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# Removal of pharmaceuticals in aerated biofilters with manganese feeding

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ABSTRACT

A tertiary treatment step is required in current wastewater treatment plants to remove trace pollutants and thus to prevent their extensive occurrence in the aquatic environment. In this study, natural MnOx ore and natural zeolite were separately used to pack two lab-scale aerated biofilters, which were operated in approximately 1.5 years for the removal of frequently occurring pharmaceuticals, including carbamazepine (CBZ), diclofenac (DFC), and sulfamethoxazole (SMX), out of synthetic and real secondary effluents. $Mn^{2+}$ was added in the feeds to promote the growth of iron/manganese oxidizing bacteria which were recently found to be capable of degrading recalcitrant pollutants. An effective removal (80–90%) of DFC and SMX was observed in both biofilters after adaptation while a significant removal of CBZ was not found. Both biofilters also achieved an effective removal of spiked $Mn^{2+}$, but a limited removal of carbon and nitrogen contents. Additionally, MnOx biofilter removed 50% of $UV_{254}$ from real secondary effluent, indicating a high potential on the removal of aromatic compounds.

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## 1. Introduction

Various pharmaceutical active compounds (PhACs) have been detected in water bodies. Although at trace concentrations, they still have a potential impact on the aquatic ecological system (Brausch et al., 2012). This impact could become complex within the interactions of various species. For instance, the antibiotics would lead to an increased resistance of microorganisms who can spread their resistance genes into other microbes (Baquero et al., 2008). It was also reported that the dramatic population decline of vultures in the India subcontinent was resulted from the residue of diclofenac (DFC) in livestock bodies which held an important position in the food chain of vultures (Green et al., 2004). Main sources of PhACs are the human and veterinary applications. PhACs from the former source would mostly enter wastewater treatment plants (WWTPs) via a sewage system while those from the latter are normally diffused. Therefore, one important strategy to control the contamination of PhACs is to upgrade the current WWTPs which currently cannot effectively eliminate all PhACs (Zhang and Geißen, 2010).

Many technologies have been studied for the removal of PhACs, including AOP, ozonation, membrane separation, sorption, etc (Basile et al., 2011). Among them, ozonation and activated carbon adsorption are most promising and have

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been installed at full scale (Reungoat et al., 2010; Zimmermann et al., 2011). However, those chemical/physical methods mostly require high investment and/or operation costs. Therefore, the development of a cost-efficient method is of great concern.

Iron/manganese oxidizing bacteria (IMOB) can mediate the oxidation of $Fe^{2+}$ and $Mn^{2+}$ to their high-valency states and thus play an important role in the natural cycle of iron and manganese (Emerson et al., 2010). IMOB widely exist in natural water bodies and technical water systems. For example, Cerrato et al. (2010) detected several strains of IMOB in the sediment of surface water, on the filter materials of drinking water treatment, and in the water distribution pipes even with the presence of chlorine. IMOB have been widely involved in the removal of $Fe^{2+}$ and $Mn^{2+}$in the drinking water treatment (Gouzinis et al., 1998).

Recently, researchers found that IMOB are also capable of degrading PhACs. One degradation mechanism is the *in vitro* adsorption and oxidation by the biogenic manganese oxides (Bio-MnOx). Sabirova et al. (2008) studied the removal of 17α-ethinylestradiol (EE2) with several IMOB strains and they found that IMOB can effectively degrade EE2 with the presence of $Mn^{2+}$. When a bacteriostatic agent (sodium azide) was applied to inhibit the manganese-oxidizing activity of IMOB, the authors still observed 80% removal of EE2. Thus they concluded that the degradation was initiated by the attack of biogenic manganese oxides (Bio-MnOx). This is in accordance with the fact that manganese oxides hold a high redox potential and both synthetic and biogenic MnOx are able to oxidize many organic and inorganic pollutants (Hennebel et al., 2009; Zaman et al., 2009; Zhang et al., 2008a). However, it was also found that the participation of active IMOB was beneficial and sometimes essential for pollutant oxidation. Murray and Tebo (2007) found that IMOB *Bacillus* sp. strain SG-1 can accelerate the oxidation of $Cr^{3+}$ compared to both synthetic and biogenic MnOx. Forrez et al. (2010) reported that the addition of either sodium azide or lysozyme (a cell lysis agent) resulted in a significant inhibition of DFC oxidation by Bio-MnOx of IMOB *Pseudomonas putida*. Meerburg et al. (2012) further reported that the heat inactivated Bio-MnOx of *P. putida* cannot remove DFC. Our previous study also observed that several IMOB strains can remove DFC but the heat inactivated biomass resulted in no removal (Zhu et al., 2012). Therefore, other mechanisms may exit to initiate the pollutant removal which occurs with the active manganese-oxidizing metabolism of IMOB, e.g. via the involvement of a ligand-bound $Mn^{3+}$ intermediate (Meerburg et al., 2012). Therefore, for real applications, the active involvement of IMOB should be guaranteed.

However, only few of studies have been published on the removal PhACs with IMOB in technical systems. De Rudder et al. (2004) used a $MnO_2$ mineral as a packing material in a filter for the removal of EE2 from tap water. They noticed that the loaded EE2 on $MnO_2$ was significantly beyond its adsorption capacity and thus they proposed that a self-regeneration process may occur. Forrez et al. (2009) compared two filters packed with the same mineral and plastic polyethylene rings. The filter with plastic rings was additionally fed with $Mn^{2+}$ and therefore the rings were expected to be covered with Bio-MnOx. Both filters can successfully remove EE2 but the biofilter with plastic rings failed to recover the effective removal after an increase of EE2 loading and also resulted in a higher $Mn^{2+}$ level in effluent than the filter with $MnO_2$ mineral. Recently, Forrez et al. (2011) added Bio-MnOx (160 mg $Mn^{4+}$ $L^{-1}$) into the membrane module of a bioreactor and achieved an effective removal of many PhACs. However, such a configuration is complex to operate and may have some negative impacts on the membrane performance, e.g. fouling, permeability, etc.

In the present study, aerated biofilters were studied, with natural MnOx ore and zeolite as packing materials. $Mn^{2+}$ was additionally spiked into the feeding wastewater to promote the growth of IMOB. Therefore, a simple configuration and active IMOB were expected with the studied aerated biofilters and the removal of three widely detected PhACs, including DFC, carbamazepine (CBZ) and sulfamethoxazole (SMX), was investigated with both synthetic and real wastewater.

## 2. Material and methods

### 2.1. Materials

MnOx ore (Aqua-mandix®) and natural zeolite (Bigadia®) were supplied by Aqua-Techniek, Netherlands, and EgeZeolit, Turkey, respectively. Their chemical compositions and physical properties are shown in Table 1. Diclofenac sodium, carbamazepine, sulfamethoxazole (all with analytical grade), and manganese(II) sulfate monohydrate with ReagentPlus® grade were purchased from Sigma Aldrich, Germany.

### 2.2. Biofilter and operation

The MnOx ore and zeolite were used to pack two biofilters, named Mn-Biofilter and Zeo-Biofilter, respectively. Both biofilters were constructed out of cylindrical acrylic glass (diameter 7 cm; effective height 45 cm; packed height 35 cm) and were aerated with a fine-bubble membrane diffuser at the bottom (Fig. 1). Aluminum foil was used to wrap the filters to prevent light. The aeration rate was regulated with a needle valve at approximately 200 mL $h^{-1}$ and 3–5 mg $L^{-1}$ dissolved oxygen was achieved in both biofilters. The biofilters were fed with wastewater (compositions described below) via a multi-channel peristaltic pump at 430 mL $d^{-1}$, which resulted in an empty bed contacting time (EBCT) of 28 h and 20 h in Mn-Biofilter and Zeo-Biofilters, respectively. In order to avoid the clogging problem, another multi-channel peristaltic pump was used to recycle water in both biofilters at 300 mL $h^{-1}$ to generate a superficial velocity of 3 and 2 m $h^{-1}$ in Mn-Biofilter and Zeo-Biofilters, respectively.

Both synthetic wastewater and effluent from a local WWTP were applied to feed the biofilters. The synthetic wastewater was produced via diluting the OECD composition (OECD, 2001) to simulate a WWTP effluent: 1-L tap water containing peptone 16 mg, meat extract 11 mg, $NH_4Cl$ 5 mg, $NaNO_3$ 10 mg, $K_2HPO_4$ 2.8 mg, NaCl 0.7 mg, $CaCl_2 \cdot 2H_2O$ 0.4 mg, $Mg_2SO_4 \cdot 7H_2O$ 0.2 mg (DOC 10 mg $L^{-1}$, TN 9 mg $L^{-1}$, pH 7.5). The collected WWTP effluent contained DOC 11 ± 3 mg $L^{-1}$, TN 15 ± 2 mg $L^{-1}$, TP 0.6 mg $L^{-1}$, conductivity 1260 ± 50 μS $cm^{-1}$, $UV_{254}$ 0.3 $cm^{-1}$, pH 7.0. In addition, 20 mg $L^{-1}$ $Mn^{2+}$ was added into both

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