

Interactions between ammonia, iron and manganese removal using pilot-scale biofilters

Qingfeng Cheng, Lichao Nengzi, Linlin Bao, Yijing Wang, Jianxing Yang and Jie Zhang

ABSTRACT

Pilot-scale biofilters treated with real groundwater were established to systemically investigate the interactions between ammonia, iron and manganese removal. When both of ammonia and manganese in influent were about 1 mg/L, they were quickly removed; but when manganese was above 3 mg/L, ammonia removal was affected significantly. When total iron was above 5 mg/L, the oxidization rate of ammonia decreased significantly. In addition, manganese and iron removal were not affected by ammonia, when ammonia was lower than 2.5 mg/L. Fe^{2+} could react with manganese oxides in the biofilter, thus manganese removal could only take place after Fe^{2+} was completely oxidized. When total iron, manganese and ammonia in influent were 11.27 mg/L, 1.20 mg/L and 1.27 mg/L, respectively, iron, ammonia and manganese were mainly removed in 0–0.3 m, 0–0.4 m and 0.2–0.8 m of the filter depth, respectively, and nitrite oxidizing bacteria were presented in 0–0.3 m of the filter depth. The pH decreased along the filter depth with the oxidation of ammonia, iron and manganese, while oxidation reduction potential increased. The results of this study were useful for the optimization and design of biofilters.

Key words | ammonia removal, biofilter, groundwater treatment, interactions, iron removal, manganese removal

Qingfeng Cheng (corresponding author)

Lichao Nengzi

Yijing Wang

Jianxing Yang

College of Resources and Environment, Chengdu

University of Information Technology,

Chengdu 610225,

China

E-mail: chqf185@163.com

Linlin Bao

Key Laboratory of Yellow River and Huaihe River

Water Environment and Pollution Control

Ministry of Education, Henan Key Laboratory of

Environmental Pollution Control,

School of Environment, Henan Normal University,

Xinxiang 453007,

China

Jie Zhang

State Key Laboratory of Urban Water Resource and

Environment,

School of Municipal and Environmental

Engineering, Harbin Institute of Technology,

Harbin 150090,

China

INTRODUCTION

Groundwaters are often mildly acidic and devoid of dissolved oxygen (DO) (Azher *et al.* 2008), therefore soluble Fe^{2+} and Mn^{2+} are usually present in groundwaters by contacting with rocks and minerals, either in dissolved mineral forms, Fe^{2+} and Mn^{2+} , or associated with various organics, minerals or chelating agents (Jusoh *et al.* 2005), especially in Northeast China (Li *et al.* 2013). A suitable water supply for people and industry has currently become more difficult (Okoniewska *et al.* 2007), because intensive development of industry branches and agriculture lead to fast degradation of the environment and simultaneously to pollution of drinking water reservoirs. Both in surface waters and groundwaters, an increase in concentration of different elements and compounds has been observed in the past

years (Kabata-Pendias & Pendias 1993). The contaminations, which come from industrial or urban wastewater, wastes, sludge, pesticides and artificial fertilizers, and their chemical compositions, that are mainly influenced by the content of industrial organic compounds, affect organoleptic properties of water, are toxic or even carcinogenic for human beings (Zaw & Chiswell 1999).

Groundwater as a reservoir for water supply systems usually contains high concentrations of iron and manganese; at the same time, a continuously increasing ammonia concentration in groundwater has been observed in the past several years (Okoniewska *et al.* 2007). The presence of ammonia, iron and manganese in drinking water should be avoided and the maximum contaminant levels

(MCLs) for ammonia of 0.5 mg/L, total iron of 0.3 mg/L and manganese of 0.1 mg/L have been established in China (GB 5749–2006). Iron and manganese are objectionable for the following reasons. (a) Iron and manganese give water a reddish and brown-black colour, respectively, when exposed to air; furthermore, their precipitates can cause stains at laundry and sanitary facilities (Azher *et al.* 2005, 2008; Tekerlekopoulou & Vayenas 2008). (b) Iron and manganese deposits build up in pipelines, reduce pipe diameter in distribution systems and eventually clog pipes, or build up in water heaters and weaken the heating efficiency. (c) Iron and manganese are substrates for the growth of bacteria in drains and water distribution systems (Azher *et al.* 2005); therefore, bad odours and unpleasant tastes may be caused by by-products of the bacteria growth and the dead bacteria (Gouzinis *et al.* 1998). In addition, when manganese exceeds the MCLs, it has been found to affect the central nervous system (Sharma *et al.* 2001). The presence of ammonia in drinking water treatment could affect the chlorination process (Tekerlekopoulou & Vayenas 2007; Hasan *et al.* 2013). This is because ammonia can react with chlorine to form disinfection by-products (Charrois & Hrudehy 2007), which could damage the human nervous system and cause a deterioration in the taste and odour of water (Richardson *et al.* 2007), and also reduce disinfection efficiency (WHO 1996). Moreover, ammonia can interfere with the manganese biofiltration process by consuming excessive oxygen during nitrification, resulting in mouldy and earthy tasting water (WHO 1996).

Chemical methods can be used to oxidize ammonia, iron and manganese, but may produce potential hazardous by-products. As well, they may introduce other pollutants into the produced water (Han *et al.* 2013). Thus, the biological removal of ammonia, iron and manganese emerged and has gradually replaced the conventional chemical treatments (Tekerlekopoulou *et al.* 2013). However, it has been reported that achieving simultaneous removal of ammonia and manganese is very difficult (Pacini *et al.* 2005; Han *et al.* 2013), since biological manganese removal can only take place after complete nitrification because of the necessary evolution of the oxidation reduction potential (ORP) (Hasan *et al.* 2012). In addition, manganese removal only takes place after Fe^{2+} is completely oxidized. Although the interactions between ammonia, iron and manganese have

been investigated in previous studies (Gouzinis *et al.* 1998; Tekerlekopoulou & Vayenas 2007, 2008) and some experimental results obtained, few researchers have systematically investigated the interactions between ammonia, iron and manganese, to know how and why ammonia, iron or manganese influence each other in the biofilter, especially when the concentrations of the pollutants were all relatively high.

In this study, pilot-scale biofilters were established for ammonia, iron and manganese removal using manganese sand as the media. In contrast to all previous reports, real feed groundwater was selected to carry out this experiment because polluted groundwater is becoming an important international issue, especially for developing countries. An approximately 200 day long-term operation was evaluated with respect to the interactions between ammonia and manganese, ammonia and iron, and manganese and iron, and the interactions among ammonia, iron and manganese in a biofilter. The main objectives of this study were to gain an in-depth insight into the interactions between ammonia, iron and manganese in the biofilters to know how and why ammonia, iron or manganese influence each other, and how ammonia, iron and manganese were removed in a biofilter, and thus to provide guidance for the optimization and design of biofilters.

MATERIALS AND METHODS

All pilot-scale biofilters were developed in a groundwater treatment plant, which is located in Harbin city, P. R. China. Each biofilter consisted of a transparent rigid plexi-glass tube 3,000 mm high; the internal diameter was 250 mm or 150 mm, and the corresponding effective working volume was 74 L or 26 L, respectively (Figure 1). At the top of the biofilter, a mixing chamber mixed the incoming waters which then flowed into the biofilter. Along the filter's depth, there were 20 sampling ports at 100 mm intervals for ammonia, total iron, manganese, DO, pH and ORP concentration measurements in the bulk liquid. In order to avoid the collision of bubbles with the deposited sludge, the aeration process was not performed in the biofilters as this could cause disturbance of the system and increase iron concentration in effluent (Katsoyiannis *et al.* 2002; Katsoyiannis & Zouboulis 2004). Downward gravity flow with a flow rate of 6 m/h was adopted in the biofilters, and the

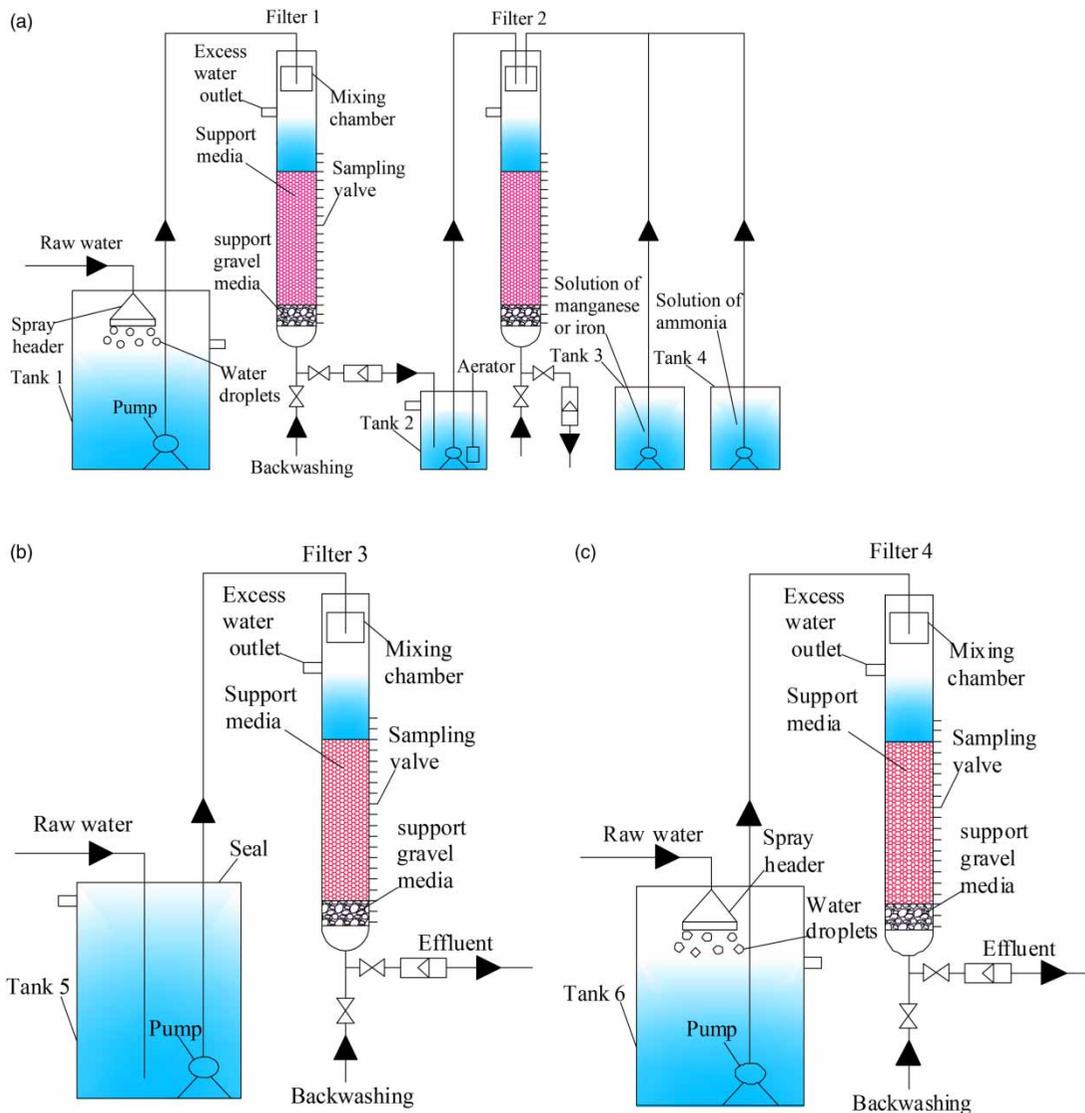


Figure 1 | Schematic drawing of the pilot-scale biofilters.

amount of the flow was controlled at the entry point. Due to pore clogging from bacteria growth and iron and manganese precipitation on the support materials' surfaces, regularly backwashing was performed about every 3 days to wash out dead bacteria and maintain the activity of the system at a high level. The support materials in the biofilters were manganese sand, and the density and bulk density of the manganese sand was 3.6 g/cm^3 and 2.2 g/cm^3 , respectively. The mean diameters of the gravels were 0.8–1 mm with specific surface areas of $3,519\text{--}3,228 \text{ m}^2/\text{m}^3$. The depth of the support materials was 150 cm in the filters and the porosity of the filters was 0.31–0.32.

Groundwater, which was extracted from wells with a depth of 40–50 m, in Harbin city, P. R. China, was used throughout this experiment. The concentration of DO, total iron, manganese and ammonia in raw groundwater was 0.15–0.25 mg/L, 9–12 mg/L, 0.9–1.3 mg/L and 0.9–1.4 mg/L, respectively. The concentration of COD_{Mn} in influent and effluent was 2.14 mg/L and 1.08 mg/L, respectively. The temperature was 7.8–8.0 °C, and pH was 6.9–7.10. In order to increase the concentration of ammonia, iron and manganese in influent, stock solutions of 10 g/L $\text{NH}_4^+\text{-N}$, 10 g/L Fe(II) and 10 g/L Mn(II) were prepared by diluting NH_4Cl , $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4\cdot \text{H}_2\text{O}$, respectively.

Water sampling from the inlet and outlet was performed every day and water sampling along the height of the filter bed was performed twice a week. To make sure the operation was stable, the biofilter was operated for about 15 days after changing influent concentration. It should be noted that all biofilters operated for about one year before this experiment.

Ammonia and manganese removal

Two pilot-scale biofilters were constructed for simultaneous removal of ammonia and manganese (Figure 1(a)); the internal diameters of filters 1 and 2 were 250 mm and 150 mm, respectively. First, raw water was sprayed into tank 1 and the DO increased to 8.0 mg/L, and then it was treated in filter 1. Next, the aerated effluent water of filter 1 in tank 2 with a DO of 11 mg/L was added to filter 2 with manganese and ammonia solutions in tanks 3 and 4, respectively. In order to investigate the influence of varying manganese concentrations on ammonia removal, the concentrations of manganese in influent was increased from about 1 to 4 mg/L, and ammonia was about 1 mg/L. The influence of varying ammonia concentrations on manganese removal was also investigated in the same way; ammonia in influent increased from about 1.5 to 2.5 mg/L, and manganese was about 1 mg/L.

Ammonia and iron removal

This experiment was operated as in the previous section except that an iron solution was prepared in tank 3. In order to investigate the influence of varying iron concentrations on ammonia removal, the concentration of total iron in influent was increased from about 0.1 to 10 mg/L, and ammonia about 1 mg/L. Then, the influence of varying ammonia concentrations on iron removal was also investigated; ammonia in influent increased from about 1.5 to 2.5 mg/L and total iron was about 10 mg/L.

Manganese and iron removal

A pilot-scale biofilter with an internal diameter of 150 mm was used for simultaneous removal of manganese and iron (Figure 1(b)). Raw water flowed to the sealed tank 5, and then was pumped to the mixing chamber of filter 3, and finally flowed to the filter. DO in the raw water increased to 3.2 mg/L

after that process. The concentration profiles of total iron and manganese along the filter depth were measured to investigate the efficiency of iron and manganese removal, when DO was insufficient to completely oxidize ferric iron (part of DO was utilized to oxidize ammonia).

Ammonia, iron and manganese removal

This experiment was done as in the previous section, except that raw water was sprayed into tank 6 (Figure 1(c)). The concentration profiles of ammonia, iron and manganese along the filter depth were measured twice a week to investigate simultaneous removal of ammonia, iron and manganese in the biofilter.

The presence of microorganism and nitrite oxidizing bacteria (NOB) in depths of 0 m, 0.1 m, 0.2 m and 0.3 m of filter 4 were detected by applying the molecular characterization method of fluorescence *in situ* hybridization (FISH) (Wagner *et al.* 1996). 4'-6-diamidino-2-phenylindole (DAPI) probe was used to target all of the microorganisms in the biofilms which revealed a significant distribution, and Nit 3 (Cy3 40 CCTGTGCTCCATGCTCCG) probe was used to target NOB groups.

Analysis methods

The pH, ORP and DO measurements were conducted using a pH meter (Ultra BASIC UB-10), an ORP meter (pH 315i-WTW) and a DO meter (Oxi 315i-WTW), respectively. Total iron, manganese and ammonia in water samples were measured by photometric method, according to *Standard Methods for the Examination of Water and Wastewater* (Method Nos 3500-Fe.B, 3500-Mn.B and 4500-NH₃.B and C, respectively) (Eaton *et al.* 2005).

RESULTS AND DISCUSSION

Ammonia and manganese removal

When the concentration of manganese and ammonia in the influent of filter 2 was 0.93 mg/L and 1.16 mg/L (Table 1), respectively, manganese and ammonia decreased to 0.02 mg/L and 0.03 mg/L in 0.1 m of the filter depth,

Table 1 | Manganese concentration profiles along the filter depth for feed concentration of about 1.0 mg/L, 2.0 mg/L, 3.0 mg/L and 4.0 mg/L, respectively, when ammonia in influent was about 1 mg/L

Filter depth (m)	Mn 1.0 (mg/L)		Mn 2.0 (mg/L)		Mn 3.0 (mg/L)		Mn 4.0 (mg/L)	
	Mn (mg/L)	NH ₄ -N (mg/L)						
0	0.93	1.16	1.98	1.07	2.93	1.13	4.24	1.12
0.1	0.02	0.03	0.07	0.06	0.47	0.17	1.40	0.35
0.2	0.00	0.03	0.00	0.05	0.09	0.08	0.34	0.10
0.3	0.00	0.03	0.00	0.04	0.00	0.06	0.00	0.09
0.4	0.00	0.02	0.00	0.03	0.00	0.04	0.00	0.07
0.8	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.04
1.2	0.00	0.03	0.00	0.02	0.00	0.03	0.00	0.03
1.5	0.00	0.02	0.00	0.02	0.00	0.02	0.00	0.01

respectively, meaning manganese and ammonia could be simultaneously removed in the biofilter. When manganese increased to about 2 mg/L, 3 mg/L and 4 mg/L, manganese in 0.1 m increased to 0.07 mg/L, 0.47 mg/L and 1.40 mg/L, respectively; surprisingly, ammonia in 0.1 m increased to 0.06 mg/L, 0.17 mg/L and 0.35 mg/L, respectively, although ammonia in influent was still about 1 mg/L. Ammonia removal was affected significantly, when manganese was higher than 3 mg/L. When manganese increased to about 3 mg/L or 4 mg/L, manganese increased along the filter depth in the first day (data not shown) while ammonia did not increase; then manganese decreased in the next few days, but ammonia increased. Thus, it may be concluded, that when manganese in influent increased to 3 mg/L or even higher, more manganese oxides were produced and covered the support materials' surface, which influenced the results of ammonia removal.

When the concentration of manganese in influent was about 1 mg/L and ammonia increased to about 1.5 mg/L, 2 mg/L and 2.5 mg/L (Table 2), respectively, ammonia slightly increased along the filter depth, but manganese concentrations hardly varied. The varying concentrations of ammonia did not affect manganese removal. Tekerlekopoulou & Vayenas (2008) investigated the interactions among ammonia, iron and manganese removal when simultaneously present in the trickling filter, and found that ammonia drastically affected manganese oxidation, which was not in agreement with our results. In our previous experiments, it was also found that manganese oxidation was affected significantly by ammonia, when nitrite in high concentrations accumulated in the

Table 2 | Ammonia concentration profiles along the filter depth for feed concentration of about 1.5 mg/L, 2.0 mg/L and 2.5 mg/L, respectively, when manganese in influent was about 1 mg/L

Filter depth (m)	NH ₄ -N 1.5 (mg/L)		NH ₄ -N 2.0 (mg/L)		NH ₄ -N 2.5 (mg/L)	
	NH ₄ -N (mg/L)	Mn (mg/L)	NH ₄ -N (mg/L)	Mn (mg/L)	NH ₄ -N (mg/L)	Mn (mg/L)
0	1.57	1.11	1.99	0.90	2.43	1.04
0.1	0.09	0.05	0.17	0.02	0.25	0.02
0.2	0.06	0.00	0.12	0.00	0.18	0.00
0.3	0.05	0.00	0.09	0.00	0.12	0.00
0.4	0.04	0.00	0.08	0.00	0.09	0.00
0.8	0.03	0.00	0.07	0.00	0.06	0.00
1.2	0.02	0.00	0.06	0.00	0.04	0.00
1.5	0.02	0.00	0.03	0.00	0.04	0.00

biofilter; but when nitrite was oxidized to nitrate, manganese oxidation was not affected by ammonia (Cheng *et al.* 2016). In this experiment, there were plenty of NOB in the biofilter, which could quickly oxidize nitrite to nitrate, and the data were measured in steady phase.

Ammonia and iron removal

When the concentration of total iron and ammonia in influent was 0.11 mg/L and 1.30 mg/L, respectively, ammonia concentration decreased to 0.12 mg/L in 0.1 m of the filter depth (Table 3). However, when total iron increased to 5.37 mg/L and 11.27 mg/L, ammonia increased to 0.50 mg/L and 0.77 mg/L in 0.1 m, respectively, and then dropped to 0.081 mg/L and 0.10 mg/L in 0.4 m, respectively; the

Table 3 | Total iron concentration profiles along the filter depth for feed concentration of about 0.1 mg/L, 5.0 mg/L and 10 mg/L, respectively, when ammonia in influent was about 1 mg/L

Filter depth (m)	Total Fe 0.1 (mg/L)		Total Fe 5 (mg/L)		Total Fe 10 (mg/L)	
	Total Fe (mg/L)	NH ₄ ⁺ -N (mg/L)	Total Fe (mg/L)	NH ₄ ⁺ -N (mg/L)	Total Fe (mg/L)	NH ₄ ⁺ -N (mg/L)
0	0.11	1.30	5.37	1.13	11.27	1.27
0.1	0.068	0.12	1.02	0.50	2.28	0.77
0.2	0.048	0.097	0.35	0.24	0.67	0.44
0.3	0.034	0.070	0.18	0.12	0.33	0.22
0.4	0.024	0.053	0.068	0.081	0.097	0.10
0.8	0.013	0.043	0.018	0.059	0.019	0.075
1.2	0.0056	0.032	0.0075	0.043	0.0095	0.053
1.5	0.0027	0.015	0.0036	0.037	0.0046	0.043

removal rate of ammonia decreased significantly with the increase of iron content. This was because when total iron was higher than 5 mg/L the oxidized ferric hydroxide covered the support materials' surface and prevented ammonia oxidizing bacteria (AOB) and NOB contacting with ammonia in the fluid, which thus affected the growth of AOB and NOB. Total iron increased along the filter depth with the increase of total iron concentration in influent.

When the concentration of total iron in influent was about 9 mg/L and ammonia was about 1.5 mg/L, 2.0 mg/L and 2.5 mg/L (Table 4), respectively, ammonia increased along the filter depth with the increase of ammonia in influent, while total iron hardly varied along the filter depth. When ammonia

Table 4 | Ammonia concentration profiles along the filter depth for feed concentration of about 1.5 mg/L, 2.0 mg/L and 2.5 mg/L, respectively, when total Fe in influent was about 9 mg/L

Filter depth (m)	NH ₄ ⁺ -N 1.5 (mg/L)		NH ₄ ⁺ -N 2 (mg/L)		NH ₄ ⁺ -N 2.5 (mg/L)	
	NH ₄ ⁺ -N (mg/L)	Total Fe (mg/L)	NH ₄ ⁺ -N (mg/L)	Total Fe (mg/L)	NH ₄ ⁺ -N (mg/L)	Total Fe (mg/L)
0	1.56	9.38	1.99	9.05	2.42	9.23
0.1	1.09	1.95	1.43	2.09	1.93	2.00
0.2	0.75	0.79	1.08	0.91	1.59	0.84
0.3	0.45	0.44	0.54	0.38	0.86	0.39
0.4	0.13	0.10	0.17	0.05	0.62	0.07
0.8	0.10	0.05	0.12	0.03	0.56	0.05
1.2	0.08	0.02	0.10	0.02	0.53	0.04
1.5	0.04	0.01	0.08	0.01	0.49	0.02

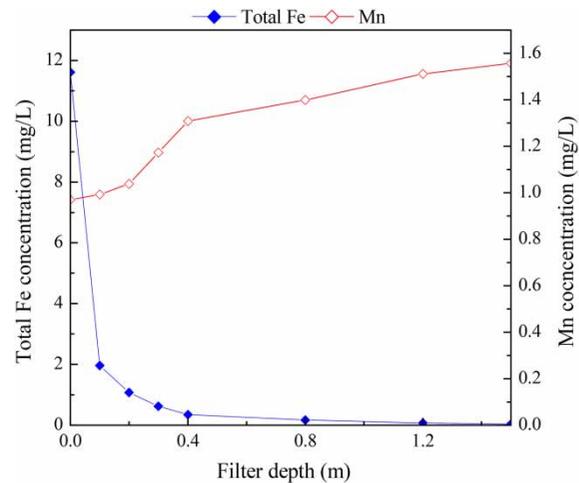


Figure 2 | Total iron and manganese concentration profiles along the filter depth, when DO in influent was 3.2 mg/L.

in influent was about 2.5 mg/L, ammonia was not completely removed because there was an insufficient amount of DO. The varying concentration of ammonia hardly affected iron removal when ammonia was lower than 2.5 mg/L.

Manganese and iron removal

Manganese and iron can be simultaneously removed in a bio-filter, which has been verified by many studies (Gouzinis *et al.*

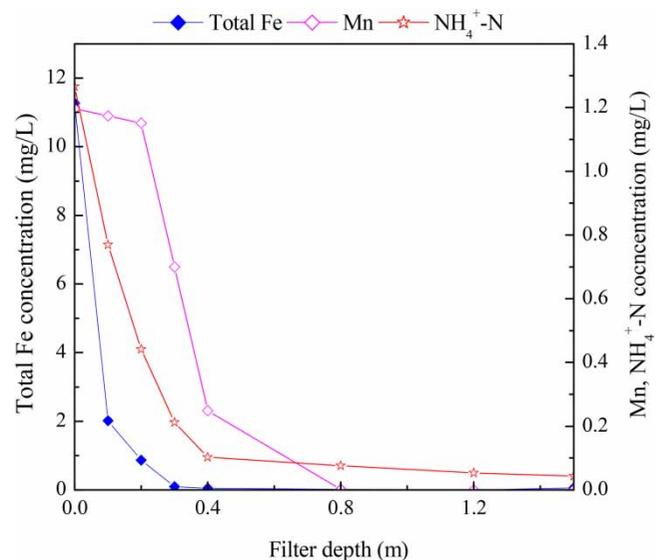


Figure 3 | Total iron, manganese and ammonia concentration profiles along filter 4 depth.

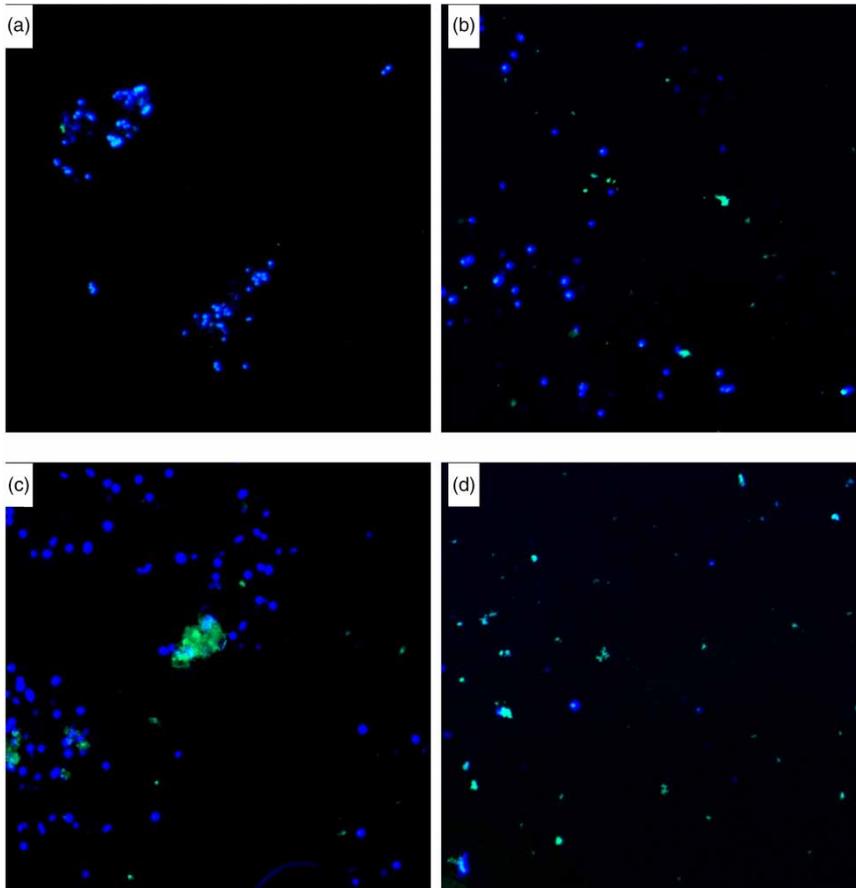


Figure 4 | Molecular characterization of the microbial community by FISH method, other broader bacterial groups characterized by DAPI and NOB in biofilms clumped characterized by FITC. (a) 0 m, (b) 0.1 m, (c) 0.2 m and (d) 0.3 m of filter 4 depth.

1998; Tekerlekopoulou & Vayenas 2007, 2008). However, few researchers have investigated simultaneous manganese and iron removal in a biofilter when DO was insufficient. When the concentration of total iron and manganese in influent was 11.61 mg/L and 0.97 mg/L (DO was 3.2 mg/L), respectively, manganese slowly increased to 1.04 mg/L in 0.2 m of the filter depth, and then quickly increased to 1.31 mg/L in 0.4 m, finally increasing to 1.56 mg/L in 1.5 m, while Fe^{2+} conversely decreased along the filter depth (Figure 2). DO was insufficient to completely oxidize Fe^{2+} (because part of the DO was utilized to oxidize ammonia), when it was 3.2 mg/L. Most Fe^{2+} was quickly oxidized by DO in 0–0.2 m where it was high. Manganese quickly increased in 0.2–0.4 m, since DO decreased to 0.38 mg/L in 0.2 m and part of Fe^{2+} reacted with manganese oxides. The increasing rate of manganese was becoming slower in 0.4–1.5 m, because Fe^{2+} was very low in that depth of the filter. Fe^{2+}

could react with manganese oxides in the biofilter, so manganese removal could only take place after Fe^{2+} was completely oxidized. Tekerlekopoulou & Vayenas (2008) investigated the interactions among ammonia, iron and manganese removal when simultaneously present in the trickling filter, and found that iron drastically affected manganese oxidation, which was in agreement with our results.

Ammonia, iron and manganese removal

When the concentration of total iron, manganese and ammonia in influent was 11.27 mg/L, 1.20 mg/L and 1.27 mg/L, respectively (Figure 3), total iron in 0.1 m, 0.2 m and 0.3 m of the filter depth was 2.02 mg/L, 0.89 mg/L and 0.09 mg/L, respectively. Manganese was adsorbed by support materials with a removal efficiency of 3.8% in 0–0.2 m and dropped to lower than 0.05 mg/L in 0.8 m. Ammonia was removed from

the top of the filter depth and dropped to 0.10 mg/L in 0.4 m. Iron and ammonia were simultaneously removed from the top of the filter depth; manganese began to oxidize when total iron was relatively low, and manganese and ammonia were simultaneously removed in 0.2–0.4 m of the filter depth.

Fe^{2+} started to oxidize when the raw water sprayed into tank 6 (Figure 1(c)); Fe^{2+} was mainly oxidized by DO in filter 4, and the residual was oxidized by iron oxidizing bacteria (IOB). Manganese oxidation required two steps: Mn^{2+} was adsorbed on bacteria cells and oxidized to manganese oxide (Hasan *et al.* 2012). The support material in the biofilter was manganese sand, which had a high ability to adsorb manganese; thus, manganese was lower than 0.05 mg/L until the 41st day in the start-up process (Cheng 2016), while in the steady phase, Mn^{2+} was adsorbed and then quickly oxidized by manganese oxidizing bacteria (MnOB). Biological ammonia oxidation occurred in the biofilter, and was carried out by two different consecutive microbial processes; nitrification-ammonia was oxidized to nitrite by AOB, and nitrification-nitrite was oxidized to nitrate by NOB. NOB were detected in 0 m, 0.1 m, 0.2 m and 0.3 m of the filter depth (Figure 4), meaning nitrite was oxidized in 0–0.3 m and ammonia was oxidized from the top of the filter, which was in agreement with the results of the previous section. A large number of microorganisms was detected in the biofilter since real groundwater was used in this experiment and the composition was complex. IOB and MnOB which belonged to microorganisms should also be present in the biofilter.

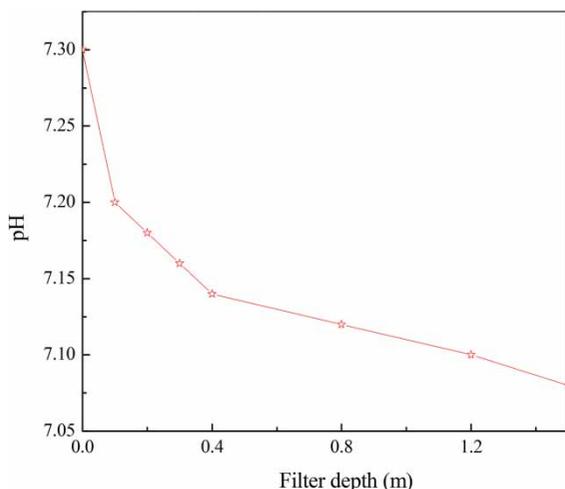


Figure 5 | The pH concentration profiles along the filter depth.

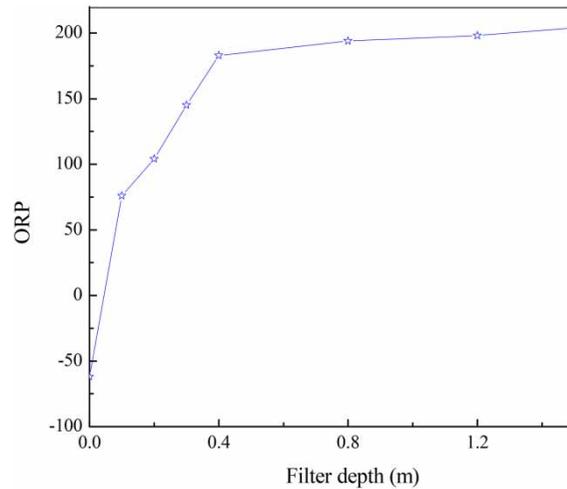


Figure 6 | ORP concentration profiles along the filter depth.

The pH and ORP were monitored along the filter depth. pH in raw water was 7.04, and increased to 7.30 after aeration (Figure 5), then obviously dropped to 7.14 in 0.4 m of the filter depth, finally dropping to 7.08 in 1.5 m. The pH decreased along the filter depth with the oxidation of ammonia, iron and manganese. ORP increased from –95 mV to –62 mV after aeration (Figure 6), and then quickly increased to 183 mV in 0.4 m, finally increasing to 204 mV in 1.5 m. The ORP profiles along the depth of the biofilter depended on the feeding concentrations and DO.

CONCLUSIONS

Ammonia and manganese, and ammonia and iron could be simultaneously removed in the biofilter, but when manganese and iron in influent were above 3 mg/L and 5 mg/L, respectively, the removal rates of ammonia decreased significantly. Iron and manganese removal was not affected by ammonia, when ammonia was lower than 2.5 mg/L. Manganese removal occurred after Fe^{2+} was completely oxidized, since Fe^{2+} could react with manganese oxides. In the biofilter for ammonia, iron and manganese removal, ammonia and iron were simultaneously removed from the top of the filter depth, and manganese removal occurred when Fe^{2+} was completely oxidized. The pH decreased along the filter depth, while ORP increased.

ACKNOWLEDGEMENTS

This work was kindly supported by the Scientific Research Foundation of Chengdu University of Information Technology (CUIT) (KYTZ201511) and Program of Education Department of Sichuan Province (16ZB0221).

REFERENCES

- Azher, N. E., Gourich, B., Vial, C., Soulam, M. B., Bouzidi, A. & Ziyad, M. 2005 Influence of alcohol addition in gas hold-up, liquid velocity and mass transfer in split-rectangular airlift bioreactor. *Biochemical Engineering Journal* **23** (2), 161–167.
- Azher, N. E., Gourich, B., Vial, C., Soulam, M. B. & Ziyad, M. 2008 Study of ferrous iron oxidation in Morocco drinking water in an airlift reactor. *Chemical Engineering and Processing* **47** (9–10), 1877–1886.
- Charrois, J. W. A. & Hruday, S. E. 2007 Breakpoint chlorination and free-chlorine contact time: implication for drinking water N-nitrosodimethylamine concentrations. *Water Research* **41**, 674–682.
- Cheng, Q. F. 2016 Competitive mechanism of ammonia, iron and manganese for dissolved oxygen using pilot-scale biofilter at different dissolved oxygen concentrations. *Water Science and Technology: Water Supply* **16** (3), 766–774.
- Cheng, Q. F., Nengzi, L. C., Xu, D. Y., Guo, J. Y. & Yu, J. 2016 Influence of nitrite on the removal of Mn(II) using pilot-scale biofilters. *Journal of Water Reuse and Desalination*. DOI: 10.2166/wrd.2016.210.
- Eaton, A. D., Franson, M. A. H., American Public Health Association, American Water Works Association & Water Environment Federation 2005 *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC.
- Gouzinis, A., Kosmidis, N., Vayenas, D. V. & Lyberatos, G. 1998 Removal of Mn and simultaneous removal of NH₃, Fe and Mn from potable water using a trickling filter. *Water Research* **32** (8), 2442–2450.
- Han, M., Zhao, Z. W., Gao, W. & Cui, F. Y. 2013 Study on the factors affecting simultaneous removal of ammonia and manganese by pilot-scale biological aerated filter (BAF) for drinking water pre-treatment. *Bioresource Technology* **145**, 17–24.
- Hasan, H. A., Abdullah, S. R. S., Kofli, N. T. & Kamarudin, S. K. 2012 Effective microbes for simultaneous bio-oxidation of ammonia and manganese in biological aerated filter system. *Bioresource Technology* **124**, 355–363.
- Hasan, H. A., Abdullah, S. R. S., Kamarudin, S. K. & Kofli, N. T. 2013 On-off control of aeration time in the simultaneous removal of ammonia and manganese using a biological aerated filter system. *Process Safety and Environmental Protection* **91** (5), 415–422.
- Jusoh, A. B., Cheng, W. H., Low, W. M., Nora'aini, A., Megat, M. J. & Noor, M. 2005 Study on the removal of iron and manganese in groundwater by granular activated carbon. *Desalination* **182** (1–3), 347–353.
- Kabata-Pendias, A. & Pendias, H. 1993 *Biogeochemia Pierwiastków Sładowych* (Biochemistry of Trace Elements). PWN, Warszawa, 364 pp. (in Polish).
- Katsoyiannis, I. A. & Zouboulis, A. I. 2004 Biological treatment of Mn (II) and Fe(II) containing groundwater: kinetic considerations and product characterization. *Water Research* **38** (7), 1922–1932.
- Katsoyiannis, I., Zouboulis, A., Althoff, H. & Bartel, H. 2002 As(III) removal from groundwaters using fixed-bed upflow bioreactors. *Chemosphere* **47** (3), 325–332.
- Li, X. K., Chu, Z. R., Liu, Y. J., Zhu, M. T., Yang, L. & Zhang, J. 2013 Molecular characterization of microbial populations in full-scale biofilters treating iron, manganese and ammonia containing groundwater in Harbin, China. *Bioresource Technology* **147**, 234–249.
- Okoniewska, E., Lach, J., Kacprzak, M. & Neczaj, E. 2007 The removal of manganese, iron and ammonium nitrogen on impregnated activated carbon. *Desalination* **206** (1–3), 251–258.
- Pacini, A. V., Ingallinella, M. A. & Sanguinetti, G. 2005 Removal of iron and manganese using biological roughing up flow filtration technology. *Water Research* **39** (18), 4463–4475.
- Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R. & Marini, D. M. 2007 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutation Research* **636** (1–3), 178–242.
- Sharma, S. K., Kappelhof, J., Groenendijk, M. & Schippers, J. C. 2001 Comparison of physicochemical iron removal mechanisms in filters. *Journal of Water Supply Research and Technology-Aqua* **50** (4), 187–198.
- Tekerlekopoulou, A. G. & Vayenas, D. V. 2007 Ammonia, iron and manganese removal from potable water using trickling filters. *Desalination* **210** (1–3), 225–235.
- Tekerlekopoulou, A. G. & Vayenas, D. V. 2008 Simultaneous biological removal of ammonia, iron and manganese from potable water using a trickling filter. *Biochemical Engineering Journal* **39** (1), 215–220.
- Tekerlekopoulou, A. G., Pavlou, S. & Vayenas, D. V. 2013 Removal of ammonium, iron and manganese from potable water in biofiltration units: a review. *Journal of Chemical Technology and Biotechnology* **88** (5), 751–773.
- Wagner, M., Rath, G., Koops, H. P., Flood, J. & Amann, R. 1996 In situ analysis of nitrifying bacteria in sewage treatment plants. *Water Science and Technology* **34** (1–2), 237–244.
- WHO 1996 *Ammonia in Drinking Water. Guidelines for Drinking-Water Quality. Health Criteria and Other Supporting Information*, Vol. 2, 2nd edn. World Health Organization, Geneva, Switzerland.
- Zaw, M. & Chiswell, B. 1999 Iron and manganese dynamics in lake water. *Water Research* **33** (8), 1900–1910.

First received 17 August 2016; accepted in revised form 3 November 2016. Available online 3 January 2017