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Efficient elimination of sulfonamides by an anaerobic/anoxic/oxic-membrane bioreactor process: Performance and influence of redox condition

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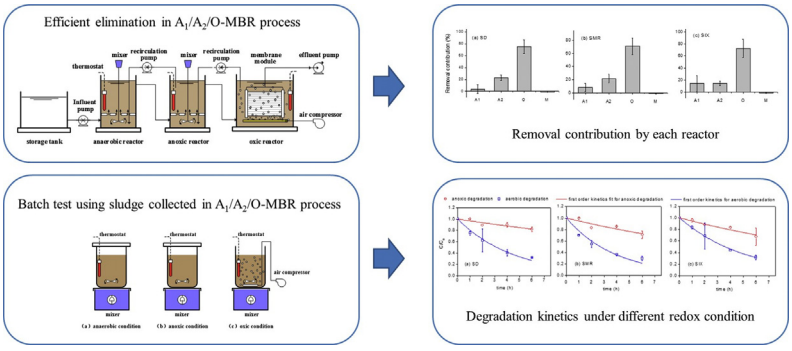
HIGHLIGHTS

- Nine sulfonamides (SAs) were efficiently eliminated by the A_1/A_2/O-MBR process.
- Aerobic reactor made the largest contribution to the total removal.
- Degradation of SAs also occurred by the collected sludge under anoxic condition.
- Removal and degradation kinetics were studied under different redox condition.
- Two SAs, SIM and SMT, exhibited less efficient removal than other SAs.

GRAPHICAL ABSTRACT



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ABSTRACT

Membrane bioreactors (MBRs) were shown contradictory results for the removal of antibiotics, such as sulfonamides (SAs), from wastewater in different studies, which highlighted the necessity for comprehensive investigation on removal mechanisms of sulfonamides in well-controlled lab-scale MBRs. In the present study, the removal performance of nine SAs by a lab-scale anaerobic/anoxic/oxic-membrane bioreactor (A_1/A_2/O-MBR) was studied at environmental relevant concentrations. The results showed that all the SAs were efficiently eliminated (93.9%–97.5%) in the A_1/A_2/O-MBR, much more efficiently than the previously reported MBR-based processes. The largest contribution to the total removal was made by the aerobic reactor (71.1%–85.3%) A small portion of SAs (7.1%–22.5%) were removed by anoxic reactor. Activated sludge in the A_1/A_2/O-MBR was harvested to conduct batch experiments to further study the removal and degradation kinetics of SAs under anaerobic, anoxic and aerobic conditions. The results indicated that only sulfisoxazole could be removed under anaerobic condition. Modest biodegradation of individual SAs (15–33%) was observed under anoxic condition. Under aerobic condition, most investigated SAs underwent an efficient and fast removal (68–77%) in 6 h without a lag phase; while sulfisomidine and sulfamethazine were removed less efficiently (approximately 47% after 6 h reaction). The aerobic and anoxic degradation of SAs fitted the first-order kinetics model well, and the obtained biodegradation rate constants (k_1) were reliable to predict removal efficiencies of SAs in the anoxic and aerobic reactor of A_1/A_2/O-MBR based on their HRTs.

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1. Introduction

Sulfonamides (SAs), which are widely used both as human antibiotics and in animal husbandry and aquaculture, are detected up to μg/L level in wastewaters (Rodriguez-Mozaz et al., 2015; Tuc et al., 2017). Conventional wastewater treatment processes could not guarantee the elimination of SAs from wastewaters (Sui et al., 2012; Garcia-Galan et al., 2012b; Zhou et al., 2013). As a result, they were found in surface water, groundwater and even drinking water supply (Shimizu et al., 2013; Yao et al., 2015). According to Zhao et al. (2016), SAs, including sulfamethoxazole (SMX), sulfadiazine, sulfamethazine, sulfathiazole, etc., were among the most frequently reported pharmaceuticals in the surface water of China, exhibited relatively high contamination levels and SMX presented the most significant environmental risk to relevant aquatic organisms (Zhao et al., 2016). For these reasons, there is a growing need to develop reliable wastewater treatment and reuse methods, which enable the efficient removal of SAs at trace levels, especially in China (Dolar et al., 2012).

Membrane bioreactors (MBRs) have become a promising wastewater treatment and reuse technology in the last few years (Shannon et al., 2008). MBRs produce a lower washout of slow-growing functional microorganisms and create richer mixed liquors, which are capable of degrading a wider range of organic pollutants (Garcia-Galan et al., 2012a; Liu et al., 2017). Previous studies indicated that MBRs showed better performance in removing SAs (Sahar et al., 2011; Garcia-Galan et al., 2012a). An MBR pilot plant in Israel achieved higher removal rates than the conventional activated sludge – ultrafiltration (CAS-UF) for SAs (Sahar et al., 2011). Garcia-Galan et al. (2012a) investigated the removal efficiencies of nine SAs and one of their acetylated metabolites in two separate pilot-scale MBRs operating in parallel to a full-scale CAS treatment, and observed the removal efficiencies in two MBRs were higher than those observed for CAS in most cases, with 100% removal for four of the SAs investigated. Thus, implementing MBRs for SA removal in wastewater treatment plants might be an interesting option with increased reliability and consistency (Larcher and Yargeau, 2012). Nevertheless, there are also contradictory results showing that MBR exhibited similar removal performance to conventional activated sludge (Sahar et al., 2011).

Therefore, removal of SAs by MBRs should be comprehensively studied to figure out the reasons for the different performances observed in various studies. However, this objective could not be easily achieved based on the field sampling results, since many uncertain factors may affect the operation of real wastewater treatment processes. Consequently, some pioneer works with well-controlled laboratory reactors have been conducted for SA removals in MBR-based process (Hai et al., 2011; Xia et al., 2012). For instance, an anoxic/aerobic membrane bioreactor (A/O-MBR) was installed in Xia et al. (2012) to investigate the effect of SRT on the removal of antibiotics, including sulfamethoxazole and sulfadiazine, and proposed that a longer SRT was suitable for antibiotics removal. However, these results were far from adequate to comprehensively elucidate the mechanisms of SA removal in MBRs.

Furthermore, removal performances and mechanisms of SAs in either conventional activated sludge processes or MBRs were mostly performed under aerobic condition. Only a few researchers have studied their degradation by activated sludge under other redox conditions (Hai et al., 2011; Alvarino et al., 2014, 2016; Oliveira et al., 2016; Jia et al., 2017). For instance, the removal efficiencies of sulfamethoxazole by an MBR were examined and compared under near-anoxic (DO = 0.5 mg/L) and aerobic (DO >2 mg/L) conditions. The results showed that an average removal efficiency of 65% of sulfamethoxazole was achieved irrespective of DO concentrations (Hai et al., 2011). Alvarino et al. (2014) indicated that SMX were highly eliminated under anaerobic conditions in an upflow anaerobic sludge blanket (UASB) reactor, and the PPCP biodegradation was correlated with the methanogenic rate. From these limited outputs already published, it could be suggested that removal efficiencies might be similar or different depending on the redox potential applied, and led to the conclusion that knowledge on the removal of various SAs under different redox conditions should be expanded.

Hence, we investigated the removal performance of nine SAs by a lab-scale anaerobic/anoxic/oxic-membrane bioreactor (A_1/A_2/O-MBR) at environmental relevant concentrations. The contribution of each unit to the total elimination of SAs was discussed. Furthermore, batch experiments were conducted to further study the removal and degradation kinetics of SAs by activated sludge in A_1/A_2/O-MBR under anaerobic, anoxic and aerobic conditions. The findings can help better understanding the performance of SAs removal by MBRs, providing some supports to develop reliable treatment methods to completely remove SAs from wastewater.

2. Materials and methods

2.1. Chemicals

The selected nine SAs, including sulfadiazine, sulfamerazine, sulfisoxazole, sulfisomidine, sulfamethoxypyridazine, sulfamethazine, sulfadimethoxine, sulfamethoxazole and sulfamonomethoxine, were purchsed from Sigma-Aldrich (Germany). Their abbreviation and physico-chemical properties were compiled in Table 1. SMT-^{13}C from Sigma-Aldrich (Germany) was used as the internal standard. HPLC-grade methanol and acetonitrile were provided by J&K (USA). Milli-Q water was produced from a Millipore purification system (Billerica, CA, USA). Solid phase extraction (SPE) cartrige (Oasis HLB, 200 mg/6 mL) was purchased from Waters (MA, USA), 0.22-μm PTFE syringe filter from Millipore (Millex-FG, 13 mm), and glass fiber filters (GF/F) from Whatman (UK). For analysis, stock solutions of individual compounds were prepared in methanol, and working solutions with different concentrations were prepared by mixing and diluting the stock solutions.

2.2. A_1/A_2/O-MBR reactors

The lab-scale A_1/A_2/O-MBR system (Fig. 1) consisted of an anaerobic reactor (A_1, 8 L, completely mixed), an anoxic reactor (A_2, 8 L, completely mixed) and an oxic reactor (O, 16 L, completely mixed) with a submerged hollow fiber polythene membrane (nominal pore size: 0.1 μm, membrane area: 0.2 m^2, Mitsubishi, Japan). A diaphragm pump (model X068, Pulsafeeder, USA) fed the raw wastewater from a 100-L storage tank to the anaerobic reactor A_1. The internal mixed liquor recirculation ratio from A_2 to A_1, from O to A_2 were at 150% and 400% of the feeding rate by a peristaltic pump (model BT100-2J, LongerPump, China). The temperatures of anaerobic (A_1), anoxic (A_2) and oxic reactors (O) were maintained at about 25 °C using thermostats. Air diffusers underneath the membrane in the oxic reactor aerated and mixed the suspensions and scored the membrane surface for reducing fouling. The dissolved oxygen (DO) concentration of the oxic reactor was maintained >4 mg/L throughout the 150-d test. The membrane effluent was drawn intermittently by a suction pump (model X030, Pulsafeeder, USA) at constant-rate mode with a filtration/idle cleaning ratio of 8 min:2 min.

Table 1
Target SAs and their physico-chemical properties.

SAs	Abbreviation	log K_{ow}	pK_a
Sulfadiazine	SD	−0.09	6.36
Sulfamerazine	SMR	0.14	6.98
Sulfisoxazole	SIX	1.01	5.00
Sulfisomidine	SIM	0.89	7.59
Sulfamethoxypyridazine	SMP	0.32	7.19
Sulfamethazine	SMT	0.89	7.59
Sulfadimethoxine	SDM	1.63	6.21
Sulfamonomethoxine	SM	0.70	6.00
Sulfamethoxazole	SMX	0.89	5.81