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Long-term operation of submerged membrane bioreactor (MBR) for the treatment of synthetic wastewater containing styrene as volatile organic compound (VOC): Effect of hydraulic retention time (HRT)

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ABSTRACT

In this study, the membrane bioreactor (MBR) was utilized to remove styrene from a synthetic wastewater having a chemical oxygen demand (COD) and styrene concentration of 1500 mg/L and 50 mg/L, respectively. At two hydraulic retention times (HRTs) of 24 h and 18 h, the MBR was operated for a period in excess of 100 days. The HRT effects were studied and it was found out that the removal efficiency of COD and styrene for both HRTs was consistently higher than 99%. Unlike conventional activated sludge processes (CASPs), no styrene was detected in the exhaust air, which meant that biodegradation was the major styrene removal mechanism at both HRTs. The transmembrane pressure (TMP) profile during the operation of the MBR showed a fairly low and constant TMP up to day 70, after which, the TMP showed a dramatic rise, as a result of the occurrence of severe membrane fouling. It was thought that an increase in styrene loading rate, when HRT was reduced to 18 h, resulted in the release of extracellular polymeric substance (EPS) from the bacterial cells, which in turn was responsible for the rise in soluble microbial product (SMP) and sludge deflocculation. The severe fouling observed during operation of MBR at HRT of 18 h was attributed to the rise in SMP concentrations and decrease in mean floc size and increase in the proportion of small particles in the activated sludge.

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1. Introduction

Styrene is one of the most important aromatic chemicals used as raw material in the production of many commercially important products such as polystyrene, acrylonitrile–butadiene–styrene (ABS), styrene–isoprene–styrene, and styrene–butadiene latexes and rubbers. The release of man-made styrene into environment can occur by various routes including the disposal of petrochemical wastewaters and pyrolysis of polystyrene. The most common method employed for degradation of hazardous volatile organic compounds (VOCs), such as styrene, in petrochemical wastewaters is the conventional activated sludge processes (CASPs). This process has been successfully used for the treatment of petrochemical wastewaters; the treated effluent from this process usually meets the industrial standards for the disposal of wastewaters [1]. However, the CASP has two major disadvantages. The first problem

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originates from the possibility of transfer of significant quantities of VOCs to the exiting air phase during the aeration of the activated sludge bioreactor [2–4]. Since styrene has been classified as a potential human carcinogen, occupational exposure limits have been set for it [5]. This means that the gaseous effluent from activated sludge plants requires further treatment. The second disadvantage is that, due to the relatively high suspended solids, the effluent from these units does not usually have the standard necessary to enable its re-use as process water [1].

According to Hsieh [4], during CASPs, the removal of VOCs from industrial wastewaters occurs by three mechanisms: stripping, adsorption, and biodegradation. Hsieh [4] stated that the percentage contribution of biodegradation to overall styrene removal can be increased through the increase of either mixed liquor suspended solids (MLSSs) or the biological rate constant for biodegradation. The latter can be achieved by using the activated sludge previously adapted to styrene, whereas the former can be attained by means of utilizing the novel processes such as membrane bioreactor (MBR).

MBR is an activated sludge process in which the sedimentation stage is replaced with membrane filtration. In this way, both a high MLSS and a very good quality effluent, suitable for process applications or may be even drinking water, can be achieved in an MBR

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process [1,6,7]. The concentration of MLSS in MBRs is reported to be typically 3–5 times that of CASPs [1].

There have been several reports on the application of MBR process for petrochemical wastewaters treatment [1,8,9]. Qin et al. [1] claimed that an MBR process with a hydraulic retention times (HRT) as low as 13 h could be used to treat a petrochemical wastewater and to obtain an effluent that meets discharge standards. Chang et al. [8] concluded that biological oxygen demand (BOD) and chemical oxygen demand (COD) removal efficiencies obtained with a MBR process, used for the treatment of ABS industrial wastewater, are higher than those which could be achieved with a CASP.

A drawback of the use of MBRs, compared to that of CASPs, is the possibility of membrane fouling which, through decrease of the membrane flux, can severely reduce the output from such processes [6]. Previous work have shown that the membrane fouling is affected by some factors such as HRT, sludge retention time (SRT), and biomass characteristics such as floc size, morphology, extracellular polymeric substance (EPS), soluble microbial product (SMP), and viscosity [10-12]. The increase in MLSS, which is necessary to reduce the contribution of stripping to VOC removal in a CASP [4], can also aggravate the membrane fouling in a MBR. A common method for reducing the membrane fouling is the air scouring of the membrane. That is, in MBRs, air sparging has the dual roles of supplying the mixed bacterial culture in activated sludge with oxygen and also reducing the formation of the foulants on the membrane. For this reason, the air rates, reportedly used in MBR processes, are usually higher than those of CASPs [13,14]. However, according to the CASP model developed by Hsieh [4] and the MBR model developed by Min and Ergas [15], increase in air rate can lead to significant increase in the removal rate of VOCs by stripping mechanism.

HRT is an important operating parameter in MBR operation [16,17]. Lower HRT values result in higher organic loading rates (OLR), which result in reduction of reactor volumes required to achieve a specified removal performance. On the other hand, higher HRTs usually result in better removal performance. Qin et al. [1] have reported that for the operation of a submerged MBR for the treatment of a petrochemical wastewater, the use of HRTs in the range 13-19h results in effluents which have acceptable qualities. Chang et al. [8] found negligible effect of HRT in the range 12-30h on the removal performance of the MBR used for treating the wastewater of an ABS unit. Visvanathan et al. [18] report similar COD and pentachlorophenol (PCP) removal performance at HRTs in the range of 12-24 h in an MBR used for treating a synthetic wastewater containing PCP. Decreasing HRT has also been reported to result in increase in the rate of membrane fouling in MBRs, although its effect seems to be mostly indirect than direct [1,8,11,17,19].

The purpose of the present work is to assess the performance of an MBR process, particularly in terms of the styrene removal mechanisms and the membranes fouling at different HRTs, for treating a synthetic wastewater which contains styrene.

2. Materials and methods

2.1. Feed wastewater characteristics

The synthetic wastewater, employed in this study, was formulated to simulate petrochemical industrial wastewater in terms of COD and styrene concentrations. For obtaining the appropriate formulation, information regarding the COD concentration of a petrochemical wastewater was obtained from the records of the treatment plant of the Tabriz Petrochemical Company in Iran, which showed a COD for the mixed effluents of the various units in the petrochemical complex in the range 700–1500 mg/L. This amount was also in the range reported by previous investigators for petrochemical effluents [1,8]. For styrene concentration, samples of mixed effluents which were fed to the CASP of Tabriz Petrochemical Company were analyzed and the concentration of styrene was found to be 50 ± 0.5 mg/L. The synthetic wastewater used in the present study had the following composition (mg/L): styrene: 50; ethanol: 645; K₂HPO₄: 32.9; KH₂PO₄: 42.14; NH₄Cl: 286.6; MgSO₄·7H₂O: 13; CaCl₂·2H₂O: 7; NiCl₂: 0.0094; MnSO₄: 0.014; Na₂MoO₄: 0.423; CoCl₂: 0.094; FeCl₃: 5; ZnSO₄: 2; EDTA: 7; NaHCO₃: 500. This resulted in a wastewater which had a COD of 1500 mg/L and contained the elements required for proper growth of the mixed bacterial population in activated sludge.

2.2. Microbial cultures

Activated sludge, used as inoculums in MBR runs, was obtained from the sludge return line at the CASP of Tabriz Petrochemical Company. After transporting to the laboratory, the activated sludge was frozen using 15% (w/w) glycerol and then stored. Before inoculating the MBR, the frozen activated sludge was thawed and grown under aeration in the above-mentioned media without styrene for a few days.

2.3. Experimental setup

A schematic diagram of the MBR experimental rig used in the present study is presented in Fig. 1. The bioreactor consisted of a 5L acrylic tank, in which a polyethylene Kubota flat sheet microfiltration membrane with a pore size of 0.4 μ m and area of 0.11 m² was immersed. The gap between the membrane and the wall was set at 7 mm to obtain efficient scouring of the membrane by the air flow [14]. Air was introduced at a distance of 10 cm beneath the membrane module through a stainless steel tube containing ten 2 mm nozzles. The air rate was 7 L/min which corresponded to an air-to-water ratio (defined as the air rate divided by the liquid rate through the MBR) of 1521 and 2016 at HRT of 18h and 24 h, respectively. The output of level sensor, pressure transmitter, dissolved oxygen (DO)-meter, pH-meter, and thermometer were connected to a data acquisition system to enable monitoring of the process parameters via a PC. The inlet and outlet peristaltic pumps were controlled (turned on or off) based on the data supplied by the level sensor.

The synthetic wastewater was stored in a feed tank prior to being pumped to the MBR. In order to avoid the escape of styrene to the gas phase of the tank, the tank was separated into two parts using a 2 cm thick Teflon sheet; the bottom section was completely filled with the synthetic media, whereas a container full of styrene was placed in the upper part. Using a feed tank with this design ensured that the concentration of styrene in the inlet to MBR throughout the experiments did not deviate from the 50 mg/L concentration by more than 0.1%. The operating conditions of the MBR system are described in Table 1.

Table T		
Operating	conditions of MBR	system.

Parameter	From day 0 to day 50	From day 51 to day 105
HRT (h)	24	18
Membrane flux (Lm ⁻² h ⁻¹)	1.89	2.5
DO (mg/L)	5.6	4.5
SRT (day)		25
Temperature (°C)		27 ± 1



Fig. 1. Schematic design of the MBR.

2.4. Analytical methods

The styrene concentrations were analyzed using a gas chromatograph (Younglin) equipped with a helium ionization detector and a 50m long capillary column. The oven temperature was maintained at 70 °C for 1 min and raised to 140 °C at the rate of 10 °C min⁻¹. The temperatures of the injector and the detector were fixed at 200 $^{\circ}\text{C}$ and 240 $^{\circ}\text{C},$ respectively. Styrene concentration in the liquid phase was estimated using the headspace method. Each gas and liquid sample was measured 3 times with a standard deviation of 0.5%. The MLSS, MLVSS and COD were estimated according to Standard Methods [21], the latter using the Merck COD kit. SMP and EPS were measured by utilizing the method described by Chang et al. [22]. Protein fraction of SMP and EPS (SMP_p and EPS_p) was measured using the folin phenol reagent method [23], whereas the corresponding polysaccharide fraction (SMP_c and EPS_c) was determined by phenol-sulfuric acid method [24]. The coefficients of variation of the analysis for SMP_p, SMP_c, EPS_p, and EPS_c based on five measurements were 0.72%, 0.93%, 1.25%, and 1.5%, respectively.

The sludge flocs were examined by light microscopy and the images were captured on a Keyence VH-Z75 microscope attached with a PC-based charge-coupled device. The particles size distribution (PSD) was determined by a Malvern Mastersizer 2000 instrument with a detection range of $0.02-2000 \,\mu$ m. Specific oxygen uptake rate (SOUR) was determined according to Standard Methods [21].

3. Results and discussion

3.1. COD and styrene removal performance of the MBR system

The COD and styrene removal efficiencies, as well as the concentration of styrene in the air exiting from the MBR system, are presented in Fig. 2. The results showed that at the both HRTs employed, COD and styrene removal efficiency from the liquid phase was consistently higher than 99%, whereas the styrene concentration in output air was consistently lower than 0.1 ppm. It can therefore be concluded that stripping mechanism did not contribute to the removal of styrene during the experiments at both HRTs. According to the paper by Hsieh [4], the contribution of adsorption mechanism to styrene removal from liquid phase by activated sludge is not usually very significant; therefore, it can be concluded that during the MBR process, even at HRT of 18 h, the styrene removal is exclusively through biological removal.

The air exiting CASPs, which are used for treatment of VOCcontaining wastewaters, usually contain significant quantities of VOCs and as a result the exiting air can be considered as a pollutant of environment [2–4]. For example, the model for the treatment of VOC-containing wastewaters by the activated sludge process developed by Hsieh [4] predicts that, at HRT = 18 h and air-to-water ratio = 35, the contribution of stripping to overall removal in the case of styrene is around 15%. The results obtained in the present study suggest that a MBR process can achieve very high removal efficiencies with negligible volatilization of styrene in the exit air stream. This can be attributed to the higher MLSS that can be achieved in MBRs compared to CASPs; in the present work the MLSS achieved at HRT = 18 h was around 5300 mg/L (Fig. 3), which compares with around 3400 mg/L as predicted by the Hsieh model for an activated sludge process at an HRT of 18 h. It should be pointed that according to the model developed by Hsieh [4] increase in the air-to-water ratio will enhance the contribution of volatilization relative to biodegradation in the overall removal of VOCs. The airto-water ratio employed in the present work was much higher than



Fig. 2. Variation of COD and styrene removal and styrene concentration in the exit air during the operation of the MBR.



Fig. 3. Variation of MLSS and MLVSS during the operation of the MBR.

that normally used in CASPs, which means that in the present work almost negligible styrene volatilizations have been achieved at airto-water ratios, which if employed in the CASP, would result in volatilization of styrene in excess of 15% in the air exit of the CASP.

Min and Ergas [15] have developed a mathematical model for treatment of VOC-containing wastewaters in MBRs which is a modified version of the model developed for CASPs by Hsieh [4]. This model, together with limited experimental data obtained for treatment of vinyl acetate synthetic wastewater in a laboratory side-stream MBR, predicts that unlike CASP processes, in MBRs, with increase in OLR (e.g. achieved through decrease in HRT) the contribution of volatilization relative to biodegradation decreases, which suggests that theoretically similar results is expected at lower HRTs in the MBR used in the present study. Chang et al. [9] have also reported decrease in volatilization relative to biodegradation of acrylonitrile with decreasing HRT in a MBR treating the wastewater of an ABS unit. However, in the present study due to the severe fouling developed at HRT=18h (see Section 3.2) operation at lower HRT was not conducted. Results reported by other researchers in MBR treating wastewaters containing other VOCs show that for VOCs which are more volatile and/or soluble than styrene such as acrylonitrile or vinyl acetate, the rate of volatilization at typical or "optimum" MBR operating conditions is not negligible but still reportedly less than 10% [9,14].

3.2. Fouling of membrane during operation of the MBR system

Characterization of fouling during the operation of MBR in the present study was performed through monitoring of transmembrane pressure (TMP). Fig. 4 shows the variation of TMP over more than 100 days operation of the MBR. This figure can be roughly separated into three phases: Phase 1 (day 1 to day 70), phase 2 (day 70 to day 98) and phase 3 (day 99 to day 110). The first phase corresponded to the operation of MBR at HRT of 24 h followed by the



Fig. 4. Evolution of TMP during the operation of the MBR.



Fig. 5. Evolution of EPS, EPS_p and EPS_c versus time.

initial period of operation at HRT of 18 h. During this period, the rate of rise of TMP with time was very slow. In the second phase the MBR was exclusively operated at HRT of 18 h. During this phase, a sharp increase in TMP over time was observed. At day 99, the membrane was taken and washed thoroughly with water to remove the cake layer. This resulted in a sharp decrease in TMP, although the initial TMP values were not restored. The results suggest that a decrease in HRT from 24 h to 18 h has resulted in a significant increase in the rate of membrane fouling such that the air scouring method was no longer able to keep the membrane clean. This general conclusion is in line with previous MBR studies on the effect of HRT on membrane fouling [1,8,19,20]. However, there is no consensus in these studies as to the reason for the effect of change in HRT on membrane fouling.

One potential reason for this effect is that by decreasing HRT, flux rises above critical flux [1,8]; in such cases, shortly after HRT is decreased, a sharp rise in the TMP profile is usually observed, whereas in the present study the significant increase in the TMP profile is observed around 20 days after HRT was decreased to 18 h. This indicates that decreasing the HRT has indirectly affected the rate of membrane fouling.

Previous works have shown that change in operation parameters of the MBR such as SRT and HRT can affect parameters which have a direct influence on the rate of membrane fouling [19,20]. These parameters include morphology of the activated sludge, PSD, production of EPS/SMP, MLSS and sludge viscosity [16,17]. For example, Meng et al. [19] found that stepwise decrease in HRT from 10-12 h down to 3-4 h resulted in significant decrease in the dissolved oxygen concentration, which in turn resulted in the overgrowth of filamentous organisms in the activated sludge; this in turn led to increase in both EPS concentration and mixed liquor viscosity, which contributed to the significant increase in membrane fouling observed at the low values of HRT. Chae et al. [20] reported that a decrease in HRT resulted in an increase in EPS and mean floc size which in turn resulted in a worsening of sludge settleability and membrane resistance. Chang et al. [8] attributed the higher rates of membrane fouling at lower HRTs to the resulting high MLSS concentrations, and/or the high membrane flux.

In order to better understand the reasons for the observed effect of decreasing HRT on the rate of membrane fouling, EPS/SMP, PSD and MLSS were measured at various times during the operation of the MBR. The total EPS, EPS_c and EPS_p profiles and the corresponding SMP, SMP_c and SMP_p profiles during the operation of the MBR are presented in Figs. 5 and 6, respectively. The results show a higher concentration of total EPS and its components in phase 1 comparing to phase 2, with these concentrations generally showing a decreasing trend during phase 2. On other hand, during most part of phase 2 the concentration of total SMP and SMP_p increased whereas the concentration of SMP_c showed a significant drop.



Fig. 6. Variation of SMP, SMP_p and SMP_c concentration along time.

EPS and SMP have both been identified as important factors in membrane fouling in MBRs [16,17,25]. There are, however, contradictory reports on the effect of EPS and SMP on membrane fouling. Some studies in MBR have identified EPS as responsible for membrane fouling [17–20,25–27] whereas others have associated SMP, instead of EPS, with membrane fouling [11,25,28–33]. What can be concluded from these studies is that although both EPS and SMP are important causes of membrane fouling, they are not the only parameters responsible for it [17].

The results in Figs. 5 and 6 seem to show that during the present study, SMP rather than EPS was one of the causes of the severe membrane fouling observed during phase 2. The TMP trend obtained in phase 3 is a further confirmation for this (Fig. 4). It shows that although water cleaning of the membrane resulted in reduction of the TMP, it did not restore the TMP values obtained in phase 1. Since, fouling due to pore blocking can only be removed by chemical cleaning, this points to the pore blocking mechanism as the major fouling mechanism during phase 2 and SMP, rather than EPS, has been mainly associated with pore blocking [11,25–27]. Meng and Yang [11] have also reported that, with deflocculated sludge, pore blocking contributes more to membrane fouling than cake layer resistance. The PSD data (Table 2) and microscopic observations of the sludge particles during phase 2 (Fig. 8), discussed below, suggest that in the MBR during phase 2 deflocculation of activated sludge flocs had indeed occurred.

There is a complex interrelationship between EPS and SMP levels inside MBR [17,25,30,34]. Meng et al. [25] have reported a direct correlation between SMP and EPS. SMP is formed either through the metabolism of substrate by the microbial culture in activated sludge or is produced by the cells usually as a result of release/hydrolysis of EPS or as a result of cell lysis. The results presented in Figs. 5 and 6 show that during phase 2, the fall in

Table 2	
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Sludge p	article size	distributions	at different HR
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Percentile	HRT = 24 h	HRT = 18 h	HRT = 18 h
	50th day	70th day	95th day
	John day	70th day	Joinday
	Size (µm)	Size (µm)	Size (µm)
10%	38.83	21.65	18.5
30%	78.07	41.96	34.62
50%	112.57	61.2	49.35
70%	157.14	89.41	68.9
80%	190.18	114.73	84.01
90%	244.13	181.59	110.03
99%	389.47	512.81	274.92
Mean size	129.45	89.76	60.53



Fig. 7. Microscopic observation of sludge from MBR at HRT = 24 h–50th day.

total EPS and EPS_{p} , roughly corresponded with the rise in total SMP and SMP_{p} , suggesting that part of the origin of the SMP generation during phase 2 is release of bound EPS.

The significant reduction in SMP_c during phase 2 can be the result of attachment to membrane and/or degradation by the mixed bacterial population and/or attachment to sludge particles. The possibility of attachment of SMPc to the membrane during phase 2 is supported by some previous reports of MBR studies: Meng and Yang [11] found that during membrane filtration of deflocculated sludge, SMP_c was a major constituent of the cake layer formed on the membrane. Viero et al. [35] have also reported the adsorption of SMP_c to the membrane in MBR, resulting in the formation of a gel layer. The formation of such a layer during phase 2 in the present study was noted through visual observations of the membrane surface. The logic for SMP_c biodegradation during phase 2 is that the micro-filtration membrane retains part of the SMP and allows a greater time for its degradation by the bacterial population [10]. This explanation is supported by the fact that the level of COD in the permeate was very low even during periods in which a rise in SMP inside the MBR was observed. The possibility of attachment of part of the SMP_c to the sludge particles is supported by the slight rise in EPSc observed during phase 2. The latter two explanations are also supported by PSD data in Table 2, which indicate decrease in mean floc sizes and increase in the proportion of small flocs during phase 2. Decreased floc sizes have been associated with better pollutant biodegradation in MBRs and CASPs due to the increase in the surface area of the flocs for adsorption of organic pollutants [10,12,26].

The drop in sludge mean particles size, together with increase in sludge supernatant turbidity – which was observed during phase 2 but not quantified – are indications of the occurrence of the phenomenon of sludge deflocculation during phase 2 [11]. Further evidence for the occurrence of deflocculation in phase 2 can be found through comparison of Figs. 7 and 8, which are microscopic pictures of sludge samples from phases 1 and 2 of the operation of MBR, respectively. It can, therefore, be concluded that the reason for the release of EPS from sludge flocs in phase 2 is sludge deflocculation. The indirect correlation between EPS and sludge flocculation in MBRs has been previously reported by Ng and Hermanowicz [12].

According to some previous studies, exposure of activated sludge to toxic chemicals can result in sludge deflocculation. Schwartz-Mittelmann [36] showed that the addition of 1000 mg/L phenol to bioreactors containing activated sludge induces sludge deflocculation. Bott and Love [37] have reported that shock loading with electrophilic (thiol-reactive) toxic chemicals results in sludge deflocculation. This occurs through activation of the glutathione-gated potassium efflux (GGKE) system in activated



Fig. 8. Microscopic observation of sludge from MBR at HRT = 18 h-90th day.

sludge communities, which is a bacterial stress response mechanism against electrophilic (thiol-reactive) toxic chemicals. The activation of this system results in release of K⁺ from the bacterial cells, which increases the localized concentration of monovalent to divalent ions within the EPS, resulting in the weakening and disintegration of the floc structure and release of bound EPS into solution.

Styrene is a weakly electrophilic thiol-reactive toxic chemical. To the knowledge of the authors, the effect of styrene on sludge flocculation/deflocculation has not been previously studied. However, based on the properties of styrene we guess that the deflocculation of activated sludge observed in phase 2 was caused by a shock loading of styrene, as a result of increase in its OLR when HRT was reduced to 18 h. It should be pointed out that the SOUR values obtained for the activated sludge during phase 2 were around $6.9 \text{ mg } O_2/\text{gVSS}$ h which was very similar to the value obtained for the activated sludge seed; this suggests that the OLR of styrene at HRT of 18h did not inhibit aerobic metabolic activity of the mixed bacterial culture inside the MBR; this is in line with previous reports which show that GGKE response mechanism is induced by thiol-reactive toxic chemicals at concentrations below their toxicity thresholds [37]. However, the confirmation of this explanation requires further study.

Finally, it should be pointed out that the size of the activated sludge particles has also been reported to be an important parameter in membrane fouling, with smaller particle sizes being associated with a more severe membrane fouling [12,13,20,25,30,38,39]. According to Lim and Bai [38] small particles can increase the specific cake layer resistance and particles with size close to pores can contribute to internal and external pore blocking. According to Meng et al. [13], small particles and colloids have a higher tendency to deposit on membrane surface. Bai and Leow [39] have reported that particles having a size smaller than 50 µm result in a greater specific cake resistance.

4. Conclusion

- (1) The treatment of a synthetic wastewater containing 50 ppm styrene in an MBR resulted in more than 99% removal of COD and styrene at HRT of 24 h and 18 h. Unlike previous reports with activated sludge reactors, where styrene removal partly occurs through air stripping, in an MBR, the mechanism of styrene removal can be exclusively through biodegradation.
- (2) A decrease in HRT from 24 h to 18 h resulted in the development of severe membrane fouling in the MBR. The EPS and SMP profiles indicated that SMP, rather than EPS, was responsible for this fouling. The increase in styrene OLR, when HRT

was reduced to 18 h, is thought to have resulted in release of EPS from the cells, which in turn caused sludge deflocculation and increase in SMP. The occurrence of sludge deflocculation was also indicated by comparison of PSD and microscopic pictures of the activated sludge particles at HRTs of 18 h and 24 h.

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