (COD) is the wastewater generated from desizing process having COD above 10 000 mg/L (Shahzad *et al.*, 2020). This high COD is the consequence of starch applied to yarn before weaving. The operating cost of combined textile wastewater treatment is very high due to high COD, requires high energy, nutrients and chemicals and produces more sludge. The overall treatment cost can be reduced drastically by anaerobic treatment of starch containing desizing wastewater. Anaerobic moving bed bioreactor (AnMBBR) was chosen for this study, as it can retain more biomass within the system for better COD degradation and good hydrodynamic conditions can reduce the acidification (Wang *et al.*, 2009). Kinetic modeling is an effective technique for explaining and predicting the performance of anaerobic treatment systems. It helps to obtain a deeper understanding of anaerobic treatment process and serves as a useful attempt to reduce complicated and laborious experimental data into simple mathematical equations (Turkdogan-Aydinol *et al.*, 2011). Different mathematical equations have been successfully developed and effectively used to forecast and describe the performance of anaerobic bioreactors for treatment of various types of wastewater (Turkdogan-Aydinol *et al.*, 2011; Faekah *et al.*, 2020). However, no information on the kinetic evaluation of starch degradation by AnMBBR is available in the literature. In this study, to determine the kinetic coefficient of Modified Stover–Kincannon, Grau second-order and First-order substrate removal models, AnMBBR was operated at different HRTs and thermophilic temperature of 55 °C. In the end of the study, these coefficients will be compared with the previously cited literature.

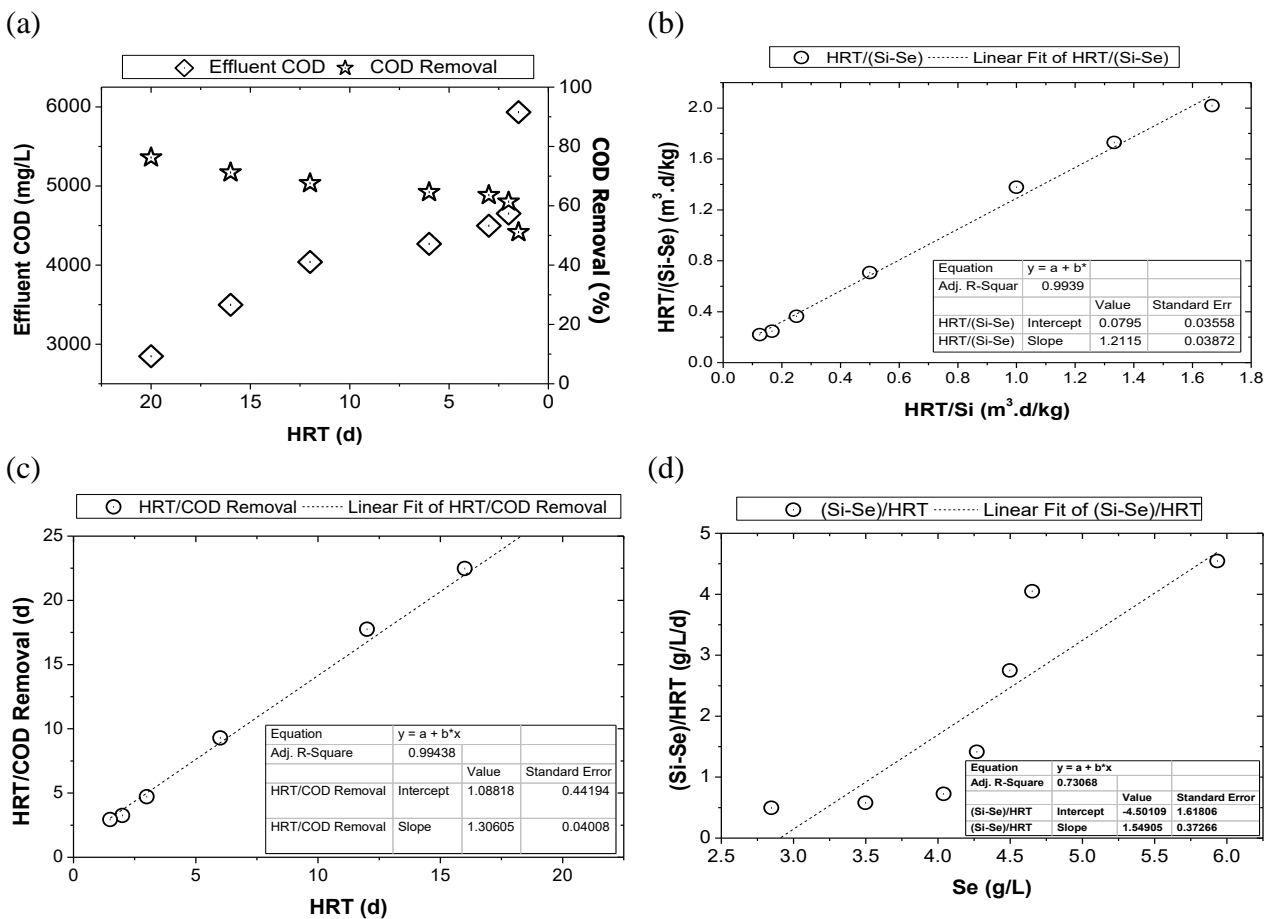
## MATERIALS AND METHODS

In this study, a lab scale AnMBBR having a total liquid volume of 12 L was used. Plastic carrier was used as a media for biofilm growth in AnMBBR. Synthetic wastewater with COD of 12 750 mg/L was fed with a peristaltic pump from the bottom of the reactor. Temperature controller (connected with heater and thermocouple) and mixer were provided in AnMBBR to control temperature at 55 °C and mixing of wastewater and media.

## RESULTS AND CONCLUSIONS

Effluent COD and COD removal from AnMBBR at steady state conditions of different HRTs are depicted in Fig. 1(a). COD removal efficiency was reduced from 76.3 % to 51.1 % with reducing the HRT from 20 to 1.5 days. From the experimental results at different HRTs, the kinetic coefficients of Modified Stover Kincannon, Grau second order and First order substrate removal models were obtained and plots of these models are shown in Fig. 1(b, c and d). Kinetic coefficients

( $K$ ) obtained from these plots are  $15.12 \text{ kg}/(\text{m}^3 \text{ d})$  ( $R^2 = 0.99$ ),  $1.31 \text{ 1/d}$  ( $R^2 = 0.99$ ) and  $1.55 \text{ 1/d}$  ( $R^2 = 0.73$ ), respectively. These findings confirmed that modified Stover–Kincannon model and Grau second-order model were found to be the best fit models for AnMBBR.



**Figure 1.** (a) Effluent COD and COD removal, (b) Modified Stover–Kincannon model, (c) Grau second-order model, (d) First-order substrate removal model.

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# Performance Evaluation of Electrocoagulation for the Removal of Nickel and Chromium from Wastewater Using Zinc Electrodes

O. A. Shaker\*, S. M. Safwat\*, and M. E. Matta\*

\* Sanitary & Environmental Engineering Division, Faculty of Engineering, Cairo University, Giza, Egypt (E-mail: [omarshaker25@yahoo.com](mailto:omarshaker25@yahoo.com); [safwat@eng.cu.edu.eg](mailto:safwat@eng.cu.edu.eg); [minerva@eng.cu.edu.eg](mailto:minerva@eng.cu.edu.eg))

## INTRODUCTION

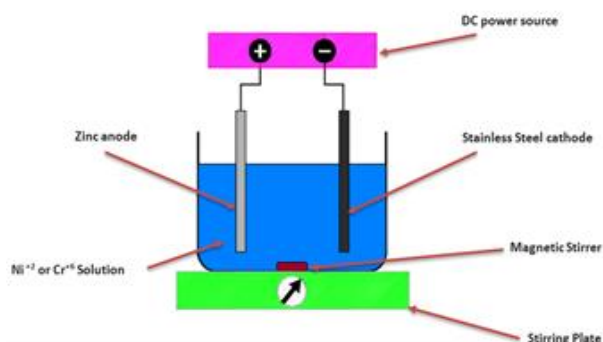
Nickel (Ni) and Chromium (Cr) are two of the most dangerous heavy metals as their presence in high concentrations can have carcinogenic effects on human and animals. Ni has been reported to be one of the most common causes of allergic contact dermatitis (Cempel and Nickel, 2006). Cr(VI) is poisonous, causing liver and kidney damage and some respiratory disorders (Sharma *et al.*, 2008). For these reasons, Nickel and Chromium must be removed from wastewater. Decreasing high initial concentrations of heavy metals to acceptable limits is a technical and economical challenge using traditional technologies.

Electrocoagulation (EC) is an electrochemical technology that depends on neutralization of charges to attract and form flocs that tend to float or settle through coagulants' generation in situ. The generation of metal ion occurs at the sacrificial anode accompanied by hydrogen gas evolution at the cathode. This technology combines the benefits of coagulation, flotation, and electrochemistry (Safwat *et al.*, 2019). It is an environmentally friendly technology as it uses simple tools and operates easily in addition to the flocs formed in EC, tends to be larger than chemical coagulation flocs (Safwat *et al.*, 2019).

This paper addresses the removal of Nickel and hexavalent Chromium from synthetic and real wastewater using electrocoagulation process. Zinc anodes were used as sacrificial anode, stainless steel as cathode, and the following operating conditions were tested: current density, initial pH, electrolysis time, spacing between electrodes, batch and continuous modes of operation, electrolyte type, and batch and continuous modes of operation. In addition to Scanning Electron Microscopy (SEM) morphology analysis for the anode to ensure the occurrence of treatment.

## MATERIALS AND METHODS

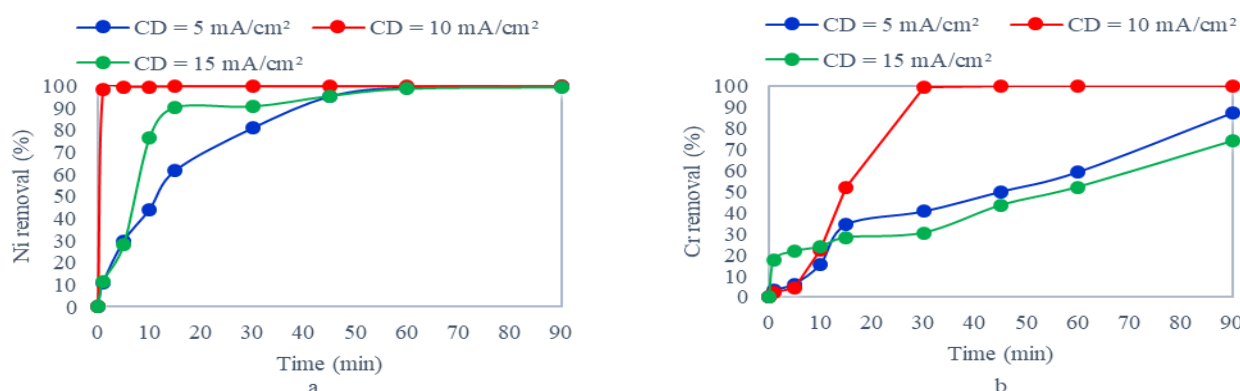
The experimental setup consisted of a 500 mL glass beaker where the electrodes were placed vertically as presented in Fig. 1. The anode material was Zn while the cathode's was stainless steel. The inter-electrode distances used were 2 cm, 4 cm, and 6 cm. The direct electric current source was a laboratory DC power source. Experiments were conducted at room temperature. Several parameters have been investigated including current density, reaction time, initial pH, electrolyte type. During each experiment, the beaker was filled with a 100 mg/L solution of either Ni or Cr, and water was stirred at 100 rpm using a magnetic stirrer for the designated time. In order to compare EC with chemical coagulation, ZnSO<sub>4</sub> was used as a coagulant with different dosages using the Jar test apparatus.



**Figure 1.** EC cell setup.

## RESULTS

Graphs describing the relationship between the obtained removal efficiencies with time at different operating conditions were drawn to understand the behavior of the EC cell in Cr and Ni removal. The following figure shows a sample of those graphs.



**Figure 2.** Ni and Cr (VI) removal efficiencies at various CDs: a) Ni removal, b) Cr (VI) removal.

## CONCLUSIONS

Using Zn electrodes in EC showed high removal efficiencies for Ni and Cr(VI) from synthetic and real wastewater. Ni had higher removal rates compared to Cr reaching 99.89 % for synesthetic wastewater and 99.4 % from real wastewater. As for the continuous mode of operation, Ni in real combined wastewater was better removed than in batch mode. The opposite was observed for Cr(VI) removal. Optimum operating conditions observed were as follows: reaction time 30 minutes, electrode gap 4 cm, electrolyte type NaCl, and basic pH for all experiments except for Cr (VI) removal where the optimum pH was in the acidic range.

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## The Mutual Interaction between Different Operational Factors within Nitrification Process

M. S. Shourjeh\*, P. Kowal\*, and J. Drewnowski\*

\* Department of Civil and Environmental Engineering, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland (E-mails: *Mehdi.shourjeh@gmail.com*; *jdrewnow@pg.edu.pl*)

### MAJOR HEADINGS

Emerging technologies in wastewater treatment plants (WWTPs) are expected to decrease the high costs of energy consumption within nitrite pathways. Several factors such as DO, temperature and pH could be incorporated into the efficiency of innovative technologies along with the application of mathematical modelling. Thus, the importance of interaction between different operational conditions and their recovery effects for each other could achieve nitrogen removal process and maintain the process stability. Conventional methods require remarkable energy to apply oxygen for nitrification and organic matters for denitrification which makes such process expensive (Dosta *et al.*, 2015; Fux and Siegrist, 2004). Nowadays, novel technologies have gained increasing attention in order to alleviate energy input used for nitrogen removal process and carbon needs for denitrification using operational factors specially dissolved oxygen, while low DO concentrations can successfully inhibit NOB activity as well as making the process more cost-effective due to the reduction of oxygen demand. Huang *et al.* (2016) investigated the use of partial nitrification in a membrane bioreactor (MBR) under DO between 0.8–0.9 mg/L, elevated temperature and FA-FNA control for restricting NOB (Huang *et al.*, 2016). In this research, a relationship between different operational factors has been developed under lab-scale environment to better understand the concept of balance within nitrification process.

### MINOR HEADINGS

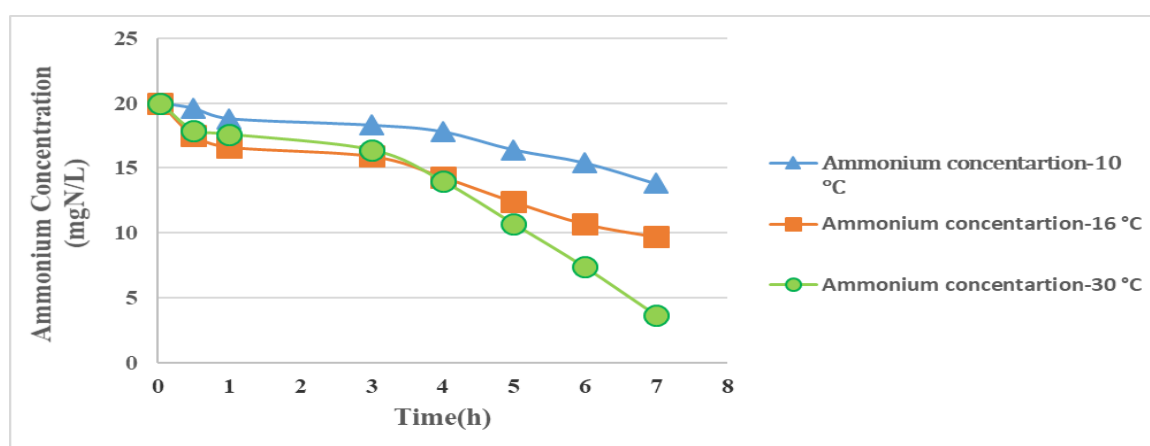
Experimental set-up and measurements of N<sub>2</sub>O production were based on series of laboratory experiments carried out in a batch reactor with a working volume of 4 dm<sup>3</sup>. The reactor was equipped with the systems for continuous monitoring and control of pH, temperature and DO concentration. On-line measurements of N<sub>2</sub>O were conducted using a clark-type N<sub>2</sub>O–R microsensor (Unisense, Aarhus, Denmark). Activated sludge originated from the local large biological nutrient removal (BNR) facility located in the city of Swarzewo. The biomass ranged from 2.0 g<sub>MLVSS</sub>/m<sup>3</sup> to 2.5 g<sub>MLVSS</sub>/m<sup>3</sup>. The nitrification tests were run at different DO set points: 0.5 g<sub>O<sub>2</sub></sub>/m<sup>3</sup>; 0.7 g<sub>O<sub>2</sub></sub>/m<sup>3</sup>; 1.0 g<sub>O<sub>2</sub></sub>/m<sup>3</sup> and 1.5 g<sub>O<sub>2</sub></sub>/m<sup>3</sup>. Ammonium constituted sole nitrogen source. At the beginning of the tests its concentration was increased to around 20 g<sub>N</sub>/m<sup>3</sup>. During each experiment, the process temperature set point was kept at 16 °C, pH remained in the range of 7.5 to 8.0, and the mixing intensity was set to approximately 200 rpm. The adequate amount of alkalinity was ensured by addition of 3 moles NaHCO<sub>3</sub> per each gram of nitrogen. In order to control the process performance, mixed liquor samples were withdrawn from the batch reactor with a set frequency, and then filtered under vacuum pressure on the Whatman GF/C. Concentrations of NH<sub>4</sub>–N, NO<sub>3</sub>–N, NO<sub>2</sub>–N were determined using Xion 500 spectrophotometer (Dr Lange GmbH, Germany). The total nitrogen concentration was determined in Total Nitrogen Measuring Unit TNM-1 (Shimadzu, Japan). Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) in the reactor were determined by the gravimetric method according to the Polish Standards (PN-72/C-04559).

## RESULTS AND DISCUSSION

The ammonium utilization and nitrate production rates (AUR-NPR) had upward trend even under low temperature conditions which confirmed the mutual influence of increasing DO concentration on process efficiency while ammonium successfully converted around 65 % even under low temperature (Table 1). However, increasing temperature from 10 °C to 30 °C played an essential role even under low DO concentration 0.5 mg/L to maintain AOB activity and the process stability by applying high temperature 30 °C. In Fig. 1 under DO = 0.5 mg/L, when temperature changed to 30 °C, ammonium conversion rate had faster slope and at the end of test the ammonium concentration decreased down to around 3.6 mg<sub>N</sub>/L and efficiency close to 81 %, demonstrating the strong relationship between operating environment which could remain the process stable.

**Table 1.** The influence of DO variations and low temperature 16 °C on nitrification rates

Parameters		Dissolved oxygen, mg/L			
		0.5	0.7	1.0	1.5
AUR	–	0.87	0.97	1.13	1.57
NPR	–	0.71	0.50	1.13	1.57
Maximum NO <sub>2</sub> <sup>-</sup>	mg <sub>N</sub> /L	0.16	0.81	2.58	1.91
Ammonium conversion efficiency	%	47	53	47	65



**Figure 1.** The influence of increasing temperature on ammonium conversion rates at DO = 0.5 mg/L.

## ACKNOWLEDGEMENT

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## Optimization of Carrier Filling Degree in the Post-Denitrification Stage at Moving Bed Biofilm Reactor Process

E. Strade<sup>\*,\*\*</sup>, M. Neibergs<sup>\*</sup>, J. Gedusevs<sup>\*</sup>, and R. Kazulis<sup>\*</sup>

<sup>\*</sup> JSC “Grindeks”, 53 Krustpils street, Riga, LV-1057, Latvia  
(E-mails: [elina.strade@grindeks.lv](mailto:elina.strade@grindeks.lv); [miks.neibergs@grindeks.lv](mailto:miks.neibergs@grindeks.lv); [janis.gedusevs@grindeks.lv](mailto:janis.gedusevs@grindeks.lv); [reinis.kazulis@grindeks.lv](mailto:reinis.kazulis@grindeks.lv))

<sup>\*\*</sup> Institute of General Chemical Engineering, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Paula Valdena 3, Riga, LV-1048, Latvia

### INTRODUCTION

The Moving Bed Biofilm Reactor (MBBR) technology is extensively used for the removal of biochemical oxygen demand and nitrogen from industrial wastewater. The utilization of biofilm carriers ensure high concentration of relevant microorganisms and provides more treatment capacity in a smaller volume compared to conventional activated sludge systems. In aerobic processes, the movement of biofilm carriers is provided by the aeration, while in the anaerobic or anoxic processes mechanical agitators are used (Ødegaard, 2006). The collision with the agitator blades causes mechanical damage of the biofilm carriers therefore they should be replaced periodically.



**Figure 1.** Mechanically damaged K3 biofilm carriers from denitrification process.

In our study the opportunity to minimise the K3 carrier filling degree in the post-denitrification stage was investigated in the lab-scale pilot plant and full scale pharmaceutical wastewater treatment plant.

### MATERIALS AND METHODS

Full scale pharmaceutical MBBR plant and laboratory scale pilot plant at scale of 1:50 000 was used in our experimental work. Design data of full-scale pharmaceutical WWTP are presented in Table 1.

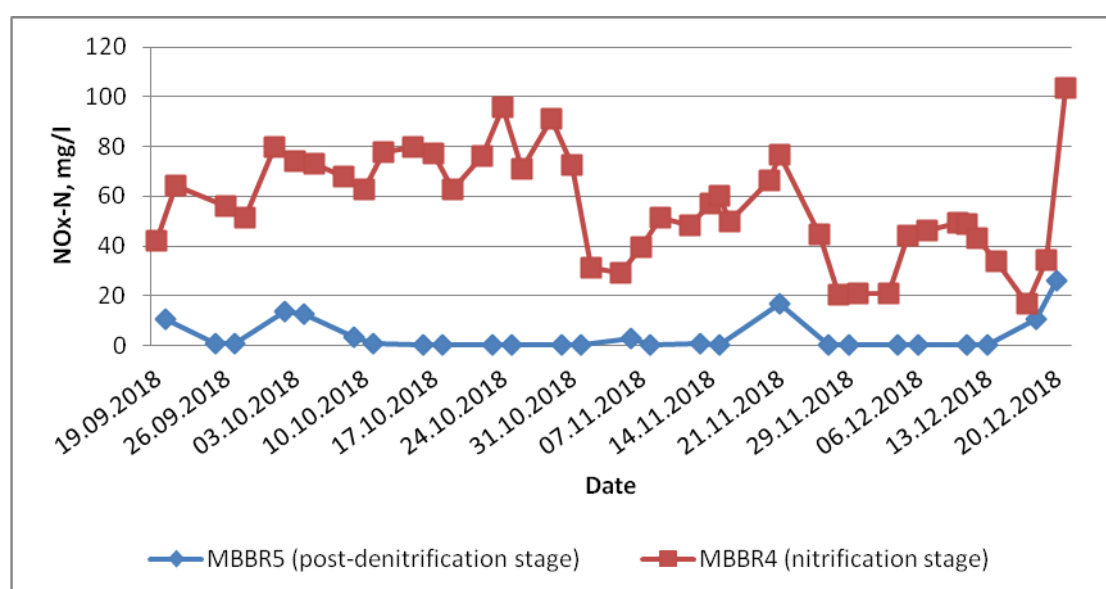
**Table 1.** Design data of pharmaceutical WWTP.

Parameter	Value	Unit
<b>Wastewater characteristics</b>		
Flow	200–500	m <sup>3</sup> /d
COD	2000–7000	mg/L
Total Nitrogen	100–200	mg/L
<b>Plant size</b>		
MBBR volume	5 × 200	m <sup>3</sup>
Carrier filling degree	50	%
Protected surface of carriers	500	m <sup>2</sup> /m <sup>3</sup>

Wastewater samples from nitrification and post-denitrification stage were filtered through 1.6  $\mu\text{m}$  glass microfiber filters. The concentration of  $\text{NO}_3\text{-N}$  and  $\text{NO}_2\text{-N}$  was measured by HACH LANGE cuvette tests using spectrophotometer DR5000. Ethanol was added as easily biodegradable carbon source in post-denitrification stage at COD:N ratio of 4:1, where N considers sum of  $\text{NO}_3\text{-N}$  and  $\text{NO}_2\text{-N}$  in the nitrification stage.

## RESULTS

In the lab-scale pilot plant, the average  $\text{NO}_x\text{-N}$  (both  $\text{NO}_3\text{-N}$  and  $\text{NO}_2\text{-N}$ ) removal rate at carrier filling degrees 35 %, 25 %, 15 % and without biofilm carriers was 99.8 %; 99.6 %, 97.2 % and 89.6 % respectively. Based on the obtained pilot plant data, the filling ratio in the full-scale post-denitrification reactor was reduced from 50 % to 15 %. Tests lasting two months confirmed that 15 % biofilm carrier filling degree is sufficient to provide complete denitrification under varying loads of  $\text{NO}_x\text{-N}$  (Fig. 2).



**Figure 2.**  $\text{NO}_x\text{-N}$  removal in a post-denitrification MBBR at 15 % biofilm carrier filling degree.

The short-term rise in  $\text{NO}_x\text{-N}$  concentration in the reactor MBBR5 indicates an insufficient dosage of the carbon source at certain moments that is related with rapid fluctuations in the incoming nitrogen concentrations.

## CONCLUSIONS

The biofilm carrier filling degree in post-denitrification MBBR could be reduced up to 15 %. Specific denitrification rate at 15 % filling degree reached up to 1.3 g  $\text{NO}_x\text{-N}$  removed per  $\text{m}^2$  per day. The minimisation of biofilm carrier filling degree reduces costs and the amount of plastic waste as well as collision and abrasion of carriers.

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# Growth Kinetics of *Acinetobacter* Strain for Phenol Removal Subjected to Substrate Inhibition with Different Kinetic Models

Sz. Szilveszter\*, D. R. Fikó\*\*, and B. Ráduly\*

\* Sapientia Hungarian University of Transylvania, Faculty of Economics, Socio-Human Sciences and Engineering, Department of Bioengineering, Libertății Sq. nr. 1, Miercurea Ciuc, Romania (E-mail: szilveszterszabolcs@uni.sapientia.ro)

\*\* Faculty of Applied Chemistry and Material Sciences, University Politehnica of Bucharest RO-011061 Gheorghe Polizu 1-7 Bucharest, Romania (Email: fiko\_robi@yahoo.com)

## INTRODUCTION

Phenol is required for several industrial processes and, being consumed mainly for the production of polycarbonate and epoxy resins, the global phenol demand in 2015 was ~10 million tons (Plotkin, 2016). Phenol can be completely oxidized and utilized as carbon and energy source by many microorganisms, even at relatively high concentrations (up to a few g L<sup>-1</sup>). Since global phenol consumption – and consequently phenolic waste generation – is expected to grow at 2.5 % per year in the next years (IHS Markit, 2016), bioprocesses aiming the degradation of phenol and phenolic compounds are in the focus of the research (Crognale *et al.*, 2012; Das *et al.*, 2016). Such bioprocesses allow for the cost-effective treatment of phenol-contaminated sites and wastewaters (Poi *et al.*, 2017). The objective of this study was determining the phenol degrading kinetic parameters of a new *Acinetobacter towneri* CFII-87 strain, isolated from landfill leachate.

## MATERIALS AND METHODS

In order to correctly account for the inhibitory effect of phenolic compounds on the specific growth of the *Acinetobacter towneri* strain, four different inhibitory growth kinetic models have been fitted to the experimental data (Table 1).

**Table 1.** Inhibitory growth kinetic models used.

Haldane (Wang and Loh, 1999)	Aiba (Aiba <i>et al.</i> , 1968)	Yano (Yano and Koga, 1969)	Edwards (Edwards, 1970)
$\mu = \frac{\mu_{max}S}{S + K_S + \frac{S^2}{K_I}}$	$\mu = \frac{\mu_{max}S}{S + K_S} e^{-\frac{S}{K_I}}$	$\mu = \frac{\mu_{max}S}{S + K_S + \frac{S^2}{K_1} + \frac{S^3}{K_2}}$	$\mu = \mu_{max} \left( e^{-\frac{S}{K_I}} - e^{-\frac{S}{K_S}} \right)$

where  $\mu_{max}$ ,  $K_S$ ,  $K_I$ ,  $K_1$ ,  $K_2$  are the biokinetic parameters, namely the maximum specific growth rate (h<sup>-1</sup>), half-saturation constant (mg L<sup>-1</sup>), inhibition constant (mg L<sup>-1</sup>), and positive constants (mg L<sup>-1</sup>), respectively.

Specific growth rate was calculated by performing linear least squares regression on the semi-logarithmic plot of biomass concentration over cultivation time in the exponential growth phase. The biokinetic parameters of the substrate inhibition models were estimated using non-linear least square curve fitting technique in Matlab 7.0 (Mathworks, Natick, Massachusetts USA).

## RESULTS AND DISCUSSION

The biokinetic parameters describing substrate inhibition are listed in Table 2.

**Table 2.** Determined biokinetic parameters for different substrate inhibition models.

Strain	Model	$\mu_{\max}$ , h <sup>-1</sup>	$K_S$ , mg L <sup>-1</sup>	$K_I$ , mg L <sup>-1</sup>	$K_1/K_2$
<i>Acinetobacter towneri</i>	Haldane	0.329	150.990	296	
	Yano	0.222	75.604	–	782.1/1607.2
	Aiba	0.223	69.760	904	–
	Edwards	0.175	72.61	1099	–

Only a couple of references can be found in the literature which investigates other substrate inhibition models than the widely accepted Haldane model. Although direct comparison of measured values and reported ones in the literature is not possible, it can be noted that the kinetic parameters are in the same order of magnitude. The  $K_S$  value shows the affinity of *Acinetobacter towneri* CFII-87 to the substrate. A higher  $K_S$  value indicates its lower affinity to phenol, while the high  $K_I$  value indicates that the inhibition effect can be observed at higher concentration ranges reflecting high phenol tolerance of the isolated strain. In the case of Haldane model, the maximum specific growth rate  $\mu_{\max}$  was 0.33 h<sup>-1</sup> and the substrate affinity constant  $K_S$  was 151 mg L<sup>-1</sup>, while for another *Acinetobacter* strain which was isolated from aerobic granules, at the same phenol concentration  $\mu_{\max}$  was 0.34 h<sup>-1</sup> and  $K_S$  between 47–740 (Adav *et al.*, 2007). The substrate affinity constant for different kinetic models ranged between 73–151 of the studied strain, which was lower than in the case of a mixed culture (ranging between 95–286) (Dey and Mukherjee, 2010). The  $K_I$  values ranged between 296 and 1099, being among the highest values found in the literature, and shows that the phenol inhibition for the studied bacterial strain can be observed only at high phenol concentrations.

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## Pharmaceuticals and Another Groups of Emerging Contaminants: Occurrence and Sources in Admiralty Bay (King George Island, Maritime Antarctica)

M. Szopińska\*, S. Fudala-Książek\*, O. Svahn\*\*, E. Björklund\*\*, and A. Luczkiewicz\*

\* Faculty of Civil and Environmental Engineering, Gdansk University of Technology, 11/12 Narutowicza St., Gdansk 80-233, Poland (E-mails: [malszopi@pg.edu.pl](mailto:malszopi@pg.edu.pl); [skisiazek@pg.edu.pl](mailto:skisiazek@pg.edu.pl); [ansob@pg.edu.pl](mailto:ansob@pg.edu.pl))

\*\* Faculty of Natural Science, Kristianstad University, SE-291 88 Kristianstad, Sweden (E-mails: [ola.svahn@hkr.se](mailto:ola.svahn@hkr.se); [erland.bjorklund@hkr.se](mailto:erland.bjorklund@hkr.se))

### INTRODUCTION

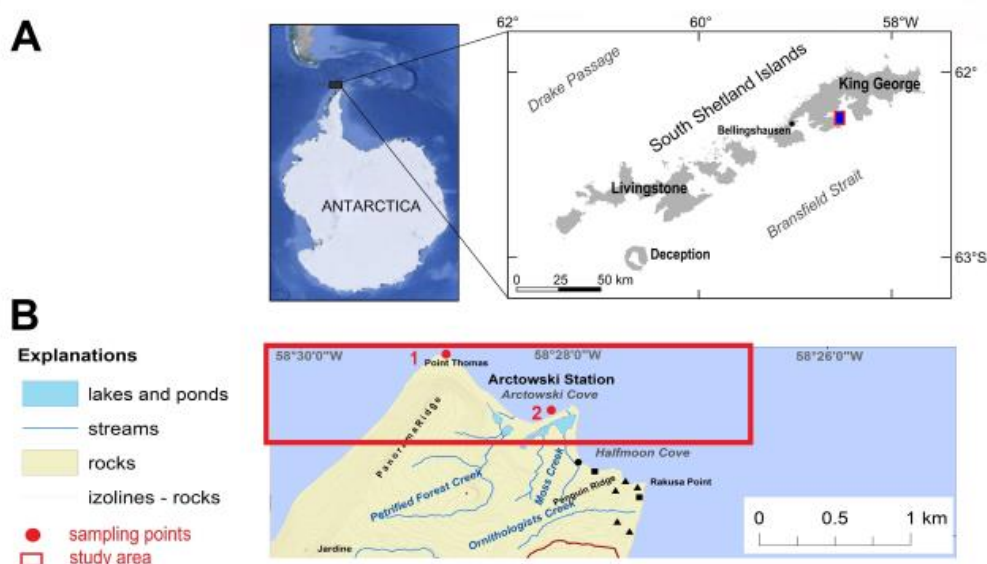
Everyday life activities may introduce a wide range of chemicals into our wastewater systems. In this study the presence of selected pharmaceuticals from the cardiovascular system group, the nervous and musculo-skeleton system group, antimicrobial agents, and genitourinary and sex hormones was examined in wastewater from the H. Arctowski Antarctic station. Additionally, the receiver of discharged wastewater (Admiralty Bay) was also analysed for its pharmaceutical content. So far, the influence of wastewater on the ecosystem in this area has only been reported in terms of microbiological pollution (fecal bacteria) (Stark *et al.*, 2016), while wastewater discharge from the Arctowski Polish Antarctic Station (on the western shore of Admiralty Bay) has not been widely investigated. Considering the construction of new station facilities in the near future, this study was undertaken to support the selection of proper wastewater management, which is crucial to mitigate the environmental impact of human activity on this precious ecosystem.

### MATERIALS AND METHODS

In this study, the dispersal and distribution of pharmaceuticals and other emerging pollutants in wastewater and sea water, after discharge into the receiver, was analysed in 2017 and 2019. Pharmaceuticals were analysed using UPLC-ESI-MS/MS, and the methodology and total list of compounds is available in a paper by Svahn and Björklund (2016). Localisation of the study area and sampling points is shown in Fig. 1. In each sample physical and chemical characteristic were analysed according to APHA.

### RESULTS AND CONCLUSIONS

Results showed the presence of pharmaceutical substances in wastewater including diclofenac, naproxen, doxycycline, propranolol at the level of ng/L. Moreover, trace amounts have also been identified in the receiving marine coastal water of Admiralty Bay. The presence of anti-inflammatory agents, antibiotics and beta-blockers in marine waters in the such a pristine environment as Antarctica can lead to long-term negative effects, which are not yet fully understood. Thus, considering the high desire for preserving the Antarctic environment, novel approaches for wastewater treatment should be considered. This includes zero discharge of emerging contaminants and non-indigenous microorganisms, as well as potential reuse of treated water as an important aspect of a circular economy.



**Figure 1.** Location of study area: (A) Localisation of King George Island; (B) Localisation of Arctowski Station and sampling points. A and B adapted and modified from Szopińska *et al.* (2018).

Nowadays electrolysis is a promising technology for small and variable flow wastewater treatment installations, due to simplicity of use and high efficiency of removal of micropollutants and reduction of by-products. Therefore technology which combines a conventional biological membrane reactor with electrolysis (e.g. BDD electrode, Fudala-Ksiazek *et al.*, 2018), enables an efficient removal of ammonium nitrogen and organic matter together with micro-pollutants and microorganisms. The treatment efficiency is expected to be high, despite the condition with high flow variability of the wastewater amount.

## ACKNOWLEDGEMENTS

This research has been supported by National Science Centre Poland project task (MINIATURA2) entitled: “*Recognition and selection of pollution markers introduced into Admiralty Bay via wastewater discharge: An example from Arctowski Polish Antarctic Station. King George Island. Maritime Antarctica*”. Agreement no. DEC-2018/02/X/ST10/01539. Authors would like to thank Dr Danuta Szumińska and the staff of Arctowski Station for the invaluable help during the field work.

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# Profiling of Amino Acids and Their Interactions with Proteinaceous Compounds for Sewage Sludge Dewatering

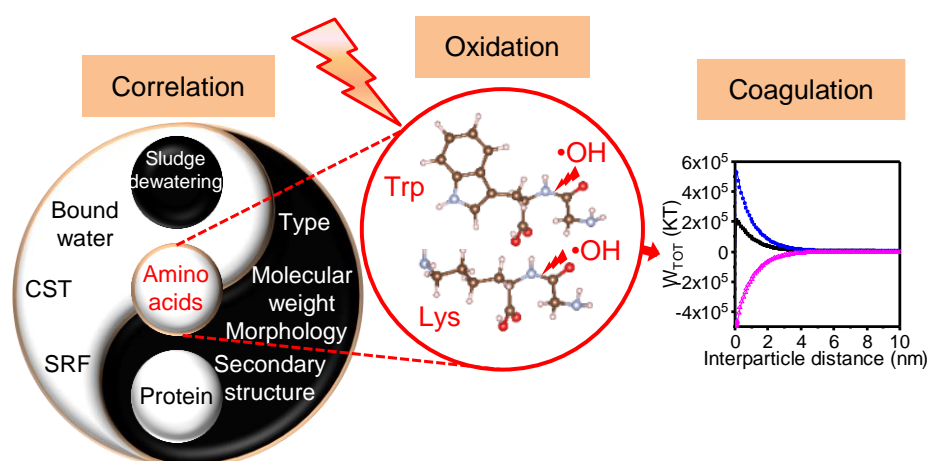
K. K. Xiao\*, Y. W. Zhu\*, and J. K. Yang\*

\* School of Environmental Science & Engineering, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, P.R. China (E-mail: xiaokeke@hust.edu.cn)

## INTRODUCTION

In wastewater treatment plants, large amounts of waste activated sludge are being generated during the biological wastewater treatment process (Cieslik *et al.*, 2015). The management of waste activated sludge is difficult since it typically contains of up to 95–99 wt. % water content (Wu *et al.*, 2018). Therefore, sludge dewatering is necessary in minimizing sludge volume and cutting costs of transportation and disposal. During advanced oxidation process for enhancing sludge dewaterability, the peptide chains of protein can be decomposed into amino acids. Protein exhibits a great impact on sewage sludge dewaterability.

However, the role of amino acids in sludge dewatering remains unclear. In this study, among the 23 types of amino acids investigated, tryptophane (Trp) and lysine (Lys) were identified as the key amino acids affecting sludge dewaterability during advanced oxidation treatment of Fenton's reagent. The content of lysine showed negative correlations with capillary suction time (CST), specific resistance to filtration (SRF), and bound water content, and the concentrations of total protein, low molecular weight protein, amines and amides, and 3-turn helix of proteinaceous compounds in bound extracellular polymeric substances (EPS), while the content of tryptophane showed positive correlations with the above parameters. The amino acids may be sourced from damage of the membrane and ribosomal proteins by hydroxyl radicals, and the peptide bonds connected with tryptophane were more inclined to be decomposed than other amino acids. Particularly, more amino acids of tryptophane can result in more hydrophobic interaction, and less necessary energy barrier for aggregation of particles. As such, regulating protein degradation towards production of tryptophane may be related with enhanced sludge dewaterability.



**Figure 1.** The main finding of this study.

**Table 1.** Correlation between dewatering characteristics (CST, SRF and bound water content) and the molecular weight,  $N$  functionalities and protein secondary structure in Bound-EPS.

		CST	SRF	Bound water content
	HB DOC	-0.684	-0.67	-0.769
	HI DOC	0.546	0.57	0.786
	HMW protein (>>20 000 Da)	0.608	0.647	0.773
	LMW protein (<20 000 Da)	0.642	0.673	0.846*
	Polysaccharide (>>20 000 Da)	-0.804	-0.859*	-0.850*
	Building blocks (<350 Da)	-0.581	-0.565	-0.162
	LMW neutrals (<350 Da)	-0.179	-0.127	0.214
	LMW acids (<350 Da)	-0.400	-0.431	-0.407
	$N_{\text{nonpr}}$ (wt. %/C)	0.704	0.735	0.871*
	$N_{\text{pr}}$ (wt. %/C)	0.054	0.181	0.278
	Aggregated strands	-0.755	-0.786	-0.860*
	$\beta$ -sheet	-0.915*	-0.919**	-0.875*
	$\alpha$ -helix	0.347	0.353	-0.029
	3-turn helix	0.870*	0.864*	0.927**
	Antiparallel $\beta$ -sheet / Aggregated strands	0.691	0.734	0.843*

\* Correlation is significant at the 0.05 level (2-tailed).

\*\* Correlation is significant at the 0.01 level.

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## A Sequential Electrocoagulation / Electrochemical Oxidation Process to Treat a Mild Sterilize Leachate

E. Yakamerca\* and A. Aygun\*

\* Department of Environmental Engineering, Bursa Technical University, Mimar Sinan Avenue, Eflak Street No: 177 16310 Yildirim/Bursa, Turkey (E-mails: [elif.yakamerca@btu.edu.tr](mailto:elif.yakamerca@btu.edu.tr); [ahmet.aygun@btu.edu.tr](mailto:ahmet.aygun@btu.edu.tr))

### INTRODUCTION

Leachate contains a high amount of organic, inorganic and some toxic substances such as heavy metals thus the biological treatment methods are not sufficient to treat, to overcome this problem electrochemical processes which are electrocoagulation, electro-oxidation and electro dialysis can be applied as a combined treatment (Ding *et al.*, 2018). Effective removal, easy operation, low cost and no additional chemical required are advantages of these processes (Sun *et al.*, 2020). Electrocoagulation can use as first step to precipitate colloidal pollutants then dissolved ones are removed by electro-oxidation (Norma *et al.*, 2012).

The purpose of the study is investigating the most proper operating condition for mild sterilize leachate removal with using sequential electrocoagulation/electro-oxidation processes under minimum the cost.

### METHODOLOGY AND RESEARCH

Electrocoagulation system contains 1 L glass vessel with the mono-polar, two parallel electrodes, anodes and cathodes are aluminium. Effective electrode area is 0.0125 m<sup>2</sup>. Experiments were carried out in batch mode with 750 mL of leachate. DC power supply (EA-PS-3022-10 B model) was used in constant voltage (0–32 V, 0–10 A). After the electrocoagulation, electro-oxidation process, which contains boron-doped diamond (BDD) anode and stainless steel cathode, was performed with 600 mL leachate.

The performance of EC-EO was determined by Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and NH<sub>4</sub> removal. pH, current density and electrolysis period were selected as the independent variable and the effects on selected pollutants removal investigate by using Box-Behnken methodology. Also, total unit cost and the amount of sludge generation was calculated. Modified quadratic models' prediction and actual values were compared statistically with variance analysis.

**Table 1.** The actual and coded levels of the input variables.

	Symbols		Actual Codes		
			-1	0	1
pH	A	EC-EO	6	8	10
Current Density, A/m <sup>2</sup>	B	EC	80	200	320
		EO	80	240	400
Electrolysis time, min	C	EC	20	40	60
		EO	240	360	480

## RESULTS AND CONCLUSION

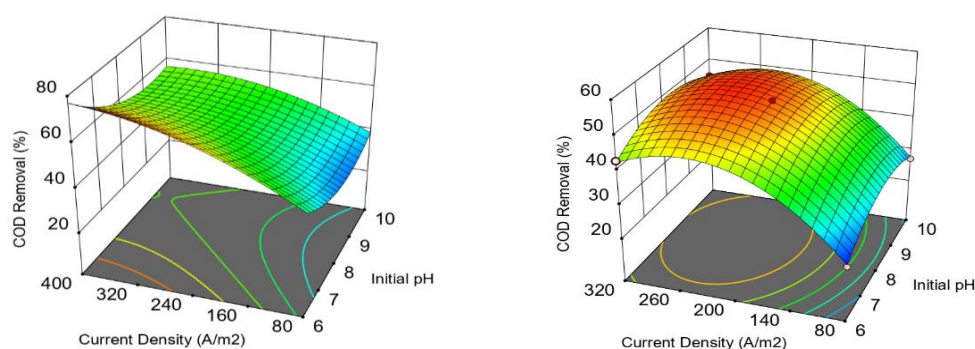
COD, TOC and NH<sub>4</sub> removal for RSM leachate were stated as modified quadratic models independent of electrode type and model equations were created each pollutant. The model equation and also 3D graph was created from RSM for COD for minimum cost and maximum remove condition were given below as an example.

### EC

$$\text{COD (\%)} = 52.15 + 1.54X_1 + 8.95X_2 + 7.46X_3 - 0.47X_1X_2 - 0.55X_1X_3 + 4.60X_2X_3 - 5.81X_1^2 - 11.78X_2^2 - 5.84X_3^2$$

### EO

$$\text{COD (\%)} = 50.85 - 6.98X_1 + 11.93X_2 + 7.20X_3 - 3.06X_1X_2 - 0.69X_1X_3 + 0.68X_2X_3 + 8.37 X_1^2 - 5.84X_2^2 - 1.72X_3^2$$



**Figure 1.** Surface plots of COD removal (Effects of current density and initial pH on COD removal).

Optimum conditions were pH: 8.6, current density: 219 A/m<sup>2</sup>, time: 35 min in electrocoagulation and under these conditions, COD, TOC and NH<sub>4</sub> removal efficiency were found as 50.5 %, 39.1 %, 28.8 % respectively. Moreover, the total operating cost was 4.69 \$/m<sup>3</sup>. On the other hand, for electro-oxidation optimum conditions were pH: 6.0 current density: 238 A/m<sup>2</sup>, time: 480 min. COD, TOC and NH<sub>4</sub> removal efficiency were found as 75.6 %, 52.5 %, 41.2 % respectively. Sequential electrocoagulation/electrochemical oxidation processes contributed to remove 87.9 % of COD, 71.0 % TOC, and 58.1 % of NH<sub>4</sub> from leachate. The model was used both effective remove and minimizing cost thus the overall cost was these process was 13.42 \$/m<sup>3</sup>. The high amount of organic compound was mineralized by using combined EC-EO treatment in reasonable time and operating cost.

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## Development of Energy-Saving Ferritisation Treatment of Zinc-Containing Electroplating Wastewater

B. M. Yemchura\*, G. M. Kochetov\*, D. M. Samchenko\*, and D. W. Pakhomov\*

\* National University of Construction and Architecture, Povitroflotsky Pr. 31, 03680, Kyiv, Ukraine (E-mails: [yemchura.b.m@gmail.com](mailto:yemchura.b.m@gmail.com); [gkochetov@gmail.com](mailto:gkochetov@gmail.com); [sama30071988@gmail.com](mailto:sama30071988@gmail.com); [pahomov4444@i.ua](mailto:pahomov4444@i.ua))

### INTRODUCTION

Heavy metals compounds belong to the most hazardous pollutants in wastewater flows of electroplating plants. Electroplating facilities generate substantial amount of zinc-containing wastewater and sludge, since zinc coatings are on the first place of application. This research study is dedicated to the development of the resource-saving technology for wastewater treatment of zinc electroplating facilities with low energy need. Analysis of existing methods of electroplating wastewater treatment suggests that the most commonly used reagent-based one is prone to low efficiency of heavy metals removal and to formation of unstable and bulky sediments (Fu and Qi, 2011). The most prospective option for introduction of the low-waste wastewater purification is associated with application of the method of ferritization. The method allows to get almost insoluble compounds of iron and zinc by wastewater treatment with an alkaline reagent and air oxygen (Kochetov *et al.*, 2018). In our previous studies the main operational parameters of the ferritization treatment were optimized. However, the effect of aeration rate on the ferritization process was not studied yet.

### MATERIALS AND METHODS

In the lab experiments treatment process was performed in concentrated wastewater of zinc electroplating units – exhausted electrolyte and other zinc-containing technological solutions with zinc concentrations  $\approx 300 \text{ g/dm}^3$  (Rubanov *et al.*, 2009). The laboratory installation was designed and used for the experiments of wastewater treatment by ferritisation at temperatures of 70 °C and aeration rate in the range from  $0.5 \text{ dm}^3/(\text{dm}^3 \text{ min})$  to  $3.5 \text{ dm}^3/(\text{dm}^3 \text{ min})$ .

Concentrations of metal ions were determined by spectrophotometer HACH DR-3900. Structural analysis of sediments was performed by powder X-ray diffraction with XRD-6000 automated diffractometer.

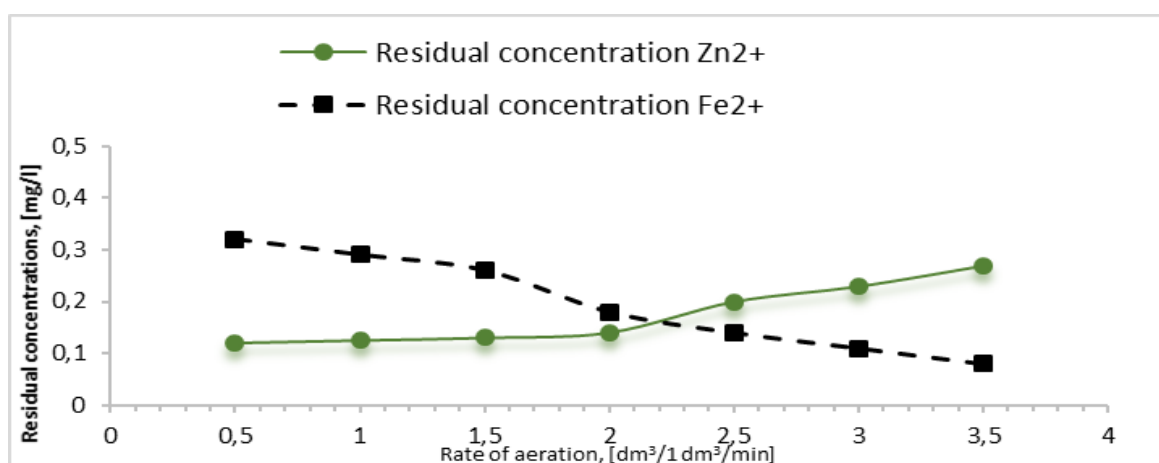
### RESULTS AND DISCUSSION

The results of removal of heavy metals from wastewater indicate that water after the ferritization treatment meets the applicable requirements for its use in industrial circulating water supply systems. The experimental data obtained suggest that with increasing aeration rates efficiency of zinc ions removal demonstrates some decrease. Efficiency of removal of iron ions from wastewater increases with increasing aeration rates.

Our research study has demonstrated that the most efficient results of the ferritization treatment were achieved at aeration rates in the range of  $0.5\text{--}1.5 \text{ dm}^3/(\text{dm}^3 \text{ min})$ , and the process duration of 15 minutes. At such process parameters, formation of stable solid ferromagnetic phases with a dispersed structure was observed. Such substances have well developed specific surface, ensuring their high adsorption capacity.

**Table 1.** Results of ferritization treatment of exhausted zinc electrolyte solution.

No.	Initial concentration, g/dm <sup>3</sup>		Rate of aeration, dm <sup>3</sup> /(dm <sup>3</sup> min)	Residual concentration, ±0.01 mg/dm <sup>3</sup>		MAC for rinsing water, mg/dm <sup>3</sup>	
	Zn <sup>2+</sup>	Fe <sup>2+</sup>		Zn <sup>2+</sup>	Fe <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sup>2+</sup>
1	3.2	16.0	0.5	0.12	0.32		
2	3.2	16.0	1.0	0.125	0.29		
3	3.2	16.0	1.5	0.13	0.26		
4	3.2	16.0	2.0	0.14	0.18	5.0	0.3
5	3.2	16.0	2.5	0.20	0.14		
6	3.2	16.0	3.0	0.23	0.11		

**Figure 1.** Dependence of residual concentrations of HMIs on aeration rates.

## CONCLUSIONS

As a result, levels of residual concentrations of HMIs in treated wastewater meet the applicable requirements for reuse of the treatment effluents in industrial circulating water supply systems.

Also, running of the ferritization process at low aeration rate makes it possible to use less powerful air compressor equipment, which in turn lowers operating costs for electricity. In addition, according to our previous research studies, it is possible to mix obtained sediments with alkaline concrete for their safe utilization.

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# CuO-NMs/Peroxymonosulfate Oxidation System for Optimization of Rhodamine B Removal Employing Taguchi Experimental Design

X. Yu\*, M. Kamali\*, P. Van Aken\*, B. Van der Bruggen\*\*, and R. Dewil\*

\* Department of Chemical Engineering, KU Leuven, De Nayerlaan 5, Sint-Katelijne-Waver 2860, Belgium (E-mails: [xiaobin.yu@kuleuven.be](mailto:xiaobin.yu@kuleuven.be); [raf.dewil@kuleuven.be](mailto:raf.dewil@kuleuven.be))

\*\* Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200F, Leuven 001, Belgium

## INTRODUCTION

Sulfate radicals (SRs) have been rapidly developed and used in recent years in advanced oxidation processes (AOPs) for the degradation of a number of recalcitrant and emerging environmental contaminants. SRs can be generated from oxidation agents (OAs) such as peroxymonosulfate (PMS) or persulfate (PS) already activated either by external sources such as heat and ultraviolet, or catalysts such as metal-based nanomaterials (Giannakis *et al.*, 2020). In this regard, metal oxides nanomaterials have received enormous attention for the activation of OAs due to some unique properties such as high specific surface areas and porous structures. Cheap and non-toxic nanomaterials such as CuO can also satisfy the sustainability considerations which can promote their wider applications for real scale wastewater treatment purposes. In this study, CuO nanoparticles was prepared through an ultrasonic assisted precipitation method for the activation of PMS towards Rhodamine B (Rh-B) degradation.

## EXPERIMENTAL DESIGN

A Taguchi L9 statistical design (Kamali *et al.*, 2019) was employed in order to identify the effects of operational parameters on the removal of Rh-B using CuO-NMs/PMS oxidation system. experiments designed are presented in Table 1.

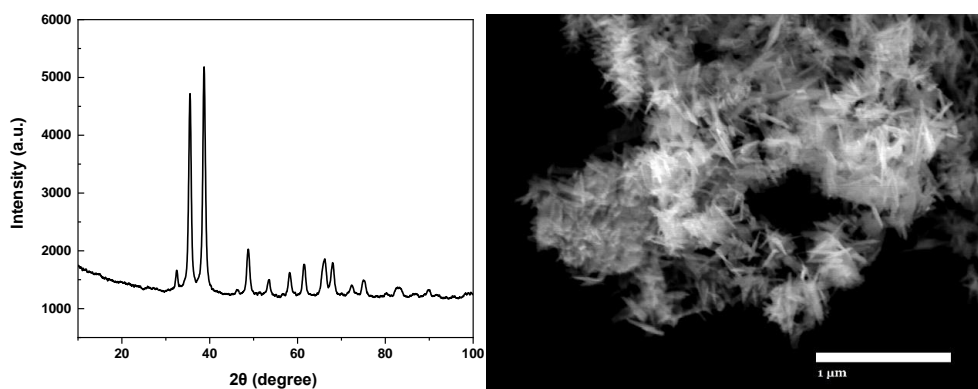
**Table 1.** L-9 orthogonal array of experiments including as studied variables oxidation system, initial solution pH and initial Rh-B concentration.

Run	System	Initial pH	Initial Rh-B concentration, mg/L
1	CuO	3	100
2	CuO	7	200
3	CuO	10	500
4	PMS	3	200
5	PMS	7	500
6	PMS	10	100
7	CuO/PMS	3	500
8	CuO/PMS	7	100
9	CuO/PMS	10	200

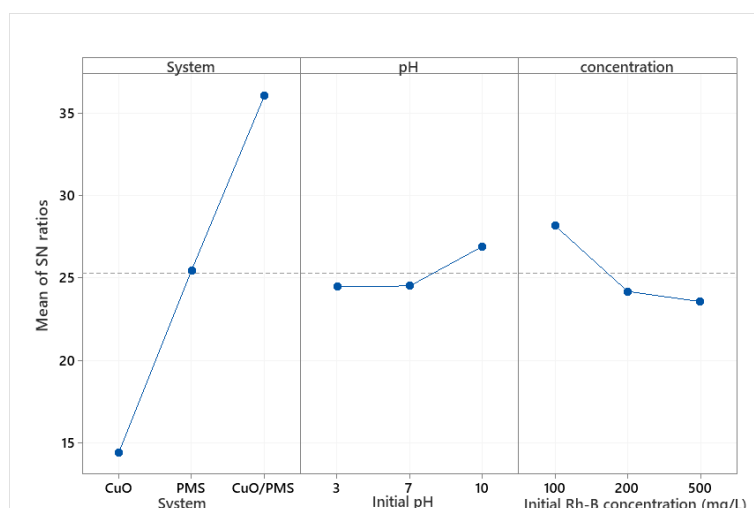
## RESULTS

### Characterization of the nanomaterials

The powders prepared were characterized using various techniques. X-ray diffraction pattern achieved is well matched with the standard XRD pattern of copper oxide (JCPDS 89-2529). Besides, the scanning electron microscopy revealed that CuO NPs are needle shape (around 100 nm in length and few nanometres in diameter with a narrow range of size distribution).



**Figure 1.** XRD pattern (Left) and SEM image (right) of CuO nanomaterials prepared.



**Figure 2.** Variation of the calculated S/N ratios.

Fig. 2 illustrates the results achieved when Taguchi experimental design was applied for the optimization of the treatment process. In this figure, signal-to-noise ( $S/N$ ) ratios demonstrate the relative importance of the studied parameters. Under optimum condition of CuO/PMS combination, initial pH of 10 (which can be attributed to more fraction of  $\text{HSO}_5^-$  instead of  $\text{H}_2\text{SO}_5$  at higher pH) and initial Rh-B concentration (100 mg/L), 92 % removal of the studied dye was observed.

## CONCLUSION

- Needle-shaped CuO NPs was synthesized using a facile method employing ultrasonic irradiation.
- Taguchi experimental design was employed in order to optimize the experimental parameters.
- The optimal conditions for Rh-B removal in CuO/PMS system were identified at pH of 10 and initial Rh-B concentration of 100 mg/L at fixed dosage of CuO and PMS.

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# Urban Runoff Quality: Preliminary Results of Case Study from Three Latvian Municipalities

M. Zemīte\*, G. Dakša\*,\*\*, V. Urbanovičs\*, and J. Rubulis\*

\* Faculty of Civil Engineering, Riga Technical University, Kalku Street 1, Riga, Latvia, LV-1050  
(E-mails: *Gints.Daksa@rtu.lv*; *Valts.Urbanovics@rtu.lv*; *Marta.Zemite@rtu.lv*;  
*Janis.Rubulis@rtu.lv*)

\*\* Jūrmalas Ūdens Ltd., Promenādes Street 1a, Jūrmala, Latvia, LV-2015

## INTRODUCTION

Urban runoff consists of various pollutants, such as solids, biodegradable organic matter, heavy metals, micropollutants, pathogens, and nutrients, originating from wet and dry deposition, vehicle tire wear, vegetation, animal excretion and corpses, fertilizers, and exhaust gases (Barbosa, 2012). Some pollutants can be toxic and can cause health impacts including neurological and carcinogenic effects (Bocca, 2004; Hamers, 2002). Therefore, it is important to monitor runoff water quality and take appropriate actions to ensure no potential pollution hazards to receiving waters.

## MATERIALS AND METHODS

Three municipalities were used to determine urban runoff quality alongside hydraulic model build-up: Liepāja, Jūrmala and Ogre. Stormwater runoff samples were collected in the final section of catchment's drainage network. Sampling was performed in the final reachable manhole before discharge into water body. If possible, a flowing dry-weather sample was collected, representing stormwater non-related inflows, i.e., groundwater drainage system.

Various physical, chemical and microbiological parameters were analysed in accredited laboratory by standard methods for water and wastewater analyses or other well-known conventional methods.

## RESULTS AND DISCUSSION

The results of stormwater runoff collected from the inflow pipeline of final accessible manhole during rain event are summarised in Table 1.

**Table 1.** Minimum, maximum and average values of stormwater drainage water quality results from Liepāja, Jūrmala and Ogre.

Parameter	Min	Max	Average
pH	7.43	7.74	7.54
$t$ , °C	14.40	16.20	15.17
EC, µS/cm	615.00	919.00	784.33
BOD <sub>5</sub> , mg/L	3.08	7.27	5.43
SS, mg/L	10.30	32.00	23.10
DOC, mg/L	0.00	18.85	6.88
TOC, mg/L	1.10	19.67	7.35
N/NH <sub>4</sub> , mg/L	0.03	6.94	2.33
N/NO <sub>2</sub> + N/NO <sub>3</sub> , mg/L	1.10	3.41	2.53
N tot., mg/L	1.61	10.60	5.69
P/PO <sub>4</sub> , mg/L	0.11	0.45	0.32

Parameter	Min	Max	Average
P tot., mg/L	0.14	1.97	0.93
Al, mg/L	0.01	0.09	0.04
As, µg/L		Not detected	
B, mg/L	0.08	0.20	0.13
Ca, mg/L	55.80	80.40	64.43
Cd, µg/L	<0.12	0.25	–
Cr, µg/L	3.26	5.22	4.19
Cu, µg/L	6.26	15.60	11.12
Fe, mg/L	0.90	2.42	1.63
K, mg/L	9.00	13.20	10.43
Mg, mg/L	7.61	21.40	15.87
Mn, mg/L	0.09	0.18	0.13
Na, mg/L	49.10	81.10	61.83
Ni, µg/L	4.03	5.99	4.92
Dissolved P, mg/L	0.12	0.60	0.42
Pb, µg/L	<0.9	2.20	–
SO <sub>4</sub> , mg/L	27.80	55.90	38.67
Si, mg/L	2.48	5.21	4.15
Zn, mg/L	0.11	0.14	0.12
<i>E. coli</i> , CFU or MPN / 100 mL	$4.00 \times 10^2$	$9.00 \times 10^4$	$3.10 \times 10^4$
Coliforms, CFU or MPN / 100 mL	$9.61 \times 10^3$	$5.00 \times 10^6$	$1.68 \times 10^6$
OI, mg/L	<0.02	0.12	–

## CONCLUSIONS

To ensure pollution free watersheds, it is extremely important to eliminate all contamination sources. Urban stormwater drainage system with direct discharge into water body is an important pollution source, therefore it is important to perform monitoring and apply further treatment measures for the flow it carries.

## ACKNOWLEDGEMENTS

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# Designing Web-App for Decision Support System for Upgrading Slum Sanitation

D. P. Apriadi\* and M. Barjenbruch\*

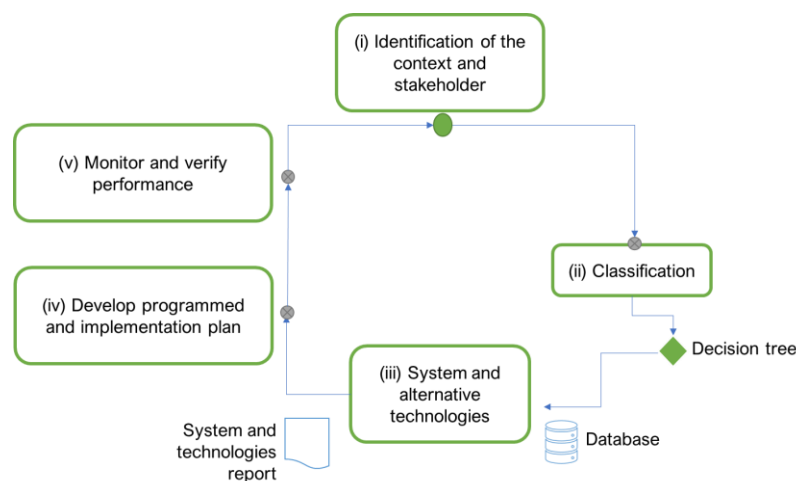
\* Department of Urban Water Management, Technical University of Berlin, Gustav-Meyer-alle 25, Berlin 13355, Germany (E-mails: [d.apriadi@campus.tu-berlin.de](mailto:d.apriadi@campus.tu-berlin.de); [matthias.barjenbruch@tu-berlin.de](mailto:matthias.barjenbruch@tu-berlin.de))

## INTRODUCTION

One of the biggest challenges of slum areas is the lack of adequate sanitation facilities. There is no best-fit-all solution to upgrading slums and to improving their sanitation facilities. Sanitation systems should be understood systematically. This study aims to create an interactive web-based platform to select sanitation technologies for slum areas. The platform will host a Decision Support System (DSS) and will be referred to as UPSS (“Upgrading Slum Sanitation”). The first screen will help identifying the slum classification (high, middle and low slum) by asking the user several questions. The following screens will identify alternative sanitation technologies. The sanitation technologies suggested by UPSS are based on the sanitation chain concept. UPSS will guide stakeholders capturing relevant data about their specific case and determining proper sanitation technologies. The complexity of sanitation systems creates a need for simplification. UPSS can be an answer to that.

## DATA/METHODOLOGY

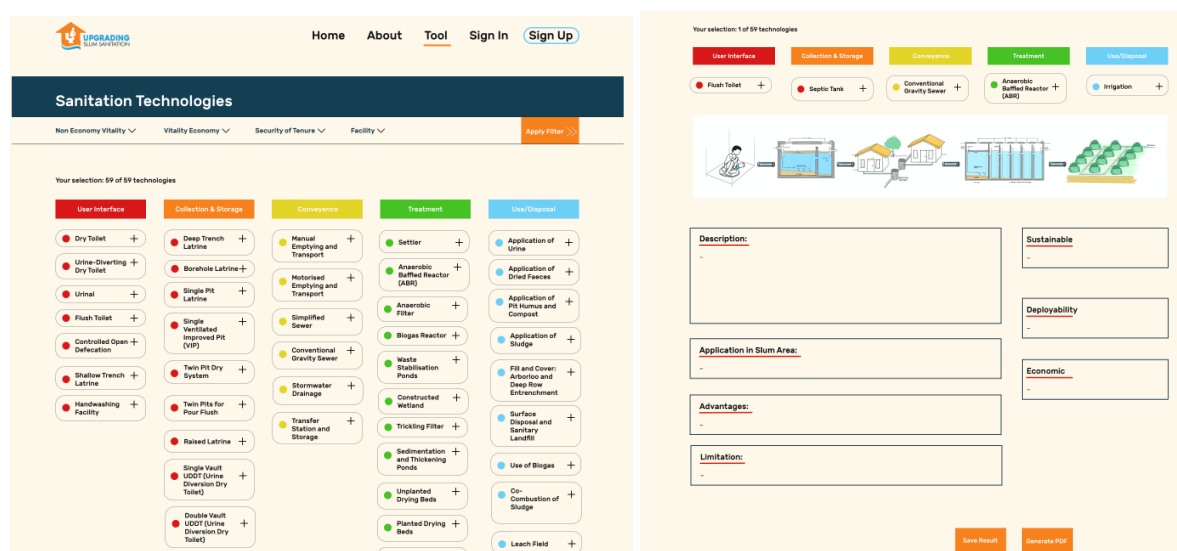
This research was conducted in the following phases: (i) review of urban slum sanitation technology and selection criteria to be included in the slum areas; (ii) development the DSS conceptual framework; (iii) web-app designing. Through the literature review, slum upgrading will be explained, the sanitation option in use or feasible in slum area would be classified and decision making influencing factors will be detected and considered in selection criteria. The design of the decision support system would then be translated into computer program. In this case, the computer program would be web-based bases.



**Figure 1.** The conceptual of DSS.

## RESULT AND FINDING

(Simiyu *et al.*, 2017) explained sanitation decision were typical with decision to invest in or construct sanitation facilities, to repair sanitation facility, to empty sanitation facility and on maintenance (cleaning) of sanitation facilities. The sanitation technologies have been used in slum area contexted. The selected technologies are further classified considering the steps of the sanitation chain concept. After all the steps, the interactive web-based platform was designed. It referred to as UPSS (Upgrading Slum Sanitation). The first screen will help identify the slum classification and following stage with screening sanitation technologies. The final decision regarding the provision of the most appropriate alternative entirely depends on the user.



**Figure 2.** User interface from UPSS.

A sanitation chain consists of several individual sanitation processes introduced in a logical order. Which are: (1) processes for excreta disposal and collection from the user-interface; (2) processes for excreta to conveyance (collection and transport); (3) processes for treatment until final disposal or reuse (treatment or disposal and reuse). In UPSS, the user needs to answer several the questionnaires that provided in the web-app, after all the final report is the output of the DSS. The final report aims at comparing the advantages and limitation of potential sanitation alternative in slum area.

## CONCLUSIONS

The development of web-app can encourage the knowledge of relevant stakeholder. A web-app is a useful tool for selecting suitable sanitation alternatives to be provided for slum areas, especially with user friendly interface. In addition, the computer – based DSS is flexible considering that each different user can introduce the stakeholder’s inputs depending on personal input.

## ACKNOWLEDGMENT

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# Naphthalene Mineralization by Supercritical Water Oxidation and Determination of By-Products Using Non-Target Analysis

H. Ates\*, M. E. Argun\*, and N. Kurt\*\*

\* Konya Technical University, Faculty of Engineering and Natural Science, Department of Environmental Engineering, Konya, Turkey (E-mails: [hates@ktun.edu.tr](mailto:hates@ktun.edu.tr); [meargun@ktun.edu.tr](mailto:meargun@ktun.edu.tr))

\*\* Konya Technical University, Institution of Graduate Education, Department of Environmental Engineering, Konya, Turkey (E-mail: [nazif.kurt94@gmail.com](mailto:nazif.kurt94@gmail.com))

## INTRODUCTION

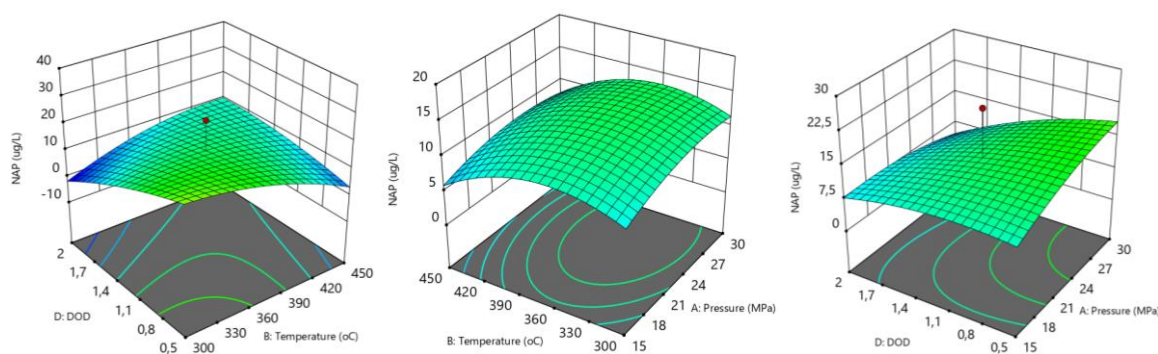
Among the polycyclic aromatic hydrocarbon (PAHs), naphthalene has been detected in the highest concentration between 0.01–15 µg/L in many aquatic environments (Ates and Argun, 2019; Kalmykova *et al.*; 2014, Oturan *et al.*; 2015, Staples *et al.*, 1985). In recent years, micropollutants have attracted significant attention because of their toxicity and possible carcinogenic and mutagenic properties. Due to its bio-resistance and toxic properties, micropollutants cannot be completely treated in conventional processes with microbiological activities. So, advanced oxidation processes (AOPs) have become a promising alternative for the mineralization of resistant organic compounds. However, further research is still needed to identify the final products of AOPs. Supercritical Water Oxidation (SCWO) is defined as one of the most effective and green treatment methods to remove refractory compounds. In this study, the fate of naphthalene which is European Union priority pollutant was investigated under the conditions of SCWO. Also, effectiveness of different operating conditions including pressure, temperature, reaction time and oxidant dose on the formation of by-products were determined.

## MATERIAL AND METHODS

Experiments were performed by SCWO with a capacity of 250 mL/min. Naphthalene solution was prepared at a concentration of 0.5 mg/L. Both quantitative analysis of naphthalene and qualitative analyses of final products were analysed by gas chromatography-mass spectrometry. Working conditions were prepared with a design expert program. The effect of four independent variables was examined with 27 runs (experiment) by using a central composite design. Treatment of naphthalene aqueous solution by SCWO was performed in the range of 250–500 °C, 3–20 min, 10–35 MPa and 0.1–2.5 DOD (dimensionless oxygen dose).

## RESULT AND DISCUSSION

The relationships between naphthalene removal and the four operating variables including temperature, pressure, time and oxidant dose were analysed for the SCWO process using response surface methodology (RSM). The model was found significant at the 5 % confidence level since the *p*-value was less than 0.05. Also, the individual effect of oxidant dose, the interaction effect of temperature and oxidant dose and second-order effect of the time were found significant on the removal of naphthalene by ANOVA test. The results of the model calculated by RSM and obtained model data were given in Table 1 and Fig. 1, respectively. According to the obtained results, naphthalene was removed between 93 % and 100 %. The minimum naphthalene removal (93 %) was obtained under the lower reaction time and oxidant dose (5 min, 0.5 DOD) at 300 °C and 30 MPa. Naphthalene was removed entirely in the operating conditions of 2.0 DOD and 15 min of reaction time for the same temperature and pressure values. Also, the degradation of naphthalene increased as the oxidant concentration increased.



**Figure 1.** Effects of independent variables on the remained naphthalene.

**Table 1.** ANOVA analysis of parameters and model.

Source	Model	A – Pressure	B – Temperature	C – Time	D – DOD	BD	C <sup>2</sup>	Lack of Fit
	<b>Significant</b>							<b>Not significant</b>
F-value	3.12	0.6110	0.6656	0.0000	<b>6.30</b>	<b>15.91</b>	<b>6.52</b>	0.2774
p-value	0.0457	0.4545	0.4356	0.9949	<b>0.0333</b>	<b>0.0032</b>	<b>0.0310</b>	0.9161

Mineralization of naphthalene by SCWO was observed to be very high for all experiments and the ratio of transformation products of naphthalene was determined as <1 %. Not only oxidation products but also thermal cracking by-products were identified throughout the treatment with non-target analysis. Some detected by-products in treated samples were benzene (with thermal cracking), p-benzoquinone, benzene acetic acid, 2,4,6-trihydroxybenzaldehyde, etc. (with oxidation). Table 2 shows both partial and full mineralization rates of naphthalene in some experimental.

**Table 2.** Mineralization and partial mineralization rates of naphthalene under some conditions.

Operation conditions	300 °C, 5 min, 0.5 DO MPa,	375 °C, 10 min, 1.25 MPa,	375 °C, 10 min, 1.25 MPa,	450 °C, 5 min, 2.0 MPa,	375 °C, 3 min, 1.25 MPa,	300 °C, 15 min, 0.5 MPa,	300 °C, 15 min, 0.5 MPa,
Mineralization, %	92.83	98.34	96.86	98.00	94.22	90.03	93.36
Partial mineralization, %	0.07	0.56	0.04	0.00	0.14	5.17	0.47
Unreacted, %	7.10	1.10	3.1	2.00	5.64	4.80	6.17

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## Effects of Organic Carbon Content on In-Situ Remediation Time Using Steam-Air Injection

W. Awandu\* and O. Trötschler\*\*

\* Department of Civil and Structural Engineering, Masinde Muliro University of Science and Technology, P.O BOX 190-50100, Kakamega – Webuye Road, Kakamega, Kenya (E-mail: [Awandu.willis@gmail.com](mailto:Awandu.willis@gmail.com))

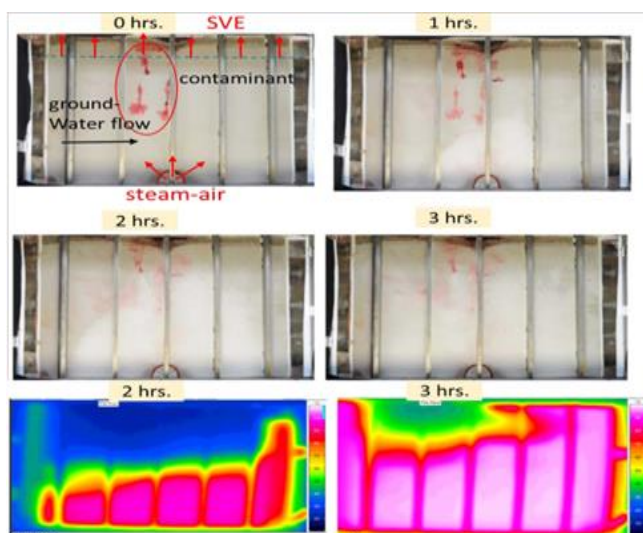
\*\* VEGAS, Universität Stuttgart, Pfaffenwaldring 61, 70569, Stuttgart, Germany (E-mail: [oliver.troetschler@iws.uni-stuttgart.de](mailto:oliver.troetschler@iws.uni-stuttgart.de))

### INTRODUCTION

A contamination with chlorinated hydrocarbons in the saturated and vadose zones threatens the groundwater sources. Thermally enhanced soil vapour extraction (TSVE) using steam-air injection has been proposed as an alternative technique (Trötschler and Weber, 2003) over traditional techniques such as pump and treat (Ochs *et al.*, 2003), to remediate contaminated soils. The application of thermally enhanced in-situ remediation is summarized in a Task Centre, UFZ Leipzig guideline (Hiester *et al.*, 2012). VEGAS, a research facility at the University Stuttgart, has conducted several pilot tests and designed and supervised several full-scale remediation systems in low permeable soils, fractured bedrock and fully saturated alluvial sediments (Trötschler *et al.*, 2019). The heat and mass fluxes of the remediation sequences and steps of the remediation design were perfectly met in the real-world scenario. The contaminant removal rates were always lower than predicted (DLI-Tool, <https://www.iws.uni-stuttgart.de/en/vegas/downloads/>). The presence of organic carbon (OC) in soils increases the adsorption of the Chlorohydrocarbons (CHC) onto the soil matrices thereby decreasing the thermal desorption rates. The dependency of the CHC-desorption-rates during steam-air injection (DLI) in 2-D remediation experiments was defined for variable soil types (e.g. sand, gravel, silt) and OC contents of 1 % and 2 %.

### EXPERIMENTAL DESCRIPTION

The laboratory 2-D Flume (box with glass) experiment was performed using 100 kg of sandy and silty soils, varying the organic matter content. TCE and PCE as CHC was used as contaminants of the source zone for the TISR with convective heat transport.



**Figure 3.** 2-D remediation process of fine sand (contaminant removal/heat propagation) (Trötschler *et al.*, 2019).

Temperature sensors were located in the target zone in a 5 cm regular spacing to monitor the heat distribution and to control the remediation process.

The contaminant retention/desorption from the soil was regularly analysed by a GC-PID (meta GmbH) to determine the mass removal rates in the extracted hot soil vapour. The remediation steps were determined from the measurement of the heat and mass fluxes of the applied remediation and treatment installation.

## RESULTS

**Table 1.** Determination of retardation factor (2-D Flume Experiments)

Soil type	Organic carbon content, %	Organic carbon realized, %	Contaminants	Retardation factor $R$
Fine sand $K = 1 \times 10^{-4}$ m/s	0–0.5–1–2	0–1–2	TCE, PCE	1–2.5–6.5
Coarse sand $K = 5 \times 10^{-4}$ m/s	0–0.5–1–2	0–1–2	TCE, PCE	1–3.3–6.8
Sandy silt $K = 3 \times 10^{-5}$ m/s	0–0.5–1–2	0–1	TCE, PCE	1–4.2

## DISCUSSION

A mixture of steam-air was injected from the bottom of the flume to heat up the soil to a co-boiling temperature of 85 °C → 100 °C. At 85 °C the co-boiling of the contaminants and water begins. The temperature rises as the contaminants are removed during the ongoing heating. The steam propagates and extends, so the contaminants removal begins. The added air provided the transport of the gaseous contaminants towards the upper and laterally located (hot) soil vapour extraction wells. The remediation process was stopped when the concentration of the contaminants in the hot soil vapour falls below the remediation goal of approx. 20 mg/m<sup>3</sup> CHC.

The retardation factor of 1.0 indicates the absence of organic carbon in the soils. A factor that is greater than 1.0 indicates the reduction of the contaminant desorption process. TCE has an octanol/water partition coefficient ( $K_{OW}$ ) of 2.42 while PCE has a coefficient of 2.88. So PCE is better adsorbed on the OC. The Henry coefficient  $H_{cc}$  of TCE is 0.392 (25 °C) and that of PCE is 0.723 (25 °C) but the aqueous solubility of TCE (1100 mg/L, 25 °C) is appr. 7× higher than that of PCE (151 mg/L, 25 °C). So PCE will remain longer in the aqueous phase compared to TCE.

The slower removal of the contaminant mixture resulted from PCE having a higher hydrophobic sorption of the chemical onto the organic phase of the porous media. Generally, the retardation of TCE is 20–40 % lower than that of PCE. Similar factors were found during the full scale remediations.

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## **Spatial Definition of Slatina Sandstones Using GIS Tools to Prove and Develop the Geothermal Potential in the City of Virovitica, North Croatia**

T. Bilić\*, D. Tumara\*\*, S. Kolbah\*\*\*, and M. Škrlec\*\*\*

\* Geotermalni izvori d.o.o., Vladimira Nazora 3, 32276 Babina Greda, Croatia  
(E-mail: [tena.bilic@gmail.com](mailto:tena.bilic@gmail.com))

\*\* Energetski institut Hrvoje Požar, 10 000 Zagreb, Croatia (E-mail: [dtumara@eihp.hr](mailto:dtumara@eihp.hr))

\*\*\* Geotermalna energija d.o.o., 10 000 Zagreb, Croatia (E-mail: [skolbah@gmail.com](mailto:skolbah@gmail.com);  
[mladen.skrlec@gmail.com](mailto:mladen.skrlec@gmail.com))

### **INTRODUCTION**

Low enthalpy geothermal water for direct utilisation in North Croatia is comparatively favourably accessible and abundant. This type of energy is constant, renewable, low – carbon and without almost any negative environmental impact. The great geothermal potential in Croatia has been originally indicated by more than 25 thermal springs and confirmed during intense hydrocarbon exploration and production by the INA company, by drilling more than 4000 deep wells. It led to the discovery of several geothermal fields for direct utilization, and the possible potential is estimate 1/3 of country demands (Kolbah and Škrlec, 2018) and one geothermal field for the electric power generation. One of these, Velika Ciglena which is, at the moment, the largest Kalina geothermal power plant operating in Europe (Živković, 2019). Within this paper, one segment of the broad application of specially organized Geographic Information System (GIS) technologies will be presented to ease procedures and decrease geological and technical risk in finding and developing the most attractive part of enormous untapped geothermal potential.

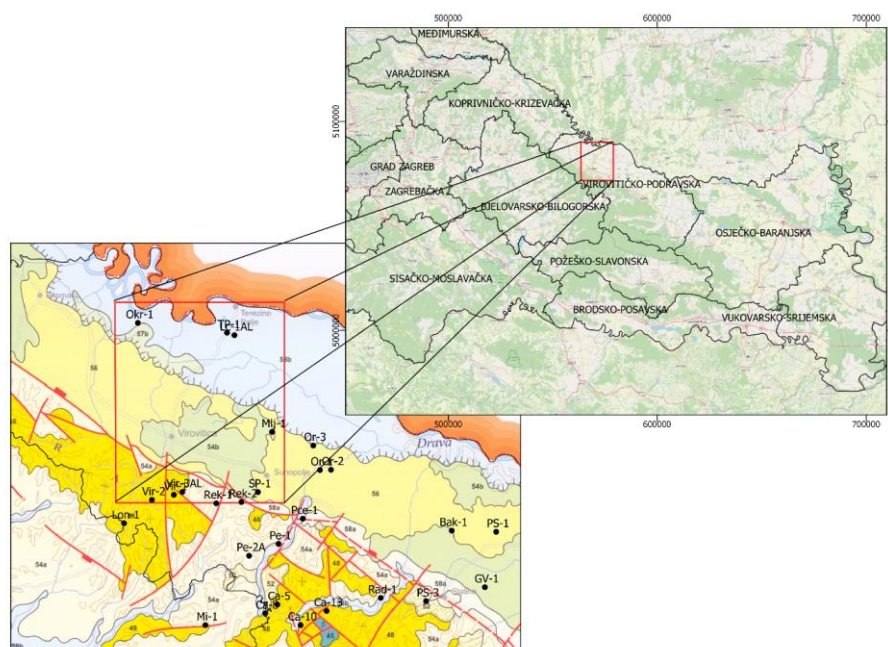
### **DISCUSSION**

Within this paper, the observed area is located around the city of Virovitica in the Virovitica-Podravina county (County), settled in the North-Eastern part of the Republic of Croatia. The County is characterised by two main ranges: the Podravina flatlands at the NE, and the Bilogora hills and Papuk highs at the SW.

Geologically, the observed area represents a segment of the Croatian part of the Pannonian basin system (CPBS), settled in the central part of the Drava depression. The deepest depocenter in the CPBS where Neogene-quaternary sediments are reaching a thickness of 7000 m in the vicinity of the city of Virovitica. Therefore, for direct utilization, the youngest permeable sandy reservoirs with geothermal water are targeted.

There, during the hydrocarbon exploration, a high geothermal gradient around 50 °C/km has been discovered. What leads that, at the depths beneath 1000 m, in the Slatina sandstones, we find geothermal water with temperatures above 70 °C, as well as possible production capacity up to 20 s<sup>-1</sup> (Kolbah, 1976). Thanks to the GIS technology possibilities, where large amounts of data sets can be easily stored and accessed, the deep structural top and bottom maps of a Slatina sandstone reservoir can be precisely modelled and presented. In this study, it was done for more certain determination of the optimal location and characterisation of the future exploration and exploitation well for utilisation of the geothermal energy. The emphasis was on the geological and tectonic settings, first time distinguished in a general geothermal potential overview in the area of the city of Virovitica (Kolbah and Škrlec, 2015) and developed by the recent drilling project. Based on the

interpretation of the geological-geophysical characteristics, the maps contain structural and geological settings of the area. Also, they show the impact of the tectonic activity of a large reverse fault zone and their side structural effects on the geothermal reservoir. Both maps are generated using GIS software. The location of the well was determined based on the results of the interpretation of the available data. GIS technologies enable dealing with available data in standard formats, opensource digital maps and other existing data obtained from the specialised agencies. The geological and geophysical surveys, as a subject of analyses and interpretations, will be presented in the form of the resulting maps, to minimize the geological-technological risk of finding the geothermal source, as well as testing it and using it.



**Figure 1.** Observed area of Virovitica-Podravina county.

## CONCLUSION

The observed area is characterized by the geothermal potential suitable for direct utilization. In this paper, the GIS software was used to analyse, interpret and present the results of the geological and geophysical surveys and deep drilling. Using GIS software, the maps of the top and bottom of the geothermal reservoir were generated, forming the special data basis ready for further development of the project. These maps can be crucial in the geothermal development of the area by confirming the existence of the geothermal source of energy. GIS technology is used to raise the ability and accuracy of confirming the existence of this source of energy. These maps could support the growth of geothermal energy share for industrial, agricultural and other purposes which could have a beneficial impact on the sustainable development of the city of Virovitica and its surroundings.

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## Evaluation of Rivers Renaturalization in Reference to Ecological Potential

J. Gervytė\*, L. Bagdžiūnaitė-Litvinaitienė\*, and A. Litvinaitis\*

\* Department of Environment Protection and Water Engineering, Faculty of Environmental Engineering, Vilnius Gediminas Technical University, Saulėtekio al. 11, Vilnius, Lithuania  
(E-mails: [justina.gervyte@stud.vgtu.lt](mailto:justina.gervyte@stud.vgtu.lt); [lina.litvinaitiene@stud.vgtu.lt](mailto:lina.litvinaitiene@stud.vgtu.lt); [andrius.litvinaitis@vgtu.lt](mailto:andrius.litvinaitis@vgtu.lt))

### INTRODUCTION

Drainage works caused irreversible changes to the river ecosystem to better conditions for agricultural activities during the 20th century. The natural riverbeds were destroyed and have been transformed into receivers of drainage systems during drainage works. The straightening has changed the shape of the rivers and their slopes. In addition to this, their riverbeds have been deepened. Straightened rivers cannot function properly and they do not undergo self-cleaning processes, as a result, rivers with poor ecological potential we have. Disappearing habitats that are vital to various macrozoobenthos organisms, spawning fish, which is inhibiting species variety are in such rivers (Nijland and Cals, 2000). 4 methods of river restoration to improve ecological potentials are applied – self-naturalization, gentle renaturalization, partial renaturalization and renaturalization. From the environmental protection side, the most suitable way to restore the river is renaturalization, when there are used natural engineering facilities such as annuals, logs, and tree debris. Using these natural engineering facilities increase natural biodiversity, which would improve the ecological potential of rivers (Geguzis and Baublys, 2015). Renaturalization of riverbeds is important for the restoration of the natural river network. The aim of this study is to evaluate to efficiency of rivers renaturalization in reference to ecological potential.

### MATERIAL AND METHODS

The ecological potential of rivers was assessed for renaturalized and representative rivers sections of Vasuoka, Viesinta and Vyzuona. The latter are straightened due drainage works. The research rivers are located in northeastern Lithuania. The area of the Vasuoka river basin is 126 m<sup>2</sup>, Viesinta – 236 km<sup>2</sup>, and Vyzuona – 415 km<sup>2</sup>.

**Table 1.** Research sections of rivers in the LKS – 94 coordinate system (Re – renaturalized section of the river, Rp – representative section of the river).

River	River section	Segment start coordinates	Segment end coordinates
Viesinta	Re	X: 545830 Y: 6181879	X: 546637, Y: 6182429
	Rp	X: 549175, Y: 6177931	X: 548750, Y: 6178846
Vyzuona	Re	X: 598610, Y: 6218602	X: 599515, Y: 6218548
	Rp	X: 595363, Y: 6218998	X: 594368, Y: 6219155
Vasuoka	Re	X: 544959, Y: 6176463	X: 544085. Y: 6176525
	Rp	X: 547918; Y: 6173558	X: 547264; Y: 6174176

The ecological potential of rivers is assessed on the basis of the Minister of Environment of the Republic of Lithuania April 29 by order no. D1-210 “On Approval of the Methodology for Determining the Status of Surface Water Bodies”. This methodology has been developed taking

into account one of the most important water protection objectives for artificial and heavily modified surface water bodies – to achieve good ecological potential. The status of a surface water body is assessed in terms of ecological potential and chemical status. One of the elements of ecological potential assessment is biological, which includes: taxonomic composition, age structure of ichthyofauna, taxonomic composition of macrozoobenthos, abundance, macrophytes.

## RESULTS

After the research, biological quality elements were obtained – Lithuanian fish index LZI, macrophyte index UMEI, macrozoobenthos index UMI.

**Table 2.** Results of the biological quality elements (Re – renaturalized section of the river, Rp – representative section of the river)

River	River section	UMEI	LZI	UMI	Ecological potential
Vyzuona	Rp	0.035	0.353	0.510	Bad
	Re	0.100	0.520	0.560	Average
Viesinta	Rp	0.090	0.606	0.540	Bad
	Re	0.400	0.628	0.540	Average
Vasuoka	Rp	0.090	0.360	0.580	Bad
	Re	0.400	0.403	0.540	Average

LZI is an important indicator for assessing the species diversity of fish, which includes indicators of the water species of the fish species, which address the water damage caused by human economic activities (Research Center of nature, 2016). From 4 % to 32 % of LZI obtained in the renaturalized sections higher to representative sections. Also, from 65 % to 78 % higher in the renaturalized sections of the macrozoobenthic index UMEI. UMEI index is important for the river ecosystem because it reveals the species diversity of macroinvertebrates that is needed to ensure the functioning of the river ecosystem. Macrophytes are important indicators for the assessment of ecological status, as they improve the oxygen regime in water of rivers, which promotes better self-cleaning processes, as the oxygen required for aerobic interpretation increases in the bottom sediment layer (Environmental Protection Agency, 2010). The macrophyte index of UMI in Vyzuona in renaturalized section is 9 % higher than in a representative section. It was found no changes in Viesinta and Vasuoka rivers. This suggests that the process of renaturalization has already begun, but need more time to capture major changes.

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# Toxicity of Widely Used Pharmaceuticals to Aquatic Organisms

Ž. Griбанова\* and M. Balode\*\*

\* Department of Hydrobiology, Faculty of Biology, University of Latvia, Jelgavas st. 1, Riga, Latvia (E-mail: [zanna.gribanova@bior.lv](mailto:zanna.gribanova@bior.lv))

\*\* Department of Hydrobiology, Faculty of Biology, University of Latvia, Jelgavas st. 1, Riga, Latvia

## INTRODUCTION

In recent years, environmental pollution due to pharmaceuticals has been rapidly increasing (Stackelberg *et al.*, 2004). This attracts the attention of researchers since potentially bioactive pharmaceutical ingredients may significantly affect aquatic ecosystems, water quality as well as human health (Pomati *et al.*, 2008). Although information on the acute toxicity of the most popular drugs is available (Cleuvers, 2004), the results for some pharmaceuticals differ significantly. Furthermore, eco-toxicological information on environmental effects is available for less than 10 % of currently known pharmaceutical substances (Amiard-Triquet *et al.*, 2015).

## METHODS

Bioassays used for toxicity detection:

1. Freshwater algal growth inhibition test with unicellular green algae *Desmodesmus communis* (LVS EN ISO 8692: 2012), test duration – 72 h;
2. Acute toxicity test: inhibition of the mobility of *Daphnia magna* Straus (LVS EN ISO 6341: 2012), test duration – 48 h (additional tests with marine crustacean *Artemia salina*);
3. *Daphnia magna* reproduction test (OECD Nr. 211, 2012), test duration – 21 days.

**Table 1.** Tested pharmaceutical products and their applications

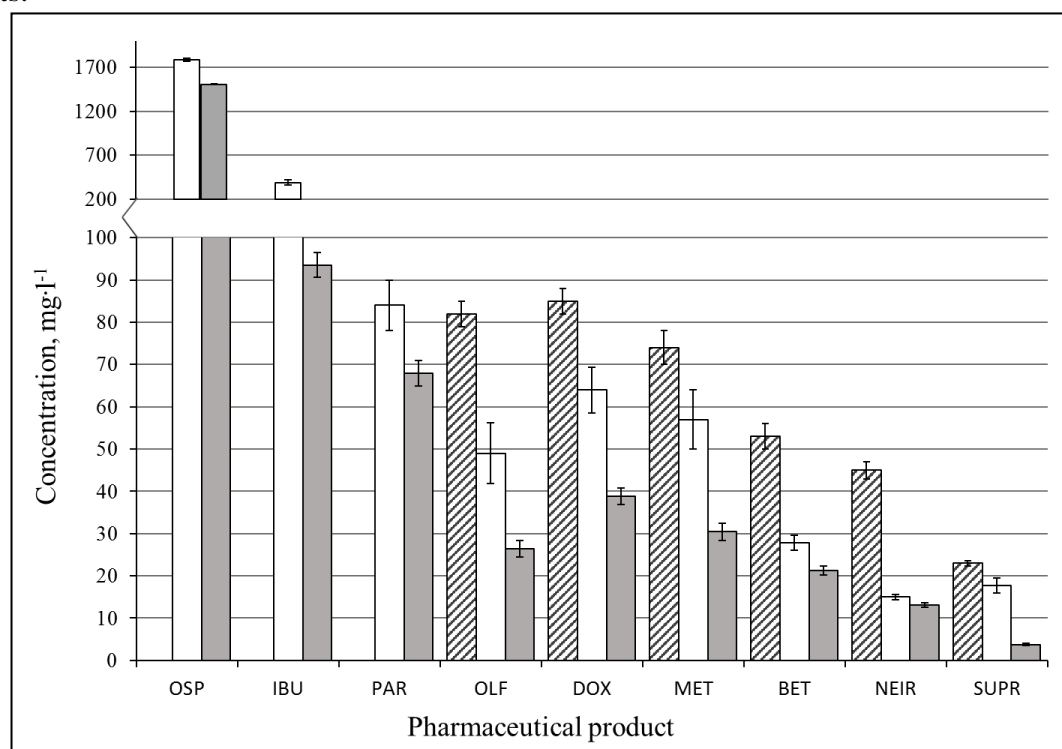
Pharmaceutical product	Active pharmaceutical ingredient (API)	Therapeutic class
“Ospamox”	Amoxicillin	Antibiotic
“Paracetamol”	Paracetamol	Analgesic, antipyretic drug
“Ibuprofen”	Ibuprofen	Nonsteroidal anti-inflammatory drug
“Olfen”	Diclofenac (Na salt)	Anti-inflammatory and antipyretic agent
“Suprastin”	Chloropyramine	Anti-allergic agent: antihistamine
“Betamaks”	Sulpiride	Antidepressant, neuroleptic agent
“Neiromidin”	Ipidacrine	NS stimulator
“Metforal”	Metformin	Biguanide (increases insulin production)
“Doxy-R-ratiofarm”	Doxycycline	Antibiotic

## RESULTS AND DISCUSSION

### Acute toxicity

The highest toxicity was demonstrated by “Suprastin” (pharmaceutical containing chloropyramine, anti-allergic agent), causing 50 % inhibition of tested organisms at concentrations ranging from 3 mg L<sup>-1</sup> (daphnia after 48 h) to 23 mg L<sup>-1</sup> (*A. salina* after 48 h). “Neiromidin” and “Betamax” that lacked eco-toxicological information also demonstrated high toxicity. Relatively low toxicity is shown by pharmaceuticals containing ibuprofen and antibiotic amoxicillin. Marine crustacean

*A. salina* demonstrated relatively low sensitivity, while *D. magna* was the most sensitive to toxicants.



**Figure 1.** LC<sub>50</sub> *A. salina* (striped columns), EC<sub>50</sub> *D. communis* (white columns) and LC<sub>50</sub> *D. magna* (grey columns) of tested pharmaceutical products (Keys: OSP – “Ospamox”, IBU – “Ibuprofen”, PAR – “Paracetamol”, OLF – “Olfen”, DOX – “Doxy-R-Ratiofarm”, MET – “Metforal”, BET – “Betamaks”, NEIR – “Neiromidin”, SUPR – “Suprastin”).

### Chronic toxicity

*Daphnia magna* reproduction tests demonstrated the highest toxicity of “Suprastin”, showing 50 % loss of *Daphnia* reproductive capacity already at a concentration of 0.25 mg L<sup>-1</sup>. Although in acute tests the product with doxycycline showed similar toxic effects with product containing metformin, in chronic tests it showed significantly higher toxicity (EC<sub>50</sub> – 3 mg L<sup>-1</sup>). Pharmaceutical products with metformin and paracetamol have medium chronic toxicity (EC<sub>50</sub> – 13 mg L<sup>-1</sup>).

Overall, long-term chronic tests showed significantly higher degree of toxicity than acute tests. Studies have shown that entering the hydro-ecosystems, many of tested drugs could significantly affect development of phytoplankton and zooplankton organisms, in particular endangering the outflow areas near pharmaceutical companies.

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## The Barsha Pump: One Way to (Cleanly) Lift Water, Many Ways to Deliver Smallholder Irrigation

J. C. Intriago Zambrano\*, J. Michavila\*\*, J. C. Diehl\*\*\*, and M. W. Ertsen\*

\* Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology. Stevinweg 1, 2628 CN Delft, Netherlands  
(E-mail: [J.C.IntriagoZambrano@tudelft.nl](mailto:J.C.IntriagoZambrano@tudelft.nl))

\*\* aQysta BV. Tel. +31 (0) 6 234 74757. Molengraaffsingel 12, 2629 JD Delft, Netherlands

\*\*\* Department of Design Engineering, Faculty of Industrial Design Engineering, Delft University of Technology. Landbergstraat 15, 2628 CE Delft, Netherlands

### INTRODUCTION

Enabling smallholders' access to irrigation water, and to its proper control and management, is one of the key interventions towards securing their production – hence potentially contributing to an increased food security – as well as to the improvement of their livelihoods (Burney and Naylor, 2012; Lowder *et al.*, 2016; Tschardt *et al.*, 2012). A way to achieve this goal is by implementing pressurized irrigation systems driven by water pumping technologies (WPTs). Given that many irrigation systems worldwide still operate on (too) cost-intensive and polluting electricity- or diesel-based pumps (Aliyu *et al.*, 2018; Chandel *et al.*, 2015), there is the potential to introduce more environmentally sound, and at times more affordable, renewable energy-based WPTs (Gopal *et al.*, 2013). Amongst these alternatives, hydro-powered pumps (HPP) present further advantages: more concentrated, continuous and predictable energy source; mechanically less complex and more robust; more cost-effective due to higher power-to-size ratio; and, typically more efficient. Nevertheless, their accessibility, successful implementation, and eventual scaling up lie much beyond their mere technical performance (Intriago Zambrano *et al.*, 2019).

The so-called Barsha pump (BP) – a waterwheel-driven manometric HPP – has become the first ever mass-produced, commercially available spiral pump, mainly intended for smallholder irrigation (Intriago Zambrano *et al.*, 2019). Though at the moment being used in a number of countries across five continents, the BP does not only still undergo many market challenges, as occurs to other WPTs (de Fraiture and Giordano, 2014; Namara *et al.*, 2014), but also has to face several on-field interpretations on how it should function related to (different) smallholders' actions and farming practices. Constraints related to the pumping benefits / technical performance, supply chains, financial affairs, ease of use, local knowledge, and even the presence of other WPTs have a(n) (in)direct influence on the acceptance and adoption of the BP. From this perspective, the main question addressed here is: which interventions ensure a better smallholder use of the BP?

### METHODOLOGY

A first part of the study was conducted face to face with smallholders between June and August 2019, in three and six different Nepali and Indonesian farming locations, respectively. Another part was carried out through online platforms with experts between April and August 2020. In total, the study included 43 individuals (19 smallholders and 24 experts).

Due to the nature of the study, which comprised several variables across a number of contexts and individuals, a triangulation of data collection techniques (e.g. direct observations, semi-structured interviews, surveys) was preferred, thereby allowing a better understanding of the integrated nature of farmers' attitudes towards the BP. The main research method was Q-methodology, an

increasingly popular inverted technique of factor analysis that combines the strengths of qualitative and quantitative research (ten Klooster *et al.*, 2008). One of its main advantages is that representativeness of the subjectivity does not depend on large samples of respondents, but rather on their diversity.

## RESULTS

On the basis of the collected evidence and further data processing, it was possible to map the current strong and weak relations between the smallholders and the BPs under a set of different contexts. Moreover, it enabled the identification of improvement opportunities to strengthen those relations, thereby ensuring: 1) an improved smallholder's BP-supplied water access and control; 2) a more sustained use of a reliable, low-cost and environmentally sound WPT; and, 3) a more (financially) sustainable business model for the technology supplier.

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## SentiLake: Development of Sentinel-2 Satellite Data-Based Service for Water Quality Monitoring in Latvian Lakes

D. Jakovels\*, A. Brauns\*, J. Filipovs\*, A. Vecvanags\*, and T. Soomets\*

\* Institute for Environmental Solutions, "Lidlauks", Priekule county/parish, LV-4126, Latvia  
(E-mail: [dainis.jakovels@videsinstitut.lv](mailto:dainis.jakovels@videsinstitut.lv))

### INTRODUCTION

Lakes and reservoirs are important ecosystems providing services such as drinking water, recreation, support for biodiversity as well as regulation of carbon cycling and climate. There are about 117 million lakes in the world and a high need for regular monitoring of their water quality. The European Union Water Framework Directive (WFD) stipulates that member states shall establish a programme for monitoring the ecological status of all water bodies larger than 50 ha, in order to ensure future quality and quantity of inland waters. But only a fraction of lakes are included in *in situ* monitoring networks due to limited resources. In Latvia, there are 2256 lakes larger than 1 ha covering 1.5 % of Latvian territory, and approximately 300 lakes are larger than 50 ha, but only 180 are included in Inland water monitoring program, in addition, most of them are monitored once in three to six years. Besides, local municipalities are responsible for the management of lakes, and they are also interested in the assessment of ecological status and regular monitoring of these valuable assets.

### APPROACH AND RESULT

Remote sensing seems the only feasible way to monitor lakes over a large region with reasonable frequency and support the WFD status assessment process. Several ecological parameters can be monitored from space – phytoplankton biomass, chlorophyll-a concentration, water transparency and frequency/intensity of algal blooms. Ocean colour sensors (e.g., MERIS, MODIS, OLCI) are specially designed for assessment of water quality parameters but have a coarse spatial resolution (250–1000 m/px) thus limiting their use only for large inland water bodies. Recently, ESA has launched a constellation of two Sentinel-2 optical satellites thus providing regular (every 5 days at the equator and 2–3 days in Latvia) and high spatial resolution (10–20 m/px) data stream for free within the Copernicus program. Sentinel-2 data is also more suitable for the assessment of water quality parameters in comparison to Landsat-8 data due to additional spectral bands, thus making it more attractive for monitoring of inland water bodies, even small ones (<1 km<sup>2</sup>).

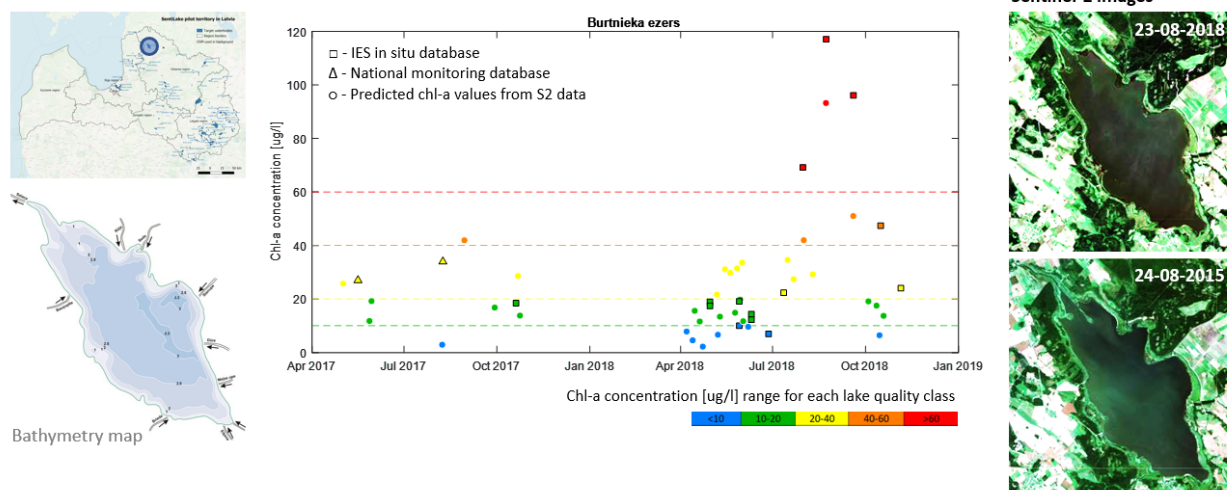
Development of Sentinel-2 based service for regular water quality monitoring in lakes is the goal of the SentiLake project (2018–2020) currently implemented within the ESA PECS for Latvia program. The pilot territory covers two regions in Latvia and includes more than 100 lakes larger than 50 ha. Automated workflow for selecting and processing of available Sentinel-2 data scenes for extracting of water quality parameters (chlorophyll-a and TSM concentrations) for each target water body has been developed. Latvia is a northern country with a frequently cloudy sky, therefore, optical remote sensing is challenging in or region. However, our results show that 1–4 low cloud cover Sentinel-2 data acquisition per month could be expected due to high revisit frequency of Sentinel-2 satellites.

The combined use of C2X (Hieronymi *et al.*, 2016) and C2RCC (Brockmann *et al.*, 2016) processors was chosen after testing of different available processors as well as band ratios showing

the satisfactory performance –  $R^2 = 0.82$  and  $RMSE = 21.2 \mu\text{g/L}$ . Chl-a assessment result is further converted and presented as a lake quality class. It is expected that SentiLake will provide supplementary data to limited *in situ* data for filling gaps and retrospective studies, as well as a visual tool for communication with the target audience. The example of Lake Burtnieks profile is shown in Fig. 1. It shows how Sentinel-2 satellite data supplements limited *in situ* data. However, it was also observed that processors tend to underestimate chl-a prediction.

## The case of Lake Burtnieks

It is a shallow brown water lake (Type 6) with an average depth of 2,9 m and area of 40 km<sup>2</sup>.



**Figure 1.** The case of Lake Burtnieks: chl-a concentration values obtained from *in situ* observations (IES and National monitoring database) as well as from Sentinel-2 satellite data.

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# Assessment of the Pollutant Removal Performance of a Rain Garden Facility Treating Urban Stormwater Runoff

M. S. Jeon\*, N. J. D. G. Reyes\*, F. K. Geronimo\*, H. S. Choi\*, and L. H. Kim\*

\*Dept. of Civil and Envi. Eng'g., Kongju National University, 1223-24 Cheonan-daero, Seobukgu, Cheonan city, Chungnam province, South Korea, 31080 (E-mail: [leehyung@kongju.ac.kr](mailto:leehyung@kongju.ac.kr))

## INTRODUCTION

The increase in impervious area due to urbanization can alter the overall water circulation. During periods of heavy rainfall, increased peak flow volume and flow duration can result to regional and local flooding in urban areas. In addition, changes in rainfall patterns due to climate change have been reported to affect the natural water cycle. Since 2004, the Korean Ministry of Environment has applied low impact development (LID) strategies to manage stormwater in urban areas and reduce non-point source (NPS) pollution. Majority of the LID facilities utilize sedimentation basins as a pre-treatment mechanism to remove particulate matters, reduce runoff volumes, and increase hydraulic retention time. In addition, NPS pollutants are managed by incorporating media filters and vegetation to promote combined physico-chemical and biological treatment mechanisms such as infiltration, filtration, adsorption, evapotranspiration, and storage. However, pollutants and sediments accumulate in the facility over time, resulting to filter media clogging, decrease in permeability, and reduced efficiency of the facility. Therefore, this study evaluated the long-term performance of rain garden through analysing the characteristics and behaviour of pollutants inside the facility.

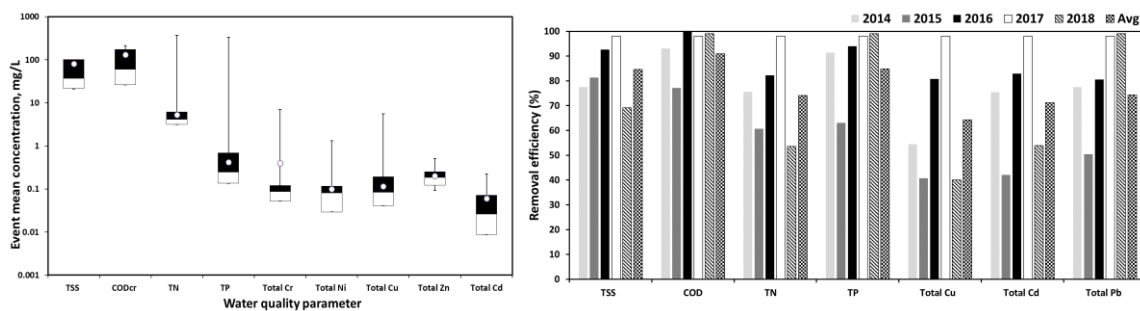
## METHODOLOGY

The rain garden facility installed in Kongju National University, Cheonan campus was designed to treat stormwater runoff from an impervious parking lot. The rain garden consists of sedimentation basin (pre-treatment zone), vegetated zone and the outflow zone. Filter media, including gravel and sand, were used in the rain garden. Storm event monitoring and water quality sampling was conducted for a total of five years from 2014 to 2018. Water quality assessment was performed by collecting water samples from inflow and outflow parts of the facility. Flow measurements were performed every five minutes as soon as the inflow and outflow were observed in the rain garden. Water samples were collected at intervals of 0 min, 5 min, 10 min, 15 min, 30 min and 60 min for the first hour of monitoring, while succeeding samples were collected at an hourly interval.

## RESULTS AND DISCUSSION

Fig. 1 exhibited the annual pollutant removal efficiency of rain garden. Monitored events were characterized by rainfall depths ranging from 0.5 mm to 40.3 mm with mean antecedent dry days and average rainfall intensity of  $(5.46 \pm 4.7)$  days,  $(5.33 \pm 6.7)$  mm/h, respectively. The concentration of TSS, COD, TN, and TP were  $(98.0 \pm 32.7)$  mg/L,  $(133.6 \pm 6.3)$  mg/L,  $(5.77 \pm 4.05)$  mg/L, and TP  $(0.54 \pm 0.03)$  mg/L, respectively. Generally, the concentration of influent was  $(44 \pm 8)$  % higher in summer than in winter. Automobile and anthropogenic activities in the catchment area during summer season was 10 % higher than in winter. Moreover, high summer temperatures resulted to increased rate of sediment drying. The dried sediments that accumulated on the impervious surfaces can be easily washed-off on storm events, thereby increasing the concentration of particulates in stormwater. The average volume reduction of the rain garden was

(96 ± 3) %. At rainfall intensities greater than 20 mm/h, the rain garden effectively reduced the runoff volume by 97 % for the first two years of operation. After the second year, it was observed that the average volume reduction of the system was reduced to 90 % for rainfall intensities greater than 14 mm/h. The five-year mean TSS removal efficiency of the system was 86 %; however, it was observed that the TSS removal efficiency in 2018 only amounted to 69 %, which was about 15 % lower as compared with the 5-year mean removal efficiency. The decrease in TSS removal can be attributed to the high frequency of overflows in the facility during periods of high rainfall intensity which cause pore blockage or filter media clogging. The mean removal efficiency of COD, TN and TP were 90 %, 76 %, and 88 %, respectively. Unlike TSS, the removal of nutrients and organics by the facility increased over time due to the continuous stabilization of the vegetative components and microbiological activities in the rain garden. The removal efficiency of Total Cu, Total Cd, and Total Pb exhibited similar trend with COD and TP since heavy metals can also be removed through physical filtration and adsorption, biological mechanisms, and plant uptake. As compared with other water quality parameters, the removal efficiency of heavy metals was relatively low due to inferior uptake mechanisms of the facility's vegetative components.



**Figure 1.** Influent Water Phase and Pollutant Reduction Efficiency.

## CONCLUSIONS

Based on the long-term monitoring of the rain garden, the following conclusions were derived.

1. The infiltration rate and storage capability of the facility decreased by 10 % due to filter media clogging and sediment deposition in the upper part of the facility over time.
2. Decrease in hydraulic residence time and filter media clogging resulted to a decreased TSS removal efficiency over time. On the other hand, the removal efficiency of nutrients and organics increased due to the stabilization of plants and other microbiological processes.
3. Continuous monitoring and further research should be conducted evaluate the factors affecting the treatment efficiency of the rain garden. Maintenance and changes in rainfall patterns should also be considered in the facility design.

## ACKNOWLEDGMENT

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# Ammonium and Phosphate Removal Using Magnetic Nanoparticles

B. Kara\*, A. Gulyás\*\*, N. Semerci\*\*\*, Z. S. Can\*\*\*\*, and S. Genç\*\*\*\*\*

\* Marmara University, Institute of Pure and Applied Sciences, Environmental Engineering Department, Kuyubaşı, Istanbul, Turkey (E-mail: *kr.busra@gmail.com*)

\*\*Marmara University, Institute of Pure and Applied Sciences, Environmental Sciences Department, Kuyubaşı, Istanbul, Turkey (E-mail: *gulyasanett93@gmail.com*)

\*\*\*Marmara University, Faculty of Engineering, Environmental Engineering Department, Kuyubaşı, Istanbul, Turkey (E-mail: *neslihan.semerci@marmara.edu.tr*)

\*\*\*\* Marmara University, Institute of Pure and Applied Sciences, Environmental Engineering Department, Kuyubaşı, Istanbul, Turkey (E-mail: *zehra.can@marmara.edu.tr*)

\*\*\*\*\* Marmara University, Institute of Pure and Applied Sciences, Metallurgical and Materials Engineering Department, Kuyubaşı, Istanbul, Turkey (E-mail: *sgenc@marmara.edu.tr*)

## INTRODUCTION

Magnetic nanoparticles (MNPs) as recent novel developed materials offer such a best alternative to improve water decontamination through their unique properties and functions. They can be promising adsorbents especially to overcome the wastewater treatment challenges due to the existence of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions. Powdered activated carbon can be synthesized with magnetite nanoparticles (i.e. PAC-MNP) as a proper for coating agent (Khodadadi *et al.*, 2017) for capturing these ions. Although different studies on phosphate adsorption with different types of MNPs exist in the literature, the fate of ammonium ions during the same application is still uncertain.

To our knowledge, there is not any study investigating the adsorption for the removal and recovery of nitrogen and phosphorus ions by employing iron-based magnetic nanoparticles from particularly sewage sludge liquors. In the current study, the efficient adsorbents Bare and Composite forms of MNPs were synthesized and then introduced to ammonium and phosphorus synthetic solutions. The further studies are planned to investigate the adsorption of dewatered sludge supernatants by boosting the adsorption performances of PAC-MNPs with the optimization studies to achieve the removal of N and P ions.

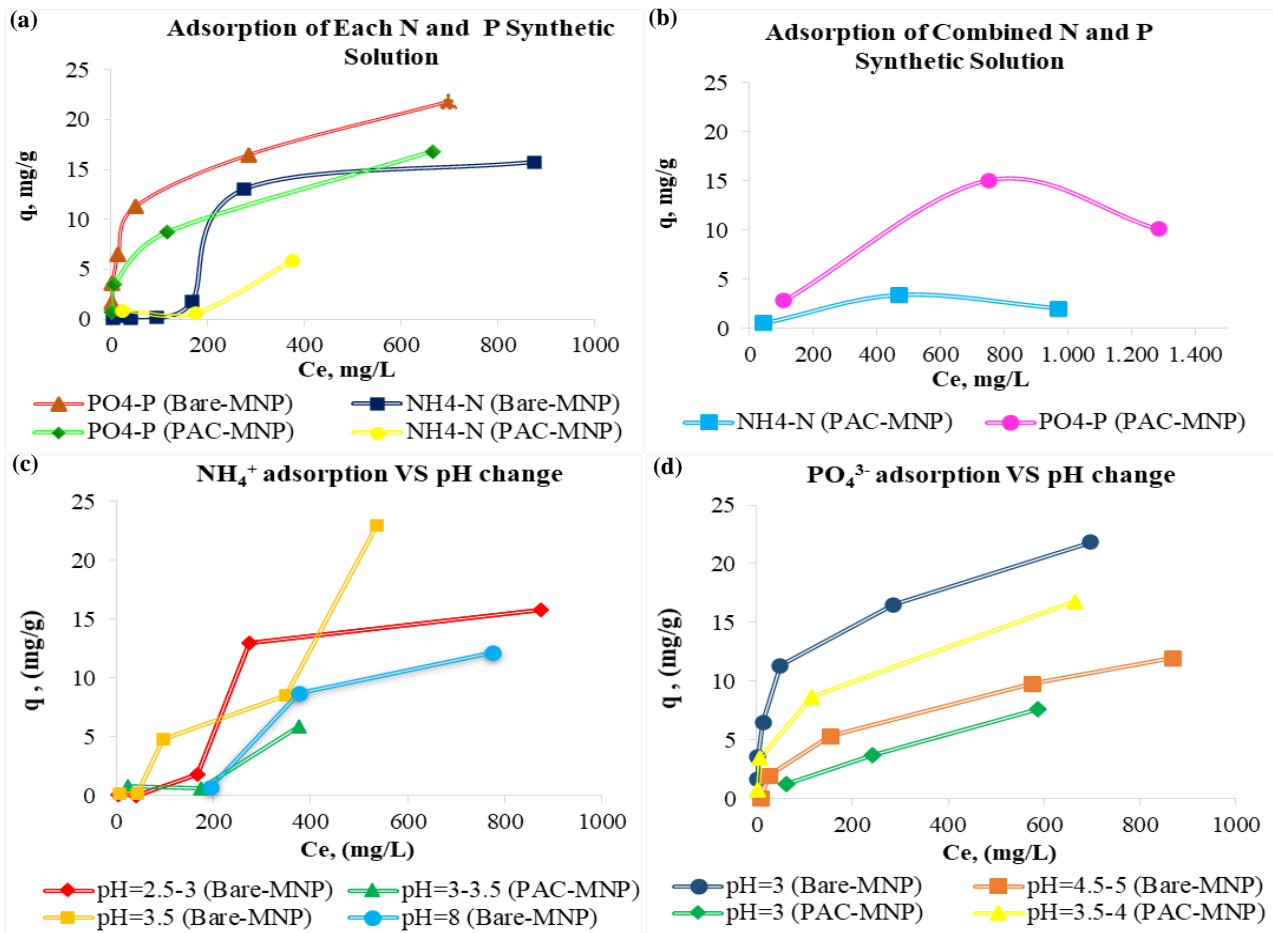
## MATERIALS AND METHOD

The co-precipitation process was used in the synthesis of Bare magnetite ( $\text{Fe}_3\text{O}_4$ ) and Composite MNPs. While Bare MNPs were synthesized with the molar ratio 2:1 of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts, Composite MNPs were generated with the molar ratio 2:1 of  $\text{Fe}_3\text{O}_4$  and PAC. Adsorption of phosphate and ammonium ions onto magnetite in synthetic solutions was studied under batch conditions. N and P synthetic stock solutions (1000 mg/L) were used for the experiments. Different initial N and P concentrations were studied. The reaction time was 24 h, with 0.3 g magnetic nanoparticles at the room temperature. Initial pHs for the each synthetic solution was set to various pH values beginning of the experiments (e.g. pH 3, 3.5, 4.5 etc.).

## RESULTS AND DISCUSSION

The adsorption of both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions were initially carried out for their each synthetic solution depending on the influent concentrations. The equilibrium adsorption capacity of Bare MNPs was increased with increasing N and P concentrations, ranged between 0.1–15.8 mg/g and 1.6–21.8 mg/g, respectively (Fig. 1). As to the adsorption capacity of PAC-MNPs, they had comparably lower equilibrium adsorption amount ( $q_e$ ), ranged between 0.8–5.9 mg/g for N ions,

and 0.7–16.8 mg/g, for P ions. The reason of why  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions could be adsorbed in the higher amounts by Bare MNPs than Composite MNPs can be ascribed that PACs have bigger pores in the sizes (e.g micropores) so that magnetites may have been inadequately impregnated (Kumar *et al.*, 2017). Furthermore, the amount of  $\text{NH}_4^+$  ions adsorbed comparably lower than  $\text{PO}_4^{3-}$  ions on both adsorbents was most probably due to the acidic pH condition reasoning the MNPs surface positively-charged (Zare *et al.*, 2016). Nevertheless, both adsorbent types could adsorb the opposite charge  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions from their the each synthetic solution, respectively. Besides, they were able to be simultaneously adsorbed by PAC-MNPs, even they were coexisting together in the same solution ( $\text{NH}_4^+$ -N adsorbed about 0.5–2.0 mg/g and  $\text{PO}_4^{3-}$ -P adsorbed about 2.8–10.0 mg/g).



**Figure 1.** (a) Adsorption of each N and P Solution; (b) Adsorption of Combined N and P Synthetic Solution; (c)  $\text{NH}_4^+$  Adsorption versus pH Change; (d)  $\text{PO}_4^{3-}$  Adsorption versus pH Change.

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## **A Cladocera Based Paleolimnological Assessment of Recent Environmental Changes in Lake from Drinking Water Supply System in Riga Vicinity, Latvia**

A. Lanka<sup>\*,\*\*</sup>, I. Zawiska<sup>\*\*\*</sup>, N. Stivrins<sup>\*\*\*\*</sup>, W. Tylmann<sup>\*\*\*\*\*</sup>,  
and I. Dimante-Deimantovica<sup>\*.\*\*\*\*\*</sup>

\* Latvian Institute of Aquatic Ecology, Agency of Daugavpils University, Voleru str. 4, Riga, LV-1007, Latvia (E-mails: [anna.lanka@gmail.com](mailto:anna.lanka@gmail.com); [inta.dimante-deimantovica@lhei.lv](mailto:inta.dimante-deimantovica@lhei.lv))

\*\* Tallinn University of Technology, Department of Geology, Ehitajate tee 5, 19086 Tallinn, Estonia (E-mail: [anlank@taltech.ee](mailto:anlank@taltech.ee))

\*\*\* Department of Geoecology and Climatology, Institute of Geography and Spatial Organization, Polish Academy of Sciences, Twarda 51/55, 00-818 Warsaw, Poland (E-mail: [izawiska@twarda.pan.pl](mailto:izawiska@twarda.pan.pl))

\*\*\*\* University of Latvia, Department of Geography, Jelgavas 1, LV-1004, Riga, Latvia (E-mail: [normunds.stivrins@lu.lv](mailto:normunds.stivrins@lu.lv))

\*\*\*\*\* Faculty of Oceanography and Geography, University of Gdańsk, Aleja Marszałka Józefa Piłsudskiego 46, Gdynia 81-378, Poland (E-mail: [wojciech.tylmann@ug.edu.pl](mailto:wojciech.tylmann@ug.edu.pl))

\*\*\*\*\* Norwegian Institute for Nature Research, Gaustadalléen 21, NO-0349 Oslo, Norway (E-mail: [inta.deimantovica@nina.no](mailto:inta.deimantovica@nina.no))

### **INTRODUCTION**

Cladocera is a group of microcrustaceans inhabiting various aquatic habitats. They play a crucial role in ecosystems as they serve for intermediate position in the food web between phytoplankton and primary consumers like fish. The structure of Cladocera carapace (consisting of chitin) allows body parts to remain in sediments for years. Hence Cladocera turns to be one of the most valuable biological proxies and can be studied for environmental changes reconstruction. Such paleolimnological research generates knowledge and may provide answers to questions on ecosystem responses to potential key drivers – deposition history will show the ecological consequences as to Cladocera before disturbance and after it, under long term and under increasing exposure. The goal of this research was to study Cladocera subfossils in order to track past environmental changes related to possible industrial footprint during the last decades in lake belonging to drinking water supply system.

### **MATERIALS AND METHODS**

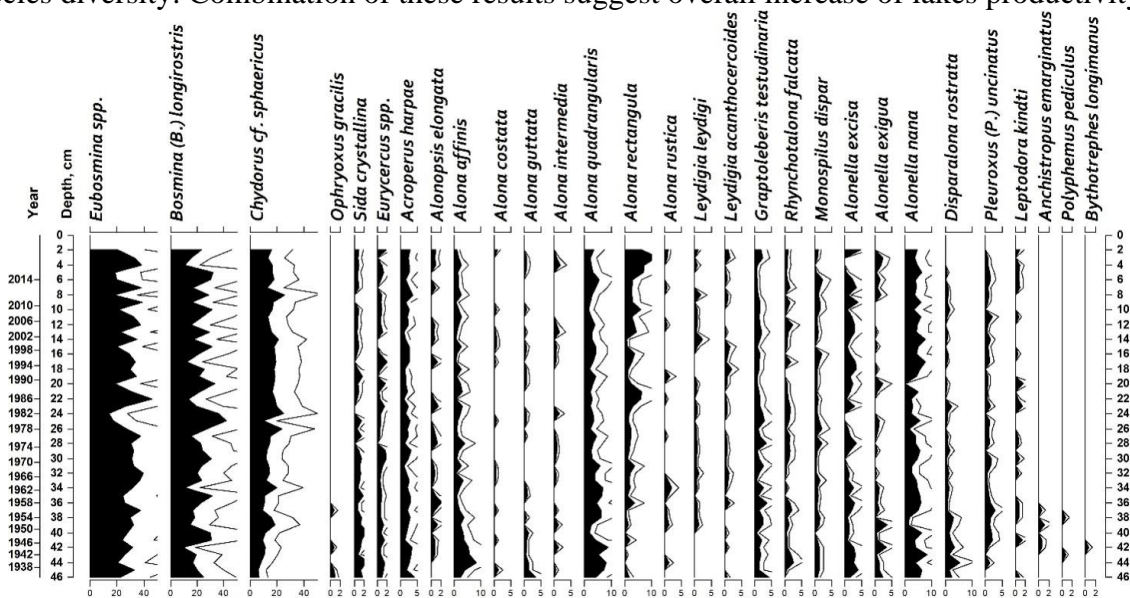
The Sekšu Lake is located East of the capital city of Latvia – Riga. It belongs to drinking water supply system, hence access to it is limited. The lake is relatively small, its area varies between 7.9 ha and 13 ha depending on the water level. Lake's average depth is about 3 meters, while maximum depth reaches 6 m. Lake bottom consists of sand and mud. In historical records from beginning of 20<sup>th</sup> century it has been mentioned as a lake with high transparency and water quality. Lake area is surrounded by forest, that decreases wind caused water mixing. There are no outflowing water streams and the only inflow is a ditch located in the southeastern part of the lake. However, that does not mean that Lake Sekšu has not suffered from external influences historically. During the times of Soviet Union, a nutrient rich water was pumped into the Lake Sekšu from nearby lake Mazais Baltezers.

Sediment samples were collected with Kayak corer in February 2019. The core of 46 cm was taken from the deepest part of the lake. The core was sectioned at 1 cm intervals. For sediment age determination <sup>137</sup>Cs and <sup>210</sup>Pb accumulation was analyzed, and age-depth model was constructed.

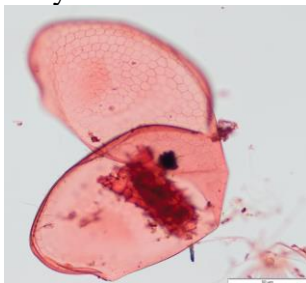
LOI was used to assess the organic and mineral content of the sediments and carbon (C), nitrogen (N) weight percent was determined. Sediment subsample of 1 cm<sup>3</sup> was prepared for subfossil Cladocera analysis.

## RESULTS

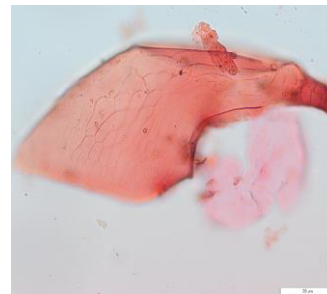
The sediment age-depth model estimated age started from approximately 1935 at the deepest part of the core. The results show that there have been considerable changes in sediment composition with increase of minerogenic sediment percentage around year 1950. The changes in sediment structure coincide with changes in Cladocera community: gradual decrease and disappearance of species that indicate oligo/mesotrophic environment [e.g. *Ophryoxus gracilis* (Sars 1862)], proportional increase of species that favor nutrient rich conditions [e.g. *Chydorus sphaericus* (Müller 1776)] and decrease in species diversity. Combination of these results suggest overall increase of lakes productivity.



**Figure 1.** Abundance of Cladocera species (only dominant species and species with indicator value are included in the graph) by location in sediment layers. On y-axis – the samples depth in sediments (number 1 is the uppermost layer and the 46 is the deepest layer) and the corresponding years for each layer.



**Figure 2.** *Chydorus sphaericus* (Müller 1776) shell. Scale bar 50 µm. Photo: A. Lanka.



**Figure 3.** *Bosmina (B.) longirostris* (Müller 1785) headshield. Scale bar 20 µm. Photo: I. Dimante-Deimantovica.

## FUNDING ACKNOWLEDGEMENTS

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# Should the Two-Phase Euler Replace the Volume of Fluid to Simulate Localised Aeration in Hydraulic Structures?

L. S. Mendes<sup>\*,\*\*</sup>, J. L. Lara<sup>\*\*</sup>, and M. T. Viseu<sup>\*</sup>

<sup>\*</sup> Laboratório Nacional de Engenharia Civil, Avenida do Brasil 101, Lisbon, Portugal  
(E-mails: [lmendes@lnec.pt](mailto:lmendes@lnec.pt); [tviseu@lnec.pt](mailto:tviseu@lnec.pt); *L. S. Mendes birth date is 1983-06-11*)

<sup>\*\*</sup> IHCantabria – Instituto de Hidráulica Ambiental, Universidad de Cantabria, Santander, Spain  
(E-mail: [jav.lopez@unican.es](mailto:jav.lopez@unican.es))

## STATE OF THE ART

Hydraulic structure free-surface flows (e.g. spillways, slope channels, weirs, impinging jets, aeration mixing tanks, energy dissipation structures and wave breaking) are typically characterized by high velocity and high turbulent regime (Chanson, 2013). Moreover, surrounding and entrained air must be evaluated to assure safe operation (Kobus, 1984). Aeration may have several effects in the flow: bulking, cavitation protection, drag reduction, increase of energy dissipation, disturbance of the turbulence field, transference of atmospheric gases (Chanson, 2004; Novak, 2001). Due to the complexity, physical modelling is the primordial tool to validate designs, in spite of the scale effects and limitations (Pfister, 2010).

In the last two decades, numerical modelling of hydraulic structures proliferated as a consequence of technological advances and proved to save costs, specially when combined with physical modelling. Nonetheless, it is extremely complex to simulate the air-bubble entrainment, transport, transformations and degassing (Shi, 2010). The most popular approaches are the single-phase Euler type models: interfacial (Volume-of-Fluid and Level-Set) and the Mixture. However, the air volume fraction is limited to 15 %. The two-phase Euler is the most complex and has no air-concentration limitation. Two continuous and interpenetrating phases have a dedicated set of continuity, momentum and energy equations. This framework demands more computational efforts, presents some stability issues and there are only few applications to hydraulic structures aerated flows (Cheng, 2012).

## METHODOLOGY

Localized air-entrainment in hydraulic structures typically occur at geometry continuities or impinging flows. Laboratory data of an impinging jet experiment (Chanson & Manasseh, 2003) is used to evaluate and compare the performance of a volume-of-fluid and a two-phase Euler models. Both are included in the open-source OpenFOAM software toolbox (OpenCFD, 2019).

A 2D cartesian wedge mesh, previously validated, is applied to a vertical jet into a 1.8 m depth plunging pool. The nozzle is 0.4 m above the pool, has a diameter of 0.025 m and an exit velocity of 3.2 m/s. Four distinct resolution mesh and both the *k-epsilon* and *k-omega SST* turbulence models are utilized. The multiphase models are evaluated against the jet centreline velocity decay, the radial velocity, turbulence and air concentration profiles.

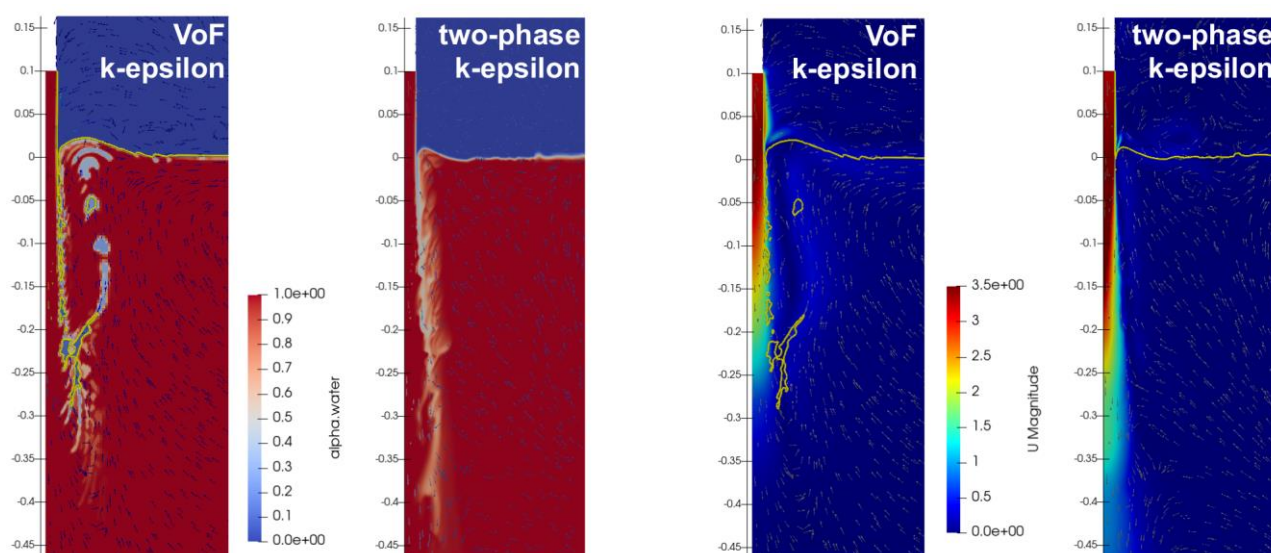
## RESULTS

The volume-of-fluid jet shear layer exhibits no mesh convergence. Trends to a thinner interface region with smaller air pockets, which leads to larger jet penetration as resolution increases. Turbulence fields resembles. Oppositely, the two-phase Euler performance is accurate for intermediate mesh resolutions and not significantly sensitive to the mesh. Moreover, the turbulence

fields values at the shear layer region are expressively smaller. The *k-epsilon* turbulence model presents higher turbulent kinetic energy and more intense jet centreline velocity decay. The *k-omega SST* is less affected by mesh resolution.

## CONCLUSION

The volume-of-fluid good results for intermediate mesh resolutions, proved to be misleading, as no mesh convergence is found. Higher mesh resolutions even deliver non-physical results. The two-phase Euler demonstrated a good reproduction of the laboratory experiment, particularly when combined with the *k-omega SST* turbulence model. Although demands higher calculation efforts, achieves accurate results with lower resolution mesh. The two-phase Euler proved to be adequate for local aeration. Notwithstanding being less stable, is an accurate and efficient tool for hydraulic structures engineering.



**Figure 1.** Water volume fraction and velocity magnitude - mesh resolution of 16 cells per nozzle diameter.

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## Identification of Pesticides in Wetland Water

I. Mihajlović\*, M. Sremački\*, M. Novaković\*, N. Živančev\*, V. Gvoić\*, I. Spanik\*\*, and M. Petrović\*

\* Department of Environmental Engineering and Occupational Safety and Health, Faculty of Technical Sciences, University of Novi Sad, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia (E-mail: [majadjogo@uns.ac.rs](mailto:majadjogo@uns.ac.rs))

\*\* Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, STU, Radlinského 9, 812 37 Bratislava, Slovakia

### INTRODUCTION

Agricultural landscapes are characterized by the high percent of arable land and increased pressures on the natural systems. Water pollution from anthropogenic and agricultural sources is a common problem (Obrovski *et al.*, 2018). The poor water quality is not only causing the loss of biodiversity in wetlands, but often makes the surface waters inadequate for irrigation (Obrovski *et al.*, 2019). The eutrophication problems and pollution of wetland in agricultural areas have to be solved for the purpose of biodiversity conservation. Habitat revitalisation and establishment of green infrastructure as water filter are required for the extension of irrigation capacities and improvement of landscape resilience. The frequent summer droughts considerably increase the costs of the afforestation and hedge planting. There is a need to find the optimal vegetation structure, adapted for local climatic conditions and effective in pollution reduction. Analyses of pollutants along the banks of surface waters could provide information on bank vegetation effectiveness in retaining the pollutants from the arable lands and be useful for the management of protected wetlands and ecological corridors, and for the surface waters quality improvement.

The main objective of study was to develop water monitoring for key physico-chemical parameters in wetland area Tompojevacki ritovi, Croatia. Evaluation of water pollution from agricultural sources will result in better management of environmental and biodiversity protection in region. The results could also be used for development of guidelines for biodiversity protection in the agricultural areas and optimal green structure adapted for local climatic conditions and effective in pollution reduction. The first sampling campaign was conducted in June 2019 in order to identify organic pollutants with special focus on pesticides in run-off water samples.

### MATERIALS AND METHODS

#### Sampling location

Sampling site is within hydrological system of watercourse recognised as ecological corridor. The wetland Tompojevacki ritovi is depression filled with water, lower than surrounding terrain for 10 to 15 m. The water flow from the underground sources at the margins of the low parts of the depression. Tompojevacki ritovi were richer in water, and therefore with flora and fauna earlier. In the last years, eutrophication of water as consequence of water pollution can be observed. Therefore, the run-off water from agricultural land was analysed.

#### Sample analysis

For the chromatographic analyses, water samples were prepared with liquid-liquid extraction (LLE) and evaporated in Kuderna–Danish apparatus. LLE was conducted 3 times per 30 minutes using 20 mL of DCM. The extract was evaporated to 1.5 mL. Screening analysis was performed on a gas

chromatogram (GC) coupled with a mass selective detector (MSD) (Shimadzu QP2010Ultra). GC injector was set to splitless operating mode. The prepared extract (1  $\mu$ L) was injected into the system. The capillary column HP-5MS (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m df) was used for the analysis. Oven temperature gradient programme was set to hold time of 10 minutes on 40  $^{\circ}$ C, then increase of 2  $^{\circ}$ C per minute was adjusted to 300  $^{\circ}$ C. MSD was used during the analysis in scan mode (m/z 45–600). Helium was used as carrier gas.

## RESULTS AND DISCUSSION

Screening analysis of run-off water indicated the presence of pesticides: Iodosulfuron-methyl-sodium, Pethoxamid, 2,4-D 2-ethylhexyl ester, Urea and Glyphosate. 2,4-D 2-ethylhexyl ester is a systemic herbicide which selectively kills most broadleaf weeds by causing uncontrolled growth in them, but leaves most grasses such as cereals, lawn turf, and grassland relatively unaffected. Urea herbicides form, together with phenoxy derivatives and triazines, the most important agricultural herbicide group. The urea-derivatives are typical pre-emergence herbicides applied usually as aqueous emulsions to the surface of soil. Pethoxamid is known as both pre-emergence and early post-emergence herbicide against mono- and dicotyledonous weeds in maize. Glyphosate is organophosphorus compound, which acts by inhibiting the plant enzyme 5-enolpyruvylshikimate-3-phosphate synthase. It is used to kill weeds, especially annual broadleaf weeds and grasses that compete with crops. Detected herbicides could cause surface and ground water pollution with negative impact on biota and human health.

## CONCLUSIONS

Screening analyses indicated water pollution with pesticides and need for detailed sampling plan and analyses. Results specified the need for comprehensive water monitoring program in order to determine the agricultural impacts which could be useful as the basis for defining of Guidelines for the establishment and management of bankside vegetation strips in the wetland area.

## ACKNOWLEDGMENTS

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## Pollution Lake Sevan (Armenia) by Selected Organic Pollutants of the EU Water Framework Directive

L. N. Mkhitarian\*, S. H. Minasyan\*, G. G. Kocharyan\*, Z. H. Manukyan\*, L. H. Harutyunyan\*, and G. A. Shahnazaryan\*\*

\* Institute of Chemical Physics, National Academy of Science RA, 5/2 P. Sevak Str., 0014 Yerevan, Republic of Armenia (E-mails: [lian1195@mail.ru](mailto:lian1195@mail.ru); [seyran\\_minasyan@yahoo.com](mailto:seyran_minasyan@yahoo.com))

\*\* Environmental Monitoring and Information Center SNCO, 5/2 P. Sevak Str., 0014 Yerevan, Republic of Armenia (E-mail: [gayane\\_shahnazaryan@yahoo.com](mailto:gayane_shahnazaryan@yahoo.com))

### INTRODUCTION

Currently, in Armenia, the practical implementation of the European Union Water Framework Directive (WFD) with regard to chemical pollution has faced some challenges. The main issue is concerning the insufficient monitoring of organic pollutants in surface waters.

This paper intends to analyse the selected organic pollutants from the WFD priority substances in waters and sediments of Lake Sevan and its basin rivers. Lake Sevan is the greatest lake in Armenia and one of the greatest freshwater high-mountain lakes of Eurasia. The lake consists of two morphometrically different basins – the deeper Minor and the relatively shallow Major Sevan (Hovhannissian, 1994). In the Lake Sevan Basin, agriculture is one of the leading sectors of the economy (12.7 %) and agricultural lands occupy about 56 % (264.36 ha) of the total land of the basin. According to the Armenian statistical data, in 2018 the annual consumption of pesticides in the Sevan basin was 1.5 kg/ha but the type of used pesticides has not been registered. Intense agriculture in Basin of Lake Sevan and untreated domestic wastewater led to the growth of content of organic matter in Lake and rivers (Minasyan *et al.*, 2018).

To investigate of pollution of the Lake Sevan by organic substances the sampling of waters and sediments were caring out in 2018. In Lake Sevan, the sampling of waters and sediment was carried out in three seasons: May, July and October, from 18 sections of the lake which have both littoral and pelagic sites. The water samples were taken from 7 m, 15 m and 30 m depths. In general, 180 water samples and 46 sediment samples were taken for three months.

### RESULTS AND DISCUSSION

Based on the analytical result, from 180 water samples of Lake Sevan organic pollutants were detected only in 65 samples. The detected main organic chemicals were heptachlor and its oxidation product (heptachlor epoxide), hexachlorobenzene, aldrin, chlordane (and isomers), endosulfan (and its degradation product: endosulfan sulfate),  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCHs, 2,4-DDD, 4,4-DDD, 2,4-DDE, 4,4-DDE, 2,4-DDT, 4,4-DDT, dicofol and chlorothalonil. The derivatives of DDD and DDT, endrin, heptachlor and chlorothalonil were rarely found in the samples. In the sediment of Lake Sevan organic pollutants were detected in 13 samples from taken 46 samples. 14 organic substances were detected and quantified in the sediment samples. The detected main organic pollutants in sediments were oxidation product of heptachlor (heptachlor epoxide), hexachlorobenzene, aldrin, trans chlordane, endosulfan (and its degradation product endosulfan sulfate),  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCHs, 4,4-DDD, 2,4-DDE, dicofol and chlorothalonil.

Relatively high concentrations of pollutants (pesticides and other agrochemicals) and the largest number of pollutants from detected chemicals have been found in May both in sediment and water

samples. In spring, by rivers and snow waters pesticides and agrochemicals are washed out from agricultural lands and carried into the lake, as a result of which a part of these compounds are accumulated in the lake sediments. During the spring, the level of the Lake Sevan rises covering and washing thousands of hectares of coastal areas, where pesticides and agrochemicals have been accumulated in the previous decades or previous agricultural season. A certain portion of these pollutants has been also precipitated in the lake's bottom. In autumn, a certain nonoxidized and nondegraded pollutants appears in the lake's sediments. The content of pesticides, in particular, heptachloro-*exo*-epoxide, DDE, in autumn, as well as in summer, was relatively high in sediments near the Gavar and Vardenis subregions. This indicates the high contamination level of agricultural lands in these regions due to accumulation of chloroorganic pesticides during several decades. Also, illegal use of these compounds in private enterprises must not be ruled out.

**Table 1.** Detected organic pollutants in some sampling sites (data presented of samples of lithoral and pelagic zones), May 2018.

Organic pollutants	Concentration, µg/L					
	1-lith-0m (Tsapatagh)	1-pel-7m (Tsapatagh)	2-lith-7m (Tsovinar)	2-pel-0m (Tsovinar)	3-lith-7m (Gavaraget)	3-pel-0m (Gavaraget)
Heptachlor epoxide	50.6	51.3	97.8	55.9	ND	ND
Hexachlorobenzene	12.7	2.2	12.7	2.1	ND	ND
Aldrin	8.7	1.5	73.1	1.0	ND	0.1
trans-Chlordane	ND	5.2	6.9	5.7	32.6	33.8
cis-Chlordane	40.3	3.2	ND	ND	12.2	53.2
α-Endosulfan	75.9	ND	45.2	ND	214.3	34.1
Endosulfan sulfate	44.1	36.5	ND	ND	ND	1794.7
α-HCH	ND	2.5	17.1	ND	8.8	22.8
β-HCH	9.8	ND	72.8	1.8	4.1	171.2
γ-HCH	10.7	1.3	1.5	97.5	80.0	28.4
2,4-DDE	1.6	ND	4.7	ND	5.2	9.7
4,4-DDD	ND	ND	ND	ND	4.6	ND
4,4-DDE	ND	ND	2.1	ND	ND	30.5
Dicofol	9.7	ND	46.7	6.5	8.7	44.2

## ACKNOWLEDGEMENTS

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# Good Practices of a Circular Economy Implementation: A Comprehensive Review in Context of Wastewater Sector

M. Preisner\*, M. Smol\*, and D. Szoldrowska\*

\* Division of Biogenic Raw Materials, Mineral and Energy Economy Research Institute,  
Polish Academy of Sciences, ul. Wybickiego 7A, 31-261 Cracow, Poland  
(E-mails: [preisner@meeri.pl](mailto:preisner@meeri.pl); [smol@meeri.pl](mailto:smol@meeri.pl); [szoldrowska@meeri.pl](mailto:szoldrowska@meeri.pl))

## INTRODUCTION

The protection of water resources and the renewal of aquatic ecosystems is one of the key actions in the field of environmental protection in the European Union (EU). Due to the deepening restrictions on access to clean water, as well as the increase in the amount of sewage generated, sustainable water and wastewater management has become a priority in many countries. The European Commission (EC) underlines that sustainable economic growth is possible by moving to a more circular economy (CE), and in the case of water and wastewater management – taking into account the use of sewage as a source of energy and valuable resources (European Commission, 2014).

The objective of this research is a comprehensive review and evaluation of the role, importance and possibilities of the wastewater sector in the implementation of the circular economy. Moreover, the study presents existing and forthcoming good practices regarding the CE concept used in municipal and industrial wastewater infrastructure in EU Member States in order to propose recommendations regarding the directions of further CE concept implementations.

## IMPORTANCE OF WASTEWATER SECTOR IN THE CE MODEL

According to the position of the EC the innovative use of sewage as a source of energy and resources, reuse of treated wastewater and closing water circuits should become important elements of water circuits, especially in the case of future water deficits. For many years, the wastewater treatment plants (WWTPs) were mainly a basic tool used to limit the loads of nutrients being discharged to wastewater receivers, but from the perspective of the current European environmental policy a wider perspective is being recommended. Due to the combination of various material flows (e.g. nutrients, water, energy and heat), WWTPs are foreseen to be one of the most promising facilities for the implementation of CE concept. It should be underlined that the transition to CE in wastewater sector should take into account an integrated approach to water and wastewater management by increasing the scope and division of responsibilities incumbent on administration and integration with other fields, including energy, transport, shipping, agriculture, forestry, fisheries, broadly understood nature protection, tourism, social communication, spatial planning as well as regional policy.

## RESULTS AND DISCUSSION

An important part of the CE implementation in wastewater sector is recovery of energy (thermal, electric) and materials (as nutrients: nitrogen – N and phosphorus – P) from wastewater, sewage sludge and sewage sludge ash. The investments in nutrient recovery (NR) technologies are considered as expensive and long-term projects and therefore, their development should be assessed in economic and environmental aspects. The paper presents the review of the selected technologies for nutrients recovery, which have been implemented into the market. Special attention was given to recovery of P, which is an important and non-renewable resource necessary for the existence of all

living organisms which cannot be replaced by any other element (Smol, 2019). Phosphorus and phosphate rock are included in the extended critical raw materials list published by the EC in 2017 (European Commission, 2017) in order to support the development of the EU policies promoting the sustainable management of P (European Commission, 2013) in the near future. Furthermore, the importance of seeking for secondary P sources results from limited primary resources of phosphates in Europe making EU Member States dependent from non-EU suppliers. In response to growing demand for P, some countries such as Germany and Switzerland have introduced legal requirements with set transition periods for an obligatory P recovery from municipal wastewater, while other countries such as Austria and Sweden are developing similar national regulations. Currently, the most applied approach is struvite precipitation from the sludge side stream or P-rich industrial wastewater, followed by calcium phosphate precipitation, and phosphoric acid production (Smol *et al.*, 2020). However, sewage sludge ash as the input for P-recovery seems to be the most reasonable in terms of the recovery efficiency (80–100 %) and the independence of sludge incineration plant and WWTP location (Shaddel *et al.*, 2019).

## CONCLUSIONS

A visible gap has been identified in the implementation of CE model. Due to the possibilities of materials and energy recovery wastewater sector was, is and will have one of the biggest potentials to foster circular solutions implementation. It could be expected that in the following years, more and more good practices of the CE in the wastewater sector will be implemented mainly from water-based waste.

## ACKNOWLEDGEMENTS

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# Incorporating Nature-Based Solutions in the Development of a Climate Change Adaptation Plan: A Case Study of Kurunegala, Sri Lanka

N. J. D. G. Reyes\*, F. K. F. Geronimo\*, H. B. Guerra\*, M. S. Jeon\*, H. S. Choi\*, and L. H. Kim\*

\* Department of Civil and Environmental Engineering, Kongju National University, 1223-34 Cheonandaero, Cheonan City 31080, Chungnam Province, South Korea  
(E-mails: [reyesnashjettdg@gmail.com](mailto:reyesnashjettdg@gmail.com); [fkgeronimo@kongju.ac.kr](mailto:fkgeronimo@kongju.ac.kr); [guerraheidib@gmail.com](mailto:guerraheidib@gmail.com); [mins91@kongju.ac.kr](mailto:mins91@kongju.ac.kr); [hyeseon27@kongju.ac.kr](mailto:hyeseon27@kongju.ac.kr); [leehyung@kongju.ac.kr](mailto:leehyung@kongju.ac.kr))

## INTRODUCTION

The Democratic Socialist Republic of Sri Lanka is considered as one of the countries severely impacted by climate change (Eckstein *et al.*, 2018). Sri Lanka's geographic location serves as a key factor affecting the country's susceptibility to various climate change-related concerns. Moreover, the lack of provisions for sustainable development can further aggravate the existing environmental conditions. In order to mitigate the adverse effects of climate change in the country, it is necessary to strategically implement development plans for creating climate-resilient communities and water-wise cities in Sri Lanka. This study was conducted to identify the risks and risk factors affecting water resources and heat stress in Kurunegala City, Sri Lanka. A climate change adaptation plan incorporating the concept of nature-based solutions (NBS) was also devised based on the identified water and wastewater management needs in the area.

## MATERIALS AND METHODS

A qualitative risk assessment focused on water scarcity and heat stress was conducted in the city of Kurunegala. A total of seven indicators listed in Table 1 were selected by the Kurunegala Municipal Council (KMC) to accurately represent climate change-related issues in the area. Additionally, 57 risk factors were specifically chosen by the council to evaluate relevant climate change scenarios. A survey questionnaire prepared by the Korea Environment Institute was handed out to 35 climate change adaptation experts from KMC to assess the weights of different risk factors. The risk factors were ranked based on the probability of occurrence and the consequence of a specific event. Finally, a climate change adaptation plan was conceptualized to assess the applicability of NBS in the study area.

**Table 1.** Risk factors for qualitative risk assessment.

Item	Risk Factor	Code
1	Drinking water resources risk/vulnerability	DWR
2	Water resources risk/vulnerability	WR
3	Health and infrastructure risk/vulnerability due to heat stress and drought	HIH
4	Sanitation risk/vulnerability due to drought and flood	SDF
5	Water management resources risk/vulnerability	WM
6	Health risk/vulnerability to flood	HF
7	Water quality and aquatic ecosystem risk/vulnerability	WQAE

## RESULTS AND DISCUSSION

DWR, WR, and HIH ranked as the major risk factors in Kurunegala City, indicating that water availability and health and sanitation were among the primary concerns in the study area. The

recorded monthly rainfall depths (2009 to 2019) in Kurunegala had a low correlation ( $r = 0.53$ ) with the number of rainy days, signifying the occurrence of extreme weather events. The annual average air temperature in Kurunegala increased by  $69\text{ }^{\circ}\text{C} \pm 0.37\text{ }^{\circ}\text{C}$  within the period of observation (2009 to 2019). Apart from increasing heat stress, warmer temperatures can promote the proliferation of pathogens and other vector-borne diseases. The climate change adaptation plan was developed to address the rising temperature, water circulation issues, and wastewater management concerns in Kurunegala City. A nature-based approach, through the application of low impact development facilities in different areas in the city, was proposed to promote sustainable development in the study area. As exhibited in Fig. 1, low impact development (LID) facilities can be installed at different institutional and public spaces to incorporate ecosystem services on existing infrastructures. Increasing green spaces can alleviate heat stress and promote efficient water circulation, whereas rainwater harvesting can be employed to supplement metered water consumption. Subsurface wetlands can also be effective for treating wastewaters in the area since these types of wetlands eliminate the risk of potential insect breeding (Kadlec and Wallace, 2009).



**Figure 1.** Proposed locations of pilot-scale LID facilities.

## CONCLUSIONS

Adaptation plans are necessary to establish climate-resilient communities. This case study successfully identified the climate change-related risks factors in Kurunegala City, Sri Lanka. Water scarcity and heat stress were found to be the primary concerns in the study area. The uneven rainfall distribution resulted in water shortage during periods of drought, whereas the continuous increase in impermeable areas also contributed to the increasing heat stress in the area. The proposed adaptation plan incorporated the concept of NBS to promote efficient water circulation and enhance the ecosystem services in Kurunegala City. Overall, the application of LID techniques in developing regions can pave the way for sustainable development through the provisions for climate change adaptation.

## ACKNOWLEDGMENT

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# Variable Speed Pump Modeling Using PID Control in EPA SWMM

Ž. M. Sretenović\*, O. R. Govedarica\*\*, Ž. A. Vasilčić\*\*, M. R. Popović\*, and A. R. Đukić\*\*

\* Jaroslav Černi Water Institute, Jaroslava Černog 80, Belgrade, Serbia  
(E-mail: [zarko.sretenovic@jcerni.rs](mailto:zarko.sretenovic@jcerni.rs))

\*\* Institute for Hydraulic and Environmental Engineering, Faculty of Civil Engineering,  
University of Belgrade, Bulevar kralja Aleksandra 73, Belgrade, Serbia  
(E-mail: [ogovedarica@grf.bg.ac.rs](mailto:ogovedarica@grf.bg.ac.rs))

## INTRODUCTION

The pumping operation can be regulated either by a control of the force main valve or a control of the impeller speed. Change in the impeller speed is a consequence of changed drive motor speed, adjusted by the frequency regulator. In contrast to the valve control, impeller speed control does not change the system characteristics. Capacity regulation by opening and closing the valve results in unnecessary loss of electric energy. Up to 70 % of energy can be saved by using Variable Frequency Drive (VFD) instead. Variations in VFD are generated using a Proportional-Integral-Differential (PID) controller, which is a generic closed-loop control scheme that attempts to maintain the setpoint of a process variable with certain corrections to the control process (Sunela and Puust, 2015; Rai *et al.*, 2017). Case study of Sewer Pumping Station (SPS) “Ušće Nova” in Belgrade is used in this paper to demonstrate variable speed pump modeling using PID control. Successful implementation of VFD in EPA SWMM is done via simulation of PID controller used to adjust pump speed to maintain the desired depth in the storage unit.

## METHODOLOGY

In the EPA SWMM software, within the Control Rules, the PID controller is used to define the level of control applied to the pump or other flow controller relative to the value of the controlled variable such as node water level, pipe flow, or simulation time. The PID control parameters contain three values, the coefficients  $K_p$ ,  $T_i$ , and  $T_d$ . The equation describing the PID controller is:

$$m(t) = K_p \left[ e(t) + \frac{1}{T_i} \int e(\tau) d\tau + T_d \frac{de(t)}{dt} \right] \quad (1)$$

where  $m(t)$  is the control signal,  $K_p$  is the proportional action factor,  $T_i$  is the integral time constant,  $T_d$  is the differentiation constant, and  $e(t)$  is the error signal. The user needs to recognize the type of reaction (i.e. direct or indirect), based on which the sign in front of the parameter  $K_p$  is determined (positive for direct, negative for indirect) (Rossman, 2010).

## CASE STUDY

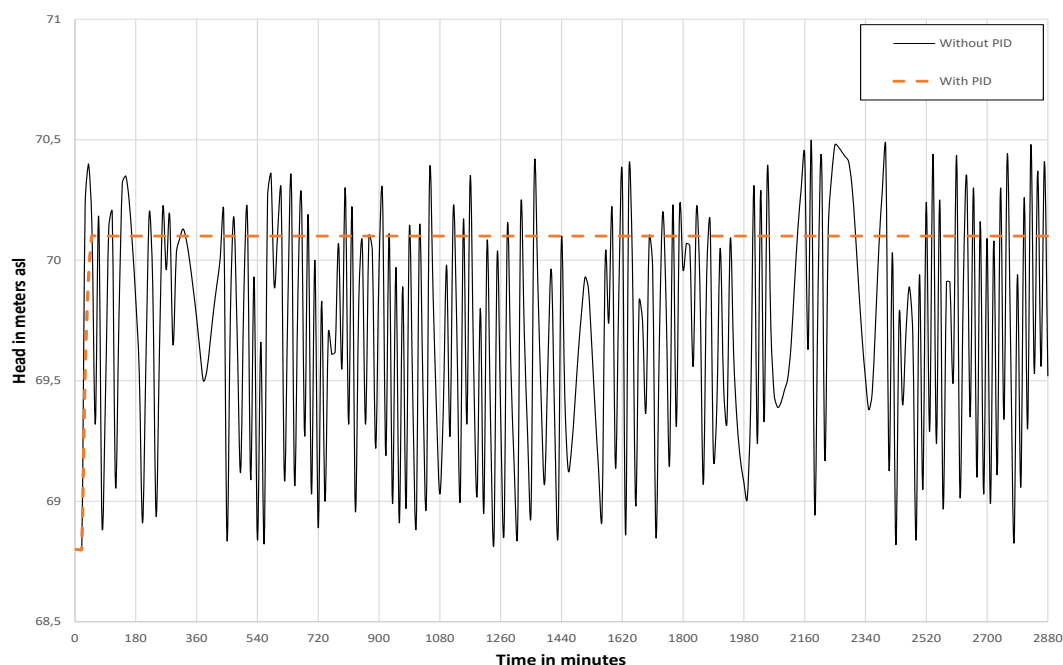
“Ušće Nova” sewer pumping station in Belgrade is used as a case study, with two scenarios being defined and modelled:

- Scenario No. 1 – the pumping station is presented with four identical pumps running in parallel, with same follow-head ( $Q$ - $H$ ) curves. Pumps start in sequence, one after the other, and stop in the reverse order. The facility operates without VFD.
- Scenario No. 2 – the pumping station is presented with the single pump, defined with the overall  $Q$ - $H$  curve of four pumps running in parallel. The PID controller adjusts pump speed

to maintain the targeted water level in the wet well.

## RESULTS

In the Scenario No. 1, the model shows marked instability with a huge number of start-ups for pumps and inconstancy of water level in the wet well. In the case of Scenario No. 2, values of PID control parameters, coefficients  $K_p$ ,  $T_i$  and  $T_d$ , are calibrated by comparing the model results with the desired water level in wet well for a series of simulations. Adopted values are  $-10$ ,  $10$ ,  $0.001$ , respectively. Diagram 1 shows levels in the wet well of the pumping station when the pump units operate with and without applied PID control (Scenario No. 1 and Scenario No. 2 of the case study).



**Figure 1.** The water level in the wet well during operation of pumps with and without applied PID control.

## CONCLUSION

Based on the diagram above and analysis of the operation of pump units without and with VFD in case study (Scenarios 1 and 2), it is concluded that pumping station operate smoothly if the pumps operate at variable speeds. The pumping station model is stable, which allows us to observe and draw conclusions about hydraulic phenomena important for the analysis and operational work of the complex system such as a SPS with a long pressurized force mains.

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# Investigation of Wave Dynamics around a Vegetation Patch in a Shallow Lake

M. Szilágyi\*, K. Homoródi\*, and T. Krámer\*

\* Department of Hydraulic and Water Resources Engineering, Budapest University of Technology and Economics, 3 Műegyetem rkp, Budapest 1111 Hungary  
(E-mails: [szilagyi.mariann@epito.bme.hu](mailto:szilagyi.mariann@epito.bme.hu); [homorodi.krisztian@epito.bme.hu](mailto:homorodi.krisztian@epito.bme.hu); [kramer.tamas@epito.bme.hu](mailto:kramer.tamas@epito.bme.hu))

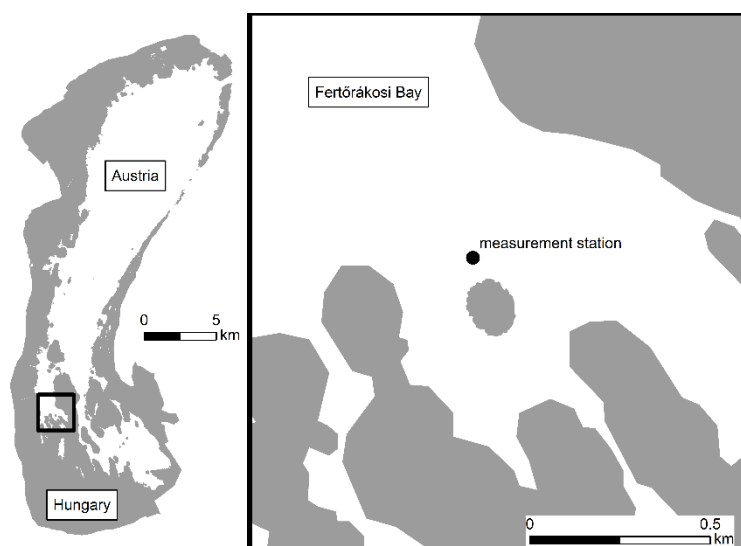
## INTRODUCTION

Emergent aquatic vegetation in shallow lakes affects wind, currents and surface waves, influencing at the same time sediment motion. Suspended particles tend to settle in the wake of a vegetation patch, which helps the vegetation spread in that direction. It is essential to understand the mechanics of these processes to predict the morphological evolution of shallow lakes. We contribute to this research by exploring surface wave dynamics around a reed patch in a shallow lake through field measurement and numerical modelling.

## METHODS

### Field measurement

Lake Neusiedl (called Lake Fertő in Hungarian), located at the Hungarian–Austrian border, is a suitable location for our case study due to its shallowness (its depth is between 1.0–1.5 m) and the large share of emergent vegetation cover. The prevailing wind direction is NNW, while SSE is also frequent. In view of this, a 100 m wide reed patch with clearly defined fetches from these directions has been chosen as the measurement site (Fig. 1). Here the water depth is 1.5 m in contrast to the SE, where it is only 0.9 m. We performed simultaneous ultrasonic wind, current and wave measurements on the NW side, to observe wave parameters under varying winds. According to the linear wave theory, bulk wave parameters such as significant wave height and wave period have been calculated.



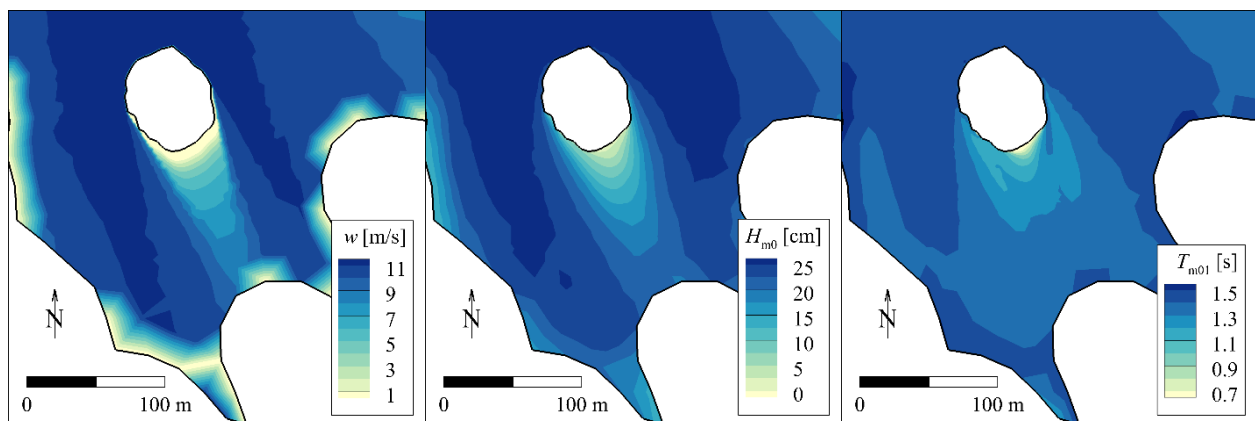
**Figure 1.** Location of the study site on the southern side of Lake Fertő.

## Numerical modelling

In order to extend the information gained from measurements towards a more detailed study with a statistically significant number of samples, we are adapting the two-dimensional spectral wave model SWAN (Booij *et al.*, 1999) to the patch and its vicinity. The model has already been tested offshore in this shallow environment (Homoródi *et al.*, 2012). Furthermore, Suzuki *et al.* (2012) applied it to investigate the impact of mangrove forest onto wave parameters. The measured information helps us calibrate and validate a model suitable to investigate longer periods and wave parameters induced by extreme wind conditions.

## RESULTS

We identify coherent signals in the modelled data to characterise wave field dynamics around the reed patch, with special interest in reflection, attenuation and diffraction. As an early result in our ongoing research, we demonstrate the significant wave height ( $H_{m0}$ ) and wave period ( $T_{m01}$ ) around the patch during a steady-state 10 m/s wind event from NNW. As it was expected, the spatial distribution of wind indicates the masking effect of the reed, at the side exposed to the wind higher significant wave height was calculated, This is the mechanism that, through many repetitions, induces morphological changes around the patch.



**Figure 2.** Spatial distribution of 10 m uniform wind speed (NNW, 10 m/s),  $H_{m0}$  and  $T_{m01}$ , respectively.

## ACKNOWLEDGEMENT

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# Deriving Nutrient Criteria Using Statistical Methods in Hungary

O. Szomolányi\* and A. Clement\*

\* Department of Civil and Environmental Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest 1111, Hungary  
(E-mails: [szomolanyi.orsolya@emk.bme.hu](mailto:szomolanyi.orsolya@emk.bme.hu); [clement.adrienne@emk.bme.hu](mailto:clement.adrienne@emk.bme.hu))

## INTRODUCTION

The objective of the Water Framework Directive (WFD) (EC, 2000) is to achieve good ecological status in surface waters by 2027. In order to make a proper evaluation of the ecological status of surface waters, it is necessary to harmonize the classification systems, therefore class boundaries for chemical and biological quality elements must be harmonized. This paper aims to determine total phosphorus and total nitrogen concentrations that support good ecological status based on the statistical evaluation of Hungarian water quality data. The research proved that basic statistical methods are not applicable for this task. Otherwise, the new approach based on random forest method demonstrates a promising tool which can be used as a decision support method for biological classification.

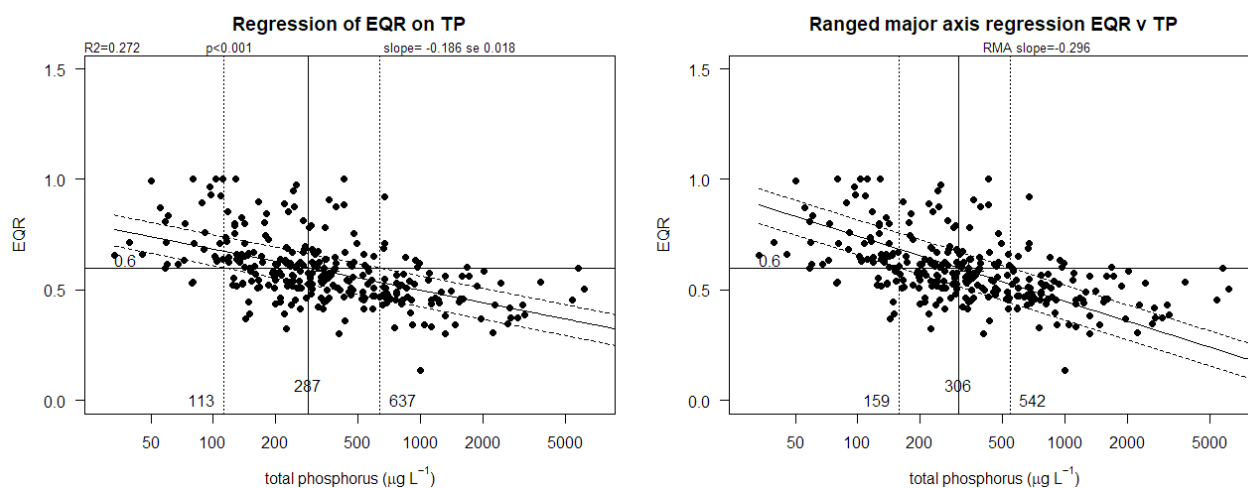
## MATERIALS AND METHODS

The statistical analysis was carried out using a guide (Phillips *et al.*, 2018) and the related “Toolkit”. As part of the “Toolkit”, we used the appended R code that contains several statistical tools and we also used RSudio 3.6.2 software to create boxplots and to build bivariate and multiple regression models. Random forest models were used for a better understanding of the stressor-response relationships and the prediction of biological status of the waters. For these analyses measured water quality (concentrations of Total P, Total N, BOD<sub>5</sub>, COD<sub>ps</sub>, DOC), hydromorphological data of the rivers and biological quality elements (EQS values of phytoplankton and phyto-benthos) were used. Statistical analyses were performed with mean nutrient concentrations and biological quality values (EQR) of Hungarian water bodies from the period 2007–2017. Analyses were conducted by using both year-round and vegetation period nutrient concentrations. Natural, artificial, and heavily modified water categories were evaluated separately. To specify nutrient criteria, we used the ordinary least squares method (OLS) and type II. ranged major axis regression (RMA). Among the categorical methods, we used the mis-match method, which has the advantage over the regression methods that it gives a good estimate even with weak nutrient-biology relationship (low  $r^2$  value).

## RESULTS

Based on the guidance we were able to perform statistical analyses and suggest nutrient class boundaries. With the long-term averages we were able to suggest nutrient class boundaries in 29 cases, with sample-site-level annual averages class boundaries were suggested in 39 cases and by using data from the vegetation period only, class boundaries could be suggested in 63 cases (highland rivers N: 1.8–6.2 mg/L, P: 180–400 µg/L; lowland rivers N: 1.4–5.0 mg/L, P: 100–350 µg/L). Generally, we could suggest thresholds in case of water types with a large amount of monitoring data (e.g. small and medium highland rivers with a mild bottom slope; small and medium lowland rivers with smooth sediment), but in these cases, the  $r^2$  values were lower than water types with fewer monitoring data. Despite the lower  $r^2$  values in the case of small and

medium rivers (Fig. 1), the analyses of phytoplankton and nutrients yielded consistent and realistic thresholds, that are similar to what other countries derived (Poikane *et al.*, 2019).



**Figure 1.** Relationship between mean total phosphorous concentration and phyto-benthos in Hungarian small and medium rivers with rough sediment. Solid lines show OLS and RMA regression, dotted lines mark the confidential interval, while the horizontal line at EQR = 0.6 shows the good-moderate biological class boundary.

Detailed analysis of stressor-response relationships with boxplots, bivariate and multivariate regression demonstrated that the relationship between biological quality elements and physicochemical stressors beyond nutrient concentrations is very complex as well. Among the investigated variables only dissolved organic carbon showed stronger linear relationship ( $0.2 \leq r^2 \leq 0.4$ ,  $p \leq 0.05$ ) with EQR. With the help of the random forest method, we selected 5 background variables that have the biggest impact on the biological status of the rivers. Based on these variables the prediction for the biological class was possible with 35–81 % error in case of phytoplankton and with 18–47 % error for phyto-benthos.

## CONCLUSIONS

The analyses highlighted that basic statistical methods cannot be used for nutrient criteria evaluation. One reason for the unsuccessful analysis lies in the small sample size and low reliability of Hungarian monitoring data. Also, the basic statistical methods such as OLS and RMA regression and the mis-match method do not consider other factors that influence the biology; therefore, we suggest using them as decision support methods supplemented with more complex methods and expertise.

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# The Analysis of Runoff Generation in Small Scale Catchments

A. Veinbergs\* and A. Lagzdins\*

\* Department of Environment and Water Management Latvia University of Life Sciences and Technologies, 19 Akademijas str., Jelgava, LV-3001, Latvia, (E-mails: [arturs.veinbergs@llu.lv](mailto:arturs.veinbergs@llu.lv); [ainis.lagzdins@llu.lv](mailto:ainis.lagzdins@llu.lv))

## INTRODUCTION

Runoff generation and hydrological pathways are still challenging to understand while necessary to estimate nutrient pathways (Deelstra *et al.*, 2014). In Latvia's monitoring system, streamflow generation is not studied in detail. Observed runoff data are not spatially sufficient to characterize the catchment's non-homogeneity. That leads to highly uncertain hydrological pathways even predicted by mathematical modeling. This study aims to reveal the spatial variations in runoff behavior caused by the catchment scale, allocation, local characteristics, and precipitation rate.

## MATERIALS AND PROCEDURES

The observational data sets of daily precipitation and runoff from 01.01.1995. to 31.12.2016. were applied to analyze hydrological regime and long-term water balance [Eq. (1)–(3)] for the monitoring stations of Berze, Mellupite, and Vienziemite in Latvia.

$$ET = \bar{P} - \bar{Q}_y, \text{ mm per year,} \quad (1)$$

$$\bar{P} = \frac{\sum_{i=1}^n P_{di}}{n_y}, \text{ mm per year,} \quad (2)$$

$$\bar{Q}_y = \frac{\sum_{i=1}^n Q_{di}}{n_y}, \text{ mm per year,} \quad (3)$$

where  $P_{di}$  is a sum of precipitations in an  $i$ th day, mm;  $Q_{di}$  is an average runoff in an  $i$ th day, mm;  $n$  is the total number of days in the data set;  $n_y$  is the total number of years in the data set.

The Nash-Sutcliffe efficiency coefficient (NSE) and Percent bias (PBIAS) (Moriassi *et al.*, 2007) were used to compare the difference between runoff from small catchments and drainage fields.

## RESULTS

This study reveals that the total amount of long-term ET and runoff is higher in the regions with relatively higher precipitation rates (Table 1). However, the higher the long-term precipitation and the higher the surface slope gradient, the higher runoff was contributing to the water balance. Similarly, the highest runoff coefficients experienced the sub-basins of highest precipitation rates at the Selke River catchment located in the central part of Germany (Sinha *et al.*, 2016). The catchments of low surface slope gradient might lead to less intense groundwater flow (Richardson and Vepraskas, 2000; Mu *et al.*, 2015), while the ET can be consequently comparatively high (Boldini *et al.*, 2014). The estimates of PBIAS (Table 2) show that the long-term average runoff is higher in the drainage fields rather than in the small catchments at the Berze and Mellupite monitoring stations. That might indicate that during the dry seasons, the existence of baseflow in the small catchment has no considerable impact on the long-term soil water balance and ET rates.

Similarly, Jones (1976) reveals that ET is insignificant from the depth higher than approximately 1.3 m below the ground surface. The estimates of NSE's indicate the different runoff behavior under the measurement scale that is more pronounced within yearly rather than monthly time scale.

**Table 1.** Long-term water balance for the monitoring stations Berze, Mellupite, and Vienziemite for the period from 1995 to 2016.

Water balance Component	Unit	Berze		Mellupite		Vienziemite	
		Small catchment	Drainage field	Small catchment	Drainage field	Small catchment	Drainage field
Precipitation ( $\bar{P}$ )	mm	601.5		678.9		730.8	
Evapotranspiration ( $ET$ and $ET_{\%}$ )	mm	430.0	421.0	435.3	434.1	452.6	462.3
	%	71.5	70.0	64.1	63.9	61.9	63.3
Runoff ( $\bar{Q}_y$ and $\bar{Q}_{y\%}$ )	mm	171.5	180.5	243.6	244.8	278.2	268.5
	%	28.5	30.0	35.9	36.1	38.1	36.7

**Table 2.** Statistical differences between the runoff from small catchment and drainage field within the period from 1995 to 2016.

Period	Berze		Mellupite		Vienziemite	
	NSE	PBIAS*	NSE	PBIAS*	NSE	PBIAS*
Monthly	0.77	5.27	0.78	0.55	0.76	-3.50
Yearly	0.60		0.71		0.42	

\*Negative value shows higher runoff from small catchment compared to the drainage field.

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# Microbiological Safety of an Indoor Pool Water Disinfected with Combined Chlorination and UV Method

M. S. Zekanovic\*, B. Pucar\*\*, and I. Gobin\*\*\*

\* Ilirija d.d., Tina Ujevica 7, 23210 Biograd na Moru, Croatia

(E-mail: [melanis@ilirijabiograd.com](mailto:melanis@ilirijabiograd.com))

\*\* Zadar Public Health Institute, Department of health ecology and environmental protection, Ljudevita Posavskog 7a, 23000 Zadar, Croatia (E-mail: [bpucar@zjz-zadar.hr](mailto:bpucar@zjz-zadar.hr))

\*\*\* Department of Microbiology and Parasitology, Faculty of Medicine, University of Rijeka, Braće Branchetta 20, 51000 Rijeka, Croatia (E-mail: [ivana.gobin@uniri.hr](mailto:ivana.gobin@uniri.hr))

## INTRODUCTION

Chlorination, the most used method of water disinfection has many drawbacks, such as the presence of chlorine-resistant microorganisms and the formation of potentially toxic disinfection by-products (DBPs) (Wyczarska *et al.*, 2020). Therefore, combined disinfection with UV irradiation is increasingly used in pools to improve the quality of swimming pool water (Ilyas *et al.*, 2018). To ensure microbial safety, the swimming pool water is regularly analyzed for the presence of different indicator organisms. Besides *Pseudomonas aeruginosa*, *Escherichia coli* is often used as a fecal indicator (Aboufotouh *et al.*, 2017). The previous research gives limited and conflicting information regarding the effects of UV-based treatment and maintenance of the pool on water microbiology in the presence of residual chlorine and the occurrence of trihalomethanes in swimming pool water (Ghasemi *et al.*, 2019, Afifi and Blatchley, 2016). So, the aim of our study was to continuously monitor the expanded range of indicators (physico-chemical and microbiological) as well as the detailed maintenance system of indoor pool a pool with combined water disinfection for one-year period (2019–2020).

## MATERIAL AND METHODS

### Indor pool characteristics

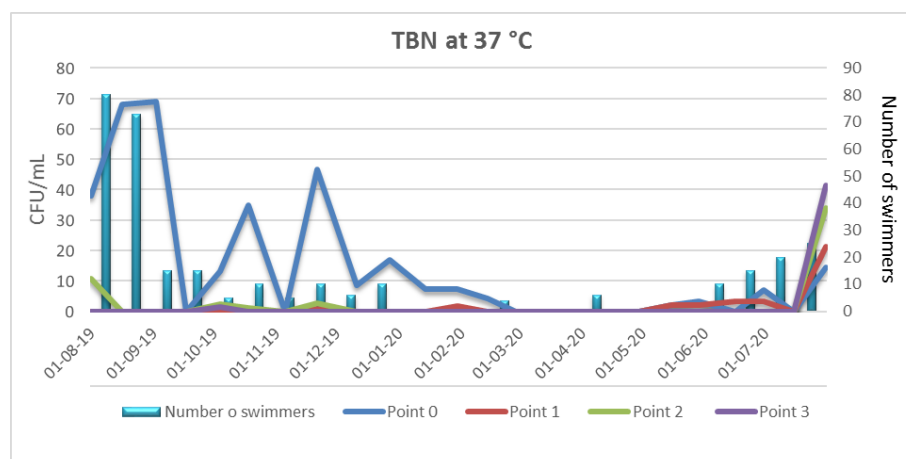
The size of the pool was 7.5 m × 14 m and is 1.45 m deep, creating a pool water volume 152.25 m<sup>3</sup>. The mean hydraulic detention time for water in the pool was approximately 5 hr. Free chlorine was applied to the pool in the form of NaClO from a tank located in pool engine room. Water disinfection is also carried out with a low pressure (amalgam) UV lamp. More than 1 % of the total amount of water is changed daily. Operation and maintenance of the pool and use of the pool by swimmers were checked every day. The research was conducted in a manner that did not interfere with use of the pool.

### Pool water quality

During a 12-month period, the basic parameters were measured once a day and the advanced parameters every two weeks. Water samples collected from approximately 30 cm below the pool water surface. As part of the basic analyses, the values of water pH, temperature, and redox potential and the concentration of free chlorine and combined chlorine were measured. The advanced analyses included chemical indicator, trihalomethanes and microbiological indicators (total number of bacteria (TNB) at 22 °C and 37 °C, *P. aeruginosa*, *E. coli*, *Clostridium perfringens*, *Enterococcus* spp., *Staphylococcus* spp. and *Legionella* spp.). Concentrations of THMs represented the sum of the concentrations of trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane.

## RESULTS

During the research due to the COVID-19 situation from March to June the pool was not closed but was maintained all the time. In terms of the analyzed microbiological indicators, the quality of the tested pool water samples was not in doubt. Fecal contamination indicators were not detected, as well as *Legionella* spp., while *P. aeruginosa* was detected in the pool at two occasions (30.1.2020. and 31.07.2020.) in small number. As it goes for *S. aureus* small number were detected at 4 occasions (21.11. and 27.12.2019., and 16.6. and 30.6.2020.). Concentrations of THMs, and other physico-chemical indicators which are daily measured, were within the permitted limits.



**Figure 1.** Total bacterial number (TBN).

## CONCLUSION

The planned research study will enable the introduction of evidence-based practice, and thus the selection of the most appropriate intervention measures and disinfection methods to improve the quality of pool water.

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