Removal of antibiotics in sponge membrane bioreactors treating hospital wastewater: Comparison between hollow fiber and flat sheet membrane systems

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Abstract

Hollow fiber (HF) and flat sheet (FS) sponge MBRs were operated at 10-20 LMH flux treating hospital wastewater. Simultaneous nitrification denitrification (SND) occurred considerably with TN removal rate of 0.011–0.020 mg TN mg VSS^{-1} d^{-1}. Furthermore, there was a remarkable removal of antibiotics in both sponge MBRs, namely Norfloxacin (93-99% (FS); 62-86% (HF)), Ofloxacin (73-93% (FS); 68-93% (HF)), Ciprofloxacin (76-93% (FS); 54-70% (HF)), Tetracycline (approximately 100% for both FS and HF) and Trimethoprim (60-97 % (FS); 47-93% (HF). Whereas there was a quite high removal efficiency of Erythromycin in sponge MBRs, with 67-78% (FS) and 22–48% (HF). Moreover, a slightly higher removal of antibiotics in FS than in HF achieved, with the removal rate being of 0.67-32.40 and 0.44-30.42 μg mg VSS^{-1} d^{-1}, respectively. In addition, a significant reduction of membrane fouling of 2-50 times was achieved in HF-Sponge MBR for the flux range.

Keywords: hospital wastewater, antibiotic, sponge membrane bioreactor, hollow fiber (HF), flat sheet (FS).

1. Introduction

Wastewater generated from hospitals and medical centers contain risk hazards including toxic substances such as organics and nutrients, infected pathogens, virus, toxic chemicals, radioactive elements and especially antibiotics (Nasr et al., 2008). These compounds directly discharged to the environment will impact not only human health but also on the ecosystem (Sonia et al., 2009). This is the reason why hospital wastewater treatment is becoming an important priority in reducing environmental risks.

Antibiotics are an important group of pharmaceutically active compounds (PhACs) which has been widely used in both human and veterinary medicine (Sapkota et al., 2008). According to the previous studies, PhACs contribute low pollution of surface water (Huang et al, 2001). Some antibiotic groups as Sulfonamide, Fluoroquinolone and Macrolide were found a high concentration in hospital wastewaters (Santos et al., 2013; Vo et al., 2016). Sulfamethoxazole, Ofloxacin, Norfloxacin, Ciprofloxacin and Azithromycin which are a generation from these groups are not considerable transformation in the environment since a high concentration is detected in the wastewater discharged. Fluoroquinolone and Tetracycline groups were decomposed slower in the environment than the others (Huang et al., 2001). Moreover, these contaminants in the environment have been found at effluent of wastewater treatment plants (WWTPs) due to ineffective removal by conventional activated sludge (CAS) (Morato et al., 2014; Vo et al., 2016).

Micropollutants in terms of antibiotics removed during wastewater treatment occurs through different mechanisms as biodegradation, abiotic transformation, sorption to biomass as well.

Commonly, biodegradation and sorption process are mainly proposed to eliminate antibiotics (Sipma et al., 2010). Currently, to date, MBR technology in wastewater treatment is challenging the traditional treatment technologies applied by CAS. It has been emerged as an innovation technology with many advantages as operation at high biomass concentration, reduction of excess sludge production, a significantly low concentration in suspended solid in the treated effluent (Wizig et al., 2002), considerable elimination of pathogens and viruses (Melin et al., 2006) as well as appreciable cost decrease of the employed membranes (Simpa et al., 2010). In addition, the higher advantages of MBR compared to CAS in the case of biodegradable micropollutants, namely antibiotics remained certainly by the previous study of Bernhard et al. (2006). In the quest to enhance micropollutant removal, Cirja et al. (2008) has been extensively studied the effects of operational parameters such as HRT and SRT on the removal performance of micropollutants by MBR treatment. Moreover, Sipma et al. (2010) indicated that the retainment of relatively long sludge ages in MBR compared with CAS help improve removal of slowly degradable antibiotics. In this study, Sipma et al. (2010) postulated that there was a significantly higher removal of antibiotics in MBR compared to CAS, with the performance efficiency being 93.5 % and 75% of Ofloxacin, 73% and 33% of Sulfamethoxazole, 57% and 11% of Trimethoprim, respectively.

In regards to the removal of antibiotics applied attached-growth processes in carriers, the studies of Falås et al. (2012) reported that there was an effective removal due to the facilitation of the growth of a slow-growing microorganism in attached growth process. Subsequent study Falås et al. (2013) indicated that a rapid removal of Diclofenac and Trimethoprim was obtained at a reactor with different carriers (Biofilm Chip M, AnoxKaldnes), with the removal rate constant (k_{bio}) in a full-scale carrier reactor ranging from 1.3–1.7 L g biomass^{-1} d^{-1} and trimethoprim from 1.0–3.3 L g biomass^{-1} d^{-1}. Another one, Luo et al. (2014) investigated the elimination of micropollutants using polyurethane sponge media as attached growth carrier. The results showed a moderated removal efficiency of Ketoprofen, Acetaminophen, Metronidazole and Gemfibrozil, ranging from 50–75%. However, with persistent as Diclofenac and Carbamazepine based on the study of Zhang et al. (2008), a slight lower removal achieved at 45.7% and 25.9%, respectively. Additionally, sponge media performed with high porosity facilitates the growth of microorganisms in anoxic condition as well as reduced membrane fouling (Ngo et al., 2008; Thanh et al., 2013). For instance, Khan et al. (2012) demonstrated that the removal efficiencies of COD, TN and TP in sponge MBR were 98%, 89% and 58%, respectively, or even extension of longer filtration due to low membrane fouling resistance. Faisal et al. (2011) evenly indicated the potential degradation of antibiotics occurring in the anoxic environment could be obtained in anoxic MBR significantly. Actually, a comprehensive literature review conducted by above studies revealed that the simultaneous coexistence of the anoxic and oxic condition can enhance not only nitrogen removal but also the elimination of micropollutants. The presence of nitrifying microorganisms in bioreactor was also found to enhance biodegradation of antibiotic compounds. More specifically, Luo et al. (2014) showed that an improved removal of Naproxen, Ethynylestradiol, Roxithromycin and Erythromycin obtains in oxic condition whereas anoxic condition enhances the degradation of Carbamazepine, Clofibric acid and Diclofenac. In addition, Dorival-García et al. (2013) reported quinolone antibiotics achieved much higher removal efficiency by biodegradation (36.2–60.0%) under nitrifying conditions in comparison with aerobic conditions (14.9–43.8%). Furthermore, Lee et al. (2015) reported that increasing ammonia oxidation activity can be an effective strategy to enhance triclosan removal in nitrifying sludge. Triclosan removal was correlated to the molar ratio of the amount of nitrate produced to the amount of ammonium removed. Approximately 36–42% of triclosan was eliminated within 24 hours by ammonia-oxidizing bacteria.

In spite of the sufficient performance of either proper MBR or sponge carrier in mitigation of micropollutants, namely antibiotics, there is still a limited amount of research on the combination of

MBR with sponge media or even evaluation of the effect of membrane types on antibiotics removal. Therefore, to date, this study focuses on the comparison of removal of common antibiotics as well as characterization of the fouling behavior between Flat sheet (FS) and Hollow fiber (HF) membranes in Sponge MBRs operated at different high fluxes.

2. Materials and methods

2.1. Hospital wastewater and seed sludge

Wastewater used this study was taken from Trung Vuong hospital. The concentration of raw hospital wastewater is in mg L^{-1} (physical-chemical parameters) and µg L^{-1} (antibiotic parameters), except for pH: COD (155-405), TSS (27-125), TKN (11.4-32.5), NH_4^+-N (3-11.2), TP (1-3), Norfloxacin (6.305-43.610), Ofloxacin (7.634-40.261), Ciprofloxacin (1.926-23.841), Sulfamethoxazole (0.378-2.078), Erythromycin (0.135-2.407), Tetracycline (0.036-1.612) and Trimethoprim (0.676-2.911).

The seed activated sludge was collected from a conventional MBR system in Ho Chi Minh City (HCMC). The mixed liquor suspended solids concentration (MLSS) added to MBR tank reached approximately 5,000 mg L^{-1}. The ratio of MLVSS/MLSS of this seed sludge is 0.79.

2.2 Operating conditions of Sponge MBRs

In this study, two glass reactors with working volume of 8 L each and dimension of L×W×H = 0.28m × 0.08m × 0.42m were used in parallel as Sponge MBRs for experiments. Each submerged membrane module was installed in each reactor. HF-Sponge MBR was equipped with a membrane module (Width×Height = 200mm × 310mm) from Mitsubishi, Japan with a surface area of 0.1 m^2 and pore size of 0.4 µm. FS-Sponge MBR was operated with a membrane module (W×H = 230mm x 300mm) from Korea with the same surface area and pore size. The cube sponges (APG, Japan) made from the polyester urethane with a porosity of 98 % and dimension of 1cm × 1cm × 1cm was added into reactors with the occupation of 20 % (v/v). Raw hospital wastewater was pumped directly into Sponge MBRs using a peristaltic pumps in order to control the feed rate whereas the permeate flow rate was controlled by a suction pump. The Sponge MBR systems is automatic operation using timers, solenoid valves and digital pressure gauges. Air diffusers were installed at the bottom of two lab-scale Sponge MBRs not only for aeration (to supply dissolved oxygen in reactor) but also for air scouring (to decrease membrane fouling). Sponge MBRs were maintained intermittent suction with filtration time of 8 mins and relaxation time of 2 mins. Basically, sludge retention time (SRT) was mainly controlled based on suspended biomass withdrawn from the reactor since the attached biomass in the sponges was retained in the reactor. No sponges were taken out of reactor except the tiny debris from broken sponges. To control SRT of 20 days, the volume of waste sludge (suspended biomass only) was 0.4 L d^{-1}. This operation is to save the sponges and slow growing bacteria retained in the real operation. For this operation, the "real SRT" maintained in the sponge MBR is slightly higher than the "control SRT", i.e. 20 days, because there is a certain amount of biomass in the sponges which is always retained in the reactor. Sponge MBRs were operated at different high fluxes of 10; 15 and 20 LMH. In addition, for each starting stage, the membrane module was externally cleaned by chemicals (0.5% NaOCl) in 4 h. The digital pressure gauges recorded the trans-membrane pressure (TMP) daily.

2.3 Analysis

2.3.1 Physical chemical parameters

Parameters such as COD, TKN, NH_4^+-N, NO_2^--N, NO_3^--N, TP, were determined according to standard methods (APHA, 1998). Trans-membrane pressure (TMP) was recorded daily and fouling rate (dTMP/dt) was determined through slope between TMP over time at the linear segment. To determine the sludge concentration, the biomass attached in sponges was converted into mixed liquor suspended solids (MLSS) concentration. Sludge in five sponges was carefully taken out by squeezing solids into a certain volume of distilled water. After washed sponges, squeezed solution contained ceramic cup were dried 105 ^{0}C overnight. And the ceramic cup was weighed with and without squeezed solution. The biomass content in squeezed solution was immediately determined as the difference in weight between with and without the weight of ceramic cup. Finally, the biomass attached in sponges was calculated based on the number of sponges MBR and suspended solids concentration in the squeezed solution (Thanh et al., 2013).

2.3.2 Nitrogen balance

Nitrogen balance was followed the Eq.1. Nitrogen assimilated into the biomass was estimated based on the assimilated nitrogen of 12 % VSS (Metcalf and Eddy, 2003). The nitrogen balance was conducted to evaluate the simultaneous nitrification-denitrification (SND) that occurred in the sponges.

$$TN_{in} = TN_{out} + TN_{assimilated} + TN_{denitrification} \quad \text{(Eq. 1)}$$

2.3.3 Quantification of antibiotics

The analytical method of antiobiotics used in this study was referenced from Dinh et al. (2011). The pre-concentration of sample was performed by SPE (Solid Phase Extraction). Oasis hydrophilic – lipophilic - balance (HLB) extraction cartridges (60 mg, 3 mL, Waters, Corp., Milford, MA) were used. Cartridges were were conditioned with 3 mL of MeOH, followed by 3 mL of UP-water. Filtered water samples were passed through the cartridges at a flow rate of 2-3 mL min^{-1}. Then, cartridges were rinsed with 3 mL of UP-water/MeOH (90:5, v/v), and dried under vacuum during 10 min. Finally, analytes were eluted with 5 mL of MeOH and extracts were evaporated under a nitrogen stream at 40◦C and reconstituted to 0.5 mL in UP-water/MeOH (90/10, v/v) with 0.1%

formic acid. Extracts were then passed through 0.2 µm syringe filters before giving the vial to analyze by Liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).

A LC-MS/MS system (Agilent1200 series) equipped with an Agilent Zorbax Eclipse Plus C_{18} column (with diameter, length and pore size of 2.1 mm, 150 mm, 3.5 µm, respectively) was used to measure the concentration of antibiotic in the feed and permeate. A sample injection volume of 10 µL. Mobile phase solvents were UP-water (Solvent A) and acetonitrile (solvent B), both solvents acidified with 0.01% formic acid (HCOOH) in an initial ratio (A:B) of 90:10. Separation was achieved at 35°C using a flow rate of 0.5 mL min^{-1} with the following (A:B) gradient: 90:10 to 75:25 in 2 min, 65:35 at 4 min, 25:75 at 7 min; 0:100 at 7.1 min for 3 min. Then, the system was equilibrated for 2.4 min prior to the next injection (total run time of 12.5 min). The LC system was coupled to a triple quadrupole mass spectrometer (Agilent 6410) with the electrospray ionization (ESI) source and it was operated in positive mode. Argon (99.9%) was used as collision gas while nitrogen was used as the nebulizing gas (11.0 L h^{-1}, nebulizer pressure 35 psi) and was produced via a nitrogen generator (Parker). Calibration always yielded standard curves with coefficients of determination (R^2) greater than 0.99 within experimental concentrations used. The quantification limit which estimated as ten times the signal of the highest peak generated by the background noise were in the 0.5-10 ng L^{-1} range.

3. Results and discussion

3.1. Removal of organic and nitrogen

The average COD concentration of feed and permeate as well as COD removal efficiency are shown in Table 1. There was not considerable fluctuation in raw hospital wastewater composition, being in the range of 265-340 mg L^{-1}. The average COD in the permeate was low with a concentration of 9-

13 mg L^{-1} at different fluxes for both Sponge MBRs. In addition, there was not a significant difference in COD removal efficiency, ranging from 96% to 97% at fluxes of 10-20 LMH. This study also showed the average COD removal rate of FS-sponge MBR and HF-sponge MBR were 0.18; 0.29; 0.28 and 0.18; 0.28; 0.33 mg COD mg $MLSS^{-1}$ d^{-1} at fluxes of 10; 15; 20 LMH, respectively. Wen et al. (2004) reported that COD in the permeate of hospital WWTP applying conventional MBR system was lower than 30 mg L^{-1} and COD removal efficiency achieved only 80%. On the other hand, the COD removal efficiency could reach a higher value of 94% by facilitating sponge MBR system (Deng et al., 2014). Another study of Ngo et al. (2008) revealed an enhanced COD removal in sponge MBR system, achieved roughly 94% efficiency. Clearly, this indicated a significant removal in COD was enhanced in sponge MBR systems.

Insert Table 1

Table 2 summarized the average concentrations of NH_4^+-N, NO_2^--N, NO_3^--N and TN in the permeate. The results showed that NH_4^+-N removal efficiency obtained at 85-92 % (FS-sponge MBR) and 85-96% (HF-sponge MBR) at fluxes of 10; 15; 20 LMH respectively.

At HRT of 10; 6.7; 5 h corresponding to fluxes of 10; 15; 20 LMH, there was not a considerable difference in NH_4^+-N permeate for sponge MBRs, with a low permeate concentration of 0.36–0.86 mg L^{-1}. However, the NH_4^+-N removal efficiency increases significantly at the higher HRT. The results also showed that a majority of deeply low NO_2^--N permeate was performed at sponge MBRs, with a concentration of below 0.06 mg L^{-1}. This revealed that the higher HRT is the lower concentration of NO_2^--N in the permeate could reach. Thanh et al. (2013) demonstrated that the concentration of NO_2^--N was very low (~ 0.03 mg L^{-1}) with HRT of 4-8 h, but greater than 1.0 mg L^{-1} with HRT of 2 h. Another study, Liu et al. (2010) performed there was not a significant improvement of nitrification process in MBR system in which operating higher HRT of 4 h. Clearly, nitrification process can occur significantly by retaining the appropriate hydraulic retention time of 5 h in sponge MBRs.

Insert Table 2

At various fluxes of 10-20 LMH, TN removal efficiencies of FS-sponge MBR and HF-sponge MBR were 51±18; 64±19; 55±17 % and 55±14; 65±20; 53±16 %, in that order. As the results, the average removal efficiency of TN in sponge MBRs was a negligible difference. Commonly, TN denitrification which is similar to two sponge MBRs is much higher than TN accumulation (Fig. 1). Simultaneous nitrification denitrification (SND) highly occurred in sponge MBRs, ranging from 35-55 % at various fluxes of 10-20 LMH. In addition, sponge MBRs performed that the nitrogen removal rate achieved at 0.011; 0.020; 0.014 and 0.012; 0.020; 0.016 mg TN mg VSS^{-1} d^{-1} for FS and HF at fluxes of 10; 15; 20 LMH, respectively. Therefore, there was the insignificant difference in nitrogen removal between sponge MBRs. However, the TN removal efficiency at 15 LMH flux was higher than the other fluxes due to the higher concentration of biomass created an anoxic condition in the sponge carriers.

In addition, the study of Liu et al. (2010) also showed a higher nitrogen removal in sponge MBR (sponge occupied roughly 50%) compared to conventional MBR, operating at HRT of 10 h and SRT of 10 days. This result is also similar to the study of Khan et al. (2011) that conducted in sponge MBR (sponge occupation of 15%), increasing by 15% of nitrogen removal compared to conventional MBR. Clearly, simultaneous nitrification denitrification considerably occurred in sponge MBRs since the growth of complex biomass captured within sponge carriers added (Khan et al., 2011). This is explained due to SND process took place in the sponge carriers as the sponge pores caught biomass inside with anoxic conditions in the pores (Zhimin et al., 2009; Thanh et al., 2013; Tin et al., 2016).

Insert Fig. 1

3.2. Removal of antibiotics

With respect to Norfloxacin (NOR), Ofloxacin (OFL), Ciprofloxacin (CIP) and Trimethoprim (TRI), there was a considerable high removal in both Sponge MBRs at fluxes of 10-20 LMH, with a low concentration in the permeate of 0.07-0.10 μg L^{-1} (FS), 0.08-0.09 μg L^{-1} (HF); 0.20-2.10 μg L^{-1} (FS), 0.22-6.73 μg L^{-1} (HF); 0.75-8.52 μg L^{-1} (FS), 0.69-8.12 μg L^{-1} (HF); 0.049-0.494 μg L^{-1} (FS) and 0.058-0.809 μg L^{-1} (HF), respectively (Fig. 2). Moreover, a significant removal of Tetracyclin (TET) was also obtained in HF-MBR and FS-MBR, with permeates of 0.000-0.106 μg L^{-1} (FS) and not detected (HF). In general, the results of the study also performed that a high removal efficiency of Norfloxacin, Ofloxacin, Ciprofloxacin, Trimethoprim achieved approximately 93-99% and 62- 86%; 73-93% and 68-93%; 76-93% and 54-70%; 60-97% and 47-93%, in FS-sponge MBR and HF-sponge MBR, respectively. The results indicated a slightly better removal of these antibiotics in FS membrane compared to HF membrane employed in sponge MBR at flux of 20 LMH. This is explained due to a higher total average MLVSS concentration in FS-sponge MBR (4546 ± 777 mg L^{-1}) compared to HF-sponge MBR (3794 ± 1243 mg L^{-1}). This is in line with the results of Garcia et al. (2013). By retaining a higher biomass concentration helps to improve higher biodegradation, dramatically increasing the removal efficiency from 63 –77% corresponding to MLSS range of 7000-15000 mg L^{-1}. Similarly, a higher removal of antibiotics was also obtained in the FS-MBR than in the HF-MBR from the previous studies of Radjenovic et al. (2009).

From the comprehensive literature of studies on removal mechanism of antibiotics, biodegradation biotransformation and sorption are the two major pathways during biological treatment (Verlicchi et al., 2012). In term of removal of sorption, it depends on hydrophobicity measured by the octanol-water partition coefficient log K_{ow} and sludge adsorption coefficient (K_d) (Tiwari et al., 2017). The study of Tadkaew et al. (2011) pointed out the Log K_{ow} can be used to evaluate the hydrophobic sorption. Even there was a clear correlation between removal efficiency and the effective octanol–water partition coefficients (log K_{ow}) (Tadkaew et al., 2011). Moreover, Wijekoon et al. (2013) assumed that with the hydrophobic compounds (Log $K_{ow} > 3.2$), adsorption was the dominant removal mechanism. However, according to previous studies, the physicochemical characteristics of Norfloxacin, Ofloxacin, Ciprofloxacin, Tetracycline, Trimethoprim was determined with the low Log K_{ow} and K_d, with the value being off -1.03-1.48; 0.84-2.10; 0.28-1.32; -1.30; 0.73-0.91 and 190; 250; > 1500; 14; 200 L kg SS^{-1}, in that order (Sipma et al., 2010; Li et al., 2015; Blair et al., 2015). Another hypothesis of sorption of Ternes et al. (2004) reported that roughly 10% of antibiotic compounds were removed by sorption with K_d value ≤ 500 L kg SS^{-1}. This reveals the removal of Norfloxacin, Ofloxacin, Tetracycline, Trimethoprim is not considered for sorption due to Log $K_{ow} <$ 2.5, indicating a low sorption potential (Verlicchi et al., 2012). The study of Luo et al. (2014) mentioned that sponge carrier can improve the removal of some moderate hydrophobic compounds (Log $K_{ow} < 2.5$), displayed biodegradation as the major removal pathway. According to the study of Radjenovic et al. (2009) reported Trimethoprim was considered as a persistent to activate sludge process, its removal efficiency negligibly obtained in sponge MBRs. Therefore, it can be predicted that enhanced biodegradation could occur in sponge MBRs in which appear the existence of anoxic, anaerobic and aerobic compartment can influence the removal of micropollutants (Faisal et al., 2011; Kim et al., 2014). Clearly, sponge MBRs can generate an attached growth process in sponge carriers which increase a large number of slow growing microbial communities with high sludge concentration (Arya et al., 2016). This leads to help the microorganism gain effective time to acclimatize and degrade to the antibiotics compounds (Zaviska et al., 2013; Arya et al., 2016).

Nevertheless, the solid retention time (SRT) has been considered to one of the most important parameters affecting the biodegradation of micropollutants, namely antibiotics (Jan et al., 2010). The results of Lesjean et al. (2005) demonstrated that the removal of pharmaceuticals increased with SRT of 26 days and inversely reduced when SRT was maintained at 8 days in MBR. Thus, by retaining SRT of 20 days in sponge MBRs seemed to be appropriate for antibiotic removal. Clearly, sponge MBRs can generate the presence of distinct zones in sponge carriers as well as higher sludge age which enhances efficient slow growing biomass and higher specific microbial (Arya et al., 2016; Tiwari et al., 2016). Meanwhile, Ciprofloxacin removal seems to be due to a significant sorption to solid with high K_d of 1500 L kg SS^{-1} (Sipma et al., 2010). This is similar to the results mentioned by Garcia et al. (2013) and Arya et al. (2016) showed that Ciprofloxacin can exhibit a high sorption into MBR sludge.

Insert Fig. 2

In regards to Erythromycin, the removal in FS-MBR is also higher than that in HF-MBR with permeate concentrations of 0.085-0.647 μg L^{-1} (FS) and 0.137-1.274 μg L^{-1} (HF). However, there was a quite high removal efficiency in sponge MBRs at various fluxes 10-20 LMH, with 67-78% (FS) and 22–48% (HF). The possibility of higher removal could be due to the better adsorption of Erythromycin on the biomass and/or on the flat sheet membrane because the operating conditions of both MBRs were similar during the operation period. Based on the results of Ternes et al (2004), the main removal mechanism of antibiotics with log K_{ow} greater than 3.0 is sorption to sludge. Erythromycin is an antibiotic with log K_{ow} of 3.06, thus its removal was better in the FS-MBR due to bioaccumulation mechanism. The average MLVSS concentration in FS-sponge MBR (4546 mg L^{-1}) was greater than HF-sponge MBR (3794 mg L^{-1}). In this study, especially Sulfamethoxazole, a known readily biodegradable compound removed significantly in MBR (Faisal et al., 2011). Sulfamethoxazole as hydrophilic with Log K_{ow} of 0.89-0.91 (Sipma et al., 2010) can be considered removal by biodegradation mechanism. Another study of Tambosi et al. (2010) showed that Sulfamethoxazole was eliminated by roughly 55 and 64% at SRT of 15 and 30 days in MBR. However, in this study, its removal was not sufficient in sponge MBRs. More specifically, Sulfamethoxazole was less removal even with low feed concentration of 0.4-2.6 μg L^{-1}. Furthermore, some samples in permeate are higher than that in the feed. This is explained due to the back conversion of N4-acetylsulfamethazole to sulfamethoxazole during degradation (Galan et al., 2012). In addition, this issue demonstrated by Jjemba et al. (2002) which reported that the derivatives of Sulfamethoxazole are N-acetyl-Sulfamethoxazole (more than 80% Sulfamethoxazole going into human body will be transformed into N-acetyl-Sulfamethoxazole, following to reformed Sulfamethoxazole due to physical chemical impacts (Gobel et al., 2007) occurring during treatment process in sponge MBRs.

3.3. Membrane fouling

Insert Fig. 3

In this study, there was the same fouling rate at fluxes of 10; 15 LMH for both Sponge MBRs (Fig. 3), with TMP increasing 1.3-2.0 kPa (FS) and 2.9-3.3 kPa (HF); 1.4-24.0 kPa (FS) and 3.6-4.6 kPa (HF) respectively. However, faster fouling rate occurred in FS-MBR compared to HF-MBR at flux 20 LMH, reaching to 40 kPa after 14 days of operation. The higher fouling observed in the flat sheet MBR was explained due to the attaching of sponge debris on the membrane surface, causing reduction of membrane surface. In addition, the results of this study were similar to the previous studies demonstrated that membrane fouling in Sponge MBRs was much higher compared to conventional MBRs (Liu et al., 2010, Ngo et al., 2008). This indicated that sponge media was more effective to HF membrane when operating at a lower flux of 15 LMH. Tin et at. (2016) found that fouling rate depended on interactive between sponge media and surface membrane, which will reduce the fouling. Total resistance (R_t) was in FS-sponge MBR is significantly higher than HF-sponge MBR at fluxes 15; 20 LMH despite relative TMP profile. The cake layer was the main fouling resistance in FS-MBR, accounting for 40-60% of R_t. By contrast, the main fouling reason (occupation of 57-61 %) in HF-MBR was caused by fouling resistance (soluble matters).

Insert Table 3

Insert Fig. 4

4. Conclusions

Sponge MBR is an effective technology for hospital wastewater treatment. Firstly, sponges improved nitrogen removal at the removal rate of 0.011–0.020 mg TN mg VSS^{-1} d^{-1}. A high removal of Norfloxacin, Ciprofloxacin, Ofloxacin, Tetracycline and Trimethoprim was obtained in sponge MBRs whereas Erythromycin was quietly removed. In contrast, a varied removal of Sulfamethoxazole occurred in sponge MBRs. Secondly, better removal of antibiotics occurred in the reactor with higher sludge concentration. Thirdly, sponges helped control fouling for MBRs. A significant reduction in fouling rate of 2-50 times was achieved in HF-Sponge MBR for the flux range of 10-20 LMH.

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Table 1. Performance of COD removal at various fluxes in Sponge MBRs

Parameters	FS-Sponge MBR			HF-Sponge MBR		
	10 LMH	15 LMH	20 LMH	10 LMH	15 LMH	20 LMH
Feed (mg L^{-1})	265±69	302±42	340±60	265±69	296±42	340±60
Permeate (mg L^{-1})	9±4	9±4	13±7	8±5	11±9	13±8
Efficiency (%)	96±2	97±1	96±2	97±3	96±2	96±2
Removal rate (mg COD mgMLSS^{-1} d^{-1})	0.18±0.03	0.29±0.05	0.28±0.05	0.18±0.05	0.28±0.04	0.33±0.06

Table 2. Concentration of nitrogen species in the permeate

Nitrogen species	FS-Sponge MBR			HF-Sponge MBR		
	10 LMH	15 LMH	20 LMH	10 LMH	15 LMH	20 LMH
TKN (mg L^{-1})	5.1±1.2	3.4±1.0	4.6±1.1	4.8±1.4	3.2±0.8	4.7±0.7
NH_4^+-N (mg L^{-1})	0.86±0.45	0.51±0.63	0.36±0.27	0.83±0.40	0.36±0.35	0.32±0.22
NO_3^--N (mg L^{-1})	7.4±4.6	3.6±2.6	5.6±3.4	6.4±2.5	3.4±2.8	5.6±3.9
NO_2^--N (mg L^{-1})	0.01±0.01	0.03±0.01	0.05±0.01	0.01±0.01	0.01±0.01	0.06±0.01
TN (mg L^{-1})	12.0±5.4	7.0±2.9	10.3±3.9	11.2±3.5	6.6±2.9	10.4±3.9

Table 3. Resistance types at different fluxes in Sponge MBRs

Resistances	FS-sponge MBR			HF-sponge MBR		
	10 LMH	15 LMH	20 LMH	10 LMH	15 LMH	20 LMH
R_c (m^{-1})	2.7×10^{11}	1.5×10^{12}	2.7×10^{12}	5.0×10^{10}	5.3×10^{10}	9.1×10^{10}
R_f (m^{-1})	2.4×10^{11}	3.3×10^{12}	4.0×10^{12}	2.0×10^{11}	2.4×10^{11}	3.4×10^{11}
R_m (m^{-1})	8.2×10^{10}	8.7×10^{10}	9.6×10^{10}	9.9×10^{10}	1.1×10^{11}	1.3×10^{11}
R_t (m^{-1})	5.9×10^{11}	4.9×10^{12}	6.8×10^{12}	3.5×10^{11}	4.0×10^{11}	5.6×10^{11}

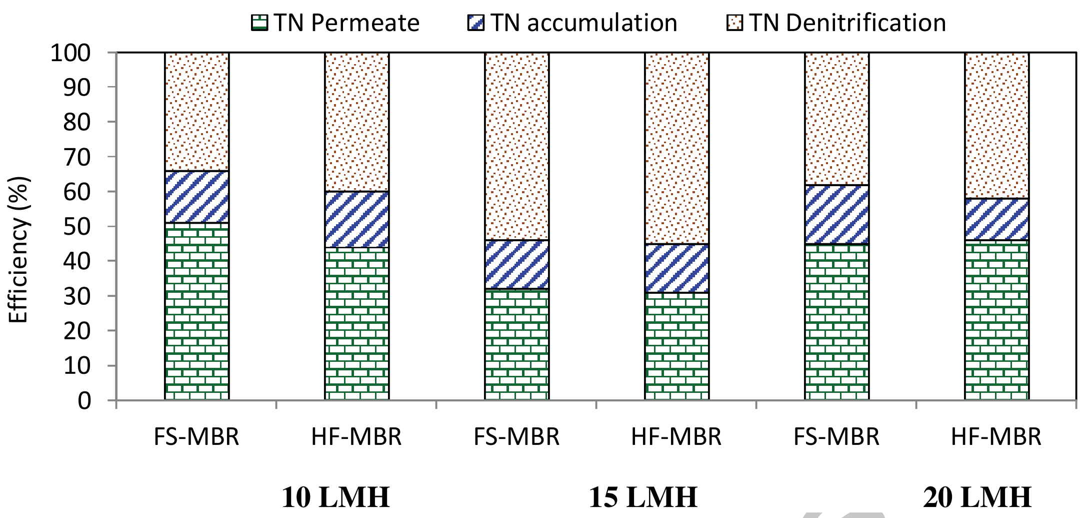

Fig. 1. Nitrogen balance in Sponge MBRs

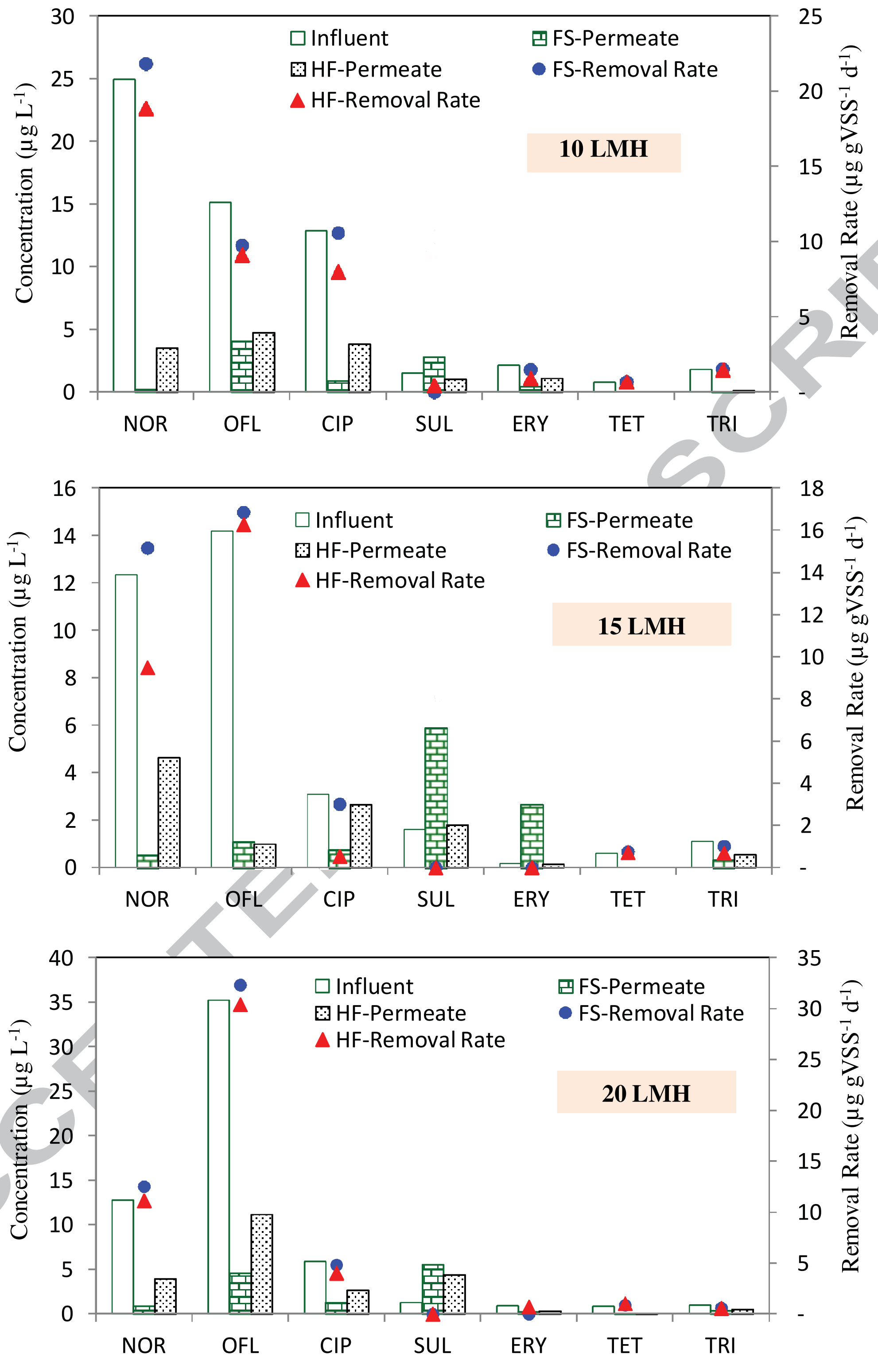

Fig. 2. Antibiotics removal in Sponge MBRs at different fluxes (FS: Flat sheet membrane; HF: Hollow fibre membrane; NOR: Norfloxacin; OFL: Ofloxacin; CIP: Ciprofloxacin; SUL: Sulfamethoxazole; ERY: Erythromycin; TET: Tetracycline; TRI: Trimethoprim)

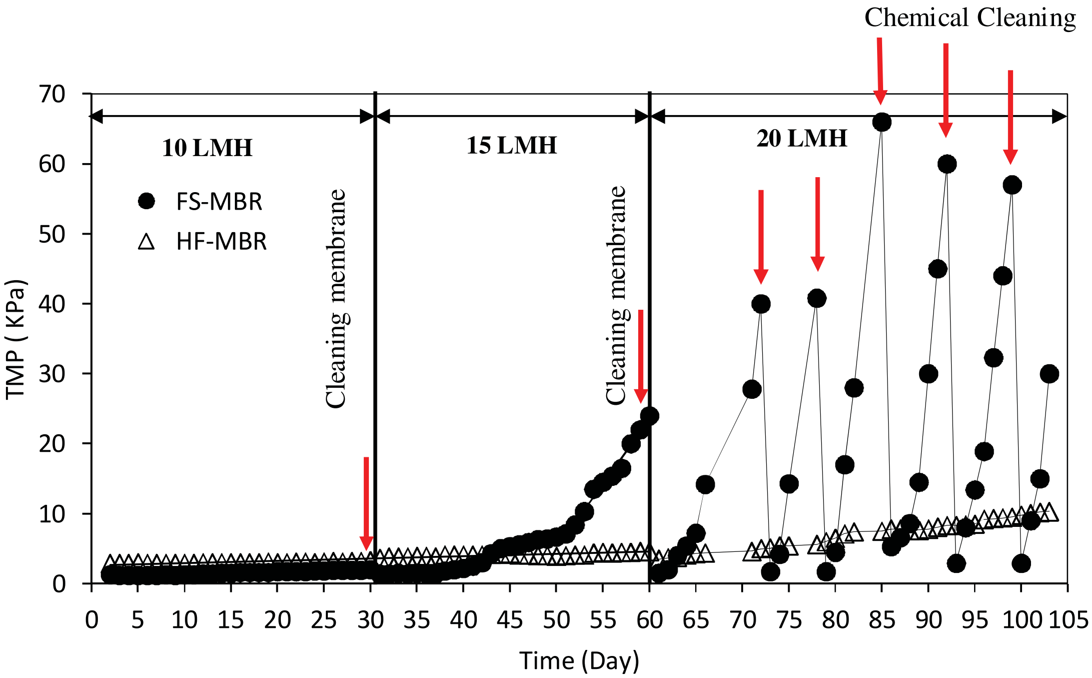

Fig. 3. Evolution of TMP in Sponge MBRs at different fluxes

Highlights for review

- Total nitrogen removal rate achieved 0.011– 0.020 mg TN mg VSS^{-1} d^{-1} for both MBRs.
- A higher removal of antibiotics was found in FS than in HF.
- Remarkable removal of antibiotics (CIP, NOR, OFL, TET, TRI, ERY) were achieved.
- Sulfamethoxazole was not significantly removed in Sponge MBRs.
- A significant reduction of membrane fouling was performed in HF-sponge MBR.