PERFORMANCE OF OZONATION PROCESS AS ADVANCED TREATMENT FOR ANTIBIOTICS REMOVAL IN MEMBRANE PERMEATE

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Abstract

There was an investigation into the removal of 6 types of antibiotics from hospital wastewater through membrane bioreactor (MBR) treatment and ozonation processes. Six types of antibiotics, namely, Sulfamethoxazole (SMZ), Norfloxacin (NOR), Ciprofloxacin (CIP), Ofloxacin (OFL), Erythromycin (ERY), and Vancomycin (VAN) which had high detection frequencies in collected samples from hospital wastewater treatment plant (HWTPs). After MBR treatment, the removal efficiencies of SMZ, NOR, OFL, and ERY were 45%, 25%, 30%, and 16%, respectively. Among of them, almost no elimination was observed for CIP and VAN since their concentrations increased by 0.24 ± 0.18 ($\mu g \cdot l^{-1}$) and 0.83 ± 0.20 ($\mu g \cdot l^{-1}$), respectively. Then, residues of the antibiotics were removed from the MBR effluent by the ozonation process. The overall removal efficiencies of SMZ, NOR, CIP, OFL, ERY, and VAN were approximately 66 %, 88 %, 83 %, 80 %, 93 %, and 92 %, respectively. The reason might be depended on different ozone consumption of those antibiotics (ABS) in a range of 313 to 1681 μg $ABS \cdot gO_3^{-1}$. Consequently, the ozonation process performed better in the antibiotics removal (e.g. CIP and VAN) so ozonation could be considered as important support for the MBR treatment to reduce the risk of antibiotic residues.

Keywords: antibiotics; membrane bioreactor; ozonation; hospital wastewater

1 INTRODUCTION

Antibiotics (ABS) have been applied for some decades. However, a number of pharmaceuticals have been detected in surface water, which indicates their ineffective removal from wastewater treated by traditional treatment technologies. Public concerns have been raised over the potential adverse effects of discharged antibiotics on public health and aquatic environment. The term “antibiotics” is used to refer to any agent with biological activity against living organisms or substrates with antibacterial activity. In Germany, there are currently about 250 different chemicals registered for use in medicine [1], but only a small proportion (less than 60 types) has been detected in wastewater and sludge. After use, antibiotics are excreted into effluent and reach a sewage treatment plant (STP). In sewage treatment plants, they are eliminated partially only. They pass through a sewage system and may end up in the environment, mainly in a major water resource. As known, antibiotic residues can reach surface water, ground water, sediments, etc. which can affect aquatic life and increase the risk to human health. For instance, ERY was determined in the STP and surface water with a dosage of 6000 and 17000 $ng \cdot l^{-1}$, respectively [2]. ERY belongs to macrolides, a subgroup of antibiotics, is highly unstable under strong acidic conditions, and so it was assessed as the main target of most of studies. In the same study, SMZ dosages of 2000, 480, and 470 $ng \cdot l^{-1}$ were also detected in effluent of the STP, surface water and ground water, respectively. SMZ was the most frequently detected in the environment, and the highest concentrations of SMZ were 5597 $ng \cdot l^{-1}$ [3] and 6000 $ng \cdot l^{-1}$ [4]. As reported by Kolpin, the CIP and NOR concentrations observed in surface water were 30 and 120 $ng \cdot l^{-1}$, respectively [5]. In some other studies, among quinolones, CIP and OFL were dominant ones with the highest detection frequencies of 4600 $ng \cdot l^{-1}$ [6] and 7870 $ng \cdot l^{-1}$ [7], respectively. VAN was recorded as “no presence observed” in municipal wastewater due to its low usage and lack of mature detection for glycopeptide subgroup.

Treatment methods are also different depending on the class structure of those antibiotics. For example, the group of macrolides (ERY) has a lactone ring that is substituted with hydroxyl (or neutral or amino sugar), alkyl, or ketone groups. Fluoroquinolones are a subgroup of quinolones with a fluorine-substitute central ring. The elimination of antibiotics can be a result of different processes such as sorption, photolysis (e.g. quinolones is a light sensitive antibiotic so they can be treated well by UV application), hydrolysis, oxidation, and biodegradation. However, antibiotics are well-known for being difficult to reduce by conventional biological treatment methods. The removal efficiencies and biodegradation rates reported for some antibiotics vary greatly among different studies. For advanced treatment, oxidation processes are usually applied such as the ozonation process. The removal of most antibiotics in the ozonation process depends significantly on the pH solution of 5.5 – 8.5 [8]. Previous studies reported that ozonation and disinfection processes are the final barrier in an STP to result in significant losses of antibiotics [9] and remove multiple classes of antibiotics in secondary effluent effectively.

In Vietnam, there was only one study carried out about antibiotic residues discharged from different sources, including the production and manufacturing of pharmaceuticals (PCs), therapeutical use of PCs for human and animals, aquaculture and plant agriculture, etc. which investigated the hospital wastewater in Hanoi, Vietnam [10]. Five antibiotics were evaluated in this study such as CIP, NOR, Levofloxacin (LEV), OFL, and Lomefloxacin (LOME); the concentrations of CIP and NOR varied in ranges of 1.1 - 44 and 0.9 - 17 µg/L, respectively. Due to that reason, there is still lack of understanding of antibiotics behaviours discharged from hospitals in Vietnam, especially, in Ho Chi Minh City. This study aims to evaluate performances of the ozonation process for antibiotic removals in permeate of MBR. Six types of antibiotics were investigated in this study, including Sulfamethoxazole (SMZ), Norfloxacin (NOR), Ciprofloxacin (CIP), Ofloxacin (OFL), Erythromycin (ERY), and Vancomycin (VAN). The results would be used to conduct further studies in the field of antibiotic removals in Vietnam.

2 MATERIALS AND METHODS

2.1 Experimental setup

The membrane bioreactor (MBR) utilized in this study was a plexi-glass tank with a working volume of 8 litres, and its dimensions of length (L), width (W), and height (H) were 0.28 m, 0.08 m, and 0.6 m, respectively. There was a module of hollow fiber membrane (W x H = 200 mm x 310 mm) submerged inside the reactor. The membrane module was purchased from Mitsubishi, Japan, with a membrane area of 0.1 m^2 and pore size of 0.4 µm. In addition, cube sponges (1 cm x 1 cm x 1 cm) made from polyester urethane with a void volume of approximately 98% were added to the MBR. Those sponges were accounted for 20% serving as the reactor volume. In order to enhance the treatment, an ozonation system was installed after the MBR (Figure 1). Basically, the ozonation process occurred in the glass tank with a volume of 2 litres and the dimensions of diameter (D) and height (H) were 8 cm and 42 cm, respectively. The flow rate of 20 – 40 mgO_3/h was supplied by an FD-3000 II model ozone generator.

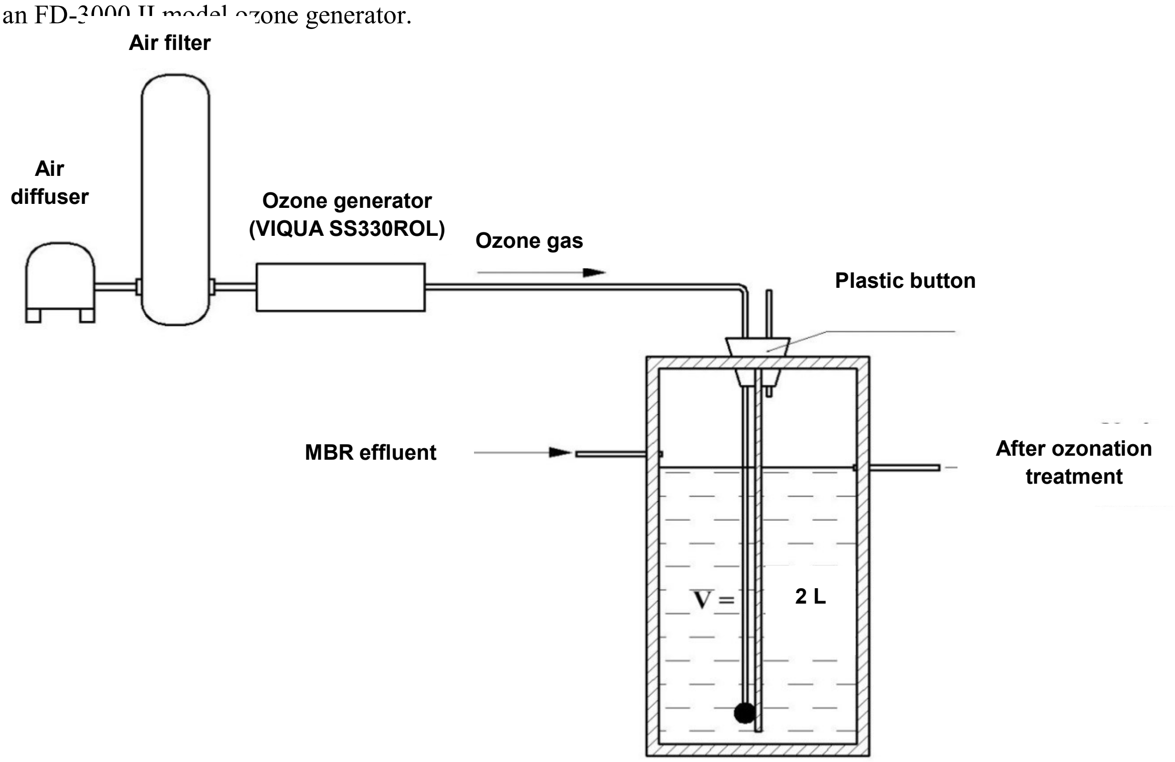

Figure 1: Schematic of ozonation process used to treat MBR effluent

2.2 Operating conditions

The inoculated sludge was collected from a full-scale MBR system. The mixed liquor suspended solid (MLSS) was approximately 5 000 $mg \cdot l^{-1}$. The MBR was operated at flux of 10 $l \cdot m^{-2} \cdot h^{-1}$ with an organic loading rate (OLR), hydraulic retention time (HRT), and sludge retention time (SRT) of 0.64 ± 0.16 kg $COD \cdot m^{-3} \cdot day^{-1}$, 10 h, and 20 days, respectively. The operating conditions of the sponge MBR were reported in a previous report [11].

Feeding substrate was collected from the equalization tank of a hospital wastewater treatment plant (HWTP). The hospital wastewater was fed directly to a lab-scale sponge MBR under the control of a feeding pump and water level sensor. There were air diffusers installed at the bottom of the MBR to maintain dissolved oxygen (DO) at a level of 4 $mg \cdot l^{-1}$ and reduce membrane fouling through air scouring. The ozonation process was conducted at pH of 8.5 and contact time of 10 minutes. The ozone dosage of 3 $mg \cdot l^{-1}$ was used as an optimal dosage for the antibiotics removal.

The target antibiotics detected in this study were: Sulfamethoxazole (SMZ), Norfloxacin (NOR), Ciprofloxacin (CIP), Ofloxacin (OFL), Erythromycin (ERY), and Vancomycin (VAN) which had concentrations of 3.37 ± 0.54 $\mu g \cdot l^{-1}$, 11.44 ± 1.39 $\mu g \cdot l^{-1}$, 12.22 ± 2.16 $\mu g \cdot l^{-1}$, 9.46 ± 1.04 $\mu g \cdot l^{-1}$, 2.94 ± 0.29 $\mu g \cdot l^{-1}$, and 2.01 ± 0.38 $\mu g \cdot l^{-1}$, respectively.

2.3 Analytical methods

In terms of antibiotics measurements, water samples were pre-treated and analysed in the laboratory of the Faculty of Environment and Natural Resources (Ho Chi Minh City, Vietnam). Firstly, the sample pH was adjusted at 6.5 to 7.5 prior to the filtration through a 0.45 µm glass fibre filter to remove suspended solids. Then, at the solid phase extraction-SPE stage, the C18 HD cartridges (HySphere, Spark Holland, 2mm×10mm) were conditioned with 3 mL of MeOH to activate the cartridges and 3 mL of distilled water to prevent the cartridges from drying, and then the samples were loaded onto the cartridges. In order to clean the cartridges after loading, 2 mL of a solvent mixture, including 5% of MeOH and 95% of distilled water, were loaded onto the cartridges for 5 minutes to wash, and after washing completion the cartridges were covered by biofilms. The samples were eluted with 5 mL of a solvent of MeOH (1L) + phormic acid (1 mL) to release the residues. Additionally, the samples were standardized by 1 mL of MeOH after being dried by the evaporation caused by nitrogen supply. At last, the final samples had to be stored at 4°C prior to be examined by HPLC-MS/MS [12-13].

3 RESULTS AND DISCUSSION

3.1 Removal of antibiotics by sponge membrane bioreactor

Theoretically, antibiotics compounds eliminated by the MBR could be result of different processes such as physical retention of sludge and antibiotics, biotransformation, air stripping, sorption, and photo-transformation [14-16]. This study applied a microfiltration membrane with the pore size of 0.4 µm which was considered to be in between of 100 and 1000 times bigger than the physical size of pharmaceutical compounds [17]. That is why no direct physical retention by the membrane bioreactor can be expected. Biodegradation and adsorption have been recently reported to be major removal routes for the antibiotic treatment in wastewater with an activated sludge process [18]. Since the sludge-water partition coefficient K_d of a compound is less than 500 L/kgSS, it indicates that it is not absorbed to activated sludge [19]. Moreover, the biotransformation of antibiotics in the MBR varies in a large range (from zero to complete) [20] and depends on the degradation constant K_{biol}. Antibiotics with K_{biol} < 0.1 L/(gSS.day) are not removed, with K_{biol} > 10 L/(gSS.day) are transformed from more than 90% and with K_{biol} in between, these are moderate removals [21]. There was almost no elimination observed in case of CIP and VAN due to low transformation rates of those antibiotics in the biological treatment (Table 1). Comparatively, the low removal efficiency of SMZ, NOR, and ERY was caused by low K_d values lower than 500 L/kgSS (260 L/kgSS) so their sorption in the MBR was not significant [22-23]. Generally, the conventional biological treatment process cannot reduce antibiotics completely [24].

Table 1: Antibiotics removal by membrane bioreactor and ozonation treatment

Antibiotics	Concentration at different points ($\mu g \cdot l^{-1}$)			Overall efficiency (%)
	Influent	MBR permeate	Ozonation effluent	
Sulfamethoxazole (SMZ)	3.37 ± 0.54	1.86 ± 0.43	1.14 ± 0.14	66.1 ± 2.3
Norfloxacine (NOR)	11.44 ± 1.39	9.16 ± 2.46	2.12 ± 0.31	87 ± 9.0
Ciprofloxacine (CIP)	12.22 ± 2. 16	12.46 ± 2.35	2.13 ± 0.29	83 ± 1.0
Ofloxacine (OFL)	9.46 ± 1.01	9.16 ± 2.463	1.83 ± 9.25	81 ± 2.3
Erythromycine (ERY)	2.94 ± 0.29	2.46 ± 0.09	0.21 ± 0.03	92.9 ± 0.4
Vancomycine (VAN)	2.01 ± 0.38	2.87 ± 0.18	0.16 ± 0.06	92.1 ± 3.0

3.2 Removal of antibiotics by ozonation

The overall removal efficiencies after ozonation are shown in Table 1. The antibiotics concentrations of SMZ, NOR, CIP, OFL, ERY, and VAN in the effluent were reduced to 1.14 ± 0.14 $\mu g \cdot l^{-1}$, 2.12 ± 0.31 $\mu g \cdot l^{-1}$, 2.13 ± 0.29 $\mu g \cdot l^{-1}$, 1.83 ± 0.25 $\mu g \cdot l^{-1}$, 0.21 ± 0.03 $\mu g \cdot l^{-1}$, and 0.16 ± 0.06 $\mu g \cdot l^{-1}$, respectively. The high removal efficiencies were for ERY and VAN, respectively, at pH of 8.5 within 10 minutes. VAN was not removed significantly by the MBR but reduced by ozonation. Perhaps, ozone attack is mainly directed towards the phenolic rings of VAN and CIP at pH of 8.5 leading to the formation of hydroxyderivative intermediates. However, SMZ was only treated from 66 ± 2.3% under the same conditions. The SMZ removal efficiency went against with Dantas et al. since they indicated that ozone had an ability to remove 95-99% of SMZ [25] while actually 66% only. These obtained results are not much different comparing to other researches. For instance, [26] reported that 99% of NOR and OFL were removed by coupling nanofiltration and ozonation. Similarly, according to [27], the efficiency of ozonation process for simultaneous degradation was shown to reduce the CIP concentration by 90%.

In terms of ozone consumption, ozone adsorption is shown in Figure 2. As can be seen from the figure, the highest consumption rate of 1681 $\mu gABS \cdot gO_3^{-1}$ was for CIP, corresponding with the increase of removal efficiency of 82.5 ± 1.06 % compared to the result of the MBR permeate. On contrary, although VAN also had a high removal efficiency of 92.1 ± 3 % after the ozonation process, the ozone consumption rate was only 313 $\mu gABS \cdot gO_3^{-1}$. It can be explained by that the occurrence of VAN in municipal wastewater was reported to be much lower than for others, mainly because of low usage in medical care [28].

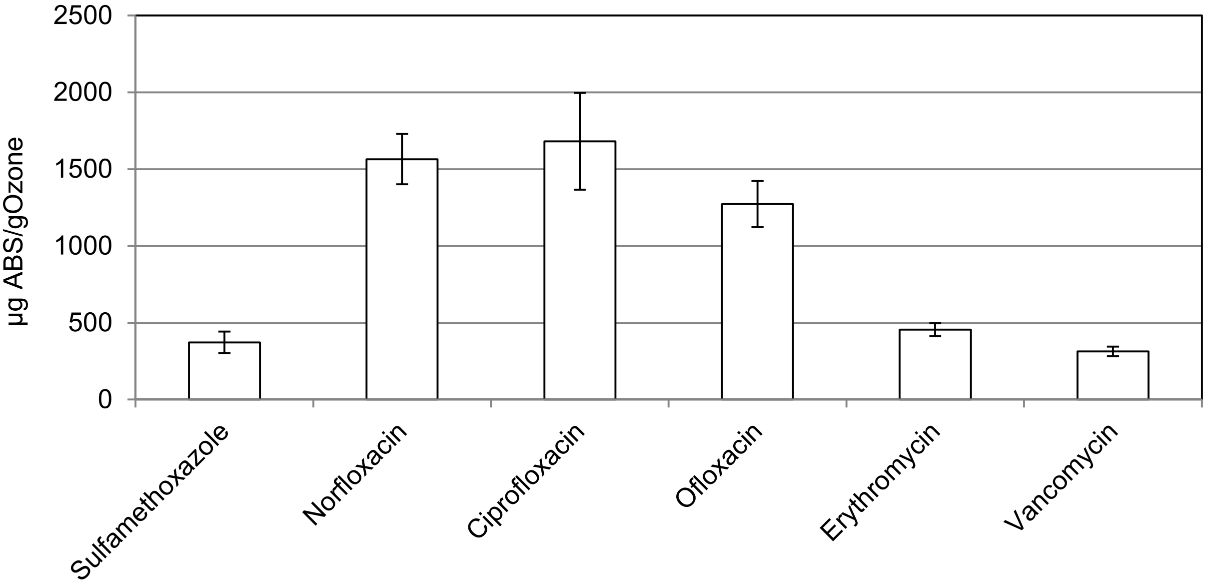

Figure 2: Comparison of ozone consumptions of different types of antibiotics

4 CONCLUSIONS

The presence of antibiotics, which are widely used for human care in pharmaceuticals, has been recorded in hospital wastewater. More complex investigations of antibiotic substances have been undertaken in order to allow an assessment of the environmental risk. In this study, target antibiotics were treated in a membrane bioreactor in connection with an advanced ozonation process. However, the antibiotics removal efficiency was not high with only the MBR treatment due to a low bio-transformation rate or a low sorption level of the antibiotics on the membrane. In order to enhance the removal efficiency, ozonation was applied to the membrane permeate and high efficiency was obtained. The highest removals were reached for ERY and VAN – over 90%, then for CIP – 82%. The results show that ozonation was effective for removing the antibiotic residues in permeate of membrane bioreactor treatment.

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