Impacts of sulfadiazine on the performance and membrane fouling of a hybrid moving bed biofilm reactor-membrane bioreactor system at different C/N ratios

Xinbo Zhang[a,b], Zumin Zhang[a,b], Ying Liu[a,b], Huu Hao Ngo[c,a,*], Wenshan Guo[c,a], Huizhong Wang[a,b], Yufeng Zhang[a,b], Dan Zhang[a,b]

[a] *Joint Research Centre for Protective Infrastructure Technology and Environmental Green Bioprocess, Department of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin 300384, China*

[b] *Tianjin Key Laboratory of Aquatic Science and Technology, Tianjin Chengjian University, Jinjing Road 26, Tianjin 300384, China*

[c] *Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NSW 2007, Australia*

*Corresponding author: E-mail address: ngohuuhao121@gmail.com (H.H. Ngo)

Abstract: The performance and membrane fouling of a hybrid moving bed biofilm reactor-membrane bioreactor (MBBR-MBR) system was evaluated when exposed to 0.5 mg/L of antibiotic sulfadiazine (SDZ). Results indicated that although SDZ reduced the removal efficiency of NH_4^+-N and TN (up to 12%) and TOC (up to 6%) at low C/N (2.5 and 4), it had no significant effect at high C/N (6 and 9). It was found that SDZ was removed 75% and 58% at high C/N of 9 and low C/N of 2.5, respectively. SDZ decreased the ratio of volatile biomass/total biomass and sludge particle size and increased the concentrations of extracellular polymeric substance (EPS) and soluble microbial product (SMP) in MBR. Consequently, this accelerated the membrane fouling rates, with an average increase of 6.85 kPa/d at low C/N (2.5) and 0.513-0.701 kPa/d at medium and high C/N (4, 6 and 9).

Keywords: sulfadiazine; hybrid moving bed biofilm reactor-membrane bioreactor system; impacts; membrane fouling; C/N ratio

1. Introduction

The large-scale use of antibiotics in human activities and the ever-rapid advances in modern detection technology, many antibiotics are now being detected in large-scale contexts (Fatehifar et al., 2018). These contaminants of emerging concern (CECs) discharged into natural water bodies through sewage treatment plants are likely to cause serious harm to aquatic animals and plants in natural water bodies (Barbosa et al., 2016; Evgenidou et al., 2015). Sulfonamide antibiotics (SAs), which constitute a commonly used pharmaceutical for treating infections, are widely used in the medical and aquaculture industries due to its high efficiency and relatively low cost (Mulla et al., 2018; Zhao et al., 2018). SAs such as sulfadiazine (SDZ) which are polar compounds with poor adsorption capacity, are widespread in wastewater bodies (Muller et al., 2013). Many municipal wastewater treatment plants (WWTPs) do not specifically design processes to remove certain antibiotics, so subsequently the existence of antibiotics triggers the spread of antibiotic resistant genes (ARGs) into the environment (Rizzo et al., 2013). For this reason, the removal of antibiotics from wastewater has become a subject of increasing research.

Hybrid moving bed biofilm reactor-membrane bioreactor (MBBR-MBR) is a new type of sewage treatment process that couples MBBR with MBR (Sombatsompop et al., 2006), on the basis of activated sludge, biofilm processes and membrane technology. Compared with a conventional membrane bioreactor (C-MBR), hybrid MBBR-MBR enhances the removal of pollutants such as organic matter, nutrients and micropollutants; it also relieves MBR unit membrane pollution (Luo et al., 2015). Although hybrid MBBR-MBR has not yet been applied to the actual sewage treatment on a larger industrial scale (Leyva-Diaz et al., 2020), many research studies have confirmed that MBBR-MBR performs excellently in removing nitrogen and organic carbon as well as micropollutants. As reported by Chen et al. (2017), high chemical oxygen demand (COD) removal were observed with average efficiencies of 94.8 ± 2.6%, 93.5 ± 1.8% and 91.5 ± 1.3%, respectively, under three different solids retention times (SRT) of 20 d, 10 d and 5 d in an MBBR-MBR system. In the meantime, more than 99% NH_4^+-N was removed at all the examined SRTs. Two aerobic MBBR-MBR systems with different biocarriers (sponge modified plastic carrier and plastic carrier) exhibited high COD and NH_4^+-N removal efficiencies (>94% and 84%) at a filling rate of 20% (Deng et al., 2016). Conversely, Jiang et al. (2018) investigated the removal of 22 frequently detected antibiotics in a hybrid MBBR-MBR at 4 different hydraulic retention times (HRTs) (24 h, 18 h, 12 h and 6 h), and most micropollutants were largely eliminated (>70%). However, the efficiencies in removing antibiotics and the performance of MBBR-MBR when antibiotics are present, constitute the research focus for the application of hybrid MBBR-MBR in the future.

SDZ is widely used and has been detected in large quantities in maricultural wastewater and pharmaceutical factories, which are sometimes discharged directly into wastewater treatment plants without treatment. This greatly affects the influent quality in wastewater treatment plants. The quality deterioration is reflected in the high concentration of antibiotics (up to mg/L) in wastewater. Some researchers investigated the removal performance of SDZ by various biological treatment processes such as MBBR, MBR and sequencing batch biofilm reactor (SBBR). Song et al. (2020) investigated the SDZ removal using polyurethane MBBR at three concentrations (1, 2 and 5 mg/L), and the average removal efficiency of 61.1±8.8% was achieved. In addition, Li et al. (2017) constructed SBBR to remove of SDZ (concentration from 0-35mg/L), and found the effluent quality deterioration is reflected under the condition of the high concentration of antibiotics (up to mg/L) in wastewater. However, to date, there is no data available on the performance of hybrid MBBR-MBR at high concentration of SDZ under different operation conditions in the literature.

Additionally, factors such as sludge particle size, extracellular polymeric substances (EPS), soluble microbial products (SMP), etc., influence membrane fouling in the MBR-based system (Nguyen et al., 2019; Yu et al., 2018). It is well known that the content of protein and polysaccharides in EPS are closely linked to membrane fouling. As an important component of sludge, EPS contains enzymes that can degrade pharmaceuticals (Shi et al., 2017; Wang et al., 2018; Tang et al., 2020). Consequently, as the pretreatment unit in a hybrid MBBR-MBR system, MBBR affects the sludge characteristics in the MBR, in turn influencing the membrane fouling problem. Therefore, membrane fouling characteristics in the hybrid MBBR-MBR need to be further explored under various operation conditions.

For the reasons stated above, to insightfully understand the impact of SDZ on the performance of hybrid MBBR-MBR system at different carbon/nitrogen (C/N) ratios, this study focused on: (i) evaluating the performance of a hybrid MBBR-MBR system with presence of SDZ in the influent; and (ii) investigating the nature of membrane fouling in the hybrid MBBR-MBR due to SDZ.

2. Materials and methods

2.1 MBBR-MBR system and operation

The hybrid MBBR–MBR system consisted of an MBBR unit (volume 6 L) and a submerged MBR unit (volume 3 L). Four hybrid MBR-MBR systems were operated in parallel named as R_1 (C/N=2.5), R_2 (C/N=4), R_3 (C/N=6) and R_4 (C/N=9), respectively. Simultaneously, the four hybrid systems were operated at room temperature of 25 ± 1 °C. The entire operation period was divided in 2 phases. In phase I, the hybrid MBBR-MBR systems were fed with wastewater (0-25 days), and the impact of C/N ratios on the performance of the hybrid system investigated. In phase II, the hybrid MBBR-MBR systems were still run under C/N in phase I, with the addition of 0.5 mg/L SDZ. The seed activated sludge was taken from a local wastewater treatment plant (Tianjin, China) and the initial mixed liquor suspended solids (MLSS) concentration amounted to approximately 5.69 g/L after acclimation. The diffusion aerators were installed at the bottom of the MBBR and MBR units to supply the oxygen and the air flow was kept at 0.1 m^3/h in four hybrid MBBR-MBR reactors (dissolved oxygen concentration of 4.5-6 mg/L). The HRT of each MBBR unit was kept at 16 h, while the MBR unit was kept at 8 h (i.e. constant flux of 9.375 L/m^2h). Each MBBR unit was filled with polyurethane sponges (the filling ratio of 20%) as biocarriers (Joyce Foam Pty, Australia) with a diameter of 10 mm, a density of 28 kg/m^3. For the MBR unit, a hydrophilic polyvinylidene fluoride (PVDF) membrane module was used with a pore size of 0.1 μm and surface area of 0.04 m^2. The sludge retention time (SRT) was retained at 60 days via sludge withdrawal. Each MBR unit operated in a continuous mode and the operation was terminated when the transmembrane pressure (TMP) exceeded 35 kPa, followed by chemical cleaning.

2.2 Synthetic wastewater

Synthetic wastewater was used to carry out the experiments, in which glucose and $(NH_4)_2SO_4$ were carbon and nitrogen sources. The influents in the experiments were different for the C/N (total organic carbon /TN) ratios: R_1(C/N=2.5). 75 mg/L total organic carbon (TOC), 30 mg/L TN; R_2(C/N=4). 120 mg/L TOC, 30 mg/L TN; R_3(C/N=6). 180 mg/L TOC, 30 mg/L TN; R_4(C/N=9). 75 mg/L TOC, 30 mg/L TN. KH_2PO_4 act as phosphorus sources. The trace nutrient solution consisted of the following: $MgSO_4 \cdot 7H_2O$, 5.068 mg/L; $FeCl_3$, 1.45 mg/L; $ZnSO_4 \cdot 7H_2O$, 0.44 mg/L; $CoCl_2 \cdot 6H_2O$, 0.422 mg/L; $CuSO_4 \cdot 5H_2O$, 0.39 mg/L; $CaCl_2 \cdot 2H_2O$, 0.372 mg/L and $MnCl_2 \cdot 7H_2O$, 0.28 mg/L. Either $NaHCO_3$ powder or H_2SO_4(1: 4) was used to adjust the pH to 7-7.2 in the hybrid MBBR–MBR. All chemicals and supplies mentioned were of analytical purity, and purchased from Tianjin, China. Sulfadiazine ($C_{11}H_{12}N_4O_2S$, >99%) has a molecular weight of 250.28 Da, and its CAS number was 68–35-9. This was obtained from Shanghai Dibai Biotechnology Co., Ltd.

2.3 Chemical analyses

Concentrations of MLSS, mixed liquor volatile solids (MLVSS), attached-growth biomass (AGBS), volatile attached-growth biomass (VAGBS), NH_4^+-N, NO_2^--N and NO_3^--N were tested based on the standard methods (APHA, 2005). TOC analyzer (TOC-V WP, Shimadzu, Japan) was used to measure the TOC of influent and effluent. The pretreatment of SDZ was based on Zhang et al. (2020). To sum up, the samples were pretreated by solid phase extraction (SPE) with Oasis (HLB) extraction cartridges (500 mg, 6 cc, Waters, USA). A high-performance liquid chromatography-triple quadrupole mass spectrometer (LC-MS, Shimadzu, Japan) equipped with a Shimadzu Shim-pack GIST C18 column (the dimensions and length are 2.1mm and 2μm) served the quantitative analysis of pharmaceuticals. The column temperature was 40 °C, flow rate was 0.4 ml/min, injection volume was 5μL, and the system's total run time lasted for 3 min. Mobile phase were 0.1 mol/L ammonium formate+0.1% formic acid water (solvent A) : acetonitrile (solvent B) = 20 : 80 (v/v).

The extraction of EPS of activated sludge has been previously documented by Deng et al. (2014). The biofilm of biocarriers was extracted into 30 ml ultrapure water by hand extrusion, and EPS of biofilm was extracted in the same method. The total amount of EPS was characterized by measuring the TOC content in the biofilm and sludge. The protein (PN) was determined by the anthrone-sulfuric acid method (Dubois et al., 1956), while the concentration of polysaccharide (PS) was found with the Coomassie brilliant blue method as employed by FØlund et al. (1995).

3. Results and discussion

3.1 Effects of sulfadiazine on the performance of MBBR-MBR at different C/N ratios

3.1.1 Nitrogen removal in hybrid MBBR-MBR system

Fig. 1 summarizes the removal efficiencies of NH_4^+-N as well as TN and simultaneous nitrification and denitrification (SND) in four hybrid reactors (C/N=2.5, 4, 6 and 9, respectively) during the operational period. Fig. 1(c) showed that the average removal efficiency of NH_4^+-N in four reactors without adding SDZ could reach 99.4% at all examined C/N ratios. However, the nitrification performance in hybrid MBBR-MBRs with adding SDZ at different C/N ratios declined to 87.59 ± 1.17%, 90.66 ± 1.69%, 92.98 ± 0.94% and 93.44 ± 0.67%, respectively. In a nutshell, compared with phase I, the removal efficiency of NH_4^+-N with SDZ fell by 12%, 9%, 7% and 6%, respectively. The removal rate of NH_4^+-N in reactors after adding SDZ reduced in different degrees because of the inhibition of NH_4^+-N functional gene (AOB amoA) by SDZ (Song et al., 2020). Moreover, the removal of ammonia nitrogen gradually rose when the C/N ratio increased, which could explain that the existence of biofilm improved the removal rate of ammonia nitrogen. Biofilm alleviated the direct impact of SDZ on microorganisms, the higher the C/N ratio, the thicker the biofilm attached to the biofilm carrier (Enaime et al., 2019). EPS was the main component of the biofilm, due to the presence of *heterotropic* bacteria in EPS, it could absorb NH_4^+-N into cell proteins (Li et al., 2020).

In phase II, all reactors' effluent under different C/N ratios could still maintain a removal efficiency of more than 88% NH_4^+-N. This was possible because SDZ was a non-hydrophilic compound, and it exerted a weak influence on the removal of NH_4^+-N. In the later stage of the reactor operation, R_3 and R_4 performed similarly on NH_4^+-N removal, indicating that the strong protection mechanism of biofilm under a high C/N ratio made it possible to maintain the high nitrification reaction.

From Fig. 1(d), it was found that the removal of TN for R_1 was the lowest, only 65.38 ± 4.21% in phase I, while the removal of TN for other reactors was as much as 70%. Table 1 shows the corresponding simultaneous nitrification and denitrification (SND) performance was above 66.66 ± 4.26%. Results confirmed that the C/N ratio had a certain effect on denitrification. The reason for the poor removal efficiency of R_1 on TN was that the activity of heterotrophic denitrifying bacteria was insufficient when the carbon source was insufficient, and low denitrification occurs. R_3 and R_4 made almost no difference in the removal efficiency of TN. This might be because a thicker biofilm was formed on the biofilm carrier in R_4, which inhibited the spread of oxygen and substrates, and thus reduced the activity of heterotrophic denitrifying bacteria. The removal efficiency of TN was therefore as same as R_3. In phase II, the removal efficiency of TN in R_1, R_2, R_3 and R_4 fell by 10.37%, 8.28%, 6.18% and 6.09%, respectively. Correspondingly, the SND performance declined by 3.39%, 3.29%, 1.65%, and 2.26%. The decrease in TN removal was caused by the addition of SDZ which impacted on the activity of nitrifying bacteria attached to the surface of the biofilm carrier. However, due to the protection mechanism of the protein in the biofilm on microorganisms, the denitrifying bacteria inside the carrier was less affected by SDZ, so the performance of SND could be maintained.

Fig.1 Variations of (a) NH_4^+-N concentrations, (b) TN concentrations, (c) NH_4^+-N removal efficiencies, and (d) TN removal efficiencies in hybrid MBBR-MBRs.

Table 1 SND performance in four hybrid MBBR-MBR systems

3.1.2 Total organic carbon removal in hybrid MBBR-MBR system

Table 2 shows the concentration changes of TOC in four hybrid MBBR-MBR systems during the entire experimental operation stages. A can be seen in Table 2, the removals of TOC by all reactors were slightly different but maintained at a high level, with an average removal efficiency of 90% or more being documented. Meanwhile the removal of TOC in phase II had been inhibited to some extent by the addition of sulfadiazine. In phase I, MBR unit membrane could trap the organics of macromolecules in the particles (Chen et al., 2018), therefore, in hybrid MBBR-MBR system, C/N had a little influence on the degradation of TOC. In phase II, after the reactors were stabilized the effluent quality of R_2, R_3 and R_4 all reached a higher level (>90%) except R_1. The removal efficiency of R_1 was lower than that of other reactors, and the reason might be that the microbial activity was reduced under low C/N. Furthermore, the addition of SDZ damaged the unstable microbial community in the system to a certain extent, which impacted on the removal efficiency of TOC.

Table 2 Removal efficiencies of TOC in four hybrid MBBR-MBR systems

3.1.3 Sulfadiazine removal in four hybrid MBBR-MBR systems

The removal efficiencies of SDZ in four hybrid MBBR-MBR systems at different C/N ratios (2.5, 4, 6 and 9) were 58.72 ± 6.07%, 69.00 ± 4.91%, 72.13 ± 2.92% and 75.63 ± 5.88%, respectively. During the experiments, all the four hybrid systems achieved more than half of the removal efficiencies when dealing with SDZ. In the experiment, the removal rate of SDZ in the four mixed systems is more than half.

The removal methods of refractory organics such as antibiotics in wastewater mainly include biodegradation, adsorption and air blowing. However, for SDZ, due to its non-hydrophilic physical and chemical properties, it is mainly removed by the biodegradation of microorganisms enriched on the carrier (Luo et al., 2014; Yu et al., 2018). When the influent C/N ratio was 3.5, the aerobic MBBR had an average removal efficiency of 61.11 ± 8.82% on SDZ with a concentration of 1-5 mg/L (Song et al., 2020). Moreover, when the aerobic submerged membrane bioreactor system was used to treat wastewater containing SDZ with a concentration of 5 μg/L and a C/N of about 5.5, the removal efficiency of SDZ reached 91%. As well, biodegradation was the main mechanism for removing SDZ (Yu et al., 2018). In the conventional MBR, the removal efficiency of SDZ was up to 100% at high C/N (>8.5) when SDZ concentration in the influent was lower than 100ng/L (Garcia Galan et al., 2012; Xu et al., 2017). However, when the SDZ concentration exceeded 1000ng/L, the removal efficiency of conventional MBR on SDZ was lower than 85% (Xu et al., 2017). Yu et al. (2018) investigated that adding sponge carrier into the conventional MBR could effectively improve the removal efficiency of SDZ by 15.2% at SDZ concentration of 5μg/L. It indicated that the attached microorganisms enhanced SDZ removal efficiency. In response to high concentration of SDZ (1mg/L), MBBR performed well with an average removal effect of 71.1±4.8% under low C/N of 3.5 (Zhang et al., 2020). Therefore, compared with the removal efficiency of SDZ by other bioprocesses, the hybrid MBBR-MBR had a good removal performance at high concentration of SDZ. With the increase in C/N ratios, the removal efficiency of SDZ also improved which was due to the co-metabolism of nutrients and SDZ. When the carbon source was sufficient, organic matter had a positive effect on SDZ' s removal, and because of high C/N, EPS in the relatively thick biofilm had a certain protective effect on microorganisms. This in turn led to better biodegradation.

3.2 Effect of sulfadiazine on sludge characteristics and membrane fouling at different C/N ratios

3.2.1 Sludge characteristics

Fig. 2 illustrates the changes of attached biomass and suspended biomass in phases I and II. As shown in Fig. 2, the order of total biomass in four hybrid MBBR-MBR systems was as follows: R_1(C/N=2.5) < R_2(C/N=4) < R_3(C/N=6) < R_4(C/N=9). The ratio of volatile biomass to total biomass in the two forms (suspended biomass and attached biomass) ranged from 0.66 to 0.73.

Fig. 2. Changes of MLSS and MLVSS in MBR as well as aAGBS and aVAGBS values in MBBR at C/N ratios (2.5, 4, 6 and 9)

MLSS content in MBBR was very small (0.241±0.060 mg/L), and the degradation effect on pollutants was negligible. Yu et al. (2020) have reported that MLSS did not contribute to the removal of refractory pollutants. Therefore, the degradation of pollutants in MBBR mainly depended on the attached biomass, and in each MBBR unit they were significantly different. They increased when an increase in C/N ratios was also evident, which may have been caused by the protective mechanism of biofilm against the degrading functional bacteria. At the same time, the attached biomass also impacted on the degradation performance of SDZ. With the increase of the attached biomass, the removal efficiency of SDZ increased correspondingly. This may be because the C/N ratio directly affected the concentration of the attached biomass and led to differences in the bacterial abundance, thus affecting the degradation performance of SDZ. Although the removal efficiency of SDZ increased with a simultaneously increase in the concentration of attached biomass in the hybrid systems, there was no conclusive evidence that a direct relationship existed between the two. It is worth noting that the suspended biomass in each MBR units were basically unchanged, remaining constant at 5.86 mg/L and 6.38 mg/L, indicating that SDZ had a small impact on the suspended biomass.

The ratio of volatile biomass to total biomass (MLVSS/MLSS and aVAGBS/aAGBS) reflects the microbial activity, the higher the ratio, the greater the microbial activity in the mixed system. It could be seen from Fig. 2 that in phase II, the microbial activity of each unit was affected after the addition of SDZ. With the increase of C/N ratios, the impact of SDZ on the microbial activity decreased gradually. MLVSS/MLSS and aVAGBS/aAGBS declined in different amounts due to the addition of SDZ (by 0.02 - 0.05 and 0.105 -0.128). After 10 days since SDZ was added, MLVSS/MLSS and aVAGBS/aAGBS ratios tended to be stable, which indicated that the hybrid systems would gradually adapt to the addition of SDZ after 10 days. However, they were still lower than in phase I, indicating that SDZ inhibited microbial activity.

In phase I, the sludge particle size was 12-28μm in MBR units at low C/N ratios of 2.5 and 4, while the sludge particle size was 15-46μm at high C/N ratios of 6 and 9. In phase II, the average particle size in all reactors decreased, at this time, the sludge particle sizes under the four C/N ratios were 8-17 μm, 10-21 μm, 14-38 μm and 16-41 μm, respectively. The phenomenon suggested that the sludge flocs began to disintegrate due to the addition of SDZ. Because SDZ was toxic to microorganisms, it might lead to the destruction of sludge floc and resulted in the sludge flocculation particles changing size. The broken floc would clog the film hole and accumulate, further leading to serious membrane fouling in the MBR unit.

Nguyen et al. (2019) confirmed that adding pharmaceuticals would affect membrane fouling due to the phenomenon of anti-flocculation caused by bacterial death of cells.

3.2.2 Changes of EPS in MBBR and MBR

EPS produced by microbial metabolism is an important factor affecting its physiological characteristics. Fig. 3 depicts the effect of different C/N ratios on the change in EPS while the system is in operation, in terms of the changes in PS and PN. The total amount of EPS was the highest in R_4 when the C/N ratio was 9, while that of the EPS in R_1 was the lowest, which was related to the total attached biomass in the MBBR units. The attached biomass in four systems was as follows: R_1 (C/N=2.5) < R_2 (C/N=4) < R_3 (C/N=6) < R_4 (C/N=9).

The content of EPS also increased in four MBBR units along with the operation time, on account of the microbes constantly accumulating on biofilm carriers. In phase II, the decline in the EPS concentration was due to the addition of SDZ, which resulted in the peeling off of the non-compacted biofilm. Additionally, the self-protection mechanism of microorganisms affected by toxins in the environment would secrete more EPS. The presence of pharmaceuticals inhibited the secretion of polysaccharides (PS), thereby impacting on the polymerization of biofilms. When the reactors stabilized, protein (PN) was basically unaffected by the pharmaceutical and still grew at a slow rate. PN was stable between 94.21 mg/L and 165.52 mg/L. Moreover, PN/PS reflected the stability of the environment in these systems (Song et al., 2020). In phase I, PN/PS in the biocarriers gradually decreased, indicating good stability of the reactors, however, in phase II, PN/PS increased to some extent. PN/PS increased with the drop in C/N ratios, suggesting that the stability of the internal environment in the reactor was easily worse under low C/N of 2.5 when SDZ was present. In contrast, at a high C/N ratio the hybrid system retained better stability. The stable hybrid systems provided favorable conditions for microbial growth, which explained the high efficiency in removing nitrogen, TOC and SDZ at high C/N ratios explained in section 3.1.

Fig. 3 Concentration of EPS, PN and PS in MBBR units with different C/N ratios

Fig. 4 describes the changes of EPS and SMP in four MBR units, and the EPS was similar after all the reactors successfully started on all the C/N ratios, with the initial EPS concentration of 4.505±0.266 mg/L. Then after adding SDZ (since day 25) the level of EPS in four MBR units gradually increased to 23.62 mg/L, 18.32 mg/L, 15.39 mg/L and 20.47 mg/L at the end of operation at C/N ratios of 2.5, 4, 6, and 9, respectively. This might be caused by a deterioration in the internal environment of the hybrid systems after SDZ is added. Due to the stimulation of SDZ, the self-protection mechanism of microorganisms was gradually improved, and EPS was then secreted. Under different C/N ratios the order of SMP in four MBR units was as follows: R_1(C/N=2.5) > R_2(C/N=4) > R_3(C/N=6) > R_4(C/N=9), in phase I, the concentrations of SMP were 20.08±0.30 mg/L, 16.12±0.83 mg/L, 10.87±0.28 mg/L and 7.22±0.80 mg/L, respectively. As SDZ was added the SMP concentration increased substantially to 25.81±0.57 mg/L, 23.79±0.64 mg/L, 20.16±0.28 mg/L and 15.25±0.80 mg/, corresponding to the C/N of 2.5,4,6 and 9, respectively. Additionally, the concentration of SMP was higher under the low C/N, which aggravated the membrane fouling rate and in effect speeded it up (Jiang et al., 2018).

Fig. 4 Variations of EPS and SMP concentrations in MBR units with different C/N ratios (2.5, 4, 6 and 9)

3.2.3 Membrane fouling

Fig. 5(a) describes the process of TMP increasing with time in four MBR units. The TMP in the MBR units reached up to 35.325 kPa, 34.524 kPa, 35.958 kPa and 35.625 kPa on days 29, 41, 45 and 42 at C/N ratios of 2.5, 4, 6 and 9, corresponding to fouling rates of 1.218, 0.842, 0.799 and 0.848 kPa/d, respectively. Therefore, membrane fouling was more likely to occur at low C/N (C/N=2.5). Especially, the TMP value remained at less than 15 kPa for 33 days (C/N ratio of 4) and 37 days (C/N ratio of 6) of operation, and even with the addition of SDZ, TMP maintained a growth rate of 0.526 and 0.511 kPa/day, respectively. The cake resistance (R_c) consisted of about 72% of fouling resistance at all C/N ratios, indicating that the main contributor to membrane fouling was formation of cake layer. In 3.2.1, it was mentioned that at high C/N, the sludge particle size was relatively large, and larger floc was not easy to plug holes, and subsequently, membrane fouling did not occur easily at high C/N. However, at a high C/N ratio, membrane fouling in R_4 reached 35kPa earlier than that in R_3, and the membrane fouling rate of R_4 (1.412kPa/day) after SDZ was added was higher than that of R_3 (1.551kPa /day). This may be explained by the high biomass concentration in R4, rapid microbial metabolism, and the production of small flocs to plug the membrane pores. This phenomenon was also related to the contents of EPS and SMP in the filter cake layer.

Fig. 5 (b) describes the contents of proteins (EPSp) and polysaccharides (EPSc) in EPS as well as proteins (SMPp) and polysaccharides (SMPc) in SMP. With the increase of C/N ratio (at medium and low C/N ratios), membrane fouling gradually improved, and the most important factor affecting membrane fouling was EPSp. In the cake layer, EPSc/EPSp reflected the hydrophobicity of the sludge floc, when the ratio was low, the hydrophobicity increased so as EPS would deposit on the membrane and further worsen the membrane fouling (Deng et al., 2016b). As can be seen in Figure 6, the ratio of EPSc/EPSp was the lowest (1.45) at low C/N (2.5), suggesting that low C/N could cause more serious membrane fouling. It was worth noting that the ratios of SMPc/SMPp were positively correlated with the growth rate of TMP, R_1 (C/N=2.5) > R_2 (C/N=4) > R_4 (C/N=9) > R_3 (C/N=6), and the ratios were 0.628, 0.604, 0.570 and 0.554, respectively. Results also showed that SMPc was a main factor affecting membrane fouling which is consistent with the view put forward by Chen et al. (2018).

According to the study by Deng et al. (2016), the TMP reached 35 kPa after 110 days or even longer with no pharmaceutical in the wastewater. In the work conducted by Jiang et al. (2018), TMP reached 36.5 kPa after 74 days when 22 micropollutants with a concentration of 5 μg/L were added to the inflow. Compared with these analyses, the rising rate of TMP in this study was faster due to the addition of 0.5 mg/L of SDZ. The results suggested after the sudden addition of SDZ, the stability of the environment in the reactor was affected. The rapid increase of SMP and EPS as well as sludge floc destroyed by SDZ were the main causes of membrane fouling. Small sludge floc was attached to the membrane surface, blocking the membrane hole and accelerating the formation of a filter cake layer, thus causing serious membrane fouling. In phase II, it was observed that the TMP in R_1 increased rapidly (33.333kPa/day), while the sludge particle size decreased sharply (from 12-28 μm to 8-17 μm). Therefore, the main reason why SDZ influenced membrane fouling in the hybrid MBBR-MBR was the filter cake layer formed by the small-sized sludge floc blocking the membrane hole.

Fig. 5 Membrane fouling of MBR unit in a MBBR-MBR hybrid system at different C/N ratios: (a) TMP profiles, (b) EPS and SMP of cake layer.

4. Conclusions

In the MBBR-MBR system. TN removal and SND performance are more inhibited by SDZ than that of TOC. However, this negative affect was curtailed at a high C/N ratio (> 4). On account of co-metabolism, the hybrid system with a high C/N ratio had better SDZ removal efficiency. Moreover, SDZ affected the sludge characteristics in terms of sludge particle size, EPS and SMP in the hybrid bioreactors. The hybrid system affected by SDZ was more likely to recover its stability under a high C/N ratio. In short, SDZ in the influent could cause more serious membrane fouling of the MBR.

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E-supplementary data for this work can be found in e-version of this paper online.

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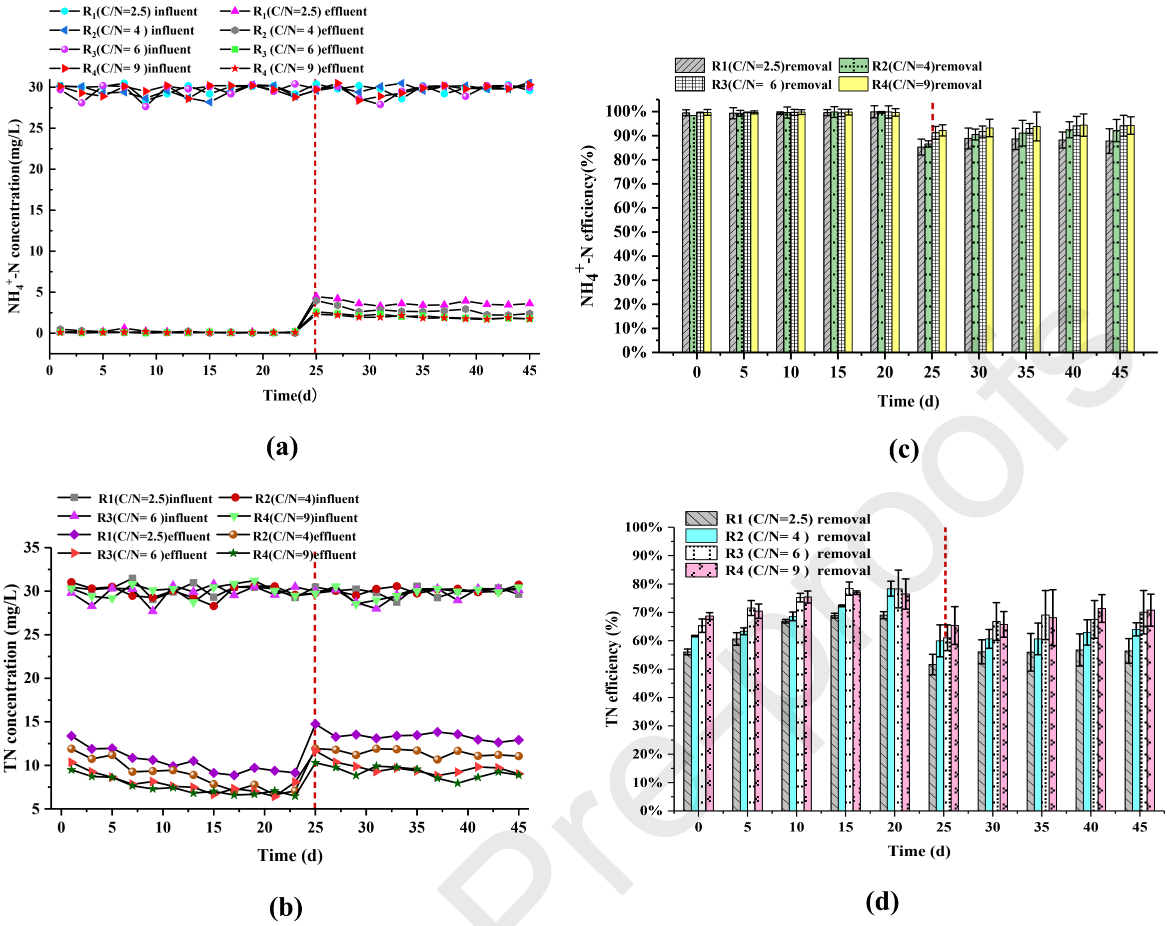


Fig.1 Variations of (a) NH_4^+-N concentrations, (b) TN concentrations, (c) NH_4^+-N removal efficiencies, and (d) TN removal efficiencies in hybrid MBBR-MBRs

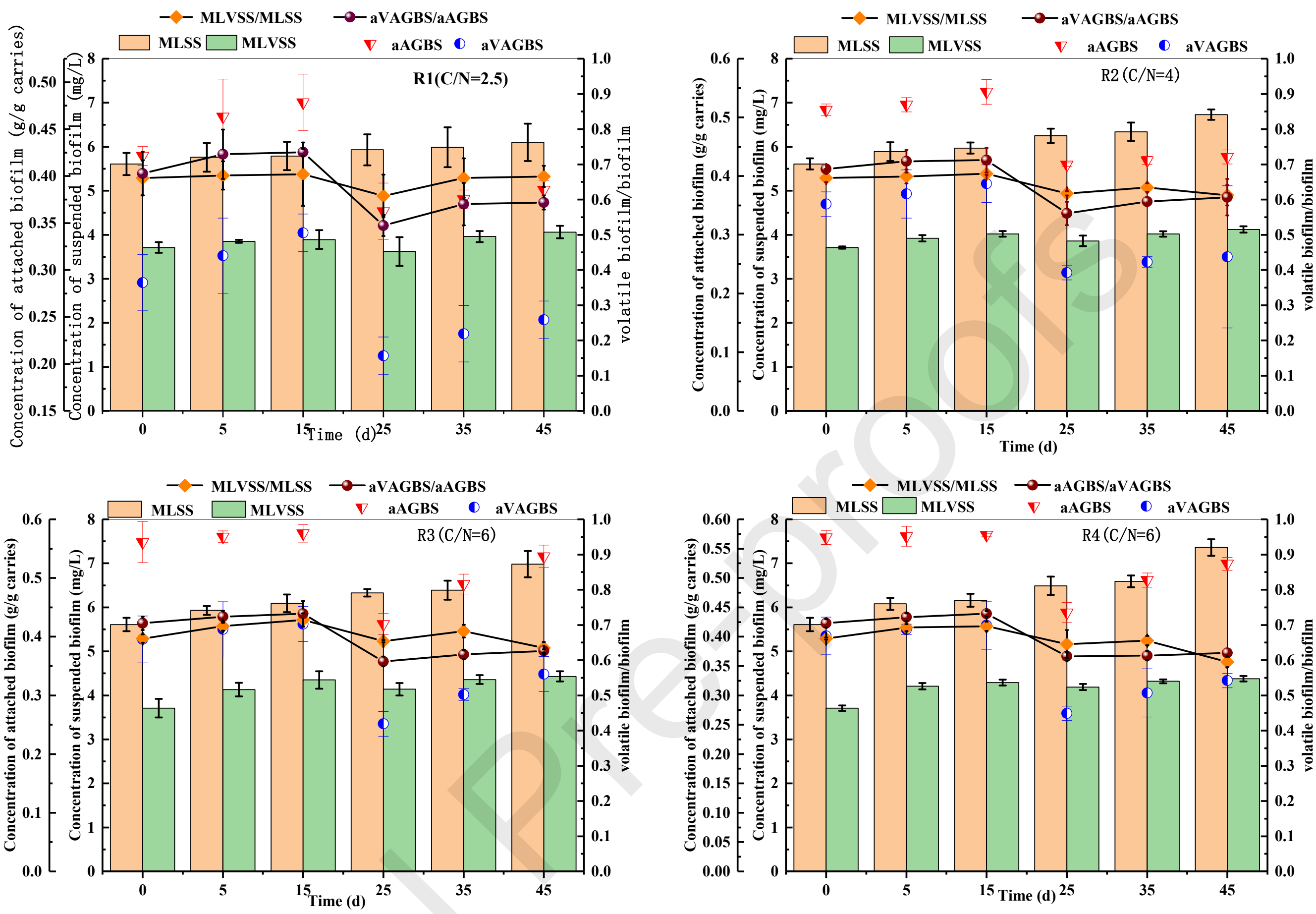


Fig.2. Changes of MLSS and MLVSS in MBR as well as aAGBS and aVAGBS values in MBBR at C/N ratios (2.5, 4, 6 and 9)

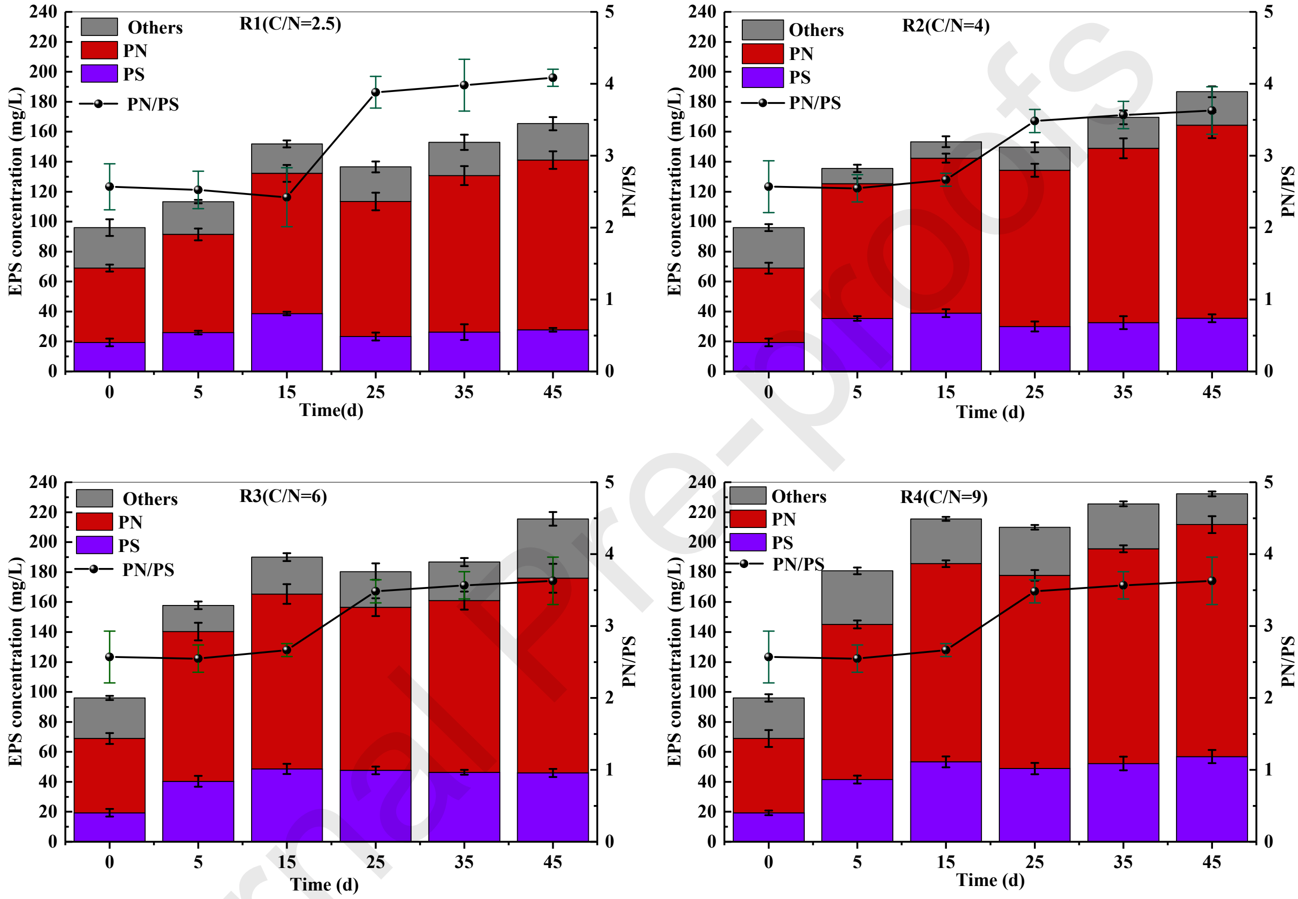


Fig. 3 Concentration of EPS, PN and PS in MBBR units with different C/N ratios

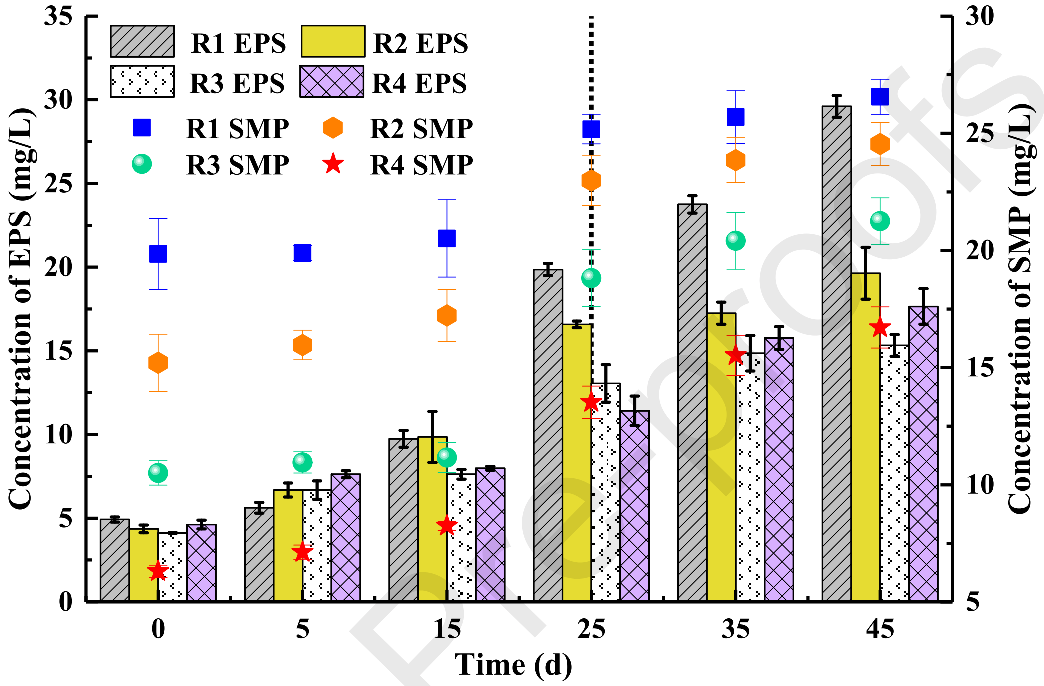
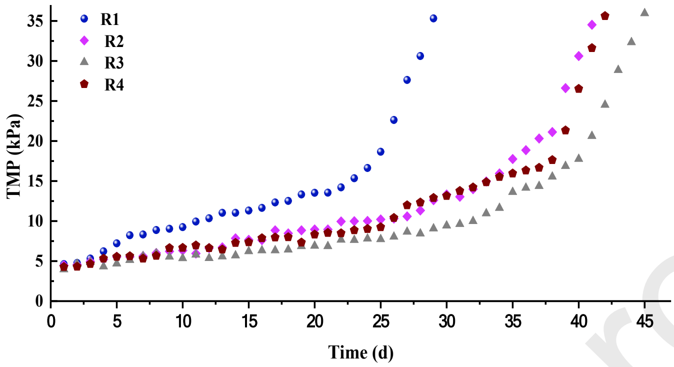


Fig.4 Variations of EPS and SMP concentrations in MBR units with different C/N ratios (2.5, 4, 6 and 9)



(a)

(b)

Fig.5 Membrane fouling of MBR unit in a MBBR-MBR hybrid system at different C/N ratios: (a) TMP profiles, (b) EPS and SMP of cake layer

Table 1 SDN performance in four hybrid MBBR-MBR systems

Period	R_1(C/N=2.5)	R_2(C/N=4)	R_3(C/N=6)	R_4(C/N=9)
Phase I (without adding SDZ)	66.66 ± 4.26%	71.84 ± 5.03%	74.23 ± 4.20%	76.41± 3.74%
Phase II (with adding SDZ)	63.26 ± 1.86%	68.55 ± 1.25%	72.58 ± 2.16%	74.15 ± 2.28%

Table 2 Removal efficiencies of TOC in a hybrid MBBR-MBR system

Period	R_1(C/N=2.5)	R_2(C/N=4)	R_3(C/N=6)	R_4(C/N=9)
Phase I (without adding SDZ)	90.10 ± 1.20%	91.29 ± 1.66%	92.29 ± 1.32%	91.21± 1.31%
Phase II (with adding SDZ)	84.33 ± 1.97%	85.69 ± 1.08%	90.35 ± 2.35%	91.08 ± 1.00%