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The investigation of paper mill industry wastewater treatment and activated sludge properties in a submerged membrane bioreactor

Hanife Sari Erkan and Guleda Onkal Engin

ABSTRACT

The paper mill industry produces high amounts of wastewater and, for this reason, stringent discharge limits are applied for sustainable reclamation and reuse of paper mill industry wastewater in many countries. Submerged membrane bioreactor (sMBR) systems can create new opportunities to eliminate dissolved substances present in paper mill wastewater including. In this study, a sMBR was operated for the treatment of paper mill industry wastewater at 35 h of hydraulic retention time (HRT) and 40 d of sludge retention time (SRT). The chemical oxygen demand (COD), NH_3-N and total phosphorus (TP) removal efficiencies were found to be 98%, 92.99% and 96.36%. The results demonstrated that sMBR was a suitable treatment for the removal of organic matter and nutrients for treating paper mill wastewater except for the problem of calcium accumulation. During the experimental studies, it was noted that the inorganic fraction of the sludge increased as a result of calcium accumulation in the reactor and increased membrane fouling was observed on the membrane surface due to the calcification problem encountered. The properties of the sludge, such as extracellular polymeric substances (EPS) and soluble microbial products (SMP), relative hydrophobicity, zeta potential and floc size distribution were also monitored. According to the obtained results, the total EPS was found to be 43.93 mg/gMLSS and the average total SMP rejection by the membrane was determined as 66.2%.

Key words | activated sludge, critical flux, extracellular polymeric substances, membrane bioreactors, paper mill industry wastewater

Hanife Sari Erkan (corresponding author)
Guleda Onkal Engin
Department of Environmental Engineering, Faculty of Civil Engineering,
Yildiz Technical University,
Davutpasa, Esenler,
Istanbul 34220,
Turkey
E-mail: *hsari@yildiz.edu.tr*

INTRODUCTION

Increasing water scarcity encountered in most of the parts of the world, along with increasing discharge limits for both municipal and industrial effluent, has created a need for new and improved wastewater treatment technologies (Johansson 2012). One of the novel technologies that have gained attention is the membrane bioreactor (MBR) technology. Today MBRs are substituted for classical activated sludge systems, as they are capable of treating high chemical oxygen demand (COD) values with relatively low hydraulic retention time (HRT) values and produce high quality effluent potentially suitable for reuse (Johansson 2012; Lin *et al.* 2012). Other advantages of MBRs are low sludge production, small foot print, and flexibility in future expansion. Application of MBR technology for industrial wastewater treatment has also gained attention because of the robustness of the process. MBR systems have been installed in thousands of municipal and industrial wastewater treatment plants in a broad range of capacities. It is known that the management units of a wide variety of challenging wastewater treatment plants such as paper mills, food processors and textile manufacturers, as well as municipal wastewater treatment plants, have decided to retrofit an existing activated sludge system, as the effluent quality does not meet the standards.

The pulp and paper industry is responsible for approximately 50% of all wastewaters discharged into receiving waters (Zhang *et al.* 2009; Kamali & Khodaparast 2015). This type of wastewater should be treated properly before discharge due to the fact that it contains high levels of organic matter, suspended solids, chlorinated organic matter, chlorate, nutrient and color (Johansson 2012; Kamali & Khodaparast 2015). On the other hand, the pulp and paper

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industry can cause slime growth, and scum formation, and may have thermal impacts (Lin *et al.* 2012). Pulp and paper mill wastewater can also include various toxic chemicals such as resin acids, unsaturated fatty acids, diterpene alcohols, juvabiones, and chlorinated resin acids depending on the type of the pulping processes. Conversely, the pulp and paper industry has been obliged to substantially reduce wastewater discharge due to the implementation of stringent regulations (Lin *et al.* 2012). High quality effluent and the possibility of internal reuse are identified as the primary driving forces for the increasing interest in MBR technology (Johansson 2012). Another reason for installing MBR technology is wastewater reduction. It was reported that pulp and paper mill companies use MBR in combination with reverse osmosis (RO) to achieve almost total recycling of the process water (reducing water usage by 75%) (Johansson 2012). Therefore, MBR processes should be adopted in the treatment of pulp and paper wastewaters to obtain high quality effluent to meet a stringent discharge limit or, even, for sustainable reclamation and reuse (Lin *et al.* 2012; Qu *et al.* 2012).

Pulp and paper wastewaters can be aerobically and anaerobically treated. Typical HRT values are reported to range within 0.5–3 and 2–10 days for aerobic and anaerobic treatment, respectively (Johansson 2012; Lin *et al.* 2012). Anaerobic treatment provides advantages of pollution decreasing with energy production. However, it was reported that anaerobic microorganisms are more sensitive to toxic substances than aerobic microorganisms, when anaerobic treatment is utilized for bleached Kraft wastewaters (Johansson 2012; Lin *et al.* 2012). For this reason, several authors investigated aerobic MBR for pulp and paper mill wastewater treatment and it was reported that the COD removal efficiencies were found to be between 86 and 99.5% (Bérubé & Hall 2000; Galil *et al.* 2003; Dias *et al.* 2005; Gommers *et al.* 2007; Lerner *et al.* 2007; Zhang *et al.* 2009).

The performance of MBR technology for different applications in the pulp and paper processes have been investigated, and the overall review indicated that this technology, in most cases, is feasible (Pokhrel & Viraraghavan 2004; Huang *et al.* 2010; Lin *et al.* 2012). Galil *et al.* (2003) compared a pilot MBR to a 'conventional' activated sludge process for the treatment of effluent obtained from an anaerobic reactor treating paper mill wastewater and it was reported that only 86% COD removal efficiency was achieved at 1 kg COD/m^3 of organic loading rate (OLR). However, in a later study conducted by Dias *et al.* (2005), it was reported that for the Kraft pulp mill foul condensate treatment at high temperature using a sMBR, the COD removal efficiencies varied between 87 and 97% for an organic loading rate of 5 kg COD/m^3. In these studies, however, the problem of scaling was not mentioned. However, it is known that membrane fouling because of calcium carbonate scaling and biofouling proved to be very serious and can cause severe flux reduction in MBR. Therefore, MBR systems treating pulp and paper mill wastewaters require proper and more complicated maintenance systems when compared to a classical activated sludge system. Lerner *et al.* (2007) who investigated full scale activated sludge plant (AS) and a pilot MBR having flat sheet membranes for the treatment of paper mill wastewater mentioned scaling problem. In a later study, Simsitich *et al.* (2012) investigated that treatment of paper mill de-inking wastewater using a sMBR under thermophilic aerobic conditions and have concluded that the COD removal rates were around only 83%. The authors have also observed calcium scaling, but reported that the scaling was negligible.

Apart from removal efficiency, the other important point is to determine is the properties of the activated sludge, as it might affect operational conditions such as HRT, OLR, F/M, and critical flux and membrane fouling. To our knowledge, until now, no study has investigated the physico-chemical properties of activated sludge from a sMBR treating paper mill industry wastewater.

The aim of this study was, therefore, to evaluate the performance of the sMBR treating paper mill industry wastewater and to focus on physico-chemical properties of activated sludge, such as extracellular polymeric substances (EPS), soluble microbial products (SMP), protein and carbohydrate, relative hydrophobicity (RH), zeta potential, and floc size distribution of activated sludge, which are known as properties affecting the operation of MBRs and membrane fouling. It should be noted that the latter contributes to the originality of this study.

MATERIALS AND METHODS

System used and operating conditions

A laboratory-scale sMBR system with a reactor volume of 10 L was operated for 103 d and the schematic diagram of sMBR system is presented in Erkan *et al.* (2016a). Aerobic sludge from municipal wastewater treatment plant was used to inoculate the sMBR for treating paper mill wastewater. Hollow fibre membrane modules with a total surface area of 0.040 m^2 was used in the sMBR. The nominal pore size of membrane was 0.4 μm. The filtration was operated continuously and the maximum trans-membrane

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pressure (TMP) was 0.8 bar. The filtration experiment was carried out without back-washing. The operating conditions in sMBR are summarized in Table 1. As shown in Table 1, the F/M ratio was 0.49 kgCOD/kgMLSS.day in the sMBR at a HRT value of 1.46 d (35 h) under steady-state conditions.

The sMBR system was operated under 7 kg/m^3.day of organic loading rate and at sludge retention time (SRT) of 40 d at steady-state conditions. The automation system was capable of adjusting the influent flow values, so that the organic loading rate was kept at the same value by the level control sensor which was placed at the bottom of the reactor. The sMBR system was operated under continuous aeration and the oxygen was supplied through an air diffuser. The sMBR was continuously fed with paper mill industry wastewater which was taken from an industry producing different paper products from recycled paper.

Characterization of wastewater and inoculum

The recycled paper mill wastewater was taken from the wastewater treatment plant of a paper mill factory located in Istanbul. The full scale treatment plant has a pre-sedimentation tank for solids separation, an anaerobic treatment followed by an activated sludge reactor. The characteristics of raw wastewater are summarized in Table 2. As can be seen in Table 2, the calcium concentration of the raw wastewater was very high, as was the case for the study carried out by Simsitich *et al.* (2012). The main problem faced by the paper mill factory in consideration was due to calcium scaling. The personnel responsible for the treatment conveyed that the main problem in anaerobic treatment was blockage in the pipelines and fractures in the pipe and the reactor itself, due to $CaCO_3$ scaling. Although the organic matter and nutrient content indicated that a combined treatment of anaerobic and aerobic treatment is suitable for the paper wastewater, the wastewater contained phenolic compounds and toxic substances which cause inhibition in the long run. The reason to select MBR technology for the treatment of paper mill wastewater was, therefore, to mitigate the above-mentioned problems. The ammonia and phosphate concentrations were very low, as was expected for paper mill wastewater. The C/N/P ratio for the studied paper mill wastewater was found to be about 100/0.7/0.069. In order to reach a C/N/P ratio suitable for aerobic treatment, known amounts of urea and ortho-phosphoric acid were added to the raw wastewater. The raw and treated wastewater samples were stored at 4 °C in a cold chamber to prevent degradation.

Table 1 | Operating conditions in the sMBR

Operating parameter	Value
pH	8.0
DO, mg/L	>3.0
Temperature, °C	21
HRT, hours	35
SRT, days	40
L_{org}, kg COD/m^3.day	7
F/M ratio, kg COD/kg MLSS.day	0.49
Membrane flux, L/m^2.h	7.2

Table 2 | Characteristics of raw paper mill wastewater

Parameter	Unit	Raw wastewater
COD	mg/L	11,415 ± 15
BOD_5	mg/L	7,155 ± 23
TS	mg/L	11,140 ± 520
TSS	mg/L	127 ± 30
TKN	mg/L	80 ± 1.5
NH_3-N	mg/L	12 ± 3
NO_3-N	mg/L	20 ± 2
TP	mg/L	7.9 ± 1.8
PO_4-P	mg/L	1.3 ± 0.15
pH	–	5.93 ± 0.08
Conductivity	mS/cm (20 °C)	6.08 ± 0.5
Alkalinity	mg $CaCO_3$/L	2,380 ± 150
Chloride	mg/L	448 ± 50
Color	Pt-Co	1,990 ± 30
Calcium	mg/L	2,074 ± 55

Sampling and analyses

Dissolved oxygen (DO), pH, temperature and TMP were continuously monitored throughout the operation of the laboratory scale sMBR. The feed and permeate samples were analyzed for COD, total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N), orthophosphate (PO_4-P), the mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) values of the activated sludge were monitored throughout the study. All the analyses were carried out according to *Standard Methods* by APHA (APHA/AWWA/WEF 2005). Measurement of DO and pH were conducted daily, whereas COD, NH_3-N, and PO_4-P analyses were carried out every other day. The EPS, SMP, protein, carbohydrate, hydrophobicity analyses were conducted once every 15 d in order to determine activated

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sludge characteristics in the sMBR. The critical flux determination, particle size distribution and zeta potential were also carried out once at steady-state conditions. All measurements were repeated three times independently. All the chemicals used were of analytical grade.

The analyses of EPS and SMP were conducted by the formaldehyde extraction method which was used by Tinggang *et al.* (2008). The carbohydrate and protein concentrations were determined by phenol-sulphuric acid (Dubois *et al.* 1956) and Lowry method (Lowry *et al.* 1951), respectively (Sheng *et al.* 2010). The analyses of RH were carried out by the MATH test (Measuring the Attachment of Bacteria to Hydrocarbons) (Chang & Lee 1998). The particle size distribution and zeta potential of activated sludge was measured using a Malvern Matersizer Instrument.

Critical flux determination

The critical flux was determined by the flux-step method (Wu *et al.* 2008; Diez *et al.* 2014). The critical flux of the sMBR system was measured using a flat sheet membrane module with a filtration area of 0.044 m^2. The flat sheet membrane was made of the same material and the same pore size of the hollow fibre membrane modules which were used in the sMBR systems. At each step of critical flux determination, a fresh flat sheet membrane was used. The obtained permeate was measured by an analytical balance (Kern PLS 6200-2A). The time intervals for each filtration step were kept constant as 30 min.

RESULTS AND DISCUSSION

Solid concentrations and permeate quality of the sMBR

The MBR was operated just over 100 d at a SRT value of 40 d. The sMBR reached the steady-state conditions after the first 28 d. The solids concentrations of the samples taken from the reactor during the operation period can be seen in Figure 1. The MLSS and MLVSS concentrations were 12.90 and 10.32 g/L and the MLVSS/MLSS ratio was found to be 0.8. The MLVSS/MLSS ratio has shown that the activity of sludge was adequate. The total solids (TS) and total volatile solids at steady-state conditions were 14.66 and 11.63 g/L, respectively. The TS concentrations increased slightly after steady-state conditions were reached. This indicated that inorganic solids present in raw wastewater accumulated in the sMBR.

The COD, ammonia and phosphate concentrations of permeate were regularly measured during the operation, and the obtained results were shown in Table 3. As shown in Table 3, the COD and biochemical oxygen demand (BOD_5) removal efficiencies were 98.0% and 99.2%, respectively. Similarly, total nitrogen (TN), NH_3-N and total phosphorus (TP) removal efficiencies were around 90.3%, 93% and 96%, respectively. It is known that application of high SRTs in sMBRs contribute to nitrification in these systems. Thus, nitrifying bacteria, which are notoriously slow growing microorganisms, are responsible for the conversion of ammonia nitrogen into nitrate (Judd 2006). It was also

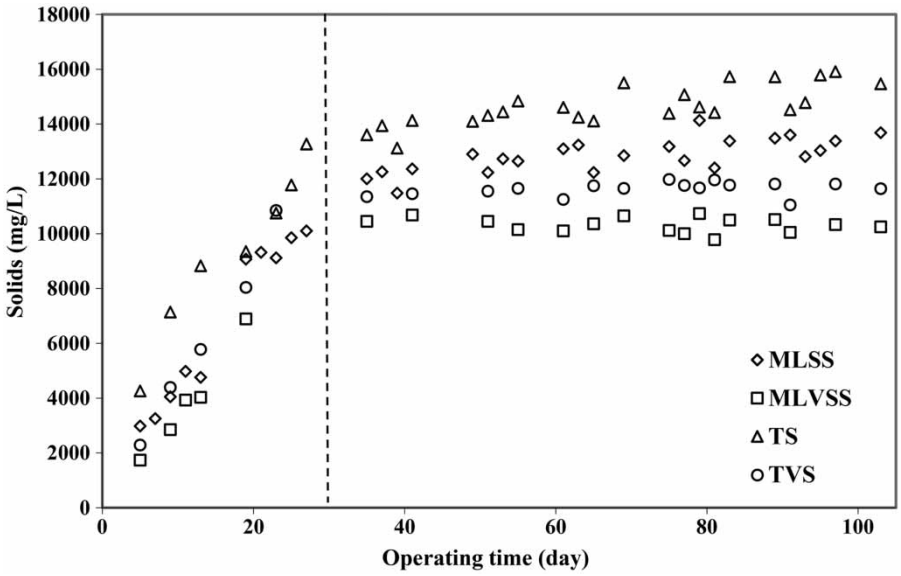


Figure 1 | Solids concentration in sMBR.

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Table 3 | Quality of permeate in sMBR

Parameter	MBR influent	MBR effluent	% Removal
COD (mg/L)	11,415 ± 15	228.3 ± 5	98.0
BOD_5 (mg/L)	7,155 ± 23	57.2 ± 10	99.2
TN (mg/L)	389 ± 7	37.8 ± 3	90.3
NH_3-N (mg/L)	301 ± 23	21.1 ± 5	93.0
TP (mg/L)	68.6 ± 3	2.5 ± 0.05	96.4
Calcium (mg/L)	2,074 ± 55	455 ± 10	78.1

reported that the TN removal efficiency in MBR is about 30% greater than conventional treatment systems (Dohare & Trivedi 2014). Significant removal of TN is not expected once the reactor is operated under fully aerated conditions (Puznava *et al.* 2001). However, it is known that due to lack of oxygen, anoxic zones can form in the inner regions of the activated sludge flocs, thereby providing convenient conditions for denitrification (Puznava *et al.* 2001). Some researchers had high phosphorus removal efficiencies in MBR systems when they were treating industrial wastewater (Farizoglu *et al.* 2007; Andrade *et al.* 2013). According to the researchers, these high removal efficiencies were due to a considerable uptake of phosphorus for new microorganism synthesis, since the MLSS concentration was high in the reactor, and due to the phosphate precipitation with the Ca^{2+} and Na^{+} ions. Both reasons account for high phosphorus removal efficiencies in this study. Zhang *et al.* (2007) investigated MBR system in order to investigate the effect of SRT on phosphorus removal. For this purpose, four comparative runs were operated at SRTs of 20, 30, 40 and 50 d. It was found that high TP removal could be achieved even when SRT was prolonged to 40 d. This was due to increased phosphorus content in the sludge with increased SRT, which allowed for reduction of excess sludge discharge while sufficient phosphorus removal was ensured. It was determined that the average influent concentration of calcium was 2,074 mg/L; towards the end of the study the calcium concentration of the permeate was found to be 455 mg/L. Therefore, average calcium reduction was around 78%. Calcium precipitation and accumulation was observed on the reactor walls, air diffuser and hollow fibre membrane surfaces. The calcification in the sMBR was observed as a result of microbial calcium removal. As mentioned before, urea was added to the system in order to balance the COD/TKN ratio of the feed wastewater. The enzymatic hydrolysis of urea caused $CaCO_3$ precipitation in the reactor. This microbiological carbonate precipitation was investigated via batch tests and it was observed that urea is degraded to ammonia and the produced ammonia reacted with the carbonate ions in presence of soluble calcium ions and precipitated as $CaCO_3$. Hammes *et al.* (2003a, 2003b) reported that it was possible to remove Ca^{2+} from industrial wastewaters such as paper recycling, bone processing and citric acid production, and landfill leachate by microbial calcium precipitation to prevent calcification and scaling problems in pipelines and reactors. However, during this study, this natural reaction occurred in the sMBR and, therefore, caused scaling on the membrane and the air diffuser. As a result, membrane flux and DO concentration decreased in the reactor.

TMP and critical flux of sMBR

Figure 2 shows the TMP of the sMBR throughout the study conducted. Dotted lines mark the operation days when chemical cleaning with citric acid and sodium hypochlorite was carried out to remove the calcium film on the membrane surface. During the operations, the permeate flux was around 7.2 LMH. The maximum fluxes acquired in sMBR for domestic wastewater were usually reported to be between 25 and 30 LMH; however, for industrial wastewaters, these values were found to be between 5 and 15 LMH (Cornel & Krause 2008). The TMP values increased sharply just after the system's initiation and reached approximately 435 mbars. On day 23, the first chemical cleaning was applied using citric acid and sodium hypochlorite. After cleaning, the TMP value remained below 285 mbars for around 24 d and increased steadily. On days 47 and 71, chemical cleaning were carried out two more times. Additionally, physical cleaning using a sponge was applied approximately once per week in order to keep the membrane flux at a steady level.

It is crucial to determine the critical flux level at the start-up of MBR. It was reported that if the initial operating flux in an MBR starts as low as possible, the rate of fouling would be retarded (Field *et al.* 1995; Park *et al.* 2015). The concept of critical flux in MBRs is simple to reach the highest initial flux for which TMP remains stable during operation of the MBR. Several methods for determining the critical flux have been suggested but, to date, no consensus was reached on a single protocol (Park *et al.* 2015). In this study, critical flux measurements using step-wise method were conducted. The critical flux determination measurements were carried out on day 30 (Figure 3) and the average critical flux value was found to be 7.5 LMH. It was reported in earlier studies that many industrial MBR systems were operated at low membrane flux values

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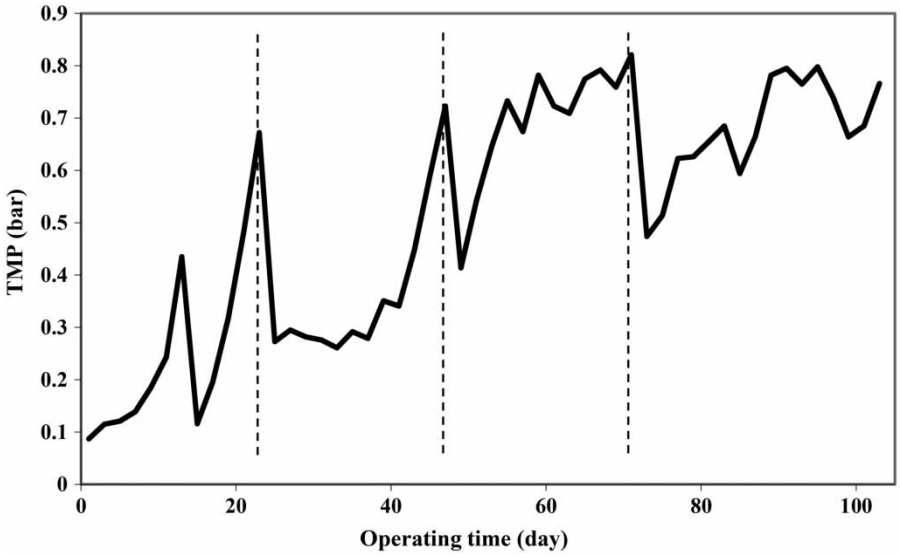


Figure 2 | TMP values of sMBR system.

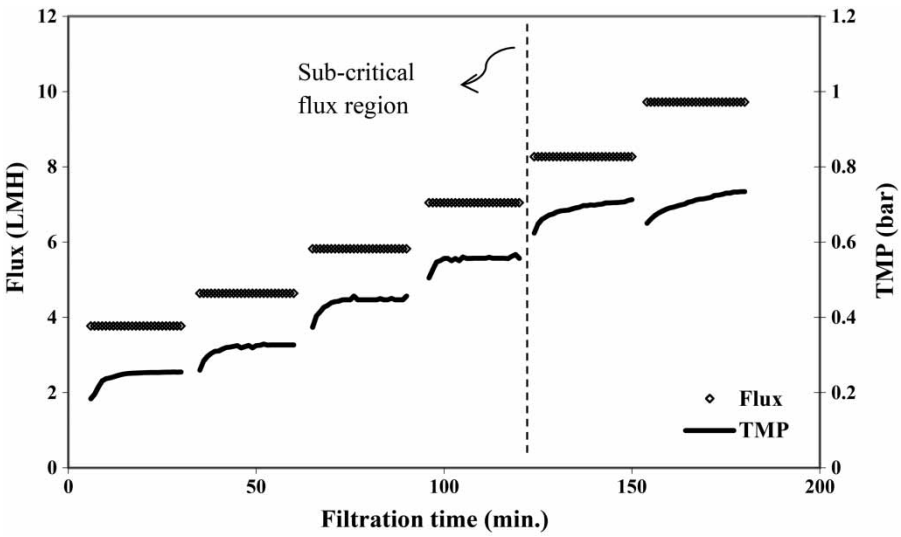


Figure 3 | Critical flux experiment for sMBR system.

(Wang *et al*. 2005; Zheng & Liu 2006; Lin *et al*. 2012). As it was stated previously, the operation flux was kept constant (7.2 LMH) under the sub-critical flux conditions throughout the sMBR operation.

SMP and EPS concentrations in MBRs

In this study, proteins and carbohydrates are considered to represent the total amount of EPS and SMP. These types are regarded as the major constituents (Erkan *et al*. 2016a). The EPS, SMP of supernatant and SMP of permeate results are shown in Figure 4. The EPS results showed that carbohydrate content was significantly higher than protein (Figure 4 (a)). At the beginning of the operation, the protein and carbohydrate contents were 43.8 and 18.645 mg/g MLSS and the total EPS content was found to be 62.445 mg/g MLSS. The carbohydrate content decreased significantly after 28 d of operation. Throughout 103 d of operation, however, the carbohydrate contents were observed to be stable between the 28th and 72nd days. No trend was observed for protein concentrations, the protein contents varied between 10.65 and 22.16 mg/g MLSS

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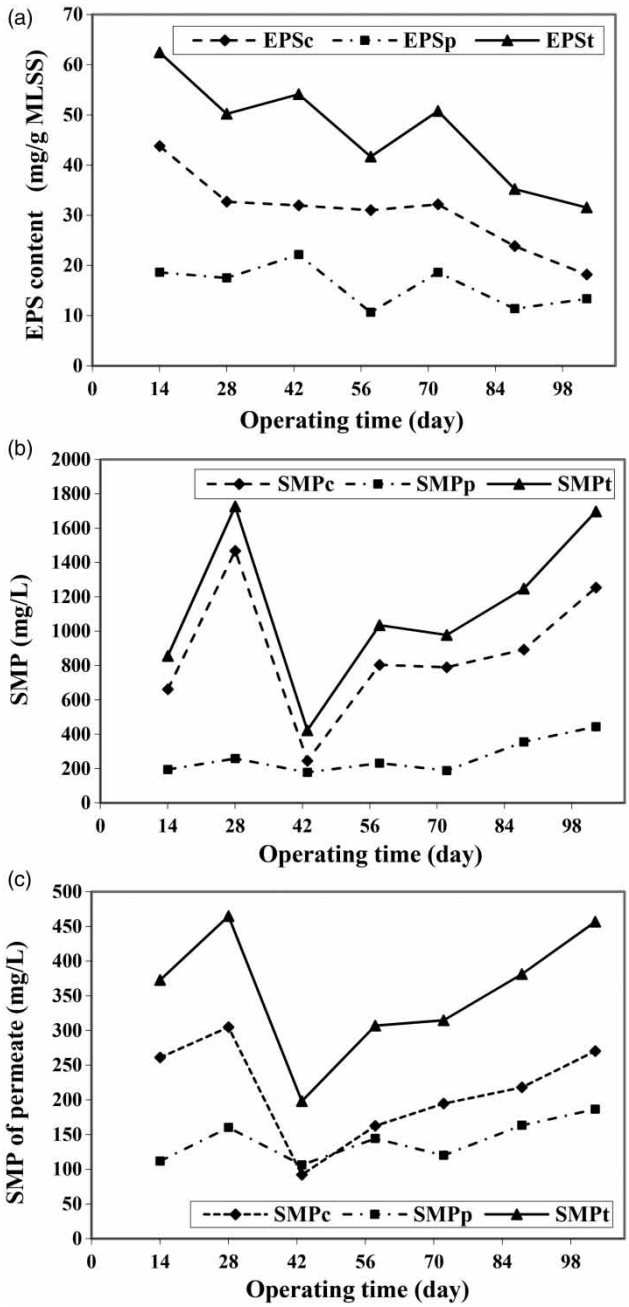


Figure 4 | EPS and SMP concentration of activated sludge: (a) EPS, (b) SMP of supernatant, (c) SMP of permeate.

throughout the study. After 88 days of operation, the total EPS concentrations decreased approximately 50% compared to the beginning levels. Sponza (2003) investigated the EPS concentrations and the physico-chemical properties of activated sludge for four different industrial wastewaters including pulp and paper industry wastewater treated in conventional activated sludge systems. The author found out that the total EPS content was roughly 85 mg/g MLVSS and the protein content was higher than carbohydrate and DNA content. As known, the protein and carbohydrate contents are highly related to influent wastewater COD and ammonia concentrations. Since nutrients in wastewater affect microbial physiology, nutrients affect the nature and content of EPS of the activated sludge, accordingly (Erkan *et al.* 2016a). Durmaz & Sanin (2003) also reported that the production of excessive carbohydrates under nitrogen-limited conditions can deteriorate the filtering property of sludge. On the other hand, Sponza (2003) reported that the active secretion of carbohydrates increased when industrial wastewater include inert and toxic substances, such as, textile or pulp and paper mill industry.

The results of supernatant SMP and permeate SMP are given in Figure 4(b) and 4(c) throughout the study. Although the SMP concentrations in the supernatant and in the permeate showed a slight decrease just after the steady-state conditions were reached, afterwards the trend was observed to be increased during the rest of the study period. The protein of SMP rejections by the membrane were varied between 36.2% and 57.9% during the operation. The maximum protein rejections were determined on the days of 88 and 103 and the rejections were found to be 54% and 57.9%, respectively. As can be seen in Figure 4(b) and 4(c), carbohydrate concentrations of supernatant was found approximately four times higher than SMP_c concentrations of permeate. The SMP_c rejection by the membrane was determined between 60.6% and 79.8% throughout the operation and the average rejection was 73.1%. As can be seen from the SMP_p and SMP_c results of the supernatant, microorganism of activated sludge secreted much higher carbohydrate compared to protein. These results indicated that more extracellular carbohydrate and less protein were produced at N-limited conditions. Consequently, the SMP_c of supernatant and permeate were higher than the protein, approximately 3.35 and 1.52 times, respectively. The reason for this observation may come from different molecular weights of the produced SMP_c and SMP_p (Erkan *et al.* 2016b). The average rejection of total SMP was found to be 66.2%.

Other properties of activated sludge

RH is a key factor in determining the adhesion potential of microorganisms to surfaces (Saini 2010). Erkan *et al.* (2016b) reported that the attachment of sludge flocs would increase when hydrophobicity increased. On the other hand, activated sludge settleability can be measured by sludge volume index (SVI) analysis. Figure 5 shows the results of

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RH and SVI of activated sludge during the treated paper mill industry wastewater. As shown in Figure 5, the RH and SVI values were higher at the start of the operation. After steady-state conditions were reached, which corresponds to 28th day of the operation, the RH and SVI values decreased to be 5.42% and 71.73 mL/g, respectively. It should be noted that the differences in the SVI values after steady-state conditions were reached were not considered to be high enough to be of practical significance, since all flocs generally settled well. It was reported that typical SVI values for pinpoint floc, normal sludge, and bulking sludge range from <50, 100–180, and >200 mL/g, respectively (Park *et al.* 2015). Li *et al.* (2008) reported that the order of fouling tendency was found to be normal sludge < pinpoint sludge < bulking sludge. After reaching the steady-state conditions, the RH showed an average value of 6.45% until day 58. Afterwards, the RH was determined to have an average value of 12.70% till the end of the operation. The reason for this increase could be attributed to the relationship between RH and P/C ratio of EPS.

Microbial floc size and zeta potential of activated sludge were also investigated on the 88th day of operation at steady-state conditions. The floc size distributions for the activated sludge can be seen in Figure 6. The mean floc sizes were found to be 105.505 ± 1.0 μm. The average floc sizes found in conventional submerged MBRs are typically around 80–160 μm depending on the microbial physiology, influent characteristics, and wastewater treatment plant site (Park *et al.* 2015). Carbohydrate and protein fractions of EPS play a major role in floc size distribution (Sheng *et al.* 2010; Xie *et al.* 2010). As seen from Figure 6, particles with sizes smaller than the nominal pore size of the membrane (0.4 μm) were not found in the activated sludge. The minimum particle size was found to be 0.955 μm which corresponded to 3% of all particle volume.

The zeta potential of microbial floc was found to be −16.0 mV. The zeta potential of activated sludge flocs was reported to range from − 50 to −10 mV in MBRs (Huang & Wu 2008; Lin *et al.* 2014). The zeta potential of activated sludge increased negatively with increasing carbohydrate fractions of EPS. Liao *et al.* (2001) reported that the EPS concentration had an influence on zeta potential of activated sludge, and pointed out that the protein/carbohydrate (P/C) ratio of EPS was more important than the quantities of individual EPS components in controlling zeta potential. As known, protein fractions of EPS that were excreted from the microbial cell would neutralize some of the negative charge of microbial floc (Lee *et al.* 2003; Sheng *et al.* 2010).

CONCLUSIONS

This study investigated the effectiveness of sMBR system for the treatment of pulp and paper mill industry at a SRT value of 40 d and HRT value of 35 h. The obtained results represented that the COD, NH_3-N and PO_4-P removal efficiencies were very satisfactory. According to the COD results obtained, the pulp and paper mill industry wastewater discharge limits (direct discharge to a receiving water body) have been met based on the standards in

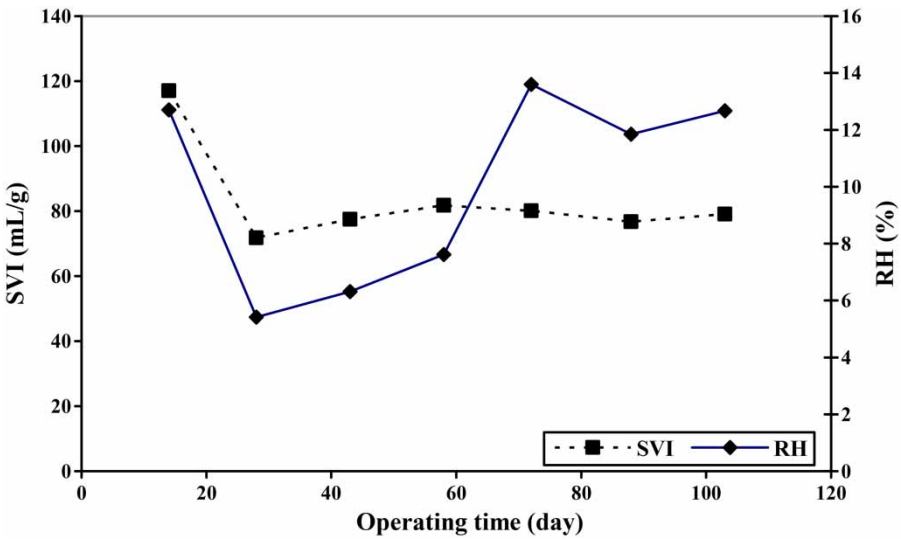


Figure 5 | RH and SVI values of activated sludge in the sMBR.

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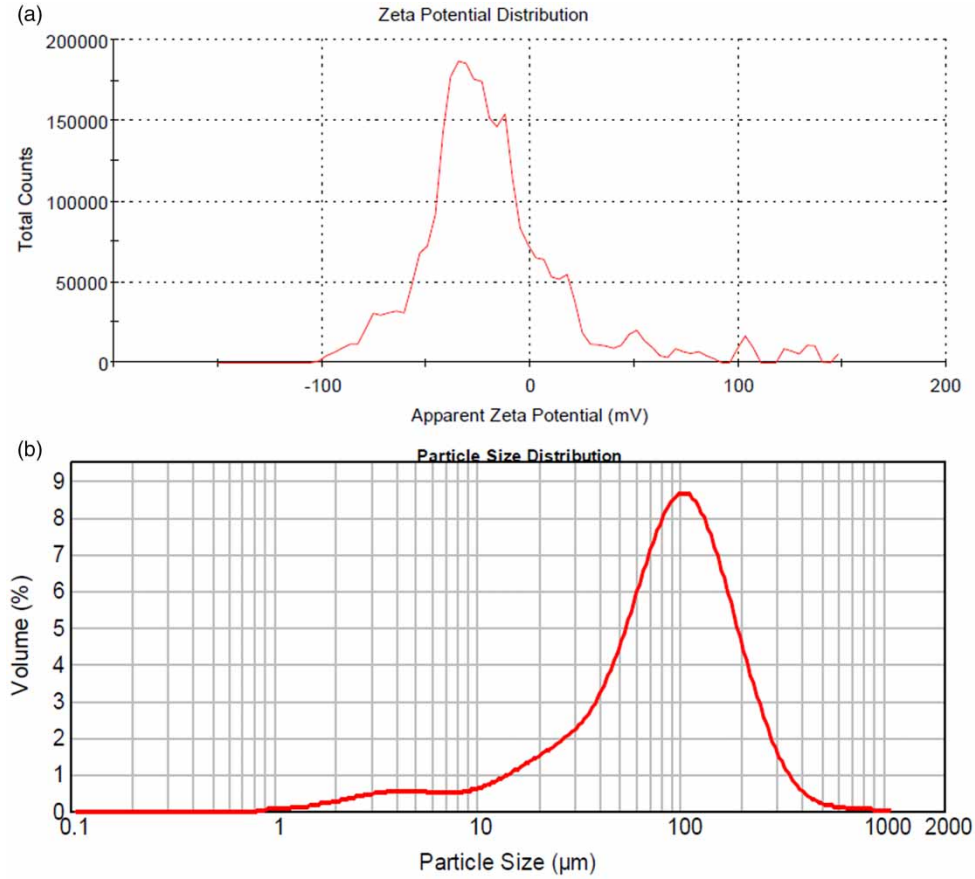


Figure 6 | Zeta potential and particle size distribution of activated sludge.

Water Pollution Control Regulation of Turkey (COD < 870 mg/L) (Ministry of Environment and Urbanization, MoEU 2004). The main operational problem was calcification in the sMBR due to the high concentration of calcium of raw wastewater and the average calcium reduction was found to be 78.06%. Particularly, calcium precipitation was observed on the reactor wall, air diffuser and hollow fibre membrane surfaces. To overcome this problem, chemical cleaning was carried out regularly. This study also focused on the activated sludge physico-chemical properties such as EPS, SMP, carbohydrate, protein fractions and so on. The results showed that the total EPS content was 43.93 mg/gMLSS and it was found that the EPS_c concentration was higher than EPS_p. On the other hand, the SMP_c concentrations of supernatant was found approximately four times greater than SMP_c of permeate. The average SMP_c rejection by the membrane was determined to be around 73%. As a final remark, it can be said that the sMBR system was found to be a feasible treatment technology for pulp and paper mill wastewater; however, the excess calcium should be removed before the wastewater is introduced to the MBR system to prolong membrane filterability.

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