*Acta hydrotechnica* **26/44 (2013)**, Ljubljana
ISSN 1581-0267


UDK/*UDC*: 574.63:628.179.2
Prejeto/*Received:* 12. 2. 2013
Izvirni znanstveni članek – *Original scientific paper*
Sprejeto/*Accepted:* 19. 11.2013

# EFFECT OF ADVANCED OXIDATION PROCESSES (AOPS) ON THE BIODEGRADABILITY OF MUNICIPAL WASTEWATER FOR ITS REUSE IN THE TEXTILE INDUSTRY

# VPLIV NAPREDNIH OKSIDACIJSKIH PROCESOV (AOPS) NA BIORAZGRADLJIVOST KOMUNALNE ODPADNE VODE ZA NJENO PONOVNO UPORABO V TEKSTILNI INDUSTRIJI

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## Abstract

Reuse of treated municipal wastewater to supplement part of fresh water is becoming more and more important. However, treated water can contain some pollutants that cannot be successfully removed with classical biological wastewater treatment processes. Aim of the study presented was to assess whether advanced oxidation processes (AOPs) and special enzymes enhance biodegradation of municipal wastewater and if treated municipal wastewater can be reused in the production process of textile industry. To test biodegradability we used a small-scale pilot wastewater treatment plant (PWWTP) consisting of six parallel bioreactors with suspended activated sludge (CAS type). Bioreactors were supplied with untreated municipal wastewater, AOP-treated municipal wastewater and AOP-treated municipal wastewater with addition of special enzymes. The results showed that AOPs contributed to better biodegradation while enzymes did not. Municipal wastewater treated by a combination of AOP and biological treatment was not suitable for reuse in the dyeing process, but could potentially be reused in some other processes in the textile industry.

**Keywords:** advanced oxidation processes (AOPs), biological treatment, municipal wastewater, water reuse, textile industry.

## Izvleček

Ponovna uporaba očiščene komunalne odpadne vode namesto dela sveže vode postaja vedno bolj pomembna. Vendar pa lahko očiščena voda vsebuje nekatera onesnaževala, ki jih ne moremo uspešno odstraniti s klasičnimi postopki biološkega čiščenja odpadnih voda. Namen prestavljene raziskave je bil ugotoviti, če z naprednimi oksidacijskimi procesi (AOPs) in s posebnimi encimi lahko povečamo biorazgradljivost komunalne odpadne vode in če lahko tako očiščeno komunalno odpadno vodo ponovno uporabimo v proizvodnem procesu tekstilne industrije. Za test biorazgradljivosti smo uporabili laboratorijsko pilotno čistilno napravo (PWWTP), sestavljeno iz šestih paralelnih bioreaktorjev s suspendiranim aktivnim blatom (CAS tip). V bioreaktorje smo dovajali neočiščeno komunalno odpadno vodo, AOP-očiščeno

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komunalno odpadno vodo in AOP-očiščeno komunalno odpadno vodo z dodatkom encimov. Rezultati so pokazali, da so AOP-ji prispevali k boljši biorazgradljivosti, medtem ko encimi niso. Komunalna odpadna voda, očiščena s kombinacijo AOP in biološkega čiščenja, ni bila primerna za ponovno uporabo v procesu barvanja, je pa potencialno primerna za ponovno uporabo v katerem drugem procesu v okviru tekstilne industrije.

**Ključne besede:** napredni oksidacijski procesi (AOPs), biološko čiščenje, komunalna odpadna voda, ponovna uporaba vode, tekstilna industrija.

## 1. Introduction

Approaches that reduce fresh water consumption are becoming more important due to diminishing water resources and increasing cost of water. However, some industries (e.g. textile industry) still require high water consumption, in spite of significant progress in BAT (Best Available Techniques) made in recent years.

Today, reuse of treated municipal wastewater instead of only using fresh water is discussed to an increasing extent. This is especially true in arid or semiarid areas where potable water and irrigation water must be imported at great expense. There are, however, some perceived risks associated with reusing treated water regarding the potential presence of pathogens, trace organics, heavy metals, nutrients, endocrine-disrupting chemicals and pharmaceutically active compounds such as antibiotics (Watkinson et al., 2007). The currently applied wastewater treatment processes and technologies are inappropriate to significantly remove some of these pollutants. Furthermore, public desire for better water quality has promoted the implementation of much stricter regulations and therefore, a need for new treatment technologies (Zhou and Smith, 2002).

Biological treatment methods are considered to be environmentally friendly and cheaper compared to chemical ones (Harrelkas et al., 2008), but the complete removal of some components due to their high chemical stability and/or low biodegradability is questionable (van der Zee and Villaverde, 2005; Oller et al., 2011). Advanced oxidation processes (AOPs) such as ozone, UV radiation (UV) and hydrogen peroxide ($H_2O_2$) can degrade complex chemical structures to more easily degradable molecules by forming hydroxide radicals (García-Montaño et al., 2006), which are highly reactive and non-selective (Gogate and Pandit, 2004). AOPs can at least partially remove the non-biodegradable chemical oxygen demand (COD) fraction from the effluent (Arslan-Alaton et al., 2004). Therefore, the main role of the AOP pre-treatment is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates which can then be treated in a conventional and less expensive way, e.g. biological wastewater treatment plant (WWTP). During pre-treatment stage the percentage of mineralization is advised to be minimal to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. However, if the pre-treatment time is too short, the reaction intermediates generated could still be structurally very similar to the original non-biodegradable and/or toxic components (Oller et al., 2011). With combining different AOPs further cost cutting can be achieved.

Within the AOP4Water project (a multinational project funded under the CORNET programme), selected combinations of different AOPs were tested with the aim to enable cost-efficient reuse of AOP-treated municipal wastewater. Biodegradability trials were performed in order to investigate the suitability of AOP-pre-treated municipal wastewater for ultimate biological treatment. Special enzymes were added to achieve better biodegradation. Our aim was to establish what overall treatment efficiency can be achieved by a combination of AOP and biological treatment and if the treated municipal wastewater could be reused in the production process of textile industry (dyeing).

## 2. Materials and methods

### 2.1 Pilot wastewater treatment configuration

The pilot wastewater treatment plant (PWWTP) consisted of six activated sludge bioreactors made of Plexiglas. To reduce costs the bioreactors were designed to be as small as possible but with dimensions that enabled installation of equipment (aerators, pumps) and maintenance (cleaning, repair). Standard aquarium aerators, i.e. membrane pump with a porous stone (Crawfish 1800, Flamingo), were used as aerators and a standard aquarium centrifugal mixing pump (NJ400, New Jet) was adopted for sludge recycling and returning. Because of the pump dimensions and in order to allow maintenance, the total bioreactor volume was 4.7 L, of which the bioreactor wetted volume was 4.0 L. Figure 1 shows a three-dimensional schematic diagram of the bioreactor used and its layout during trials. Each bioreactor consisted of a selector, an anoxic chamber, an aerobic chamber, and a sedimentation chamber. The bioreactors were continuously supplied with municipal wastewater at a flow rate of 2.0 L per day, with a residence time of 48 h. This long residence time compared to the usual time of a few hours was selected in order to be able to prepare enough waste-water for the whole series of the reactors. Feeding mixture consisting of municipal wastewater and nutrients (for nutrients recipe see Table 1) was added into the 10 L plastic tanks next to the bioreactors and was continuously pumped to the bioreactors with pulse pumps (Mikro+polo).

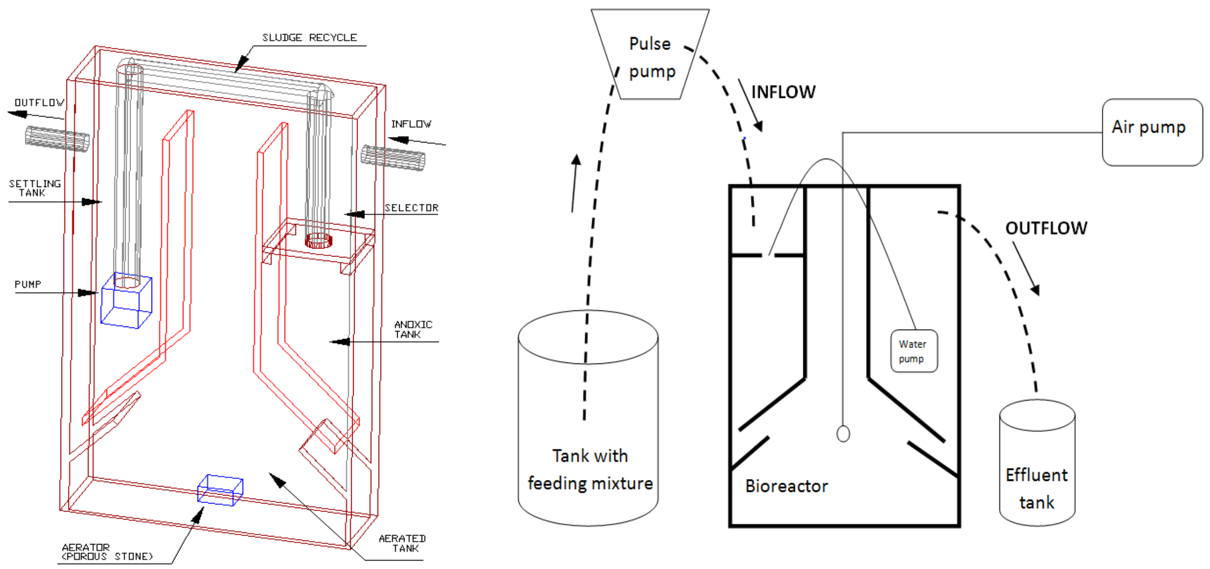


***Figure 1:*** *Left: three-dimensional schematic diagram of the bioreactor showing inflow, selector, anoxic/anaerobic tank, aerated tank, settler with sludge return to aerated tank, and sludge recycle. Right: layout of an individual bioreactor during trials showing tank with feeding mixture, pulse pumps, bioreactor, water pump, air pump and effluent tank. Arrows indicate the flow of the wastewater from the tank with feeding mixture through the bioreactor into the effluent tank.*

***Slika 1:*** *Levo: tridimenzionalni shematski prikaz bioreaktorja z dotokom, zbiralnikom, anoksično/anaerobno komoro, prezračevalno komoro, usedalnikom z vračanem blata v prezračevalno komoro in recikliranje blata. Desno: Postavitev posameznega bioreaktorja med poskusi prikazuje posodo s hranilno mešanico, pulzne črpalke, bioreaktor, vodne črpalke in posodo za iztok. Puščice kažejo tok odpadne vode iz posode s hranilno mešanico preko bioreaktorja v posodo za iztok.*

***Table 1:*** *Recipe for nutrients mixture added to the bioreactors.*

***Preglednica 1:*** *Recept za hranilno mešanico, ki smo jo dodajali v bioreaktorje.*

| Nutrient/Hranilo | Concentration/ Koncentracija |
|---|---|
| Meat extract (Sigma-Aldrich) | 0.108 g/L |
| Peptone (Sigma-Aldrich) | 0.108 g/L |
| Yeast extract (Sigma-Aldrich) | 0.108 g/L |
| NH4COOCH3(Merck) | 0.264 g/L |
| NH4Cl (Carlo Erba) | 0.033 g/L |
| K2HPO4(Carlo Erba) | 0.019 g/L |
| KH2PO4(Sigma-Aldrich) | 0.007 g/L |
| CaCO3(Sigma-Aldrich) | 0.083 g/L |
| MgCO3(Sigma-Aldrich) | 0.083 g/L |
| NaCl (Sigma-Aldrich) | 0.033 g/L |
| FeSO4 x 7H2O (Sigma-Aldrich) | 0.004 g/L |

Pulse pumps were set on a timer to maintain flow rate and ensure the appropriate residence time. Nutrients were added to maintain sufficient growth of microbial biomass and better treatment performance because the municipal wastewater used for trials was not heavily loaded (COD 75 mg/L, $BOD_5$ 44 mg/L). Due to relatively simple aquarium aerators we were not able to sufficiently regulate the oxygen concentration in the aerobic part of the bioreactors, which varied from 2.0 mg/L to 7.4 mg/L (average 5.96 mg/L) and in anoxic part of the bioreactors from 0.08 mg/L to 7.72 mg/L (average 2.48 mg/L). For PWWTP start-up we used activated sludge from a sequencing batch bioreactor (SBR). Sludge acclimation time was 45 days. During that time all bioreactors were fed with the same feeding mixture mentioned above. In Figure 2 the layout of the PWWTP is shown.

## 2.2 Biodegradability trials

Biodegradability trials were performed in the beginning of July 2012 at the Faculty of Civil and Geodetic Engineering, University of Ljubljana. Each trial was performed in two parallels. Municipal wastewater was collected from the inflow to the experimental SBR located at the premises of the Faculty where access to the municipal wastewater sewerage of the city of Ljubljana is enabled. The raw municipal wastewater was filtered with black ribbon filters (Sartorius-stedim, Grade 388, 10-15 µm, basis weight 84 g/m2) to remove solid compounds and then used as feed water to the PWWTP.

The PWWTP consisted of six parallel bioreactors. Two bioreactors, R1a and R1b, were fed with untreated municipal wastewater (except filtration), two bioreactors, R2a and R2b, were fed with AOP-treated municipal wastewater and two bioreactors, R3a and R3b, were fed with AOP-treated municipal wastewater with added commercially available enzyme product (Biocomplex 200, Eko Gea Ltd., www.ekogea.com) to enhance activated sludge performance. AOP treatment was a combination of ozonation and UV irradiation and was performed for 2 hours on the AOP treatment plant. Chosen combination of AOPs and duration of the treatment have proved to be the most effective in previous experiments (see Krivograd-Klemenčič et al., 2012).

The AOP treatment plant consists of a plastic wastewater tank, a water pump (Iwaki Magnet Pump, Iwaki co. LTD), an air pump (KNF Neuberger), an air dryer module (Lufttrockner module LTM 110-60, AquaCare), an $O_3$ generator (BasiTech III, AquaCare, 500 mg/h), an $O_3$ reactor (Ozonreaktor OZR 75, AquaCare), an $O_3$ analyser (BMT 964 C, BMT Messetechnik), a rotameter (GEMÜ 55/21/14), a benchtop meter (multi-parameter analyser C3040, Consort) and a UV lamp (Sterilight copper, Viqua, 12 W). The volume of the wastewater tank is 2.2 L while the total volume of the pilot plant is 4 L. $O_3$ is produced from dried air with maximum $O_3$ production of 500 mg/h and flow rate of the gas stream 60 L/h. In the $O_3$ reactor, the $O_3$-containing gas is led over a porous stone and rises through the water to be ozonised. Part of the $O_3$ contained in the gas diffuses into the water, is dissolved and reacts with the substances contained in the water. The system operates in a continuous mode with a flow rate of the water stream 60 L/h maintained with the rotameter, but the residence time was increased by returning the wastewater back to the beginning of the system. Consequently the system operates in a batch mode with the water being completely mixed.

Before adding AOP-treated wastewater into feeding tanks, water was stirred with a magnetic stirrer in order to remove the excess of ozone. Product with special enzymes was first activated in tap water and then added into AOP-treated water in 1:1.000.000 dilution (according to the manufacturer's instructions; personal communication). Duration of the treatment trials was five days.

### 2.3 Chemical analyses

During the trials effluents from bioreactors were collected in 3 L effluent tanks (Figure 1) for analyses of pH, electric conductivity (EC), chemical oxygen demand (COD), biochemical oxygen demand in five days ($BOD_5$), colour at 436 nm, 525 nm and 620 nm and total suspended solids (TSS). Chemical parameters were analysed every second day, taking into account the 48 h retention time. The listed chemical analyses were also performed on the feeding mixture as a control. At the end of each trial effluents from bioreactors were analysed for total dissolved solids (TDS), total hardness, sulphate ($SO_4$), chloride, iron (Fe), manganese (Mn), copper (Cu), nitrate ($NO_3$), nitrite ($NO_2$), alkalinity and turbidity (NTU) in order to determine if the treated municipal wastewater could be reused in the production process of textile industry (dyeing). In Table 2 methods and equipment used for chemical analyses are shown.

***Figure 2:*** *Pilot wastewater treatment plant showing bioreactors, plastic tanks with feeding mixture and pulse pumps.*

***Slika 2:*** *Pilotna čistilna naprava z bioreaktorji, plastičnimi posodami s hranilno mešanico in pulznimi črpalkami.*

***Table 2:*** *Methods and equipment used for chemical analyses.*
***Preglednica 2:*** *Metode in oprema, ki smo jih uporabili za kemijske analize.*

| ParameterParameter | Method/Metoda | Equipment used/ Uporabljena oprema |
|---|---|---|
| Electric conductivity (EC) | electrometry | Multimeter HACH HQ40d |
| Total hardness | colorimetry | Spectrophotometer HACH DR 2800 |
| Total dissolved solids (TDS) | gravimetry | Analytical balance Mettler Toledo AL204 |
| Turbidity | spectrophotometry | Spectrophotometer HACH DR 2000 |
| Colour | spectrophotometry | Spectrophotometer HACH DR 2800 |
| Alkalinity | titration | Burette |
| pH | ISO 10523 | pH meter Eutech Ion 510 |
| Total suspended solids (TSS) | SIST ISO 11923 | Analytical balance Mettler Toledo AL204 |
| Copper (Cu) | porphyrin | Spectrophotometer HACH DR 2800 |
| Iron (Fe) | SIST ISO 6332 | Spectrophotometer HACH DR 2800 |
| Nitrite (NO2) | SIST EN 26777 | Spectrophotometer HACH DR 2800 |
| Nitrate (NO3) | SIST ISO 7890-1 | Spectrophotometer HACH DR 2800 |
| Chloride (Cl) | DIN 38405 | Spectrophotometer HACH DR 2800 |
| Sulfate (SO4) | SIST ISO 10530 | Spectrophotometer HACH DR 2800 |
| Manganese (Mn) | PAN | Spectrophotometer HACH DR 2800 |
| Chemical oxygen demand (COD) | ISO 6060 | Spectrophotometer HACH DR 2800 |
| Biochemical oxygen demand in five days (BOD5) | SIST EN 1899 - 2 | Manometer WTW Oxi top |

### 2.4 Microbiological analyses

Microbiological analyses were performed at the end of the biodegradability trials with municipal wastewater. Feeding mixtures for bioreactors (untreated and AOP-treated municipal wastewater) and effluents from bioreactors were analysed for total bacterial count, coliforms, faecal coliforms, *E. coli*, Enterococci and aerobic spores (*Bacillus*). Total bacterial count was done at 22 °C and 37 °C for 72 hours and 48 hours of incubation, respectively (SIST EN ISO 6222), using Nutrient broth and Agar agar (both Biolife, Italia). *E. coli*, coliforms and faecal coliforms counts were done using MacConkey and ENDO media (both Merck, Germany) (SIST EN ISO 9308-1, Microbiology Manual Merck) at 44 °C (*E. coli* and faecal coliforms) and 37 °C (coliforms) for 24 hours of incubation. For confirmation of *E. coli* we used biochemical identification test API 10 S (bioMerieux, France). Detection of Enterococci (SIST EN ISO 7899-2) was done using Slanetz Bartley media at 37 °C for 24 hours of incubation. Aerobic spores (*Bacillus*) count (SIST EN ISO 7932: 2004) was done using MYP media (Merck, Germany) at 30 °C for 24 hours of incubation.

## 3. Results and discussion

### 3.1 Chemical analyses

Table 3 shows the physical and chemical parameters measured in the effluents from bioreactors during biodegradability trials with municipal wastewater. Limit values for discharges into sewage and surface waters are added according to the Slovenian legislation (OG RS

7/2007). No measured values exceeded the legislation limits.

Figure 3 shows average values of physical and chemical parameters measured in biodegradability trials with municipal wastewater. Figure 4 shows average removal efficiencies that were achieved with biological treatment. In all three bioreactors pH values of effluents were lower after biological treatment; the highest pH value was measured in bioreactor R2 and the lowest in bioreactor R1. In bioreactors R1 and R2 EC values of effluents were lower after biological treatment while in bioreactor R3 they were higher, probably due to the addition of enzymes. Enzymatic product consists of thick brown liquid containing solid particles which could cause a rise in EC.

***Table 3:*** *Physical and chemical parameters measured in effluents from bioreactors filled with municipal wastewater. Average values and standard deviations (SD) were calculated and compared with Slovene legal requirements. R1 – bioreactors filled with untreated municipal wastewater, R2 – bioreactors filled with AOP-treated municipal wastewater, R3 – bioreactors filled with AOP-treated municipal wastewater + enzymes.*

***Preglednica 3:*** *Fizikalni in kemijski parametri, izmerjeni v iztokih iz bioreaktorjev, napolnjenih s komunalno odpadno vodo. Povprečne vrednosti in standardne odklone (SD) smo primerjali s slovenskimi zakonodajnimi vrednostmi. R1 – bioreaktorji napolnjeni z neočiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno odpadno vodo + encimi.*

| Parameter | R1 | | R2 | | R3 | | Limit values (SI legislation*)//Mejne vrednosti (SI zakonodaja*) | |
|---|---|---|---|---|---|---|---|---|
| | Average/ Povprečje | SD | Average/ Povprečje | SD | Average/ Povprečje | SD | Sewage/ Odpadna voda | River/ Vodotok |
| pH | 7.2 | 0.2 | 7.8 | 0.2 | 7.7 | 0.3 | 6.5 - 9.5 | 6.5 - 9.5 |
| EC (µS/cm) | 0.871 | 0.030 | 0.902 | 0.027 | 0.950 | 0.049 | / | / |
| COD (mg/L) | 15.0 | 2.6 | 5.3 | 1.5 | 14.0 | 3.6 | (h) | 200 (i) |
| BOD5 (mg/L) | 8.0 | 2.0 | 4.2 | 2.7 | 7.8 | 1.3 | / | 30 |
| colour 436 nm (m-1) | 0.828 | 0.046 | 0.355 | 0.038 | 0.370 | 0.037 | (b) | 7.0 |
| colour 525 nm (m-1) | 0.444 | 0.051 | 0.079 | 0.015 | 0.184 | 0.013 | (b) | 5.0 |
| colour 620 nm (m-1) | 0.322 | 0.032 | 0.020 | 0.007 | 0.126 | 0.015 | (b) | 3.0 |
| TSS (mg/L) | 3.0 | 1.0 | 1.3 | 0.6 | 1.7 | 0.6 | (a) | 80 |

**According to Decree on the emission of substances and heat in the discharge of wastewater from devices for production, processing and treatment of textile fibres (Official Gazette of the Republic of Slovenia, No 7/2007).*

*(a) limit concentration of suspended solids and surfactants in industrial wastewater shall be determined in the environmental permit on the basis of opinion of the public sewer or municipal wastewater treatment plant manager on the value that has no adverse effects on sewerage or does not interfere with the operation of municipal wastewater treatment plant,*

*(b) use of provisions of the third paragraph within Article 3 of the Decree on the emission of substances and heat in the discharge of wastewater from devices for production, processing and treatment of textile fibres,*

*(h) wastewater disposal is allowed if the biodegradability level of wastewater, expressed in terms of COD or TOC, is at least 70 percent rate of biodegradation of the wastewater in the municipal sewage treatment plant,*

*(i) if the monthly average of the 24-hour representative sample analysis shows that COD value in raw industrial wastewater at the inlet of biological stage of industrial wastewater treatment plant is greater than 1.350 mg/L, the limit, instead of the COD, is threshold for the treatment effect of the industrial wastewater treatment plant, which may not be less than 80 percent. In this case treatment effect is calculated as the average ratio of 24-hour wastewater load measured by COD at the inlet and outlet of the treatment plant.*

Comparing COD and $BOD_5$ values of R1 feeding mixture (untreated municipal wastewater) and R2 + R3 feeding mixture (AOP-treated municipal wastewater), we can see that pre-treatment with AOPs contributed to better results as some COD and $BOD_5$ had already been removed (16% and 11%, respectively). In all three bioreactors COD and $BOD_5$ values of effluents were significantly lower after biological treatment. The lowest COD and $BOD_5$ values were reached in bioreactor R2 while COD and $BOD_5$ values in bioreactors R1 and R3 were similar after biological treatment. The highest COD removal was obtained in bioreactor R2 (92%) due to the effect of pre-treatment. AOPs helped by degrading complex chemical structures into more easily degradable ones, which were then more efficiently treated in the biological stage. COD removal was the lowest in bioreactor R3 (78%), where the enzyme product probably caused the rise of COD. Similarly, the highest $BOD_5$ removal was in bioreactor R2 (89%) and the lowest in bioreactor R3 (80%). The enzyme product obviously had some effect on COD and $BOD_5$ values in bioreactor R3 because they were still slightly higher than in other two bioreactors.

***Table 4:*** *Concentrations of physical and chemical parameters measured at the end of the municipal wastewater trial in comparison with process water requirements for dyeing. Exceeded values are marked in bold. R1 – bioreactors filled with untreated municipal wastewater, R2 – bioreactors filled with AOP-treated municipal wastewater, R3 – bioreactors filled with AOP-treated municipal wastewater + enzymes.*

***Preglednica 4:*** *Koncentracija fizikalnih in kemijskih parametrov izmerjenih na koncu poskusov s komunalno odpadno vodo v primerjavi z zahtevano kvaliteto vode za industrijski proces barvanja. Prekoračene vrednosti so označene odebeljeno. R1 – bioreaktorji napolnjeni z neočiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno odpadno vodo + encimi.*

| Parameter | Bioreactor/Bioreaktor | | | Process water requirements for dyeing*/ Zahtevana kvaliteta vode za industrijski proces barvanja* |
|---|---|---|---|---|
| | R1 | R2 | R3 | |
| Turbidity (FTU) | 6 | 13 | 8 | max. 10 |
| TDS (mg/L) | 930 | 580 | 554 | max. 150 mg/L |
| Total hardness (mg CaCO3/L) | 0.58 | 1.02 | 1.07 | max. 25 mg CaCO3/L |
| NO2 (mg/L) | 0.235 | 0.054 | 0.53 | max. 5 mg/L |
| NO3 (mg/L) | 37.1 | 5.9 | 15.6 | max. 50 mg/L |
| SO4 (mg/L) | 27 | 28 | 25 | max. 30 mg/L |
| Chloride (mg/L) | 70.4 | 75.4 | 47.1 | max. 30 mg/L |
| Mn (mg/L) | 0.028 | 0.021 | 0.018 | max. 0.03 mg/L |
| Fe (mg/L) | 0.01 | <0.01 | 0.01 | max. 0.15 mg/L |
| Cu (mg/L) | 0.005 | 0.001 | 0.002 | max. 0.005 mg/L |

*personal communication/*osebna komunikacija

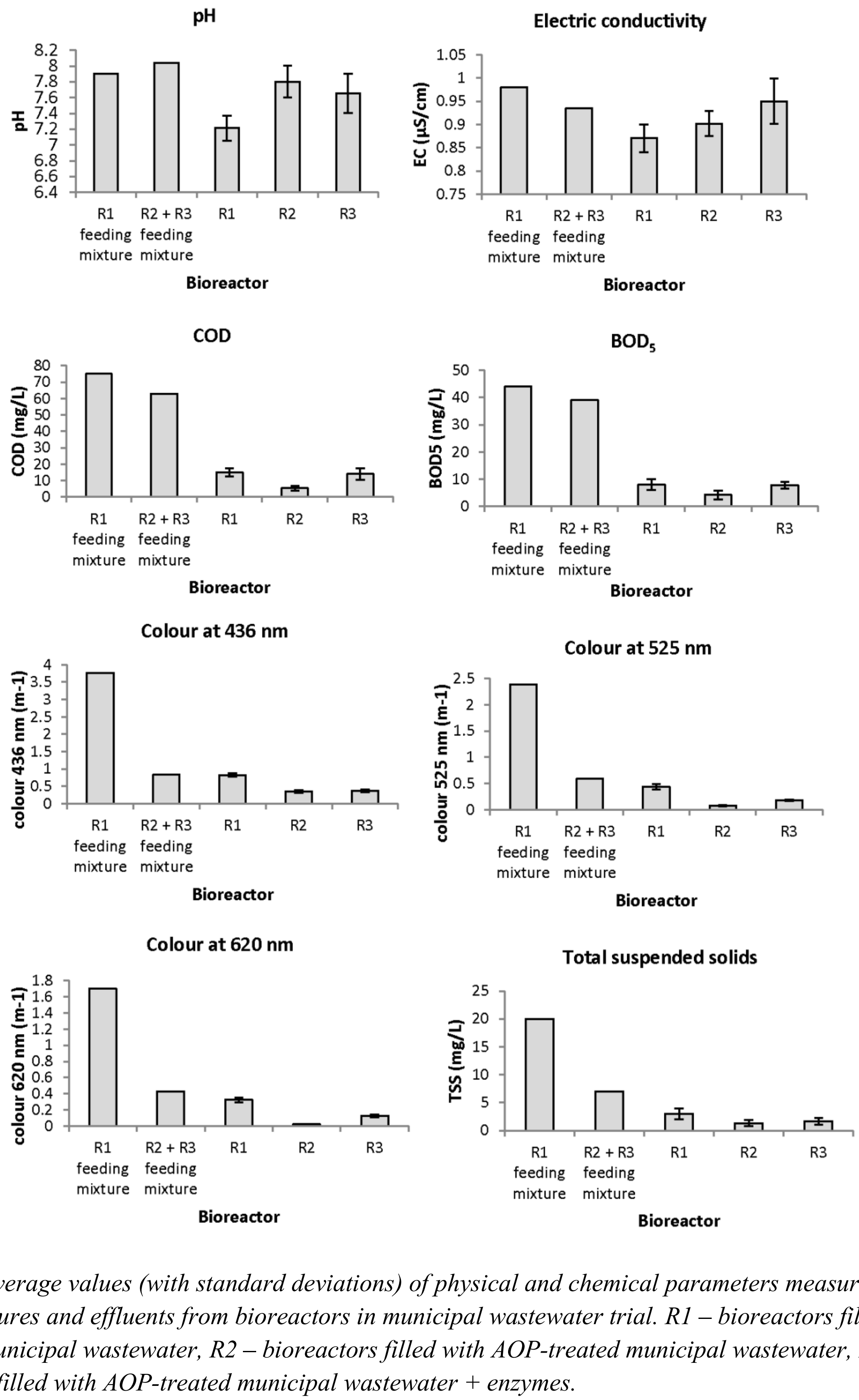


***Figure 3:*** *Average values (with standard deviations) of physical and chemical parameters measured in feeding mixtures and effluents from bioreactors in municipal wastewater trial. R1 – bioreactors filled with untreated municipal wastewater, R2 – bioreactors filled with AOP-treated municipal wastewater, R3 – bioreactors filled with AOP-treated municipal wastewater + enzymes.*

***Slika 3:*** *Povprečne vrednosti (s standardnimi odkloni) fizikalnih in kemijskih parametrov, izmerjenih v hranilnih mešanicah in iztokih iz bioreaktorjev pri poskusih s komunalno odpadno vodo. R1 – bioreaktorji napolnjeni z neočiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno odpadno vodo + encimi.*

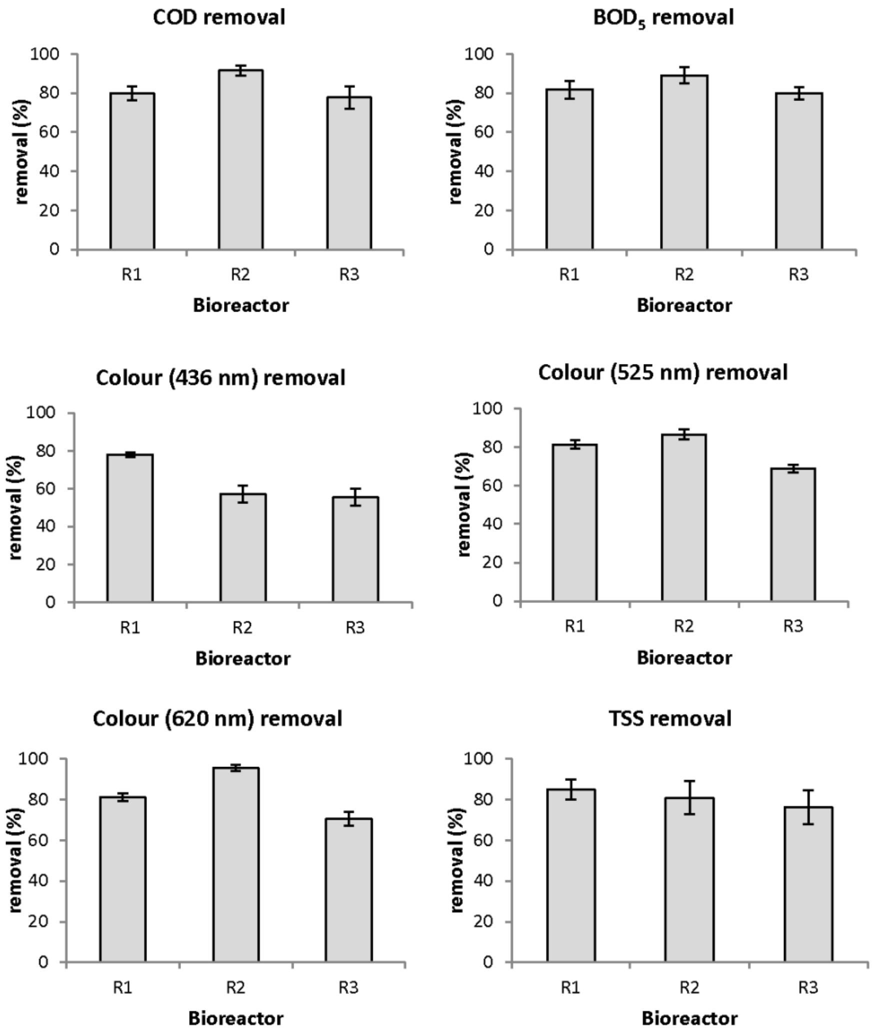


***Figure 4:*** *Average removal efficiencies (with standard deviations) for parameters measured in municipal wastewater biodegradability trial. R1 – bioreactors filled with untreated municipal wastewater, R2 – bioreactors filled with AOP-treated municipal wastewater, R3 – bioreactors filled with AOP-treated municipal wastewater + enzymes.*

***Slika 4:*** *Povprečna uspešnost odstranitve (s standardnimi odkloni) za parametre izmerjene pri poskusih s komunalno odpadno vodo. R1 – bioreaktorji napolnjeni z neočiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno odpadno vodo + encimi.*

Pre-treatment with AOPs also significantly lowered colour (75-78% removal) and TSS values (65%) in municipal wastewater if we compare colour values of R1 feeding mixture (untreated municipal wastewater) and R2 + R3 feeding mixture (AOP-treated municipal wastewater). In all three bioreactors colour values (measured at three wavelengths) were additionally lowered after biological treatment. The highest removal of colour at 436 nm was reached in bioreactor R1 (78%) while colour removal in bioreactors R2 and R3 was similar (57% and 56%, respectively). The highest colour removal at 525 nm was in bioreactor R2 (87%) and the lowest in bioreactor R3 (69%). The highest colour removal at 620 nm was in bioreactor R2 (95%) and the lowest in bioreactor R3 (76%). Overall, the removal of colour was the poorest in bioreactor R3, which could be caused by addition of the dark-coloured enzyme product. TSS values of effluents were lower after biological treatment; the highest TSS removal was in bioreactor R1 (85%) and the lowest in bioreactorR3 (76%).

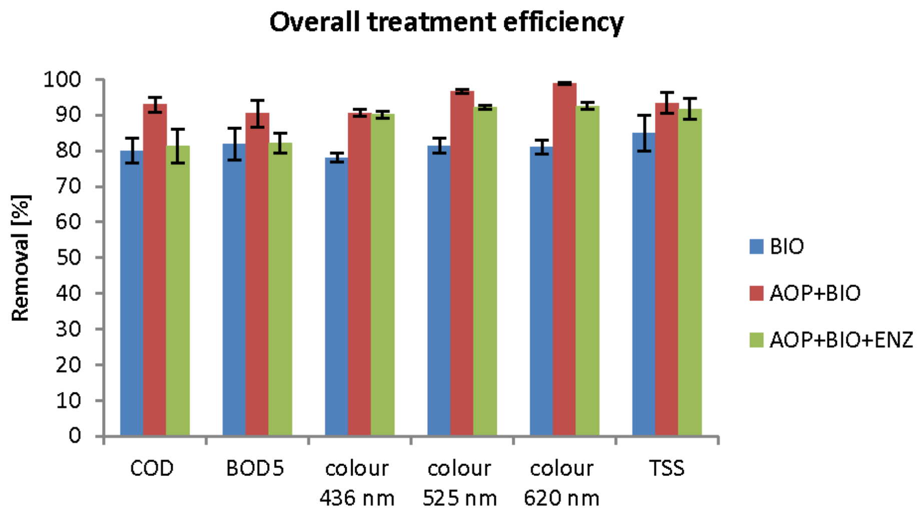


***Figure 5:*** *Average overall treatment efficiency (with standard deviations) for selected parameters achieved with different combinations of AOP and biological treatment of municipal wastewater. BIO – biological treatment alone, BIO+AOP – combination of AOP and biological treatment, BIO+AOP+ENZ – combination of AOP, biological treatment and enzymes.*

***Slika 5:*** *Povprečna skupna učinkovitost čiščenja (s standardnimi odkloni) za izbrane parametre dosežena z različnimi kombinacijami AOP in biološkega čiščenja komunalne odpadne vode. BIO – samo biološko čiščenje, BIO+AOP – kombinacija AOP in biološkega čiščenja, BIO+AOP+ENZ – kombinacija AOP, biološkega čiščenja in encimov.*

Figure 5 shows average overall treatment efficiencies achieved with different combinations of AOP and biological treatment of municipal wastewater. For all selected parameters the highest overall treatment efficiency was achieved with a combination of AOP and biological treatment (90-99% removal), while with biological treatment alone 78-85% removal was achieved. Addition of the enzyme product did not improve the overall treatment efficiency for any of the selected parameters as better results were achieved with a combination of AOP and biological treatment alone.

Table 4 shows the physical and chemical parameters that were measured at the end of the biodegradability trial with municipal wastewater in order to see if the treated municipal wastewater could be reused in the production process of textile industry (dyeing). Process water requirements for dyeing are added. Values for turbidity were exceeded, but only in bioreactor R2. Values for TDS and chloride were exceeded in all three bioreactors. Turbidity could be removed by an additional step of membrane filtration or coagulation, while chloride, being part of the mineralization process, cannot be so easily removed. One option for chloride removal would be ion exchange, but this would also remove most of the other ionised substances. There were no exceeded values for total hardness, nitrate, nitrite, sulphate, manganese, iron and copper. According to the results of the measured parameters and the requirements for dyeing, municipal wastewater treated by a combination of AOP and biological treatment would not be suitable for reuse in the dyeing process in the textile industry, but could potentially be reused in some other processes of the textile industry, such as rinsing or maintenance of production facilities and machines (toilet flushing, cleaning).

### 3.2 Microbiological analyses

Figure 6 shows the results of microbiological analyses performed on feeding mixtures (untreated and AOP-treated municipal wastewater) and on effluents from bioreactors. Comparing microbiological parameters measured in R1 feeding mixture (untreated municipal wastewater) and R2 + R3 feeding mixture (AOP-treated municipal wastewater), it can be seen that we achieved significant reduction of microorganisms with the AOP treatment. AOPs lowered total bacterial count, total coliform count and Enterococci count and completely removed faecal coliforms and aerobic spores (*Bacillus*). For reuse of treated municipal wastewater microbiological safety is very important and AOPs proved to be effective in disinfecting municipal wastewater. Depending on the requirements, AOP-treated municipal wastewater could be reused in production processes of textile industry, such as washing, and also in the production process of pulp and paper industry. However, not all biodegradability trials that followed were so successful. In bioreactor R1 all measured microbiological parameters were reduced, except aerobic spore count, which was slightly higher after biological treatment. In bioreactor R2 all microbiological parameters rose after biological treatment, except total bacterial count, which remained unchanged. The same occurred in bioreactor R3, where most of the microbiological parameters were even higher than in bioreactor R2. Higher values of some microbiological parameters after biological treatment can be explained by an inefficient sampling method; effluents from bioreactors were collected in effluent tanks, where some contamination could occur. Also, there could be some leakage of suspended microbial biomass from bioreactors into the effluent tanks, which could cause rise in microbial parameters in the effluents. Poor results in R3 could be caused by the addition of the enzyme product, which also promotes microbial growth. Presence of *E. coli* was not detected.

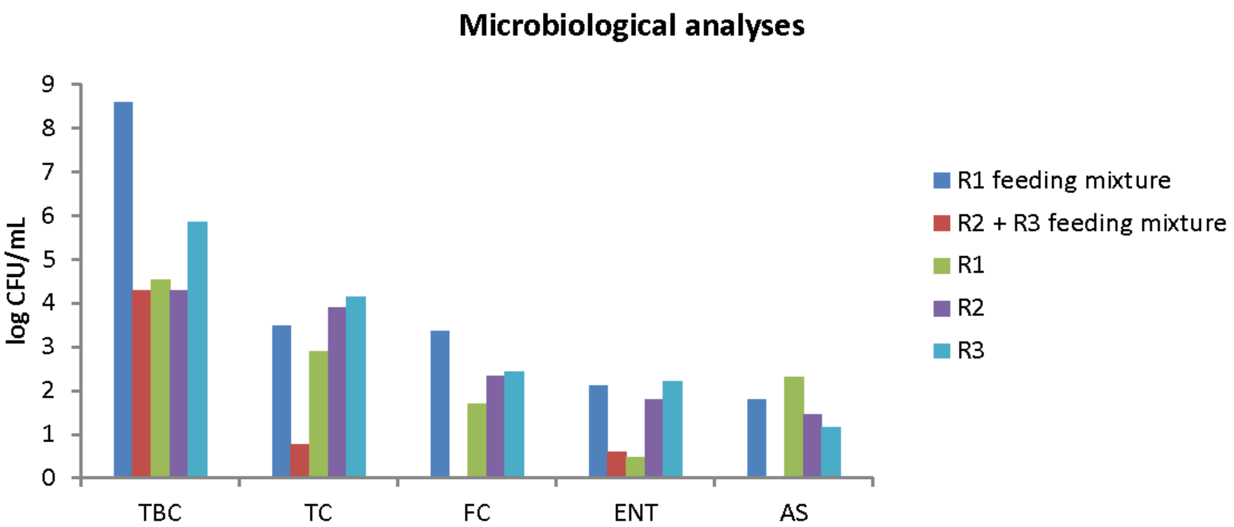


***Figure 6:*** *Microbiological analyses of feeding mixtures and effluents from bioreactors performed in trial with municipal wastewater. R1 feeding mixture – untreated municipal wastewater, R2 + R3 feeding mixture – AOP-treated municipal wastewater, R1 – bioreactors filled with untreated municipal wastewater, R2 – bioreactors filled with AOP-treated municipal wastewater, R3 – bioreactors filled with AOP-treated municipal wastewater + enzymes. TBC – total bacterial count, TC – total coliforms, FC – faecal coliforms, ENT – Enterococci, AS – aerobic spores (Bacillus).*

***Slika 6:*** *Mikrobiološke analize hranilnih mešanic in iztokov iz bioreaktorjev, ki smo jih izvedli med poskusi s komunalno odpadno vodo. R1 hranilna mešanica – neočiščena komunalna odpadna voda, R2 + R3 hranilna mešanica – AOP-očiščena komunalna odpadna voda, R1 – bioreaktorji napolnjeni z neočiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno komunalno odpadno vodo, R2 – bioreaktorji napolnjeni z AOP-očiščeno odpadno vodo + encimi. TBC – skupno število mikroorganizmov, TC – skupne koliformne bakterije, FC – fekalne koliformne bakterije, ENT – enterokoki, AS – aerobne spore (Bacillus).*

## 4. Conclusions

Pre-treatment with AOPs helped with initial reduction of colour, COD and $BOD_5$ in municipal wastewater. With further biodegradability trials we achieved significant removal of COD and $BOD_5$ as well as colour in all three bioreactors. AOPs also significantly lowered initial values of microbial parameters and proved to be an effective disinfectant, but in further biodegradability trials, some parameters were again increased due to potential contamination and leakage of microbial biomass from bioreactors into the effluents. AOPs contributed to better biodegradation, while addition of special enzymes did not. According to the results of chemical parameters and based on requirements, municipal wastewater used in our trials and treated by a combination of AOP and biological treatment is not suitable for reuse in the dyeing process in textile industry. Nevertheless, it showed good results regarding chemical and physical parameters after treatment and could potentially be reused in the rinsing process in textile industry, for toilet flushing, cleaning of production facilities and machines. Results could potentially be improved by optimising the biological stage of treatment (higher hydraulic retention time, better aeration, etc.) and in this way the treated municipal wastewater could also be reused in the dyeing process in textile industry.

## 5. Acknowledgements

The study was performed within the CORNET project AOP4Water (www.cornet-aop4water.eu), which was co-funded by the Slovenian Ministry of Higher Education, Science and Technology (MVZT) under the Cornet programme and was performed together with other European institutions. Significant financial support has been provided by University of Ljubljana, Institute for Water of the Republic of Slovenia, and Echo Ltd.

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