Removal of pharmaceuticals in aerated biofilters with manganese feeding

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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. Mn²⁺ 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 Mn²⁺, but a limited removal of carbon and nitrogen contents. Additionally, MnOx biofilter removed 50% of UV254 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 sub-continent 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
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 Fe²⁺ and Mn²⁺ 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 Fe²⁺ and Mn²⁺ in the drinking water treatment (Gouzis 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 Mn²⁺. 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 Cr³⁺ 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 exist to initiate the removal PhACs with IMOB in technical systems. De Rudder et al. (2004) used a MnO₂ mineral as a packing material in a filter for the removal of EE2 from tap water. They noticed that the loaded EE2 on MnO₂ 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 Mn²⁺ 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 Mn²⁺ level in effluent than the filter with MnO₂ mineral. Recently, Forrez et al. (2011) added Bio-MnOx (160 mg Mn⁴⁺ 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. Mn²⁺ 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 mL h⁻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, NH₄Cl 5 mg, NaNO₃ 10 mg, KH₂PO₄ 2.8 mg, NaCl 0.7 mg, CaCl₂·2H₂O 0.4 mg, MgSO₄·7H₂O 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, UV₂₅₄ 0.3 cm⁻¹, pH 7.0. In addition, 20 mg L⁻¹ Mn²⁺ was added into both
feedings. SMX, CBZ and DFC were also spiked in both feedings at concentrations described below.

The biofilters were initially filled with a solution of 10-d old IMOB strains (Leptothrix sp. and Pseudomonas sp.) which were separately cultivated in a liquid medium (leptothrix strains media 2) prepared according to (Atlas, 1997). After 2 d, the biofilters were continuously fed with the synthetic wastewater.

Both biofilters experienced the following operation phases: A) starting with 2 mg L\textsuperscript{−1} PhACs in synthetic wastewater; B) working phase with the same feeding; C) feeding with 1.5 mg L\textsuperscript{−1} extra PhACs in WWTP effluent; D) feeding with 1.5 mg L\textsuperscript{−1} extra PhACs in WWTP effluent without feeding Mn\textsuperscript{2+}. The final concentrations of SMX, CBZ and DFC in WWTP effluent were 2, 5, 4 mg L\textsuperscript{−1}, respectively. The biofilters were assumed to enter the working phase (Phase B) when an effective SMX removal was observed. A transition period of 2–4 weeks occurred between the other sequent operation phases.

3 samples were taken per week in the operation Phase A and B and 2 samples in the other phases. After filtration with 0.45 μm cellulose nitrate membrane, all samples were stored at 4 °C for the collective analysis.

### 2.3. Control tests

Some carrier materials were taken from both biofilters and a defined amount (wet weight: 10 g Mn ore, 20 g zeolite) was added into 50 mL WWTP effluent spiked with 2 mg L\textsuperscript{−1} PhACs. A control test with the presence of sodium azide (50 mg L\textsuperscript{−1}) was also conducted for both materials. Samples of water were taken in intervals during 10 d and analyzed with HPLC after centrifugation.

### 2.4. Sample analysis

PhACs at the high concentration were analyzed with HPLC-UV (Agilent 1200) system equipped with a Gemini-NX C18 column (250 × 4.6 mm, 5 μm) and a SecurityGuard pre-column. The column temperature was set at 30 °C. The injection volume was 50 μL. Elution was conducted with Millipore water (0.1% formic acid) and acetonitrile, at a flow rate of 1.0 mL min\textsuperscript{−1} with the following gradient: 40% acetonitrile at 0 min, 60% at 8 min, 90% at 9 min, 60% at 14 min, and 40% at 15 min (the end). The eluted SMX, CBZ and DFC were detected by a UV detector at 265 nm, 285 nm, and 275 nm, respectively. The limit of quantification was 50 μg L\textsuperscript{−1} for all three PhACs.

The samples with low concentrations of PhACs were analyzed with a HPLC-MS system, consisting of Agilent 1260 HPLC and AB SciexQTrap 5500 MS with an electrospray ionization interface. Analysis was carried out in positive ion mode. A Synergi Hydro-RP column (150 × 3 mm) with a Security Guard column AQ C18 was used for the chromatographic separation. 70 μL of sample was injected into the HPLC-MS system. The column oven temperature was set to 40 °C. The elution solution consisted of Millipore water with 0.1% formic acid and ammonium formate (A) and methanol with 0.1% formic acid (B). The gradient elution program was set as follows: 0–4 min, 98% (A); 5 min, 60%; 16.5 min, 0%; 22 min, 0%; 22.1 min, 98%. The run time was 28 min and the flow rate was 0.50 mL min\textsuperscript{−1}.

Dissolved organic carbon (DOC) and total Nitrogen (TN) were analyzed with a DOC/TN analyzer (AnalytikJena multi N/C 3100). DOC was measured as non-purgeable organic carbon. Mn\textsuperscript{2+} was analyzed by atomic absorption spectroscopy (PerkinElmer PinAAcle 900 Z). The absorbance of ultraviolet at 254 nm (UV\textsubscript{254}) was measured with a photo spectrometer (DR5000, Hach Lange GmbH). Total phosphorus (TP) was measured with a cuvette test from Hach Lange GmbH.

### 3. Results

#### 3.1. Removal of PhACs

Fig. 2a shows the removal efficiencies of SMX, CBZ, and DFC in Mn-Biofilter at different operation phases. About 95% of DFC...
was removed immediately after starting the biofilter. On the contrary, only 10% of SMX was removed in the starting period of 3 months. However, thereafter the removal of SMX rapidly increased to >90% in several days (defined as the start of operation Phase B) and kept stable. The removal of both SMX and DFC was dropped to 70% and 80% (median value), respectively, after switching to the trace concentration (Phase C). More interestingly, both removal efficiencies were elevated with WWTP effluent (Phase D): 90% of SMX and 96% of DFC. After excluding Mn$^{2+}$ in the feeding (Phase E), the removal of both SMX and DFC was slightly decreased and a broader variation was also observed here than in the previous phase.

CBZ obtained a negative removal efficiency in Mn-Biofilter after the trace feeding concentrations were applied, which indicates that the removal of CBZ in Phase A and B, although at very low efficiencies, was probably due to the sorption onto the carrier material.

The removal of SMX, CBZ, and DFC in Zeo-Biofilter is shown in Fig. 2b. It can be found that all three substances were poorly removed in the approximately 4-month starting phase. However, an effective removal of SMX appeared quickly after the starting phase, just like the Mn-Biofilter. An escalation of DFC removal was clearly observed through the operation phases and finally a median removal of 88% was achieved in phase D after about 1-year operation. A slightly decreased removal of SMX (79%) and DFC (74%) was also found in Phase E, similar to Mn-Biofilter. This biofilter also resulted in a limited removal of CBZ in Phases A-D but it was very interesting that CBZ was slightly removed (<20%) in Phase E.

UV–vis spectroscopy was applied to evaluate the evolution of aromatic contents in the treated wastewater. At the end of Phase E, 10 mg L$^{-1}$ DFC or SMX was separately fed into both biofilters and the effluents were scanned with UV–vis spectroscopy. The UV–vis spectra of SMX and DFC are shown in Fig. 3. It can be found that Mn-Biofilter effectively destroyed the aromatic structure of DFC while SMX was only partially removed (Fig. 3a). An opposite result was observed in Zeo-Biofilter where the aromatic structure of SMX was completely eliminated (Fig. 3b). Nevertheless, the partial removal of DFC or SMX may be due to the high loading, it might be possible that the aromatic structure of both...
substances can also be destroyed at a trace level. However, the transformation products were not identified in this study, which makes the degradation pathways still unclear. A control test was conducted in order to clarify the biological and chemical effects of the biomass on both carrier materials. As shown in Fig. 4, the presence of sodium azide significantly depressed the elimination of SMX by both carrier materials, indicating that the elimination of SMX can be attributed to the biological oxidation of manganese in both biofilters. Azide also negatively influenced DFC removal with the inoculated zeolite but its influence on DFC removal with inoculated MnOx ore was limited, which indicates a significant removal by chemical reactions.

3.2. Removal of DOC, TN, TP, and UV\textsubscript{254}

DOC and TN were monitored during the whole operation of biofilters while TP and UV\textsubscript{254} only when WWTP effluent was applied. Fig. 5 shows the C/C\textsubscript{0} ratios of DOC and TN in three phases: feeding with synthetic wastewater plus Mn, with WWTP effluent plus Mn, and with WWTP effluent without Mn.

The absolute concentrations of DOC and TN can also be found in Supplementary Information (Fig. 1s). In general, both biofilters resulted in a limited removal of DOC and TN. DOC removal was slightly enhanced in both biofilters when they were fed with WWTP effluent plus Mn: Median values of C/C\textsubscript{0} were decreased from 83% to 64% and 92%–76% in Mn-Biofilter and Zeo-Biofilter, respectively. However, when Mn was excluded in the feed, the value was slightly increased to 68% in Mn-Biofilter and 95% in Zeo-Biofilter. On the other hand, the TN removal in both biofilters was dropped down after WWTP effluent plus Mn was applied. The median C/C\textsubscript{0} ratios of TN were increased from 86% to 93% in Mn-Biofilter and from 73% to 93% in Zeo-Biofilter. The median C/C\textsubscript{0} value of TN was decreased to ~86% in both biofilters when Mn was excluded.

The removal efficiencies of UV\textsubscript{254} and TP are present in Fig. 6. Zeo-Biofilter showed a moderate removal of TP with a median value of 41% which was much higher than the removal in Mn-Biofilter (23%). However, UV\textsubscript{254} was more effectively removed in Mn- than Zeo-Biofilter: 51% vs. 22% of median value. UV\textsubscript{254} in the original WWTP effluent was approximately 0.3 cm\textsuperscript{-1} and median values of UV\textsubscript{254} were 0.15
and 0.24 cm\(^{-1}\) in the effluents of Mn-Biofilter and Zeo-Biofilter, respectively. A significant influence of Mn in the feed was not found on the removal of UV\(_{254}\) and TP in both biofilters.

3.3. Residual manganese

Manganese is normally not controlled for the effluent discharge. WHO suggests a provisional value of 0.5 mg L\(^{-1}\) manganese for the hazardous control of drinking water while a ten-fold lower value (50 \(\mu\)g L\(^{-1}\)) is recommended by USA and Europe to avoid odor and staining effects of manganese.

The spiked manganese was effectively removed with both biofilters and its concentration in effluent was generally below the ahead mentioned standards in all operation stages as shown in Fig. 7. However, a slightly elevated Mn concentration was observed in the effluents of both biofilters when the real WWTP effluent was applied to replace the synthetic wastewater. Without spiking Mn in the real wastewater, only a trace amount of Mn was detected in both biofilters, which was in the range of Mn content of applied WWTP effluent. It also indicated that Mn was not released from the previously fixed Mn on the packing materials.

4. Discussion

Current WWTPs cannot effectively remove SMX and DFC (Larcher and Yargeau, 2011; Zhang et al., 2008b). Our results provide an alternative solution to remove both substances with a simple reactor and an ease operation. However, adaptation is required for both biofilters to effectively remove SMX: 1 month in Mn-Biofilter, 1.5 month in Zeo-Biofilter. It might be related to the development of some SMX-degrading IMOB since the removal of SMX should be a result of biological manganese oxidation as shown in the control test. It is highly possible that the Mn\(^{3+}\) intermediate formed during the biological oxidation of Mn\(^{2+}\) was involved in the degradation of SMX, like the degradation of DFC by P. putida (Meerburg et al., 2012). Nevertheless, a high level of SMX (2 mg L\(^{-1}\)) was used during the adaptation in this study. Baumgarten et al. (2011) found that the high concentration of SMX can largely shorten the adaptation time for SMX removal in aerobic sand filters (HRT ~14 d). Therefore, it might be possible that both biofilters in this study would need a longer adaption time when starting immediately with secondary effluent where the concentration of SMX is in the range of low \(\mu\)g L\(^{-1}\).

It took about 1 year to obtain an effective removal of DFC in Zeo-Biofilter. It is interesting to notice that the removal of DFC in Zeo-Biofilter was gradually increased along the operation time, during which the spiked manganese should be biologically fixed in the form of MnO\(_x\) on the zeolite (estimated as ~1.5 mg Mn per g zeolite according to the mass balance). After the whole operation period, one can clearly found the black biofilm on zeolite (Fig. 2s in Supplementary Information). A lot of manganese was also detected on zeolite in the elementary analysis with energy dispersive X-ray spectroscopy (Fig. 3s in Supplementary Information). This Bio-MnO\(_x\) on zeolite can still eliminate DFC even with the presence of azide, however, with a lower kinetic rate than without azide as shown in Fig. 4. It indicates that the involvement of biological Mn oxidation is beneficial for the activity of Bio-MnO\(_x\), which is in agreement with the study of Forrez et al. (2010).

On the other hand, Mn-Biofilter can achieve an immediate removal of DFC, which should be attributed to the catalytic effects of mineral MnO\(_x\), as demonstrated by the recent study of Huguet et al. (2013). They also found that the oxidation capacity of MnO\(_x\) was gradually diminished during the reaction with DFC (~20 mg L\(^{-1}\) in clean water). After the treatment of 350 empty-bed volumes, the oxidation capacity disappeared, which the authors attributed to the reductive dissolution and saturation of the active sites. In this study, the biofilters were fed with approximately 400 empty-bed
Villalobos et al. (2003). The structure of Bio-MnOx may change during the reaction and consequently its activity could decrease. Recently, Learman et al. (2011) analyzed the evolution of structure and activity of Bio-MnOx from Roseobacter sp. AzwK-3b during the in vitro oxidation of Mn^{2+}. They found that 78% of Bio-MnOx hexagonal symmetry was gradually transferred to a pseudo-orthogonal symmetry in 5 d and the latter almost lost its activity of Mn^{2+} oxidation. It indicates that a continuous generation of Bio-MnOx may be required to sustain the catalytic activity. However, the structure evolution of MnOx may also occur during the reaction with organic pollutants, which is still not reported according to our knowledge.

UV_{254} indicates the color and aromatic contents (e.g. humic substances) in wastewater, which may be problematic, e.g. by forming disinfection byproducts in chlorination and causing membrane fouling (Tripathi et al., 2011; Zheng et al., 2010). Wert et al. (2009) also found a strong correlation between UV_{254} removal and pharmaceutical elimination from tertiary treated wastewater by O_3 and O_3/H_2O_2. In their study, 4–8 mg L^{-1} of ozone dosage was required to remove 50% of UV_{254}. However, UV_{254} cannot be effectively removed by most biofilters. For example, the slow sand filters can only remove 5–6% of UV_{254} from a secondary effluent (Zheng et al., 2010). Wang et al. (2008) combined an ozonation column and a biofilter with a clay media to treat a WWTP secondary effluent. They obtained 60% and 15% removal of UV_{254} in ozonation (8 mg L^{-1} dosage) and biofilter, respectively. Lee et al. (2012) applied a MBR to treat a WWTP secondary effluent, which was followed by an ozonation column and a biofilter packed with anthracite coal at EBCT of 20 min. They found that 56% of UV_{254} in the MBR effluent was removed with ozone at a dosage of 8 mg L^{-1} (Lee et al., 2012). The subsequent biofilter removed negligible UV_{254}. In the present study, about 50% of UV_{254} was removed in Mn-Biofilter without the complex operation. It indicates that Mn-Biofilter might also be applied as a pretreatment for membrane separation and drinking water chlorination.

The low removal of carbon contents in both biofilters is in accordance with other biofilters for the treatment of secondary effluent; e.g. 25% COD removal (Wang et al., 2008), 20% of DOC removal of pre-ozonated effluent (8 mg L^{-1} ozone dosage) (Lee et al., 2012). Both biofilters had a sufficient oxygen supply (dissolved oxygen 3–5 mg L^{-1}) and thus the denitrification cannot significantly occur. Therefore, the limited removal of TN was found in both biofilters. Nevertheless, a higher removal of DOC can be noticed in Mn-Biofilter than Zeo-Biofilter (Fig. 9). It may be due to the oxidation of humics by MnOx. It has been found that chemically synthesized MnOx can mediate the oxidation of humic substances to generate low-molecular-weight organic compounds, including pyruvate, acetone, formaldehyde, etc. (Sunda and Kieber, 1994). That also partially explained the better removal of UV_{254} by Mn-Biofilter. However, the presence of humic substances could inhibit the oxidation of organic pollutants. Li et al. (2012) found that humic acid can dramatically decrease the mineralization of phenolic monomers (catechol and p-coumaric acid) by chemical MnO_2.

It is also worth mentioning that the material cost of MnOx ore per volumetric unit is more expensive (3–5 times) than granular activated carbon. Therefore, the initial investment for a MnOx filter should also be higher. However, activated carbon is usually suffered from the declined adsorption capacity and consequently decreased removal of organics. Mn-Biofilter did not encounter this problem. It is also possible that activated carbon can further remove recalcitrant organics thanks to the biofilm (Reungoat et al., 2012). However, the development of mature biofilm may takes a long term, up to several years. The natural zeolite is a less expensive material but it took Zeo-Biofilter a long adaption term to degrade DFC in this study. Its adaption may be shorten, e.g. by increasing the loading of manganese, which surely should be confirmed with another study.

5. Conclusions and outlook

The following conclusions can be made from this study:

1) SMX and DFC can be effectively removed in the aerated biofilter packed with natural MnOx and zeolite. However, Zeo-Biofilter required a long adaption time (~1 year) to remove DFC. Mn-Biofilter and Zeo-Biofilter can also effectively eliminate the aromatic contents of DFC and SMX, respectively.

2) DFC was mainly removed by the oxidation of MnOx while SMX during the biological oxidation of manganese. The bioactivity was also beneficial for the removal of DFC by MnOx.

3) Spiked Mn^{2+} can be effectively removed and therefore environmental impact of manganese feeding is minimal.

4) Both biofilters resulted in a limited removal of DOC and TN. However, Mn-Biofilter obtained ~50% removal of UV_{254} from the secondary effluent, indicating a high potential of eliminating aromatic contents in wastewater.

Further studies are required to shorten the adaption time of Zeo-Biofilter, e.g. via increasing the loading of manganese and to identify the crystal structure of Bio-MnOx and its influence on the elimination of DFC.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.01.009.

REFERENCES

