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The effect of HRT and carriers on the sludge specifications in MBR to remove VOCs from petrochemical wastewater

Hossein Hazrati, Jalal Shayegan*, S. Mojtaba Seyedi

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran, Tel. +98 2166165420; Fax: +98 2166022853; email: shayegan@sharif.edu (J. Shayegan)

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ABSTRACT

This work employs two membrane bioreactors (with and without carrier) to evaluate the influence of carrier and hydraulic retention time (HRT) on the sludge specifications when removing organic volatile compounds (e.g. styrene and ethylbenzene) from petrochemical wastewater. This study is conducted during three various HRTs. The results indicate that the optimum HRT (e.g. 15 h.) was achieved in the reactor with carrier during biological removal and membrane fouling minimization. During the optimum HRT, the biological removal efficiency for styrene, ethylbenzene, and COD is 99.8 ± 0.1%, 99.8 ± 0.1%, and 99 ± 0.8%, respectively, and the concentration of styrene and ethylbenzene in the exit air reached to the minimum concentration (e.g. 0.1 and below 0.1 ppm, respectively). The fluctuation of the transmembrane pressure indicates a slight variation for the reactor with carrier rather than without carrier. Further, the sludge particle distribution in reactors demonstrates that the HRT reduction decreases the sludge particle size. This is also validated by flocculation ability tests. Finally, the alteration of soluble microbial product (SMP) and extracellular polymeric substance (EPS) in two reactors during all the HRTs show that the SMP is the main reason for fouling of the membranes and the EPS is not the main factor for sludge flocculation.

Keywords: Membrane bioreactors; Suspended carrier; Sludge specifications; VOC and HRT

1. Introduction

The emission of volatile organic compounds (VOCs), especially styrene and ethylbenzene that are the most common contaminants in petrochemical wastewaters, has been concerned many environmental organizations and research centers. These contaminants not only have destructive effect on the environment but also raise health concerns for workers. Wastewater treatment processes have been established to respond appropriately and relief various anxieties about the public health [1]. These methods include physical techniques such as activated carbon adsorption [2], chemical procedures such as ozonation [3], and biological methods such as conventional activated sludge (CAS) process [4], rotating biological contactor process [5], and stabilized biofilm [6]. Biological methods compared with other methods cover a wide spectrum of advantages as they are compatible to the nature. Among the biological methods, CAS has been employed in many industries as well as the petrochemical industry. It was reported that

*Corresponding author.

biodegradation, stripping, and absorption are three main mechanisms that cause the removal of VOCs in the CAS systems. Meanwhile, the absorption mechanism is not effective enough in the removal of VOCs [7]. To increase the mixed liquor suspended solid (MLSS) concentration in the activated sludge systems, which causes the increase in the biological removal, a membrane could be used instead of secondary settling tank. Therefore, the removal of VOCs through the biodegradation mechanism increases in comparison with the stripping mechanism. Several researches used the MBR systems for the petrochemical wastewater treatment [8–12]. Chang et al. [9] found minor effect of hydraulic retention time (HRT) in the range of 15–30 h on the removal efficiency of the MBR used for the treatment of high-strength acrylonitrile–butadiene–styrene wastewater. It was also reported similar pentachlorophenol removal efficiency at HRTs in the range of 12–24 h in an MBR used for treating a synthetic wastewater [13]. Another study offered that the retention time of 13 h can be applied for petrochemical wastewater [11]. Moreover, Fallah et al. [10] showed that the styrene removal efficiency from synthetic wastewater was over 99 percent during the HRT of 18 h. It should be considered that the authors only used styrene as substrate, while in the actual wastewater of poly styrene plants (P.S.P), ethylbenzene is always present with styrene. Therefore, consideration of the inhibition effect of ethylbenzene is a major contribution for the improvement of the petrochemical wastewater treatment. Another study offered that the HRT of 13 h can be applied for petrochemical wastewaters [11]. Despite several advantages of MBR systems, they have limited disadvantages. The main disadvantage of a MBR is the reduction of permeate flux due to the membrane fouling [14]. The membrane fouling increases both operation and maintenance costs [15]. Previous works showed that membrane fouling is related to the operating parameters such as HRT, sludge retention time (SRT), and sludge specifications (e.g. floc size, extracellular polymeric substance (EPS), soluble microbial product (SMP), and sludge viscosity) [16–18]. The value of HRT is one of the important parameters in MBR systems [8,11]. For a fixed flow of wastewater, the volume of system could be reduced when the HRT decreases but with the increase in HRT, system works with high efficiency due to the reduction of the organic loading rate (OLR). However, the reactor should need more volume. It has also been demonstrated that the reduction of HRT leads to further membrane fouling caused by the reduction of particle size distribution and the SMP enhancement [10]. Previous studies tried to alter the sludge specifications such as SMP and EPS by adding carrier or chemical material to the reactor [19–21]. There are, however, contradictory reports on the effect of carrier on membrane fouling [18,19,22]. Chun et al. [22] showed that membrane fouling increased with dosage of 5% (v/v) and with density of 978 kg/m^3 suspended carrier due to the big flocs' breaking. This happening released a higher amount of SMP content. Further, Jin et al. [19] demonstrated that the addition of about 6 percent (in volumetric scale) carriers with density of 573 kg/m^3 to the MBR reduced the membrane fouling due to the formation of larger flocs. It has been presented in several papers that the SMP is one of the significant parameters in membrane fouling [18,19]. For example, Geng and Hall [21] observed that the SMP concentration in sludge was an important parameter in the membrane fouling while the EPS concentration was not related to the clogging issue directly.

The aim of this study was to simultaneously examine the effect of both HRT and carrier on the removal efficiency of VOCs and sludge specifications which leads to membrane fouling. In addition, the sludge specifications (e.g. EPS concentration, SMP concentration, flocculating ability, sludge particle size, and specific oxygen uptake rate (SOUR)) are determined in three different HRTs and two MBR reactors (the MBR reactor with and without carrier). Furthermore, the optimum HRT for both reactors is well-defined.

2. Materials and methods

2.1. Experimental setup and operation condition

In this study, two identical laboratory-scale MBRs (R1 without carrier and R2 with the carrier) was manufactured. The dimensions of both MBRs were 60 cm × 22 cm × 6.5 cm. Fig. 1(a) depicts schematic diagram of the MBRs that were operated in parallel situation in order to investigate carrier's effects. Fig. 1(b) shows the side view of these two reactors. The effective volume in each reactor was 7 l, and they were composed of four main sections which will be discussed in following sentences: (1) sides: the designed MBRs were made of two layers: the inner part that forms the main reactor's basin in which the biological reactions occur, and the outer part through which the warm/cold water can flow during the temperature flow. Since the temperature variations were not studied in this study, all the biological processes were performed at 25˚C, (2) membrane: the employed membrane in this study was a micro-filtration (MF) type with an effective area of 0.1 m^2 and pore nominal diameter of 0.4 µm. The membrane is produced by the Kubota® Company and is made of polyethylene (PE),

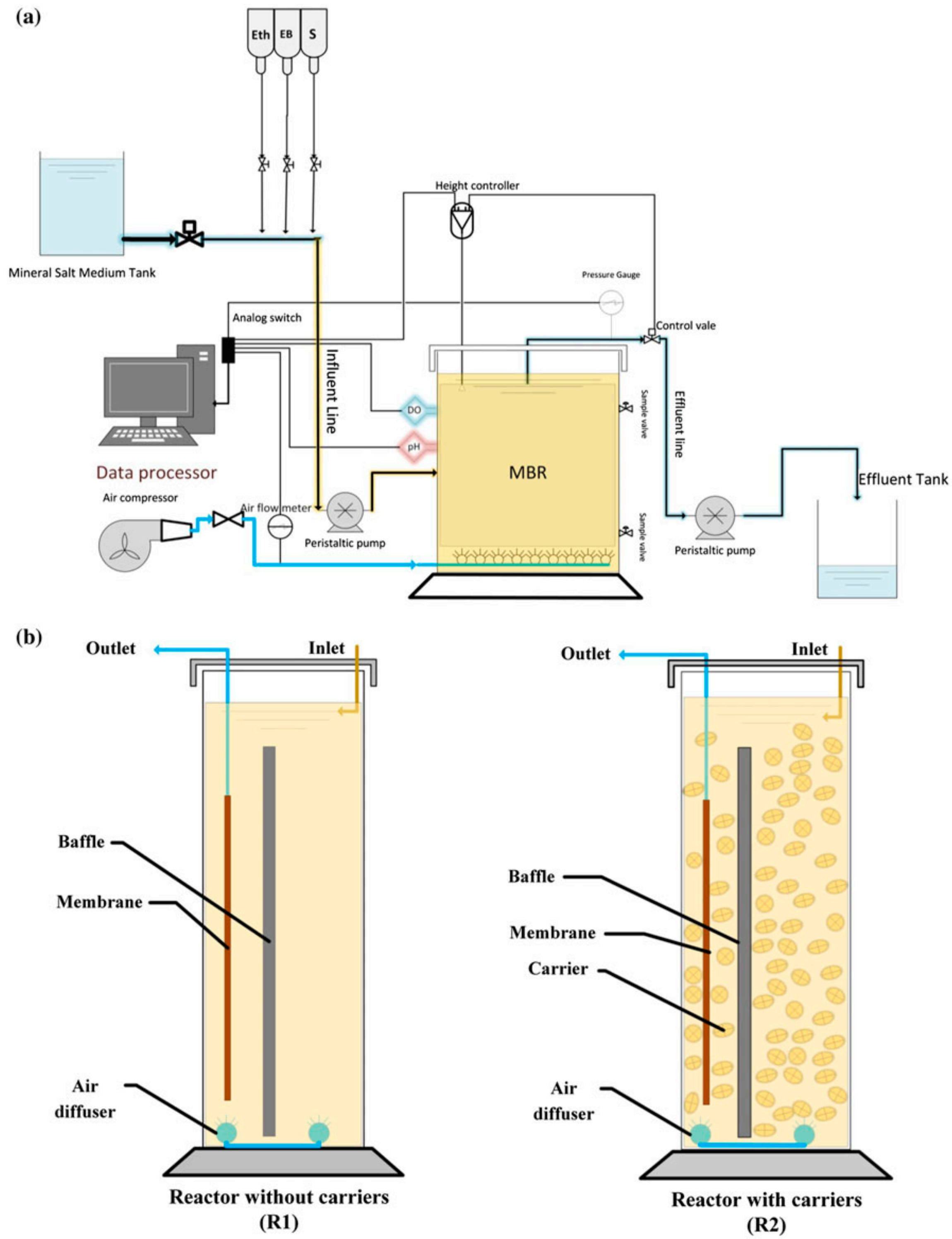

Fig. 1. (a) Schematic process flow diagram and (b) side view of the two reactors.

(3) conductor blade or baffle: the aeration process in MBRs was completed for two purposes, first is to supply the oxygen needed for biological processes and second is to clean the membrane surface and reduce the fouling rate. To achieve the second goal, a polymethyl methacrylate plate was used as a baffle to keep

the air bubbles near the membrane surface so that they can make proper tensions with it to remove any visible sediment particles adhering to the membrane surface. The distance of the baffle from the membrane and the basin side was set to 2 and 1.5 cm, respectively, (4) the height sensor: in this apparatus, the main bar length of the sensor is about 25 cm, which was installed on the MBR where it indicates the 7 l volume of the basin. The aerobic sludge used in the MBRs basin was supplied from the activated sludge of the Tabriz Petrochemical Company with MLSS and MLSS/MLVSS of 2,000 mg/l and 0.83, respectively. The sludge was adapted with synthetic feed for one month. For this purpose, the initial influent styrene and ethylbenzene concentration was set to around 10 mg/l and then increased to 100 mg/l with a few step changes during one month. The operating conditions of the MBR systems are described in Table 1.

2.2. Influent wastewater

The synthetic wastewater used in this research was formulated to simulate petrochemical industrial wastewater in terms of COD, styrene, and ethylbenzene concentrations which were 1,200, 100, and 100 mg/l, respectively. Ethanol was used as a carbon source which created a COD concentration of about 1,200 mg/l. Moreover, to avoid the VOCs' stripping to air from the feed, the VOCs separately injected to the feed stream. To ensure that the influent VOC and COD concentrations have not decreased, these parameters were analyzed periodically. The synthetic wastewater compositions used in this study are described in Table 2.

2.3. Carriers

The porous and suspended carriers used in this work have a dimension of 10 mm in length, 8 mm in width, and 12 mm in height. It was made of polyethylene with a large surface area of 525 m^2/m^3 and a density of 645 kg/m^3. The carriers could be easily circulated throughout the whole reactor providing scouring effect on the membrane surfaces through aeration. A dosage of 2.0% (v/v) suspended carriers was introduced into reactor 2 (R2).

Table 2
The synthetic wastewater compositions used in this work

Components	Concentration (mg/l)
Ethanol	320
Styrene	100
Ethylbenzene (EB)	100
NH_4Cl	560
K_2HPO_4	35
KH_2PO_4	45
$MgSO_4{\cdot}7H_2O$	13
$CaCl_2{\cdot}2H_2O$	7
$FeCl_3$	5
$ZnSO_4$	2
$NaHCO_3$	500
EDTA ($C_{10}H_{16}N_2O_8$)	7

2.4. Analytical methods

The styrene and ethylbenzene concentration was analyzed using a gas chromatograph (GC). The GC (Young Lin, ACME-6100) was set with a flame ionizing detector and the attached silica capillary column (DB-5, 0.53 mm I.D., 30 m length, 1 mm film thickness) that was designed to be well suited for the analysis of volatile components. The carrier gas was helium flowing at 15 ml/min. The oven temperature was maintained at 70℃ for 1 min duration and raised to 140℃. The temperatures of the injector and the detector were fixed at 200 and 240℃, respectively. The styrene and ethylbenzene concentrations in the liquid phase were estimated using the headspace method [10]. The gas flow rate from the bioreactors' headspace was measured using a

Table 1
Operating parameters for membrane bioreactors

Parameter	Dimension	Reactor	From 0 to 43rd days	From 43rd to 86th days	From 87th to 125th days
HRT	h	R1 and R2	20	15	10
SRT	d	R1 and R2	20	20	20
Effluent flux	l/m^2 h	R1 and R2	3.18	4.24	6.36
OLR	kg/m^3 d	R1 and R2	1.44	1.92	2.88
Air flow rate	l/min	R1	8	8	8
		R2	5	5	5
DO	mg/l	R1	4.2–5.1	3.2–4.3	5.1–5.9
		R2	3.1–4.4	2.1–3.3	3.5–4.5

flowmeter. To quantify the concentration of VOCs within the exit air, the gas collection was done using water displacement method. Then, the intended gas samples were collected using 100 µl gas tight syringe (Hamilton). The samples were analyzed directly through manual injection in the GC using the same program condition mentioned above. The MLSS, MLVSS, COD, and SOUR were estimated according to the standard methods [23]. The flocculating ability was measured with the method described by Jorand et al. [24]. The SMP and EPS concentration were measured utilizing the method described by Chang et al. [25]. The protein concentration was measured by Bradford's method using bovine serum albumin as the standard [26], whereas the corresponding polysaccharide fraction was determined by phenol–sulfuric acid method [27]. The particles size distribution was determined by the Fritsch "analysette 22" NanoTec laser-particle-sizer with a detection range of 0.01–1,000 µm.

3. Results and discussion

3.1. The effect of HRT and carriers on removal efficiency

3.1.1. The effect of HRT on removal efficiency

According to a previous study by Eckenfelder [28], the absorption of a pollution by the activated sludge could be only considered as an important mechanism when the logarithm of partition coefficient of octanol–water (log K_{ow}) is more than 4, while for styrene and ethylbenzene, it is about 3.15 and 2.85, respectively [7,29]. Moreover, previous studies revealed that the styrene absorption by sludge as a removal mechanism is insignificant [10]. Thus, during styrene and ethylbenzene elimination process, the impact of absorption is negligible. Therefore, it was assumed that the overall removal efficiency for styrene and ethylbenzene is through biological and stripping removal.

The overall removal efficiency of styrene, ethylbenzene, and COD is presented in Fig. 2. As it can be seen, in the steady state condition during the HRT of 20 h, the removal efficiency of COD in the R1 (reactor without carrier) is around 98 ± 1 percent and the removal efficiency of both styrene and ethylbenzene is more than 99.9 ± 0.8 percent. Similar to R1, the removal efficiency of styrene and ethylbenzene is more than 99.9 ± 0.1 percent in the R2 (reactor with carrier), while the removal efficiency of COD is better than R1 with a negligible difference (more than 99 ± 0.1%). In addition, the concentration of ethylbenzene and styrene in the exit air from the reactor was measured on a daily basis. Fig. 3 shows that during the HRT of 20 h, the concentration of ethylbenzene and styrene in the R1 exit air and in the steady state condition is 0.7 ± 0.1 and 1 ± 0.1 ppm, respectively. Further, these concentrations in R2 exit air are 0.4 ± 0.1 and 0.6 ± 0.1 ppm, respectively. Except during the first few days (days 44 to 47th) that the removal efficiency extremely reduced in both reactors, the removal efficiencies of COD, styrene, and ethylbenzene were increased during the HRT of 15 h. Eventually, COD, styrene, and the ethylbenzene removal efficiency in the steady state condition reached 98 ± 1, 99.8 ± 0.1, and 99.8 ± 0.1 for the R1 and 99 ± 0.8, 99.8 ± 0.1, and 99.8 ± 0.1 for the R2, respectively. Due to the sudden increment of the OLR in the reactors at day 44, the microorganisms were under shock. Therefore, a decline trend was observed during the mentioned days. Right after this stage when microorganisms adapt themselves with the new condition, the removal efficiency of systems gradually increased and eventually reached the steady state condition. Following the variation of the HRT from 20 to 15 h, the biological removal efficiency of styrene and ethylbenzene in both reactors were increased. The results could be explained by two factors which affect the removal efficiency when the retention time is reduced. The first factor is the slight increment of the OLR which boosts the concentration of the MLSS in the reactor. The second factor is contact time between contaminants and the sludge which is reduced in the reactor. It is reasonably inferred that the increase in MLSS has a positive effect and the reduction of contact time between contaminants and sludge has a negative impact on the biological removal efficiency (it is worthy to mention that this factor has also a positive effect due to the reduction of the contaminants' removal through volatility). Since MLSS concentration in both the reactors increased, this happening in both reactors neutralized the probability negative effect of the contact time, and as a result, the removal efficiency increased. The concentration of ethylbenzene and styrene in the exit air located in R1 at steady state condition were 0.4 ± 0.1 and 0.8 ± 0.1 ppm, respectively. In R2, the concentrations were about zero and less than 0.1 ppm for ethylbenzene and styrene, respectively. Comparison of the results reveals that by the reduction of HRT from 20 to 15 h, the removal of contaminants through volatility was reduced. In a previous study, it was also reported that the HRT reduction decreased the removal efficiency through volatility [9]. This could be attributed first to the MLSS concentration increase caused by the increment of the OLR in the system and thereafter to the retention time of wastewater reduced in the system. When the HRT reduced to 10 h, the OLR in the system increased extremely. On the other hand, the contact time between the activated sludge and wastewater

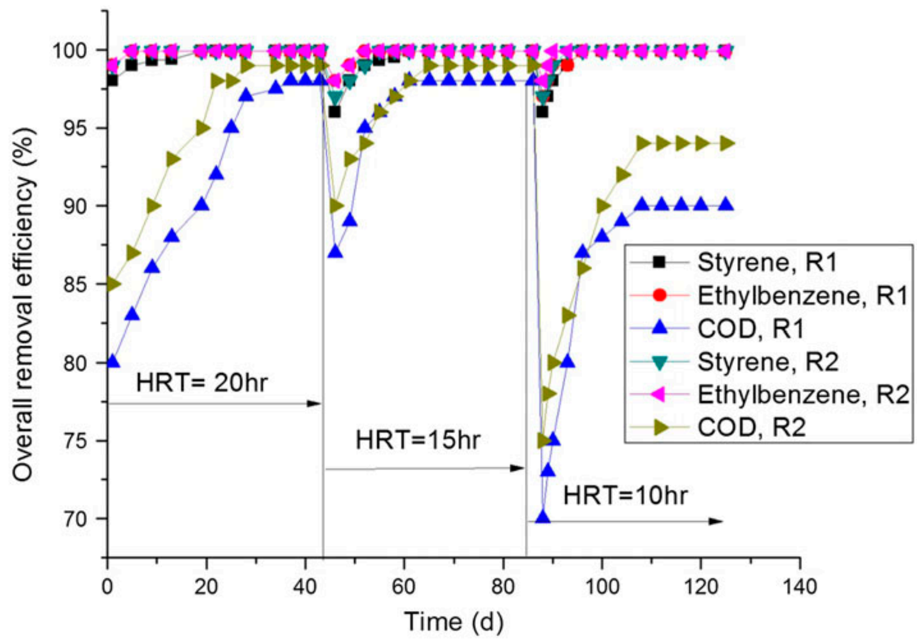

Fig. 2. Variations of COD, styrene, and ethylbenzene removal during the operation of the MBRs HRT of 20 h (days 0–43rd), 15 h (days 44–85th), and 10 h (days 86–125th).

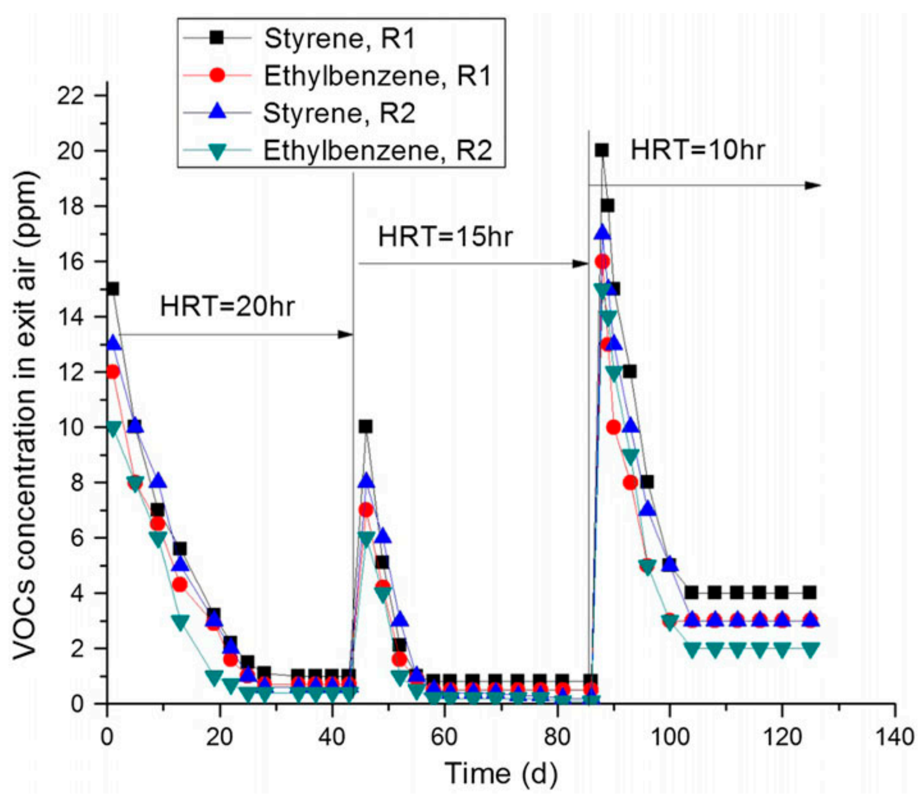

Fig. 3. Ethylbenzene and styrene concentration in the exit air during the operation of the MBRs HRT of 20 h (days 0–43rd), 15 h (days 44–85th), and 10 h (days 86–125th).

decreased significantly compared to the previous states (e.g. in HRTs of 20 and 15 h). Therefore, the biological removal efficiency in both reactors reduced significantly. During this HRT, the removal efficiencies of COD, styrene, and ethylbenzene were 90 ± 2.5, 99.8 ± 0.1, and 99.8 ± 0.1 percent in R1 and 94 ± 2.3, 99.8 ± 0.1, and 99.8 ± 0.1 percent in R2, respectively. The concentration for styrene and ethylbenzene existent in the exit air were 4.5 ± 1.3 and 3.4 ± 1.1 ppm in R1 and 2.8 ± 0.9 and 1.5 ± 0.6 ppm in R2. It is worth noting that since the concentration of exit gases increased due to the MLSS concentration reduction, the removal efficiency using the biodegradation mechanism was reduced during the HRT of 10 h compared with two previous HRTs. Therefore, it is inferred that the optimum HRT and OLR in pilot scale for petrochemical wastewater is 15 h and 1.92 kg/m^3 d, respectively.

3.1.2. The effect of carriers on removal efficiency

The results of Section 3.1.1 indicate that styrene and ethylbenzene removal in both reactors was not by stripping mechanism. Therefore, the removal mechanism in the reactors is mainly through biodegradation mechanism. The small amount of emissions of organic compounds in R2 compared with R1 could be explained by the lower aeration rate in R2 and the presence of carriers in R2 which lead to a higher contact area between sludge and wastewater. This leads the biomass to remove the compound more effectively. This clearly indicates that the COD reduction rate in R2 is lower than R1 when the HRT is reduced to 10 h. Hence, it can be claimed that the second reactor is more resistant to the increment of the organic load than the first reactor.

From the obtained results, it could be observed that the MBR systems compared with the CAS ones show better performance among the removal of VOCs. But it is possible that the removal rate by the stripping mechanism increases in these systems due to their need for higher aeration and reduces the membrane fouling. Therefore, to decrease the fouling rate, carriers were used and aeration rate was decreased. This is the main cause for the reduction of stripping in the R2. It is worth noting that the exit air from the aeration tank of a CAS system was too much and did not meet the environmental standards [30,31]. For example, it was shown that styrene removal using the stripping mechanism in the CAS system is about 15% [7]. In another study, it was reported that the removal efficiency of chlorinated and nonchlorinated VOCs through stripping by CAS was about 50 and 20%, respectively [32]. Battacharya et al. [33] also showed that the removal of VOCs by this mechanism was above 2% while in this study, the stripping removal efficiency was below 0.5%.

3.2. Sludge specifications and the microbial activity

3.2.1. MLSS, MLVSS, and microbial activity variations in reactors

The variation of MLSS concentration at different times is shown in Fig. 4. As it can be seen, the MLSS concentration increased in the first stage and fixed to 4,200 ± 36 mg/l in the final stage during the HRT of 20 h in both reactors. Furthermore, Fig. 4 depicts that when the HRT reduces from 20 to 15 h, the OLR increases from 1.44 to 1.92 kg/m^3 d. After a slight reduction in the biomass concentration due to the shock posed to the system, the biomass concentration starts to increase. From day 77, MLSS concentration reached to its steady state condition, eventually the MLSS concentration in R1 and R2 reached to about 4,600 ± 42 and 5,000 ± 37 mg/l, respectively. When HRT reduced to 10 h, the concentration of the MLSS decreased to 2,900 ± 62 mg/l. Besides, the fluctuation of the MLVSS concentration is shown in Fig. 4, too. This parameter almost followed the similar trend to MLSS. It is worth noting that the MLSS concentration in the MBR is about 2.5 times of seed concentration which was for CAS system. Therefore, it can be observed that MBR systems show better performance among organic compounds' removal compared with CAS.

In order to evaluate the oxygen transfer in the reactors and to determine the HRT effect on the bacterial activities, the SOUR parameter was measured for the activated sludge which accumulated in the reactors. Table 3 shows the SOUR amount and the flocculating ability during the HRT of 10, 15, and 20 h for both reactors. With the reduction of HRT from 20 to 15 h, the effects of reduction of sludge particle size prevailed on the increasing OLR; therefore, the SOUR (which is influenced by both of them) slightly increased. With the further reduction of HRT from 15 to 10 h, the effects of increasing OLR prevailed on the reduction of sludge particles; therefore, the SOUR decreased. In HRT of 10 h, the OLR amount was higher than the amount that the microorganisms can tolerate for their activity. Therefore, MLSS concentration significantly decreased, and as a result, the SOUR reduced during this HRT. The effect of OLR and the sludge particle size on SOUR more will be further explained in Section 3.2.2. Although particle size distribution in the HRTs will be discussed in Section 3.2.2, in this section the reason for the particle size reduction is investigated by the flocculation ability test. The

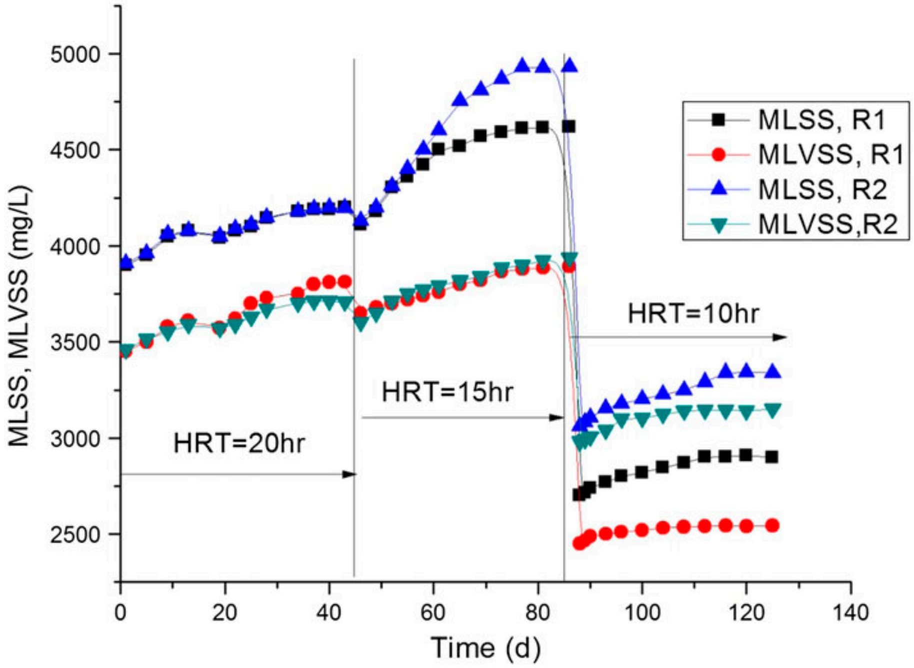

Fig. 4. Variations of MLSS and MLVSS during the operation of the MBRs HRT of 20 h (days 0–43rd), 15 h (days 44–85th), and 10 h (days 86–125th).

Table 3
The SOUR variation and flocculation ability in the both reactors in varying HRTs

Rectors	HRT (h)	SOUR (mg O_2/h gVSS)	Flocculating ability (%)
R1 (without carrier)	20	19.2 ± 2.1	38 ± 5
	15	20.2 ± 1.8	24 ± 3
	10	14.2 ± 1.7	20 ± 4
R2 (with carrier)	20	17.3 ± 1.5	63 ± 6
	15	18.6 ± 1.6	51 ± 6
	10	12.1 ± 1.4	48 ± 4

flocculating ability was measured on the suspended biomass in both reactors. It can be seen that flocculating ability during the HRT of 20 h was higher than HRT of 15 h (see Table 3). The floc particle size reduction causes the oxygen transfer rate to reduce. Besides, when the HRT reduced to 10 h, the SOUR amount decreased in both the reactors. This might be due to the enhancement of the OLR on biological mass. Section 3.2.2 discusses the reasons in further detail. It is worthwhile noting that the flocculating ability during all HRTs for R2 is higher than R1 caused by the sludge floc occurred due to the presence of suspended carrier. Other researchers also demonstrated that the addition of carrier to the MBR can reduce the membrane fouling due to the formation of larger flocs [19].

3.2.2. Particle size distribution during various HRTs for both MBRs

One of the major impacts of morphological changes in activated sludge is particle size distribution. Membrane fouling rapidly occurs when the activated sludge contains fine particles. Thus, the sludge particle size is considered as the key element for membrane fouling issue [34,35]. Meng et al. [36] revealed that the smaller particles of sludge show more tendency to stick to the membrane surface. In other words, the smaller flocs (less than 50 μm) will increase membrane fouling which was also reported by Bai and Leow [37]. The particle size distribution of sludge in the reactors with the HRT of 20, 15, and 10 h is shown in Table 4. The average particle size (APS) during the HRT of 20 h in both reactors (R1 = 65, R2 = 110 μm) is more than the HRT of 15 h (R1 = 30, R2 = 72 μm). The increase in OLR leads to the separation of sludge floc which is the main reason for the reduction of particle size in the sludge. However, this increase in the OLR had no effect on the sludge biological activities, and therefore, the oxygen transmission rates did not decrease. Also, due to the particle size reduction, the amount of SOUR slightly increased. Further, the sludge flocs' breakup is caused by the shock and increase in the loading rate of styrene and ethylbenzene during the HRT of 10 h. (APS for reactors: R1 = 22, R2 = 55 μm). Nevertheless, biological activities (SOUR) were reduced during this HRT, which indicates that the loading of styrene and ethylbenzene was greater than the amount that the microorganisms can tolerate for their activity. Thus, in this condition, styrene and ethylbenzene could be toxic for microorganisms. Therefore, the removal efficiency has reduced significantly during the HRT of 10 h. Another study has been publicized that there was a significant contributor to activated sludge deflocculation caused by shock loads of toxic electrophilic chemicals. This happening occurs through activating glutathione-gated potassium efflux system in microbial population in activated sludge that microorganism's response to toxins. Activation of this system causes the release of K^+ ions from microorganisms. Hence, in the extracellular polymers, the amount of monovalent ions increased more than divalent ions that leads to weakening of flocs and release of extracellular polymers [38]. On the other hand, it can be noted that existing carriers in the R2 caused bigger sludge particle size than the R1 in all of the HRTs. Huang et al. [20] stated that using carriers more than a certain amount due to their strong rotation in the reactor would break down the flocs. They demonstrated that the addition of 5 percent (in volumetric scale) carriers to the MBR reduced the particle size distribution. However, sludge particle size increased when the volume of carriers was reduced from 5 to 1%. In their study, the density of carriers was 978 kg/m^3. It can therefore be concluded that high density in larger volumes leads to the breaking down of floc, while in this study, due to the application of lower density and longer carriers, even in 2% (v/v), large flocs were formed.

3.3. Membrane fouling

3.3.1. TMP variation with HRT in both MBRs

One of the major limitations of membrane bioreactors is membrane fouling. Thus, to evaluate this parameter, the transmembrane pressure (TMP) variation was measured continuously. The TMP variation during operation for both reactors is shown in Fig. 5. As it can be seen in Fig. 5, during the HRT of 20 h, the fouling rates for both reactors were less accelerated compared with the HRT of 15 and 10 h. In the second part, when HRT was reduced to 15 h after a few days, the TMP was increased faster in both reactors. Finally, the TMP value in R1 and R2 reached 110 and 60 mbar, respectively. The main reason for the sharp slope during the HRT of 15 h compared with the HRT of 20 h in both reactors could be the reduction of sludge particle size as consequences of the increase in OLR in each system that caused the floc to break down. Eventually, by reducing the HRT to 10 h, the fouling rate raised with almost the same steep of previous stage, and accordingly, the TMP amount increased to 170 and 90 mbar in R1 and R2. Furthermore, Fig. 5 illustrates that the TMP variations in R2 occurred with less acceleration than R1. These observations show that carriers are able to moderate membrane fouling. Even though in R2, fouling has

Table 4
The distribution of sludge particle size in the reactors with HRT 20, 15, and 10 h

HRT	20 h		15 h		10 h	
Percent	R1 (34th day) size (μm)	R2 (34th day) size (μm)	R1 (75th day) size (μm)	R2 (75th day) size (μm)	R1 (110th day) size (μm)	R2 (110th day) size (μm)
10	22.1	25.3	11.4	21.8	10.3	18.8
30	38.8	53.4	18.6	34.5	15.4	32.2
50	54.3	70.2	30.1	52.3	23.1	43.4
70	73.5	118.4	35.3	76.5	25.6	62.1
80	90.1	180.3	43.1	98.3	34.8	87.2
90	120.5	254.3	56.3	160.8	45.6	103.4
99	238.1	457.3	180.4	450.5	170.3	270.3
Mean size	65.4	110.3	30.7	75.2	22.5	55.1

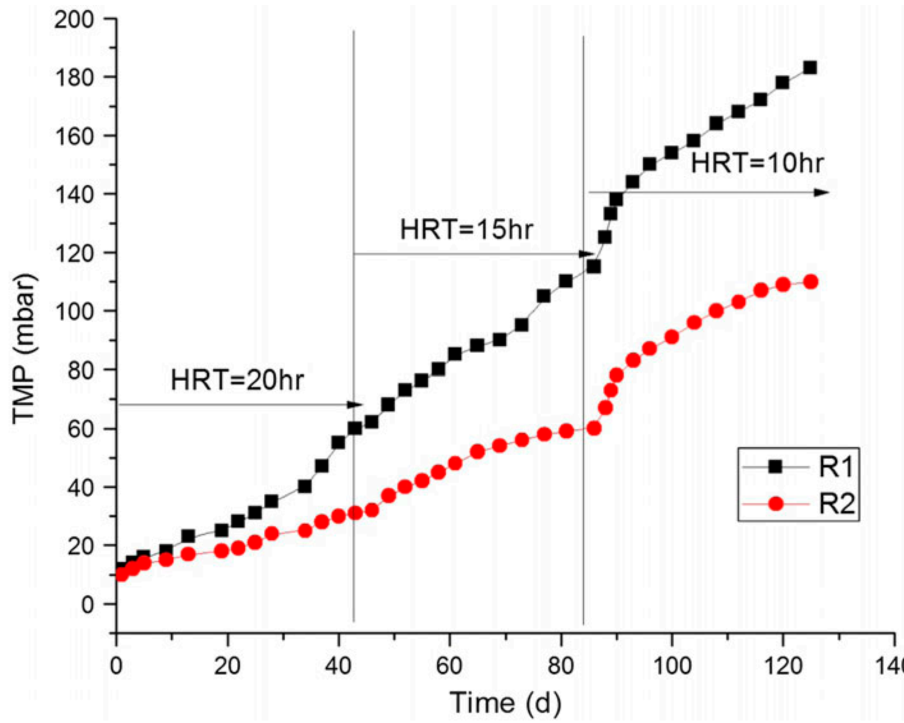

Fig. 5. Variations of TMP during operation HRT of 20 h (days 0–43rd), 15 h (days 44–85th), and 10 h (days 86–125th).

increased during the HRT of 15 h compared with 20 h, the TMP at the end of the HRT of 15 h was equal to the TMP value in the HRT of 20 h in R1. Huang et al. [20] showed that by the addition of 1% of carrier to the MBR system, membrane fouling was reduced. Membranes were taken out on day 120 and it can be seen that the sludge cake in the first membrane reactor was more than the second reactor. In fact, the sludge cake was not observed in the R2 membrane. Thus, the carriers on the membrane surface have positive effects on the removal of cake layers due to their shear stress with the membrane surface.

3.3.2. The effect of SMP and EPS on the membrane fouling

Previous researches showed that the SMP has major impact on the membrane fouling, and even some researchers have expressed that the effect of SMP is much stronger than EPS [19,22]. Zhao and Gu [39] reported that the SMP compounds which stuck to membrane surface in early days of operation could be easily separated with the physical methods. Meanwhile, in long run, it could cause irreversible membrane fouling which can be washed out only by chemical compounds. Nevertheless, while most researchers consider SMP as the responsible parameter for membrane fouling [19–21,31], some other studies have identified the EPS in charge for this event [34,40,41]. Even EPS has been reported as the main factor in membrane fouling and there is a close relationship between EPS and specific cake resistance [40]. Ahmed et al. [41] demonstrated that with increase in the EPS concentration, the resistance of cake layer would be increased. Furthermore, previous studies show that HRT variation can change SMP and EPS concentration which are important factors in membrane fouling [10].

In this study, the total SMP in both reactors is composed of two parts including protein and carbohydrates which is shown in Fig. 6(a). This figure depicts that the total SMP concentration and the protein part (SMP_p) were severely increased compared with the carbohydrate part (SMP_c) by the HRT reduction. These variations imply that when the HRT decreased, the sludge particle size was reduced, and as a result, the total SMP was increased in the mixed liquor. The SMP increased the membrane fouling by blocking the pores on the membrane surface. In previous sections such as in Section 3.2.1, it was concluded that with the reduction of HRT, the membrane fouling was increased. Besides, these products (SMP) were effective on cake formation.

Moreover, the SMP concentration in R2 was always smaller than the R1 because of the formation of larger flocs. Jin et al. [19] also examined the effect of carriers

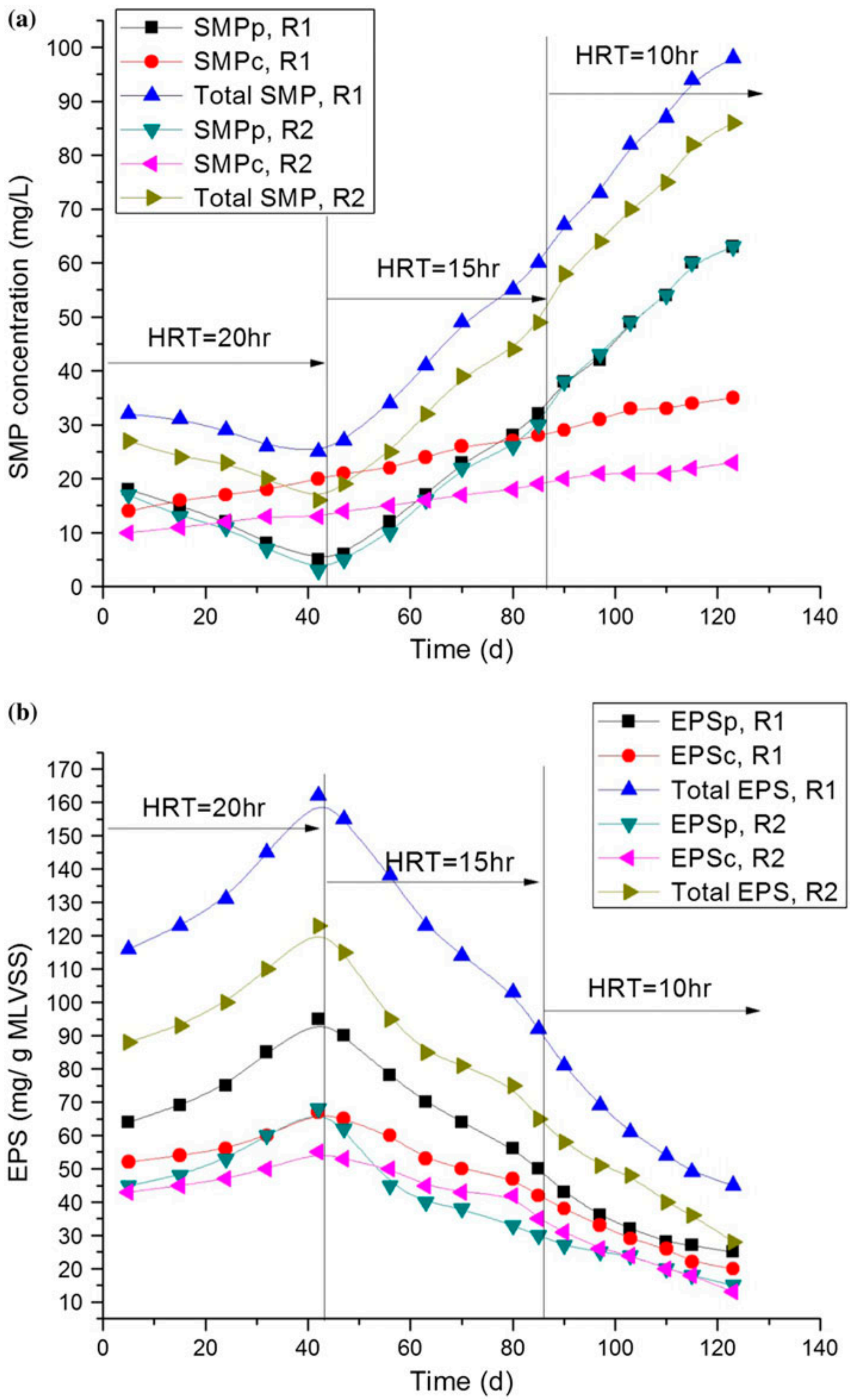

Fig. 6. (a) Variation of SMP, SMP_p, and SMP_c concentration and (b) variation of EPS, EPS_p, and EPS_c concentration during the operation of the MBRs.

on the MBR and found that by the addition of carriers, the SMP concentration would be decreased. This study demonstrated that a decrease in the SMP concentration and the reduction of membrane fouling occurred by two factors: (1) the increase in HRT and (2) the presence of carriers in reactor. In another study, it was also reported that the SMP concentration is an important parameter in the sludge properties and has a significant influence on membrane fouling. However, EPS concentration is not directly related to membrane fouling [21].

Fig. 6(b) exhibits changes for the whole EPS and its components including carbohydrate (EPS_c) and protein (EPS_p) during the operational period. From Fig. 6(b), it is easy to understand that total EPS concentration was reduced after the HRT reduction from 20 to 15 h and then to 10 h. Likewise, during this period, both the EPS_p and EPS_c were reduced. The decrease in total EPS accompanied occurred by changing of the sludge morphology from floc to dispersed growth due to the reduction of sludge particle size. Although the main flocculation mechanism is not entirely specified, EPS could be considered as one of the main factors for floc formation. It can be noted that the sludge particle size in the reactor containing carriers (R2) is larger and floc formation in this reactor is more than R1 which has the less EPS during the whole retention time. Therefore, in this research, EPS cannot be considered as the main factor for the floc formation and the membrane fouling would not be directly related to EPS.

4. Conclusion

The operation of the two MBR systems for the biological removal of VOCs demonstrated the 15 h time as an optimum HRT for the biological removal of volatile contaminants such as styrene and ethylbenzene. The reactor with carrier showed an enhanced performance in both liquid effluent and exit air compared with the reactor without carrier during this HRT. Moreover, the membrane fouling rate for the reactor with carrier and the HRT of 15 h was equal to the membrane fouling rate for the reactor without carrier and HRT of 20 h. This study further found that the reduction of the HRT causes variation on the sludge morphology such as the sludge particle size. The results also demonstrated bigger size for sludge particles in the reactor with carriers than that of without carriers. Finally, the study showed that while the high SMP concentration is the primary factor for membrane fouling, the EPS factor could not be the main reason for the floc formation.

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