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IMPRESSUM

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EDITORIAL TEAM

Editor-In-Chief opening remarks

Dear readers,

It is a great honor to introduce you the new *Special Issue: WATER FOR ALL* number of the journal *Environmental Engineering-Inženjerstvo okoliša* published by Faculty of Geotechnical Engineering, University of Zagreb, Croatia.

In this number the topic was water, with a Guest Editor prof. Mirna Habuda-Stanić, from the Department of Applied Chemistry and Ecology, Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Croatia.

Prof. Habuda-Stanić was the organizer of a very successful 8th International Conference WATER FOR ALL 2019 held in Osijek. The selection of the best papers from the conference seemed to be a logical step in supporting the *Special Issue: WATER FOR ALL* number.

Prof. Habuda-Stanić has done a remarkable work and the new issue is in front of you - six accepted papers, including 4 original scientific, 1 preliminary report and 1 professional paper; and authors from 3 different countries. The papers covered different fields of water and water related issues; from vacuum sewer systems, case study of water status on the waste landfill, electrocoagulation of water, advanced oxidation treatments of wastewater, photocatalytic degradation of dyes and solid-phase extraction of residues from water.

I am also proud to note that in cooperation with the National and University Library in Zagreb and the Crossref, a Digital Object Identifier (DOI) number has been assigned to the journal *Environmental Engineering-Inženjerstvo okoliša*. The DOI numbers will be assigned to all papers published in 2019 and ongoing.

I hope this issue is a small step in promotion of importance of water and water related issues for a better future.

At the end, I would like to give my gratitude to prof. Habuda-Stanić, all team members and to our sponsors.

I hope you will enjoy it.

With best regards,

Assoc. Prof. Dr. Nikola Sakač
Editor-in-Chief

Unit for Chemical Sensors
Department of Environmental Engineering
Faculty of Geotechnical Engineering
University of Zagreb

Guest Editor introduction

Dear readers,

Water covers 70 % of our beautiful and unique planet Earth. However, although present in such enormous amounts in our environment, and in our bodies, the clean water that we need in our everyday life during the past decades became incredibly rare. This increased the awareness how fragile and precious natural resource it is.

In this sense, with greatest honour and happiness I accepted the invitation of Editor-in-Chief, prof. Sakač to be the Guest Editor of the *Special Issue: WATER FOR ALL*.

As the main organizer of the very successful conference "8th International Conference WATER FOR ALL 2019" held in Osijek from 21st to 22nd March 2019, I decided to select the papers presented at this conference for the Special Issue, since the conference was supported by 359 authors from 10 countries and 112 paper.

The International Conference WATER FOR ALL 2019 was held on the World Water Day with the aim of gathering and exchanging experiences of scientists and experts in the field of water management, environmental protection and preservation of water resources. The conference was organized by Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek (my home institution) and a network of institutions, while our international partners in organization were International Federation of Environmental Health (IFEH), European Hygienic Engineering & Design Group (EHEDG) and Danube Parks.

The 8th International Conference WATER FOR ALL 2019 was held under auspice of the President of the Republic of Croatia, Mrs. Kolinda Grabar Kitarović, while the scientific part of the Conference was under the auspices of the Croatian Academy of Arts and Sciences.

At the conference we made an open student contest for “The best WATER PHOTO”. The selected student photo was used as a cover photo of this Special Issue. The author of the cover photo is Lucija Prebeg, a student of the Faculty of Agrobiotechnical Sciences Osijek.

I hope that this Special Issue of the journal *Environmental Engineering - Inženjerstvo okoliša* will contribute to awareness of increasing global problem of water scarcity, as well to give small contributions in finding solutions for water preservation and water safety for generations yet to come.

Kind regards,

Assoc. Prof. Dr. Mirna Habuda-Stanić
Guest Editor

Department of Applied Chemistry and Ecology
Faculty of Food Technology Osijek
University of Osijek
Croatia

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C O N T E N T

MAINTENANCE ISSUES OF THE VACUUM SEWER SYSTEM

Dino Obradović [1,*], Marija Šperac [1] and Saša Marenjak [1]
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Abstract: *A sewer system is an indispensable part of every settlement which contributes to the protection of the environment and people. There are many types of sewer systems. In addition to the standard sewer systems (mixed, separated, etc.), there are the alternative, non-standard systems, and one of them is a vacuum sewer system. In order for a sewer system to function correctly and to perform its tasks successfully, it needs to be maintained properly and regularly. Generally speaking, maintenance is considered to be a series of activities performed in order to achieve that constructed buildings allow an adequate use and functionality for the purpose they were designed for. Considering these systems are relatively new and still rarely used, there is no general practice or rules for use and maintenance of the same, and, most importantly, there is no user experience or people responsible for managing the work and maintenance. The paper will present the general characteristics and parts of vacuum sewer systems. Maintenance recommendations will be given, and maintenance costs specified making reference to the literature available to the authors.*
Keywords: *sewer system, maintenance, costs, vacuum sewer system*

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Professional paper

1. INTRODUCTION

Proper functioning of the sewer system is very important. The sewer system carries wastewater away from family houses, buildings, factories, as well as streets, into the wastewater treatment plants, which is a prerequisite of indispensable public hygiene. Because of that reason, the maintenance of wastewater system and wastewater pipes is of great importance (Obradović 2017; Obradović 2018b; Obradović et al. 2019) and a serious attention should be given to the maintenance (Šperac et al. 2012). The sewer system consists of pipelines, conduits, pumping stations, force mains, and all other facilities used to collect wastewater from individual residential, industrial, and commercial sources and convey it to the treatment facilities (KCNRK 2018) Generally, maintenance can be defined as the process of implementing the necessary activities to keep a building, all its parts, system or equipment to the specified operable condition and to preserve the value and purpose of buildings, systems and equipment (Obradović & Marenjak 2017). Urbanization is becoming more and more evident, and there is a growing need for sewer maintenance and its renovation, using as little work on the terrain surface as possible (Obradović 2018a).

In the light of all the aforementioned considerations, the importance of a proper maintenance of the sewer system, as well as a more cost-effective utilization of money for design, maintenance, reconstruction and eventually the replacement of the sewer system and its components is clear. Moreover, not every type of terrain is suitable for any type of a sewer system. In order to try to solve some of the problems mentioned (and ultimately, each issue comes down to money), among other things, the invention of a vacuum sewer has been made as an alternative sewer system with a forced flow. The main reasons for the realization of such sewer systems were the requirements for a fully sealed sewer system, the rationalization of the quantity of the embedded material, the reduction of the work required during the sewer system construction and the efforts made to reduce the negative impacts on the environment during construction and exploitation (Šanta & Fabry 2016; Hrskanović 2016). In many countries, this system has been widely used (Elawwad 2015), even in our neighbouring countries, such as: Hungary, Slovenia, Romania, Serbia, Germany, etc. In the Republic of Croatia, the vacuum sewer system was built in Županja and in one part of the town of Sisak. Relatively very few towns in the Republic of Croatia have such a system and there is little existing knowledge about the system and the way it is operated and maintained.

The sections of this article are structured as follows. Section 2 is intended to show brief history, technology of vacuum sewer system, advantages and disadvantages. Maintenance of vacuum sewer system and maintenance costs are given in Section 3. Section 4 gives brief discussion about dealt topic and provides some conclusions at the end of the paper.

2. VACUUM SEWER SYSTEM

2.1. History of vacuum sewer system

Concepts of vacuum sewer system appeared already by the end of the 19th century (Tang et al. 2013), when technological developments allowed engineers to construct devices to pump sewage (Miszta-Kruk 2016). It is not entirely clear who can be named the inventor of vacuum sewer system and exact year of invention. A Dutch engineer and former Captain in the US army Charles Thieme Liernur, invented pneumatic system in 1868 (somewhere dated 1886) (Liernur 1892; Scott 1975; Petrešin & Nekrep 2008; Redivac Limited 2014; Gikas 2017) where sewers were laid at uniform depth regardless of gradient and sewage was drawn through cast-iron pipes under half an atmosphere of vacuum (Read 2004). The Pneumatic System was first put in operation in 1871 in two districts in Amsterdam (Scott 1975). As can be seen from **Figure 1** Liernur's system was used to collect sewage from domestic houses and consisted of an underground storage tank into which the effluent was received via iron pipes under gravity flow (Redivac Limited 2014).

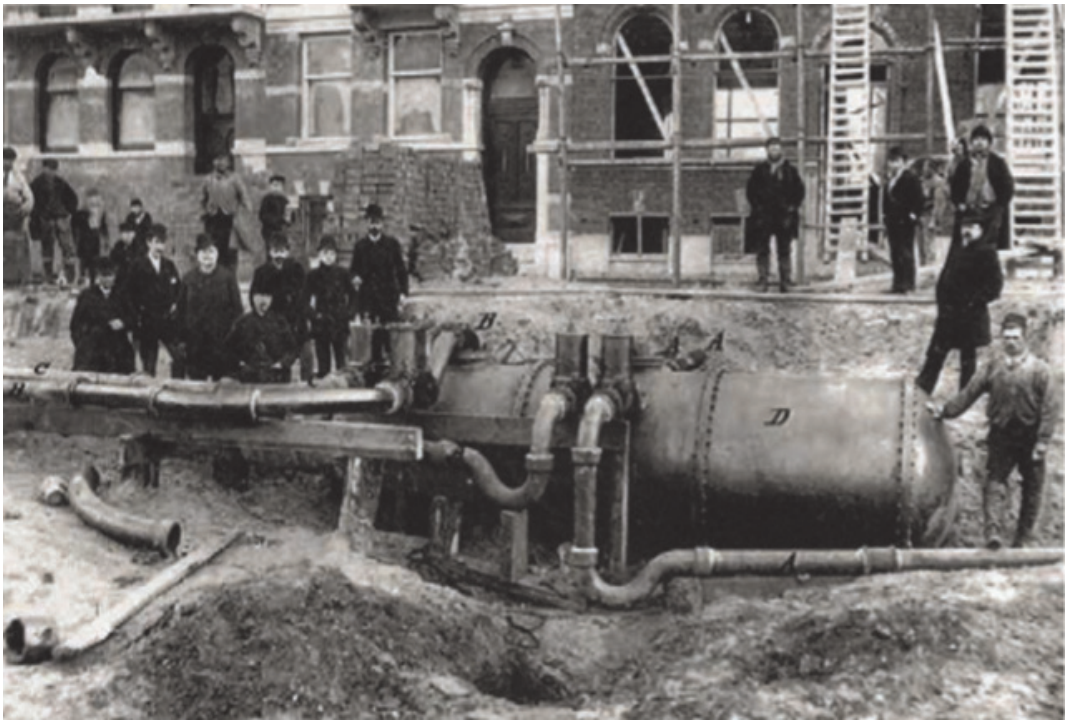

Figure 1. *Vacuum sewer system in Amsterdam (Redivac Limited 2014; Schluff 2013)*

By other authors (Lemarquand 1887; Miszta-Kruk 2016; Shafiqul Islam 2017; Gikas 2017) the first vacuum wastewater collection system was patented in 1888 in the United States by Adrian LeMarquand. And, at the end, by the third group of authors (Averill & Heinke 1974; Read 2004; WEF 2007; Schluff 2013; Miszta-Kruk 2016) the first vacuum sewer system was patented in Sweden by Joel Liljendahl and was originally called the Liljendahl Vacuum Sewage System. In fact, Liljendahl continued to develop the vacuum sewerage system and tested it in the residential district in the north of Stockholm. It was employed first in 1959.

2.2. Technology of vacuum sewer system

The term vacuum sewer system has been widely used for simplification reasons and marketing purposes. Technically "vacuum" is not the correct term (for using in name "vacuum sewer system") since a vacuum is a void space free of any matter. Vacuum sewer system operates under negative pressure compared to the atmospheric pressure (Mohr 2016). However, because the term "vacuum sewer" is already established and common it will be used in this paper. The fundamental principle of the vacuum sewer system is the transport of wastewater by air pressure rather than by the gravity - induced flow of water. Vacuum sewer systems have two distinct advantages over conventional gravity systems: the vacuum system can function using much less water than gravity systems, and wastewater transport is not restricted to following hydraulic grade lines (Averill & Heinke 1974).

Although there are several types and methods of its construction, each of these vacuum sewer systems operates on the same principle. **Figure 2** shows the typical layout of a vacuum sewer system.

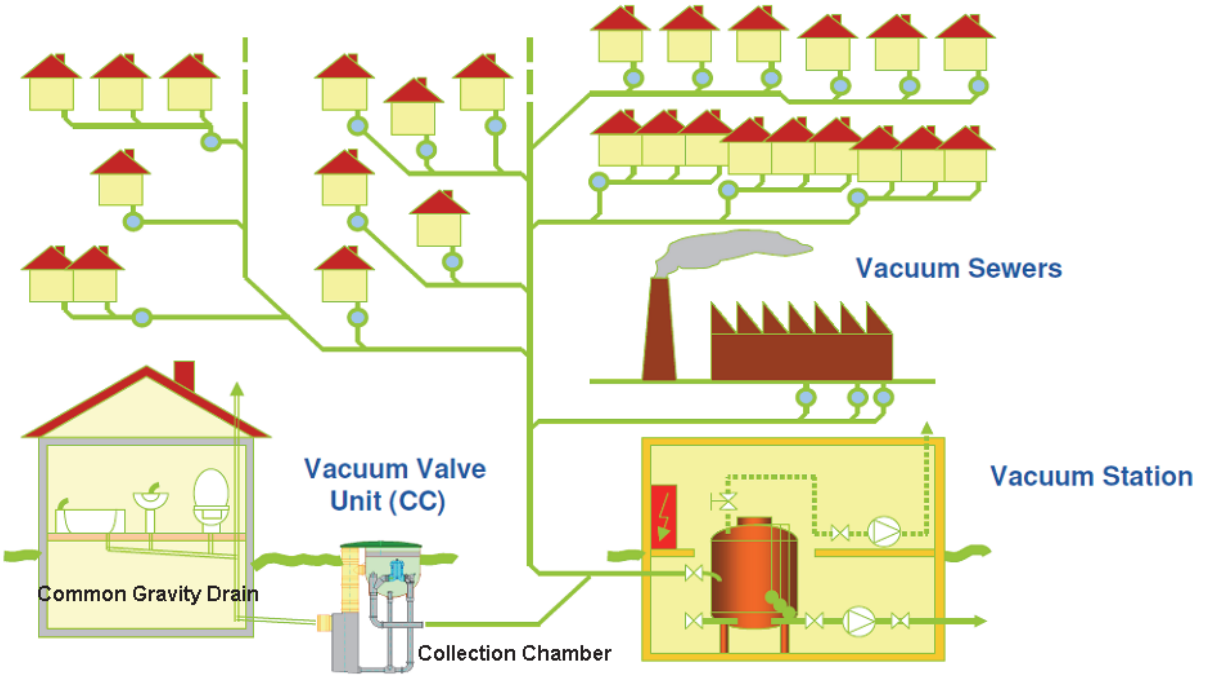

Figure 2. *Overview of a typical vacuum sewer system with the vacuum valve unit, vacuum mains and the central vacuum station (Bilfinger Berger - Roediger 2007; Bilfinger Berger 2011; Becket 2017; Mohr et al, 2016; Stauffer & Spuhler 2018; Mohr et al. 2018)*

The vacuum in the vacuum sewer system is drawn by one or more vacuum pumps located in a central pumping station. There are no electrical components at the individual connections to the system (at the home) (Pipeline 1996; Aquate 2019). The wastewater that accumulates at the building level flows into the closely located collection chamber via a gravity line (Beckett, 2017). When the wastewater in the collection chamber reaches a certain level, a sensor prompts a pneumatic valve to open, and the entire plug of wastewater is violently sucked into the lines by the vacuum in the sewer main. The valve stays open a few seconds to also allow some air to be sucked in after the wastewater (Pipeline 1996). The amount of air that enters with the sewage is controlled by the length of time that the valve remains open. When the vacuum valves close, atmospheric pressure is restored inside the valve pit (Buchanan et al. 2010). As a standard practice, the necessary sub pressure (lower pressure than atmospheric) for operation of the vacuum system normally in range of 60 to 70 kPa (0.6 to 0.7 bars) or 40 to 30 kPa absolute pressures. This pressure should be maintained by vacuum pumps (Shafiqul Islam 2017; Beckett 2017; Ciobotici et al. 2014; Panfil et al. 2013).

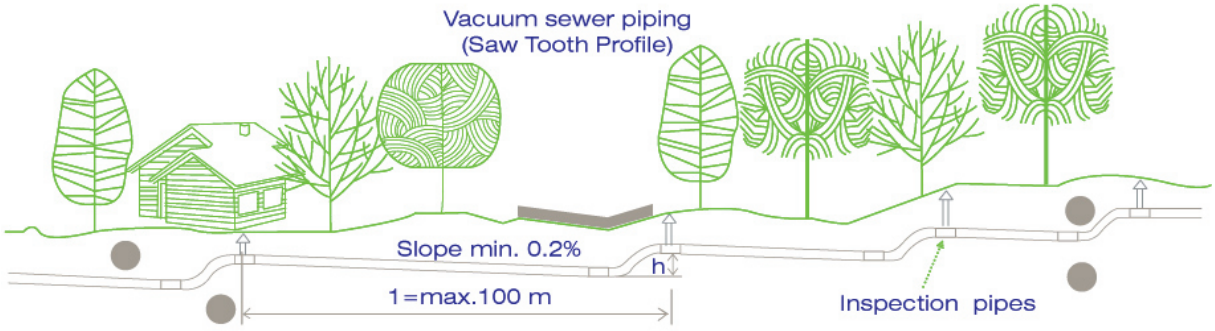

Figure 3. *Saw-tooth profile (UW Tech 2019)*

For vacuum sewer networks a saw-tooth pipe profile design is required (Bilfinger Berger 2012) (**Figure 3**). It means that the sewer line is composed of "lifts" and positive slopes towards the vacuum station. On the positive slopes the sewage is moved by gravity and on the negative slopes the sewage is moved by the differential pressure behind and in front of the sewage slug. The purpose of the saw-tooth-profile is to keep the trench depth shallow (1.0 to 1.2 m), to transport the sewage uphill and to prevent the pipes from becoming sealed by keeping an open passage way on top of the sewer (WEF 2007; Mäkinen 2016).

2.3. Advantages and disadvantages of vacuum sewer system

Many characteristics of vacuum sewer system can lead to benefits over other sewer systems. However, despite its flexibility a vacuum sewer system does not give a solution to every problem. In **Table 1** are given advantages and disadvantages (please note this is partly subjective) of vacuum sewer system compared to other sewer system and technologies (Mohr et al. 2016).

Table 1. Summary of advantages and disadvantages of vacuum sewer system (Elawwad et al. 2014; Mohr et al. 2016; Ljubisavljević & Obrenović 2010; Bilfinger Berger - Roediger 2007; Bilfinger Berger 2011; WEF 2007; UW Tech 2019; Gibbs 2016; Ma et al. 2015)

Advantages	Disadvantages
Small pipes diameter (90 to 250 mm)	High energy consumption
Shallow and narrow trenches (1.0 to 1.20 m)	Additional cost for vacuum valves and vacuum stations
No exfiltration in vacuum systems	Expert design is needed
Better in flat areas (saw tooth profile)	Needs energy to maintain vacuum
Minimum potential for blockage (v = 6 m/s)	Network length is limited
Shorter construction period	Skilled operators are required – training necessary
Less water is needed for transport to centralized treatment facility	Design guidelines and operation and maintenance are not well known in developing countries
No manholes are required	Number of system providers limited
Fault detection is quick	Faults at individual valves can affect the entire systems
Installation in the same trench as water supply lines possible	System components not quickly available everywhere
Applicable in water protection zones	
No infiltration of stormwater or groundwater due to tight system	
Minimum maintenance at vacuum valves and collection chambers	
Only one source of power, at the vacuum station, is required	
Can be used in very narrow streets	
Flexible pipeline construction independent from topography	
Field changes can easily be made as unforeseen underground obstacles can be avoided by going over, under, or around them	
Minimum impact to the environment from construction	
Vacuum sewer systems are the only systems allowed to be installed in ecologically sensitive areas and drinking water protection zones	
Little impact on local traffic	
No dependence on external circumstances	
Earthquake proof, no rat trouble, no animals are caught in the sewer net	

2.4. Maintenance of vacuum sewer system

A long-term and trouble-free operation of the sewer system requires a suitable design and its execution, but also properly performed preventive maintenance and repairs of the property. These periodically repeated activities (**Table 2**) are crucial for the sustainability and adequate service life of the sewer system (Mazák et al. 2017).

Table 2. Maintenance tasks and their frequencies (Mohr et al. 2016; Mäkinen 2016; Buchanan et al. 2010)

Frequency	Maintenance Tasks
Daily	General inspection at the station Visually check gauges/ charts Record all pump run times Check oil level in vacuum pump sight glass Check alarms at the control cabinet Fill out daily equipment check-up log book Check alarm dialer function
Weekly	Exercise generator (if applicable) Check vacuum system for leaks with manometer and record findings Check oil level Check for unusual noises Check vacuum pump exhaust filter gauge Visually/audibly check vacuum station operation
Monthly	Change oil and oil filters (depends on manufacturer's recommendations) Remove and clean inlet filters on vacuum pumps Test all alarm systems Check all motor couplings and adjust (if needed) Clean all sight glasses Exercise all shut off valves (vacuum station) Check appearance of station (cleanliness and accessibility) Check biofilter (humidity, odours, appearance) Check sump for proper valve cycling Check vacuum sensor (absolute pressure)
Semi-annually to annually	Conduct external leak test on all vacuum valves Check electrical connections at the station Check tank for deposits and remove them Check alarm signals of the vacuum pumps Check pump motors and couplings (wear, misalignment, deterioration, overheating)
Every year	Exercise division valves Inspect vacuum and sewage pumps for wear Visual inspection of all pits and valves Check valve timing and adjust if needed Check functionality of alarms Change oil of vacuum pump Change oil filter of vacuum pump Check state of construction of the station (e.g. corrosion, structures, etc.) Floating switch cleaning and testing
Every 3 years	Rebuild controller (buffer tank valves only)
Every 5 years	Rebuild controller (most valves)
Every 15 to 25 years	Replace a vacuum station equipment

If the vacuum sewer system is properly designed and constructed, there are very few things that can deteriorate in the vacuum sewer channel. Proper coordination of components and their individual properties is crucial. It is imperative to determine the amount of wastewater and select the components according to the required capacities. This applies not only to vacuum and sewerage pump capacities but also to the diameter of the vacuum mains. Due to lower transport velocities vacuum mains which have a large pipe diameter are more prone to scaling and precipitation from compounds contained in the wastewater. This can affect the durability of

the selected material and thus the life span (Mohr et al. 2016). As with any sewer system, pipe cracking may occur due to land subsidence or landslide resulting in the loss of vacuum in the system. This is revealed by means of an alarm generated by the control system signalling the - vacuum loss, with the exact location of the crack that can be located by opening and closing the segment valves in a logical sequence along the pipeline. Another potential problem is the excessive amount of water in the system. If the system maintenance records are kept (and they should be kept in order for the maintenance to be performed properly), periodic inspections will be required with regards to the identified problems and the parts of the sewer system that are prone to malfunctions.

Preventive inspections and repairs are shown in **Table 2**. The time periods for the replacement of deteriorated parts and the preventive inspections are determined by the equipment manufacturers. Preventive action approaches minimize the risk of failures before they emerge. The availability of components needs to be checked and ensured when choosing a vacuum sewer system. In the event of system failure or material wear individual parts need to be available to ensure quick recovery of the sewer function. Therefore, sufficient stock and long-term material supply need to be assured (Mohr et al. 2016).

Emergency maintenance is mainly related to improper vacuum valve operation. The cause of this is usually a low vacuum level in the system or some other water in the system with the valves in the open position during the failure. This results in a vacuum loss because the system is open to the atmospheric pressure. If the inlet valve breaks in the open position, the monitoring system will detect the malfunction and alert the personnel responsible for the system operation and maintenance (Hrskanović 2016).

Operation and maintenance costs can vary significantly on how well the system is designed and how repair of the system failures is managed. Electricity and personnel costs are the major cost components (Mohr et al. 2016; Beckett 2017). However, material costs are also important but usually much lower than the electricity and personnel costs. In a comparative study on vacuum sewers in Germany electricity consumption of vacuum sewers was found to be in 15 to 30 kWh/person/year or 0.2 to 0.4 kWh/connection/day (Mohr et al. 2016). **Table 3** provides cost estimation (and/or by experience) for the materials, installation, and maintenance of a vacuum sewer system.

Table 3. Approximate costs of materials, installation and maintenance of a vacuum sewer system (Schluff 2013; Buchanan et al. 2010)

Component	Approximate cost [in EUR]
Pipe costs depending of the diameter	10 to 50 EUR/m
Domestic connection, incl. control and supervision plant	3,000
Pump station, ready to be operated	350,000
Annual operation and maintenance (for 100 vacuum pits)	72,920 to 109,400
Annual electricity	8,500 to 12,500

The vacuum sewer system is not very widespread in the Republic of Croatia. One part of the town of Županja has it (Komunalac Županja 2016), as well as the suburban village of Galdovo - near the town of Sisak (Grad Sisak 2008; Sisački vodovod 2019).

It exists in some other towns or its construction is being considered, but to a lesser extent. The following section of the paper presents the vacuum sewer maintenance costs according to available data and research (Hrskanović 2016). A vacuum system maintenance comes down to maintaining a vacuum station, constituting the largest part of the costs. The sewage pipeline of the vacuum system does not require cleaning, except in cases of clogging, which is extremely rare, since the wastewater flow rates in the vacuum sewer system are very high and the vacuum pipeline is considered to be self-cleansing. **Table 4** shows the electricity cost of the energy requirement for one vacuum station. Vacuum stations use one vacuum pump and one sewage pump, and both have a spare one in case of failure or service.

It is important to emphasize that a sewage system may consist of multiple vacuum stations (and usually it does), but the tables below show the maintenance costs of a single pumping station or costs per one unit. From all of the aforementioned, it is not a problem to calculate costs for, for example, a vacuum sewer system consisting of five vacuum stations. All the costs are expressed in monetary units - Croatian Kunas (HRK) and Euros (EUR) according to the Croatian National Bank's exchange rate on October 23, 2019 (Croatian national bank 2019).

Table 4. Electricity costs for a vacuum station (Hrskanović 2016, edited)

Component	Engine power	Hours a day	Days a year	Electricity price [HRK/kWh]	Cost [in HRK]	Cost [in EUR]
Vacuum pump	2.5	8	220	0.529	2,327.60	313.10
Sewage pump	0.4	8	220	0.529	372.42	50.10

Vacuum stations should undergo routine daily and monthly inspections and annual cleaning. Labour costs for daily, weekly, monthly and annual inspections and checks are shown in **Table 5**. Moreover, the vacuum pump is dismantled and cleaned once a year, which is usually performed by the manufacturer or an authorized person and represents a significant portion of the annual maintenance costs, since this service is "external" and is paid separately by an external contractor. **Table 6** shows the total cost of maintaining and operating a single vacuum station.

Table 5. Vacuum station inspection costs (Hrskanović 2016, edited)

Task	Workers	Hours a day	Days a year	Labor cost [HRK/h]	Total cost [in HRK]	Total cost [in EUR]
Inspection	1	0.5	365	60.00	10,950	1,472.96
Pump replacement	1	0.5	12	60.00	360.00	48.43
Maintenance	1	2	1	60.00	120.00	16.14
Cleaning	-	-	1	-	35,000	4,708.10

Table 6. Total cost of maintaining and operating a single vacuum station (Hrskanović 2016, edited)

Item	Costs [in HRK]	Costs [in EUR]
Electricity cost of the vacuum pump	2,327.60	313.10
Electricity cost of the sewage pump	372.42	50.10
Inspection	10,950	1,472.96
Pump replacement	360.00	48.43
Maintenance	120.00	16.14
Cleaning	35,000	4,708.10
Repair of vacuum pump	6,762.50	909.69
TOTAL	55,892.52	7,518.51

3. CONCLUSION

Vacuum sewer system is considered an alternative wastewater collection system. Vacuum sewer systems have many advantages, such as water savings, shallow and narrow trenches, smaller pipe diameter, good sanitation conditions, flexible pipeline construction independent from topography, shorter construction period, etc. However, the investment and operational costs, as well as the applicability can vary significantly between regions and the need for them to be assessed under local conditions. Vacuum sewer systems show less negative environmental and social impacts than the conventional system. Under appropriate conditions and with a proper maintenance, the vacuum sewer system does not present any additional requirements with respect to the inevitable operating costs and the necessary resources of the operator. As with any building, a timely and proper maintenance is very important. Proper coordination of components and their individual properties is crucial. Preventive action approaches minimize the risk of a failure before it occurs, and because of this, a preventive maintenance should be performed on time and must be carefully planned.

Although there are a lot of aforementioned advantages and benefits of the vacuum sewer system, there is some unease and scepticism because of the unfamiliarity with the technology from all the groups including users, operators, planners and construction companies. As the infrastructure is becoming obsolete, the importance of circular concepts and circular economy is becoming vital, including water reuse, nutrient recovery etc. The vacuum sewer systems can be a viable alternative for the improvement or further development of the sewer system. Moreover, considering the increasing efforts being made to tackle water-related issues, the economic and social sustainability of the vacuum sewer system should be considered as a potential alternative to the sewer system in near future.

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MONITORING OF WATERS STATUS ON THE AREA OF THE WASTE LANDFILL – CASE STUDY PIŠKORNICA

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Abstract: *The remediation of the municipal waste landfill reduces the harmful effects of inadequately disposed waste in the environment and reduce the risks on human health. The aim of this paper is to evaluate the efficiency of the remediation (2005 to 2012) of waste landfill of Piškornica. Groundwater from piezometers (P2, P3, P4 and P5) at Piškornica and surface water from the Gliboki stream (upstream and downstream) were analyzed, before and after the remediation. The results of the analyzed parameters (KPK, BPK_5, electroconductivity, iron) showed significant decrease in values ($p < 0.05$) and up to 82% (BPK_5 in P5) after remediation. The most significant decrease in the value of the indicators was determined in the P5, which is nearest and downstream from the landfill body. Significant difference ($p < 0.05$) was not found at the upstream and downstream locations of the Gliboki stream basin before and after remediation. The numerical model of the groundwater flow shows that groundwater pollution will not occur even in the worst scenario (the largest possible pumping of 420 l/s) of the current capacity of the Ivanščak source. The results contributed to decisions on water management and further monitoring of water plans on landfill area.*
Keywords: *waste landfill, remediation, monitoring of waters, numerical model.*

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1. INTRODUCTION

Municipal solid waste (MSW) disposal is a global problem in developing countries and the rise in the urban population in the past few decades point out the necessity to develop environmentally sustainable management system (Hossain et al 2014; Hui Liu et al. 2010; Sumathi et al. 2008). The high production volume of dangerous materials and industrial waste and their impact on the human health and environment, have become one of the most important decisions in urban management. Solid waste management is a difficult task and includes the control of generation, collection, transfer and disposal of solid waste in an environmentally acceptable manner (Barjinder et al. 2014). Landfill is the simplest and cheapest effective method of disposing of solid waste (Hossain et al. 2014; Barjinder et al. 2014). The most landfills are open dumps landfills. Therefore, due to ecological and socioeconomic criteria, it is essential to find an optimal location which has the lowest environmental risk and economically favorable (Danesh et al. 2019). The waste placed in landfills can influence on groundwater quality by infiltration of leachate. Municipal landfill leachate is highly concentrated complex effluents which contain disolved inorganic or organic compounds, heavy metals or other toxic substances (Hui Liu et al. 2010; Barjinder et al. 2014). Environmental pollution from landfills depends on various interconnected factors such as landfill location characteristics, waste amount and type, the amount of precipitation and leachate. Considering these factors, landfills urgently requiring remediation based on multicriteria decision making, in which hazards must be evaluated (Ubavin et al. 2017). Remediation of old landfills with no leachate collection system is demanding and costly operation. It requires control of environment and the landfill body, since the pollutants are still present in the landfilled waste for decades after the site has been closed (Thomas et al. 2007). Most remediation methods involve a wide range of activities that result in social, economic and environmental impacts. It is suggested that natural attenuation is a feasible approach but is demanding and complicated (Thomas et al. 2007), therefore the largest and most obvious impacts (cost and duration) will ussualy be taken into account when selecting an appropriate technology and remediation methods to be used (Harbottle et al. 2008). Landfills may pose serious threat to the both groundwater and surface water quality if incorrectly secured and improperly operated. Groundwater is known as major source of water supply and its contamination is a major heath concern (Longe & Balogun 2010). Therefore, assesment of groundwater quality and monitoring surface water near municipal landfill site during work and remediation of the landfill reduces the risk to the environment and people health (Longe & Balogun 2010; Talalaj 2014; Ogundiran & Afolabi 2008). The risk also depends on local hydrogeology and soil stratigraphy beneath the landfill base and these are important factors in the natural attenuation of leachate constituents in the groundwater body (Longe & Enekwechi 2007). Groundwater in piezometers close to the landfill is under a strong landfill impact (Talalaj

2014; Chapuis & Sabourin 1989; Cherry et al. 1983). Some researces (Cherry et al. 1983) have established networks of different types of devices for multilevel groundwater monitoring and in these way they determined migration of contaminants in groundwater at a landfill (Chapuis & Sabourin 1989; Cherry et al. 1983). Some devices are particularly well suited for use in aquifers composed of sand or gravel that have little clay and groundwater flow is primarily horizontal (Cherry et al. 1983). Lopes et al. (2012) defined leachate plume and located groundwater monitoring wells using different geophysical technique in order to evaluate groundwater contamination in the surrounding area of a landfill. In general, industrial or municipal waste and agricultural runoff are the most often antropogenic pollution sources. Rivers and streams are also exposed to pollution sources. Therefore it is important to investigate the origin of each surface water quality variable due to land use activities based on spatial water quality assessment using environmetric techniques. The aplication of environmetric methods can reveal meaningful information on the spatial variability of river water quality data (Juahir et al. 2011). The river surface water is greatly exposed to the risk of contamination from leachate unless proper leachate management is carried out. The influence of leachate on river water quality depend on many factors as leachate characteristics, precipitation, surface runoff or applied treatment (Cherry et al. 1983). Improper treatment practise leads to high levels of contaminants in the streams or rivers near the rehabilitated or closed landfills. Some studies (Yusof et al. 2009; Zafar & Alappat 2011) have shown that chemical analysis of surface waters at corresponding river section which is affected by the presence of landfill surface runoff, is very important part of waste management. In the studies, a series of indicators (pH, conductivity, COD, total solids, anions, cations, heavy metals, nitrogen anorganic compounds, organic compounds etc.) were investigated with the aim identifying one of the largest sources of environmental pollution, such as a landfill (Yusof et al. 2009; Zafar and Alappat 2011).

The main aim of this paper has been to evaluate the impacts of landfill on groundwater and surface water quality and the efficiency of the remediation of waste landfill of Piškornica (Koprivnica-Križevci county, northwest Croatia) as well. Groundwater from piezometers (P2, P3, P4 and P5) at the location of the landfill and surface water from the Gliboki stream (upstream and downstream from the landfill location) were analyzed, before and after the remediation. Grundwater is the major source of drinking water supply in the study area and its contamination is a major and environmental concern. Therefore, the numerical model (Ackerer et al. 1999) of the groundwater flow and transfer of pollutant was done with aim to show possible influence on the groundwater of the source Ivanščak (public water supply) located 5-6 km from the landfill. The study was carried out in the period from 2002 to 2018 (piezometers) and from 2008 to 2018 (the Gliboki stream) to assess the physical and chemical parameters of groundwater and surface water during all seasons. The remediation was carried out from 2005 to 2012.

2. MATERIALS AND METHODS

2.1. Study area

The Piškornica landfill is situated in Koprivnički Ivanec (x=5640168.50 and y=5122332.05), close to Koprivnica, the largest city of Koprivnica-križevci county. It started operations in the year 1982 and covered an area of about 10 hectares (**Figure 1**). Between 1982 and 2000 (before remediation), 223000 tonnes of MSW was land filled. Wastes are of different types, ranging from organic to inorganic, hazardous and non-hazardous. Remediation started in 2005 year. The remediation was carried out by constructing the bottom sealing layer and collecting system for leaches and on such arranged plateau, old waste was moving and new-arrived waste was land filled.

The wider area of the location of Piškornica belongs to the low Panonian and Peripanonian area. The layout of surface and groundwater as well as their interconnections are determined by the morphological and hydrogeological features of the wider area of the Piskornica. The waste landfill is located on clustery, mostly aluvial deposits with a lower top layer of clay-dusty material with humus (Duić & Urumović 2007). Study area belongs to Drava river catchment. The most important tributary of the Drava river on study area is the Gliboki stream, 250 m away from the landfill.

The mean monthly temperature ranges from -4 °C in January to 20 °C in July. The minimum and maximum annual temperatures are -26 °C and 35 °C, respectively. Average rainfall range from 800 to 900 mm. The highest amount of precipitation is during the period from April to July (60 to 80 mm/m^3). On study area the moderately warm climate predominates (State Hydrometeorological Institute).

At a distance of 5 to 6 km from the landfill there is the source Ivanščak (public water supply) which supplies about 30000 inhabitants of Koprivnica city and surrounding settlements.

2.2. Sampling and analysis

To assess the extent of groundwater contamination, 4 piezometers (P2, P3, P4 and P5) were selected. Positions of piezometers inside landfill are shown on **Figure 1**. Samples were collected in average 4 time in year during 2002 to 2018. in clean 5000 ml plastic container after the extraction of water (with pump) from a piezometer. The

water has flowed (before sampling) to ensure the discharge of 5 to 6 volumes of water from the piezometer and up to stabilization of EC of water. Each bottle was labelled according to sampling location while all the samples were preserved at 4°C and transported to the laboratory. All the samples were analysed for the physico-chemical parameteres and iron (**Table 1**).

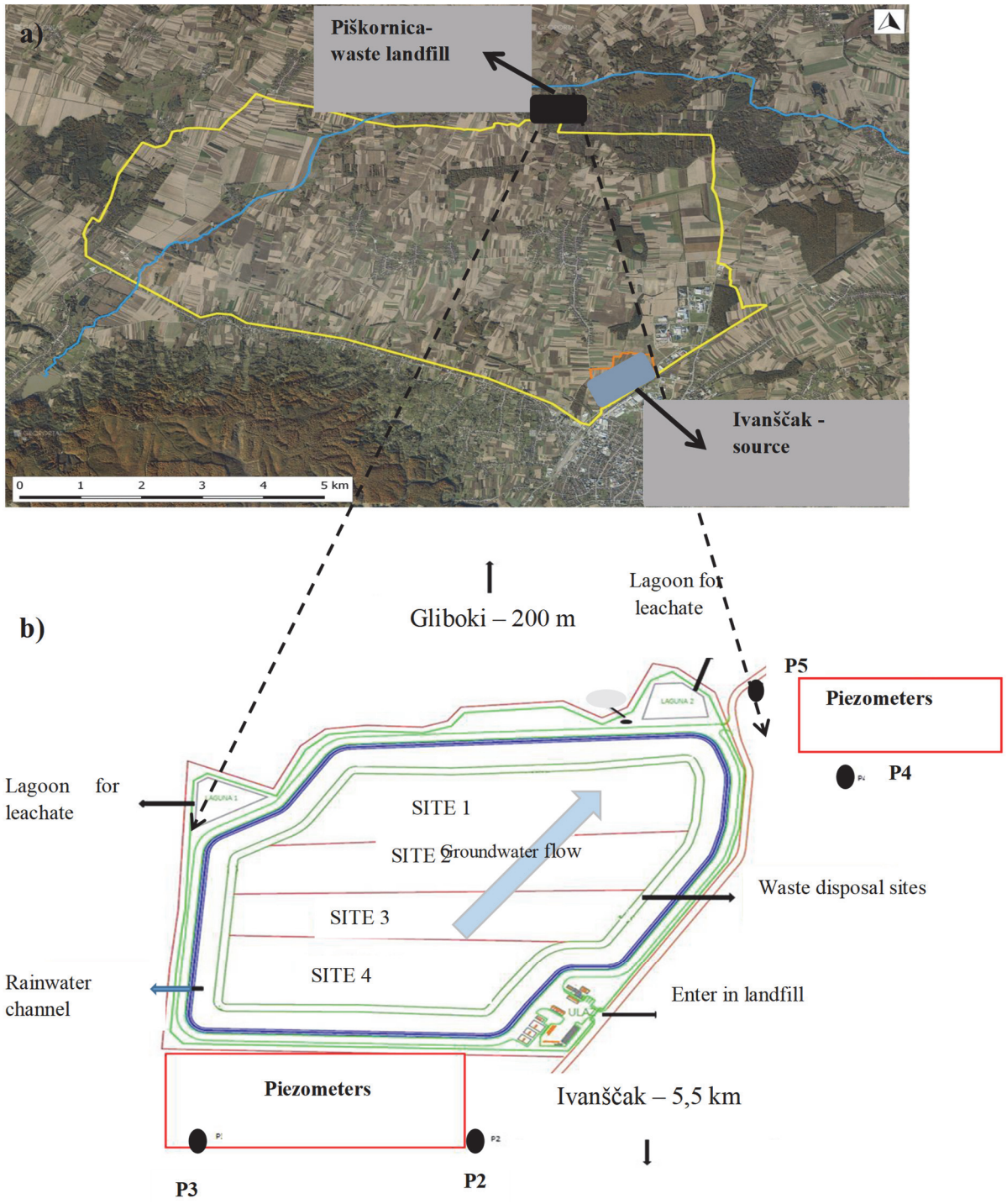


Figure 1. a) Study area – waste landfill Piškornica and source Ivanščak locations
b) waste landfill Piškornica – piezometer locations (P2, P3, P4, P5)

Surface water samples from Gliboki stream (**Figure 1**) were collected from distances of 400 m upstream and 600 m downstream from the landfill. Samples were collected with a container at a depth of about 30 cm below the surface of stream and transferred to a 5000 ml plastic clean container. Each container was labelled according to sampling location and all the samples were preserved at 4 °C and transported to the laboratory and were analysed for the parameters in **Table 1**.

The analysis was done within the next 48 hours which is recommended for better result and in minimizing the quality change. All the samples were analysed according to internationally accepted procedures (**Table 1**), standard methods (Rice et al. 2012) and Norms.

Table 1. Methods (Norms) used in analysis of physico-chemical parameters of water samples

PARAMETER	METHOD
Chemical oxygen demand (COD)	HRN ISO 15705:2003
Biochemical oxygen demand (BOD_5)	HRN EN 1899-1:2004
Electroconductivity (EC)	HRN EN 10523:2012
Iron (Fe)	HRN ISO 8288:1995

3. RESULTS AND DISSCUSION

3.1. Groundwater quality

Analytical results of physico-chemical characteristics of groundwater samples from piezometers include general indicators of pollution as electrical conductivity (EC), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and iron (Fe). The results of monitoring of groundwater samples are presented at **Figure 2a, 2b, 2c** and **2d**.

Electrical conductivity (**Figure 2a**) in P2, P3 and P4 was high but below standard limits. High EC is a symbol of high ionic load and indicates that organic and inorganic matter has washed into groundwater on that location. Groundwater on P5 location is highly contaminated by organic and inorganic matters (Hossain et al. 2014) and it has been observed that value is higher than standard limits of 2500 µS/cm (National Newspaper 125 2017). After remediation, the trend of decrease of the conductivity value in Piezometer P5 (**Figure 2a**) has been observed. This suggests a reduced impact of leachate and drainage of the contents of the landfill into the environment or groundwater. It is assumed that the decrease of the conductivity is a result of the remediation of the landfill (Ubavin et al. 2017; Talalaj 2014).

Chemical oxygen demand and biochemical oxygen demand indicate the presence of inorganic or organic pollutants. According to the results (**Figure 2b**) the COD value is the highest on piezometer P5, then piezometer P2 while lower values are determined in piezometers P3 and P4. Some scientists (Lopes et al. 2012) found low BOD_5 values at groundwater in the surrounding area of a landfill, however, COD values were determined at 40 times higher than the concentration of BOD_5. It is also visible (**Figure 2c**) that the BOD_5 values are also the highest in piezometer P5. The figures also show that the values for both parameters decreased, indicating the effect of landfill remediation (Barjinder et al. 2014).

Heavy metals are often present on landfill sites in leachate. Their concentrations depend on the composition of the waste and on the stage of waste construction (Talalaj 2014; Ogundiran & Afolabi, 2008). Also, the concentration of metal in groundwater depends on the geological composition of the soil (the natural origin of metals). Considering the significant concentrations of iron of natural origin (Duić & Urumović, 2007) found in the study area, the concentrations were monitored at the piezometers of the landfill. Iron is most commonly found in groundwater in the form of Fe^{2+} and and is bound in organic molecules. It indicating also the possibility of binding of Fe^{2+} to organic matter derived from the landfill (Yusof et al. 2009). Under anaerobic conditions, iron is dissolved, which may result in an increased concentration of iron in the groundwater. On the study area the alluvial deposits is rich in iron salts which can contribute to increased concentration in groundwater. The results of the movement of iron concentrations are shown in **Figure 2d**. The highest concentrations were recorded in the period from 2004 to 2008 and thereafter a significant decrease in concentration in all piezometers is visible (Hossain et al. 2014; Talalaj 2014).

According to the results of the statistical analysis (t-test) of measured groundwater indicators before (V1) and after (V2) landfill remediation, average values has shown (**Table 2**) a statistically significant difference (p=0.05; 95%). It has been shown that values before remediation are significantly higher than the values after remediation, which indicates the impact of the observed factor (remediation) on groundwater quality. The differences are particularly visible in piezometer P5 where for EC, COD and BOD_5 values V1 are greater than V2. COD and BOD_5 values have shown a statistically significant difference in piezometer P2 indicating groundwater contamination before remediation at that location (Ubavin et al. 2017). The mean iron concentration have not changed significantly after the landfill remediation pointing out to the natural sources of iron on study area (Duić & Urumović 2007), however, higher concentration variability is visible before landfill remediation.

The relationship measured variables (indicators) between the individual piezometers was estimated by the analysis of variance (ANOVA). The results of the mean values of the measurement of all indicators before (V1) and after (V2) remediation used for ANOVA test are shown in **Table 2**. If the variability between the groups was

greater than the variability within the group, it was concluded that the differences are statistically significant (F> Fcrit.; p=0.05).

According to the results of the EC, by comparing before (F=71, Fcrit=2.69) and after (F=8.57, Fcrit=2.81) the remediation of the landfill, significant changes were found only at location P5. However, the ANOVA test found that the values for P5, despite the decrease after remediation, are still higher than other locations (P2 to P4).

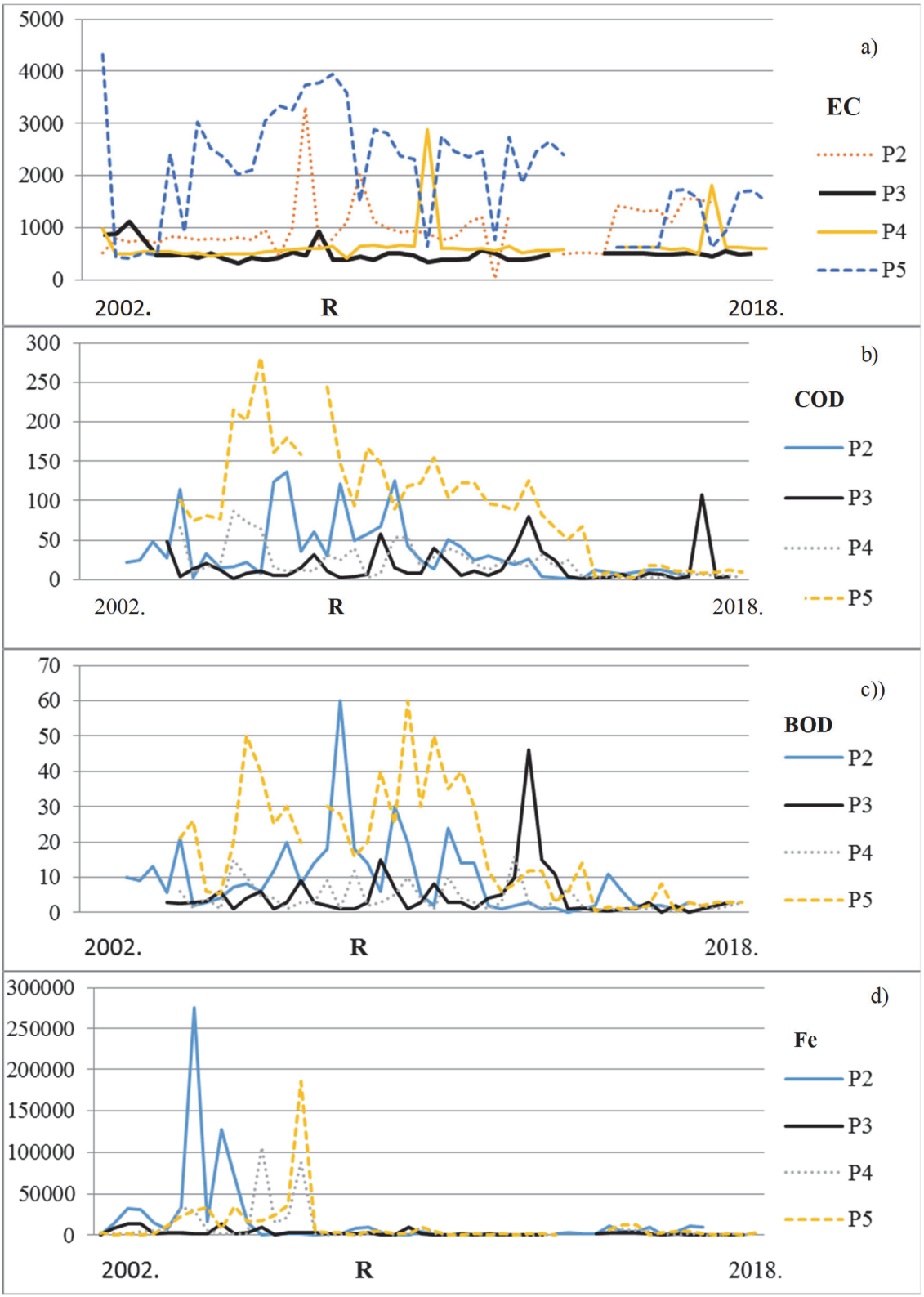


Figure 2. Monitoring of groundwater (piezometers) quality; R-the beginning of remediation
a) electrical conductivity (EC); b) chemical oxygen demand (COD; c) biochemical oxygen demand (BOD); d) iron (Fe)

According to the ANOVA result test, COD values at P5 location are significantly higher than those at other locations (P2 to P4). However, the differences between the piezometers after remediation (F=5.2, Fcrit=2.76) are less than the difference between locations prior to remediation (F=54.5, Fcrit=2.70).

Analysis of variance has shown that there are significant differences in BOD_5 values for individual locations before landfill remediation (F = 33.9, Fcrit = 2.70) due to high BOD_5 values at P5 location. After the landfill remediation, this value at P5 location significantly decreased, so the variance of analysis results has shown that there are no significant differences (F=0.68, Fcrit=2.77) among the mean BOD_5 values.

ANOVA results also showed that there were no significant differences before (F=1.73, Fcrit=2.69) and after (F=1.68, Fcrit=2.81) remediation of landfill among the mean values of the iron obtained at piezometers P2 to P5.

The results of the mean values of the measurement of all indicators before (V1) and after (V2) remediation used for ANOVA test are shown in **Table 2**.

Table 2. Indicator values before and after remediation at locations of piezometers P2, P3, P4, P5 (t-test, 95 % significance level; N-number of samples)

INDICATOR	PIEZOMETER	V1 N = 23-27	V2 N=12-15	T-EKSP.	RELATION V1 AND V2
EC (µS/cm)	P2	949	923	0.15	V1=V2
	P3	515	472	1.13	V1=V2
	P4	649	682	0.24	V1=V2
	P5	2330	1454	2.45	V1>V2
COD (mg/l)	P2	50	17	3.56	V1>V2
	P3	15	15	0.04	V1=V2
	P4	31	11	3.65	V1>V2
	P5	142	43	5.93	V1>V2
BOD5 (mg/l)	P2	13	6	2.44	V1>V2
	P3	4	7	1.15	V1=V2
	P4	5	3	1.47	V1=V2
	P5	29	5	7.55	V1>V2
Fe (µg/l)	P2	25191	3548	1.96	V1=V2
	P3	2993	1579	1.99	V1=V2
	P4	11676	2682	2.02	V1=V2
	P5	15292	4354	1.77	V1=V2

V1-before remediation; V2-after remediation

3.2. Surface water quality

For monitoring of the surface water quality of the Gliboki stream, general pollution indicators have been selected as EC, COD and BOD_5 (Juahir et al. 2011). Concentration trends during the monitoring are shown in **Figure 3a**, **3b** and **3c**. Valuable indicators in the Gliboki stream indicate on the variability, but there is no significant difference of values between upstream and downstream from the landfill site. However, **Figure 3c** shows a high concentration of BOD_5 of 9 mg/l in the Gliboki downstream of the landfill (September 2012.). It is assumed to be related to the uncontrolled discharge of untreated waste water (organic pollution) from agriculture, in the environment. The results of the t-tests for the mean values of EC, COD and BOD_5 obtained by examination of the surface water quality from the Gliboki stream are shown in **Table 3**. According to the results, the difference in the values of the measured parameters, before and after remediation of the landfill, is not obtained, except for G2 (downstream) where BOD_5 has shown decrease after remediation. Given that the values decreased upstream and downstream from the landfill, it is assumed that BOD_5 decrease is not affected by the landfill but depends on a number of other environmental factors on the study area (Danesh et al. 2019; Zafar & Alappat 2011).

The results showed that the values of measured indicators were similar upstream and downstream and no statistically significant difference ($p = 0.05$) was demonstrated. It follows that the landfill does not affect the quality of surface water from the Gliboki stream. The results of other scientists (Hui Liu et al. 2010) have also shown that the proximity of the landfill is not necessarily a risk for surface water pollution. It is important to take into account all environmental risk factors such as agriculture, industry or natural (Danesh et al. 2019; Longe & Balogun 2010).

3.3. Evaluation of the landfill impact on the source Ivanščak

The location of the Ivanščak source is shown in **Figure 1**. The source is located about 5.5 km from the landfill and has a significant influence on the hydrodynamics of the groundwater flow. Excessive pumping of groundwater could cause a direct connection between the source and the landfill. The existing exploitation of drinking water has not shown the impact of landfill on the quality of drinking water from the source. However, due to the importance of the source on study area, the need for a greater amount of water and increased pumping capacity in the future can be expected. Therefore, several scenarios (S1-S5) of pumping were analyzed in numerical models:

S1 Q=0 (m^3/s) - no pumping;
S2 Q=100 (m^3/s) - corresponds to the current average pumping;
S3 Q=200 (m^3/s) - corresponds to the current maximum pumping;
S4 Q=420 (m^3/s) - corresponds to the current maximum with regard to the pumping capacity;
S5 Q=600 (m^3/s) - corresponds to the pumping that would cause a direct hydrodynamic connection between the source and the landfill Piškornica.

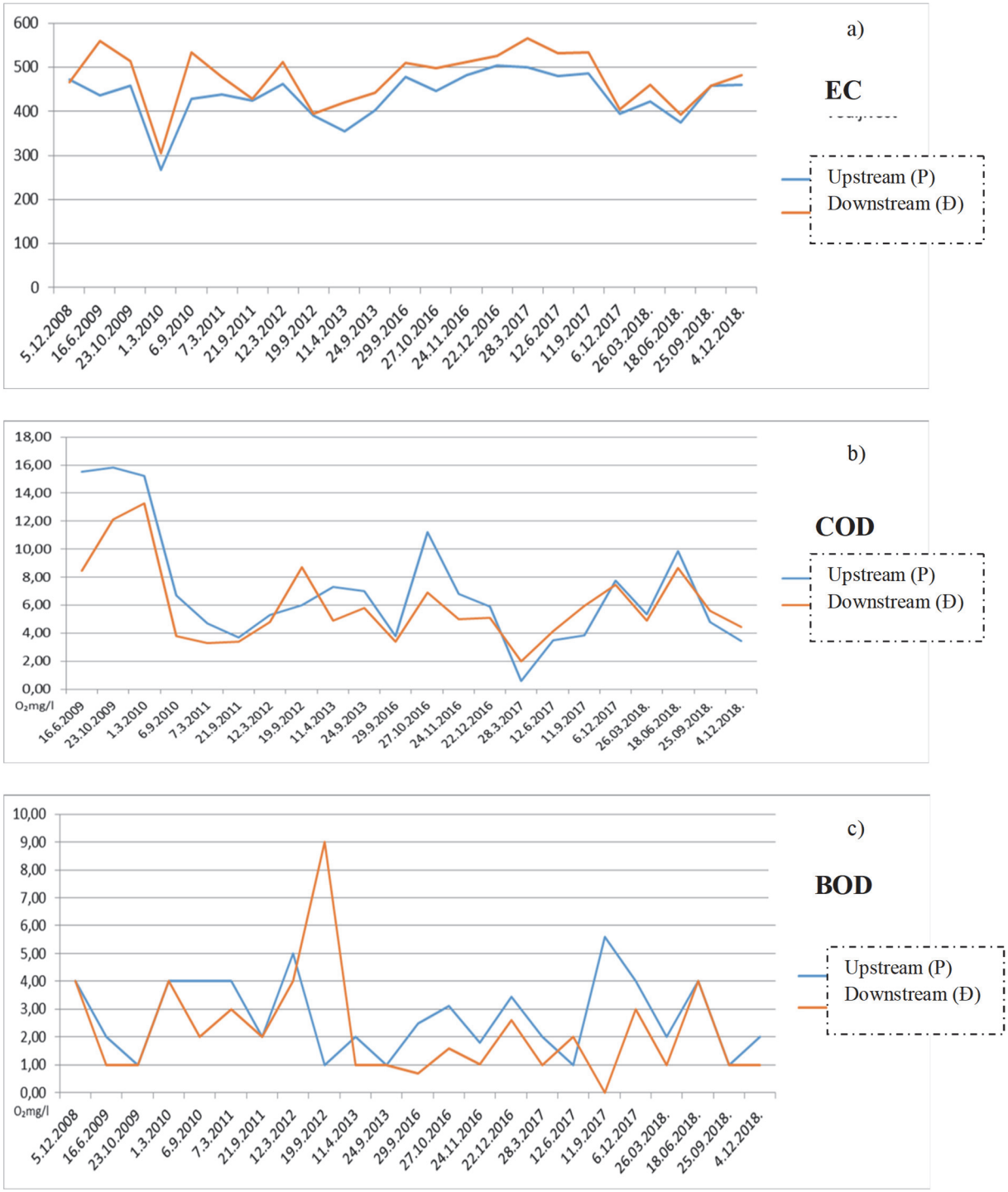


Figure 3. Monitoring of surface water quality: a) electrical conductivity (EC); b) chemical oxygen demand (COD); c) biochemical oxygen demand (BOD); P-Pustakovec, Đ-Đelekovec

3.4. Numerical models of surface water and transmission of contaminants

Numerical models were used to show the transmission of the contaminants at a certain pumping capacity (Welty & Gelhar 1992). The most important and interesting scenarios are S3 and S5. The hydrodynamics of the flow of water at 200 L/s (S3) is shown at **Figure 4**. According to the results, the groundwater flow is not directed to the source and potential contaminants do not affect the water quality at the source. The models show that in all other scenarios (S1, S2, S4) a hydrodynamic connection between the landfill and the source is also not possible. It is estimated that under such conditions of pumping (discharge) it is not possible to transfer contaminants from the landfill to the source (Longe & Balogun 2010) Under the worst conditions shown for scenario S5 at pumping 600 l/s (**Figure 5**), groundwater flow indicates a hydrodynamic connection between the landfill and source. However, this capacity of pumping is not possible currently, indicating that the landfill is not a risk for groundwater quality at the Ivanščak source in the near future. It is assumed that a relatively large distance between landfills and sources and environmental factors contributes to good water quality (Longe & Balogun 2010).

Table 3. The difference between the value of the indicators measured before (V1) and after (V2) landfill remediation on the Gliboki stream

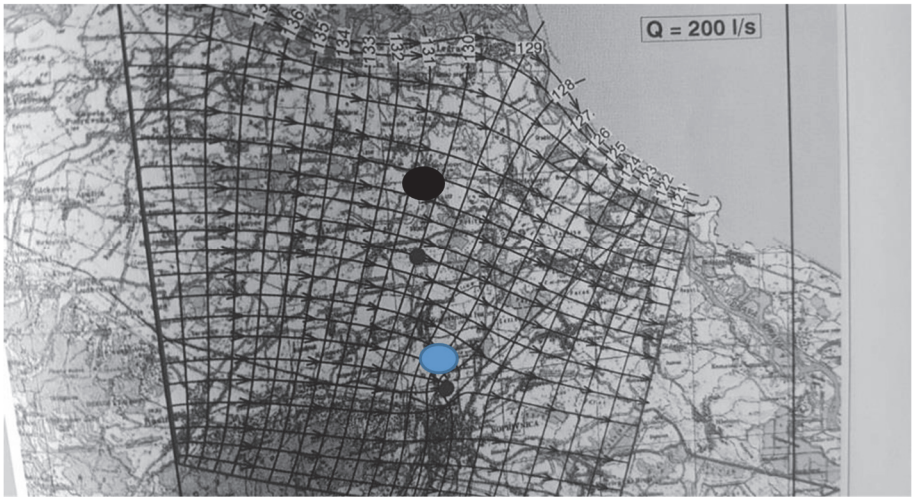
INDICATOR	GLIBOKI STREAM	V1 N = 9	V2 N=13	T-EKSP.	RELATION V1 AND V2
EC (µS/cm)	G1	420	445	1.05	V1=V2
	G2	466	481	0.54	V1=V2
COD (mg/l)	G1	10	6	1.97	V1=V2
	G2	9	5	1.67	V1=V2
BOD5 (mg/l)	G1	3	3	0.68	V1=V2
	G2	3	2	2.07	V1=V2

G1-upstream; G2-downstream

Table 4. The difference between the value of the indicators measured upstream (G1) and downstream (G2) of the Gliboki

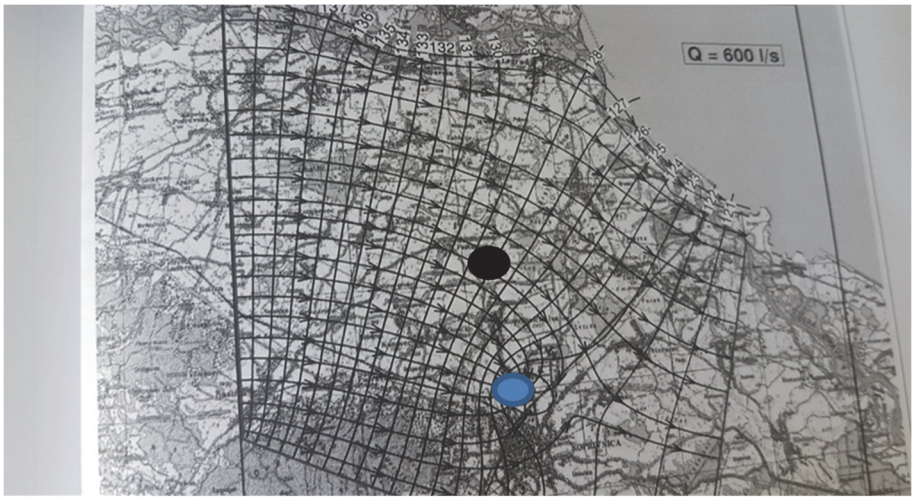
INDICATOR	GLIBOKI STREAM	G1	G2	T-EKSP.	RELATION G1 AND G2
EC (µS/cm)	V1	420	466	1.37	G1=G2
	V2	445	481	1.77	G1=G2
COD (mg/l)	V1	10	9	0.48	G1=G2
	V2	6	5	0.65	G1=G2
BOD5 (mg/l)	V1	3	3	0.68	G1=G2
	V2	3	2	2.12	G1=G2

V1-before remediation; V2-after remediation



(● - Piškornica location; ● - Ivanščak location)

Figure 4. Scenario (S3) of hydrodynamics of the water flow (pumping capacity Q=200 l/s)



(● - Piškornica location; ● - Ivanščak location)

Figure 5. Scenario (S5) of hydrodynamics of the water flow (pumping capacity Q=600 l/s)

4. CONCLUSIONS

Municipal landfills are considered a big risk to their surrounding urban environment. They are the source of pollution especially for groundwater and surface waters. From the study it has been observed that improper practices of solid waste management impact on the groundwater. However, landfill remediation contributed to improving the quality of groundwater from individual piezometers at the landfill site. After the remediation, the value of the indicators decreased in piezometer P5 which is located downstream of the landfill. It is due to the transfer of contaminants to P5 and the impact of improper disposal of waste to groundwater. Examination of surface water of the Gliboki stream near the landfill has not confirmed contamination from the landfill. Pollution has been observed in the upstream and downstream of the landfill, pointing to other sources of environmental pollution. Given the location of the source Ivanščak (public water supply) near the landfill, the mathematical model estimates that the landfill has no effect on groundwater quality from the source. It is concluded that the landfill distance from the source and the groundwater flow direction additionally ensures a reduction of the groundwater quality risk in the near future. The results contributed to decisions on water management and it is suggested that the local government and the management of the landfill corporation should take necessary initiatives for the monitoring of groundwater and surface water quality and that ensure quality water from the public water supply.

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APPLICATION OF ELECTROCOAGULATION FOR WATER CONDITIONING

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Abstract: *Water conditioning is a method of removing altering minerals, chemicals and contaminants from a water source and it is carried out on facilities equipped with the corresponding electro-mechanical equipment. Although efficient, conventional processes typically use several complex devices connected to a single functional unit, which are often expensive to maintain and occupy large areas. Therefore, the aim of this paper is to present the electrocoagulation (EC) method as an alternative to conventional water conditioning processes. The examples of previous studies of the EC process application is presented in this paper. The focus of the paper is to investigate the influence of the certain operational parameters such as pH, temperature, electrode material, etc., on the efficiency of pollutant removal such as Escherichia coli and elevated concentrations of iron, arsenic, manganese, ammonia and others. Further, an economic analysis is made, which, from an economic point of view, shows when it is feasible to use the EC in the conditioning process. Furthermore, a case study of electrocoagulation process for Total Nitrogen (TN) removal is presented. According to results, 69.7 % of TN was removed with aluminum electrodes after 240 minutes. For this case, total operating costs were 7.60 €/m^3.*
Keywords: *electrocoagulation, water conditioning, operative parameters, total nitrogen*

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Original scientific paper

1. INTRODUCTION

Access to clean drinking water is a basic human right. According to the Council Directive 98/83/EC (Official Journal L 330) on the quality of water intended for human consumption, drinking water shall be wholesome and clean if it is free from any micro-organisms, parasites and substances which in numbers or concentrations constitute a potential danger to human health, whereby must meet minimum requirements regarding microbiological and chemical properties, radioactivity and physical properties.

In case of unsatisfactory values of certain parameters established by the Council Directive 98/83/EC (Official Journal L 330), appropriate activities shall be undertaken to ensure the quality of the water and, where necessary, to prohibit or limit the use of the water. Water conditioning is a method of removing altering minerals, chemicals and contaminants from a water source and it is carried out on facilities equipped with the corresponding electro-mechanical equipment (Vuković 2017).

According to (Croatian Institute of Public Health 2018) in 69 % of water supply areas water is not processed before the distribution to the consumers. In the remaining 31 % of water supply areas, the water is treated, dominating the filtration process, and a combination of aeration and filtration, a combination of filtration, coagulation, flocculation and precipitation, and manganese and/or iron removal are also used (**Figure 1**). Although efficient, conventional processes typically use several complex devices connected to a single functional unit, which are often expensive to maintain and occupy large areas. Therefore, the aim of this paper is to present the electrocoagulation (EC) method as an alternative to conventional water conditioning processes.

Furthermore, (Croatian Institute of Public Health 2018) analyzed the quality of water for human consumption and stated that the most common cause of its malfunction is the presence of *Escherichia coli (E. coli)* and total coliforms, as well as the elevated concentrations of iron, arsenic, manganese, ammonia, color, smell and turbidity. Therefore, the focus of the paper is to investigate the influence of the certain operational parameters such as pH, temperature, electrode material, etc., on the efficiency of removing the mentioned contaminants.

An economic analysis is also made, which, from an economic point of view, shows when it is feasible to use EC in the conditioning process.

Additionally, the influence on total nitrogen removal efficiency was evaluated for some of the process parameters on a full-scale EC unit. For this specific case, operating costs are also determined.

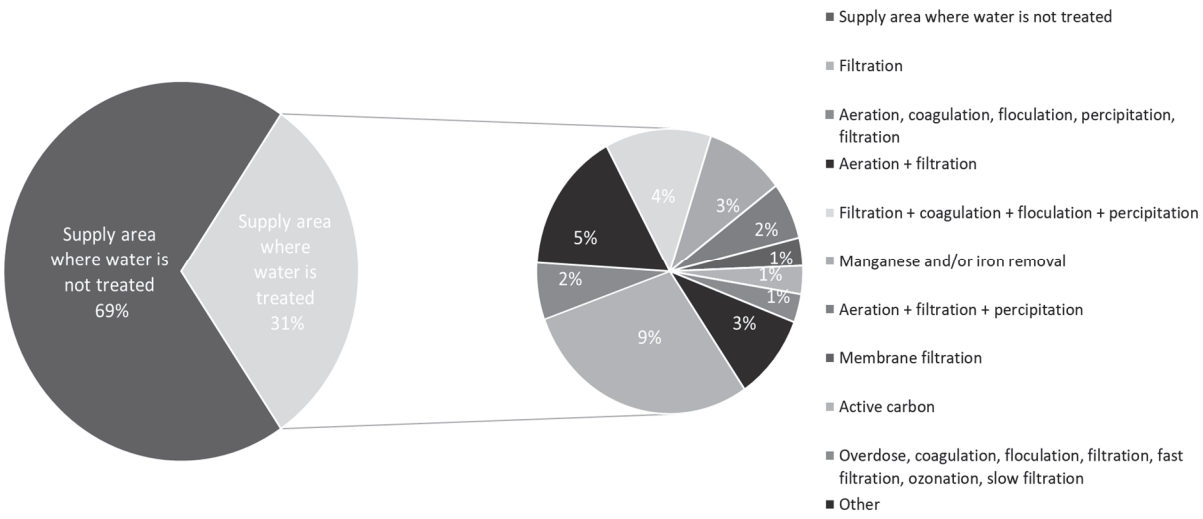

Figure 1. *Water conditioning technologies (Croatian Institute of Public Health, 2018)*

2. THEORY OF ELECTROCOAGULATION

The EC process, **Figure 2**, combines the benefits of coagulation, flotation or precipitation and electrochemistry (Moussa 2017). It includes coagulation and precipitation of pollutants (suspended solids and solutes) from the wastewater by the use of electricity and sacrificing electrodes for the "in situ" coagulant production (Gardić 2007). In the EC reactor, the wastewater flows between electrodes while the direct current is applied to them. Electrodes are usually made of metal, mostly iron (Fe) or aluminum (Al), because these materials are cheap, available, non-toxic and proven effective. The choice of electrode material and the arrangement of electrodes depend on the wastewater contamination and the required effluent quality. Usually, aluminum is used for the drinking water treatment and iron for the wastewater treatment (Chen and Hung 2007; Shammas et al. 2010; Kuokkanen et al. 2013; Hakizimana 2017).

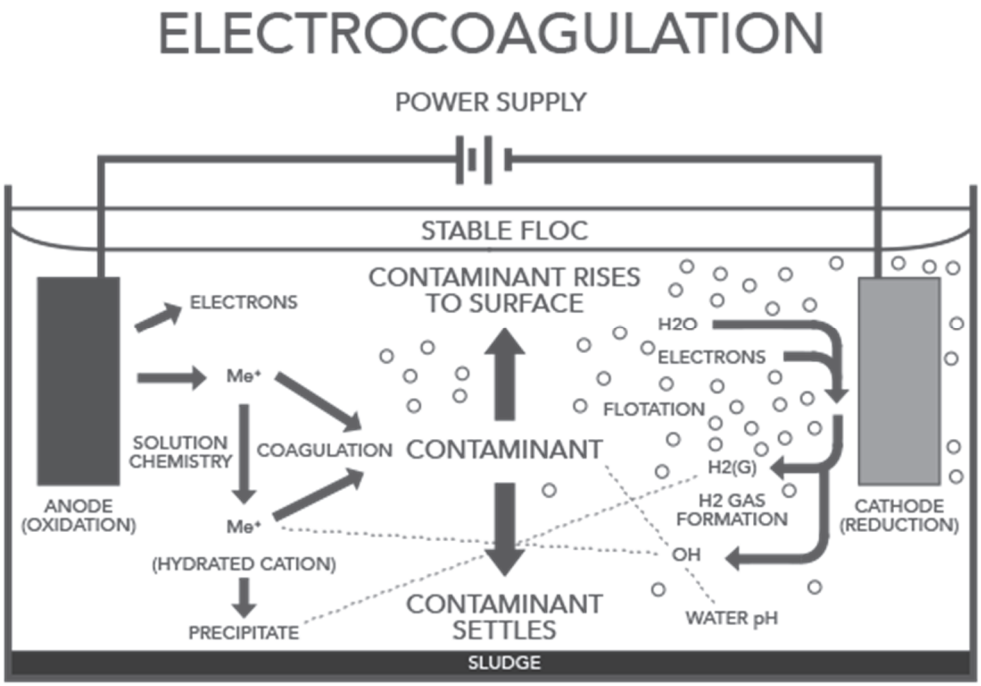

Figure 2. *Electrocoagulation process*
(https://www.crs-reprocessing.com/en/crs-solutions/electrocoagulation/, Accessed March 11 2019)

According to the **Equation 1**, when the current is passed through metal electrode, the metal (M) from the anode is oxidized to its cations (M^{n+}). Simultaneously, water is reduced to hydrogen gas and the hydroxide ion (OH^-) on the cathode (**Equation 2**) (Kabdaşli et al. 2012):

$$M \rightarrow M^{n+} + ne^- \quad (1)$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (2)$$

By forming monomeric and polymeric hydroxides, metal cations (M^{n+}) destabilize colloidal particles, i.e. trap colloidal particles and create flocs which can be easily removed from water by sedimentation or flotation (Kabdaşli et al. 2012; Pirkarami & Olya 2017).

Some of the advantages of the EC process are: effluent contains less total dissolved solids compared to the other chemical processes, easy maintenance of the device, more efficient and faster degradation of organic matter compared to chemical coagulation, larger and more stable flocs are formed than those produced by chemical coagulation, it is not necessary to control the pH of the water, except in extreme cases, no chemicals are required, reduces residue, it can process multiple pollutants which can easily be removed, operating costs are much lower compared to most conventional technologies, the device is smaller and simpler than the coagulation device so it can be used as decentralized process and if the solar panels are used, the device can be used as a batch process in rural areas that don't have access to the electricity for processing the smaller quantities of wastewater (Vepsäläinen, 2012; Kuokkanen et al. 2013; Marriaga-Cabarales & Machuca-Martínez 2014; Hakizimana et al. 2017).

However, some of the EC disadvantages are: in some countries, the use of electricity may be expensive, possible passivation of anode due to the oxygen presence and the deposition on the cathodes (can be overcomed by switching the electrode poles), the electrodes need to be regularly replaced which increases the maintenance costs, the high conductivity of the wastewater is required, the high concentrations of iron and aluminum need to be removed from the effluent, in some cases, the gelatinous hydroxides may be dissolved in water, it is not effective for the removal of the soluble substances such as sugars, organic acids, solvents, phenols, alcohol and similar (Vepsäläinen 2012; Kuokkanen et al. 2013; Marriaga-Cabarales & Machuca-Martínez 2014; Hakizimana et al. 2017).

3. APPLICATION OF ELECTROCOAGULATION FOR WATER CONDITIONING

Water health parameters for human consumption are determined by the Ordinance on conformity parameters, analytical methods, monitoring and drinking water safety plans, and keeping register of legal entities which provide public water supply (Official Gazette 125/17). The aim of monitoring these parameters is to protect human health from the adverse impact of any contamination of water intended for human consumption and to ensure its health. According to the (Official Gazette 125/17), drinking water should be free of color, taste and smell. Maximum permissible concentrations of E. coli, iron, arsenic, manganese, ammonia, color, smell and turbidity, according to the (Official Gazette 125/17), are shown in **Table 1**.

Table 1. Chemical and indicator parameters

PARAMETER	UNIT	MAXIMUM PERMISSIBLE CONCENTRATIONS
Ammonia	mg/l	0.50
Arsenic	µg/l	10
Escherichia coli	*E. coli*/100 ml	0
Iron	µg/l	200
Manganese	µg/l	50
Color	mg/PtCo	20
Smell	/	-
Turbidity	NTU	4

3.1. Removal of E. coli

Microbiological contamination of water can be effectively counteracted by disinfection measures. Disinfection is the last stage of water preparation for the purpose of eliminating or decreasing the number of microorganisms in it. Mostly, chemical disinfection uses chlorine, chlorine dioxide or ozone. However, water disinfection is, most often, just one step in the water treatment and is often combined with other chemical processes (Andrija Stampar Teaching Institute of Public Health 2017). The examples in **Table 2** show that EC has very high efficiency of *E. coli* removal. It can be noticed that 30 min is enough for complete *E. coli* removal with Al electrodes.

Table 2. Recent applications of EC for *E. coli* removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
0.5 l	Al electrodes; Electrode distance: 5 cm; 12 V; treatment time 30 min	100	-	Ghernaout et al. (2008)
1 l	Al electrodes; Electrode distance: 2 cm; 30 V; 22 A; treatment time: 30 min	99.8	-	Ricordel et al. (2014)

3.2. Iron removal

The presence of iron in drinking water is not directly harmful to human health, but problems with discoloration, turbidity and unpleasant taste occur (Doggaz et al. 2018). There are several methods for removal of iron from drinking water, but aeration and separation are the most common methods (Gosh 2007). Some of the recent applications of EC for iron removal are shown in **Table 3**. Most commonly Al electrodes or their combinations with other materials are used. Also, the increase of current density influences the treatment efficiency and shortens the electrolysis time.

Table 3. Recent applications of EC for iron removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
3 l	Al electrodes; Electrode distance: 0.5 cm; treatment time 35 min	99.2	5.35	Gosh et al. (2007)
1 l	Mn anode, Fe cathode; 6 A/m^2; treatment time: 60 min	98.4	-	Vasudevan et al. (2009a)
1 l	Al anode, SS cathode; 6 A/m^2; treatment time: 60 min; pH 6.5	98.8	-	Vasudevan et al. (2009b)
2.2 l	Al electrodes; Electrode distance: 0.5 cm; 15 A/m^2; treatment time: 20 min; pH 6	98.5	0.20	Hashim et al. (2017)

3.3. Arsenic removal

Among several investigated technologies for removal of arsenic from drinking water, most common are ion-exchange, precipitation, coagulation/adsorption and membrane treatment systems. Although these processes produce high quality water, they require expensive resins, replaceable adsorption media and chemicals (Alferness 2016). It can be noticed that EC is a very efficient method for arsenic removal (**Table 4**). Total arsenic removal can be achieved under less than 30 min with Fe electrodes at an inter-distance of about 1 cm. Applied voltage should be around 12-15 V.

Table 4. Recent applications of EC for arsenic removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
1 l	Fe electrodes; Electrode distance: 2 cm; 12 V; treatment time 30 min; pH 7	100	-	Wan et al. (2011)
1.4 l	Fe electrodes; Electrode distance: 0.5 cm; 0.54 mA/cm^2; treatment time: 30 min; pH 4	99.5	-	Can et al. (2014)
20 l	Al electrodes; Electrode distance: 0.55 cm; 5.5 mA/cm^2; treatment time: 15 min	92.2	-	Flores et al. (2014)
10 l	Fe and Al electrodes; Electrode distance: 1 cm; 6 A; 15 V; treatment time: 20 min	100	-	Oreščanin et al. (2014)
13.2 l	SS electrodes; Electrode distance: 2.2 cm; 6 V; treatment time: 60 min	96.7	0.47	Alferness et al. (2016)

3.4. Manganese removal

The presence of manganese and other metals in drinking water may be responsible for its coloration. Conventional methods for removing manganese include chemical precipitation, coagulation, flotation, ion-exchange, oxidation/filtration, adsorption and membrane filtration (Alvarez-Bastida et al. 2018). Some of the recent applications of EC for manganese removal are shown in **Table 5**. Manganese removal efficiency varies from 50-100 %, depending on the treatment time and applied voltage. It can be assumed that the optimal operative parameters are Fe electrodes, electrode distance of 2 cm, 90 min of treatment time, pH 7 and current density of 15 mA/cm^2. Also, the addition of supporting electrolyte, such as SO_4^{2-}, helps to increase the removal efficiency. More research on manganese removal needs to be done, and until then, it is suggested to combine it with other water treatments.

Table 5. Recent applications of EC for manganese removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
0.5 l	Fe electrodes; Electrode distance: 2 cm; 2 A; treatment time 90 min; pH 6	99	-	Gatsios et al. (2015)
0.5 l	Fe electrodes; Electrode distance: 2 cm; 10 mA/cm^2; treatment time: 60 min; pH 7	50	-	Xu et al. (2017)
0.5 l	Fe electrodes; Electrode distance: 2 cm; 15 mA/cm^2; treatment time: 120 min; pH 7; addition of electrolyte: 25 mmol/l SO_4^{2-}	85.5	-	Xu et al. (2018)

3.5. Ammonia removal

Ammonia in wastewater can originate from many sources such as fertilizer manufacturing, food processing, landfill leachate, agriculture, slaughterhouses and tanneries. Ammonia is considered as one of the most toxigenic contaminants, and high ammonia concentrations can cause eutrophication of rivers and lakes, thus disrupting the ecological balance. Till now, the main ammonia removal processes involved: air stripping, biological nitrification, denitrification, chemical treatment and selective ion exchange method (Desai et al. 2016). However, these methods are limited because of their cost, low efficiency and the use of toxic chemicals (Aoudj et al. 2017). Therefore, EC seems as an interesting solution for ammonia removal, and some results are shown in **Table 6**. According to results,

EC is not effective for ammonia removal. The removal efficiency is less than 50 % in all the mentioned research. Since it has been shown that EC is not effective enough to meet the standards determined by the Ordinance on conformity parameters, analytical methods, monitoring and drinking water safety plans, and keeping register of legal entities which provide public water supply (Official Gazette 125/17), it is suggested that EC needs to be combined with other water treatment processes.

Table 6. Recent applications of EC for ammonia removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
1.8 l	Al electrodes; 3 A; treatment time 60 min; pH 8	24	-	Son et al. (2017)
2 l	Al electrodes; Electrode distance: 2 cm; 1.5 A; 15 V; treatment time: 90 min	47	-	Desai et al. (2016)
90 l	Al electrodes; 150 A/m^2; treatment time: 120 min; pH 7	36	1.95	Lončar et al. (2019)

3.6. Color removal

Colored water is not suitable nor for drinking nor for many industrial purposes such as food industry or cloth washing. There are two types of color in water, true and apparent color. True color is the result of soluble substances that cannot be isolated by filtration, and apparent color is the result of suspended solids and colloid particles that can be separated by filtration (Malakootian and Fatehizadeh 2010). It can be noticed that EC has high color removal efficiency (97 %), but the choice of optimal operative parameters differs (**Table 7**). Therefore, more research on color removal by EC needs to be done.

Table 7. Recent applications of EC for color removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
1.5 l	Al electrodes; 300 A/m^2; treatment time 120 min; pH 5.2	97.2	-	Kara et al. (2013)
3 l	Fe electrodes; Electrode distance: 5 cm; 2.07 mA/cm^2; treatment time: 45 min; pH 7.6	97	0.26	Khansorthong and Hunsom (2016)

3.7. Turbidity removal

Water turbidity is caused by suspended solids and colloidal particles of clay, sludge, fine organic matter, microorganisms and other. The precipitation of particles depends on their density and size. Particles with higher density precipitate due to gravity and smaller particles, especially ones whose density is similar as water density, such as bacteria and colloidal particles, don't precipitate, but remain suspended in water and need to generate larger flocs. Conventional treatments for turbidity removal have several disadvantages, such as the use of large amounts of chemicals and generating large amounts of sludge which causes disposal problems and the loss of water (Gulić 2003). It has been shown that EC is good for removing water turbidity (more than 95 %) and some results of previous research are shown in **Table 8**. According to previous research, optimal operative parameters very much differ. Since all mentioned types of the electrode material have high removal efficiency, their price can be a deciding factor. Suggested optimal operative parameters are Al electrodes, 2 cm of electrode distance, 20 V voltage and 40 min of treatment time.

Table 8. Recent applications of EC for turbidity removal

VOLUME TREATED	OPTIMAL OPERATIVE PARAMETERS	% REMOVAL	OPERATING COSTS [€/m^3]	REFERENCE
2 l	Fe electrodes; Electrode distance: 5 cm; 5.62 mA/cm^2; treatment time 40 min; pH 5.2	95	-	Ni'am et al. (2007)
3 l	Al electrodes; Electrode distance: 2 cm; 20 V; treatment time: 10 min	97	-	Rahmani (2008)
1 l	SS electrodes; Electrode distance: 2 cm; 20 V; treatment time 180 min; pH 7	98	-	Adapureddy and Goel (2012)
3 l	Al electrodes; Electrode distance: 2 cm; 30 V; treatment time 25 min; pH 7	95	0.12	Moosavirad (2017)

4. ECONOMY ANALYSIS AND THE COMPARISON OF REMOVAL EFFICIENCY

Economy analysis, along with the removal efficiency analysis, plays an important role in the selection of optimal water treatment. The economic factors that can influence this choice are chemicals, coagulation resins, membranes, electricity, work, maintenance, etc. Only few papers analyzed the cost of EC, and most of the experiments were conducted on small batch units (Vepsäläinen 2012). Therefore, only rough estimation and approximate cost comparison of EC and similar water treatments can be given. Operative costs of some previous research are shown in **Tables 3-8**, and cost and efficiency comparisons between EC and several water treatments are given in **Figures 3-6**.

The first comparison is for turbidity and **Figure 3** shows that EC has higher removal efficiency than the combination of ultrafiltration/coagulation by 10 %. Also, operative costs of EC are lower than for the combination of ultrafiltration/coagulation by 0.20 €/m^3 (**Figure 4**). Therefore, it is justified to use EC for removal of turbidity.

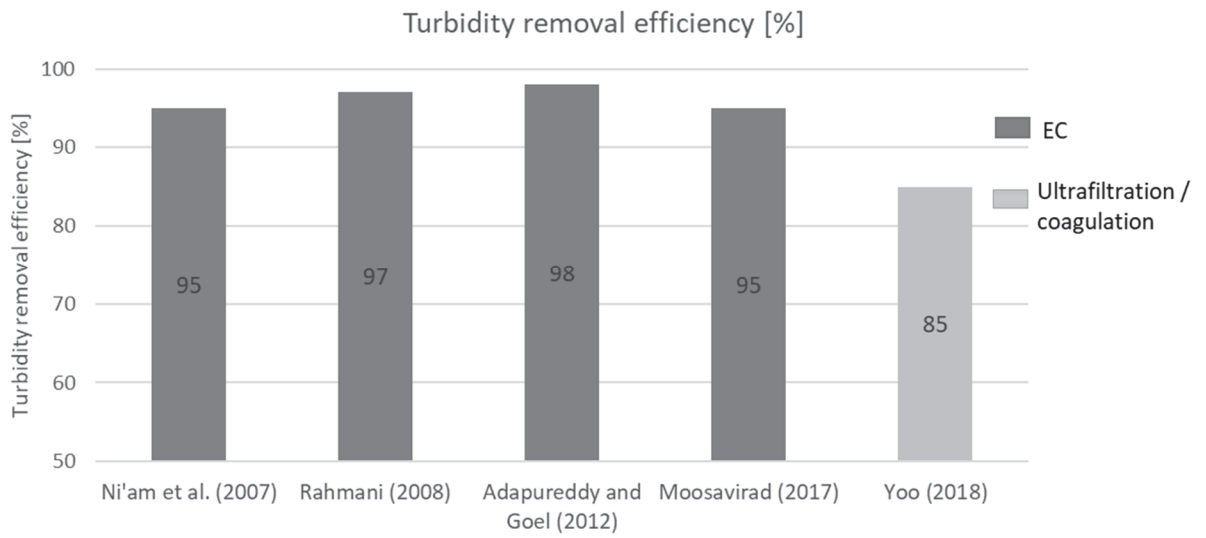

Figure 3. *Comparison of turbidity removal efficiency*

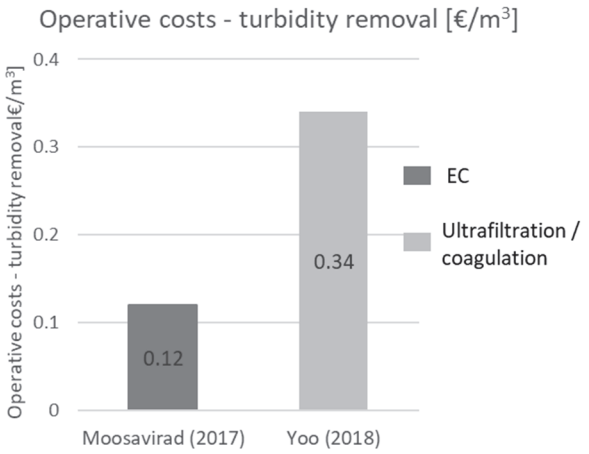

Figure 4. *Comparison of operative costs for turbidity removal*

The second comparison is for arsenic removal efficiency. Reverse osmosis and EC process both have very high removal efficiencies and similar operative costs (**Figure 5** and **Figure 6**). But since more research was carried out on it, the advantage is given to reverse osmosis. It is noted that all studies were conducted on units with similar capacity.

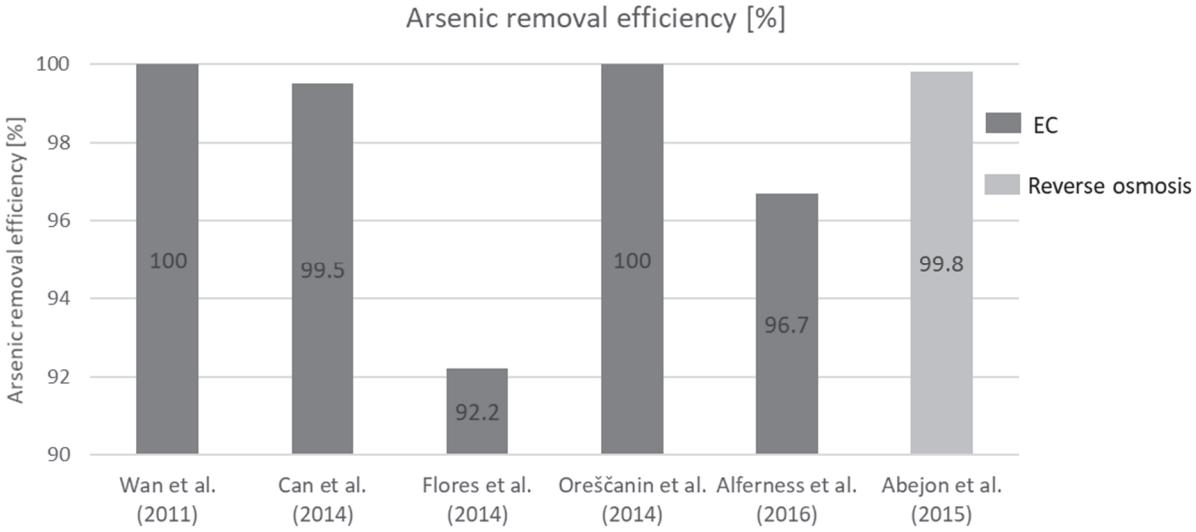

Figure 5. *Comparison of arsenic removal efficiency*

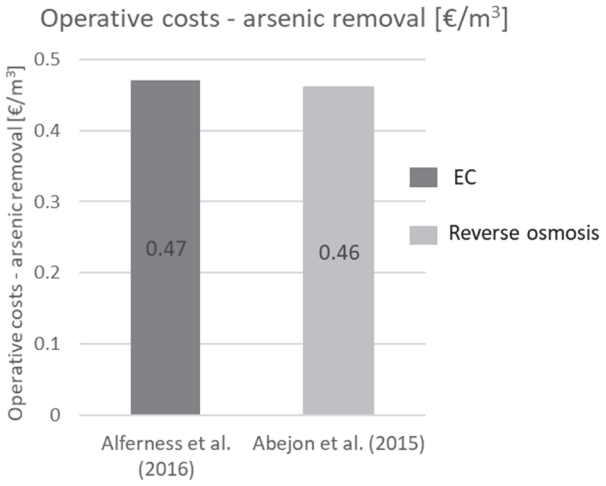

Figure 6. *Comparison of operative costs for arsenic removal*

4.1. Removal of Total Nitrogen on a full-scale electrocoagulation reactor

A case study with Al electrodes was performed on a full-scale batch EC unit made from stainless steel, **Figure 7**. The unit has two rectangular chambers (tanks), whose dimensions are 0.80 m × 0.55 m × 1.10 m. In the study, 90 L of water was used as the operating volume. The first tank is used for EC process, from which water can circulate (by pump) between two rectangular Fe, Al or SS electrode plates, while the second one is used as a settling tank. The total surface of Al electrodes was 0.063 m^2 and the electrode distance was 0.5 cm.

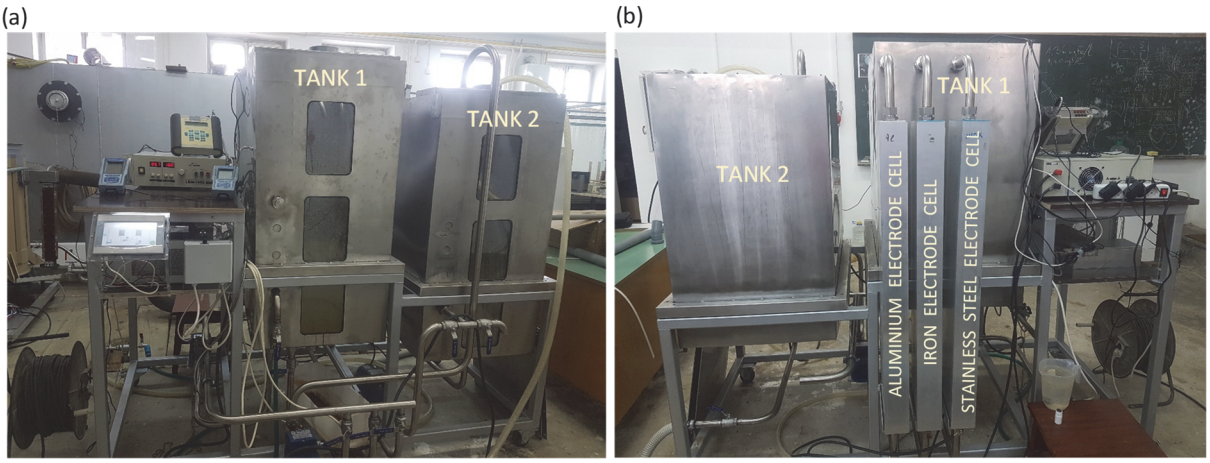

Figure 7. *(a) The front and (b) the back of the EC unit*

In the tank 1 (**Figure 7**), 100 mL of 25 % NH_3 solution was mixed with 90 L of drinking water from public water supply system in order to obtain Total Nitrogen (TN) concentration just over 200 mg/L. Also, 180 g of NaCl was added in order to increase the solution conductivity and obtain its concentration around 2 g/L. Everything was mixed for several minutes. The initial pH was 9.8 and total treatment time was 240 min. Water samples were taken before the beginning of the treatment, at every 60 min, and at the end of the process. TN concentrations were measured with NANOCOLOR 500D (by Eutech) Test 0-88 (TNb 220). Flow (Q = 0.03 L/s) was measured with ultrasonic water meter FLUXUS F601 (by Flexim), and the current was maintained approximately constant at 12 A by the MC Power LBN-1990 lab power supply. After 240 min, TN was decreased to 63 mg/L, corresponding to removal efficiency of 69.7 % (**Figure 8, Table 9**).

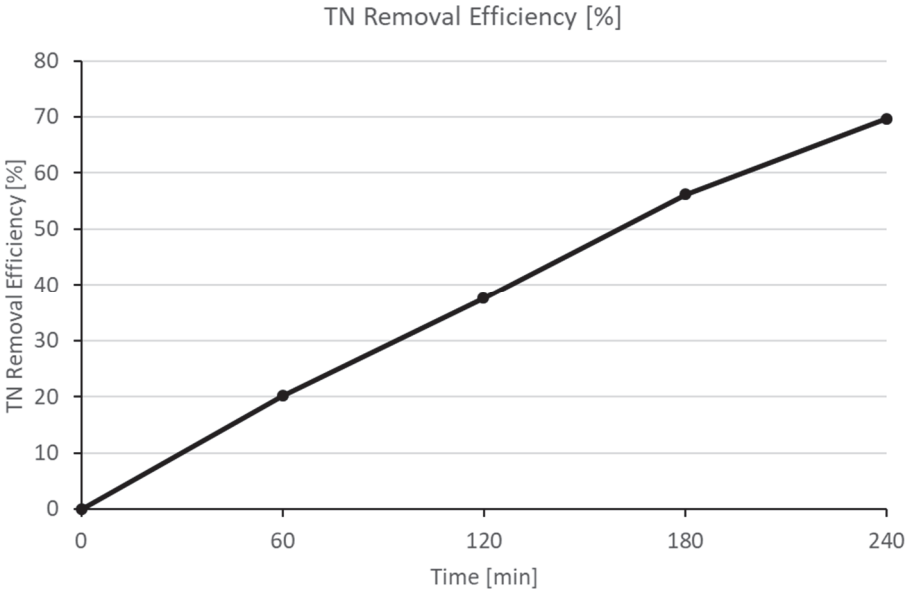

Figure 8. *TN removal efficiency*

According to **Figure 8**, a linear trend of TN removal can be noticed, approximately 33 mg/L per hour. In comparison with some previous results (Posavčić et al., 2018), it is assumed that flow significantly affects the removal efficiency and is better that the water runs slower through the electrodes because there is more time for the formation of Al hydroxides.

Further, the operating costs are determined for this case (**Table 9**). An assessment of the operational costs of the EC process is given regarding energy cost, consisting of electricity and pump (power) costs, and material (electrodes) cost according to **Equation 3**:

$$Operating\ costs = a\ (C_{electricity} + C_{pump}) + b\ C_{material} \qquad (3)$$

where: $C_{electricty}$ is electrical energy cost of 1 m^3 of treated water (kWh/m^3), C_{pump} is the energy cost of the pump for 1 m^3 of treated water (kWh/m^3) and $C_{material}$ (kg Al/m^3) is the cost of the electrode material used in 1 m^3 of the treated water. *a* is the average electricity price of 0.13 €/kWh (according to the national tariff models), and *b* is the average market price of aluminum given as 1.54 €/kg. After 240 min, total operational costs were 7.60 €/m^3.

Table 9. TN removal efficiency (%) and operating costs for energy (electricity and pump) and material (electrode)

TIME [min]	TN [mg/L]	% REMOVAL	$C_{electricity}$ [kWh/m^3]	C_{pump} [kWh/m^3]	$C_{electrode}$ [kg/m^3]	OPERATING COSTS [€/m^3]
0	208	-	-	-	-	-
60	166	20.19	8.00	5.56	0.09	1.90
120	130	37.50	16.00	11.11	0.18	3.80
180	91	56.25	24.00	16.67	0.27	5.70
240	63	69.70	32.00	22.22	0.36	7.60

5. CONCLUSION

According to previous research, EC is suitable for removal of *E. coli*, iron, arsenic, color and turbidity. However, in cases with manganese and ammonia, it has been shown that EC is not effective enough to meet the standards determined by the Ordinance on conformity parameters, analytical methods, monitoring and drinking water safety plans, and keeping register of legal entities which provide public water supply (Official Gazette 125/17) and needs to be combined with other water treatment processes.

Generally, most of the previous research were conducted on "small-scale" units, i.e. small capacity devices (up to 10 L), where received results (operative costs and operative parameters), are not applicable in real conditions. Therefore, in order to obtain more credible results, more research on pilot devices need to be done.

In this paper, a case study is also presented. Observed linear change indicates that the EC process for TN removal, with specified reactor setup, can be modelled with a simple linear rule with the average removal rate of 33 mg/L·h for 0.03 L/s flow rate.

Linear change can be attributed to the approximately constant current that was maintained at 12 A. Also, what was not previously reported is that during the study the current was constantly slowly decreasing. Approximately every 15 minutes current dropped for 1 A. In order to keep the current constant, the voltage was increased accordingly.

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ADVANCED OXIDATION TREATMENTS OF OLIVE MILL WASTEWATER

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Abstract: *New and innovative advanced oxidative processes for wastewater treatments are currently in the focus of scientific research and development for possible industrial implantation. The main aim of this study was to investigate the effect of cold plasma treatment, high intensity ultrasound and UV radiation with the addition of additives: H_2O_2, TiO_2, $FeCl_3$ x $6H_2O$ on degradation and removal of complex organic compounds from olive mill wastewater (OMWW). Olive mill wastewater represents a potential ecological problem when it is raw disposed into the environment, because of its high organic load. OMWW samples (with and without additives) were treated by high-voltage plasma discharge at frequencies 60 Hz and 120 Hz in combination with pumped gases (nitrogen, air and oxygen) for 30 minutes, by UV radiation for 30 minutes and 10 minutes by high intensity ultrasound. Physico-chemical parameters of quality, chemical oxygen demand (COD), and total dissolved carbon (TOC) were determined. The results have shown the efficacy of plasma treatment in degradation of organic compounds as well as degradation and reduction of polyphenolic compounds. Reduction of colour and total dissolved carbon occurred in all treated samples, mostly with the addition of $FeCl_3$ x $6H_2O$. Treatment with UV radiation and ultrasound proved to be the most efficient resulting in the 50% reduction of organic compounds after a 10-minute treatment.*
Keywords: *wastewater, cold plasma, OMWW, ultrasound, UV radiation*

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1. INTRODUCTION

The food industry is a large consumer of water but also acts as one of the biggest generators of wastewater. Olive mill wastewater (OMWW) is one of the most loaded and complex agro-industrial wastewater with hardly biodegradable constituents and it is necessary to process it prior to discharge into the aquatic environment or the public drainage system.

OMWW is a mixture of vegetation water, soft tissue from olive fruit and water used in various stages of oil pressing process; water added during centrifugation, water from filters and water from the washing equipment. It contains olive fruit pulp, pectin, oil, and other substances suspended in a relatively stable emulsion. According to its physico-chemical characteristics olive mill wastewater is a dark coloured liquid characterized by expressed odour, high organic loads (Chemical oxygen demand (COD) from 47-178 gO_2 L^3), high concentration of phenols (0,5-0,7 gL^{-3}), low pH (pH= 4-5), high conductivity (5,50-10 dSm^{-1}) and high ratio of suspended particles (to 20 gL^{-1}) (Paredes et al. 1997; Akar et al. 2009; Morillo et al. 2009).

OMWW contains organic compounds such as soluble phenols (hydroxytyrosol, tyrosol, catechol, methylcatechol, caffeic acid, vanillic acid, p-coumaric acid, etc.), polyphenols, polyalcohols, sugars, tannins, lipids, and pectins originally from olives (Tsagaraki et al. 2007). In addition, several studies have shown that phenolic compounds are responsible for the phytotoxicity of OMWW (Niaounakis & Halvadakis 2006; Quaratino et al. 2007; Kallel et al. 2009). It has been established that organic loads, especially phenolic compounds, inhibit the efficacy of anaerobic digestion and therefore, in some cases, advanced oxidation methods are considered to be an extraordinary alternative (Kallel et al. 2009).

Due to the diversity of potential contaminants in OMWW and the problem of their removal, research is directed towards the development of new technologies, and the current emphasis of the research is on reducing the harm and toxicity of advanced oxidation processes (AOPs) that have proven to be exceptionally high performance for removing highly degradable compounds.

AOPs are defined as processes based on the formation of various oxidation agents in sufficient quantity for complete mineralization of organic substances. The main mechanism of AOP is to generate highly reactive free radicals that effectively react with carbon-carbon double bonds and attack the aromatic nucleus (Zaviska et al. 2009). AOP includes: chemical processes (O_3, O_3/H_2O_2, Fe^{3+}/H_2O_2) (Nesheiwat & Swanson, 2000), mechanical processes (cavitation generated by ultrasonic radiation or using compression such as valves or openings in hydraulic devices) (Adewuyi 2001), photochemical or photocatalytic processes (by

ultraviolet radiation in the presence of oxidants or catalysts) (Bhatkhande et al. 2002) and electrical processes ("corona" discharge or "glow" discharge). The resulting hydroxyl radicals are strong oxidation reagents with a 2.33 V oxidation potential and show very rapid oxidation reactions compared to conventional oxidants such as hydrogen peroxide or $KMnO_4$ (Gogate et al. 2004).

1.1. Cold plasma

Plasma coming from the Greek word “plasma” in free translation means self-forming material (Mott-Smith & Langmuir 1926). It consists of positive and negative ions, free radicals, gas atoms, molecules, electrons and neutral particles (Roya & Hosseini 2014). The term "plasma" was first used in 1928 by Irving Langmuir to define the fourth state of the substance with partial or completely ionized gas status. Changing the phase of a solid, liquid and gaseous state is generated by increasing the energy intake and also the further increase of energy above a certain level in the gaseous phase causes the ionization of molecules resulting in plasma formation (Thirumdas et al. 2014). Plasma can be created by subjecting the gas to the electric field (between the two electrodes) of a constant or changed high frequency amplitude. Applied energy can be from a variety of sources (thermal, electrical, magnetic), causing an increase in kinetic energy of the electron, resulting in increased collisions with neutral molecules and plasma formation, divided into two major categories - thermal and non-thermal plasma (Cheng et al. 2007).

Plasma generates oxidizing agents OH, O, H_2O_2 which have a high oxidative potential for oxidation of organic compounds and purification of water (Li et al. 2007). Plasma can be created directly in the liquid, in the air above the liquid, or in the case of a hybrid reactor, both in liquid and in the air. Research has focused on the use of non-thermal plasma for the oxidation of phenols, dyes, degradation of pharmaceutical compounds and pesticides. Non-thermal plasma has a tendency of energy transfer through the aqueous medium being treated. When treating wastewater, plasma is generated as a result of high-voltage discharge that is generated by the current electrical and magnetic field. The electromagnetic field is capable of sterilizing wastewater and therefore plasma technology is considered to be more effective in treating wastewater (Cheng et al. 2007).

1.2. Ultrasound

Great attention to research on the use of ultrasound in environmental protection is directed to the exploitation of the cavitation effect on the destruction of chemical and biological substances in wastewater as an example of an advanced oxidation process (Mason & Tiehm 2001).

Ultrasonic waves are mechanical vibrations that spread through a medium that contains elastic properties such as solid, liquid or gas. The effect of ultrasound treatment is basically the result of ultrasonic induced cavitation by using sound wave in the lower frequency range. It is mainly applied in the range of 20-40 kHz, but there is an increasing interest for the effects of higher frequencies, but not above the MHz frequency where cavitation is difficult to achieve without the use of high power (Mason & Lorimer 2002). Ultrasound has more and more potential for wastewater treatment. The use of sonochemical oxidation, which results in cavitation or formation of growth, and subsequent breakdown of bubbles or cavities created in an extremely small time interval (microseconds) and the release of large amounts of energy. Under these conditions, the organic compounds are dissociated directly by pyrolytic cleavage. On the other hand, the hydroxyl radicals formed by pyrolysis also participate in the degradation of organic substances (Babuponnusami & Muthukumar 2013).

1.3. UV radiation

UV radiation is a part of electromagnetic radiation wavelengths of 100-400 nm, which due to the release of large amounts of energy, effectively cleaves the chemical bonds within the molecules.

The photochemical processes of degradation are increasingly attributed to the importance of wastewater because chemical reactions are characterized by the formation of free radicals that can be easily produced by UV radiation (Mazzarino et al. 1999). Molecules absorb the energy of UV radiation and move to an excited state, but in such a state they remain very short and return to their ground state or break down to the radical. The resulting radicals are reactive and react with organic substances in reactions where the final products are of low molecular weight.

Research has shown that UV radiation at 253.7 nm wavelength (UV-C) efficiently breaks down industrial chemicals, hydrocarbons, fuel, dye and odour molecules. Also, ultraviolet radiation processing has proven to be effective when used as a pre-treatment or in combination with other processing technologies such as adsorption on activated carbon, biodegradation, ion exchange and membrane bioreactor treatment.

2. MATERIAL AND METHODS

Wastewater from the production of olive oil (OMWW) was supplied from an oil mill in Northern Dalmatia and stored in plastic containers in a freezer at -18 °C. Before the treatment, to remove agglomerated particles, OMWW was tempered to room temperature and filtered through a 0.45 μm pore paper filter. The treated OMWW had the following physico-chemical characteristics: pH 5.04, electrical conductivity 872 μScm^{-1} and 29.8 % saturation.

2.1. Methods

Physical characteristics of OMWW were measured in samples before and after treatment using a digital meter (HANNA instruments, Woonsocket, USA), pH value with pH electrode (HI11310), electrical conductivity with the electrode (HI763100) and oxygen saturation with the electrode (HI764080).

Pulse high-voltage generator (Spellman, UK) of 1200 W output power was used to generate plasma. A generator is connected to the circuit with resistors 9.5MΩ and capacitor with capacity 0.75 nF. Plasma frequencies used for treatment were 60 Hz and 120 Hz and the voltage was measured by the Tektronix P6015A voltage-probe connected to the oscilloscope (Hantek DS05202BM, China).

A hybrid plasma reactor is a glass reactor with a total volume of 500 mL (working volume of 200 mL), with rubber caps and adapted opening for the electrodes and gas injection (**Figure 2**). During treatment through high-voltage electrode (stainless steel needle Microlance TM 3.81 cm) located at the bottom of the reactor and placed in the liquid phase, gases were blown N_2 (flow = 4 $Lmin^{-1}$), O_2 (flow = 6 $Lmin^{-1}$) or air (flow = 6 $Lmin^{-1}$), which also enabled mixing of the sample. A ground electrode was placed on the upper side of the reactor, in the gas phase. This type of reactor enables discharge on the top of the electrode in the liquid and on the surface, where it discharges through the bubbles on the surface.

Table 1. Cold plasma treated samples

Sample	Treatment		t (min)
A	untreated		0
B	60 Hz	N_2	30
C		air	30
D		O_2	30
E	120 Hz	N_2	30
F		air	30
G		O_2	30
H	untreated + $FeCl_3$ x $6H_2O$		30
I	60 Hz	N_2+ $FeCl_3$ x $6H_2O$	30
J		air + $FeCl_3$ x $6H_2O$	30
K		O_2+ $FeCl_3$ x $6H_2O$	30
L	120 Hz	N_2+ $FeCl_3$ x $6H_2O$	30
M		air + $FeCl_3$ x $6H_2O$	30
N		O_2 + $FeCl_3$ x $6H_2O$	30

In UV radiation treatment was used UV-C lamp of 16 W power placed in stainless steel tube (Spa Dealers - Lux Style, Finland). The peristaltic pump (SP 311 VELP Scientifica, Italy) provided a constant circulation of wastewater from the reactor through UV lamp.

In order to have most effective further wastewater treatment, chemical requirements were decreased by up to 70 %. OMWW samples of 200 mL volume were treated for 30 minutes with the previous addition of: 51.5 μL H_2O_2 (c = 1 gL^{-1}), 0.2 g TiO_2 (c = 1 gL^{-1}) and 33 μL of $FeCl_3$ x $6H_2O$ (c = 1 $molL^{-1}$).

Table 2. UV radiation treated samples

Sample	Treatment	t (min)
1.	H_2O_2 / UV	30
2.	TiO_2 / UV	30
3.	$FeCl_3$ x $6H_2O$ / UV	30
4.	H_2O_2 + $FeCl_3$ x $6H_2O$ / UV	30

The ultrasonic processor - Misonix Sonicators S-4000 (Connecticut, USA) was used to generate high intensity ultrasound for ultrasonic treatment. The device has a maximum power of 600 W, a voltage of 120 - 240 V and a frequency of 20 kHz. The thermocouple was immersed in the sample during the entire treatment and connected to an ultrasonic processor. In the study was used an ultrasound probe of 12.7 mm diameter. Ultrasonic power loss occurs by passing through the medium due to heat development and because of it treatment time was

limited to 10 minutes without cooling the reactor chamber. OMWW volumes of 200 ml were treated for 10 minutes with the previous addition of: 51.5 µL H_2O_2 (c = 1 gL^{-1}), 0.2 g TiO_2 (c = 1 gL^{-1}) and 33 µL $FeCl_3$ x $6H_2O$ (c= 1 $molL^{-1}$).

Table 3. Ultrasound treated samples

Sample	Treatment	t (min)
5.	H_2O_2 / US	10
6.	TiO_2 / US	10
7.	$FeCl_3$ x $6H_2O$ / US	10
8.	H_2O_2 + $FeCl_3$ x $6H_2O$ / US	10

Determination of sample colour was tested on Specord 50 Plus Spectrophotometer (AnalytikJena, Jena, Germany) with measurements of L*, a* and b* values on the 10 mm mesh mask. Coordinates of the CIE Lab colour system are based on Hering's theory of opposite colour pairs representing the system's axis. The chromatographic characteristics of the wastewater according to the CIE system are described by the following parameters: achromatic axis L* (lightness) indicates luminance in the range of 0 % to 100 %, with 0 % black and 100 % white; axis a* represents the range of colours red-green and axis b* range of colours yellow-blue (Mohammadi et al. 2008; Sharma & Rodríguez-Pardo 2012; de Mendonça et al. 2016). All measurements were performed in SCI (Specular Component Included) mode.

Samples are defrosted and stored at room temperature prior to colour determination. The transmittance measurement was carried out in plastic cuvette at wavelengths of 380 to 780 nm, each 5 nm, with the D65 illuminator and the viewing angle of 10 ° versus distilled water as a blank probe. The tested sample L*, a*, b*, C and h values are calculated with automatic data processing using CIE Lab software support. It expresses colour as three values: L* for the lightness from black (0) to white (100), a* from green (−) to red (+), and b* from blue (−) to yellow (+). Based on the measured parameters L*, a* and b* values, the total colour change ΔE is calculated according to **Equation 1**:

$$\Delta E* = \sqrt{(L* - L_{ref}*)^2 + (a* - a_{ref}*)^2 + (b* - b_{ref}*)^2} \qquad (1)$$

L*- the colour brightness of the examined sample in the L* a* b* system
a*- colour parameter of the examined sample
b*- colour parameter of the examined sample
L_{ref}*- the colour brightness of the reference sample
a_{ref}*- colour parameter of the reference sample
b_{ref} *- colour parameter of the reference sample

Dissolved Organic Carbon (DOC) was measured on the TOC Analyser (TOC-VCPH, Shimadzu, Japan) by the (NPOC) non-purgeable organic carbon method. The combustion catalytic oxidation method achieves total combustion of samples by heating them to 680°C in an oxygen-rich environment inside TC combustion tubes filled with a platinum catalyst. Since simple oxidation principles are used through heating and combustion, pre-treatment and post-treatment are not required. Carbon dioxide generated by oxidation is detected by an infrared gas analyser (NDIR). By adopting the newly designed highly sensitive NDIR, the TOC-L series achieves high detection susceptibility with a detection limit of 4 μgL^{-1}, the highest level for the catalytic combustion oxidation method.

The DOC and TOC determination method requires the removal of all inorganic carbons from the sample before the sample is analysed for the organic carbon content. If inorganic carbon is not completely removed, there will be a significant error. Inorganic carbon disturbance is removed by converting inorganic carbon into CO2 by acidification of the sample at pH 2-3 and sifting inert gas to remove the generated CO2. The sample is then injected into the instrumental TOC system and the organic carbon is oxidized to CO2 released from the sample and detected as DOC or TOC (Shimadzu 2018).

The OMWW content of DOC depends significantly on the raw material, climatic conditions and operating conditions of the plant. Because of the presence of suspended material, TOC and DOC significantly differ and therefore can be expected results variability.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical characteristics

In the treated samples, the physical characteristics of pH value, electrical conductivity and oxygen saturation were measured and the following results were obtained. In the treated samples a decrease in the pH value was

observed after cold plasma treatment, especially in treatment with $FeCl_3$ x $6H_2O$ supplementation. The pH elevation was observed in UV radiation treatment while ultrasonic treatment did not change pH value.

The difference in pH value of the treated samples is due to the different effect of the individual treatments. Acidification of the solution in plasma treatment can be explained by the partial oxidation of the phenolic compounds into low molecular weight carboxylic acids, which predominantly occurs within the first stage of the Fenton process (Esteves et al. 2018). In contrast, UV radiation treatment raises the pH due to the influence of different ions on the absorption of UV light and the reaction of undesirable substances with hydroxyl radicals.

Different values of pH and conductivity after the ultrasound treatment can be explained on the basis of the main factors limiting acoustic cavitation like degassing of liquid, high atmospheric pressure, temperature elevation, and irradiation with increasing US frequencies (Herrmann 1999).

Due to the development of high temperatures during ultrasound processing (> 60 °C), the treatment time was 3x shorter, compared to UV treatment. Ultrasound leads to the formation, growth and breakdown of the bubble, which is followed by the generation of very high local temperature. In the range of 20 to 80 °C, the temperature-dependent degradation is weak, but cooling is recommended for temperatures above 80 °C due to a drastic decrease in activity and reaction rate (Herrmann 1999).

After treatment in a hybrid plasma reactor, values of electrical conductivity have increased as well as in ultrasonic treatment with H_2O_2 supplementation, whereas in the UV and US treatments there is usually a decrease in electrical conductivity. The agglomerates present in the OMWW are degraded by the cold plasma treatment and contribute to the increase of electrical conductivity. Also, nitrate and nitric products dissolving in water during plasma treatment can induce a steep pH lowering of the solution and an increasing of conductivity as well as participate in various reactions (Jiang et.al. 2014). Oxygen saturation increases after treatments where air or oxygen was blown into samples, while in samples where nitrogen was blown oxygen saturation decreased.

3.2. Colour intensity

OMWW treatments in a hybrid plasma reactor with selected process sizes and using UV radiation and/or US treatments gave the following results. Using the colourimetric method prior to treatment (**Figure 1**) and after treatment (**Figure 2**), the colouring intensity decreased. The most significant colour change occurred in samples treated with cold plasma with nitrogen and air blow at a frequency of 120 Hz with addition of $FeCl_3$ x $6H_2O$, whereas colour change in treated US and/or UV radiation is most pronounced in samples in which H_2O_2 was added.

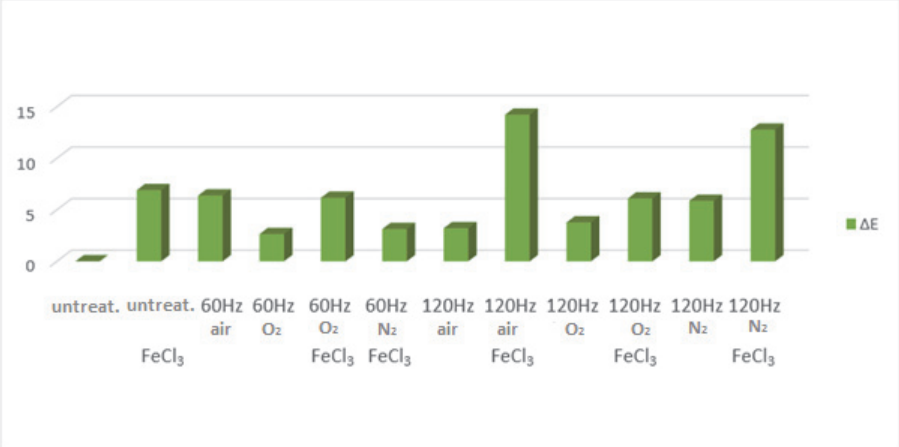

Figure 1. *Colour change in samples treated with cold plasma*

In the samples to which Fenton's method was applied, the colour change is more significant in cold plasma treated samples, while in US and/or UV treated samples, the colour change is lower. The reason for this is that the efficiency of the Fenton process is affected by the amount of added iron ion, the concentration of H_2O_2, the concentration of contaminated substances and pH. At pH values above 4, Fe^{2+} ions are highly unstable and easily transfer to a more stable Fe^{3+} ion that creates complexes with a hydroxyl ion (Niaounakis & Halvadakis 2006). pH values of cold plasma treated samples ranged between 3.34 and 5.05 while pH in samples treated with US and/or UV radiation ranged between 5.01 and 5.76, which influenced the efficacy of Fenton's method.

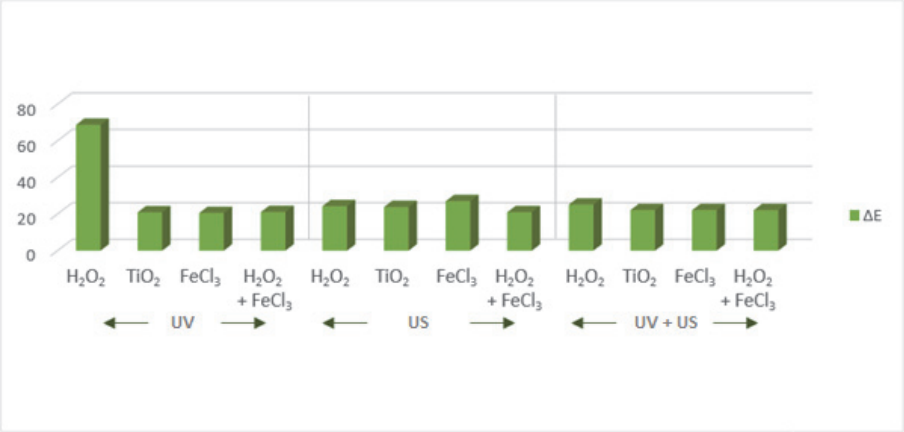

Figure 2. *Colour change in samples treated with US and/or UV radiation*

Since the photooxidation process is very limited, ultraviolet light is used in combination with a strong oxidant such as H_2O_2 or TiO_2 catalyst. (Daneshvar et al. 2008). According to the results of the research, Rezaee et al. (2008), under the optimal dose of H_2O_2 (2.5 $mmolL^{-1}$) and UV radiation (55 W) for less than 30 minutes, the solution was fully decolourized. The percentage of decolourization is linearly increased by UV radiation and the nonlinear increase of the initial concentration of H_2O_2. According to this research, the best result of ultrasonic removal and/or ultraviolet radiation is achieved by UV treatment with the addition of H_2O_2.

3.3. Colour intensity

Figure 3 presents the concentrations of total dissolved carbon in samples after treatment in a hybrid plasma reactor at selected process conditions. From the obtained values is apparent that in relation to the DOC value in the untreated sample, the highest reduction in DOC was obtained in the sample treated with cold plasma at a frequency of 60 Hz with nitrogen and addition of $FeCl_3$ x $6H_2O$.

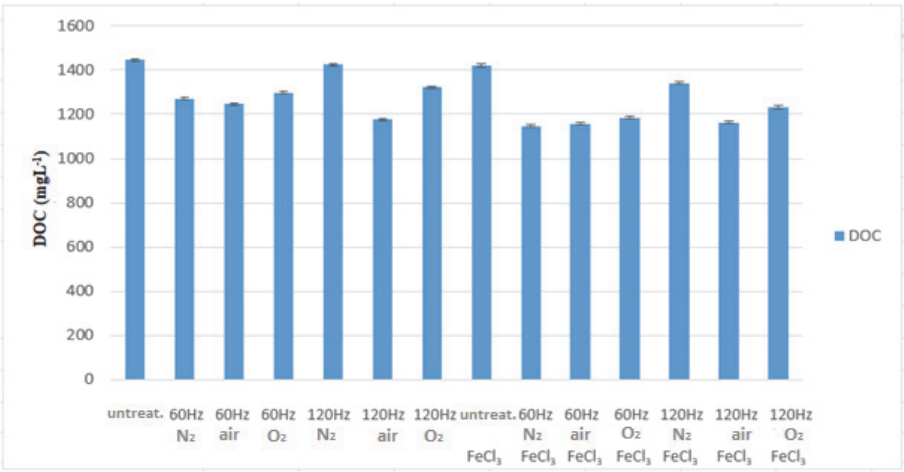

Figure 3. *DOC values in samples after cold plasma treatment*

The values of total dissolved carbon in the samples treated with ultrasound and/or UV radiation with the previous addition of H_2O_2, TiO_2 and $FeCl_3$ x $6H_2O$ with the selected process conditions are shown in **Figure 4**. It is apparent that the highest value of total dissolved carbon (2546 mgL^{-1}) is obtained by ultrasonic and UV radiation treatment with the prior addition of 30 % H_2O_2 in a volume of 51 µL. The disadvantage of this combination is that H_2O_2 has a poor absorption of UV radiation and most of the light input in wastewater treatment will be wasted (Crittenden et al. 2005).

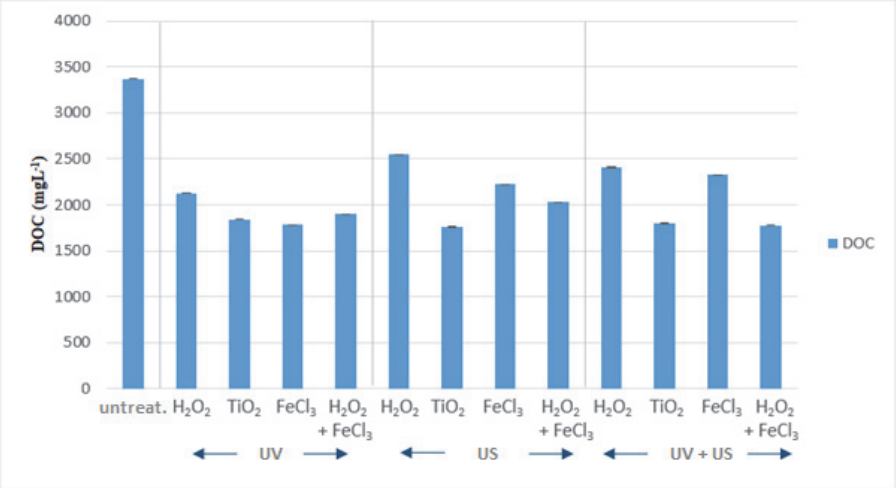

Figure 4. *DOC values in samples after UV and/or US treatment*

The combination of H_2O_2 and UV radiation with the Fenton reagent proved to be very effective in reducing the DOC value to 1897 mgL^{-1}. Compared to the combination of UV radiation, H_2O_2 and Fenton reagent with the Fenton reagent itself, the combination produces more hydroxyl radicals and thus increases the rate of degradation of organic contamination. The required amount of iron salt for treatment is considerably lower in the combination of US/UV compared to the Fenton method itself where the iron ions have to be added at regular intervals for the reaction to flow.

Furthermore, the addition of 0.2 g of TiO_2 with ultrasound and UV treatment have caused the most significant change in the DOC value. Wastewater treatment with TiO_2 and UV radiation has been intensively used in wastewater treatment since TiO_2 is cheap and highly available chemical, biologically inert and stable, capable of oxidizing organic compounds into harmless compounds such as H_2O and CO_2. El-Hajjouji et al. (2008), in their research, investigated the effect of 1 gL^{-1} TiO_2 and UV radiation on wastewater from olive oil production. After 24 hours, 22 % COD and 94 % phenol were removed. Almost 30 % of DOC was removed in the presence of 0.5 and 1 gL^{-1} TiO_2 over a period of 50-60 minutes.

Figure 3 and **Figure 4** present a significant difference in total dissolved carbon values. After cold plasma treatment values of DOC ranges from 1148 mgL^{-1} to 1421 mgL^{-1}, which is a significant reduction compared to the untreated sample. The DOC values after ultrasound and UV radiation treatment are in the range of 1761 mgL^{-1} to 2409 mgL^{-1}.

4. CONCLUSION

After the research conducted, it can be concluded that the most significant colour changes, as well as the greatest reduction of total dissolved carbon, are in samples treated with cold plasma and in samples with the addition of Fenton reagent. After 30 minutes of UV treatment, 10 minutes by ultrasound or combination of US and UV radiation for 10 minutes, the biggest colour change was observed by applying the combination of UV treatment with the addition of strong oxidants H_2O_2 and the catalyst. The value of total dissolved carbon was almost double reduced by ultrasound treatment with the addition of TiO_2 catalyst in comparison to the untreated sample.

Observing the influence of all conducted treatments, advanced oxidation treatments has proved to be effective treatments for olive mill wastewater and it is useful to conduct further extensive research for possible effective industrial applications in the future.

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THE EFFECT OF DIFFERENT NANOCATALYSTS FOR PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

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Abstract: *The aim of this study was to investigate photodegradation of Methylene Blue (MB) in water by using ZnO and TiO_2 nanoparticles. Adsorption and photocatalytic oxidation studies were carried out by using produced TiO_2, commercial TiO_2 and commercial ZnO nanoparticles. In order to evaluate performance tests, 5 mg/l of MB solution was used. The samples were mixed in the dark for 2 hours for establishing adsorption-desorption equilibrium. The photocatalytic tests of the samples were performed by assessing the decomposition rate of MB solutions under UV light. The results of the photocatalytic showed that the highest color removal efficiencies was obtained by TiO_2 catalyst where Methylene blue solution was completely degraded.*

Keywords: *TiO_2, ZnO, Photocatalytic Degradation, Methylene Blue*

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Preliminary report

1. INTRODUCTION

Water plays an important role in human, animal life, and ecosystem, but any unwanted addition of chemical substances leads to contamination or pollution and makes it unfit for consumption. Lately, environmental pollution is becoming the world debating and challenging problem. Among all those problems, water pollution is of prime concern. Water pollution has become an important problem at the global scale. Anthropogenic and industrial activities are responsible for this pollution. Effluents are discharged directly or indirectly by the industries into the nearby water resources without proper treatment (Ameta et al. 2013).

The degradation of dyes in industrial effluent has attracted great attention in the recent years because of increasing environmental awareness and the application of environmental rules. However, some treatments for colour removal from these effluents do not guarantee the absence of other secondary toxic substances, often arising from the treatment process itself (Immich et al. 2009).

In recent years, photocatalytic specialized materials and devices are increased not only in academic case but also in industrial applications. This dramatic rise is accompanying the population growth and wastes which are increased by them. New technological improvements are invented continuously. Owing to the environmental pollution, these new approaches should be eco-friendly. In 1969, according to a Japan researcher called Fujishima, photocatalysts were used for the treatment process. Honda-Fujishima developed a prototype: fine powders which are doped with metal and/or metal oxide particles were used as a photocatalyst in chemical reactions. These fine powders were semiconductor. Photocatalytic reactions using TiO_2 were discovered. Among these years many researches were done to improve the photocatalytic systems (Kodama & Suzuki 2007).

In photocatalysis, light of energy greater than the band gap of the semiconductor, excites an electron from the valence band to the conduction band (**Figure 1**). In the case of anatase TiO_2, the band gap is 3.2 eV, therefore UV light ($\lambda \leq 387$ nm) is required. The absorption of a photon excites an electron to the conduction band (e-CB) generating a positive hole in the valence band (Pelaez et al. 2012).

One of the advanced oxidation processes convenient for drinking water is heterogeneous photocatalysis with semiconductor titanium dioxide (TiO_2). TiO_2/UV photocatalytic oxidation process is generally with solar energy (hν) and TiO_2 surface. The main aim is to generate hydroxyl radical (OH•) which is a strong oxidizer and participates in different reactions with adsorbed substances on this surface (Çakıroğlu 2011).

Zinc oxide (ZnO) nanomaterials provide great usage because of their specifications in electronics, optics and photonics. Due to this reason, the properties of ZnO nanostructures, which have application potential in different areas, and ZnO is an environmentally friendly (Guo 2017).

Methylene blue is an aromatic chemical compound. The papers, hair dye, fabric dying and wool dying industry widely use MB as a colourant. The most MB is used in textile industry. It is commonly used in dyestuff applications and as a redox indicator. The mostly used wavelengths of MB are 291 and 664 nm (Yao and Wang 2010).

The aim of this study was to perform the photocatalytic degradation tests of MB in water by using ZnO and TiO_2 nanoparticles. Adsorption and photocatalytic oxidation studies were carried out by using produced TiO_2, commercial TiO_2 and commercial ZnO nanoparticles.

2. MATERIALS AND METHODS

2.1. Preparation and supplying of materials

TiO_2, ZnO and Methylene Blue (MB) were used in the experiment. TiO_2 was produced in Electronical Materials Production and Application Center of Dokuz Eylul University (99.55 % purity, 18 nm, anastas) (Yıldırım et al. 2016); commercial TiO_2 (99 %purity) and ZnO (99.5 %purity) 30-50 nm were bought from Nanograph Company. MB (Sigma-Aldrich, 97 %) solution was prepared by adding 5 mg of MB to 1 liter of deionized water. For providing the homogeny mix, 30 minutes of stirring was done with using magnetic mixer.

For every experiment, the beakers were filled up to 50 ml and the nanoparticles of TiO_2, commercial TiO_2 and ZnO placed on the testing apparatus as shown in Figure 1. ZnO, TiO_2 and commercial TiO_2 were added in MB solutions as 0,05g/50 ml, 0,1 g/50ml and 0,2 g/50ml, respectively. In the beginning, adsorption study was performed in the dark for 2 hours to establish adsorption-desorption equilibrium. After this step, photocatalytic studies were performed under UV lamp. Control sample (CS) were a reference samples without any photocatalyst. CS1 and CS2 were used to observe the effect of adsorption and photocatalytic studies. Schematic experiment apparatus was used in adsorption and photocatalytic studies as shown in **Figure 1**.

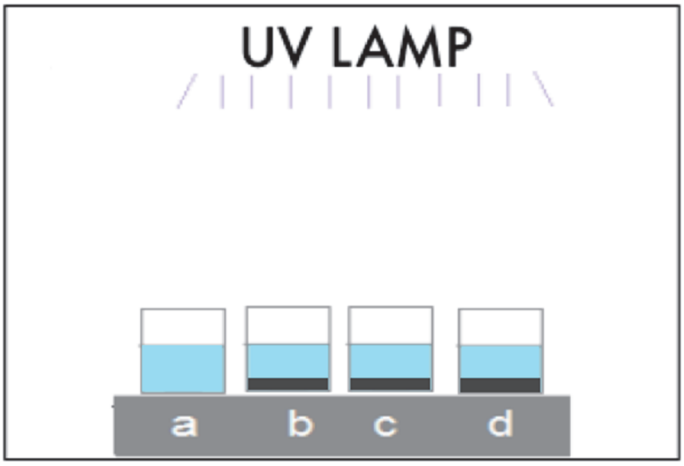

Figure 1. *Schematic experiment apparatus, (a) Control Sample, (b) MB soluton with ZnO nanoparticle, (c) MB solution with commercial TiO_2, (d) MB solution with produced TiO_2*

Initial absorbance was determined as Ao, and absorbance value of different times was determined as Ai, following the **Equation 1**:

$$\% \text{ Degradation rate} = (A_o - A_i)/A_o \times 100 \quad (1)$$

The degradation rate was calculated by using the **Eq. 1**. All samples were shaked in WISD Orbital Shaker (Korea) device for 2 hours in dark to establish the equilibrium for adsorption. 10 ml from each sample was taken for measurement of absorbance. Absorbance measurements were performed with Shimadzu UV-mini 1240 UV-Vis spectrophotometer (Japan). Photocatalytic degradation performance tests were carried out under UV lamp for 5 hours. After UV lamp exposure, all samples were taken for measurement of absorbance values. SEM analysis was performed to investigate surface morphology and characteristics of TiO_2 by using JEOL JSM-6060 SEM (United States).

3. RESULTS AND DISCUSSION

3.1. Characterization

The TiO_2 samples were characterized by using Scanning Electrone Microscope (SEM) and XRD. The morphology of the TiO_2 nanoparticle was found to be affected by solution concentration and illustrated in **Figure 2**. The size distribution of TiO_2 nanoparticles was homogeneous. Spectrophotometric measurement results are shown in **Figures 4-5**. The morphology of the films is an important parameter that affects photocatalytical properties (Bakuy 2009). It is noted that TiO_2 nanoparticles distribution is non-uniform.

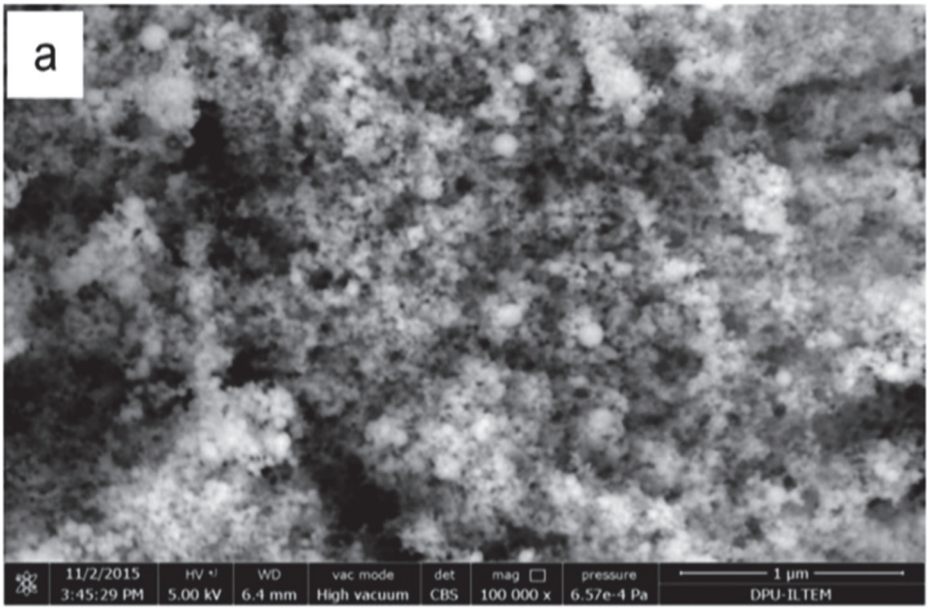

Figure 2. *SEM micrograph of TiO_2*

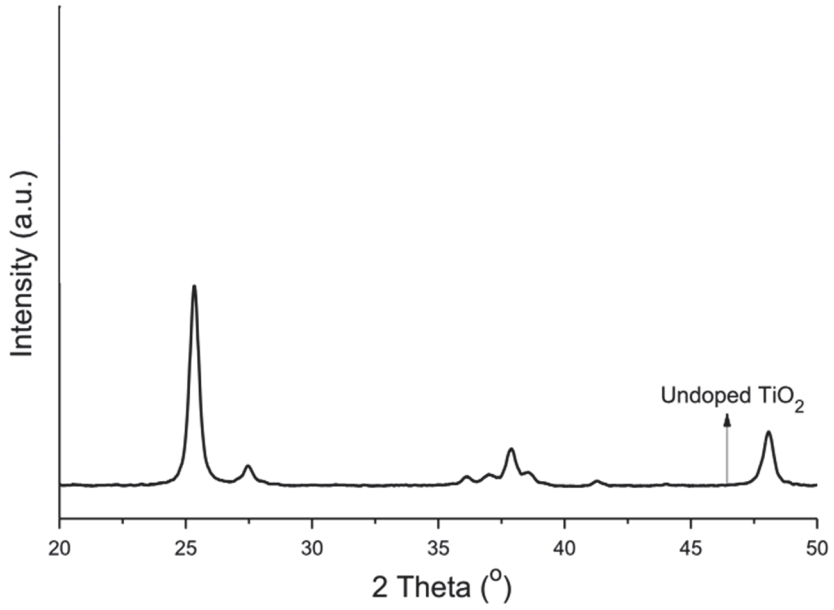

Figure 3. *XRD graph of TiO_2*

Phase identification of the TiO_2 was performed using X-Ray Diffraction (XRD) and illustrated in **Figure 3**. It was noted that strong and sharp peaks of the patterns confirmed. The obtained diffraction peaks were matched very well with the JCPDS Card no.: 21-1272 and 86-0148 demonstrating the phases of TiO_2 (Yıldırım et al. 2016).

3.2. Degradation

The degradation of the color during adsorption study was shown in **Figure 4**. It was noted that there was no significant color change after the adsorption study for all three nanoparticle photocatalysts; commercial TiO_2 - 1, prepared TiO_2 - 2 and ZnO (at three different concentrations of photocatalysts 0.05, 0.1 and 0.2). As expected, during the photocatalysis the colr removals appeared (**Figure 5**) for all three nanoparticle photocatalysts; commercial TiO_2 - 1, prepared TiO_2 - 2 and ZnO (at three different concentrations of photocatalysts 0.05, 0.1 and 0.2). The higherst degradation rates were obtained by the use of both types of TiO_2 nanoparticles - commercial TiO_2 - 1, prepared TiO_2 - 2.

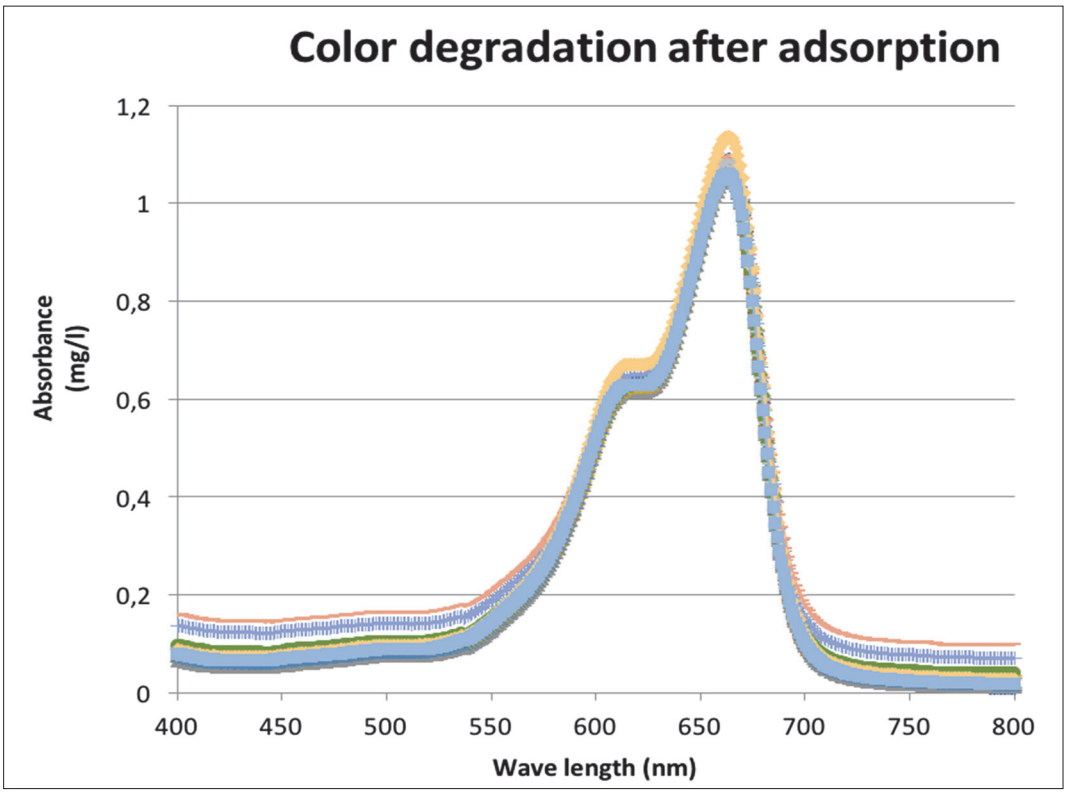

Figure 4. *Color degradation after adsorption on commercial TiO_2 - 1, prepared TiO_2 - 2 and ZnO nanoparticles; at three different concentrations of photocatalysts*

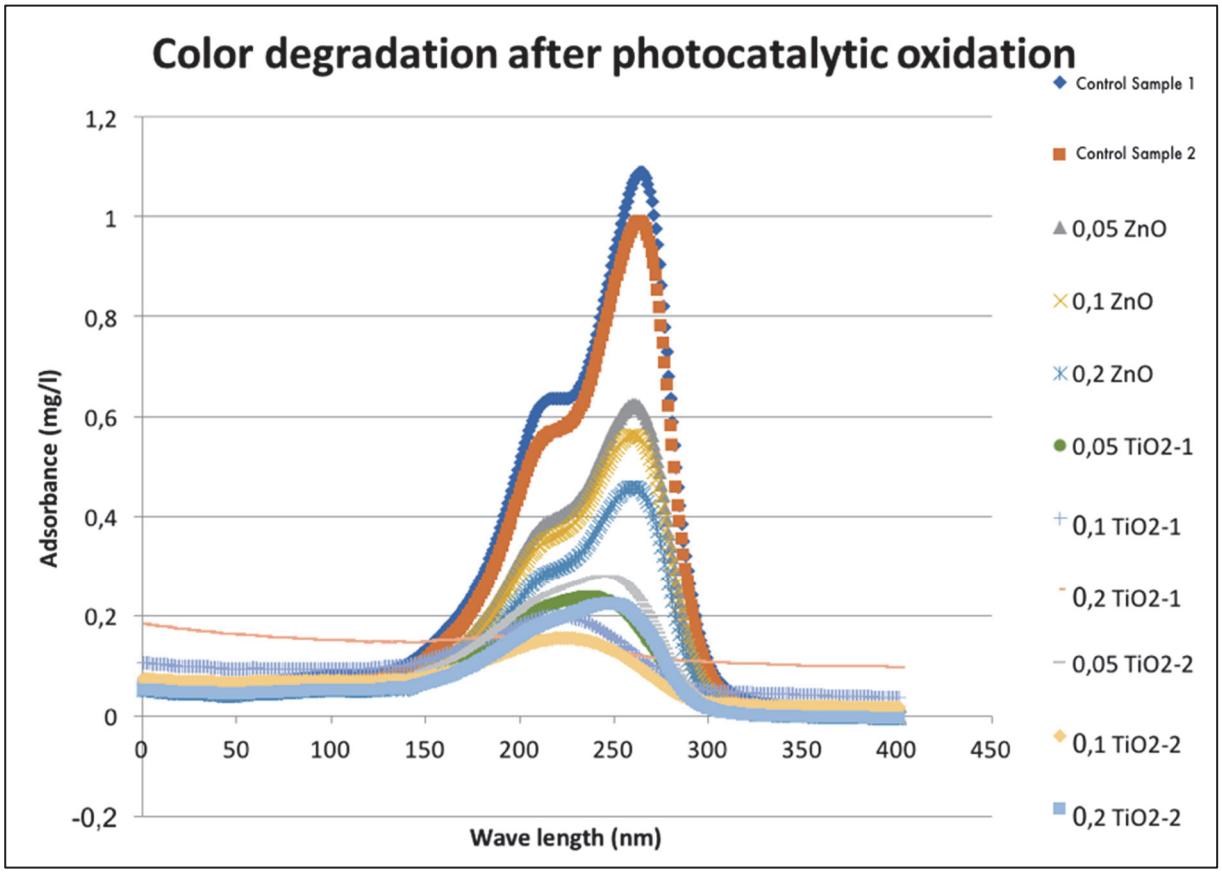

Figure 5. *Photocatalytic color degradation after adsorption on commercial TiO_2 -1, prepared TiO_2 - 2 and ZnO nanoparticles; at three different concentrations of photocatalysts*

The photocatalytic experiment results are illustrated in **Table 1** and shown in **Figure 5**. A slight change can be seen at reference (control) sample during the test. It was found that the samples with TiO_2 photocatalyst was removed totally MB in water, successfully. The MB degradation was very weak with ZnO catalyst in comparison with TiO_2 catalyst. Although it was found that 72 % degradation efficiency, it is possible to make nanoparticle more effective using on thin film coating with different dopant elements (Yang et al. 2009).

Table 1. Percentage of degradation after photocatalytic oxidation

NAME OF SAMPLE	RESIDUE MB CONCENTRATION (mg/l)	EFFICIENCY (%)
Control Sample	4,55	11
0.05 ZnO	2,37	54
0.1 ZnO	2,02	61
0.2 ZnO	1,43	72
0.05 TiO_2 (p)*	0	100
0.1 TiO_2-1 (p)*	0	100
0.2 TiO_2-1 (p)*	0	100
0.05 TiO_2 (c)**	0	100
0.1 TiO_2 (c)**	0	100
0.2 TiO_2 (c)**	0	100

**Produced TiO_2 in EMUM(Yıldırım et al., 2016) **Commercial TiO_2*

4. CONCLUSION

Adsorption and photocatalytic oxidation studies with ZnO, commercial TiO_2 and produced TiO_2 catalysts were performed successfully. As a result of the photocatalytic performance studies, the highest efficiencies were reached with the TiO_2 (both commercial and produced TiO_2 obtained 100 % efficiency) compared to ZnO nanoparticles (up to 70 % efficiency).

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SOLID-PHASE EXTRACTION OF NEONICOTINOIDS RESIDUE FROM WATER: COMPARISON BETWEEN EXTRACTION CARTRIDGES

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Abstract: *The Commission Implementing Decision (EU) 2018/840 established the watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC and Commission Implementing Decision (EU) 2015/495. This Decision establishes additional substances and their maximum acceptable method detection limits including neonicotinoids (9-500 ng/L). During the pesticides extraction from water, the solid-phase extraction (SPE) column was used. Bakerbond spe™ SDB-1 SPE and Bond Elut Plexa were evaluated for the SPE of neonicotinoids (imidacloprid, thiamethoxam, acetamiprid, thiacloprid and clothianidin) from water. The comparation of the results of these two types of columns, was performed by spiking water samples at two levels (0.05 and 0.1 μg/L) in three replicates. The Bakerbond™ column quantitatively adsorbed these pesticides, with the obtained recoveries: 36.9 % for imidacloprid, 43.2 % for thiacloprid, 119.3 % for clothianidin, 64.6 % for acetamiprid and 53.6 % for thiamethoxam. Using Bond Elut Plexa the obtained recoveries were 66.9 % for imidacloprid, 72.9% for thiacloprid, 103.4 % for clothianidin, 67.4 % for acetamiprid and 45.2% for thiamethoxam. Both colums have low recovery values for thiametoxam, while the highest values were obtained by Bond Elut Plexa for thiacloprid, imidacloprid and acetamiprid. Great recoveries were achieved for clothianidin using both SPE columns.*
Keywords: *neonicotinoids, SPE extraction, water, LC-MS/MS.*

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Original scientific paper

1. INTRODUCTION

Water is one of the essential resources for life and its multiple uses are indispensable for a series of activities, such as agriculture, generation of energy, public and industrial supply, among others (Stojanović et al. 2017). Water covers about 70 % of the earth, but only 3 % of the world's water is fresh and twothirds of that amount is tucked away in frozen glaciers or otherwise unavailable for our use (Lomsadze et al. 2018). The problem of watercourses pollution has become the main topic of discussion among numerous scientists and experts in the field of environmental protection. Unfortunately, this problem was observed relatively late (at the end of the 1980s), after the chemicals in water caused the disappearance of many aquatic organisms. Particular attention is paid to pesticides that can migrate to surface and groundwater after the application to plants or soil (Ismail et al. 2012). Very often, agricultural producers, after finishing spraying, throw away empty containers into the local channels or leave them near the field, which is another source of pollution (Bursić et al. 2013). Although pesticides are considered to be extremely toxic substances in the environment, there is very little information about their distribution and use in Serbia (Antić et al. 2013).

Neonicotinoids are nowadays the most widely used insecticides in the world and include imidacloprid, thiamethoxam, acetamiprid, thiacloprid and clothianidin, as well as a metabolite 6-chloro nicotinic acid (Bursić et al. 2016). Despite these potential advantages, nowadays, the use of neonicotinoids is a matter of concern due to their high mobility in plants and environmental matrices, having been detected in the surface water samples, obtained in the vicinity of agricultural areas, from different regions of the planet (Casadol et al. 2016). Apart from their direct impact in honey production, their toxicity for bees presents a threat for the biodiversity of ecosystems. Commission Implementing Decision (EU) (2018) 2018/840 of 5 June 2018 established a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495. This Decision establishes additional substances and their maximum acceptable method detection limits like oxadiazon (8.8 ng/L), methiocarb (10 ng/L) and neonicotinoids (9-500 ng/L).

Among the different pre-treatment approaches, SPE (solid-phase extraction) offers a good compromise between robustness, rapidity, convenience, clean-up efficiency, scope for automation and solvent consumption

and is, therefore, ideally suited to routine analysis (Xie et al. 2011). SPE columns, mostly OASIS HLB cartridges, are widely used for neonicotinoids residue analysis for different samples such as vegetable and fruits (Obana et al. 2003; Xie et al. 2011), cottonseed cake (Mohan et al. 2010) and wine (Rodriguez-Cabo et al. 2016).

The low maximum residue limits (MRLs) have fostered the development of more powerful sensitive analytical methods to meet the requirements in the complex samples, such as food, water and soil. In this sense, liquid chromatography–tandem mass spectrometry (LC–MS/MS) with triple quadrupole in multiple reaction monitoring (MRM) mode has become so far, the most widely used technique for the quantitation of neonicotinoid insecticides in different matrices as reported extensively in the literature.

During the imidacloprid, thiamethoxam, acetamiprid, thiacloprid and clothianidin (**Figure 1**) extractions from water, the SPE column was used. This study reports the comparison between extraction cartridges: Bakerbond spe™ SDB-1 Solid Phase Extraction Columns (J.T. Baker™, USA) and Bond Elut Plexa (Agilent Technologies, USA) in the terms of neonicotinoid insecticide recoveries from water using LC-MS/MS.

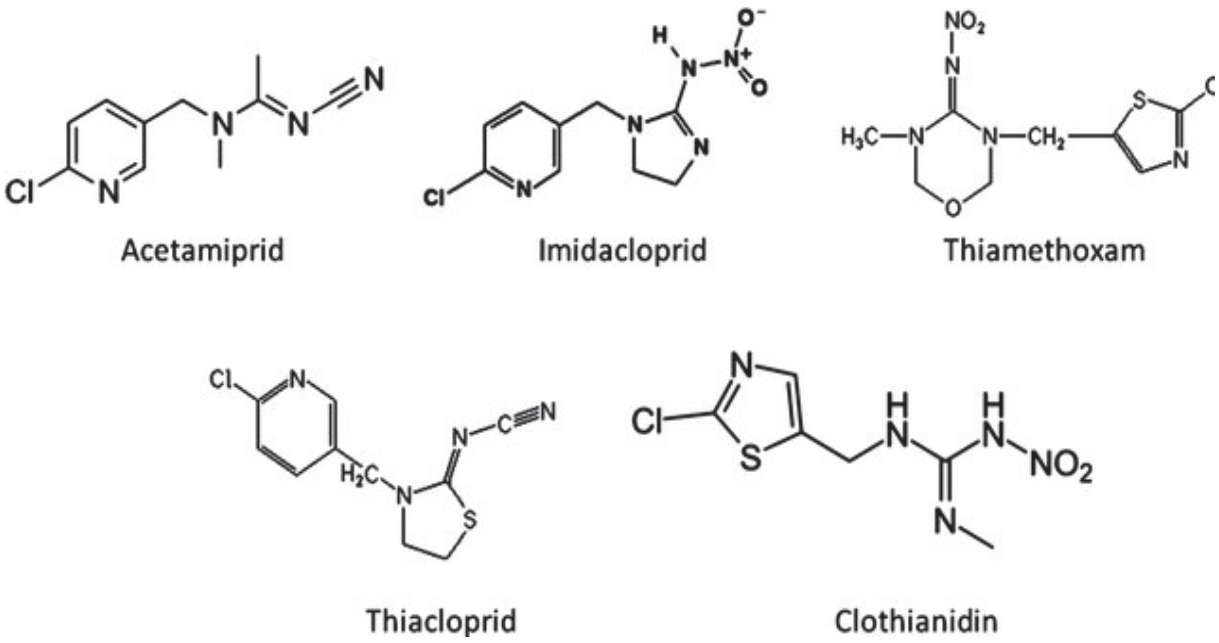

Figure 1. *Chemical structures of five neonicotinoid pesticides (Ghanim & Ishaaya 2011)*

2. MATERIALS AND METHODS

2.1. Standards, solvents and sorbents

HPLC grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Formic acid (purity 98 %, *w/w*) was from Sigma–Aldrich (Steinheim, Germany). The water used was purified with a Milli-Q water purification system from Millipore (Bedford, MA, USA). Cartridges used for solid-phase extraction were Bakerbond spe™ SDB-1 Solid Phase Extraction Columns (200 mg, 6 mL - J.T. Baker™, USA) and Bond Elut Plexa (60 mg, 3 mL - Agilent Technologies, USA). PTFE syringe filter (Millex LCR, Millipore, Milford, MA, USA).

Individual standard pesticide stock solutions (≈0.50 mg/mL) were prepared in methanol and stored at −20 °C. Working standard (multi component solution – 10 µg/mL) was prepared by diluting stock solution with the chromatographic mobile phase (acetonitrile/water (0.1 % formic acid) 30:70, v/v) and was used for spiking tap water samples.

2.2. Spiking samples

The recoveries were done at two concentration levels (0.05 and 0.1 µg/L) in three replicates. The method precision is expressed as the repeatability (RSD %) based on the recovery experiments (SANTE/11813/2017).

2.3. Solid-phase extraction

Before the use, the activation Bakerbond spe™ SDB-1 and Bond Elut Plexa were conditioned with 5 mL of methanol and 5 mL of deionized water. The samples were percolated through the cartridges and left to flow through

under the action of gravity. The cartridges were eluted with 5 mL of methanol and the eluate was evaporated to dryness on a steam of nitrogen. The dried extract was reconstituted in 0.2 mL of mobile phase, vortex mixed for 60 s. The final solution was filtered through a 0.22 μm PTFE syringe filter and injected in LC–MS/MS.

2.4. LC-MS/MS conditions

An Agilent series 1200 HPLC system (Agilent Technologies) equipped with a G1312B binary pump, a G1367D auto sampler, a G1379B degasser, a G1316B column compartment thermostat, The HPLC system was coupled to an Agilent triple quadrupole mass spectrometer (6410B) coupled to an electrospray ionization source (ESI+). A Zorbax XDB C18 column (50x4.6 mm, 1.8 μm particle size) from Agilent (San Jose, CA, USA) was employed for the separation. The chromatographic determination of neonicotinoids was carried out employing a binary mobile phase with methanol (0.1 % HCOOH, v/v - A) and an aqueous solution of formic acid (0.1 %, v/v - B). A gradient elution started at 60 % of B at the flow rate of 0.4 mL/min. This composition was reduced to 30 % B in 10 min, and held for 5 min. The system was equilibrated during 5 min. The injection volume was 5 μL and column temperature was kept at 30 ºC. The ESI source values were as follows: drying gas (nitrogen) temperature 350 °C, drying gas flow rate 10 L/min, nebulizer pressure 40 psi and capillary voltage 4000 V. The detection was performed using the multiple reactions monitoring mode (MRM). The Agilent MassHunter software (version B.06.00 Agilent Tehnologies, 2012) was used for the optimization and quantification.

3. RESULTS AND DISCUSSION

The LC-MS/MS (ESI+) fragmentation of the protonated molecular ions of the investigated neonicotinoid insecticides, which yielded two product ions, respectively given in **Table 1**.

Table 1. MRM transitions, fragmentation (FRAG), colision energies (CE) and retention times (t_R)

PESTICIDE	MW	TRANSITION (m/z)	CE (V)	FRAG (V)	t_R (min)
Acetamiprid	222.67	223.1→55.7 223.1→125.8	15 20	100	16.288
Imidacloprid	255.66	256.0→174.6 256.0→208.7	20 15	100	9.176
Clothianidin	249.68	250.0→132.1 250.0→169.1	15 10	90	12.696
Thiamethoxam	291.71	292.0→181.0 292.0→211.0	20 10	80	7.179
Thiacloprid	252.72	253.0→126.0 253.0→186.0	20 10	110	19.240

*MW-molecular weight

The average recoveries were calculated from the gained recovery values of spiking water samples at concentrations of 0.05 and 0.1 μg/L, in three replicates. Compared average recoveries using Plexa and JBT columns are given in **Table 2**, while the graphic recovery comparison of investigated neonicotinoids is shown in **Figure 2**.

Table 2. Obtained average recovery

	THIAMETHOXAM		CLOTHIANIDIN		THIACLOPRID		IMIDACLOPRID		ACETAMIPRID	
	Plexa	JTB	Plexa	JTB	Plexa	JTB	Plexa	JTB	Plexa	JTB
Average recovery, %	45.2	53.6	103.4	119.3	72.9	43.2	66.9	36.9	64.3	66.9
SDEV	1.28	8.09	18.74	14.08	7.91	4.23	13.82	20.34	3.94	1.67
RSD, %	2.84	15.07	18.12	11.81	10.84	9.79	20.64	55.11	6.12	2.49

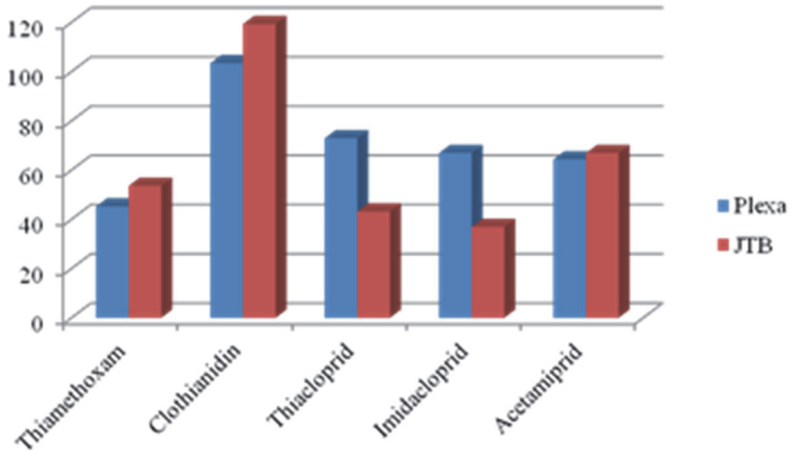

Figure 2. Graphic comparison of obtained average recovery

The LC-MS/MS total ion chromatogram (TIC) from a blank water sample spiked with all the analytes at the contrentation level of 0.1 μg/L is shown in **Figure 3**. The retention times of the investigated neonicotinoide pesticides are given in Table 1. First peak at 7.179 min was the peak of thiamethoxam, followed by imidacloprid, clothianidin, acetamiprid and thiacloprid.

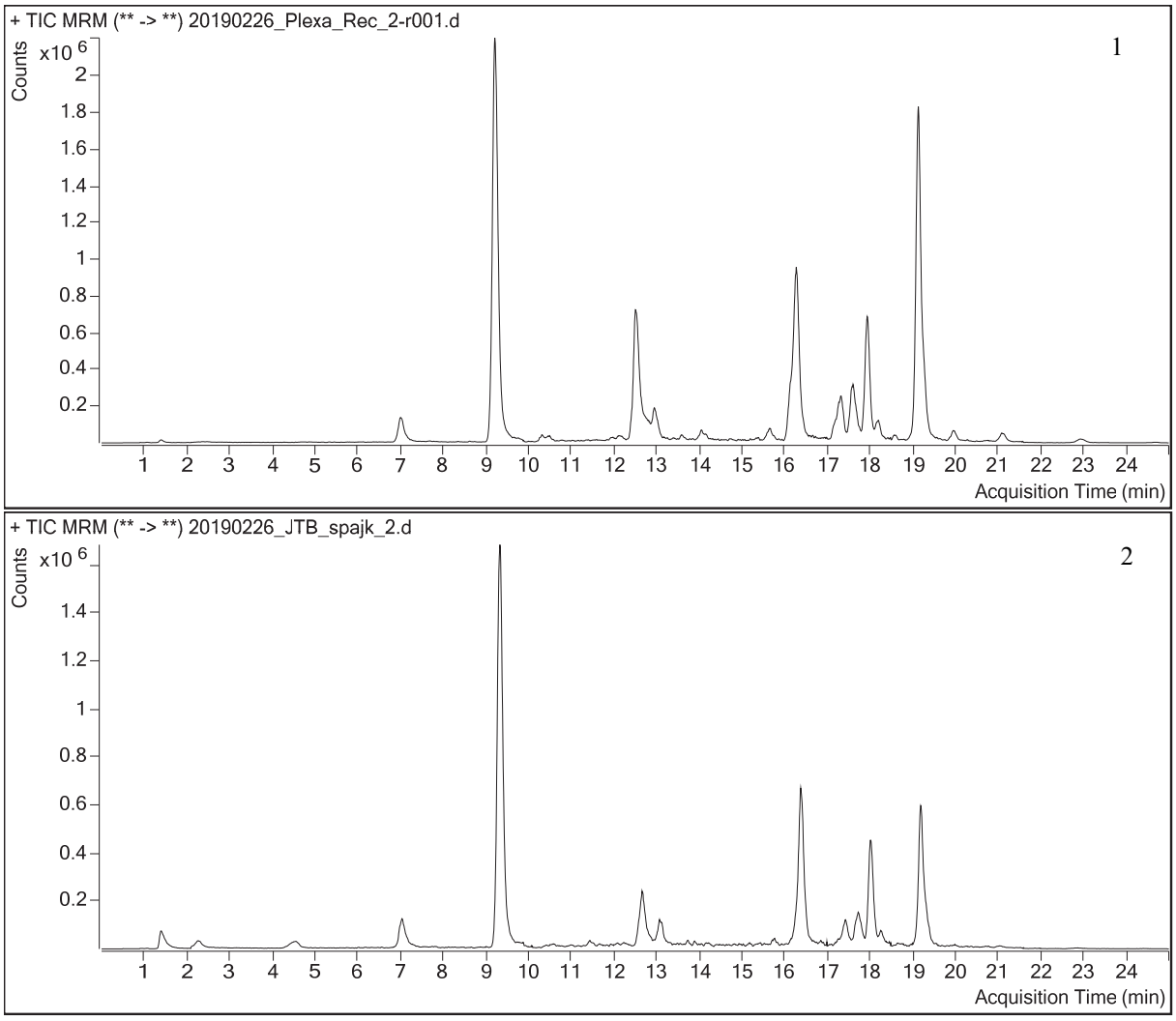

Figure 3. TIC chromatogram of spiking sample obtained by Plexa (1) and JBT column (2)

In order to statistically compare the two types of columns, the null hypothesis is defined, which implies that there are no significant differences in the means of each sample. The hypothesis was tested using t-test: Two-Sample Assuming Equal Variances and F-test Two-Sample for Variances, and the results are presented in **Table 3**. The significant differences in the precision of the results for two data sets were detected only for imidacloprid, so the null hypothesis was accepted in this case. The performances of the tested column types demonstrated significant differences in the results accuracy for thiacloprid (T-test) and the precision of the results for imidacloprid (F-test).

Table 3. The results of T- and F-test

	THIAMETHOXAM	CLOTHIANIDIN	THIACLOPRID	IMIDACLOPRID	ACETAMIPRID
F	0.025	1.77	3.50	0.46	5.58
F Critical	0.157	6.39	9.12	0.11	9.28
F<Fcrit.	Yes[1]	Yes	Yes	No[3]	Yes
t Stat	-2.30	-1.52	6.74	2.44	0.09
t Critical two-tail	2.31	2.31	2.36	2.57	2.36
$t_{stat.}<t_{crit.}$	Yes	Yes	No[2]	Yes	Yes

[1] Since the p – value is less than our alpha (0.05). the null hypothesis that there are no significant differences in each sample means is rejected

[2] Significant difference in the accuracy results for two data sets

[3] Significant difference in the precision of the results for two data sets

4. CONCLUSION

The comparison of the results of Bakerbond™ column with styrene-divinylbenzene (SDB) copolymer/ 6 mL capacity, 200 mg bed weight and Bond Elut Plexa (60 mg, 3 mL) with unique polymeric architecture, a no retentive, hydroxylated, amide-free surface, and a nonpolar PS-DVB core for retaining small molecules column types was performed by spiking water samples at two levels (0.05 and 0.1 μg/L) in three replicates. The obtained statistical data using t- and F-test, indicate the presence of the significant differences in the results for two data sets in the results accuracy for thiacloprid and the precision of the results for imidacloprid (T-test and F-test, respectively).

5. ACKNOWLEDGMENTS

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Laboratorijska djelatnost kao jedna od vodećih na tržištu laboratorijskih usluga u Republici Hrvatskoj djeluje više od 25 godina, dok je nagli razvoj započeo 2005. g. dobivanjem prve potvrde o akreditaciji prema međunarodnoj normi HRN EN ISO/IEC 17025. Od tada se područje akreditacije svake godine kontinuirano proširuje novim metodama ispitivanja, te je više od 180 metoda ispitivanja akreditirano prema novom izdanju norme HRN EN ISO/IEC 17025 iz 2017. g. U Laboratoriju za ekologiju ispituju se svi tipovi voda, različite vrste otpada (uključujući i kruta oporabljena goriva), tla, mulja, sedimenta i naftnih proizvoda prema važećim zakonskim propisima. Uzorkovanje obavljaju tehničari na cijelom području Hrvatske, kao i u drugim zemljama.

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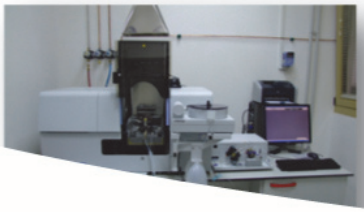
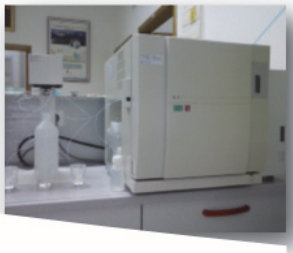




SVEUČILIŠTE U ZAGREBU
GEOTEHNIČKI FAKULTET
Hallerova aleja 7, 42 000 VARAŽDIN
tel.: 042 / 408 – 900
fax: 042 / 313 – 587
M.B. 03042316

GEOTEHNIČKI FAKULTET
Zavod za hidrotehniku
Laboratorij za geokemiju okoliša
tel.: 042 / 408 – 937
fax: 042 / 313 – 587

LABORATORIJ ZA GEOKEMIJU OKOLIŠA

- osnovan je 2006. godine sa znanstvenom, stručnom i obrazovnom svrhom
- opremljen instrumentima i pratećom opremom za prikupljanje uzoraka tala, sedimenata, prirodnih i otpadnih voda
- vrši terenske i laboratorijske analize prikupljenih uzoraka
- obavlja usluge agrokemijskih analiza tla za poljoprivrednike na temelju kojih se daje preporuka za gnojidbu

Zavod za hidrotehniku

LABORATORIJ ZA GEOKEMIJU OKOLIŠA

Tel.: 042 / 408 – 937
Fax: 042 / 313 – 587
E-mail: lgo@gfv.unizg.hr

LABORATORIJ ZA GEOKEMIJU OKOLIŠA

Laboratorij za geokemiju okoliša osnovan je u sklopu Zavoda za hidrotehniku Geotehničkog fakulteta u Varaždinu. Laboratorij sudjeluje u izvođenju praktične nastave iz kolegija preddiplomskog i diplomskog studija te Združenog međunarodnog doktorskog studija kao i u znanstvenim te stručnim projektima. Na taj način ispunjava svoju obrazovnu, znanstvenu i stručnu svrhu. Smješten je na 100 m² prostora i opremljen modernom opremom za provedbu geokemijskih terenskih i laboratorijskih ispitivanja, što uključuje prikupljanje uzoraka tla, sedimenata i vode. U laboratoriju se obavljaju i usluge agrokemijskih analiza tla.

Pokazatelji koje mjerimo u uzorcima voda, eluata tala i sedimenata:

~ atomskom apsorpcijskom spektrometrijom: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sr, Ti, V, Zn
~ amonijak, nitriti, nitrati, ukupni dušik
~ bromidi, fenoli, fluoridi, fosfati, jodidi, kloridi
~ silikati, sulfidi, sulfati, sulfiti
~ suspendirana tvar, mutnoća, KPK
~ alkalitet, ukupna tvrdoća, karbonatna tvrdoća, nekarbonatna tvrdoća, kalcijeva tvrdoća, magnezijeva tvrdoća
~ slobodni CO_2, koncentracija otopljenog kisika i zasićenost kisikom
~ pH, električna vodljivost, ukupna otopljena tvar – TDS
~ trasiranje podzemnih tokova (koncentracija natrijevog fluoresceina)
~ ukupni organski ugljik i ukupni dušik – TOC/DOC/TN
~ razaranje tla zlatotopkom
~ ekstrakcija izmjenjivih kationa iz tla amonijevim acetatom i kalijevim kloridom

Provođenje agrokemijskih analiza tla u svrhu modernizacije poljoprivredne proizvodnje, racionalizacije gnojidbe, povećanja prinosa i zaštite prirodnih resursa.

Ispitivanje fizikalnih i kemijskih svojstava prirodnih i otpadnih voda.

Određivanje pH, pKCl, ukupnog $CaCO_3$, NO_3^-, NO_2^-, NH_4^+, fosfora i kalija, humusa, teških metala i drugih kemijskih svojstava tla.

Ispitivanje sastava eluata otpada.

Kontakti: izv.prof.dr.sc. Anita Ptiček Siročić
voditeljica laboratorija
tel: 042 / 408 – 957
e-mail: anita.pticek.sirocic@gfv.unizg.hr

dr.sc. Dragana Dogančić
stručna suradnica
tel: 042 / 408 – 956 ili 042 / 408—937
e-mail: ddogan@gfv.unizg.hr

Saša Zavrtnik, dr.med.vet.
laborant
tel: 042 / 408—937
e-mail: lgo@gfv.unizg.hr

SVEUČILIŠTE U ZAGREBU GEOTEHNIČKI FAKULTET
Hallerova aleja 7, 42 000 Varaždin

GEOTEHNIČKI LABORATORIJ

Tel: 042/408 909, 408 938 Fax: 042/313 587 E-mail: geolab@gfv.hr

LABORATORIJSKA ISPITIVANJA OPĆENITO

- Oformljen 1974. god. u sastavu tadašnje Više geotehničke škole
- Godine 2006. potpuno obnovljen, moderniziran i proširen
- Član udruge Hrvatski laboratoriji CROLAB
- Akreditiran od HAA prema normi HRN EN ISO/IEC 17025

Sudjeluje u
- Znanstvenim projektima čiji su nositelji djelatnici Geotehničkog fakulteta
- Stručnim i gospodarskim projektima iz područja geoinženjerstva, inženjerstva okoliša i graditeljstva

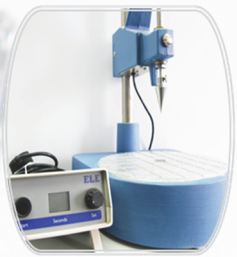
- Opremljen za provođenje svih standardnih geomehaničkih ispitivanja tla prema zahtjevima nacionalnih i svjetskih normi
- Raspolaže s modernom opremom za znanstvena istraživanja iz područja mehanike tla
- Razvija vlastite uređaje za specijalna ispitivanja

Opća fizikalna svojstva tla

- vlažnost
- gustoća ; vlažna, suha, najmanja, najveća, čvrstih čestica tla
- relativna zbijenost nekoherentnog tla
- poroznost
- zasićenost vodom

2. Klasifikacijski testovi

- Atterberg-ove granice koherentnog tla: tečenja, plastičnosti, stezanja
- granulometrijski sastav: metoda sijanja, metoda areometriranja



3. Čvrstoća tla

- aksijalna čvrstoća sa slobodnim bočnim širenjem
- posmična čvrstoća; izravni posmik: UU, CD, reversni, po metodi Krey-Tiedemann
- troosni posmik: UU, CIU, CID
- nedrenirana čvrstoća: krilnom sondom, konusnim penetrometrom

4. Deformabilnost tla

ispitivanja u:
- standardnom edometarskom uređaju
- hidrauličkom edometarskom uređaju s mjerenjem pornog tlaka
- hidrauličkom edometarskom uređaju s ćelijom promjera 50 cm
- troosnom uređaju s dirigiranim odnosima vertikalnih i horizontalnih deformacija ili opterećenja

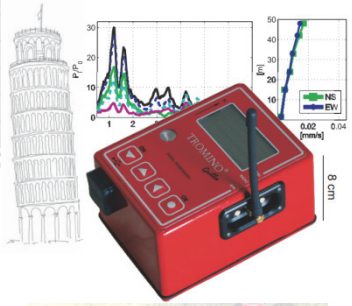
5. Posebna svojstva tla

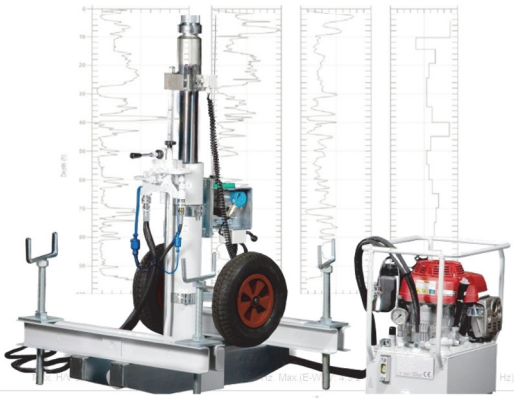
- koeficijent hidrauličke vodljivosti (vodopropusnost) u ćelijama tipa FH i CH
- optimalna vlažnost prema standardnoj ili modificiranoj energiji zbijanja
- sadržaj organskih i gorivih tvari
- sadržaj kalcij-karbonata
- kut trenja suhog, rahlo nasipanog tla
- pH vrijednost

Sveučilište u Zagrebu
GEOTEHNIČKI FAKULTET

ZAVOD ZA GEOTEHNIKU

GEOFIZIČKO-GEOTEHNIČKI ISTRAŽNI RADOVI





GEOFIZIČKI ISTRAŽNI RADOVI

- Geoelektrična istraživanja (sondiranje, profiliranje, tomografija)
- Seizmička refrakcija (P i S valovi)
- Višekanalna analiza površinskih valova (MASW)
- Seizmička karotaža
- Seizmički efekti miniranja
- Mikrotremor
- Georadar

GEOTEHNIČKI ISTRAŽNI RADOVI

- Istražno bušenje u svim vrstama tla i stijena
- Statički penetracijski test (CPT, CPTU, SCPT)
- Standardni penetracijski test (SPT)
- Bušenje, ugradnja i pokusno crpljenje zdenaca i piezometara
- Izrada geotehničke dokumentacije (izvješća, elaborati, projekti)
- Geotehnički nadzor i savjetovanje

Varaždin, Hallerova aleja 7, Tel: + 385 (0) 42 408 900, Faks: + 385 (0) 42 313 587
E-mail: ured.dekana@gfv.unizg.hr, www.gfv.unizg.hr

BESTSDI Project Objectives

The wider objectives of the BESTSDI project is to improve the quality of higher education in Geographical Science and Technology field, SDI and geodesy, enhance its relevance for the labour market and society and to improve the level of competences and skills in HEI's by developing new and innovative education programmes within the field of SDI. These wider objectives are fully compliant with the priorities of the Capacity Building projects within the Erasmus+ program.The specific project objectives are to develop, test and adapt new curricula, courses, learning

BESTSDI Expected Results

To develop appropriate curricula, courses and their content for both target groups (SDI providers and SDI users) of academic institutions. This includes the development of:

- SDI compulsory course for undergraduate study programs in geodesy
- SDI modules for graduate study programs in geodesy and geoinformatics
- SDI user course components for undergraduate study programs of partner faculties
- SDI elective courses for graduate study program of partner faculties (SDI users)
- Development of sustainable training courses (life-long education) of broad scope of professionals.

Additional benefits:

- New level of communication and cooperation among the partner universities with the emphasis on SDI but expanding it on institutional and project cooperation.
- Exchange of students and staff will be fostered through the project activities and information about activities conducted by the partners communicated among the partner universities.

BESTSDI Partners

Coordinator: **University of Zagreb, Faculty of Geodesy, Croatia**
Partner: **University of Zagreb, Faculty of Geotechnical Engineering, Croatia**

Other Partners:

Katholieke Universiteit Leuven (Catholic University of Leuven), Belgium
Sveučilište u Splitu (University of Split), Croatia
Univerzitet "Sv. Kiril i Metodij" Skopje (Ss. Cyril and Methodius University in Skopje), Macedonia
Hochschule Bochum (Bochum University of Applied Sciences), Germany
Universiteti Politekniki i Tiranës (Polytechnic University of Tirana), Albania
Universiteti Bujqesor i Tiranes (Agricultural University of Tirana), Albania
Univerzitet u Banjoj Luci (University of Banja Luka), Bosnia and Herzegovina
Sveučilište u Mostaru (University of Mostar), Bosnia and Herzegovina
Univerzitet u Sarajevu (University of Sarajevo), Bosnia and Herzegovina
Javna Ustanova Univerzitet u Tuzli Universitas Studiorum Tuzla (University of Tuzla), Bosnia and Herzegovina
Universiteti Nderkombetar per Biznes dhe Tehknologji UBT (University for Business and Technology), Kosovo
Javna ustanova Univerzitet Crne Gore Podgorica (University of Montenegro), Montenegro
Unvierzitet u Beogradu (University of Belgrade), Serbia
Univerzitet u Novom Sadu (University of Novi Sad), Serbia
Universiteti "Ukshin Hoti" ne Prizren (University of "Ukshin Hoti" in Prizren), Kosovo

Associated Partners:

Republic Administration for Geodetic and Property Affairs of Republika Srpska, BiH
Federal Administration for Geodetic and Property Affairs of Federation of Bosnia and Herzegovina, BiH
Agency for Real Estate Cadastre, Macedonia

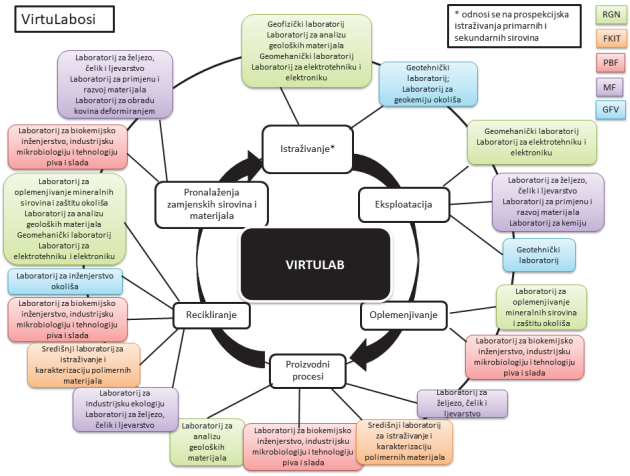
Subcontractors:

Lantmäteriet (Swedish National Mapping and Cadastre Authority), Sweden
Novogit AB, Sweden

PROJEKT VIRTULAB - INTEGRIRANI LABORATORIJ ZA PRIMARNE I SEKUNDARNE SIROVINE

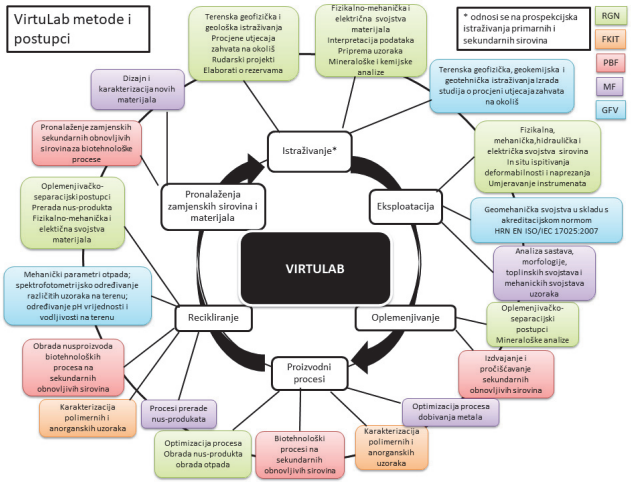
A great step forward was made in the preparation for the realization of the VIRTULAB project, whose goal is to strengthen the scientfic and exploratory capacity of fifteen labs of the five Faculties at the University of Zagreb. The Ministry of Science, Education and Sports recognized this project as strategic for the Republic of Croatia and thus it was place on the Ministry's indicative list. The intention is to begin the setting up of the University exploratory center for primary and secondary raw materials in the next period.

Projektom će se ulagati u opremanje laboratorija na pet fakulteta Sveučilišta u Zagrebu (Rudarsko-geološko-naftni fakultet - RGN, Fakultet kemijskog inženjerstva i tehnologije - FKIT, Metalurški fakultet - MF, Prehrambeno-biotehnološki fakultet - PBF i Geotehnički fakultet - GFV), s ciljem jačanja njihovih znanstveno-istraživačkih kapaciteta i uspostave virtualnog istraživačkog centra za primarne i sekundarne sirovine koji će omogućiti višu kvalitetu izvođenja nastave, ojačat će znanstvenoistraživački rad na fakultetima, omogućit će im ravnopravno sudjelovanje u KIC inicijativi, a istovremeno će stvoriti prostor za komercijalizaciju rezultata znanstvenih istraživanja i praktičnu primjenu inovacija u gospodarstvu. Projektni partneri nastavit će rad s korisnicima usluga u gospodarstvu, a istovremeno će nastojati proširiti postojeću suradnju.



Grafički prikaz VIRTULAB-a nakon integracije pet fakulteta – VirtuLabosi

Grafički prikaz VIRTULAB-a nakon integracije pet fakulteta – metode i postupci



Ključni problem koji se rješava provedbom projekta VIRTULAB jest to što ne postoji sveučilišni znanstveno-istraživački centar za primarne i sekundarne sirovine zbog slabih i nedostatnih nastavnih i znanstveno-istraživačkih kapaciteta pet sastavnica Sveučilišta u Zagrebu zbog čega se sektor nalazi na razini koja ne zadovoljava EU i svjetske standarde te nema praktične primjene rezultata istraživanja u gospodarstvu.

Posebnost projekta „VIRTULAB – Integrirani laboratorij za primarne i sekundarne sirovine" jest njegova međunarodna komponenta, to jest sudjelovanje ovog projektnog konzorcija i njihovih industrijskih partnera u KIC (Knowledge Innovation Community) programu za mineralne sirovine, a koji je u nadležnosti Europskog instituta za tehnologiju te je osnovan potkraj 2014. godine.

KIC za mineralne sirovine (eng. raw materials) jest dugoročno integrirano partnerstvo više od 100 europskih organizacija iz znanstvenog i gospodarskog sektora koje s ciljem implementacije rezultata klasičnih R&D projekata prema tržištu. „Raw materials", odnosno mineralne sirovine su ne-energetske sirovine: metali, nemetali, kamen, drvo, biomasa i sekundarne sirovine (eng. reused).

Sveučilište u Zagrebu se priključilo konzorciju koji čine Austrija, Belgija, Danska, Estonija, Finska, Francuska, Grčka, Irska, Italija, Mađarska, Nizozemska, Njemačka, Poljska, Portugal, Rumunjska, Slovačka, Slovenija, Španjolska, Švedska i Velika Britanija. Glavni koordinator za područje istočne i jugoistočne Europe je Sveučilište u Leobenu (Montanuniversität Leoben), a koordinator za Sveučilište Zagrebu je Rudarsko-geološko-naftni fakultet.

Koordinator projekta na Geotehničkom fakultetu: izv. prof. dr. sc. Igor PETROVIĆ

Suradnici na projektu s Geotehničkog fakulteta:

- *Izv.prof.dr.sc. Nikola SAKAČ*
- *Izv.prof.dr.sc. Anita PTIČEK SIROČIĆ*
- *Doc.dr.sc. Ivana GRČIĆ*
- *Dr.sc. Vitomir PREMUR*
- *Damir ŠTUHEC, dipl.ing.geot.*
- *Nikola KANIŠKI, mag.ing.amb.*
- *Nikola HRNČIĆ, mag.ing.geoing*

Trajanje projekta: 18 mjeseci

Ukupna vrijednost projekta: 14.186.222,23 kuna

Ukupni prihvatljivi troškovi: 12.300.603,45 kuna

Iznos financiranja za Geotehnički fakultet: 1.035.042,83 kuna

SVEUČILIŠTE U ZAGREBU
GEOTEHNIČKI FAKULTET

RawMaterials
Connecting matters

USPOSTAVNI ISTRAŽIVAČKI PROJEKT

ISPITIVANJE I MODELIRANJE MEHANIČKOG PONAŠANJA BIOOSUŠENOG OTPADA KAO PREDUVJET ENERGETSKE OPORABE – WtE

TESTING AND MODELLING OF MECHANICAL BEHAVIOUR OF BIODRYED WASTE AS A WASTE-TO-ENERGY PREREQUISITE

Visit us on web page: http://wte.gfv.hr/index_en.html

Projekt je primarno orijentiran na detaljno eksperimentalno ispitivanje i numeričko modeliranje mehaničkog ponašanja bioosušenog otpada.

Biosušenje je varijacija aerobne razgradnje koja se primjenjuje za parcijalnu stabilizaciju komunalnog otpada.

Nakon biosušenja, otpad se upućuje u daljnju mehaničku rafinaciju gdje se izdvaja organski bogata sitnozrnata frakcija koja je pogodna za odlaganje na bioreaktorsko odlagalište.

Jednom odložena, ova se frakcija ponovno podvrgava postupku vlaženja, s ciljem intenziviranja procesa razgradnje i proizvodnje bioplina.

Proizvedeni bioplin potom se može iskoristiti za energetsku oporabu kroz proizvodnju toplinske i/ili električne energije.

Trenutno u Republici Hrvatskoj postoje dva funkcionalna MBO postrojenja s tehnološkim procesom obrade čiji je izlazni proizvod pogodan za odlaganje na bioreaktorsko odlagalište.

Pravilnik o načinima i uvjetima odlaganja otpada, kategorijama i uvjetima rada za odlagališta otpada (NN 114/15) prepoznaje bioreaktosko odlagalište kao odlagalište otpada za neopasni otpad - podkategorija 1.

Unatoč tome što su u RH bioreaktorska odlagališta dozvoljena i već postoje postrojenja čiji je izlazni produkt pogodan za energetsku oporabu, u RH trenutno ne postoji niti jedno bioreaktorsko odlagalište.

Trajanje projekta: 01.01.2018. – 31.12.2022.

Iznos financiranja: 920.000,00 kuna

Web stranica projekta: wte.gfv.hr

Hrvatska zaklada za znanost

Kao jedan od razloga ovakvoj situaciji svakako se može istaknuti nedovoljan broj eksperimentalnih podataka o geotehničkim parametrima sitnozrnate frakcije bioosušenog MBO otpada.

Drugi razlog je nedostatak prikladnog numeričkog modela za ovu vrstu otpada.

Uslijed ovih nedostataka projektiranje bioreaktorskog odlagališta nije moguće.

Stoga je glavni cilj novog istraživanja, na temelju utvrđenih eksperimentalnih podataka, razviti prikladan konstitutivni model za opisivanje 3-D stanja naprezanja i deformacija sitnozrnate frakcije bioosušenog otpada.

Razvijeni model tada bi se mogao koristiti za potrebe projektiranja bioreaktorskih odlagališta ne samo u RH već i u drugim zemljama regije kod kojih MBO tehnologija tek treba biti implementirana.

Stjecanjem ekspertize u provođenju pokusa i numeričkom modeliranju bioosušenog otpada na Geotehničkom fakultetu Sveučilišta u Zagrebu omogućit će se otvaranje specifičnog područja istraživanja, visoko komplementarnog s postojećim istraživačkim iskustvom u Hrvatskoj.

Rezultati ovog projekta dozvolit će racionalniji pristup u projektiranju odlagališta otpada.

Osim toga, rezultati pokusa će pružiti sveobuhvatan skup dobro kontroliranih, novih generičkih mjerila za računalnu validaciju različitih aspekata modeliranja MBO otpada te doprinijeti unaprjeđenju njegove prediktivne snage za potrebe projektiranja odlagališta otpada.

Cilj projekta je stvoriti specifičnu i dugoročnu istraživačku nišu za Eksperimentalni i numerički laboratorij na Geotehničkom fakultetu Sveučilišta u Zagrebu, u suradnji s centrom izvrsnosti u Austriji.

Spomenuta suradnja temelji se na višegodišnjoj ekspertizi u području numeričkog modeliranja profesora Ericha Bauera s Tehničkog sveučilišta u Graz-u.

Voditelj projekta: izv. prof. dr. sc. Igor PETROVIĆ, Geotehnički fakultet

Suradnici:

- *Erich BAUER, Dipl.-Ing. Dr.techn., habil., ao.Univ.-Prof., Institute of Applied Mechanics, Graz University of Technology, Austria*
- *Doc.dr.sc. Ivan HIP, Geotehnički fakultet*
- *Izv.prof.dr.sc. Anita PTIČEK SIROČIĆ, Geotehnički fakultet*
- *Doc.dr.sc. Boris KAVUR, Geotehnički fakultet*
- *Dr.sc. Marko PETRIC, Geotehnički fakultet*
- *Linke LI, Graz University of Technology, Austria*

Doktorandi zaposleni na projektu:

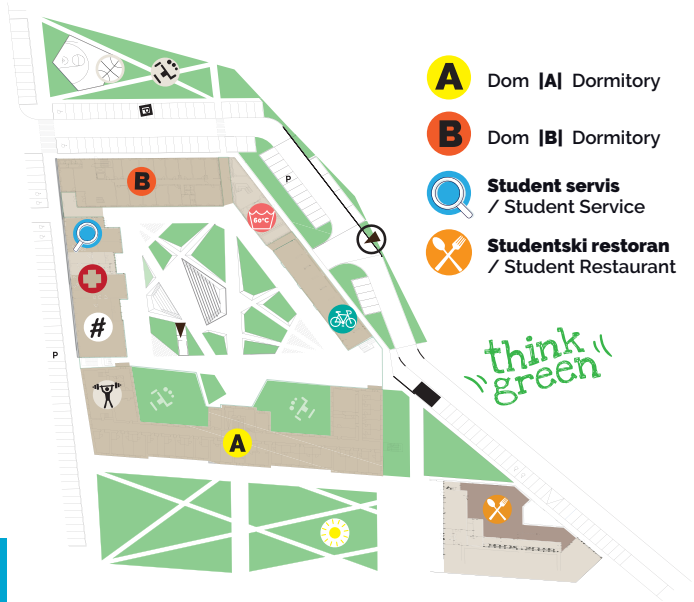
- *Nikola Kaniški, mag.ing.amb., Geotehnički fakultet*
- *Nikola Hrnčić, mag.ing.geoing., Geotehnički fakultet*

Sveučilište u Zagrebu
GEOTEHNIČKI FAKULTET

Sveučilište u Zagrebu • University of Zagreb

STUDENTSKI CENTAR VARAŽDIN

Student Centre Varaždin



- **A** Dom |A| Dormitory
- **B** Dom |B| Dormitory
- **Student servis** / Student Service
- **Studentski restoran** / Student Restaurant
- **Studentski klub** / Student Club
- **Studentska ambulanta** / Student Infirmary
- **Gym**
- **Praonica rublja** / Student Laundry Room
- **Spremište za bicikle** / Bicycle Storage
- **Sportsko igralište** / Sports Playground
- **Fitness park** / Fitness Park
- **Solarni park** / Solar Park
- **Ulaz u podemnu garažu** / Underground Garage Enterence

www.scvz.unizg.hr

scvarazdin

HDiG Hrvatsko društvo inženjera geotehnike

www.jobclub.uig.hr
projekti@uig.hr

JOB CLUB VARAŽDIN

Mlad si i nezaposlen?
Tražiš posao?

Posjeti našu web stranicu ili piši na naš e-mail
i saznaj kako ti možemo pomoći!

Sadržaj oglasa isključiva je odgovornost Hrvatskog društva inženjera geotehnike.

Projekt je sufinancirala Europska unija iz Europskog socijalnog fonda.

Student Council
Faculty of Geotechnical Engineering

- ✓ As the student representatives we promote student interests and take care of the student standard at the Faculty council.
- ✓ We take care on student rights, encourage students to be involved in international mobility, advise students in their needs, etc.

- ✓ We are participating in many projects; form student promotions, study promotions, to scientific and professional project with our professors.
- ✓ We are working on the networking of current students with former students and potential employers.
- ✓ Through various activities our goal is to be the leader of the student standard promotion in Varaždin.

✓ **Every student is important to us.**

CONTACT:
Email: studentski.zbor@gfv.unizg.hr

Studentski zbor
Geotehničkog fakulteta

KRITERIJI ZA UPIS

Lista poretka prijavljenih kandidata za upis sastavlja se prema sljedećem sustavu bodovanja:

a) Na temelju uspjeha u srednjoj školi = do 500 bodova

b) Na temelju položenih ispita na državnoj maturi
- matematika (osnovna razina) = do 500 bodova

c) Na temelju provjere posebnih sposobnosti = nema bodova

d) Temeljem dodatnih postignuća učenika = IZRAVAN UPIS (1000 bodova)
- osvojeno jedno od prva tri mjesta na državnim natjecanjima u RH iz matematike, fizike, kemije, biologije, informatike, astronomije, statistike ili tehničkih znanosti za vrijeme srednjoškolskog obrazovanja.

AKADEMSKI NAZIVI

Završetkom preddiplomskog studija Inženjerstvo okoliša stječe se 180 ECTS bodova te akademski naziv sveučilišni prvostupnik/prvostupnica inženjer/inženjerka Inženjerstva okoliša (univ.bacc.ing.amb.).

Završetkom diplomskog studija Inženjerstvo okoliša stječe se 120 ECTS bodova te akademski naziv magistar/magistra inženjer/inženjerka Inženjerstva okoliša (mag.ing.amb.).

Završetkom doktorskog studija Inženjerstvo okoliša stječe se 180 ECTS bodova te akademski naziv doktora znanosti (dr.sc.).

DODATNE INFORMACIJE

TAJNIŠTVO: pon-pet: 07:00 - 15:00
tel: 042/408-901
ured.tajnika@gfv.unizg.hr

REFERADA: pon-pet: 09:00 - 12:00
tel: 042/408-904
studentska.referada@gfv.unizg.hr

Točne datume upisa i ostale relevantne informacije možete potražiti na web stranicama fakulteta: www.gfv.unizg.hr

ADRESA: Geotehnički fakultet Sveučilišta u Zagrebu, Hallerova aleja 7, 42000 Varaždin

Studij inženjerstva okoliša – Geotehnički fakultet

inzenjerstvo_okolisa

STUDIJ INŽENJERSTVA OKOLIŠA

FAKULTET
KOJIM ĆEŠ
MIJENJATI SVIJET
NA
BOLJE

STUDIJ INŽENJERSTVA OKOLIŠA

Geotehnički fakultet Sveučilišta u Zagrebu

Opis zvanja - kompetencije i osposobljenost

Završetkom sveučilišnoga **preddiplomskog studija** na Geotehničkom fakultetu steći ćeš osnovne kompetencije u identificiranju, definiranju i rješavanju inženjerskih zadaća u Inženjerstvu okoliša.

Od praktičnih znanja kao prvostupnik Inženjerstva okoliša posjedovat ćeš sposobnost korištenja laboratorijske i terenske opreme, promatranja, bilježenja i analize podataka dobivenih laboratorijskim i terenskim ispitivanjima. Znat ćeš izraditi tehničke nacrte ručno i pomoću računala, te pripremiti prezentaciju tehničkih izvješća.

Znanja i kompetencije koja stekneš završetkom sveučilišnoga preddiplomskog studija odgovarajuća su za praćenje diplomskoga sveučilišnog programa na Geotehničkom fakultetu, a omogućavaju ti i praćenje diplomskih studija iz srodnih područja na drugim tehničkim studijima te praćenje različitih programa cjeloživotnog obrazovanja.

Diplomski studij Inženjerstvo okoliša traje dvije godine, a uključuje smjerove Geoinženjerstvo okoliša, Upravljanje vodama i Upravljanje okolišem. Ovaj studij mogu upisati studenti koji su završili sveučilišni preddiplomski studij ili strani studij ekvivalentnog programa.

Završetkom diplomskoga studija bit ćeš osposobljen upravljati okolišem na održiv način i preuzeti osobnu i timsku odgovornost za strateško odlučivanje i uspješnu provedbu zadataka pri izradi elaborata, studija i projekata iz inženjerstva okoliša, kao i primijeniti legislativu iz područja zaštite okoliša te preuzeti društvenu i etičku odgovornost za posljedice.

Doktorski studij Inženjerstvo okoliša traje tri godine, a njegovim završetkom stječu se kompetencije za provođenje samostalnog istraživačkog rada.

Mogućnost zaposlenja

Znanstvenu karijeru možeš nastaviti razvijati upisom na poslijedoktorski studij Inženjerstvo okoliša na našem Fakultetu. A ako si bio vrlo uspješan student, možda započneš svoju akademsku karijeru kao asistent na našem Fakultetu.

Izvan akademske ili znanstvene sredine, popis mogućih poslodavaca kod kojih se možeš zaposliti doista je raznolik. To su sve institucije državne i lokalne uprave, kao i svi gospodarski subjekti koji zapošljavaju osobe za obavljanje stručnih poslova zaštite okoliša, kao što su na primjer komunalna poduzeća, centri za gospodarenje otpadom, pročišćivači otpadnih voda, eksploatacijska polja. Nadalje, to su i svi oni gospodarski subjekti koji se bave obnovljivim izvorima energije te oni koji svojim proizvodnim procesom mogu naštetiti okolišu.

Ako želiš možeš postati i inspektor za zaštitu okoliša, a s ovim stručnim nazivom ti ni vrata Europske unije neće biti zatvorena.

Pogodnosti studiranja

Tijekom studiranja na našem Fakultetu kao student Sveučilišta u Zagrebu na raspolganju imaš razne pogodnosti. Detaljnije o pogodnostima možeš saznati u našem vodiču za brucoše:
http://www.gfv.hr/modules/m_gfv/datoteke/vodic_za_brucose_a5_final_v1.pdf

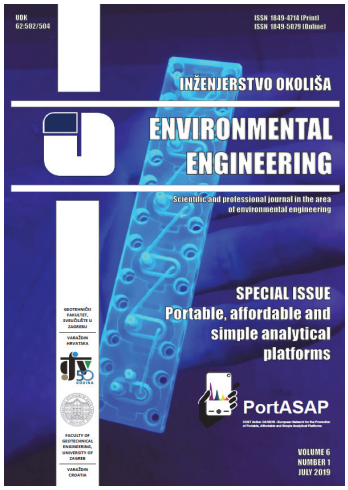
Znanost i suradnja s gospodarstvom

Na Geotehničkom fakultetu provode se i znanstvena istraživanja. Fakultet raspolaže akreditiranim geotehničkim laboratorijem, kao i laboratorijem za inženjerstvo okoliša, laboratorijem za geokemiju okoliša, informatičkim centrom za GIS. Primjereno smo opremljeni i za terenske istraživačke radove. Budući da istraživači koji ih provode sudjeluju i u izvođenju nastave, studentima se prenose najnovije spoznaje i rezultati istraživanja.

Velik doprinos nastavi i znanstvenom radu daje znanstvena i stručna suradnja Geotehničkog fakulteta sa srodnim visokoškolskim institucijama u Republici Hrvatskoj i svijetu. Usporedno s nastavom i znanstveno-istraživačkim radom, Fakultet održava i razvija i suradnju s gospodarstvom kroz izradu mnogobrojnih studija i projekata iz područja Inženjerstva okoliša.

PREVIOUS ISSUES

http://www.gfv.unizg.hr/hr/journalio_online_library.html



INSTRUCTIONS FOR AUTHORS

The journal „*ENVIRONMENTAL ENGINEERING-INŽENJERSTVO OKOLIŠA*“ publishes scientific and technical papers and other articles in the interdisciplinary area of environmental engineering. The scientific topics covered by the Journal include geo-engineering, water resources management, technical aspects of environmental protection and similar areas. The journal publishes papers in English. Papers are accepted for publication after they have received a positive review and are categorized as an original scientific paper, preliminary comunications, review paper or technical paper.

The journal is published biannually. There are no charges for printing the paper. As a rule, the length of the paper is not limited. However, it is recommended that it should not be longer than 15 single-spaced A4 pages, all figures included.

Figures are printed in greyscale, and authors should take it into account when preparing their manuscript. However, authors may, in agreement with the editorial board, prepare figures in colour when they deem it necessary for the understanding of what the figure shows. The figures in colour approved by the editorial board will not be additionally charged.

When a paper is submitted for review, this implies that the paper has not been previously published or that it is not being reviewed by another journal. The author is responsible for the content of the paper and for obtaining consent, where applicable, to publish particular data.

The first page should contain the title of the paper, the authors' names, the institution of employment, the authors' email addresses, the abstract and keywords. It is recommended that the title of the paper should be illustrative and clearly reflect the content of the paper. If the title contains local names, then a generally recognizable name in a wider region should be included. The abstract should not exceed 300 words, and there should be 4 to 6 keywords. If none of the authors has been specified as lead author, the editors will exclusively contact the first mentioned author.

Authors should submit their paper by e-mail to: **casopis@gfv.unizg.hr**. The paper should be prepared in Microsoft Word in A4 page format, with 25 mm margins and 1.5 line spacing, in one column aligned to both sides. The text should be written in 10 pt Times New Roman, and the pages should have automatic numbering in the bottom right corner. Depending on the content, the text should be divided into several sections whose headings are in 11 pt bold and aligned to the left. The paper should be written in the third person singular and has to be terminologically harmonized with legal regulations in force and the international system of units (SI). All equations have to be numbered; tables and figures should also be numbered with a heading and inserted in the appropriate place in the article. **For citation of equations, figures and table in text use bold font**. All figures (images, diagrams, photographs) have to be prepared for graphic reproduction at a minimum resolution of 300 dpi and submitted in a separate map.

When **citing papers in the text** with blue colour, only previously published papers should be mentioned. If authors consider it necessary, personal communication and unpublished papers may be cited in the paper, but in an appropriate manner, either as part of the text or in acknowledgements at the end of the paper. **References** include an alphabetical list of published papers that have been cited in the text. The **Harvard citation** and referencing style should be used**.**

If the paper is accepted for publication, the authors are obliged to harmonize the paper with the instructions given by the reviewers/editors. If the authors do not accept the reviewers'/editors' remarks or if they do not submit the corrected version of the paper within three months, the editorial board will deem that the authors have withdrawn their paper from the procedure and no longer wish to have it published.

Prior to its publication, the authors will receive the paper for inspection and final revision.

The paper which has been through all the phases of text preparation will first be published online, and then in the printed edition. Authors will receive a separate in pdf format as well as one copy of the journal in which the paper was published.