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Obdelava tekstilnih odpadnih voda z membranskim bioreaktorjem

Izvirni znanstveni članek

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Izvleček

Uporaba membranskega bioreaktorja (MBR), ki pomeni biološko razgradnjo odpadnih voda z aktivnim blatom v kombinaciji s fizikalnim procesom membranske filtracije, je postala zanimiva predvsem zaradi številnih prednosti pri čiščenju tekstilnih odpadnih voda in hitrega razvoja v zadnjem desetletju. Namen dela je bil očistiti modelno odpadno vodo z membranskim bioreaktorjem ter določiti njegovo učinkovitost čiščenja modelne tekstilne odpadne vode, pripravljene v laboratoriju po recepturi iz industrije. Cilj je bil vzpostaviti obratovalne razmere in stabilnost celotnega sistema, ki bi dal maksimalen izkoristek čiščenja z želeno kakovostjo očiščene vode. S spremljanjem obratovalnih parametrov, kot so pretok vhodne odpadne vode, dovajanje kisika v biološki del obdelave ter spremljanje tlaka ultrafiltracije, smo nameravali zagotoviti optimalne obratovalne razmere. S fizikalno-kemijskimi analizami smo dokazali, da so se vrednosti KPK in koncentracije barvila, izražene kot spektralni absorpcijski koeficient (SAK), znižale, in sicer za 70 do 90 odstotkov. Iz rezultatov je razvidno, da je bila učinkovitost zniževanja KPK okoli 90-odstotna, učinkovitost zniževanja vsebnosti barvil pa doseže do 97 odstotkov. Iz navedenega lahko povzamemo, da je tehnologija MBR, ki je kombinacija biološkega in fizikalnega čiščenja, zelo učinkovita pri čiščenju tekstilne odpadne vode.

Ključne besede: reaktivna azobarvila, tekstilne odpadne vode, membranski bioreaktor, aktivno blato.

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Abstract

The use of a membrane bioreactor (MBR) has been rapidly developing over the last decade. This technology is based on the biodegradation of wastewater with activated sludge in a combination with the physical process of membrane filtration and has become of particular interest due to its numerous advantages during wastewater treatment. The objectives of this work were to treat laboratory-prepared wastewater using MBR, in order to determine its effectiveness regarding wastewater treatment, and to establish operational parameters and system stability which would provide optimum treatment. The operational parameters, e.g. inlet wastewater flow, concentration of oxygen within a bio-unit and the monitoring of ultrafiltration pressure, were adjusted during the treatment process. By measuring individual parameters and implementing the chemical analysis, a satisfactory functioning of the MBR system was demonstrated, since the efficiency value regarding COD reduction and the elimination of dyes, expressed as SAC (Spectral Absorption Coefficient), reached 70–90% for both parameters. The results show that the removal efficiency of COD was 90% and of the dyes 97%, respective-

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ly. It can be concluded that the MBR technology, as a combination of biological and physical treatments, is very effective for the textile wastewater treatment.

Keywords: reactive azo dyes, membrane bioreactor, wastewater treatment, activated sludge

1 Introduction

The textile finishing process requires large amounts of water and, consequently, generates a large quantity of wastewater. The average consumption of water ranges between 100–150 m³ per tonne of textile material [1]. During the textile dyeing processes, vast quantities of chemicals (dyes, auxiliaries) are consumed, which strongly charge the wastewater. The textile wastewater contains large amounts of dissolved organic matter and inorganic substances, a high pH value and low BOD/COD (biological oxygen demand/chemical oxygen demand) ratio. The wastewater contains heavy metals, sulphide components, fats, oils and fibres. The residues of non-biodegradable dyes remain mostly in the wastewater, being the result of incomplete binding of dyes to the textile fibre. The average rate of dye-fixation when dyeing with reactive dyes is 60–80%. The residues of non-fixed colours are washed from the textile and thus contaminate the wastewater [1, 2]. The textile dyes are distinguished by their high thermal stability and photo-stability; therefore, the degradation of dyes is slow and the process is rather complex. It is well-known that the decomposition products of reactive dyes are in the vast majority of cases colourless compounds which are generally more toxic than the dye itself (aromatic amines, derived from the degradation of azo dyes) [3, 4].

Several methods have been developed for the decolourization of textile wastewater; however, due to the complex structure of textile wastewater (the multiplicity and diversity within the chemical structures of compounds), a suitable universal purification process has still not been established. With regard to the wastewater characteristics, the type of treatment is chosen in order to remove dangerous impurities from the water. There are different textile wastewa-

1 Uvod

Plemenitenje tekstilnih materialov zahteva velike količine vode in posledično nastajajo velike količine odpadne vode. V povprečju se porabi od 100 do 150 kubičnih metrov vode na tono tekstilnega materiala [1]. Pri procesih barvanja tekstilij se porabi velika količina kemikalij (barvila, tekstilna pomožna sredstva), ki po končanih procesih močno obremenjujejo odpadno vodo. Tekstilne odpadne vode imajo velik delež raztopljenih organskih in anorganskih snovi, visoko pH vrednost in nizko razmerje BPK/KPK (biokemijska potreba po kisiku/kemijska potreba po kisiku) vrednosti. Vsebujejo težke kovine, sulfidne komponente, maščobe in olja ter vlakna. Največkrat se v njih zadržujejo ostanki biološko nerazgradljivih barvil, ki so rezultat nepopolne vezave barvila na tekstilno vlakno. Pri barvanju z reaktivnimi barvili je povprečna stopnja fiksiranja barvila od 60 do 80 odstotkov. Ostanek nefiksiranega barvila se izpere iz tekstilij in kontaminira odpadno vodo [1, 2]. Tekstilna barvila odlikujeta visoka termična obstojnost in fotostabilnost, zato je njihova razgradnja v okolju počasen in zapleten proces. Znano je, da so produkti razgradnje reaktivnih barvil v veliki večini brezbarvne spojine, ki so veliko bolj toksične kot samo barvilo (aromatski amini, ki nastanejo pri razgradnji azobarvil) [3, 4].

Za razbarvanje tekstilnih odpadnih voda je bilo razvitih kar nekaj uporabnih metod, vendar zaradi zapletene sestave tekstilne odpadne vode (številnosti in raznolikosti v kemijski strukturi spojin) še vedno ni primernega univerzalnega postopka čiščenja. Glede na karakteristike odpadne vode se določi vrsta postopka, s katerim se odstranijo nevarne snovi iz vode. Za čiščenje tekstilne odpadne vode se uporabljajo različni postopki, in sicer: klasični (fizikalno-kemijski), biološki (aerobno-anaerobna biorazgradnja) ter membranska filtracija. Ena od perspektivnih alternativ čiščenja tekstilnih odpadnih voda je uporaba membranskega bioreaktorja (MBR) [5]. Obdelava vode z uporabo membranskega bioreaktorja (MBR) je čiščenje odpadnih voda na podlagi biološkega čiščenja v kombinaciji z membransko filtracijo. Membrana omogoča zadrževanje kosmov aktivnega blata in suspendiranih snovi, poleg tega pa lahko zadrži večino mikroorganizmov in tudi velik delež raztopljenih snovi. Po uporabi procesa MBR najdemo v očiščeni vodi manj kot 2 mg/L suspendiranih delcev, medtem ko pri klasičnih postopkih najmanjša vrednost suspendiranih snovi presega 10 mg/L. V odpadni vodi so količina hrane in razmere za razmnoževanje odvisni od sestave odpadne vode in koncentracije kisika.

Aromatski amini, ki nastanejo pri razgradnji azobarvila, so odporni na aerobno razgradnjo, saj aerobne bakterije niso sposobne razgraditi molekul z aromatskim obročem [6]. Zato je kombinacija anaerobnega in anoksičnega dela bioenote v membranskem bioreaktorju primerna za nastajanje razmer za rast mešane kulture mikroorganizmov, ki je odgovorna za učinkovito čiščenje obarvanih tekstilnih odpadnih voda. Anoksična biorazgradnja je eden ključnih korakov pri čiščenju obarvanih tekstilnih odpadnih voda, saj *ter treatment methods, e.g. conventional (physical – chemical), biological (aerobic – anaerobic biodegradation) and membrane filtration. One of the more promising textile wastewater treatment alternatives is the use of a membrane bioreactor (MBR) [5]. The wastewater treatment using a membrane bioreactor (MBR) is based on biological treatment in combination with membrane filtration. The membrane allows for the retention of activated sludge flakes and suspended solids, and can also retain the majority of microorganisms and higher amounts of dissolved substances. Less than 2 mg/L of suspended solids can be found in the treated water after the MBR process is finished, whilst with conventional processes, the lowest level of suspended solids exceeds 10 mg/L. The amount of food and reproductive conditions depends on the composition of the wastewater and its oxygen concentration.*

Aromatic amines are formed during the degradation of azo dyes, which are resistant to aerobic degradation, as the aerobic bacteria are unable to degrade the molecules with aromatic rings [6]. Therefore, a combination of anaerobic and anoxic parts of the bio-unit within a membrane bioreactor is suitable for creating conditions for the growth of mixed cultures of microorganisms, which are responsible for any effective treatment of coloured textile wastewater. Anoxic biodegradation is one of the key steps in the treatment of coloured textile wastewater, since it achieves the degradation of aromatic rings. An efficient biodegradation of azo dyes is achieved with a diverse community of microorganisms found within activated sludge, which means that the system of biodegradation should include both the aerobic and anaerobic parts [7, 8]. In consequence, the treated wastewater exhibits improved physical and chemical properties, and complete decolourisation is achieved in most cases. The wastewater can be reused in the industrial sector through an additional treatment, e.g. nanofiltration or reverse osmosis [9].

The Zenon ZW-10 pilot plant is composed of anoxic and aerobic parts, and a filtration unit with hollow-fibre membranes. The aim of this study was to establish the operating conditions and stability for the whole laboratory MBR sys-

z njo dosežemo razgradnjo aromatskih obročev. Učinkovita biorazgradnja azobarvil se doseže z raznoliko združbo mikroorganizmov, ki se nahajajo v aktivnem blatu, kar pomeni, da mora sistem biorazgradnje zajemati tako aerobni kot anaerobni del [7, 8]. Tako očiščeni odpadni vodi se izboljšajo karakteristične fizikalne in kemijske lastnosti, prav tako se v večini primerov tudi popolnoma razbarva. Očiščena odpadna voda se lahko s pomočjo dodatne obdelave, kot sta nanofiltracija ali reverzna osmoza, ponovno uporabi v industrijskem sektorju [9].

Modelno tekstilno odpadno vodo smo čistili s pilotno napravo Zenon ZW 10, ki je sestavljena iz anoksičnega in aerobnega dela ter iz filtracijske enote z votlo–vlaknasto membrano. Namen raziskave je bil vzpostaviti obratovalne razmere in stabilnost celotnega sistema laboratorijskega MBR, ki bi dal maksimalen izkoristek čiščenja z želeno kakovostjo očiščene vode za izpust v kanalizacijo. Gre za izvirno raziskavo, saj v literaturi nismo zasledili, da bi se s kombinacijo anoksične in aerobne faze v MBR izboljšala kakovost tekstilne odpadne vode. S spremljanjem obratovalnih parametrov, kot so pretok vhodne odpadne vode, dovajanje kisika v biološki del obdelave ter spremljanje tlaka ultrafiltracije, je bil namen raziskave zagotoviti optimalne obratovalne razmere.

2 Eksperimentalni del

2.1. Barvila in kemikalije

Po navodilih podjetja Beti Pletiva, d. o. o., smo pripravili odpadno vodo (preglednica 1). Postopek plemenitenja bombaža je bil sestavljen iz petih stopenj. Na prvi stopnji poteka beljenje surovega bombaža z vodikovim peroksidom (H_2O_2). V 10 litrih vode smo raztopili pripadajočo količino kemikalije *CHT-entschaumer mi*, emulgirano maščobno spojino *Biavin 109*, detergent *Imerol jsf*, belilni regulator *Sirrix sb*, bazično raztopino NaOH in belilo H_2O_2. Vodo s surovim bombažem smo segreli na 98 °C in jo pustili pri tej temperaturi 30 minut. Po 30 minutah smo odpadno vodo odlili v rezervoar, bombaž pa uporabili na naslednji stopnji barvanja. Na drugi stopnji barvanja bombaža je potekalo encimsko razškrobljevanje, kjer smo v 10 litrih vode raztopili ocetno kislino in hibridni encim katalazo *Bactosol arl*. Po 20-minutnem segrevanju mešanice bombaža in raztopljenih kemikalij pri temperaturi 50 °C smo nastalo odpadno vodo odlili v rezervoar z odpadno vodo, ki je nastala pri prvi stopnji barvanja bombaža. Na tretji stopnji smo bombaž barvali z reaktivnimi azobarvili. Ponovno smo v 10 litrih raztopili *CHT-entschaumer mi*, zaščitno izolirno sredstvo *Meropan dpe*, emulgirano maščobno spojino *Biavin 109*, omakalno sredstvo *Alviron rfr*, NaCl, reaktivno barvilo *Drimaren blau hf–lr*, *Drimaren gelb hf–r* in barvilo *Drimaren rot hf–3b*, kalcirano sodo in bazično raztopino NaOH. Mešanico smo segreli do 60 °C ter jo pri tej temperaturi pustili eno uro in jo nato odlili v skupen rezervoar. Na četrti stopnji barvanja bombaža je sledilo izpiranje nezreagiranih

tem to achieve the maximum pollutant removal efficiency with the desired quality of treated water being discharged into the sewer. This was a novel investigation, since nothing could be found in the literature about the combinations of anoxic and aerobic phases in MBR to improve the quality of textile wastewater. The objective of this research was to ensure optimal operating conditions by monitoring the operating parameters, e.g. wastewater flow, oxy-

snovi. V 10 litrih vode smo raztopili pripadajočo količino ocetne kisline in jo za 10 minut segreli na 60 °C. Po 10 minutah smo jo odlili v rezervoar s preostalo odpadno vodo, ki je nastala pri prejšnjih stopnjah barvanja. V zadnji fazi barvanja bombaža smo raztopili v 10 litrih vode kemikaliji *Cotoblanc n sr* in emulgirano maščobno spojino *Biavin 109* ter jo za 10 minut segreli na 98 °C. Iz kopeli smo odstranili pobarvan bombaž, nastalo odpadno vodo pa dolili v rezervoar s preostalo modelno odpadno vodo.
Tako je bila pripravljena odpadna voda, ki smo jo morali še ohladiti na sobno temperaturo, preden smo jo začeli čistiti.

Table 1: List of chemicals for preparing 100 L of modelled wastewater in accordance with recipe by Beti Pletiva

<table>
<tr><th>Chemical</th><th>Concentration</th><th>Quantity (g)</th><th>Temperature of chemical cooking (°C)</th><th>Time of chemical cooking (min)</th></tr>
<tr><td colspan="5">1st phase</td></tr>
<tr><td>CHT-ENTSCHAUMER MI</td><td>0.2 g/L</td><td>20</td><td rowspan="6">98</td><td rowspan="6">30</td></tr>
<tr><td>BIAVIN 109</td><td>0.5 g/L</td><td>50</td></tr>
<tr><td>IMEROL JSF</td><td>1%</td><td>100</td></tr>
<tr><td>SIRIX SB</td><td>1.2%</td><td>120</td></tr>
<tr><td>NaOH</td><td>1.36%</td><td>140</td></tr>
<tr><td>H_2O_2</td><td>5%</td><td>500</td></tr>
<tr><td colspan="5">2nd phase</td></tr>
<tr><td>ACETIC ACID</td><td>0.3 g/L</td><td>30</td><td rowspan="2">50</td><td rowspan="2">20</td></tr>
<tr><td>BACTOSOL ARL</td><td>0.5%</td><td>50</td></tr>
<tr><td colspan="5">3rd phase</td></tr>
<tr><td>CHT-ENTSCHAUMER MI</td><td>0.2 g/L</td><td>20</td><td rowspan="10">60</td><td rowspan="10">60</td></tr>
<tr><td>MEROPAN DPE</td><td>1 g/L</td><td>110</td></tr>
<tr><td>BIAVIN 109</td><td>0.5 g/L</td><td>50</td></tr>
<tr><td>ALVIRON RFR</td><td>1 g/L</td><td>100</td></tr>
<tr><td>NaCl</td><td>60 g/L</td><td>6000</td></tr>
<tr><td>DRIMAREN BLAU HF-RL</td><td>1.1%</td><td>110</td></tr>
<tr><td>DRIMAREN GELB HF-R</td><td>0.7%</td><td>70</td></tr>
<tr><td>DRIMAREN ROT HF-3B</td><td>0.48%</td><td>50</td></tr>
<tr><td>CALCINED SODA</td><td>5 g/L</td><td>500</td></tr>
<tr><td>NaOH</td><td>0.88 g/L</td><td>90</td></tr>
<tr><td colspan="5">4th phase</td></tr>
<tr><td>ACETIC ACID</td><td>0.5 g/L</td><td>50</td><td>60</td><td>10</td></tr>
<tr><td colspan="5">5th phase</td></tr>
<tr><td>COTOBLANC N SR</td><td>0.3 g/L</td><td>30</td><td rowspan="2">98</td><td rowspan="2">10</td></tr>
<tr><td>BIAVIN 109</td><td>0.5 g/L</td><td>50</td></tr>
</table>

gen concentration in the biological part of MBR and transmembrane pressure.

2 Experimental

2.1 Dyes and chemicals

Modelled textile wastewater was prepared in a laboratory using the recipe provided by the company Beti Pletiva (cf. Table 1). The process consisted of five stages. The bleaching of raw cotton with hydrogen peroxide (H_2O_2) took place during the first stage. Certain amounts of chemicals CHT-entschaumer mi, emulsified fatty compound Biavin 109, detergent Imerol jsf, bleaching regulator Sirrix sb, alkaline solution of NaOH and H_2O_2 were dissolved in 10 L of water. Water with raw cotton was heated at 98 °C for 30 minutes. In the second stage of cotton dyeing, acetic acid and hybrid enzyme catalase Bactosol arl were dissolved in 10 L of water. After 20 minutes of heating at a temperature of 50 °C, the wastewater was poured into the collection tank together with the wastewater generated during the first stage of cotton dyeing. During the third stage, the cotton was coloured with reactive azo dyes. CHT-entschaumer mi, protective insulating mean Meropan dpe, emulsified fatty compound Biavin 109, wetting agent Alviron rfr, NaCl, reactive dye Drimaren blau hf-lr, Drimaren Gelb hf-r and dye Drimaren hf-rot 3b, bicarbonate and NaOH were dis-

2.2. Pilotna naprava MBR – Zenon ZW 10

Modelno tekstilno odpadno vodo smo čistili v membranskem bioreaktorju Zenon, model ZW – 10 z votlo-vlaknasto hidrofilno membrano, s površino 0,93 m^2 in velikostjo por 0,04 µm, ki je delovala pri največ 0,2 bara podtlaka. Pilotna naprava (slika 1) je obratovala od začetka aprila 2009 do konca julija 2009. Membranski bioreaktor je sestavljen iz bio-enote, kjer poteka biološko čiščenje odpadne vode z aktivnim blatom, in iz filtracijske enote z membranskim modulom z votlo–vlaknasto membrano. Tekstilna odpadna voda se črpa iz rezervoarja s pomočjo črpalke v bioenoto (anoksično in aerobno cono), kjer poteka biološka razgradnja barvil, ogljikovih in dušikovih spojin. Tako mikrobiološko obdelana odpadna voda teče v filtracijsko enoto, kjer se nahaja ultrafiltracijska membrana in v prisotnosti podtlaka poteka filtracija vode skozi votlo-vlaknaste membrane. Po končani ultrafiltraciji se očiščena odpadna voda zbira v posebnem zbiralniku.

Membranski bioreaktor je obratoval kontinuirano, pri čemer smo zagotovili neprekinjen dotok modelne odpadne vode s pretokom med 0,3 in 1,16 L/h. Za preprečitev ireverzibilnega mašenja membrane smo med obratovanjem spremljali tlak filtracije do maksimalne vrednosti podtlaka 0,2 bara. Membrano smo mehansko čistili s povratnim tokom permeata skozi pore membran pri tlaku do največ 0,25 bara.

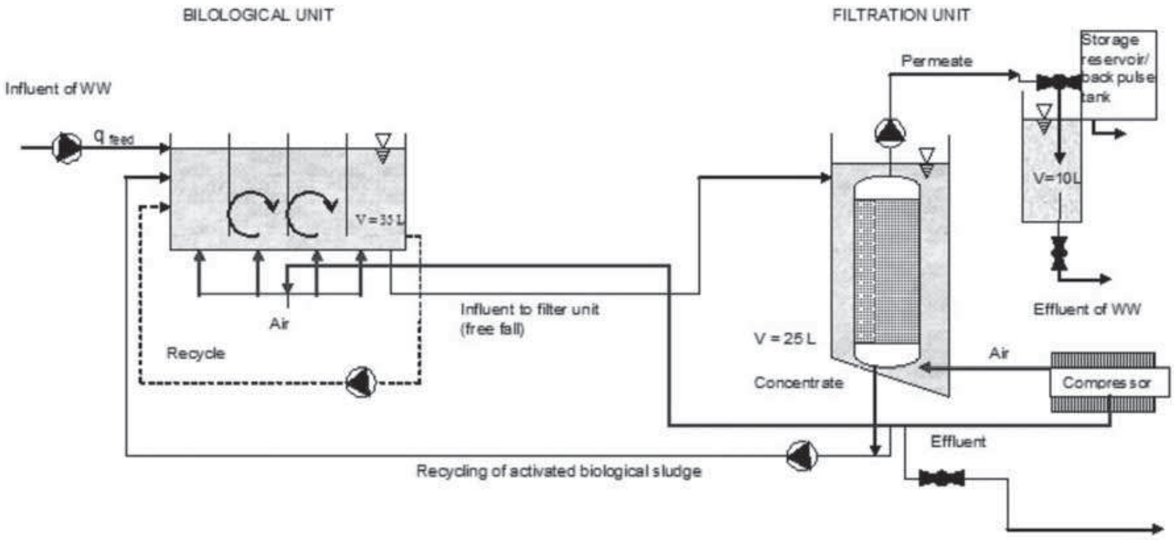

Figure 1: MBR pilot plant

Učinkovitost delovanja MBR lahko izračunamo po enačbi 1:

$$R_E = \left(1 - \frac{\gamma_{j,\,i}}{\gamma_{j,\,v}}\right) \times 100\% \quad (1)$$

kjer je:

R_E – učinkovitost [%]

$\gamma_{j,\,i}$ – masna koncentracija j-te komponente na iztoku [mg/L]

$\gamma_{j,\,v}$ – masna koncentracija j-te komponente na vtoku [mg/L] *solved in 10 L of water. This mixture was heated at 60 °C for 1 hour and then poured into the collection tank. During the fourth stage of cotton dyeing, acetic acid was dissolved in 10 L of water and heated at 60 °C for 10 minutes. Afterwards, it was poured into the collection tank. During the final stage, Cotoblanc n sr and emulsified fat compound Biavin 109 were dissolved in 10 L of water and heated at 98 °C for 10 minutes. The generated wastewater was then poured into the tank.*

2.2 Pilot plant MBR – Zenon ZW-10

The modelled textile wastewater was purified using the Zenon membrane bioreactor, model ZW-10 with a hollow-fibre hydrophilic membrane. The membrane area of 0.93 m² and pore-size of 0.04 µm were used. MBR operated at up to 0.2 bar of vacuum. The pilot plant (cf. Figure 1) operated April–July 2009. The membrane bioreactor was composed of a bio-unit with an activated sludge biological wastewater treatment, and a filtration unit with a hollow-fibre membrane. The textile wastewater was

3 Analizne metode

Merjeni parametri, ki smo jih določali odvzetim vzorcem, ter standardne metode in aparati so prikazani v preglednici 2.

Table 2: Measured parameters, standard methods and apparatus

Parameter	Standard	Method	Apparatus
Temperature, T (°C)	DIN 38404-C4	/	Thermometer
pH value	SIST ISO 10523	electrometric	pH meter Iskra MA 5740
Concentration of dissolved oxygen, γ_{O_2} (mg O_2/L)	SIST EN 25814	electrometric	Oximeter WTW
Concentration of activated sludge, γ (g/L)	APHA, 1995	gravimetric	Scales MetllerAE 100
Total nitrogen, TN (mg/L)	SIST ISO 10048 DIN EN ISO 11905-1 (digestion) ISO 789-1 (determination like NO_3–N)	quick test (Merck)	Thermoreactor Merck 620, spectrophotometer Merck NOVA 60
Ammonium nitrogen – NH_4^+, N (mg/L)	SIST ISO 6778	spectrophotometric	Perkin – Elmer
Nitrate nitrogen – NO_3^-, N (mg/L)	ISO 7890	spectrophotometric	Perkin – Elmer
Chemical oxygen demand, COD (mg O_2/L)	SIST ISO 6060	titrimetric	Thermoreactor Lovibond ET 108
Water colour, SAC (m^{-1})	SIST EN ISO 7887/3	spectrophotometric	Perkin – Elmer

4 Rezultati in razprava

Iz rezervoarja, kjer smo skladiščili modelno pripravljeno odpadno vodo, smo vsak dan odvzeli vzorec za analizo. Drugi vzorec smo odvzeli na iztoku iz bioenote, kjer se voda preliva v ultrafiltracijsko enoto. Vzorec permeata smo odvzeli po končani ultrafiltraciji. Obarvanost vzorcev je razvidna iz slike 2.

Figure 2: Sample of permeate (purified water within MBR system), sample from bio-unit (wastewater after biological treatment) and fed solution

pumped from the tank into the bio-unit (anoxic and aerobic zone) responsible for the biodegradation of dyes, and carbon and nitrogen compounds. The biologically-treated wastewater flowed into the filtration unit with an ultrafiltration membrane, where any mixed liquor was separated from the wastewater. The purified wastewater was collected in a special tank. The membrane bioreactor operated continuously at 0.3–1.16 L/h. In order to prevent irreversible membrane fouling, transmembrane pressure during the operation was monitored to a maximum value of 0.2 bar of vacuum. The membrane was mechanically cleaned using a reverse-current permeate flow through the membrane pores at a pressure of up to 0.25 bar. The efficiency of the MBR-operation can be calculated according to Equation 1, where:

R_E *– efficiency [%],*

$\gamma_{j,I}$ *– mass concentration of* j^{th} *component at outflow [mg/L],*

$\gamma_{j,v}$ *– mass concentration of* j^{th} *component at inflow [mg/L].*

3 Analytical methods

The measured parameters, standard methods and equipment are enumerated in Table 2.

4 Results and discussion

Samples for the analysis were taken daily from the reservoir where the modelled wastewater was stored. A further sample was taken at the effluent of the bio-unit, where the water was poured into the ultrafiltration unit. A sample of permeate was taken after the ultrafiltration. The samples are shown in Figure 2.

Activated sludge was taken from the municipal wastewater treatment plant. The adaptation of microorganisms into the modelled wastewater lasted for about a month.

The activated sludge growth and the efficiency of the wastewater treatment were significantly affected by the temperature and pH values of the fed wastewater. The microorganisms which are normally developed under such conditions were very specific and sensitive to major changes in pH or temperature [10]. At unfavourable pH values, the bacteria were no longer able to

Za biološko predelavo odpadne vode smo uporabili aktivno blato iz komunalne čistilne naprave. Potrebno je bilo približno mesec dni, da so se mikroorganizmi adaptirali na modelno odpadno vodo.

Na rast aktivnega blata in s tem na učinkovitost čiščenja odpadne vode pomembno vplivata temperatura in pH vhodne odpadne vode, odpadne vode iz bioenote in permeata. Mikroorganizmi, ki se po navadi pri tem razvijejo, so zelo specifični in senzibilni na velike spremembe pH ali temperature v sistemu [10]. Ob neprimerni pH-vrednosti se bakterije niso več sposobne vezati med seboj in kosmi aktivnega blata začnejo razpadati. Iz slike 3 so razvidne vrednosti temperatur tekstilne modelne odpadne vode v bioenoti in izmerjene pH-vrednosti vhodne odpadne vode, biološko čiščene vode v bioenoti ter permeata v odvisnosti od časa obratovanja procesa.

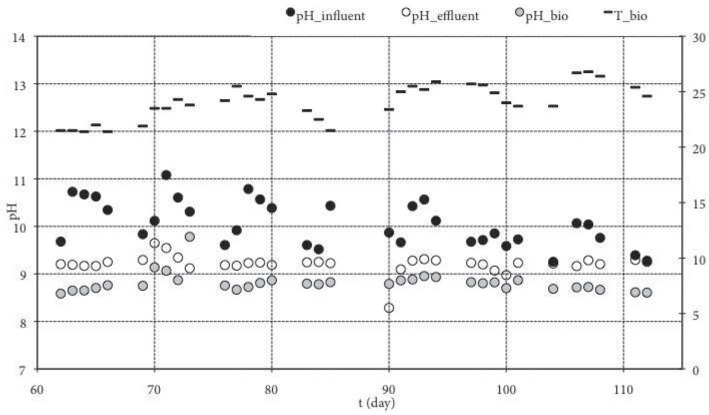

Figure 3: pH value and temperature depending on time

pH- vrednosti modelne odpadne vode so bile med 8,5 in 11, medtem ko je optimalna pH-vrednost za biološko čiščenje okrog 7 [1]. Če je pH-vrednost prenizka ali previsoka, kosmi izgubijo na trdnosti, ker se bakterije niso več sposobne vezati med seboj. Tudi pH izhodne vode je ostal relativno visok. Aktivnost mikroorganizmov je občutljiva na zunanje razmere, med katere spada tudi pH, zato je treba pred biološko predobdelavo regulirati pH.

Določali smo koncentracije KPK (slika 4) laboratorijsko pripravljene vode in očiščene vode na izhodu iz membrane UF, ki je bila pred tem biološko obdelana v bioenoti. Povprečne vrednosti KPK pripravljene odpadne vode so bile od 2000 do 2500 mg/L, medtem ko so le-te na izhodu iz MBR znašale med 200 in 600 mg/L. Bistveno zmanjšanje vrednosti KPK je rezultat kombinacije biološke enote in nadaljnjega čiščenja v sistemu z membrano, kar omogoča biološko obdelavo odpadne vode in nadaljnje fizikalno čiščenje. Nekatere rezultate kemijskih analiz za KPK smo ovrednotili z učinkovitostjo čiščenja (R_E), iz katere smo lahko razbrali, ali smo dosegli zadovoljivo stopnjo učinkovitosti čiščenja modelne tekstilne odpadne vode. Učinkovitost zmanjševanja KPK in starost vode v MBR med obratovanjem v juniju in juliju 2009 prikazuje slika 5.

bind together and the activated sludge flakes began to fall apart. Figure 3 shows the temperature and measured pH values as a function of the operational process time, as measured in the modelled textile wastewater, in the bio-unit, and the permeate.

The pH values of the modelled wastewater were 8.5–11, whilst it is known that the optimum pH value for a biological treatment is about 7 [1]. If pH is too low or too high, the strengths of the flakes decrease, as the bacteria are no longer able to bind together. The pH value for the wastewater leaving the bio-unit remained relatively high. The microbial activity is sensitive to external conditions, e.g. pH value; therefore, it was necessary to adjust pH before the biological pretreatment.

The COD values (cf. Figure 4) of the modelled wastewater and permeate were determined. The COD values of the modelled wastewater averaged between 2000 to 2500 mg O_2*/L, whilst after the MBR treatment, the permeate COD averaged between 200 and 600 mg* O_2*/L. A significant reduction in the COD value was a result of the combination of biological and membrane treatments within the MBR system.*

The COD removal efficiency (R) was calculated according to Equation 1, which showed whether a satisfactory level of the purification performance was achieved for the modelled textile wastewater. The COD removal efficiencies and hydraulic retention times within MBR during the operations during June and July 2009 are shown in Figure 5.

The hydraulic retention time is the time the wastewater remains in the tank. The purpose of measuring these parameters was to show the correlation of hydraulic retention time and COD removal efficiency. It is well-known that a higher hydraulic retention time enables a lower oxygen demand for the same effect at lower mixed liquor suspended solids MLSS in activated sludge [11]. The lower the MLSS, the lower the operational costs. Figure 5 shows the linear correlation of COD removal and hydraulic retention times until day 4, then the COD removal decreased. The average COD removal efficiencies were between 60 and 90%, which is lower than that found in the literature [12]. Detailed calculations showed that the COD re-

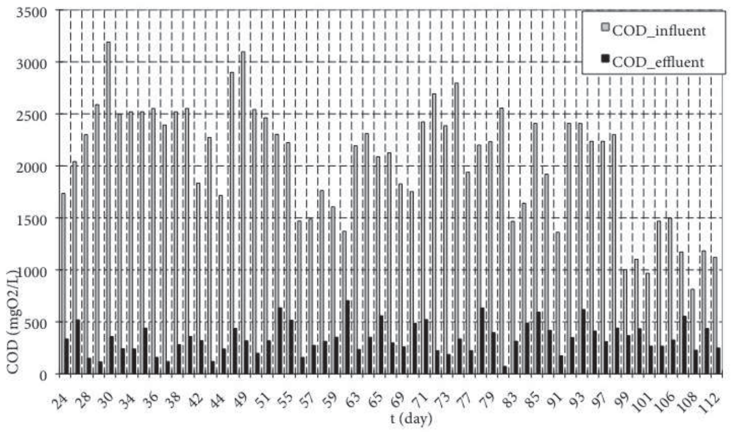

Figure 4: COD concentration depending on time

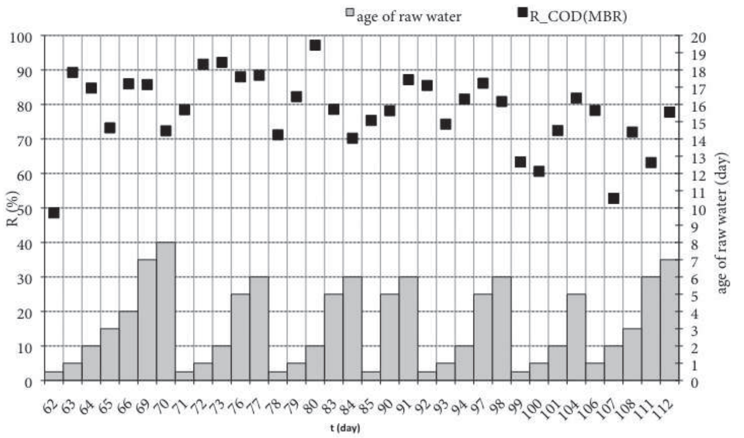

Figure 5: COD removal efficiency and correlation using hydraulic retention time

S parametrom starost odpadne vode smo hoteli prikazati, kako dolgo se je modelna odpadna voda nahajala v rezervoarju in kako starost odpadne vode vpliva na učinkovitost razgradnje KPK. Ugotovili so namreč, da je z višjo starostjo odpadne vode potrebnega manj kisika za enak učinek čiščenja pri nižji koncentraciji aktivnega blata [11], kar občutno zniža obratovalne stroške. Iz slike 5 je razvidno, da znižanje vrednosti KPK narašča linearno s starostjo modelne odpadne vode do 4. dne, nato začne upadati. Povprečne učinkovitosti zmanjševanja KPK so med 60 in 90 odstotki, kar je nekoliko nižje, kot navajajo drugi avtorji [12]. Iz podrobnejših izračunov in primerjave med učinkovitostjo biološkega čiščenja in spremembo učinkovitosti po ultrafiltraciji smo ugotovili, da se večji del modelne tekstilne odpadne vode očisti biološko po kombinaciji aerobnega in anoksičnega dela. Ultrafiltracija je izboljšala učinek zmanjševanja KPK vrednosti predvsem takrat, ko je bila učinkovitost v bioenoti nizka (R_{EKPK} < 50 %). V povprečju se je po ultrafiltraciji izboljšala učinkovitost zmanjševanja KPK za 10 do 20 odstotkov.

Slika 6 prikazuje koncentracijo amonijevega dušika v odvisnosti od časa obratovanja procesa. Ker je za nitrifikacijo potrebna zado-

moval efficiency was the highest after the biological treatment and lower after the ultrafiltration. The latter improved the COD removal efficiency in the case of low efficiency in the bio-unit (R_{ECOD} < 50%). The average improvement in the COD removal efficiency after the ultrafiltration was calculated at between 10 to 20%.

Figure 6 shows the concentration of ammonia nitrogen depending on time. The nitrification runs at a certain oxygen level; therefore, the measurements of oxygen concentrations were conducted within the aerobic zone. They were between 0.5 and 3 mg/L O_2. NH_4^+ was determined in the modelled wastewater (NH_4^+_influent) together with the biologically-treated wastewater (NH_4^+_bio) and MBR-treated wastewater (NH_4^+_effluent). Figure 6 shows a NH_4^+ concentration decrease, which means that complete nitrification could be reached.

The colour of the water was determined at three wavelengths, i.e. 436 nm (yellow range), 525 nm (red range) and 620 nm (blue range), for the dye blend. The results are presented in Figure 7.

The SAC values for the modelled wastewater at λ = 436 nm oscillated between 400 and 650 m^{-1}, and at λ = 525 nm and λ = 620 nm between 250 and 500 m^{-1}. The higher the hydraulic retention time, the higher the SAC value determined as a consequence of the suspended solid sedimentation in the modelled wastewater. The permeate SAC at λ = 436 nm oscillated between 100 and 200 m^{-1}, and at λ = 525 nm and λ = 620 nm between 0 and 100 m^{-1}. If the modelled wastewater SAC decreases, the dye concentration also decreases. The colour removal efficiency at all three wavelengths was high and oscillated at between 75 and 95%, whilst at λ = 620 nm, it was between 85 and 98%.

The colour removal efficiency of the modelled textile wastewater at λ = 525 nm oscillated between 80 and 90% until day 56, then further between 60 and 80%. The worst results were due to the oscillation in the oxygen concentration within the anoxic phase, where the aerobe organisms developed and prevailed over the anoxic ones due to a high oxygen concentration [13].

The colour removal efficiency of the modelled textile wastewater at λ = 436 nm ($R_{SAC(436)}$) was

stna količina kisika, smo opravili potrebne meritve koncentracije kisika v bioenoti in so znašale od 0,5 do 3 mg/L O_2. Koncentracijo NH_4^+ smo spremljali v modelno pripravljeni odpadni vodi (NH_4^+_vhod), biološko predelani odpadni vodi (NH_4^+_bio) ter očiščeni odpadni vodi z MBR (NH_4^+_izhod). Iz slike 6 je razvidno upadanje koncentracije NH_4^+, kar je posledica popolne nitrifikacije procesa.

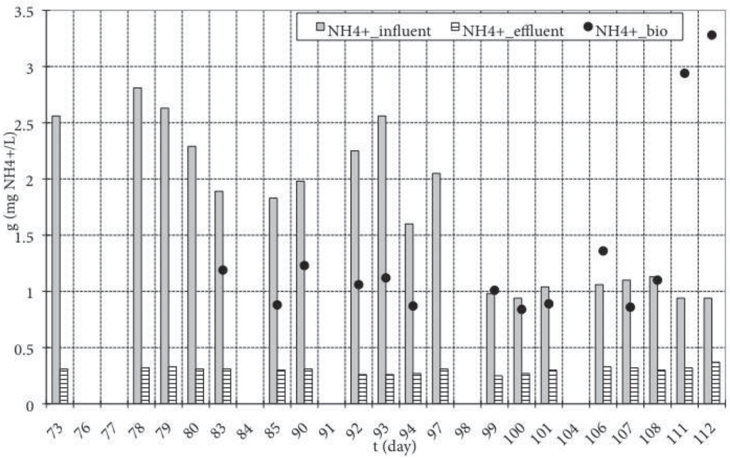

Figure 6: Concentration of NH_4^+ depending on MBR operational time

Obarvanost vode smo določili fotometrično pri treh valovnih dolžinah, in sicer pri 436 nm v rumenem območju, 525 nm v rdečem območju in 620 nm v modrem območju za mešanico barvil. Rezultati meritev so prikazani na sliki 7.

Vrednosti SAK vhodne raztopine pri λ = 436 nm nihajo v povprečju med 400 in 650 m^{-1}, pri valovnih dolžinah λ = 525 nm in λ = 620 nm pa med 250 in 500 m^{-1}. S staranjem odpadne vode se SAK povečuje, kar je posledica usedanja suspendiranih organskih in anorganskih snovi v vhodni modelni odpadni vodi. Vrednosti SAK permeata pri λ = 436 nm nihajo med 100 in 200 m^{-1}, pri λ = 525 nm in λ = 620 nm so vrednosti SAK med 0 in 100 m^{-1}. Zmanjšanje absorpcijskega spektralnega koeficienta (SAK) kaže na zmanjšanje koncentracije barvila v očiščeni tekstilni modelni odpadni vodi. Učinkovitost zniževanja obarvanosti modelne tekstilne odpadne vode je pri vseh treh valovnih dolžinah visoka in se giblje med 75 – 95 odstotki, pri λ = 620 nm pa je v povprečju med 85 in 98 odstotki.

Učinkovitosti zniževanja obarvanosti modelne tekstilne odpadne vode pri λ = 525 nm nihajo med 80 in 90 odstotki do 56. dneva obratovanja, medtem ko v nadaljnjih dneh nihajo med 60 in 80 odstotkov. Slabši rezultati so posledica nihanja v koncentraciji kisika na anoksični stopnji, pri čemer se razvijejo aerobni organizmi, ki prevladajo nad anoksičnimi [13].

Učinkovitosti zniževanja obarvanosti modelne tekstilne odpadne vode pri λ = 436 nm ($R_{SAK(436)}$) je v primerjavi z drugimi vrednostmi ($R_{SAK(620)}$ in $R_{SAK(525)}$) relativno majhna. Zmanjšana učinko-

relatively low in comparison with λ = 525 and λ = 620 ($R_{SAC(620)}$ and $R_{SAC(525)}$). The reason was the low biodegradability of the yellow dye. Until day 56, $R_{SAC(436)}$ was between 70 and 90%. After day 56, $R_{SAC(436)}$ decreased and was 45–70%.

5 Conclusion

This research into wastewater treatment using MBR showed the effectiveness of the MBR technology. The COD values for the MBR-treated wastewater were between 200 and 600 mg O_2/L, which indicates the removal efficiency of COD being between 50 and 97%, depending on the hydraulic retention time. The optimal hydraulic retention time was determined to be 3–4 days. The efficiency was not influenced by the wastewater flow. The research confirmed that the oxygen concentration within the aerobic and anoxic zone is crucial for the wastewater quality. The chemical analysis showed the removal efficiencies of the blue and red dyes to be 70–90%. The yellow dye was not biodegradable and the removal efficiency was thus lower. Ammonia nitrogen was satisfactorily removed. All these facts prove the effectiveness of MBR for the textile wastewater treatment. The type of MBR is very important, including the separated tanks for the nitrification and denitrification of azo dyes. If the legislation is taken into account (UL RS 7/2007), NH_4^+ could be successfully removed for a discharge into the environment; as 0.3 mg/L NH_4^+ was below the allowed value of 5 mg/L. Nevertheless, the COD and SAC values were too high for a discharge: COD was above 200 mg O_2/L and at λ = 436 nm, the permitted value is set at 7.0, whilst the results were between 100 and 200 m^{-1}; at λ = 525 nm, the permitted value is set at 5.0 m^{-1}, whilst the results were between 0 and 100 m^{-1}, and at λ = 620 nm, the permitted value is set at 3 m^{-1}, the results being between 0 and 100 m^{-1}. In regard to the removal efficiency, the results were satisfactory (50–97%), since they reduce the operating costs regarding ecological taxes. The nanofiltration or reverse osmosis additionally improved the wastewater quality. Such treated water could be reused in various industrial processes.

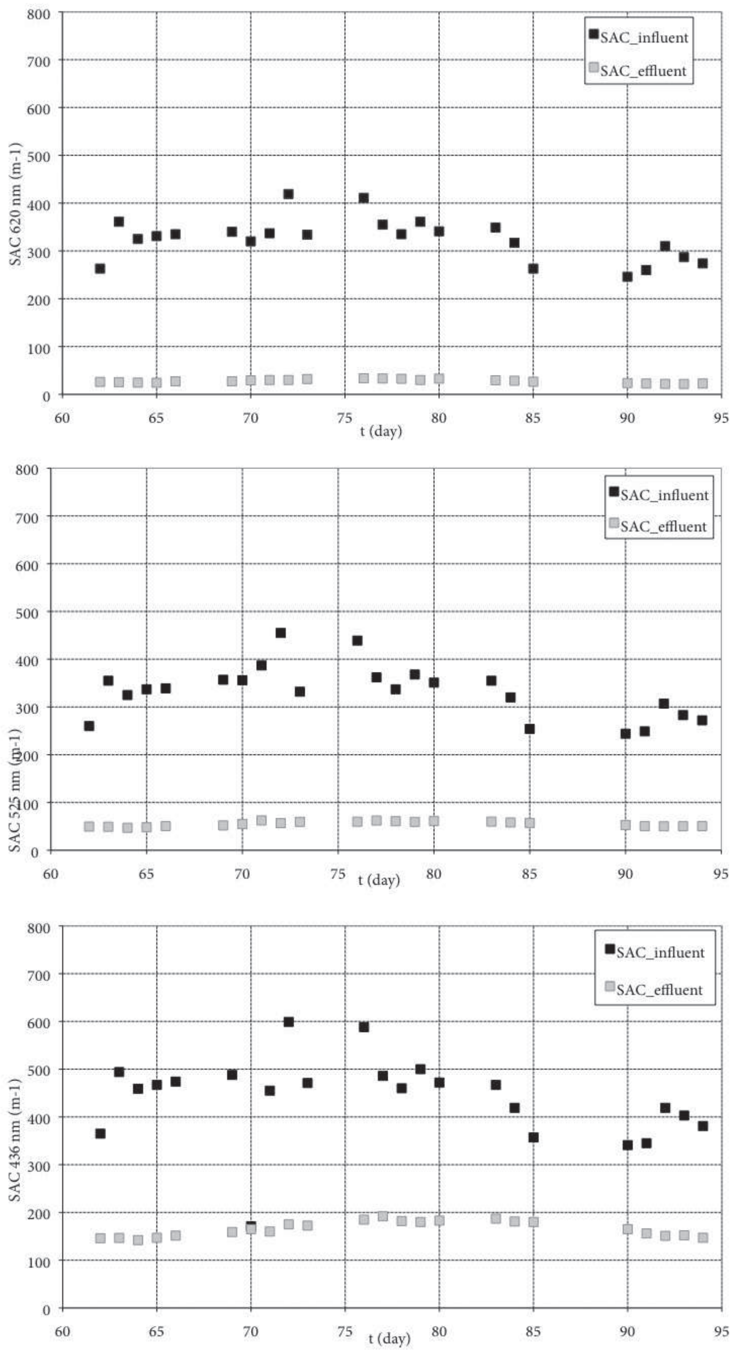

Figure 7: Modelled textile wastewater expressed with SAC as function of operational process time for a) λ = 620 nm, b) λ = 525 nm and c) λ = 436 nm

vitost SAK je posledica težje razgradljivosti rumenega barvila. Do 56. dneva obratovanja znaša $R_{SAK(436)}$ od 70 do 90 odstotkov. Od 56. dneva naprej se $R_{SAK(436)}$ zmanjša in znaša v povprečju od 45 do 70 odstotkov.

5 Sklep

V raziskavi obdelave modelne odpadne vode z MBR smo pokazali, da smo dosegli zadovoljive rezultate izhodne očiščene odpadne vode glede na vhodne vrednosti. Vrednosti KPK na izhodu iz MBR so bile od 200 do 600 mg O_2/L, kar pomeni od 50- do 97-odstotno učinkovitost odstranjevanja, to je odvisno od starosti pripravljene modelne odpadne vode. Najvišji učinek znižanja KPK smo dosegli pri 3 do 4 dni stari odpadni vodi. Pretok vode ni bistveno vplival na čiščenje modelne tekstilne vode. Naše raziskave so potrdile, da je koncentracija kisika v aerobni in anoksični coni izjemno pomemben dejavnik, ki vpliva na kakovost očiščene vode. Iz kemijskih analiz očiščene vode je razvidno, da smo pri odstranjevanju modrega in rdečega barvila dosegli od 70- do 90-odstotno učinkovitost. Odstranjevanje rumenega barvila iz modelne tekstilne odpadne vode je bilo zmanjšano, kar pripisujemo njegovi težji razgradljivosti v biološkem delu bioreaktorja. Dosegli smo zadovoljive vrednosti zmanjšanja koncentracij amonijevega dušika. Vse navedene raziskave dokazujejo primernost tehnologije membranskega bioreaktorja za čiščenje tekstilnih odpadnih voda. Pri tem je pomembna izvedba posebnega reaktorja z ločenimi rezervoarji, ki omogočajo nitrifikacijo in denitrifikacijo za razgradnjo azobarvil, ki prevladujejo v odpadnih vodah tekstilne industrije. Če upoštevamo ustrezno uredbo (UL RS 7/2007), lahko za dosežene vrednosti merjenih parametrov povzamemo, da bi glede na vrednosti NH_4^+ ionov permeate lahko odvajali neposredno v vode, saj s povprečno vrednostjo koncentracije 0,3 mg/L ne presegajo mejne vrednosti 5 mg/L, medtem ko vrednosti KPK v večini primerov presegajo mejno vrednost 200 mg O_2/L za odvajanje neposredno v vode, prav tako tudi SAK, in sicer pri vseh treh valovnih dolžinah (pri λ = 436 nm je mejna vrednost 7,0 dosežene vrednosti pa med 100 in 200 m^{-1}; pri λ = 525 nm je mejna vrednost 5,0 m^{-1}, dosežena pa med 0 in 100 m^{-1} in pri λ = 620 nm je mejna vrednost 3 m^{-1}, dosežena pa 0–100 m^{-1}). Kljub temu smo lahko zadovoljni z visoko učinkovitostjo odstranjevanja omenjenih parametrov (50–97 odstotkov), saj bi tako lahko močno zmanjšali stroške plačevanja okoljskih dajatev ob izpustu v javno kanalizacijo. Ob dodatni uporabi membranskih filtracij, kot je nanofiltracija oz. reverzna osmoza, pa lahko dosežemo visoko kakovost očiščene odpadne vode, ki bi ustrezala zahtevam po ponovni uporabi te vode kot tehnološke vode v industrijskih procesih.

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