



## The study of electron equivalent fluxes about decomposition of sulfamethazine and sulfathiazole using oxygen-based membrane biofilm reactor

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### ABSTRACT

The subject of this research was electron equivalent fluxes about the decomposition of pharmaceuticals (sulfamethazine and sulfathiazole) using an oxygen-based membrane biofilm reactor (MBfR). The influent concentrations in pharmaceuticals feed-medium were (in ppb): sulfamethazine (40) and sulfathiazole (85). The oxygen-based MBfR system consisted of two membrane modules connected to a recirculation loop. The main membrane module contained a bundle of 32 hydrophobic hollow-fiber membranes inside a polyvinyl-chloride pipe shell and the other module contained a single fiber used to take biofilm samples. Pure O<sub>2</sub> was supplied to the inside of the hollow fibers through the manifold at the base, and the O<sub>2</sub> pressure for both reactors was 13 kPa. (1 kPa = 0.0099 atm = 0.145 psi). HRT was 3 h. The decomposition ratio of pharmaceuticals (sulfamethazine and sulfathiazole) using oxygen-based MBfR was (%): sulfamethazine (77 ± 2) and sulfathiazole (87 ± 2). In all cases, nitrification was the largest provider of electrons, together accounted for at least 99.98% of the total electron flux.

*Keywords:* Electron equivalent flux; Oxygen; Membrane biofilm reactor; Sulfamethazine; Sulfathiazole

### 1. Introduction

The presence of pharmaceuticals in the environment is a growing concern. The number of reports of measurable concentrations of pharmaceuticals found in the environment is growing. Despite the numerous reports on the environmental occurrence of pharmaceuticals at levels in the range of nanogram to low microgram/liter,

the environmental significance of their presence is largely unknown. With a growing population and an increased demand for medicine, the amount of pharmaceuticals entering the environment is steadily growing. Pharmaceuticals enter the environment through various routes. Pharmaceutical compounds, including their metabolites and conjugates, are mainly excreted in urine or feces. They enter municipal sewage treatment systems where they can be degraded, absorbed to

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sewage sludge, or eventually diluted into surface water. Sewage treatment facilities are not always effective in removing active pharmaceuticals from wastewater. Pharmaceuticals that adsorb into sludge can reach the terrestrial environment and enter surface water and groundwater, and eventually reach the aquatic environment. In addition to excretion from human bodies, effluent from pharmaceutical plants, hospital wastewater containing various pharmaceuticals at relatively high levels, and the direct dumping of excess or expired medication from households can be significant sources of pharmaceuticals in the environment.

The membrane biofilm reactor (MBfR) takes advantage of a naturally occurring partnership between a membrane and a biofilm [1]. Biofilm grows on the outside of a gas-transfer membrane that has a gas-phase substrate on the inside of the membrane. The substrate diffuses through the wall of the membrane and is consumed by the bacteria in the biofilm. Thus, the biofilm accumulates on an “active” surface, or one that delivers substrate to the bacteria. The substrate can be an electron donor or an electron acceptor, as long as it is a gas.

The concept underlying the MBfR can be traced back to 1960, when Schaffer et al. [2] utilized permeable plastic films to transfer  $O_2$  and developed slimes on the outside walls. The discovery of more advanced membrane materials in the 1970s through the 1990s led to development of a range of  $O_2$ -based MBfR systems used for nitrification, and combined nitrification and denitrification [3–7]. These aerobic systems, often called membrane-aerated biofilm reactors [8], demonstrated the possibility of delivering a substrate directly to a biofilm.

The MBfR overcomes the problems of sparging, because the  $O_2$  is delivered directly to the biofilm by its diffusion through the wall of a gas-transfer membrane. Bubbleless  $O_2$  transfer eliminates the problem of creating a combustible atmosphere. It also makes  $O_2$  delivery nearly 100% efficient, and virtually self-regulating [9]. In essence, the bacteria in the biofilm “pull” the  $O_2$  through the membrane wall when they consume  $O_2$  (in proportion to the reduction rate(s) of the reduced contaminant(s)), and generate an  $H_2$  gradient in the biofilm and across the membrane wall [10–12]. One of the strengths of the MBfR is that it is a platform technology that can be used for waters contaminated with one or more reduced contaminants in many different settings: drinking-water sources, ground or surface waters that must be bioremediated, industrial and agricultural wastewaters, and municipal wastewater requiring advanced nutrient removal [13–19].

In this study, the bio-oxidation of sulfamethazine and sulfathiazole in an  $O_2$ -based MBfR and electron

equivalent fluxes were investigated. A nitrifying reactor was used in this study, because the nitrification process was an oxidation process of  $NH_4^+$ . Furthermore, nitrification was investigated to determine whether it acted as an inhibitor to the bio-oxidation of sulfamethazine and sulfathiazole.

## 2. Materials and methods

### 2.1. Experimental setup

A schema of the MBfRs used in this study is shown in Fig. 1, and the reactor characteristics are provided in Table 1. The MBfR was the same as those described in Chung et al. (2006). The MBfR system consisted of two glass tubes connected with Norprene tubing and plastic bared fittings. One glass tube contained a main bundle of 32 hollow-fiber membranes (Model MHF 200TL, a composite bubbleless gas-transfer membrane produced by Mitsubishi Rayon), each 25 cm long. The MBfR was covered with aluminum foil to preclude the growth of phototrophs. A single peristaltic pump (Gilson Miniplus 3, Middleton, WI) was used to give a feed rate of 0.078, 0.104, and 0.310 ml/m for ammonia + sodium acetate + sulfamethazine + sulfathiazole medium. The recirculation rate was 150 ml/m, which promoted complete mixing. The high recirculation rate also helped in the formation of a dense biofilm (Chang et al., 1991, Lee and Rittmann, 2002), and minimized the accumulation of excessive biofilm that might otherwise clog the reactor. Pure  $O_2$  was supplied to the inside of the hollow fibers through the manifold at the base and the  $O_2$  pressure for both reactors was 13.7, 20.6, and 27.5 kPa. (1 kPa = 0.0099 atm = 0.145 psi). Retention times were 1, 3, and 4 h.

### 2.2. Feed medium, stock solution, and mixed influent

The composition of the feed-medium was (in g/L):  $(NH_4)_2SO_4$  (0.09432),  $MgSO_4 \cdot 7H_2O$  (0.05),  $NaHCO_3$  (0.252),  $KH_2PO_4$  (0.0454),  $CH_3COONa$  (0.043), yeast extract (0.005), and 1 ml/L of trace mineral solution. The trace mineral solution (mg/L) consisted of  $ZnSO_4 \cdot 7H_2O$  (100),  $MnCl_2 \cdot 4H_2O$  (30),  $H_3BO_3$  (300),  $CoCl_2 \cdot 6H_2O$  (200),  $CuCl_2 \cdot 2H_2O$  (10),  $NiCl_2 \cdot 6H_2O$  (10),  $Na_2MoO_4 \cdot 2H_2O$  (30), and  $Na_2SeO_3$  (30). The influent concentrations in the pharmaceuticals feed-medium was (in ppb): sulfamethazine (40) and sulfathiazole (85). The concentration of pharmaceuticals was based on “Development of analytical method and study of exposure of pharmaceuticals and personal care products in environment, National Institute of Environmental Research, Korea.” It was prepared in a 10-L

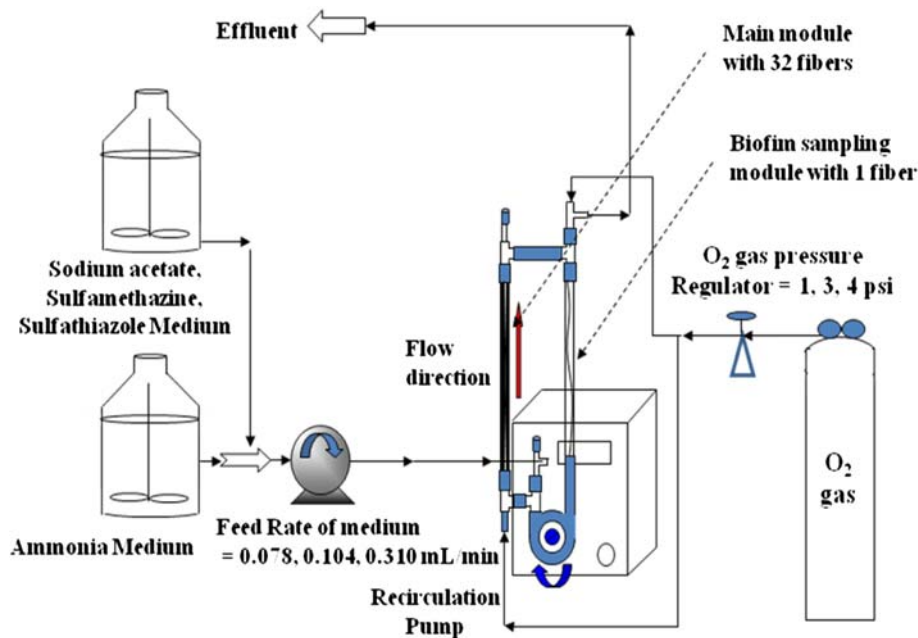


Fig. 1. Schema of the bench-scale MBfR used to investigate the oxidation of sulfamethazine and sulfathiazole.

Table 1  
Physical characteristics of the main module of the MBfR

	Value	Units
Fiber surface area	72	cm <sup>2</sup>
Fiber's outside diameter	280	µm
Tube length	27	cm
Tube's inside diameter	0.6	cm
Volume	23.9	ml

glass bottle and the prepared 10-L influent was sterilized in the autoclave.

2.3. Operating condition

The experiment was performed with two settings as shown in Table 2. The inocula came from oxic unit in wastewater treatment at Uiwang-si, Kyungki-do.

Start-up began when O<sub>2</sub> was supplied to the membrane, and the liquid in the reactor was recirculated for 24 h to establish a biofilm. In set I, by changing HRT and O<sub>2</sub> gas, the performance of the reactor was estimated. Based on the results of set I, the operating conditions of set II were decided.

2.4. Flux Computations

The flux of each contaminant gives us detailed information about the removal capacity of the target contaminant by the biofilm. Eq. (1) shows the computation for flux. Eq. (1) was applied for COD, NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N, sulfamethazine, and sulfathiazole. Eq. (2) shows the computation for electron-equivalent flux. Eq. (2) was applied for NH<sub>4</sub><sup>+</sup>-N, sulfamethazine, and sulfathiazole. Eq. (3) shows the computation for surface loading. Eq. (3) was applied for NH<sub>4</sub><sup>+</sup>-N, sulfamethazine, and sulfathiazole.

Table 2  
Experimental conditions

Exp. setting	Set I (Without sulfamethazine and sulfathiazole)					Set II (Including sulfamethazine and sulfathiazole) Run
	Run 1	Run 2	Run 3	Run 4	Run 5	
Term (days)	0–24	25–38	39–52	53–66	67–80	81–113
HRT (h)	4	3	1	3	3	3
O <sub>2</sub> gas (kPa)	13.7	13.7	13.7	20.6	27.5	13.7

$$J_s = Q(S_0 - S)/A \quad (1)$$

where  $J_s$  is the flux target parameter ( $\text{g}/\text{m}^2\text{-d}$ ),  $Q$  is the influent flow rate ( $\text{m}^3/\text{d}$ ),  $S_0$  the influent concentration of target parameter ( $\text{g}/\text{m}^3$ ),  $S$  is the effluent concentration of target parameter ( $\text{g}/\text{m}^3$ ), and  $A$  is the membrane surface area ( $\text{m}^2$ ).

$$J_e = \frac{Q \Delta S}{aVEW} \quad (2)$$

where  $J_e$  is the electron flux target parameter ( $\text{eq}/\text{m}^2\text{-d}$ ),  $Q$  is the influent flow rate ( $\text{m}^3/\text{d}$ ),  $\Delta S$  is the concentration of target parameter ( $\text{g}/\text{m}^3$ ),  $aV$  is the total biofilm surface ( $\text{m}^2$ ), and  $EW$  is the number of electrons per mole of target parameter ( $\text{g}/\text{eq}$ ).

$$SL = \frac{Q_x S_0}{A} \quad (3)$$

where  $SL$  = surface loading ( $\text{g}/\text{m}^2\text{-d}$ ),  $Q$  is the influent flow rate ( $\text{m}^3/\text{d}$ ),  $S_0$  is the influent concentration of target parameter ( $\text{g}/\text{m}^3$ ), and  $A$  is the membrane surface area ( $\text{m}^2$ ).

### 2.5. Sampling and analysis

The performance of the MBfR was monitored through the analysis of analyzing influent and effluent samples on a daily basis. Samples were immediately filtered through a 0.2- $\mu\text{m}$  membrane filter (Whatman Corp.). The pH was determined using a glass electrode pH meter (Orion, Model 525A). Soluble COD was determined using the HACH digestion vials (HACH, DR/2012).  $\text{NO}_3^-$  was determined using ion chromatography (DX-120, Dionex Inc.) and  $\text{NH}_4^+$  was determined using ion chromatography (DX-500, Dionex Inc.).

The concentrations of sulfamethazine and sulfathiazole were analyzed using solid-phase extraction (SPE) and liquid chromatography/mass spectrometer (LC/MS). To enrich the sample, TurboVap LV concentrator (Caliper Lifescience Co., Seattle, WA, USA) was used. Oasis HLB (200 mg, 6 cc) and Oasis MCX (150 mg, 6 cc) (Waters Co., Milford, Massachusetts, USA) were used as cartridges of SPE and a vacuum manifold (Supelco, Bellefonte, PA, USA) was used. Sulfamethazine and sulfathiazole of Sigma-Aldrich (St Louis, MO, USA) were used. Sulfamethazine-6-13C (Cambridge Isotope Laboratories Co., Andover, MA, USA) was used for surrogate, and terbutylazine (Fluka Co., Seelze, Germany) was used as the internal standard.

Agilent 1100 series HPLC (Palo Alto, CA, USA) with autosampler (Agilent 1100 series G1313A) was used, and triple–quadruple tandem mass spectrometer

(Quattro Micromass, UK Ltd, Manchester, UK) was used for determining the molecular weight of separated material. An amount of 0.1  $\mu\text{g}/\text{mL}$   $\text{Na}_2\text{-EDTA}$  0.5 mL and 10  $\mu\text{g}/\text{mL}$  sulfamethazine-6-13C was pipetted into 500 mL of sample and pH was fixed at 3 using 3.5 M  $\text{H}_2\text{SO}_4$ . After Oasis HLB (200 mg, 6 cc) and Oasis MCX (150 mg, 6 cc) cartridges were installed at vacuum manifold, 2 mL of distilled water and 2 mL of methanol were allowed to flow. A volume of 2 mL of 5% ammonia–methanol solution, 2 mL of distilled water, and 2 mL of distilled water (pH 3.0) were passed sequentially for conditioning. After HLB cartridge was installed at the upper part of MCX cartridge, sample was loaded at a rate of 10 mL/min. After separating the cartridge, HLB was washed using 2 mL of distilled water and 2 mL of methanol was loaded. MCX was washed using 2 mL of distilled water. After cartridge was connected again, 2 mL of methanol was loaded and 6 mL of methanol was used to elute. After HLB cartridge was removed, MCX cartridge was eluted using 4 mL of 5% ammonia–methanol solution. A volume of 25  $\mu\text{L}$  of internal standard (10  $\mu\text{g}/\text{mL}$  terbutylazine) was pipetted into this eluted solution. After evaporating using a nitrogen-evaporator, 500  $\mu\text{L}$  of ammonium acetate (20 mM) was used for dissolving. After filtering using a 0.45- $\mu\text{m}$  filter, sample was pipetted into a 2-mL vial (brown in color). The operating conditions of LC/ESI-MS/MS were: column (Luna 3u Phenyl-Hexyl column, 3 mm I.D. 150 mm (Phenomenex, Torrance)), mobile phase (A: 20 mM ammonium acetate (pH 6.5) and B: Acetonitrile), gradient (Time(min) 0, 10, 11, 15, 15.1, and 17, Solvent B(%) 30, 65, 100, 100, 30, and 30), column flow rate (300  $\mu\text{L}/\text{min}$ ), injection volume (10  $\mu\text{L}$ ), column temperature (25°C), ionization mode (positive ion electrospray), capillary voltage (3.20 kv), cone voltage (30 V), source temperature (120°C), desolvation temperature (300°C), cone gas flow (50 L/hr), and desolvation gas flow (550 L/hr).

## 3. Results and discussion

### 3.1. Nitrification and removal of COD

Fig. 2 shows the steady state results of soluble  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  and the COD in influent and effluent from MBfR. In Run 1 (4 HRT, 13.7 kPa) and Run 2 (3 HRT, 13.7 kPa), nitrification efficiency of  $\text{NH}_4^+\text{-N}$  was stably maintained above 93%, and concentration of  $\text{NH}_4^+\text{-N}$  in effluent was maintained below 1.5 mgN/L. In Run 3 (1 HRT, 13.7 kPa), nitrification efficiency of  $\text{NH}_4^+\text{-N}$  was decreased from 90% to 75–79%, and concentration of  $\text{NH}_4^+\text{-N}$  in effluent was increased from  $1.2 \pm 0.2$  to 3.0–3.7 mgN/L. These results indicate that nitrification was controlled by

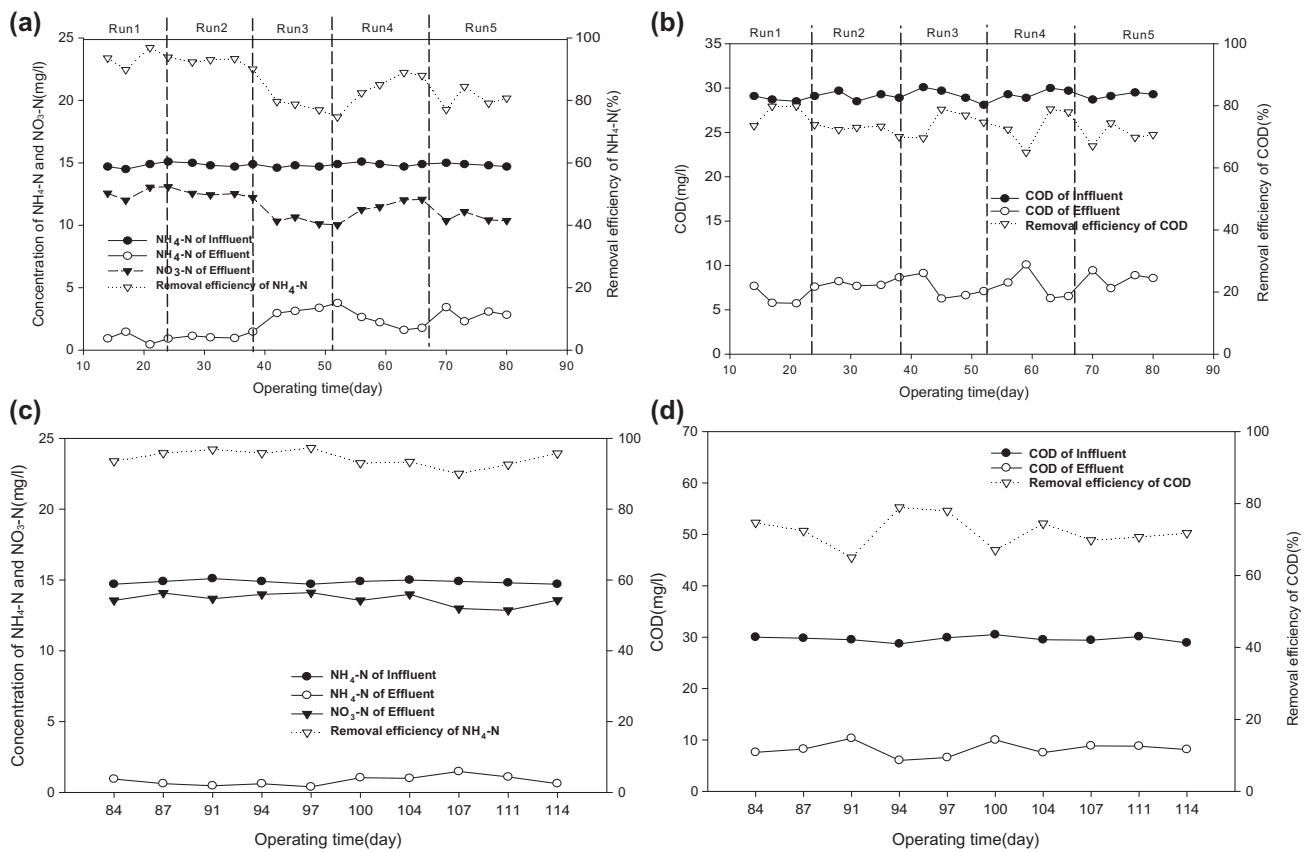


Fig. 2. Results of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , and COD according to experimental conditions. (a) Concentrations and removal efficiency of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  without sulfamethazine and sulfathiazole, (b) Concentrations and removal efficiency of COD without sulfamethazine and sulfathiazole, (c) Concentrations and removal efficiency of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  including sulfamethazine and sulfathiazole, and (d) Concentrations and removal efficiency of COD including sulfamethazine and sulfathiazole.

HRT. In Run 4 (3 HRT, 20.6 kPa), nitrification efficiency of  $\text{NH}_4^+\text{-N}$  was increased from 75–79% to 82–88%, and concentration of  $\text{NH}_4^+\text{-N}$  in effluent was decreased from 3.0–3.7 to 1.7–2.6 mgN/L. In Run 5 (3 HRT, 27.5 kPa), nitrification efficiency of  $\text{NH}_4^+\text{-N}$  was decreased from 82–88% to 77–80%, and concentration of  $\text{NH}_4^+\text{-N}$  in effluent was increased from 1.7–2.6 mgN/L to 2.8–3.4 mgN/L. These results indicate that nitrification was also controlled by  $\text{O}_2$  pressure. However, removal efficiency of COD was maintained at  $73 \pm 3\%$ , and concentration of COD in effluent was maintained at  $7.8 \pm 1.1$  mg/L regardless of HRT and  $\text{O}_2$  pressure. From these results, operating condition of set II was determined to be 3 HRT and 13.7 kPa. As shown in Fig. 2(c), nitrification efficiency of  $\text{NH}_4^+\text{-N}$  was stably maintained above 93%, and concentration of  $\text{NH}_4^+\text{-N}$  in effluent was maintained below 1.5 mgN/L. These results indicate that nitrification was not affected by sulfamethazine and sulfathiazole.

As shown in Fig. 2(d), removal efficiency of COD was maintained at  $72 \pm 3\%$ , and concentration of COD in effluent was maintained at  $7.7 \pm 1.1$  mg/L. These results indicate that the removal of COD was not affected by sulfamethazine and sulfathiazole.

### 3.2. Decomposition of sulfamethazine and sulfathiazole

Fig. 3 shows the steady state results of sulfamethazine and sulfathiazole in influent and effluent from MBfR. Sulfamethazine and sulfathiazole were removed immediately, and concentrations of sulfamethazine and sulfathiazole in effluent were  $9 \pm 0.5$   $\mu\text{g/L}$  and  $10 \pm 0.5$   $\mu\text{g/L}$ , respectively. Removal efficiency of sulfamethazine was  $77 \pm 1\%$ , while the removal efficiency of sulfathiazole was  $87 \pm 1\%$ . The effluent pH was  $7.6 \pm 0.2$ , and was slightly higher than the influent pH (7.4). Intermediate and final products of sulfamethazine and sulfathiazole were not analyzed.

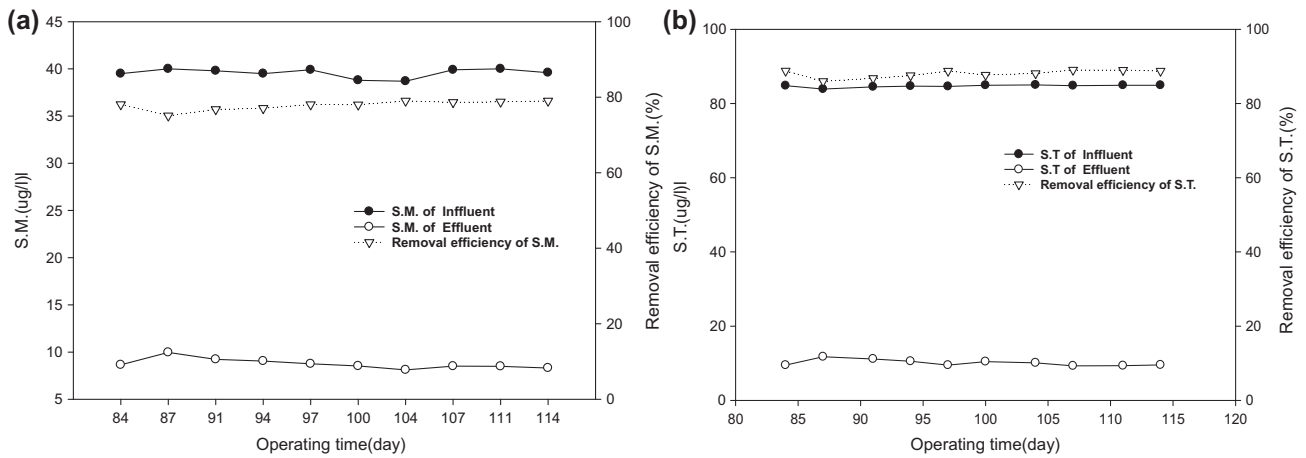


Fig. 3. Experimental results of sulfamethazine (S.M) and sulfathiazole (S.T). (a) Concentrations and removal efficiency of sulfamethazine in set II experiment and (b) Concentrations and removal efficiency of sulfathiazole in set II experiment.

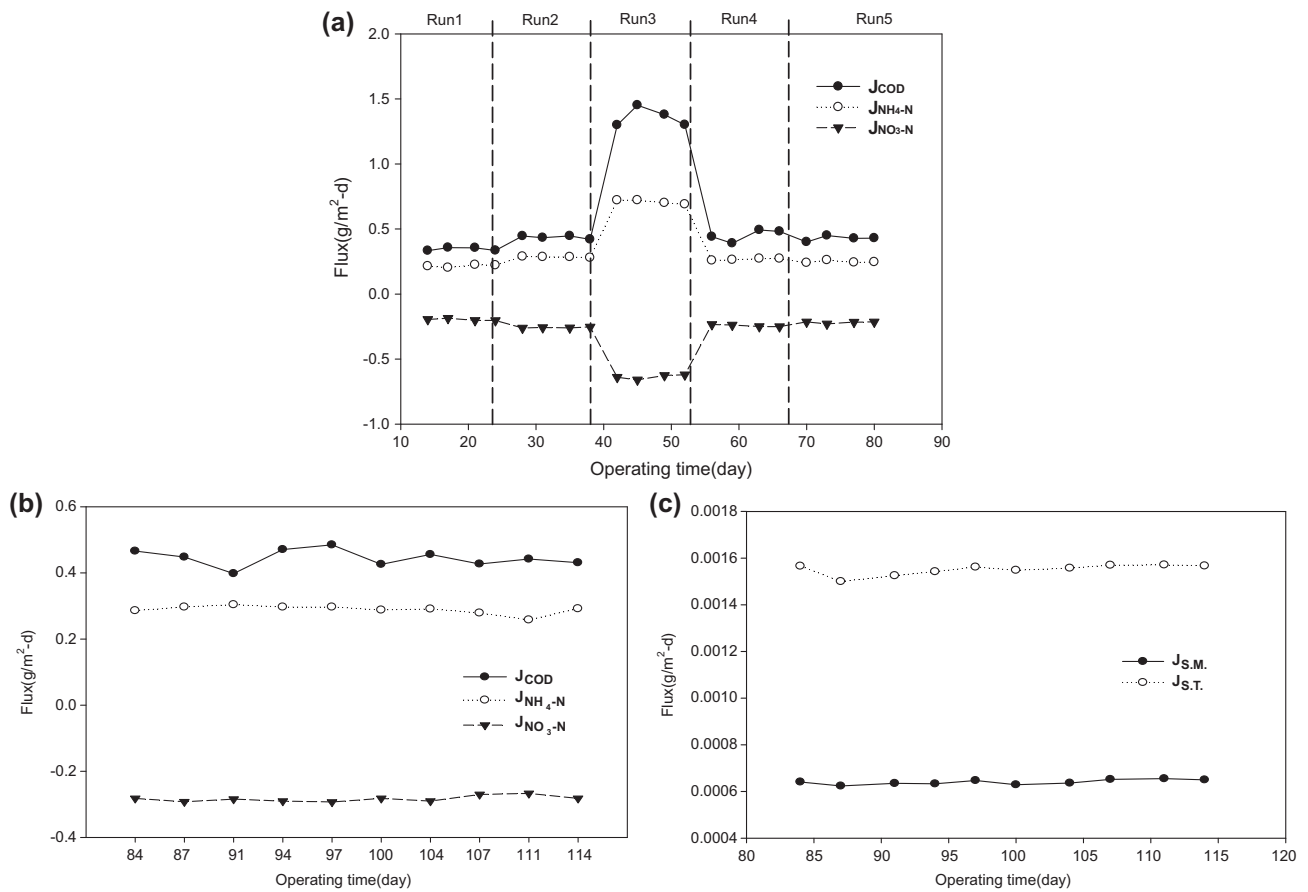


Fig. 4. Results of  $J_{\text{COD}}$ ,  $J_{\text{NH}_4^+-\text{N}}$ ,  $J_{\text{NO}_3^--\text{N}}$ ,  $J_{\text{S.M.}}$ , and  $J_{\text{S.T.}}$  according to experimental condition. (a)  $J_{\text{COD}}$ ,  $J_{\text{NH}_4^+-\text{N}}$ , and  $J_{\text{NO}_3^--\text{N}}$  without sulfamethazine and sulfathiazole, (b)  $J_{\text{COD}}$ ,  $J_{\text{NH}_4^+-\text{N}}$ , and  $J_{\text{NO}_3^--\text{N}}$  including sulfamethazine and sulfathiazole, and (c)  $J_{\text{S.M.}}$  and  $J_{\text{S.T.}}$ .

Table 3  
Surface loading and fluxes for NH<sub>4</sub><sup>+</sup>-N, sulfamethazine, and sulfathiazole

Operating time (day)	Flux (eq m <sup>-2</sup> d <sup>-1</sup> )			Surface loading(eq m <sup>-2</sup> d <sup>-1</sup> )		
	NH <sub>4</sub> <sup>+</sup> -N	S.M.	S.T.	NH <sub>4</sub> <sup>+</sup> -N	S.M.	S.T.
84	2.86 × 10 <sup>-1</sup>	6.41 × 10 <sup>-4</sup>	15.66 × 10 <sup>-4</sup>	3.05 × 10 <sup>-1</sup>	8.21 × 10 <sup>-4</sup>	17.63 × 10 <sup>-4</sup>
87	2.97 × 10 <sup>-1</sup>	6.24 × 10 <sup>-4</sup>	15.00 × 10 <sup>-4</sup>	3.09 × 10 <sup>-1</sup>	8.32 × 10 <sup>-4</sup>	17.45 × 10 <sup>-4</sup>
91	3.04 × 10 <sup>-1</sup>	6.35 × 10 <sup>-4</sup>	15.25 × 10 <sup>-4</sup>	3.14 × 10 <sup>-1</sup>	8.27 × 10 <sup>-4</sup>	17.57 × 10 <sup>-4</sup>
94	2.97 × 10 <sup>-1</sup>	6.33 × 10 <sup>-4</sup>	15.42 × 10 <sup>-4</sup>	3.09 × 10 <sup>-1</sup>	8.21 × 10 <sup>-4</sup>	17.61 × 10 <sup>-4</sup>
97	2.97 × 10 <sup>-1</sup>	6.47 × 10 <sup>-4</sup>	15.62 × 10 <sup>-4</sup>	3.05 × 10 <sup>-1</sup>	8.29 × 10 <sup>-4</sup>	17.59 × 10 <sup>-4</sup>
100	2.88 × 10 <sup>-1</sup>	6.29 × 10 <sup>-4</sup>	15.48 × 10 <sup>-4</sup>	3.09 × 10 <sup>-1</sup>	8.07 × 10 <sup>-4</sup>	17.65 × 10 <sup>-4</sup>
104	2.91 × 10 <sup>-1</sup>	6.36 × 10 <sup>-4</sup>	15.57 × 10 <sup>-4</sup>	3.12 × 10 <sup>-1</sup>	8.04 × 10 <sup>-4</sup>	17.68 × 10 <sup>-4</sup>
107	2.79 × 10 <sup>-1</sup>	6.52 × 10 <sup>-4</sup>	15.70 × 10 <sup>-4</sup>	3.09 × 10 <sup>-1</sup>	8.29 × 10 <sup>-4</sup>	17.63 × 10 <sup>-4</sup>
111	2.58 × 10 <sup>-1</sup>	6.55 × 10 <sup>-4</sup>	15.71 × 10 <sup>-4</sup>	3.07 × 10 <sup>-1</sup>	8.32 × 10 <sup>-4</sup>	17.65 × 10 <sup>-4</sup>
114	2.91 × 10 <sup>-1</sup>	6.50 × 10 <sup>-4</sup>	15.67 × 10 <sup>-4</sup>	3.05 × 10 <sup>-1</sup>	8.23 × 10 <sup>-4</sup>	17.65 × 10 <sup>-4</sup>

3.3. Flux analysis

3.3.1. Fluxes for COD, NH<sub>4</sub><sup>+</sup>-N, NH<sub>3</sub><sup>-</sup>-N, sulfamethazine, and sulfathiazole

Fig. 4 shows the results of J<sub>COD</sub>, J<sub>NH<sub>4</sub><sup>+</sup>-N</sub>, J<sub>NO<sub>3</sub><sup>-</sup>-N</sub>, J<sub>S.M.</sub>, and J<sub>S.T.</sub> according to experimental condition. In Run 1, Run 2, Run 4, and Run 5, J<sub>COD</sub> was 0.45 ± 0.05 g/m<sup>2</sup>d and J<sub>NH<sub>4</sub><sup>+</sup>-N</sub> was 0.25 ± 0.02 g/m<sup>2</sup>d. However, in the Run 3, J<sub>COD</sub> was 1.30–1.45 g/m<sup>2</sup>d and J<sub>NH<sub>4</sub><sup>+</sup>-N</sub> was 0.69 ± 0.72 g/m<sup>2</sup>d. These results indicate that J<sub>COD</sub> and J<sub>NH<sub>4</sub><sup>+</sup>-N</sub> were affected by HRT, regardless

of O<sub>2</sub> pressure. Fig. 4(b) shows that J<sub>COD</sub> and J<sub>NH<sub>4</sub><sup>+</sup>-N</sub> were not affected by sulfamethazine and sulfathiazole. This means that nitrification and the removal of COD using MBfR can be performed regardless of the presence of sulfamethazine and sulfathiazole.

3.3.2. Surface loading for NH<sub>4</sub><sup>+</sup>-N, sulfamethazine, and sulfathiazole

The surface loading(SL) for each target parameter was computed from Eq. 3. The surface load equals the

Table 4  
Electron-equivalent fluxes for NH<sub>4</sub><sup>+</sup>-N, sulfamethazine, and sulfathiazole

Operating time (day)	Electron-equivalent flux (eq m <sup>-2</sup> d <sup>-1</sup> )			Sum up the fluxes in electron equivalents (eq m <sup>-2</sup> d <sup>-1</sup> )	Distribution of fluxes (%)		
	NH <sub>4</sub> <sup>+</sup> -N <sup>a</sup>	S.M <sup>b</sup>	S.T <sup>c</sup>		NH <sub>4</sub> <sup>+</sup> -N	S.M	S.T
84	0.163	8.97 × 10 <sup>-6</sup>	23.4 × 10 <sup>-6</sup>	0.16303237	99.98	0.05 × 10 <sup>-1</sup>	0.14 × 10 <sup>-1</sup>
87	0.169	8.73 × 10 <sup>-6</sup>	22.5 × 10 <sup>-6</sup>	0.16903123	99.98	0.05 × 10 <sup>-1</sup>	0.13 × 10 <sup>-1</sup>
91	0.173	8.86 × 10 <sup>-6</sup>	22.8 × 10 <sup>-6</sup>	0.17303166	99.98	0.05 × 10 <sup>-1</sup>	0.13 × 10 <sup>-1</sup>
94	0.169	8.86 × 10 <sup>-6</sup>	23.1 × 10 <sup>-6</sup>	0.16903196	99.98	0.05 × 10 <sup>-1</sup>	0.13 × 10 <sup>-1</sup>
97	0.169	9.05 × 10 <sup>-6</sup>	23.4 × 10 <sup>-6</sup>	0.16903245	99.98	0.05 × 10 <sup>-1</sup>	0.13 × 10 <sup>-1</sup>
100	0.164	0.88 × 10 <sup>-6</sup>	23.2 × 10 <sup>-6</sup>	0.16402408	99.98	0.05 × 10 <sup>-1</sup>	0.13 × 10 <sup>-1</sup>
104	0.166	0.89 × 10 <sup>-6</sup>	23.3 × 10 <sup>-6</sup>	0.16602419	99.98	0.05 × 10 <sup>-1</sup>	0.14 × 10 <sup>-1</sup>
107	0.159	9.12 × 10 <sup>-6</sup>	23.5 × 10 <sup>-6</sup>	0.15903262	99.97	0.05 × 10 <sup>-1</sup>	0.14 × 10 <sup>-1</sup>
111	0.147	9.17 × 10 <sup>-6</sup>	23.5 × 10 <sup>-6</sup>	0.14703267	99.97	0.06 × 10 <sup>-1</sup>	0.15 × 10 <sup>-1</sup>
114	0.166	9.17 × 10 <sup>-6</sup>	23.5 × 10 <sup>-6</sup>	0.14703267	99.97	0.06 × 10 <sup>-1</sup>	0.15 × 10 <sup>-1</sup>

<sup>a</sup>Calculated by = J<sub>e</sub> =  $\frac{Q \Delta S}{a V E W}$ , where Q is in m<sup>3</sup>/d, ΔS is in g- NH<sub>4</sub><sup>+</sup>-N/m<sup>3</sup>, aV is in m<sup>2</sup>, EW is 14 in g-NH<sub>4</sub><sup>+</sup>-N/8 e<sup>-</sup> equivalent for oxidation of NH<sub>4</sub><sup>+</sup>-N to NH<sub>3</sub><sup>-</sup>-N, and J is in g-NH<sub>4</sub><sup>+</sup>-N/m<sup>2</sup>d. It was assumed that there were eight electrons per mole for NH<sub>4</sub><sup>+</sup>-N oxidation to NH<sub>3</sub><sup>-</sup>-N.

<sup>b</sup>Calculated by = J<sub>e</sub> =  $\frac{Q \Delta S}{a V E W}$ , where Q is in m<sup>3</sup>/d, ΔS is in g-sulfamethazine/m<sup>3</sup>, aV is in m<sup>2</sup>, EW is 278 in g-sulfamethazine/4 e<sup>-</sup> equivalent for oxidation, and J is in g-sulfamethazine/m<sup>2</sup>d. It was assumed that there were four electrons per mole for sulfamethazine oxidation.

<sup>c</sup>Calculated by = J<sub>e</sub> =  $\frac{Q \Delta S}{a V E W}$ , where Q is in m<sup>3</sup>/d, ΔS is in g-sulfathiazole/m<sup>3</sup>, aV is in m<sup>2</sup>, EW is 255 in g-sulfathiazole/4 e<sup>-</sup> equivalent for oxidation, and J is in g-sulfathiazole/m<sup>2</sup>d. It was assumed that there were four electrons per mole for sulfathiazole oxidation.

flux when  $S=0$ , corresponding to full removal or maximum efficiency (100%). Thus, system performance is easily determined by comparing the values of flux and surface loading. Table 3 shows surface loading and flux of  $\text{NH}_4^+-\text{N}$ , sulfamethazine, and sulfathiazole.

### 3.3.3. Electron-equivalent fluxes for $\text{NH}_4^+-\text{N}$ , sulfamethazine, and sulfathiazole

Table 4 shows the electron-equivalent fluxes of electron donors,  $\text{NH}_4^+-\text{N}$ , sulfamethazine, and sulfathiazole, along with the sum. In all cases, nitrification was the largest provider of electrons, together accounted for at least 99.98% of the total electron flux. These results presented here demonstrate that sulfamethazine and sulfathiazole were bio-oxidized to a major extent in an  $\text{O}_2$ -based MBfR in which the electron-equivalent fluxes from  $\text{O}_2$  reduction were dominated by nitrification (>99.98%).

## 4. Conclusions

Pharmaceutical compounds are developed and manufactured for specific biological effects, and have been administered for human and animal health care, and livestock farming. Because of their physicochemical and biological properties, when released into the environment, it may be possible for them to exert serious impacts on non-target species, for example, aquatic and terrestrial organisms. Therefore, there are growing concerns about ecological risks of the pharmaceutical residues on ecosystem. Reduced pharmaceutical compounds can be a significant challenge to water utilities; as such, compounds frequently are not removed by conventional wastewater treatment and advanced wastewater treatment processes are expensive. Sulfamethazine and sulfathiazole were bio-oxidized by up to 78% and 88%, respectively, in the  $\text{O}_2$ -based MBfR, and the rate of oxidation responded in the normal manner to  $\text{O}_2$  pressure and competing electron donors. Although this study was not able to identify the final oxidation product(s), it clearly

documented that sulfamethazine and sulfathiazole are susceptible to bio-oxidation when  $\text{O}_2$  is available as the electron acceptor. Also, the  $\text{O}_2$ -based MBfR can be used a versatile platform for oxidizing reduced contaminants in many water-treatment settings: drinking water, ground water, wastewater, and agricultural drainage.

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