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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.

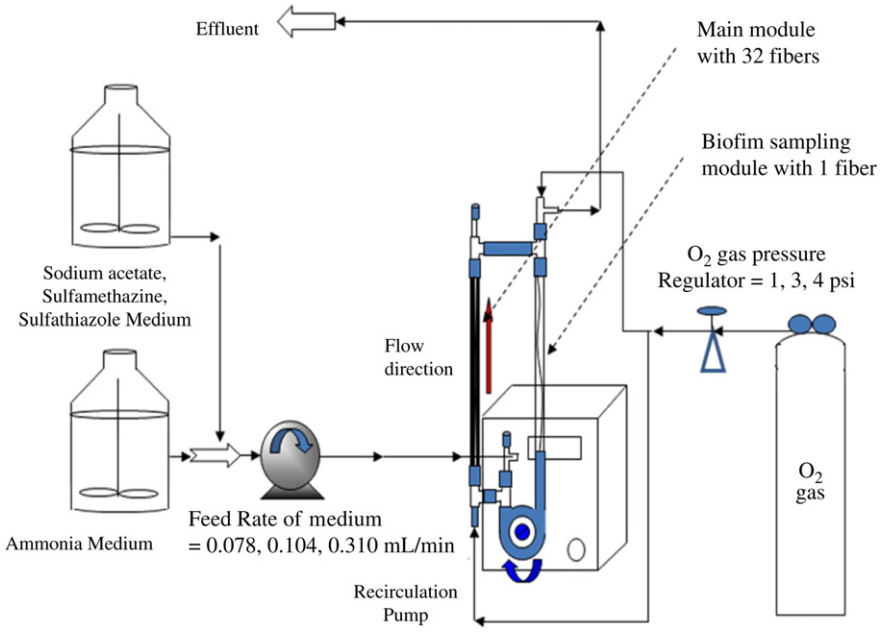

Fig. 1. Schematic of the bench-scale MBfR used to investigate the oxidation of sulfamethazine and sulfathiazole.