Environmental Engineering and Management Journal

November 2018, Vol. 17, No. 11, 2667-2676 http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu



"Gheorghe Asachi" Technical University of Iasi, Romania



TREATMENT OF AN AZO DYE - CONTAINING WASTEWATER IN INTEGRATED ANAEROBIC-AEROBIC MEMBRANE SEQUENCING BATCH REACTOR (MSBR) AT DIFFERENT HYDRAULIC RETENTION TIMES (HRTS)

Maryam Hasani Zonoozi^{1,2*}, Mohammad Reza Alavi Moghaddam¹, Reza Maknoon¹

¹Civil and Environmental Engineering Department, Amirkabir University of Technology, Hafez Ave., Tehran15875-4413, Iran ²Civil Engineering Department, Iran University of Science and Technology, Narmak, Tehran, 16846-13114, Iran

Abstract

In this study, application of integrated anaerobic-aerobic membrane sequencing batch reactor (MSBR) for treatment of an azo dyecontaining wastewater was investigated. For this purpose, three lab-scale MSBR systems were operated at various hydraulic retention times (HRT) of 48, 24 and 16 h with constant value of solid retention time (SRT) for all reactors. The treatment performance and the decolorization kinetic of the systems as well the fouling rate of the membranes were evaluated during the experiment period. Based on the results, COD removal efficiency was not significantly influenced by HRT, while the decolorization efficiencies declined considerably by decreasing the HRT. Incomplete decolorization of the dye, even during the longest anaerobic stage (HRT of 48 h), revealed that a longer anaerobic period was still required for complete decolorization of the selected dye. Decolorization profiles of all MSBRs followed zero-order kinetics. These profiles experienced faster descending rates at lower HRTs. Lower HRTs of 16 and 24 h resulted in higher TMP (transmembrane pressure) rising rates. The most acceptable performance of the MSBR system from the viewpoint of decolorization efficiency and membrane fouling was obtained for the MSBR operating at the highest HRT (48 h).

Key words: azo dye-containing wastewater, hydraulic retention time, integrated membrane sequencing batch reactor

Received: September, 2013; Revised final: January, 2015; Accepted: February, 2015; Published in final edited form: November, 2018

1. Introduction

Dyes are one of the most important groups of chemical compounds, which are widely used in many industrial sectors. Among the different classes of dyes, azo dyes represent the largest class of dyes applied in majority of the dye-consuming industries (Saratale et al., 2011; Van der Zee and Villaverde, 2005). More than 50% of the dyes and colorants produced annually and used worldwide are of the azo class, which are characterized by one or more nitrogen-nitrogen double bond (-N=N-), called azo group, as part of their

molecular structure (Meng et al., 2012; Stolz, 2001). Besides the aesthetic problems, toxicity, carcinogenicity and mutagenicity of many azo dyes and their breakdown products to human and aquatic life have been proven (Saratale et al., 2011; Van der Zee and Villaverde, 2005). Therefore, their removal from wastewaters before discharging into the receiving natural environments is of high importance.

Various physical, chemical and biological treatment technologies have been applied to remove azo dyes from wastewaters, and each of them has its advantages and drawbacks (Pajootan et al., 2016;

^{*}Author to whom all correspondence should be addressed: e-mail: mhzonoozi@iust.ac.ir, maryamzonooz@yahoo.com; Phone: +98-21-7322-8194; Mobile: +98-912-2898341; Fax: +98-21-77240398.

Saratale et al., 2011; Van der Zee and Villaverde, 2005). Owing to complete mineralization of the azo dyes and other organic pollutants at relatively low costs, biological processes have been recognized as eco-friendly and cost-competitive options for treatment of azo dye-containing wastewaters (Ozkan-Yucel and Gokcay, 2017; Saratale et al., 2011; Spagni et al., 2010). Bacterial decolorization and degradation of the azo dye molecules, generally arises through a two-stage anaerobic-aerobic process. Briefly, anaerobic stage involves the reductive cleavage of the dye's azo linkages, resulting in the formation of potentially hazardous colorless aromatic amines, while through aerobic stage, degradation of the aromatic metabolites occurs (Van der Zee and Villaverde, 2005).

Among different biological methods. sequencing batch reactor systems (SBRs) and their modified configurations (modified SBRs) have been efficiently used for treatment of azo dye-containing wastewaters due to some advantages of SBRs such as high operational flexibility and tolerance against shock loads and peak flows (Hakimelahi et al., 2016; Lotito et al., 2011). Some researchers (You and Teng, 2009a, 2009b; You et al., 2010; Zuriaga-Agusti et al., 2010) have recently investigated coupling of membrane separation with SBR technology as a novel modified SBR system for dye-containing wastewater treatment. In most of the mentioned studies, a fully anaerobic SBR was coupled with a fully aerobic membrane bioreactor (MBR), each operating in separate reactors. To the best of our knowledge, precise reports on the use of integrated anaerobicaerobic membrane sequencing batch reactors (integrated MSBRs) for treatment of azo dyecontaining wastewaters are not available. As well, the influence of important operational parameters, especially hydraulic retention time (HRT), on the performance of these systems and on the azo dye decolorization kinetics has not been clearly studied.

The main aim of the present work was to evaluate the treatment performance and the decolorization kinetics of integrated anaerobicaerobic MSBR system for treatment of azo dyecontaining wastewater, at three different HRTs. The influence of HRT on membrane fouling was also investigated.

2. Material and methods

2.1. Composition of the synthetic wastewater

The synthetic dye-containing wastewater was prepared using tap water and composed of 750 mg/L glucose (corresponding to about 750 mg/L readily biodegradable COD), urea (80 mg/L), KH₂PO₄ (33.5 mg/L) and azo dye, AR18 at concentration of 100 mg/L (corresponding to about 60 mg COD/L). The azo dye AR18 was of commercial grade with the purity of more than 98% and purchased from AlvanSabet Company (Iran). It is among the most widely used dyes in textile industry in Iran. The main characteristics of the dye AR18 are summarized in Table 1.

2.2. Experimental set-up and operating conditions

Three MSBRs were made up of Plexiglas with a working volume of about 14 L each. Each reactor had a 190 cm² trapezoidal cross-section with 90 cm height. A 0.4 μ m polyethylene Kubota flat sheet membrane with area of 0.11 m² was located in the lower part of each reactor. Fig. 1 shows a schematic representation of the MSBRs set-up.

Table 1. Chemical structure and general characteristics of
the dye AR18 (Hosseini Koupaie et al., 2013)

Parameter	Value				
Color Index	16255				
CAS Number	2611-82-7				
Chemical formula	$C_{20}H_{11}N_2Na_3O_{10}S_3$				
Molecular weight (g/mol)	604.5				
λ_{max} (nm)	507				
Molecular structure					

The reactors were run for about three months according to a time-schedule consisting of four phases including feeding, reaction, drawing and idle. The reaction phase included the subsequent alternating anaerobic and aerobic stages. Anaerobic and aerobic conditions of each reactor were provided using a magnetic stirrer (rotation speed of 100 rpm) and two air compressors (total flow rate of 10 L/min for each reactor), respectively. Aeration was done through a Plexiglas diffuser containing 2 mm holes with 2 cm intervals, located underneath the membrane module to supply air for biological aeration and air-scouring of the membranes, as well. Feeding of the reactors was done by the use of an injection pump (Etatron, DLS-MA, Italy) and permeate was extracted using a peristaltic pump (Heidolph, PD 5201, Germany) sited on the permeate line.

The volume exchange ratio (VER) of 0.5 was kept constant during the experiments for all reactors. Thus, in the filling phase (the first 20 minutes of the anaerobic stage), about 7 liters of new synthetic wastewater was supplied to each reactor and in the drawing phase (the last 120 minutes of the aerobic stage), the same amount of the effluent was withdrawn through the membranes. Operation modes of the three MSBRs are shown in Fig. 2. A sludge retention time (SRT) of about 23 days was imposed to the three reactors by daily purging of a constant volume of mixed liquor before permeate extraction through the membranes.



Fig. 1. A schematic diagram of the MSBR lab-scale set-up (1 - inlet section, 2 - converging section, 3 - throat, 4 - diffuser, 5 - outlet section, 6 - spray nozzle, 7 - mist eliminator)

All experiments were conducted at room temperature. Other key operating parameters of MSBR systems are listed in Table 2.

Table 2. Key operating parameters of MSBR systems

Parameter	Reactors				
1 arameter	MSBR1	MSBR2	MSBR3		
HRT (h)	48	24	16		
Treatment cycles per day	1	2	3		
Cycle time	24	12	8		
Organic loading rate	810	1620	2430		
$(OLR) (mg COD/L.d)^*$	mg/L.d	mg/L.d	mg/L.d		
Flux (L/m ² h)	36.4	36.4	36.4		
Filtration mode	Intermittent suction mode: 260s on/40s off				

The operation of the cycles in three MSBRs was controlled using a laboratorial program and a controller, which linked between the program and the set-up elements including solenoid valves, peristaltic and injection pumps, level sensors (for announcing in the case of any malfunction), air pumps and stirrers.

Transmembrane pressure (TMP) was also monitored using a pressure transmitter (Sensys, Korea) located in the effluent line. Data of TMP were recorded by the aforementioned laboratorial program every 60 seconds during each of the filtration events.

2.3. Seeding of the reactors

Activated sludge from a local municipal wastewater treatment plant (Sahebgharanieh Wastewater Treatment Plant, Tehran, Iran) was used for seeding of the MSBRs. After seeding, the sludge was allowed to acclimate to the synthetic wastewater by gradual increasing of the COD and dye concentrations until reaching the final desired values. Membranes were introduced into the reactors after the complete adaptation period.

2.4. Analytical methods

Chemical oxygen demand (COD), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured according to the procedures outlined in Standard Methods for Examination of Water and Wastewater (APHA, 1998). The maximum absorbance of the dye AR18 (λ max=507), was determined according to the scanning pattern performed on HACH spectrophotometer DR/4000 (USA), with the background of tap water. The dye concentration of the samples and the decolorization efficiencies were determined by using the previously developed absorbance-concentration curve of the dye. Samples for measurement of the dye and COD concentrations were centrifuged at 6000 rpm for 10 min, before the analysis. MATLAB software (release v. 7.10) was used for fitting the decolorization kinetic data to the kinetic models.

2.5. Statistical analysis of data

In order to find out whether the differences observed between the three MSBRs are meaningful or not, the experimental data were analyzed by one-way ANOVA (95% confidence interval) using MINITAB software.



Fig. 2. Operation modes of the three MSBRs

For this purpose, the experimental data obtained after reaching the steady state condition (approximately the last 40-45 days of the operation period) were utilized.

3. Results and discussion

3.1. Effect of HRT on biomass concentration

Three reactors reached a steady state condition in terms of MLSS concentration after about 35 days of operation, when MLSS concentrations became relatively constant. As illustrated in Fig. 3, with decreasing the HRT, the MLSS values increased. The mean steady state MLSS concentrations were about 2694±354, 3966±278 and 5176±301 mg/L, for HRTs of 48, 24 and 16 h in reactors 1, 2 and 3, respectively. Statistical analysis showed significant difference between the mean MLSS concentrations in three MSBRs (P<10⁻³, F=173.4). The F/M ratio also showed a meaningful increase with decreasing the HRT. The mean steady state F/M ratios for MSBRs 1, 2 and 3 were 0.31±0.04, 0.41±0.03 and 0.47±0.03 mg COD/mg MLSS. d, respectively (P<10⁻³, F=66.6). The results can be explained in terms of the organic loading rate (OLR) in three MSBRs. As presented in Table 2, by decreasing the HRT from 48 h in MSBR1 to 16 h in MSBR3, the OLR increased from 810 mg/L.d to 2430 mg/L.d. This increase in the OLR resulted in an increase in the F/M ratio from MSBR1 to MSBR3 and consequently the MLSS concentration increased as well. Increase of MLSS concentration with decreasing the HRT has also reported by other researchers (Pajoum Shariati et al., 2011; Scheumann and Kraume, 2009).

3.2. Effect of HRT on COD removal efficiency

Changes of the COD removal efficiency and the effluent COD concentration at the end of the

aerobic stage during the operation time of three MSBRs are shown in Fig. 4.



Fig. 3. Variation of MLSS concentrations in three MSBRs during the operation time



Fig. 4. Variation of the COD removal efficiency and the effluent COD concentration at the end of the aerobic stage in three MSBRs

As seen in Fig. 4, the COD removal efficiency in all MSBRs was high and relatively constant during the entire experiment period. It is noteworthy that the slight decrease in the COD removal efficiency recorded around the 35th day of the operation (marked with dashed line) was simultaneous with the dye insertion into the reactors. Data of the mean COD removal efficiency during different stages of the treatment cycle after the 40th day of the MSBRs operation are presented in Table 3. According to the table, there are small differences between three MSBRs in terms of the COD removal efficiency during different stages of the treatment cycle. However, statistical analysis using one-way ANOVA (95% confidence interval) indicated that the observed differences were not meaningful (P>0.05). Therefore, it can be concluded that changing the HRT between 16-48 h did not have significant effect on the COD removal efficiency. This result is in agreement with those reported by Viero and Sant'Anna Jr (2008), according to which, in treatment of a synthetic wastewater containing easily biodegradable compounds, HRT did not influence the COD removal efficiency of MBR system. While, for treatment of a complex industrial wastewater (petroleum refinery), even small variation on HRT affected the COD removal efficiency of the same system (Viero and Sant'Anna Jr, 2008).

According to Table 3, most portion of COD removal was achieved in the anaerobic stage in all three MSBRs. The results of the COD removal kinetics study for three MSBRs (data not presented) showed that about 80% of the influent COD was consumed rapidly in the first hours of the anaerobic stage. This result is in agreement with those reported by some other researchers (Hakimelahi et al., 2012; Kapdan and Ozturk, 2005; Yasar et al., 2012; Zuriaga-Agusti et al., 2010). Adsorption of organic matter onto the biomass flocs and the rapid assimilation of the readily biodegradable organic matter by certain aerobic bacteria subjected to stress conditions in anaerobic phase, were the main reasons reported by the study group of Zuriaga-Agusti (2010) for this phenomenon. Yasar et al. (2012) also explained that since anaerobic stage was the first stage of the treatment cycle, the primary substrate was rapidly consumed in the anaerobic stage by microorganisms to serve as electron donor.

Another noticeable point regarding the data given in Table 3 is that the removal of the remained COD during the aerobic stage (inside the reactor) was very low for all three MSBRs (only about 3%). Inadequate amount of the remained organic matter after the anaerobic stage has been reported as the main reason for such low COD removal rate during the aerobic stage (Kapdan and Ozturk, 2005; Yasar et al., 2012).

Measuring the COD of the aerobic samples extracted from the membranes showed that membrane filtration slightly increased the overall COD removal efficiencies of the MSBRs. This could be explained by the layer of biofilm that was formed on the membranes' surface and acted as the final consumer of the COD existing in wastewater crossing the membrane. In agreement with this result, Qu et al. (2009) reported that in a bioaugmented MBR system, the average values of COD removal for the supernatant and the membrane effluent were about 30% and 50%, respectively. Wang et al. (2009) also reported that the dense layer of biofilm formed on the membrane surface enhanced the COD removal of MBR system due to rejection capability of large soluble molecules.

3.3. Effect of HRT on decolorization process of AR18

As shown in Fig. 5, the relative steady color removal in three MSBRs was achieved on the 50th day of the operation (about 20 days after the first dye insertion into the reactors). The results of the UV-Vis spectrum analysis (data not presented) showed that the main drop of the influent absorbance peak at 507 nm occurred at the end of the anaerobic stage and the contribution of the aerobic stage to decolorization was almost none.

Decreasing the length of the anaerobic stage as a consequence of decreasing the HRT resulted in considerable reductions in color removal efficiencies. The mean steady state decolorization efficiency at the end of the anaerobic stage was 78.7±4.9%, 59.9±5.3% and 52.9±4.1% for HRTs of 48, 24 and 16 h, respectively. The meaningful differences between the color removal efficiencies of three MSBRs (P<10-3, F=46.1) indicated the significant influence of HRT/length of the anaerobic stage on decolorization of the dye AR18. In addition, as the color removal did not complete even during the longest anaerobic stage in MSBR1, it could be concluded that a longer period for anaerobic stage is required to attain complete decolorization of AR18 from aqueous solution with dye and COD concentrations of 100 and 750 mg/L, respectively.

 Table 3. Mean values of COD removal efficiency during different stages of the treatment cycle after the 40th day of the MSBRs operation

Treatment stage		ANOVA analysis results			
	MSBR1	MSBR2	MSBR3	F	Р
Anaerobic stage (samples from inside the reactor)	88.0 ± 3.0	86.8 ± 3.3	84.4 ± 1.2	2.6	0.11
Aerobic stage (samples from inside the reactor)	3.2 ± 2.9	2.5 ± 2.4	2.6 ± 2.8	0.11	0.9
Membrane filtration (samples extracted from the membranes)	3.6 ± 2.2	3.7 ± 2.2	6.5 ± 3.1	2.2	0.16



Fig. 5. Variations of the anaerobic AR18 decolorization efficiency during the operation time

Other researchers (Dos Santos et al., 2005; Van der Zee and Villaverde, 2005; Yasar et al., 2012) have also reported positive relation between the color removal efficiency and the length of the anaerobic stage. Dos Santos et al. (2005) who studied the decolorization of an azo dye in expanded granular sludge bed reactor (EGSB) at different HRTs reported that decreasing the HRT from 10 to 5 and then, to 2.5h in their bioreactor decreased the decolorization efficiency from 56 to 37 and to 13%, respectively.

However, Firmino et al. (2010) obtained different results as they reported that changing the HRT from 24 h to 12 h did not significantly affect the decolorization efficiency, indicating that the electron transfer was not a concern. Consequently, they concluded that the dye used in their study (Direct Red 28) was not a very recalcitrant dye. They also explained that since the effect of HRT on the decolorization efficiency is influenced by the dye structure and type of the reactor, different results are reported in literatures (Firmino et al., 2010).

The standard ORP-time profiles of three MSBRs are presented in Fig. 6. According to the figure in comparison with MSBRs 2 and 3, MSBR1 with the longest HRT exhibited a slightly more negative E_0 values during the anaerobic stage. Generally, it can be concluded from Fig. 6 that the ORP values during the anaerobic stages of the MSBRs, particularly MSBRs 2 and 3, were not sufficient for obtaining complete decolorization efficiency.

3.4. Effect of HRT on the dye decolorization kinetics

Kinetic studies of azo dye decolorization have been performed by some other researchers (Dafale et al., 2008; Hakimelahi et al., 2012; Hosseini Koupaei et al., 2012; Hosseini Koupaei et al., 2013; Kokabian et al., 2013; Lourenco et al., 2011, 2006; Yu et al., 2001). However, there is no or limited number of previous reports considering the effect of HRT on the azo dye decolorization kinetics. Therefore, the main aim of the present section is to allow a better understanding of the influence of HRT on the decolorization kinetic model and decolorization rate constants for the selected dye in MSBR systems

The most widely used model of the decolorization kinetic developed by Yu et al. (2001) is presented in Eq. (1):

$$\frac{dC}{dt} = -kM^m C^n \Rightarrow \left(\frac{C}{C_0}\right)^{l_n} = l - \frac{(l-n)kM^m}{C_0^{(l-n)}} t \quad (n \neq l)$$
(1)

where *t* is the time (min), *M* and *m* are the cell mass concentration (MLSS, mg/L) and its partial reaction order, *C* and n are the dye concentration (mg/L) and its partial reaction order, and *k* is the specific decolorization rate with a unit depending on the values of *m* and *n* (mg⁽¹⁻ⁿ⁾.L^(m+n-1)/mg^m.min).

Assuming a negligible cell growth or death during a steady state MSBR cycle (i.e., M^m = constant), Eq. (1) can be simplified to Eqs. (2) and (3) as zero and first order reaction models. In these models, kM^m is replaced by K_0 (zero-order decolorization rate constant, mg/L.min) and K_1 (first-order decolorization rate constant, 1/min). In order to find out the most appropriate kinetic model for anaerobic decolorization of AR18 in MSBRs, zero and first order kinetic models were investigated (Eqs. 2-3).

$$C = (-K_0 t) + C_0 \quad (n = 1)$$
 (2)

$$C = C_0 \exp(-K_1 t) \quad (n = 1)$$
(3)

Time-course profiles of the anaerobic AR18 decolorization and the obtained values of the two models' constants as well as the R-Square (R^2) and root mean standard error (s) values are presented in Table 4 and Fig. 7. According to Table 4, relative higher values of R^2 and lower values of s were obtained for zero-order kinetic model, indicating that the zero-order model gave a slight better fit of the experimental data than the first-order model. Furthermore, very small values of the first-order decolorization rate (K_1) imply that the AR18 decolorization profile actually followed zero-order kinetic in all three MSBRs.

Hosseini Koupaei et al. (2013) also studied the decolorization kinetics of the same dye (AR18) in anaerobic-aerobic fixed-bed sequencing batch biofilm reactor and reported that the decolorization profiles followed first-order kinetics. The difference between the results reported by the research group of Hosseini Koupaei and obtained in the present study were presumably due to the different operational and experimental conditions applied in the two studies. The most important different operational conditions in the two studies were the inocula type, the initial substrate (electron donor) and the treatment procedure. Based on the literature information reported by Lourenco et al. (2006), mono-azo dye decolorization has been reported to follow first-order kinetics by several authors, whereas other reports mentioned zero-order or even half-order kinetics.



Fig. 6. Standard ORP profile of three MSBRs during one treatment cycle (transition from anaerobic condition to aerobic condition is shown with arrows)

Table 4. Zero and first-order kinetic constants obtained for anaerobic decolorization in three MSBRs

	Kinetic order							
Reactors	Zero-order kinetic				First-order kinetic			
	Ko (mg /L.min)	$C_0(\text{mg/L})$	\mathbb{R}^2	S	K_l (1/min)	$C_0 (\mathrm{mg/L})$	\mathbb{R}^2	<i>S</i>
MSBR1 (HRT: 48 h)	0.052	60.17	0.989	1.039	12×10-4	63.08	0.974	1.586
MSBR2 (HRT: 24 h)	0.082	75.15	0.997	0.470	14×10 ⁻⁴	76.64	0.992	0.806
MSBR3 (HRT: 16 h)	0.108	81.57	0.994	0.554	16×10 ⁻⁴	82.30	0.992	0.639



Fig. 7. Time-course profile of anaerobic AR18 decolorization in three MSBRs and the fitted curves (a) zero-order kinetic, (b) first-order kinetic

They explained that different experimental conditions used in the reported studies might be responsible for such apparently contradictory kinetic results. Van der Zee et al. (2001) who studied the substrate dependency of an azo dye decolorization, also reported that the substrate type influences the decolorization rate of azo dyes. It is also noteworthy that according to the kinetic data shown in Fig. 7, the decolorization process started from the beginning of the anaerobic stage and continued until the end of the same stage. On the other hand, as mentioned previously, about 80% of the influent glucose (as the main electron donor) was consumed rapidly in the early hours of the anaerobic stage.

This implies that the required reducing equivalents for the reductive cleavage of the dye molecules' azo bonds were generated at a similarly high rate in all three MSBRs, however, transferring of them to the dye molecules via enzymatic activity continued until the end of the anaerobic stage. Comparing the decolorization rates in three MSBRs indicate that with decreasing the HRT the zero-order decolorization rate (K_0) increased. However, by normalizing the K_0 values by the corresponding biomass concentrations (normalized $K_0=K_0/MLSS$), a relative linear relationship was found between the MLSS concentration and the decolorization rate showing that the decolorization ability of biomass in a

certain length of time did not changed much by varying the HRT from 48 h to 16 h (Table 5).

Table 5. Ko and normalized Ko in three MSBRs

Parameter	Reactor				
1 urumeter	MSBR1	MSBR2	MSBR3		
K_0 (zero-order decolorization rate) (mg dye/L.min)	0.053	0.082	0.108		
<i>MLSS</i> concentration at the day of kinetic study (mg/L)	2804	4138	5450		
Normalized K_0 ($K_0/MLSS$) (mg dye/mg MLSS.min)	0.190× 10 ⁻⁴	0.198× 10 ⁻⁴	0.198× 10 ⁻⁴		

3.5. Effect of HRT on the TMP in three reactors

Data of the transmembrane pressure recorded by the laboratorial program during the operation period are shown in Fig. 8. Each point in the TMP graphs represents the average of more than 100 TMP data recorded during each of the filtration events. The scattered TMP values in the initial segment of the figure (marked with dashed ellipsoids) show the results of a pretest period for selecting the appropriate amounts of the flux (36.4 L/m².h) and the intermittent on/off suction time (260s on/40s off).Considering the results presented in Fig. 8, it can be found that the TMP rising rate in MSBRs 2 and 3 was much higher than that in MSBR1, which resulted in more frequent physical/chemical cleaning of the membranes in MSBRs 2 and 3. The mean TMP values during the operation time (except for the pretest period) for MSBRs 1, 2 and 3 were about 138.5, 164.2 and 173.2 mbar, respectively.

The obtained TMP data can be explained in terms of MLSS concentration in three MSBRs. Putting together the data presented in Figs. 3 and 8 suggests that membrane fouling rate increased with an increase in MLSS concentration. Some researchers (Chang and Kim, 2005; Psoch and Schiewer, 2006; Trussell et al., 2007) also reported that increase in MLSS concentration seemed to aggravate the membrane fouling. The filtration frequency can also be considered as another influencing factor on membrane fouling rates. Lower HRTs in MSBR systems correspond with more numbers of treatment cycles per day and consequently, higher filtration frequency and smaller relaxation time between two successive filtration periods. Increase of permeate withdrawal frequency per day has been accounted by Pajoum Shariati et al. (2011) as one of the causes for increase of the TMP rising rate with decreasing the HRT. Furthermore, prolonged relaxation periods have been reported by some authors (Bessiere et al., 2005; Vargas et al., 2008) to help the fouled membrane surface to be recovered and lead to decrease in the membrane fouling rate. The membrane fouling mechanisms of the MSBRs under the influence of HRT is discussed precisely in the previous work of the authors (Hasani Zonoozi et al., 2017).



Fig. 8. Comparison of the TMP trend between (a) MSBR1 (HRT: 48 h), (b) MSBR2 (HRT: 24 h) and (c) MSBR3 (HRT: 16 h)

4. Conclusions

According to the results, MLSS concentration, decolorization efficiency and TMP trend of three MSBRs were significantly influenced by HRT. Increasing the HRT from 16 to 48 h resulted in lower MLSS concentrations. However, better dye removal efficiencies were observed for higher HRTs. This implied that the length of the treatment period was more effective on decolorization efficiency than the MLSS concentration.

Moreover, more bio-fouling problems were exhibited for the two lower HRTs corresponded to higher MLSS concentrations and more filtration numbers per day. Other parameters including COD removal efficiency and decolorization kinetics were not much influenced by HRT.

Acknowledgements

The authors gratefully acknowledge the Amirkabir University of Technology (AUT) and the Iran National Science Foundation (INSF) for their funds and financial supports to provide the research materials and equipments. Ms. Lida Ezzeddinlou and Mr. Ehsan Hosseini Koupaie (former MSc. student) are also acknowledged for their kind assistance during the work.

References

- APHA, (1998), Standard Methods for the Examination of Water and Wastewater, 19th Edition, American Public Health Association, Washington, DC, USA.
- Bessiere Y., Bacchin P., Jefferson B., (2005), Dead-end filtration of natural organic matter: experimental evidence of critical conditions, *Desalination*, **175**, 29-36.
- Chang I.S., Kim S.N., (2005), Wastewater treatment using membrane filtration – effect of biosolids concentration on cake resistance, *Process Biochemistry*, **40**, 1307-1314.
- Dafale N., Wate S., Meshram S., Nandy T., (2008), Kinetic study approach of remazol black-B use for the development of two-stage anoxic–oxic reactor for decolorization/biodegradation of azo dyes by activated bacterial consortium, *Journal of Hazardous Materials*, 159, 319-328.
- Dos Santos A.B., Traverse J., Cervantes F.J., Van Lier J.B., (2005), Enhancing the electron transfer capacity and subsequent color removal in bioreactors by applying thermophilic anaerobic treatment and redox mediators, *Biotechnology and Bioengineering*, **89**, 42-52.
- Firmino P.I.M., Da Silva M.E.R., Cervantes F.J., Dos Santos A.B., (2010), Colour removal of dyes from synthetic and real textile wastewaters in one- and two-stage anaerobic systems, *Bioresource Technology*, **101**, 7773-7779.
- Hakimelahi M., Alavi Moghaddam M.R., Hashemi S.H., (2012), Biological treatment of wastewater containing an azo dye using mixed culture in alternating anaerobic/aerobic sequencing batch reactors, *Biotechnology and Bioprocess Engineering*, **17**, 875-880.
- Hasani Zonoozi M., Alavi Moghaddam M.R., Maknoon R., (2017), Investigation of HRT Effects on membrane fouling in Sequencing Batch Membrane Bioreactor

with Respect to Batch Filtration Mode, *Environmental Progress & Sustainable Energy*, **36**, 1785-1793.

- Hosseini Koupaie E., Alavi Moghaddam M.R., Hashemi S.H., (2012), Investigation of decolorization kinetics and biodegradation of azo dye Acid Red 18 using sequential process of anaerobic sequencing batch reactor/moving bed sequencing batch biofilm reactor, *International Biodeterioration and Biodegradation*, **71**, 43-49.
- Hosseini Koupaie E., Alavi Moghaddam M.R., Hashemi S.H., (2013), Evaluation of integrated anaerobic/aerobic fixed-bed sequencing batch biofilm reactor for decolorization and biodegradation of azo dye Acid Red 18: Comparison of using two types of packing media, *Bioresource Technology*, **127**, 415-421.
- Kapdan I.K., Ozturk R., (2005), Effect of operating parameters on color and COD removal performance of SBR: Sludge age and initial dyestuff concentration, *Journal of Hazardous Materials*, **123**, 217-222.
- Kokabian B., Bonakdarpour B., Fazel S., (2013), The effect of salt on the performance and characteristics of a combined anaerobic-aerobic biological process for the treatment of synthetic wastewaters containing Reactive Black 5, *Chemical Engineering Journal*, **221**, 363-372.
- Lotito A.M., Di Iaconi C., Fratino U., Mancini A., Bergna G., (2011), Sequencing batch biofilter granular reactor for textile wastewater treatment, *New Biotechnology*, 29, 9-16.
- Lourenco N.D., Novais J.M., Pinheiro H.M., (2001), Effect of some operational parameters on textile dye biodegradation in a sequential batch reactor, *Journal of Biotechnology*, **89**, 163-174.
- Lourenco N.D., Novais J.M., Pinheiro H.M., (2006), Kinetic studies of reactive azo dye decolorization in anaerobic/aerobic sequencing batch reactors, *Biotechnology Letters*, 28, 733-739.
- Meng X., Liu G., Zhou J., Fu Q.S., Wang G., (2012), Azo dye decolorization by *Shewanella aquimarina* under saline conditions, *Bioresource Technology*, **114**, 95-101.
- Ozkan-Yucel U.G., Gokcay C.F., (2017), Modeling of dye reduction by sludge digestion: combined effect of biochemical and chemical reduction, *Environmental Engineering and Management Journal*, **16**, 1543-1550.
- Pajootan E., Arami M., Bahrami H., (2016), Optimization of the combined UV/electrocoagulation process for dye removal from textile wastewater using Response Surface Methodology, *Environmental Engineering and Management Journal*, **15**, 189-198.
- Pajoum Shariati S.R., Bonakdarpour B., Zare N., Zokaee Ashtiani F., (2011), The effect of hydraulic retention time on the performance and fouling characteristics of membrane sequencing batch reactors used for the treatment of synthetic petroleum refinery wastewater, *Bioresource Technology*, **102**, 7692-7699.
- Psoch C., Schiewer S., (2006), Anti-fouling application of air sparging and backflushing for MBR, *Journal of Membrane Science*, 283, 273-280.
- Qu Y.Y., Zhou J.T., Wang J., Xing L.L., Jiang N., Gou M., Salah Uddin M., (2009), Population dynamics in bioaugmented membrane bioreactor for treatment of bromoamine acid wastewater, *Bioresource Technology*, 100, 244-248.
- Saratale R.G., Saratale G.D., Chang J.S., Govindwar S.P., (2011), Bacterial decolorization and degradation of azo dyes: A review, *Journal of the Taiwan Institute of Chemical Engineers*, 42, 138-157.

- Scheumann R., Kraume M., (2009), Influence of hydraulic retention time on the operation of a submerged membrane sequencing batch reactor (SM-SBR) for the treatment of greywater, *Desalination*, 246, 444-451.
- Spagni A., Grilli S., Casu S., Mattioli D., (2010), Treatment of a simulated textile wastewater containing the azodye reactive orange 16 in an anaerobic-biofilm anoxicaerobic membrane bioreactor, *International Biodeterioration & Biodegradation*, **64**, 676-681.
- Stolz A., (2001), Basic and applied aspects in the microbial degradation of azo dyes, *Applied Microbiology and Biotechnology*, 56, 69-80.
- Trussell R.S., Merlo R.P., Hermanowicz S.W., Jenkins D., (2007), Influence of mixed liquor properties and aeration intensity on membrane fouling in a submerged membrane bioreactor at high mixed liquor suspended solids concentrations, *Water Research*, **41**, 947-958.
- Van der Zee F.P., Bouwman R.H.M., Strik D.P.B.T.B., Lettinga G., Field J.A., (2001), Application of redox mediators to accelerate the transformation of reactive azo dyes in anaerobic bioreactors, *Biotechnology and Bioengineering*, **75**, 691-701.
- Van der Zee F.P., Villaverde S., (2005), Combined anaerobic–aerobic treatment of azo dyes-A short review of bioreactor studies, *Water Research*, **39**, 1425-1440.
- Vargas A., Moreno-Andrade I., Buitron G., (2008), Controlled backwashing in a membrane sequencing batch reactor used for toxic wastewater treatment, *Journal of Membrane Science*, **320**, 185-190.

- Viero A.F., Sant'Anna Jr G.L., (2008), Is hydraulic retention time an essential parameter for MBR performance?, *Journal of Hazardous Materials*, **150**, 185-186.
- Wang J., Lu H., Jin R., Zhou J., Liu G., Xing L., (2009), Decolorization of 1-amino-4-bromoanthraquinone-2sulfonic acid in bioaugmented membrane bioreactor, *Process Biochemistry*, 44, 812-816.
- Yasar S., Kevser C., Ozer C., (2012), The effect of cyclic anaerobic–aerobic conditions on biodegradation of azo dyes, *Bioprocess* and *Biosystems Engineering*, 35, 449-457.
- You S.J., Damodar R.A., Hou S.C., (2010), Degradation of Reactive Black 5 dye using anaerobic/aerobic membrane bioreactor (MBR) and photochemical membrane reactor, *Journal of Hazardous Materials*, 177, 1112-1118.
- You S.J., Teng J.Y., (2009a), Anaerobic decolorization bacteria for the treatment of azo dye in a sequential anaerobic and aerobic membrane bioreactor, *Journal of the Taiwan Institute of Chemical Engineers*, **40**, 500-504.
- You S.J., Teng J.Y., (2009b), Performance and dyedegrading bacteria isolation of a hybrid membrane process, *Journal of Hazardous Materials*, **172**, 172-179.
- Yu J., Wang X., Yue P., (2001), Optimal decolorization and kinetic modeling of synthetic dyes by *Pseudomonas strains*, *Water Research*, **35**, 3579-3586.
- Zuriaga-Agusti E., Iborra-Clar M.I., Mendoza-Roca J.A., Tancredi M., Alcaina-Miranda M.I., Iborra-Clar A., (2010), Sequencing batch reactor technology coupled with nanofiltration for textile wastewater reclamation, *Chemical Engineering Journal*, **161**, 122-128.