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Decompostion of pharmaceuticals (sulfamethazine and sulfathiazole) using oxygen-based membrane biofilm reactor☆

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ABSTRACT

The subject of this research was the decomposition of pharmaceuticals (sulfamethazine and sulfathiazole) using an oxygen-based membrane biofilm reactor. The influent concentrations in pharmaceuticals feed-medium were (in ppb): sulfamethazine (40) and sulfathiazole (85). The oxygen-based membrane biofilm reactor 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_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 kPa. (1 kPa = 0.0099 atm = 0.145 psi). HRT was 3 h. The decomposition ratio of pharmaceuticals (sulfamethazine and sulfathiazole) using oxygen-based membrane biofilm reactor was (%): sulfamethazine (77 ± 2), and sulfathiazole (87 ± 2).

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 ng to low μg/L, 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 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 (MABRs) [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].

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In this study, the bio-oxidation of sulfamethazine and sulfathiazole in an O_2-based MBfR was 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 set-up

A schematic 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 completely mixed conditions. 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 kPa, 20.6 kPa, and 27.5 kPa. (1 kPa = 0.0099 atm = 0.145 psi). Retention times were 1 h, 3 h, 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 glass bottle and the prepared 10-L influent was sterilized in the autoclave.

Table 1
Physical characteristics of the main module of the MBfR.

	Value	Units
Fiber surface area	72	cm^2
Fiber outside diameter	280	μm
Tube length	27	cm
Tube inside diameter	0.6	cm
Volume	23.9	ml

Table 2
Experimental conditions.

Exp. setting	Set I (Without sulfamethazine and sulfathiazole)					Set II (Including sulfamethazine and sulfathiazole)
Variable	Run 1	Run 2	Run 3	Run 4	Run 5	Run
Term (days)	0–24	25–38	39–52	53–66	67–80	81–113
HRT (hours)	4	3	1	3	3	3
O_2 gas (kPa)	13.7	13.7	13.7	20.6	27.5	13.7

2.3. Operating condition

The experiment was performed with two settings as showed in Table 2. The inoculums came from oxic unit in wastewater treatment at Uiwang-si, Kyungki-do. Start-up began when O_2 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_2 gas, the performance of the reactor was estimated. Based on the results of set I, the operating conditions of set II were decided.

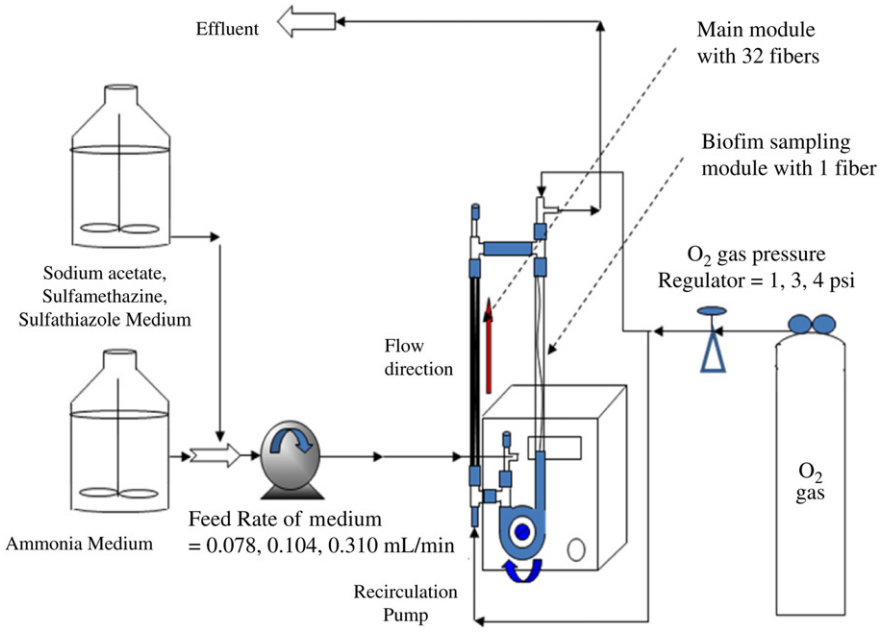

Fig. 1. Schematic of the bench-scale MBfR used to investigate the oxidation of sulfamethazine and sulfathiazole.

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_4^+-N, NO_3^--N, sulfamethazine, and sulfathiazole.

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

J_s	flux target parameter (g/m^2 d)
Q	influent flow rate (m^3/d)
S_0	influent concentration of target parameter (g/m^3)
S	effluent concentration of target parameter (g/m^3)
A	membrane surface area (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-μm membrane filter (Whatman Corp.). pH was determined using a glass electrode pH meter (Orion, Model 525A). Soluble COD was determined using the HACH digestion vials (HACH, DR/2012). NO_3^- was determined using ion chromatography (DX-120, Dionex Inc.) and NH_4^+ was determined using ion chromatography (DX-500, Dionex Inc.).

The concentration of sulfamethazine and sulfathiazole was 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 for cartridge of SPE and vacuum manifold (Supelco, Bellefonte, PA, USA) was used. Sulfamethazine and sulfathiazole of Sigma-Aldrich (St Louis, MO, USA) were used. Sulfamethazine-6-^{13}C (Cambridge Isotope Laboratories Co., Andover, MA, USA) was used for surrogate and terbutylazine (Fluka Co., Seelze, Germany) as internal standard was used.

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. 0.1 ug/mL Na_2-EDTA 0.5 mL and 10 ug/mL sulfamethazine-6-^{13}C was pipetted into 500 mL of sample and pH was fixed at 3 using 3.5 M H_2SO_4. After Oasis HLB (200 mg, 6 cc) and Oasis MCX (150 mg, 6 cc) cartridge was installed at vacuum manifold, 2 mL of distilled water and 2 mL of methanol was flowed. 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 cartidge was eluted using 4 mL of 5% ammonia–methanol solution. 25 uL of internal standard (10 ug/mL terbutylazine) was pipetted into this eluted solution. After evaporating using a nitrogen-evaporator, 500 uL of ammonium acetate (20 mM) was used for dissolving. After filtrating using a 0.45 um 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), B: Acetonitrile), gradient (Time(min) 0 10 11 15 15.1 17, Solvent B(%) 30 65 100 100 30 30), column flow rate (300 uL/min), Injection volume (10 uL), 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/h), and desolvation gas flow (550 L/h).

3. Results and discussion

3.1. Nitrification and removal of COD

Fig. 2 shows the steady-state results of soluble NH_4^+-N, NO_3^--N, and 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 NH_4^+-N was stably maintained above 93%, and concentration of NH_4^+-N in effluent was maintained below 1.5 mgN/L. In Run 3 (1 HRT, 13.7 kPa), nitrification efficiency of NH_4^+-N was decreased from 90% to 75%–79%, and concentration of NH_4^+-N in effluent was increased from 1.2 ± 0.2 mgN/L to 3.0–3.7 mgN/L. These results indicate that nitrification was controlled by HRT. In Run 4 (3 HRT, 20.6 kPa), nitrification efficiency of NH_4^+-N was increased from 75%–79% to 82%–88%, and concentration of NH_4^+-N in effluent was decreased from 3.0–3.7 mgN/L to 1.7–2.6 mgN/L. In Run 5 (3 HRT, 27.5 kPa), nitrification efficiency of NH_4^+-N was decreased from 82%–88% to 77%–80%, and concentration of NH_4^+-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 controlled also by 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 ± 1.1 mg/L regardless of HRT and 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 NH_4^+-N was stably maintained above 93%, and concentration of NH_4^+-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 ± 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 ± 0.5 μg/L and 10 ± 0.5 μg/L, respectively. Removal efficiency of sulfamethazine was 77 ± 1 %, while the removal efficiency of sulfathiazole was 87 ± 1 %. The effluent pH was 7.6 ± 0.2, and was slightly higher than the influent pH (7.4). Intermediate and final products of sulfamethazine and sulfathiazole were not analyzed. Fig. 4 shows the expected decomposition pathway of sulfamethazine and sulfathiazole. O_2 as the electron acceptor received the electron of N, and sulfamethazine and sulfathiazole were decomposed as a hetero compound and sulfide compound.

3.3. Flux anaylsis

Fig. 5 shows the results of J_{COD}, JNH_4^+-N, JNO_3^--N, $J_{S.M.}$, and $J_{S.T.}$ according to experimental condition. In Run 1, Run 2, Run 4, and Run 5, J_{COD} was 0.45 ± 0.05 g/m^2 d and JNH_4^+-N was 0.25 ± 0.02 g/m^2 d. However, in the Run 3, J_{COD} was 1.30–1.45 g/m^2 d and JNH_4^+-N was 0.69 ± 0.72 g/m^2 d. These results indicates that J_{COD} and JNH_4^+-N were affected by HRT, regardless of O_2 pressure. At Fig. 5 (b), J_{COD} and JNH_4^+-N 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.

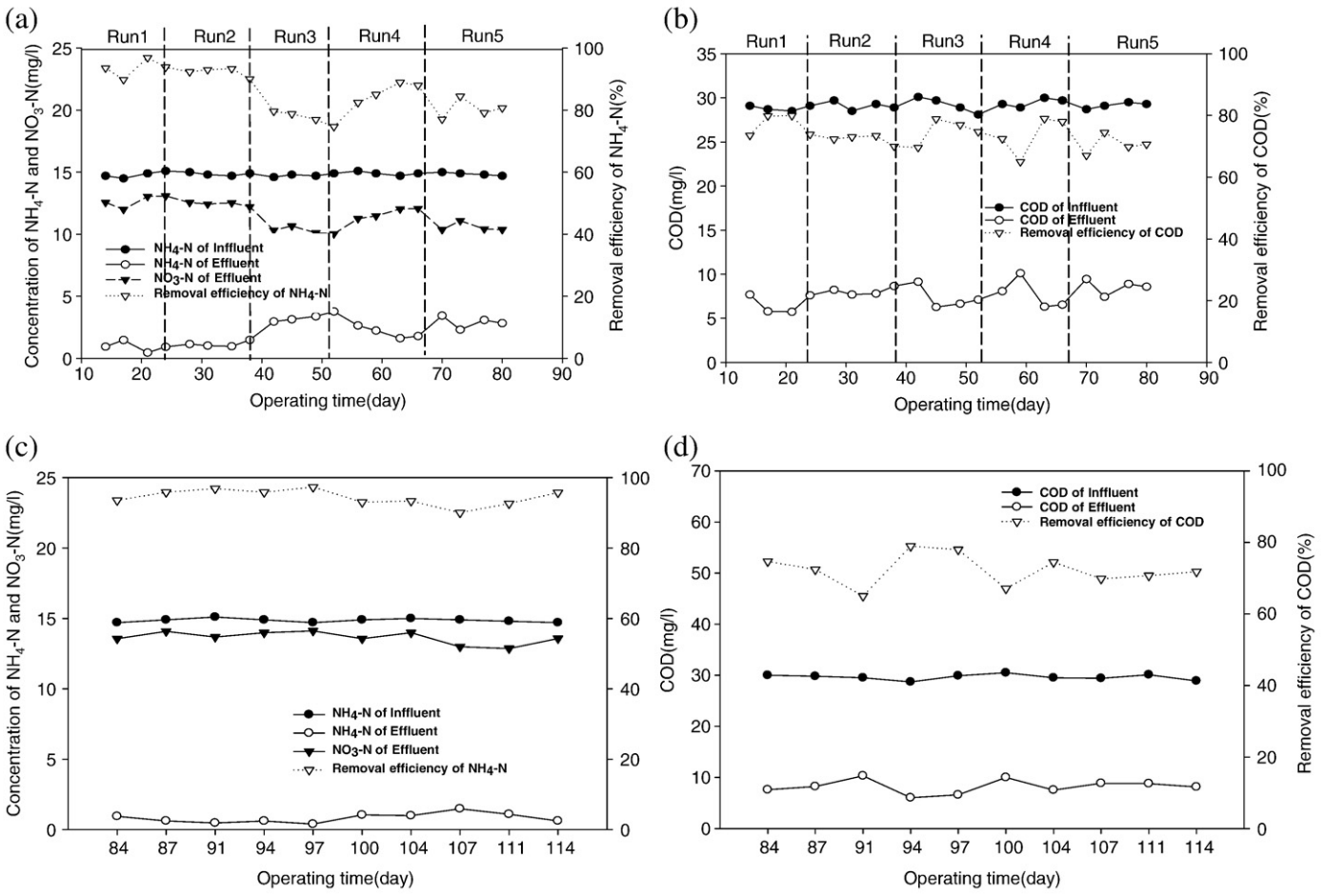

Fig. 2. Results of NH_4^+-N, NO_3^--N, and COD according to experimental conditions. (a) Concentrations and removal efficiency of NH_4^+-N and NO_3^--N without sulfamethazine and sulfathiazole. (b) Concentrations and removal efficiency of COD without sulfamethazine and sulfathiazole. (c) Concentrations and removal efficiency of NH_4^+-N and NO_3^--N including sulfamethazine and sulfathiazole. (d) Concentrations and removal efficiency of COD including sulfamethazine and sulfathiazole.

4. Conclusions

Frequently, trace compounds such as pharmaceuticals appear in the effluent of wastewater treatment plants. In addition, while some WWTPs are able to remove these compounds, others are not. In this study, the decomposition of sulfamethazine and sulfathiazole in synthetic wastewater was investigated using oxygen-based MBfR. The oxidation of sulfamethazine and sulfathiazole occurred rapidly under

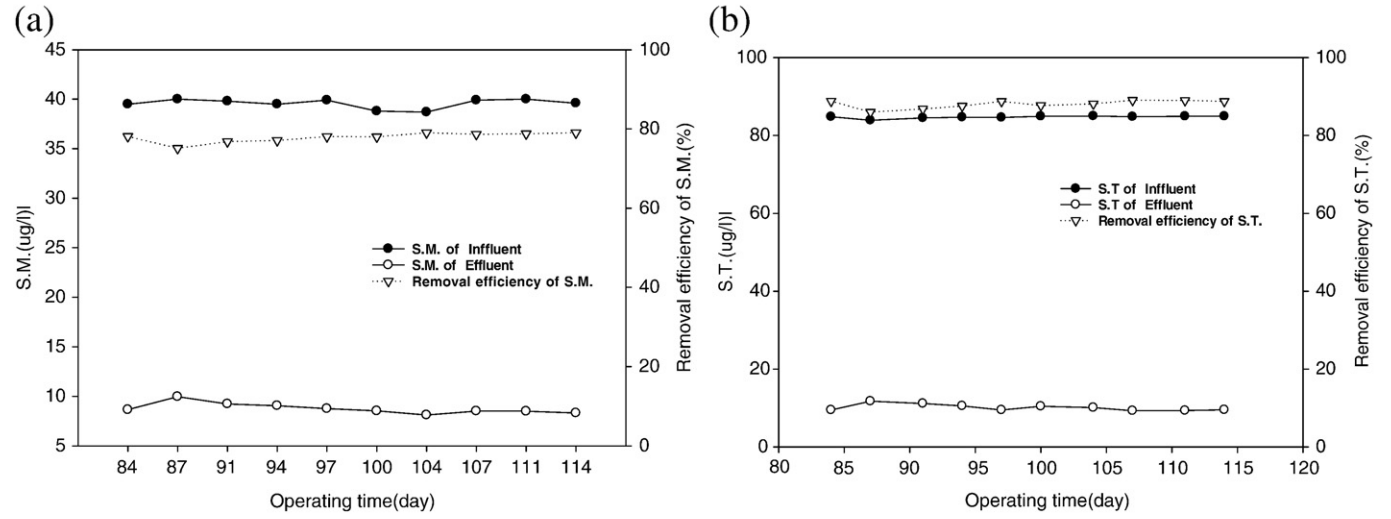

Fig. 3. Experimental results of sulfamethazine (S.M.) and sulfathiazole (S.T.). (a) Concentrations and removal efficiency of sulfamethazine in set II experiment. (b) Concentrations and removal efficiency of sulfathiazole in set II experiment.

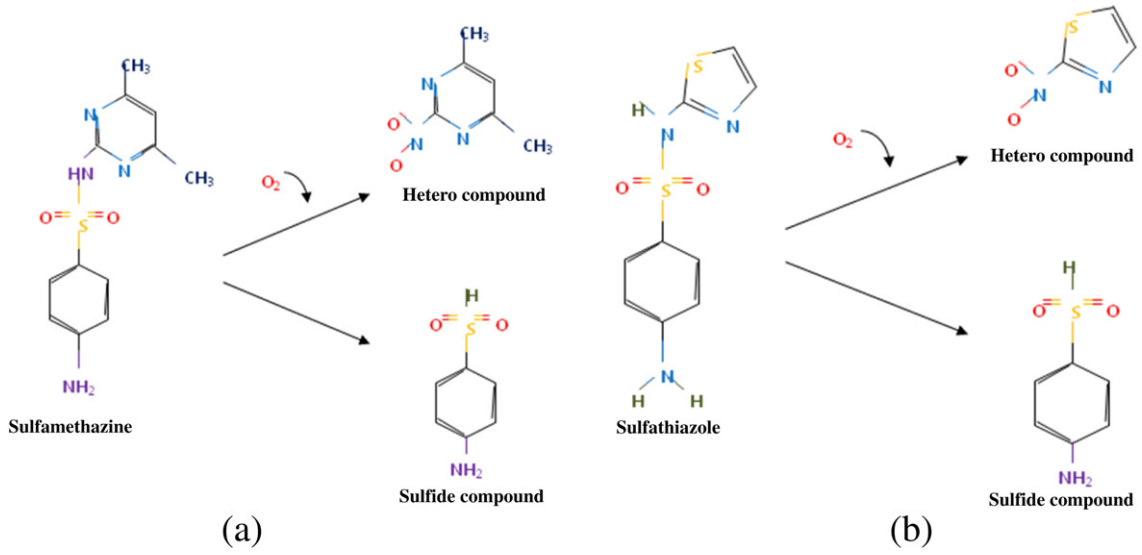

Fig. 4. Expected decomposition pathway of sulfamethazine and sulfathiazole. (a) Pathway of sulfamethazine. (b) Pathway of sulfathiazole.

normal oxygen-based MBfR nitrifying conditions, without a special inoculum. These results show that the oxygen-based MBfR can be performed for the treatment of sulfamethazine and sulfathiazole in drinking water and wastewater. Additional studies are required to examine the influence of HRT, O_2 pressure, the variation of sulfamethazine and sulfathiazole, and pH.

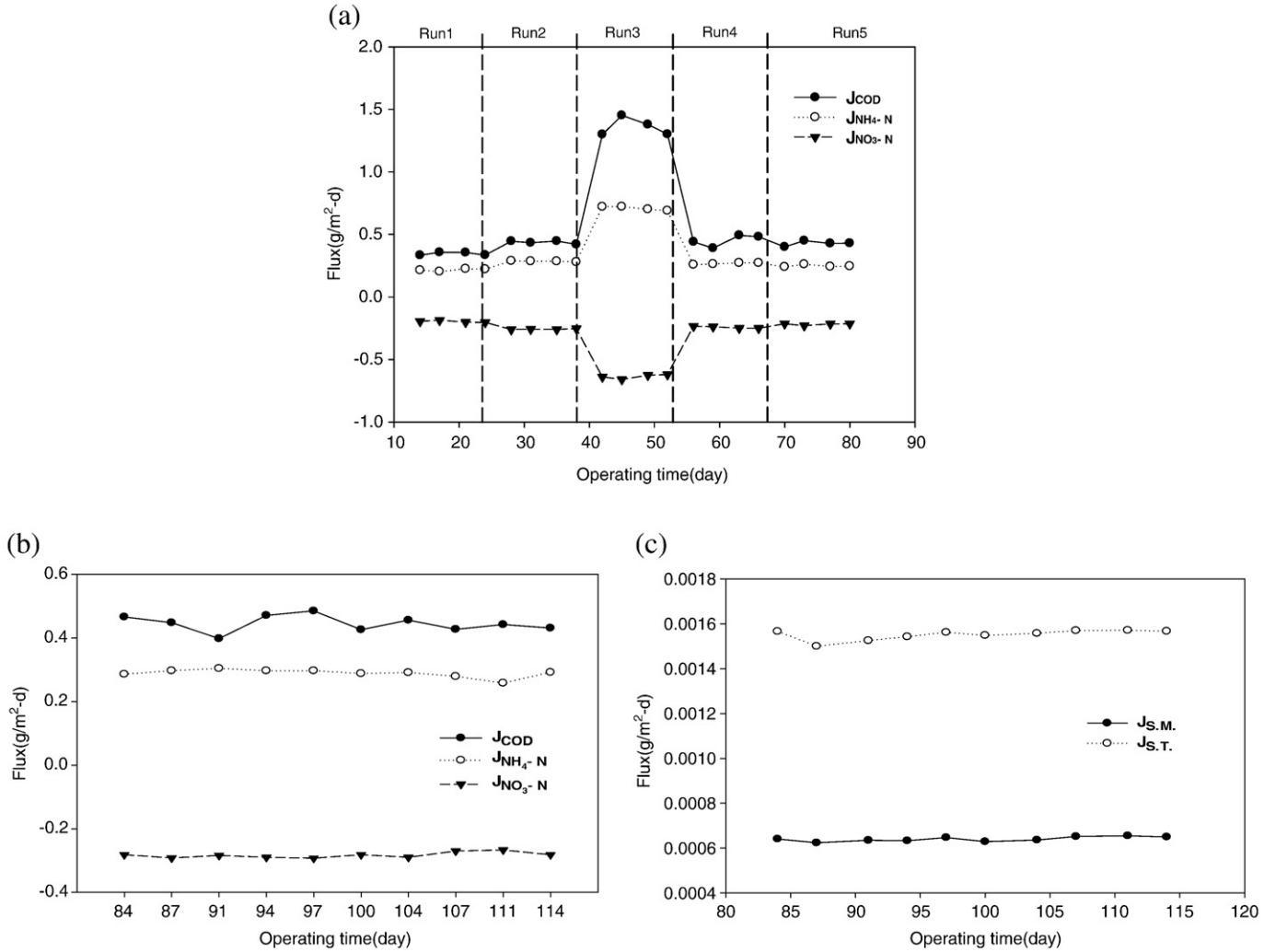

Fig. 5. Results of J_{COD}, JNH_4^+-N, JNO_3^--N, $J_{S.M.}$, and $J_{S.T.}$ according to experimental conditions. (a) J_{COD}, JNH_4^+-N, and JNO_3^--N without sulfamethazine and sulfathiazole. (b) J_{COD}, JNH_4^+-N, and JNO_3^--N including sulfamethazine and sulfathiazole. (c) $J_{S.M.}$ and $J_{S.T.}$

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