



Article Influence of Nitrite on the Removal of Organic Matter and Manganese Using Pilot-Scale Biofilter: A Kinetic Study

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Abstract: Nitrite produced during ammonia oxidation can inhibit the activity of microorganisms. To provide guidance for the optimization and design of a biofilter, a pilot-scale biofilter was established to investigate the influence of nitrite on organic matter and manganese removal and on the kinetics. The results demonstrated that COD_{Mn} , ammonia, and manganese in effluent were 2.77, 0.034, and 0.026 mg/L in the steady phase, respectively. Organic matter and manganese removal were affected by nitrite during the start-up process, as well as in the ammonia increasing process. When ammonia increased from about 0.5 to 1 and 2 mg/L, organic matter, and manganese removal were affected at 4 and 3 days and 6 and 5 days, respectively. When organic matter, ammonia, and manganese in the influent were 6.27, 2.07, and 1.19 mg/L, respectively, organic matter, ammonia, and manganese oxidation all followed a first-order kinetic rate. The *k*-value was 0.0268, 0.268, and 0.216 min⁻¹, and the half-life time was 24.236, 2.583, and 3.202 min, respectively. The influence of nitrite on the structure of microbial communities in the biofilter will be investigated in the future.

Keywords: organic matter; ammonia and manganese removal; biofilter; nitrite; drinking water; kinetics



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1. Introduction

Water is the source of life and the crucial substantial foundation of social and economic development. However, it is currently more difficult to provide a suitable water supply for humans and industry [1], since intensive development of industry branches and agriculture leads to fast degradation of the environment, as well as pollution of drinking water reservoirs [2,3]. Moreover, both in surface waters and groundwaters, growing evidence of increasing pollution has been observed in the past years [4]. These contaminants generated from industrial and urban wastewater, wastes, sludge, pesticides, andartificial fertilizers are potentially toxic and carcinogenic for human beings; furthermore, the chemical compositions of these contaminants are mainly influenced by the concentrations and compositions of industrial organic compounds [1,5].

Organic matter, ammonia, and manganese are major pollutants in sources of drinking water, such as lakes, groundwaters, and rivers in China. When the concentration of contaminants in water is beyond regulated limits, it becomes dangerous to human health [6]. The presence of high concentrations of organic matter can lead to the depletion of dissolved oxygen and to the development of septic conditions [7]; some kinds of organic matter are even toxic to humans, such as antibiotics and pesticides. In drinking water treatment, the presence of ammonia can affect the chlorination process [8]. This is because ammonia reacts with chlorine to form disinfection byproducts [9,10], which could damage the human nervous system [11], deteriorate the taste and odor of water [12], and reduce disinfection efficiency [13]. Moreover, excessive oxygen is consumed during the nitrification process, which interferes with the biological manganese oxidization process, resulting in earthy and moldy-tasting water [13]. Another parameter is manganese, which can lead to aesthetic and

operational problems, such as staining on plumbing fixtures and laundry [14], substrates for the growth of bacteria, and causing defects in industrial products [15]. Furthermore, manganese affects the central nervous system when it exceeds 0.05 mg/L [16]. As a result, drinking water containing high levels of organic matter, ammonia, and manganese needs to be treated before it can be used in industry and humans. The maximum contaminant level (MCLs) of COD_{Mn} of 3 or 5 (when the concentration of COD_{Mn} in raw water was above 6 mg/L) mg/L, ammonia of 0.5 mg/L, and manganese of 0.1 mg/L have been established in China (GB 5749-2006).

Organic matter, ammonia, and manganese are generally removed by chemical or biological technologies. Recently, simultaneous biological removal of organic matter, ammonia, and manganese by one or more biofilters has emerged and gradually replaced conventional chemical treatments in the current circumstances [17]. Since no extra chemicals are needed, no new pollutants can be introduced into the produced water and no potentially hazardous by-products can be produced [18]. Simultaneous removal of chemical oxygen demand (COD_{Mn}), ammonia ($NH_4^+ - N$), and manganese (Mn^{2+}) in a biological aerated filter were investigated by several researchers [19]. However, nitrite which is toxic to microorganisms, is generated in the biofilter during the start-up period, or when ammonia in the influent is suddenly increased, as the rate of nitritification (ammonia is oxidized to nitrite) is faster than the rate of nitratification (nitrite is continually oxidized to nitrate) [20]. To the best of our knowledge, there is no investigation into the influence of nitrite on simultaneous organic matter and manganese removal using a biofilter; although the influence of nitrite on manganese removal was investigated by several researchers [21].

Contaminant removal kinetics in water treatment can provide information on the time required to efficiently remove a specific contaminant, which is necessary for sizing treatment units [22]. Therefore, the kinetics of simultaneous biological organic matter, ammonia, and manganese oxidation in biological systems were worth studying. In addition, it is recommended to include the biofilter system as an additional system prior to the chlorination process to avoid the potential risk of bacterial contamination.

In this study, a pilot-scale biofilter was established to remove organic matter simultaneously, ammonia and manganese from simulated potable water. The influence of nitrite generated during the start-up process and the ammonia increasing process on the organic matter and manganese removal were investigated, and the variation of organic matter, ammonia, nitrite, and manganese along the filter layer was also investigated. Moreover, the removal kinetics of biological organic matter, ammonia, and manganese oxidation were calculated to provide information about the required time that the specific contaminant needs to be removed efficiently. The main objectives of this study were to investigate the influence of nitrite generated in the biofilter on simultaneous organic matter, ammonia, and manganese removal to provide guidance for the optimization and design of biofilter.

2. Materials and Methods

A pilot-scale biofilter system was developed for the simultaneous removal of organic matter, ammonia, and manganese. The pilot-scale biofilter consisted of a 44.16 L transparent rigid plexiglass column with an inner diameter of 150 mm and a height of 2500 mm (Figure 1). At the top of the biofilter, the water is first mixed in the mixing chamber and then flows into the biofilter. Meanwhile, at the bottom of the biofilter, an aerator was used to control the concentration of dissolved oxygen (DO). Along the filter depth, there were 17 sampling ports at 100 mm intervals for DO, pH, oxidation-reduction potential (ORP), organic matter, ammonia, and manganese concentration measurements. During the long run of the biofilter, a high flow rate backwash is performed regularly every 7 days to flush out dead bacteria and maintain a high level of activity in the system. The backwashing time was 3 min, and the backwashing intensity was 12 L/(s·m²). Tank 1 (volume was 500 L) was used to collect tap water. A stock solution of 10 g/L Mn(II) and 5~20 g/L NH₄⁺-N was prepared in tank 2 (volume was 30 L) by diluting MnSO₄·H₂O and NH₄Cl,

respectively. Tank 3 (volume was 500 L) was used to collect real river water from the river on the campus. $MnSO_4 \cdot H_2O$, NaOH, KI, HgI_2 , HCl, NH_4Cl , and the other chemical reagents were of analytical grade (Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China). In this study, manganese sand with a height of 1500 mm and an average diameter of 2~4 mm was packed in the biofilter. It should be noted that the upper part of the media (200 mm) was matured manganese sand collected from a groundwater treatment plant (GWTP) for ammonia, manganese, and iron removal, and the lower part (1300 mm) was new manganese sand. In addition, the presence of manganese oxidizing bacteria (MnOB) in the layer of the biofilter in the GWTP was verified by several researchers [4,23]. The concentration of organic matter, ammonia, and manganese in the simulated source water was 5.5~7.0, 0.45~2.20, and 0.95~1.35 mg/L, respectively. The temperature was kept at 15~20 °C (Table 1).



Figure 1. Schematic drawing of the pilot-scale biofilter system.

Properties	Value	Properties	Value		
Temperature	15~20 °C	NO ₂ -	~0.02 mg/L		
pH	~7.0	NH_4^+	0.45~2.20 mg/L		
Total Fe	~0.1 mg/L	COD _{Mn}	5.5~7.0 mgO ₂ /L		
Mn	0.95~1.35 mg/L	DO	6.0~8.0 mg/L		
NO_3^-	~0.1 mg/L	Alkalinity	60~100 mg CaCO ₃ /L		
Turbidity	0.2~0.4 NTU	Conductivity	280~320 μs/cm		

Table 1. Physicochemical characteristics of the simulated source water.

2.1. Start-Up Process Strategy

To shorten the start-up period, bacteria that oxidized organic matter, ammonia, and manganese were inoculated in the biofilter. About 2 L activated sludge from a wastewater treatment plant containing ammonia oxidizing bacteria (AOB) was collected and discharged into the biofilter as inoculated water, and about 2 L activated sludge was collected from the place where the river water was obtained and discharged into the biofilter too. The waters in tanks 1, 2, and 3 were pumped into the biofilter with a suitable proportion to ensure the concentration of organic matter, ammonia, and manganese in influent were about 5.5~7.0, 0.45~0.65, and 0.95~1.35 mg/L, respectively. In addition, the biofilter was intermittently operated for about 2 days to make sure that the AOB and organic matter oxidizing bacteria (OMOB) adhered to the media of the biofilter. Then, the biofilter was continuously operated from the 3rd day, and the concentration of organic matter, ammonia, and manganese was measured from the 4th day. Moreover, the flow rate was controlled at 3 m/h. When the effluent organic matter, ammonia, and manganese were lower than 3, 0.1, and 0.1 mg/L, respectively, the biofilter was started up successfully.

2.2. Influence of Nitrite on Organic Matter and Manganese Removal in a Biofilter

In order to investigate the influence of nitrite on simultaneous organic matter and manganese removal, the influent ammonia sharply increased to about 1 mg/L to generate nitrite. After the biofilter was steadily operated for about a month, the influent ammonia sharply increased to about 2 mg/L.

2.3. Kinetics of Biological Organic Matter, Ammonia, and Manganese Oxidation

The kinetics of biological organic matter, ammonia, and manganese oxidation were investigated in this experiment. The determination of empty bed contact time (EBCT) of groundwater in a biological filter is based on the following formula:

$$EBCT = filter bed (m)/linear velocity (m/h)$$
(1)

2.4. Analysis Methods

The pH, DO, and ORP measurements were conducted using a pH meter (Ultra BASIC UB-10), a dissolved oxygen meter (Oxi 315i-WTW), and an ORP meter (pH 315i-WTW), respectively. Concentrations of organic matter, ammonia, and manganese were measured according to the Standard Methods for the Examination of Water and Wastewater [24].

2.5. The Kinetics of Biological COD_{Mn} , $NH_4^+ - N$, and Mn^{2+} Oxidation

The COD_{Mn} , NH_4^+ –N, and Mn^{2+} removal from the BAF was evaluated using the following equation:

$$\frac{d[\text{COD}_{Mn}/\text{NH}_4^+ - \text{N}/\text{Mn}^{2+}]_t}{dt} = -k[\text{COD}_{Mn}/\text{NH}_4^+ - \text{N}/\text{Mn}^{2+}]_t$$
(2)

where *k* is the rate constant, min^{-1} .

After the separation of variables and integration of Equation (2), the following Equation (3) was obtained:

$$\ln \frac{[\text{COD}_{\text{Mn}}/\text{NH}_{4}^{+} - \text{N}/\text{Mn}^{2+}]_{t}}{[\text{COD}_{\text{Mn}}/\text{NH}_{4}^{+} - \text{N}/\text{Mn}^{2+}]_{0}}$$
(3)

where $[COD_{Mn}/NH_4^+ - N/Mn^{2+}]_0$ is the influent concentration and $[COD_{Mn}/Mn^{2+}]_t$ is the concentration at the EBCT of t.

3. Results and Discussion

3.1. Overall Performance of the Biofilter in the Start-Up Process

In the biofilter, organic matter and ammonia removal were achieved by OMOB and AOB, respectively, while manganese was removed by physicochemical (such as adsorption of manganese sand) and biological (such as oxidation of manganese oxidizing bacteria (MnOB)) processes. At the beginning of this experiment, manganese was completely removed (Figure 2), since manganese sand had a high adsorption capacity for manganese, and the matured manganese sand attached plenty of MnOB which could oxidize manganese. Only a small number of OMOB and AOB were inoculated in the biofilter, and the bacteria needed time to adapt to the new circumstances, therefore, the efficiency of organic matter and ammonia removal was relatively low (Figures 3 and 4). Subsequently, with the growth of OMOB and AOB, the efficiency of organic matter and ammonia removal increased, as the removal efficiencies on the 26th day increased to 22.49% and 83.54%, respectively. The removal efficiency of ammonia was much higher than that of organic matter. The reasons were as follows: (a) organic matter removal was affected by nitrite which was generated in the start-up process; (b) the influent ammonia was lower; and (c) organic matters in the influent were mainly refractory organic matters [19]. The removal efficiency of organic matter and ammonia continually increased as time went on. Surprisingly, the efficiency of manganese removal decreased to 59.23% on the 26th day, since the manganese sand was saturated with manganese adsorption and the activity of MnOB was inhibited

by nitrite [20]. The influent manganese increased to 0.54 mg/L at the 29th day and then decreased gradually possibly due to the growth and reproduction of MnOB. When the nitrite was completely oxidized to nitrate, the efficiency of organic matter and manganese removal quickly increased. In addition, the effluent organic matter, ammonia, and manganese were lower than 3, 0.1, and 0.1 mg/L from the 51st day, respectively, suggesting that the biofilter was started up successfully.



Figure 2. Long-term performance of the biofilter with respect to Mn²⁺ removal.



Figure 3. Long-term performance of the biofilter with respect to COD_{Mn} removal.

The variation of organic matter, ammonia, and manganese along the filter depth was also investigated. On the 16th day, the inoculated AOB did not adapt to the new environment, and the removal rate of ammonia was only 15.10% (Table 2). AOB was quickly accumulated in the biofilter from day 16 to 32 since the removal rate of ammonia increased to 92.68%, and ammonia was mainly removed in 0~0.8 m. On the 45th and 73rd days, ammonia in 0.4 m decreased to 0.18 and 0.13 mg/L, respectively, and ammonia in 0.8 m was lower than 0.1 mg/L. The effluent organic matter decreased to 5.62 mg/L on the 16th day, and the corresponding removal rate was only 12.90% (Table 2). As only a small

quantity of OMOB was accumulated in the biofilter, organic matter removal was achieved by OMOB. On the 32nd day, the removal rate of organic matter increased to 27.19% with the growth and reproduction of OMOB; organic matter quickly decreased to 5.06 from 5.71 mg/L in 0.4 m, decreased to 4.37 mg/L in 1.2 m, and slowly decreased to 4.16 mg/L in 1.5 m. The organic matter along the filter depth decreased on the 45th day and decreased to 3.83 and 3.41 mg/L in 1.2 and 1.5 m, respectively. This is due to the fact that OMOB was rapidly grown after nitrite was completely oxidized (data not shown). On the 73rd day, organic matter was mainly removed in 0~0.8 m and decreased to 2.68 mg/L in 1.5 m.



Figure 4. Long-term performance of the biofilter with respect to NH₄⁺–N removal.

Table 2. Ammonia, organic matter, and manganese concentration profiles along the filter depth in the start-up process.

T 11.	Effluent (mg/L)											
Filter Depth (m)	Ammonia	Day 16 Organic Matter	Manganese	Ammonia	Day 32 Organic Matter	Manganese	Ammonia	Day 45 Organic Matter	Manganese	e Ammonia	Day 73 Organic Matter	Manganese
0	0.53	6.45	1.14	0.62	5.71	1.37	0.51	6.61	1.22	0.46	6.27	1.19
0.4	0.50	6.12	0.85	0.38	5.06	0.92	0.18	5.19	0.79	0.13	4.13	0.73
0.8	0.48	5.89	0.65	0.203	4.65	0.73	0.060	4.44	0.47	0.043	3.43	0.24
1.2	0.46	5.72	0.27	0.091	4.37	0.62	0.039	3.83	0.22	0.029	2.95	0.064
1.5	0.45	5.62	0.037	0.045	4.16	0.45	0.031	3.41	0.035	0.026	2.68	0.022

The influent manganese on the 16th day was 1.14 mg/L (Table 2), and manganese quickly decreased to 0.85 mg/L in 0.4 m of the filter depth, since manganese was oxidized by MnOB, which attached to the matured manganese sand, and was adsorbed by manganese sand. Manganese in the influent was preferably adsorbed by the upper part of the media; therefore, when the media in $0.4 \sim 0.8 \text{ m}$ was getting saturated, the adsorption region extended to $0.8 \sim 1.5 \text{ m}$, and manganese in 1.5 m decreased to 0.037 mg/L. On the 32nd day, manganese quickly decreased to 0.92 from 1.37 mg/L in 0.4 m possibly due to the growth and reproduction of MnOB; the effluent manganese obviously increased to 0.45 mg/L, as the adsorption capacity of the media in $0.4 \sim 1.5 \text{ m}$ was getting saturated and biological manganese removal was inhibited by nitrite [2]. MnOB quickly grew after nitrite was completely oxidized; manganese in effluent decreased to 0.035 mg/L on the 45th day, and the concentration of manganese along the filter depth decreased compared with the 32nd day. In the steady phase (day 73), manganese was mainly removed in $0 \sim 0.8 \text{ m}$ and decreased to 0.022 mg/L in 1.5 m.

3.2. Influence of Nitrite on Organic Matter and Manganese Removal

The biological oxidation of ammonia is carried out by two continuous microbial processes, nitritification, and nitratification [25]. During the nitritification process, ammonia is oxidized to nitrite, and during the nitratification process, nitrite is converted to nitrate. It should be noted that the nitritification rate is faster than that of nitratification [20], thus when the influent ammonia increased to about 1 mg/L on the 78th day (Figure 4), nitrite was accumulated in the biofilter. Moreover, the effluent ammonia increased to 0.18 mg/L from 0.026 mg/L, however, it quickly decreased to 0.074 mg/L on the 79th day with the growth and reproduction of AOB. Organic matter and manganese removal were inhibited by nitrite, and the effluent organic matter and manganese increased to 3.60 and 0.16 mg/L from 2.61 and 0.016 mg/L, respectively (Figures 2 and 3). Organic matter and manganese in the effluent decreased with the decreasing of nitrite and decreased to 2.52 and 0.042 mg/Lat the 83rd and 81st days, respectively. When the influent ammonia increased to about 2 mg/L on the 108th day, nitrite was also accumulated, and organic matter and manganese removal were affected too. When the influent ammonia suddenly raised or the biofilter was started up, nitrite accumulated in the biofilter and then inhibited organic matter and manganese removal [4].

In order to analyze the removal mechanism of organic matter, ammonia, and manganese after ammonia increased, variation of the pollutants along the filter depth was investigated. When the influent ammonia increased to 1.04 from 0.49 mg/L on the 78th day, ammonia quickly decreased to 0.63 mg/L in 0.4 m of the filter depth, decreased to 0.45 mg/L in 0.8 m, and slowly decreased to 0.18 mg/L in 1.5 m (Table 3a). The concentration of nitrite in the influent was 0.0028 mg/L, quickly increased to 0.082 mg/L in 0.4 m, increased to 0.13 mg/L in 0.8 m, and slowly increased to 0.14 mg/L in 1.5 m (Table 3b). Nitrite increased along the filter depth with the decrease of ammonia concentration, since nitrite was produced in the nitrification process. With the growth of AOB, ammonia in the effluent decreased to 0.074 mg/L on the 79th day, and ammonia along the filter depth continually decreased as time went on. Nitrite was mainly generated in 0~0.4 m of the filter depth since the removal amount of ammonia was highest in that depth. On the 79th day, nitrite increased to 0.11 mg/L in 0.8 m, and then slowly decreased to 0.095 mg/L in 1.5 m. The biofilter was steadily operated on the 83rd day, ammonia was mainly removed in 0~0.8 m, and decreased to 0.11 and 0.033 mg/L in 0.8 and 1.5 m, respectively. In addition, nitrite increased to 0.013 mg/L in 0.4 m and decreased to 0.0039 mg/L in 1.5 m.

Organic matter and manganese removal were inhibited on the 78th day due to the accumulation of nitrite in the biofilter. The effluent organic matter and manganese increased to 3.60 and 0.16 mg/L (Table 3c,d), respectively, which exceed the MCLs. On the 79th day, organic matter and manganese in 0.4 and 1.5 m were 4.76 and 0.83 and 3.48 and 0.12 mg/L, respectively, which was slightly lower than that on the 78th day. In the next few days, nitrite along the filter depth continually decreased, and OMOB and MnOB gradually adapted to the nitrite-presented condition. Therefore, organic matter and manganese along the filter depth decreased. Manganese in the effluent decreased to 0.088 mg/L on the 80th day, which was lower than the MCLs; but the organic matter was dropped to lower than 3 mg/L until the 82nd day; the reason may be that OMOB was more sensitive to nitrite than MnOB [8]. Finally, organic matter and manganese decreased to 2.52 and 0.042 mg/L on the 83rd and 81st days.

When the influent ammonia increased to around 2 mg/L on the 108th day, nitrite was accumulated in the biofilter, too, and organic matter and manganese removal were also inhibited (Table 3). Organic matter and manganese were dropped to lower than 3 and 0.1 mg/L on the 113th and 112th day, respectively. Manganese was lower than 0.1 mg/L 3 days later after ammonia increased to around 1 from 0.5 mg/L, while manganese was lower than 0.1 mg/L. The reasons were as follows: (1) the concentration of nitrite was much higher on the 108th day (0.24 mg/L) than that on the 78th day (0.14 mg/L), (2) nitrite was present in the biofilter 4 days with high concentration (>0.1 mg/L) after ammonia increased to about

2 from 1 mg/L, while nitrite was present 2 days after ammonia increased to about 2 from 1 mg/L. In addition, organic matter and manganese decreased to 2.82 and 0.025 g/L on the 114th and 113th day, although nitrite in 0.8 m was 0.43 mg/L, meaning OMOB and MnOB adapted to the nitrite presented condition. Therefore, in order to reduce the impact of nitrite on biological organic matter and manganese removal, suitable inoculating bacteria should be collected from the biofilter for organic matter, manganese, and ammonia removal, since the presence of NOB would quickly oxidize the generated nitrite, and the OMOB and MnOB and MnOB would adapt to the nitrite presented conditions.

Table 3. (a) Ammonia concentration profiles along the filter depth when ammonia increased to 1 and 2 mg/L, respectively. (b) Nitrite concentration profiles along the filter depth when ammonia increased to 1 and 2 mg/L, respectively. (c) Organic matter concentration profiles along the filter depth when ammonia increased to 1 and 2 mg/L, respectively. (d) Manganese concentration profiles along the filter depth when ammonia increased to 1 and 2 mg/L, respectively. (d) Manganese concentration profiles along the filter depth when ammonia increased to 1 and 2 mg/L, respectively.

Filter Depth (m)	(a) Ammonia (mg/L)												
0	1.04	1.06	1.08	1.00	1.08	1.07	1.93	2.02	2.04	2.09	2.01	2.07	2.00
0.4	0.63	0.59	0.55	0.49	0.49	0.48	1.30	1.27	1.24	1.23	1.16	1.16	1.13
0.8	0.45	0.31	0.21	0.17	0.11	0.084	0.87	0.74	0.61	0.49	0.38	0.31	0.29
1.2	0.29	0.15	0.11	0.070	0.065	0.052	0.56	0.34	0.24	0.19	0.10	0.062	0.071
1.5	0.18	0.074	0.039	0.048	0.053	0.033	0.33	0.24	0.11	0.05	0.026	0.015	0.050
(b) Nitrite (mg/L)													
0	0.0028	0.0016	0.0043	0.0046	0.0042	0.0030	0.0026	0.0018	0.0032	0.0015	0.0020	0.0012	0.0013
0.4	0.082	0.065	0.047	0.037	0.021	0.013	0.041	0.053	0.030	0.011	0.014	0.013	0.011
0.8	0.13	0.11	0.085	0.066	0.035	0.010	0.26	0.24	0.19	0.15	0.11	0.086	0.043
1.2	0.14	0.11	0.081	0.054	0.024	0.0073	0.29	0.22	0.17	0.13	0.097	0.041	0.012
1.5	0.14	0.095	0.064	0.035	0.0091	0.0039	0.24	0.16	0.13	0.092	0.058	0.0025	0.0017
	(c) Organic Matter (mg/L)												
0	5.96	5.80	6.51	6.01	6.41	5.85	5.82	6.02	6.27	5.98	6.36	6.07	6.21
0.4	5.01	4.76	5.01	4.48	4.33	3.77	4.83	4.57	4.64	4.30	4.39	3.95	4.09
0.8	4.35	4.06	4.36	3.49	3.83	3.07	4.19	4.00	4.08	3.83	3.75	3.34	3.37
1.2	3.93	3.65	3.90	3.07	3.32	2.73	3.81	3.64	3.61	3.41	3.47	3.07	3.04
1.5	3.60	3.48	3.53	3.25	2.97	2.52	3.63	3.38	3.38	3.17	3.25	2.90	2.82
(d) Manganese (mg/L)													
0	1.17	1.17	1.12	1.17	1.12	1.18	1.22	1.22	1.24	1.19	1.22	1.27	1.29
0.4	0.86	0.83	0.80	0.75	0.72	0.70	0.87	0.85	0.85	0.79	0.77	0.76	0.077
0.8	0.57	0.53	0.48	0.37	0.29	0.23	0.61	0.55	0.51	0.42	0.36	0.28	0.28
1.2	0.34	0.29	0.24	0.15	0.095	0.054	0.43	0.38	0.31	0.21	0.13	0.076	0.072
1.5	0.16	0.12	0.088	0.042	0.025	0.021	0.29	0.24	0.17	0.11	0.083	0.033	0.025

3.3. Kinetics of Biological Organic Matter, Ammonia, and Manganese Oxidation

Contaminant removal kinetics in water treatment can provide information on the time required to efficiently remove a specific contaminant, which is necessary for sizing treatment units [20]. Therefore, the removal kinetics of organic matter, ammonia, and manganese in the biofilter for simultaneous removal of the pollutants was investigated, since kinetics were valuable for the optimization and design of the biofilter.

3.3.1. Kinetics of Biological Organic Matter Oxidation

It was well established that organic matter could be removed from potable water by biological systems, and the efficiency of organic matter removal in the biofilter has been calculated. In this experiment, the influent organic matter was 6.27 mg/L, and the residual concentration was 2.68 mg/L, which was lower than the MCL (Figure 5a). In addition, the results have been expressed as $ln[(COD_{Mn})_t/(COD_{Mn})_o]$ versus time (EBCT) (Figure 5b). At constant DO concentration and pH value, it was found that organic matter



oxidation followed a first-order kinetic rate from the linearity of the curves, given by the following equation:

Figure 5. COD_{Mn} concentration profiles along the filter depth for COD_{Mn} feed concentration of approximately 6 mg/L (**a**), linear regression analysis of COD_{Mn} depletion in relation with the empty bed contact time (**b**).

The kinetic constant was 0.0268 min⁻¹, and the calculated half-life constant of organic matter oxidation was 24.236 min. The calculated half-life constant was high because organic matters in the influent were mainly refractory organic matters.

3.3.2. Kinetics of Biological Ammonia Oxidation

The kinetics of biological ammonia oxidation was also investigated. Ammonia in the influent was 2.07 mg/L, and the removal rate of ammonia was higher than 99% (Figure 6a). In addition, the results have been expressed as $ln[(NH_4^+ - N)_t/(NH_4^+ - N)_o]$ versus time

(EBCT) (Figure 6b). From the linearity of the curves it was found that ammonia oxidation followed a first-order kinetic rate, given by the following equation:

$$-\frac{d(NH_4^+ - N)}{dt} = k(NH_4^+ - N)$$
(5)

for constant DO concentration and pH value. The kinetic constant was 0.268 min^{-1} , and the calculated half-life constant of ammonia oxidation was 2.583 min.



Figure 6. $NH_4^+ - N$ concentration profiles along the filter depth for $NH_4^+ - N$ feed concentration of approximately 2 mg/L (a), linear regression analysis of $NH_4^+ - N$ depletion in relation with the empty bed contact time (b).

3.3.3. Kinetics of Biological Manganese Oxidation

In the biofilter for simultaneous organic matter, ammonia, and manganese removal, the influent manganese was 1.19 mg/L (Figure 7a). The effluent manganese decreased to 0.022 mg/L, and the corresponding removal rate was 98.12%. Based on the results obtained, the oxidation kinetics of manganese can be calculated by assuming that all manganese is

(6)

oxidized and then removed by a biofilter. By keeping DO constant and pH constant, the manganese loss rate will be first-order kinetics, i.e.:



Figure 7. Mn^{2+} concentration profiles along the filter depth for Mn^{2+} feed concentration of approximately 1 mg/L (a), linear regression analysis of Mn^{2+} depletion in relation with the empty bed contact time (b).

A plot of $\ln[(Mn^{2+})_t/(Mn^{2+})_o]$ versus time (EBCT) would be linear if the kinetics of manganese oxidation were indeed first order, and the slope of such a plot would be -k value. Figure 7b indicated that the $\ln[(Mn^{2+})_t/(Mn^{2+})_o]$ versus time (EBCT) was linear. The value of k was 0.216 min⁻¹ and the half-life time for the depletion of manganese was 3.202 min in this experiment, which was much higher than 1.010 min [20]. The reasons were as follows: (1) Although a similar biofilter was used, only a kind of contaminant (manganese) was removed in their experiment, while organic matter, ammonia, and manganese were simultaneously removed in this experiment. (2) The diameter of manganese sand in their biofilter was only 0.8–1 mm, which was much smaller than that in this experiment (8~10 mm). The size of the filter material plays a key role in the removal efficiency of contaminants [14]; the smaller size of the filter material, the higher the removal efficiency of the contaminants. The value of k (0.216 min⁻¹) in this experiment was higher than 0.174 min⁻¹ [22] and 0.153 min⁻¹ [18].

The results clearly showed that the rate of ammonia oxidation was faster than manganese oxidation, and the rates of ammonia and manganese oxidation were much faster than organic matter oxidation under the specified experimental conditions.

4. Conclusions

The efficiency of organic matter and manganese removal was adversely affected by nitrite generated in the biofilter during the start-up process, and their removal efficiency quickly increased after the nitrite was completely oxidized. Organic matter, ammonia, and manganese were mainly removed in 0~0.8 m of the filter depth in the steady phase. The efficiency of organic matter and manganese removal was also adversely affected during the process of influent ammonia increase, and the efficiency of organic matter removal was more adversely affected. The longer the nitrite was present in the biofilter, the higher efficiency of organic matter, and manganese removal was adversely affected. Biological organic matter, ammonia, and manganese oxidation in the biofilter all followed a first-order kinetic rate. The influence of nitrite on the structure of microbial communities in the biofilter will be investigated in the future.

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