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Simultaneous removal of iron, manganese and ammonia from groundwater: upgrading of waterworks in northeast China

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ABSTRACT

The municipal water supply of Songbei District in Harbin, Northeast China, relied on local groundwater which contained high concentration of iron (about 15 mg/L), manganese (about 1.5 mg/L) and ammonium (about 1.1 mg/L). The waterworks had a two-stage filtration process, including the first purification filters for the removal of iron and the second one for the removal of manganese and ammonium. The total treatment capacity was 10,000 m^3/d. In order to double it to meet the increasing water-supply demand, the upgrading of the waterworks from operation in series to operation in parallel by the simultaneous removal of iron, manganese and ammonium in single biofilter was recommend. After inoculation of bacterial solution, aeration was enhanced from about 4.5 mg/L to almost 10 mg/L, by adding of cascaded aeration and perforated pipe spargers, to meet the oxygen demand in the biofilter. And the filter-layer was optimized, by adopting the dual-media filter, to reduce the effect of ferrous on biofilter for manganese removal. Finally, the waterworks was successfully transferred into the one-stage filtration process and the concentration of iron, manganese and ammonium in the treated water was about 0.20, 0.05 and 0.17 mg/L, superior to the national standards for drinking water (GB5749-2006). Adequate dissolved oxygen and dual-media filter are beneficial to biological manganese removal from groundwater, in the condition of high concentration of ammonia nitrogen and ferrous ion.

Keywords: Iron; Manganese; Ammonium; Groundwater; Simultaneous removal

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1. Introduction

Groundwater is used not only for people's living but also for industrial and agricultural production almost everywhere in the world, and sometimes it is the only water resource available in many areas. However, groundwater is often contaminated by inorganic pollutants [1]. It is a common phenomenon for the groundwater to contain iron and manganese [2]. And the widely use of fertilizers induces the increasing of the concentration of ammonium in the groundwater [3]. Iron and manganese cause aesthetic, organoleptic and operating problems [4]. In addition, manganese is adverse for the central nervous system [5]. When water is disinfected with chlorine (Cl_2), ammonium can react with chlorine and produce carcinogenic materials [6,7]. In China, according to the last directive, the standards for drinking water quality (GB5749-2006) [8], the maximum admissible concentration (MDC) for these pollutants are: 0.30 mg/L for iron, 0.10 mg/L for manganese and 0.50 mg/L for NH_4^+–N.

The processes available for the removal of iron and manganese are either physico-chemically or biologically based. Iron and manganese most appear as soluble ions (Fe^{2+}, Mn^{2+}) in groundwater, and Fe^{2+} can be easily removed by simple aeration, subsequently precipitation or filtration. But the

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oxidation of Mn^{2+} by oxygen alone is a slow process unless the pH is raised above neutrality [9]. However, under the catalysis of the manganese oxidizing bacteria (MOB), the Mn^{2+} oxidation rates increase by at least 3–5 orders of magnitude [10]. For the removal of manganese, there is a preference to add chemical oxidants, such as chlorine, ozone and potassium permanganate, sometimes lime in the USA [11], while in Europe which is preferably avoided. Various biological iron and manganese removal systems have been widely used for decades [12]. Comparing with the chemical treatment, the biological process is more efficient and economical. Similarly, because of the high costs and undesirable products induced by the chemical process, biological ammonium removal is preferably adopted [13].

Ammonium, iron and manganese are often simultaneously present in groundwater above the MDC for human consumption, and the diverse Redox potentials needed for the oxidation of these pollutants made the simultaneous biological removal difficult [14]. Mouchet brought forward a three-stage process: biological iron removal, nitrification of ammonium in a granular aerated biofilter, final biological filtration for the complete nitrification and manganese removal [12]. However, the simultaneous removal process has been studied intensely. It is said that two-stage filtration process is needed for the removal of iron and manganese from groundwater, when the iron and manganese concentration exceeds 5 and 1.5 mg/L, respectively [15]. However, in Northeast of China, using the "one cascaded aeration/one filtration" biological process, two plants has been built and achieved the simultaneous removal for the high concentration of iron and manganese from groundwater (For Lanxi Plant: $10 < \text{TFe} < 15$, $0.65 < \text{TMn} < 1.1$; For Jiamusi Plant: $14 < \text{TFe} < 18$, $0.5 < \text{TMn} < 1.0$; unit: mg/L) [16,17], but the mature periods of the biofilters were longer than half a year. Many researchers find that the removal of manganese follows the complete nitrification of NH_4^+–N, and the start-up period of a biofilter for the removal of manganese is typically 1–2 months, while when the groundwater contains both NH_4^+–N and Mn^{2+} it can take several months [18]. Simultaneous biological removal of ammonium, iron and manganese from potable water using a trickling filter has been extensively studied [19,20], and the filter presented good performance with the feed concentration varying in a low levels.

This research was about the simultaneous removal of iron, manganese and ammonium in a higher concentration level (Fe^{2+}: 14~18 mg/L; Mn^{2+}: 1.1~2.8 mg/L; NH_4^+–N: 1.1 mg/L) by rapid sand biofilter, and all derived from the upgrading of a waterworks for the groundwater treatment, where a two-stage filtration process had been adopted, and could remove high concentration of ammonium, iron and manganese from the groundwater. Recently, its production capacity needed to expand to meet the ever increasing water-supply demand. However, due to the limitation of land occupation, it was impossible to build a new process, and there was only one way to excavate the potential of the original treatment process. So the one-stage filtration process with simultaneous removal of ammonium, iron and manganese for the upgrading of the waterworks was adopted. By converting the two-stage filtration in series into one-stage filtration in parallel, the waterworks doubled the treatment capacity and only some pipeline transformation have been done, with a little adjustment of aeration and filter units. The whole process was presented in detail as follows. The mature process of biological manganese removal filter was summarized, including the effects of high concentration of Fe^{2+} and NH_4^+–N and the solution put forward.

2. Materials and methods

2.1. Treatment unit of the former process

The waterworks was built in 1997 in Harbin which is the capital city of the Heilongjiang province of China and the total treatment capacity was 10,000 m^3/d. At the beginning, the plant was designed to remove only iron and manganese from the groundwater, and the concentration of the iron and manganese was about 3 and 2 mg/L during the monitoring period (1996–1997). But recently the concentration of iron and ammonium increased (Table 1). The treatment process consisted of 6 stages, as shown in Fig. 1a: (1) cascaded aeration, (2) filtration for the removal of iron, (3) intermediate lifting, (4) mechanical aeration, (5) filtration for the removal of manganese and (6) disinfection using Cl_2.

- Firstly the groundwater was subjected to cascaded aeration, and the height of the cascade was about 1.5 m. After the cascaded aeration, the raw water contained dissolved oxygen (DO) of about 4.5 mg/L.
- The first purifying room had 5 rapid sand filters ($1^{\#}$~$5^{\#}$) which were in the same scale, the filter area of each filter was 20 m^2. The filter layer consisted of sand of total height 1m, and the diameter of sand grains was 0.6~1.2 mm. The design filtration velocity was 5 m/h, and backwashing took place once every 3~4 d, operated at an intensity of 15~17 L/sm^2 for 5~7 min. The removal of iron by the first-stage filtration almost based on chemically, and the concentration of iron in the effluent could be reduced to 0.2~0.4 mg/L, but the concentration of ammonium and manganese almost remained same.
- The effluent of the first stage filtration was collected in the intermediate reservoir and pumped into the mechanical aeration tank.

Table 1
Characteristics of the groundwater

Parameter	Value	MDC
Temperature(°C)	7	
pH	6.7~6.9	6.5~8.5
DO mg/L	0	
Fe^{2+} mg/L	14~18	TFe < 0.3
Fe^{3+} mg/L	0.1~0.5	
Mn^{2+} mg/L	1.1~2.8	0.1
NH_4^+–N mg/L	1.1	0.5
NO_2^-–N mg/L	<0.01	
NO_3^-–N mg/L	<0.04	20
SO_4^{2-} mg/L	30.77	250
Total hardness, $CaCO_3$ mg/L	220	450
Alkalinity, $CaCO_3$ mg/L	232	
Conductivity, us/cm	502	

- The mechanical aeration tank was used to increase the pH and DO of the water for the manganese removal, and the depth was 4 m. The hydraulic retention time was 20 min, after that the DO in the water could increase to 10 mg/L.
- The second purifying room was the same with the first in the scale, but the filters (6#~10#) had biological activity and they were efficient for the removal of manganese and ammonium. Backwashing took place once in every 15 d, with the intensity of 15~17 L/sm^2 for 7 min.
- The water was disinfected with Cl_2 in the last stage, and by controlling the residual chlorine of the treated water in the concentration of 0.3~0.4 mg/L, microbiological contamination during the water supply could be avoided.

2.2. Upgrading of the waterworks

Fig. 1b shows the one-stage filtration process, which was used for the upgrading of the plant to double the production capability. So two key tasks were needed to be completed to ensure effluent quality, one was the cultivation of the biological activity of the first-stage filters for the removal of Mn and NH_4^+–N, and the other was making the second-stage biofilters have not only the ability to removal Mn and NH_4^+–N but also the ability to removal high concentration of iron. The series filtration process had been used all though the upgrading process until it was confident that the effluent quality of the one-stage filtration could reach the national standards after upgrading, so that the water supply for the people could be guaranteed. And during the operation of parallel, in the condition of total iron 15 mg/L, and the final filtration velocity of 5 m/h, the backwash cycle was set as 24 h with the strength of 12~15 L/sm^2 and time of about 6~10 min.

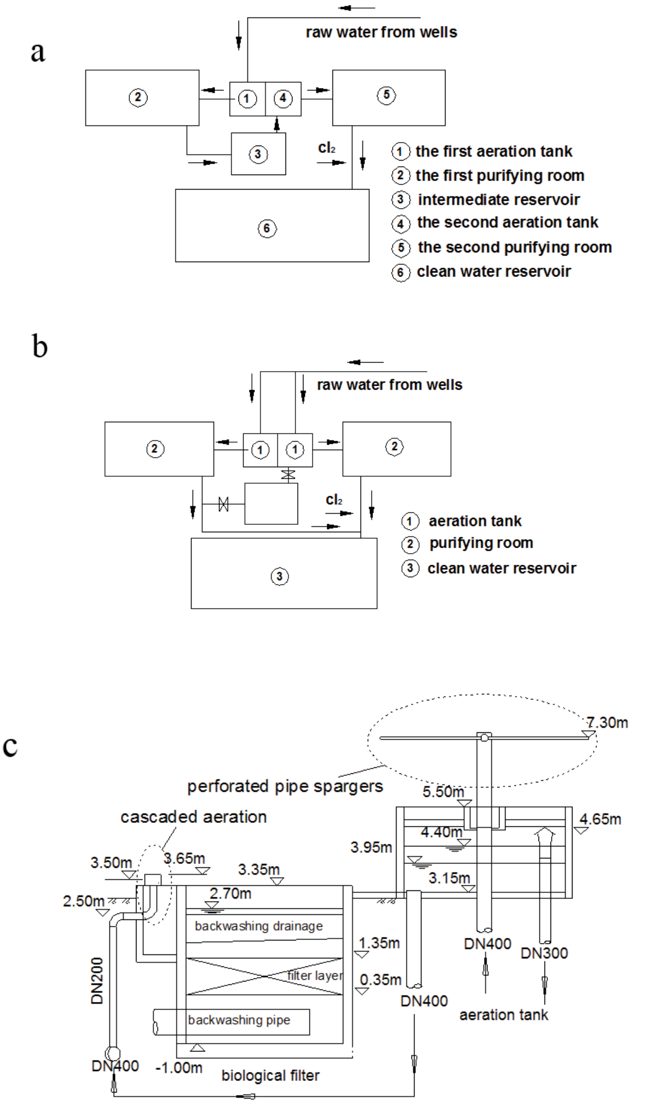

Fig. 1. Flow chart of waterworks: (a) Two-stage filtration process in series, (b) One-stage filtration process in parallel and (c) Sketch map of the aeration enhancement for the waterworks.

2.3. Groundwater characteristics

The groundwater was pumped from wells (depth 30~50 m), and because of the latitude of the Waterworks, the raw water temperature was only 7°C. It contained high concentration of iron and manganese, which was typical for most area of Heilongjiang province in China. The chemical composition of the groundwater is presented in Table 1, together with the MDC by the national standards for drinking water quality (GB5749-2006) of China. There were 11 wells in all in the waterworks, and the chemical composition of the raw water varied with the scheduling of the wells slightly.

2.4. Analytical methods

The influent was taken from the reserved sampling port of the inlet pipe of the cascaded aeration tank and the effluent was taken from the outlet pipe of the biofilter. All samples are analyzed immediately in the laboratory of the Water Treatment Plant, so no storage measures were adopted. All iron, manganese and ammonia nitrogen analyses were performed by the spectrophotometer in accordance with standard methods [21]. Dissolved oxygen was measured by the Dissolved Oxygen Meter (oxi340i, WTW), pH were determined using an electrode (pH/oxi340i, WTW).

Sand samples were taken from the surface, in depth of 20, 40 and 80 cm in the stable operation biofilter, then loaded into the sterilized 50 mL centrifuge tube, and refrigerated at –20°C immediately. Single-strand conformation polymorphism (SSCP) was carried out as previous reports [22,23].

3. Result and discussion

3.1. Inoculation and cultivation of biofilters for manganese removal

3.1.1. Early stage of the inoculation and cultivation process for first-stage biofilters

Native bacteria were collected from the water supply system, and then iron oxidizing bacteria (IOB) and MOB were isolated to domestication and multiplication according to the method described by Li et al. [24]. Finally 1,500 L bacteria solution was prepared, and it was inoculated into filters 1#~5# uniformly. In order to create a friendly environment and accelerate the formation of the biological filter layer, the backwashing intensity was reduced to 10~12 L/sm^2.

After the inoculation for the filters $1^\#$~$5^\#$, the concentration of iron and manganese in raw water and filtrate were measured daily. The culture course of the five filters were almost the same, and the data (averaged for 3 d) of $3^\#$, $5^\#$ are shown in Fig. 2. The manganese removal ability for the filters increased soon after the inoculation, this could be attributed to the function of biology, the inoculated IOB and MOB flowed deep into the filters, some of them were intercepted and subsequently adsorbed to the filter media. Under the weak backwashing, some bacteria could dwell long in the filters and secrete the enzyme for the oxidation of iron and manganese [25].

However, the manganese removal rate halted around 20% for the next 4 months. This can be explained by our previous filter column experiments [26,27], for the simultaneous removal of iron, manganese and NH_4^+–N in the biofilter, almost Fe^{2+} got oxidized and removed in the upper part, for almost NH_4^+–N in the upper and the middle parts, for almost Mn^{2+} in the middle and the lower parts. So when the DO in the influent is not ample, the oxygen can be depleted quickly in the upper part of biofilter by the reductive material including Fe^{2+}, NH_4^+–N and others, and the lower part of the biofilter can present anaerobic. In the treatment process of this plant, the DO in the water after the cascaded aeration was only about 4.5 mg/L, and oxygen had not been detected in the filtrate all the time. It was suggested that the filters maybe presented anaerobic in the lower part and where the MOB couldn't get enough oxygen for the biological oxidation of Mn^{2+}. Actually the all demand oxygen for the oxidation of Mn^{2+} is only 0.435 mg/L according to the chemical reaction equation (Mn^{2+} account as 1.5 mg/L).

In this condition the MOB couldn't accumulate in the filters and of course the manganese removal ability of the biofilters didn't increase along the time. And unfortunately the increasing of Fe^{2+} in the raw water induced the even more quickly consumption of the DO in the water, the effluent turned even more badly later, sometimes with the manganese concentration larger in the effluent than in the influent, which indicated the manganese was released.

For ammonia nitrogen in effluent, it fluctuated between 0.8 and 1.0 mg/L. There was no downward trend. It is no doubt that the removal of ammonia nitrogen from effluent was limited by dissolved oxygen exactly as the removal of manganese. However, the concentration of iron ion in effluent has been further reduced, stabilized less than 0.3 mg/L, which met the national maximum allowable concentration standard of China (0.3 mg/L), basically between 0.1 and 0.2 mg/L. This was attributed to that the iron oxides produced in the filter layer were better intercepted and removed due to the trapping effect by microorganisms [28].

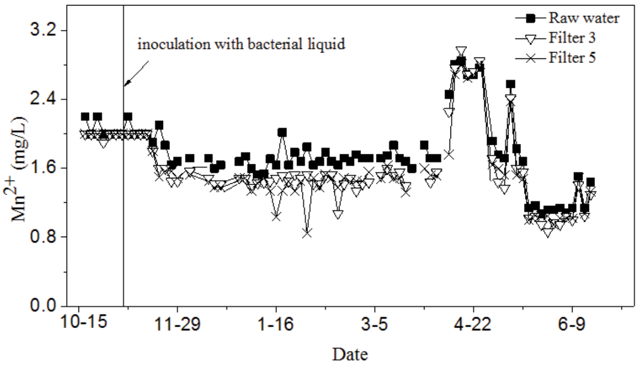

Fig. 2. Variation of Mn in raw water and filtrate of the filters.

3.1.2. Aeration enhancement

The groundwater abounds with reductive Fe^{2+}, Mn^{2+} and NH_4^+–N, and is lack of NO_3^-–N and SO_4^{2-}, and it is strictly anoxic (DO = 0). The purification of these contaminants in the groundwater all based on oxidation, chemically or biologically, so the concentration of DO is significant. According to the chemistry reaction equations, the demand oxygen for simultaneous removal of these pollutants can be estimated, as shown in Eq. (1), and the portion contributed by oxygen loss and consumption of other reductive materials, such as H_2S and organic matters, is not included.

$$[O_2] = 0.143[Fe^{2+}] + 0.29[Mn^{2+}] + 4.6[NH_4^+\text{–N}] \tag{1}$$

Using the highest concentration of Fe^{2+}, $Mn^{2+}$and NH_4^+–N for the rough estimate, the needed concentration of DO is about 8.5 mg/L. Obviously the former cascaded aeration tank can't afford ample DO for the purification, and the enhancement is needed, which has been done finally, as shown in Fig. 1c. Firstly cascaded aeration was added in the purification room, and the DO in the raw water was increased to 5.5 mg/L from the former 4.5 mg/L, but it is not enough all the same. Until the perforated pipe spargers were adopted in the aeration tank to enhance the aeration, and the DO was increased to 10 mg/L. In order to keep the same hydraulic conditions and reduce the electricity charge, the mechanical aeration tank in the second-stage was also transformed into the same before the waterworks was operated in parallel, so the cascaded aeration was added in the second purification room.

After the aeration system was strengthened, the dissolved oxygen of the inlet water into the filter was increased from the original 4.5 mg/L to more than 8.5 mg/L. The specific influent DO value was shown in the Table 2, it was reached above 8.5 mg/L after the spray aeration, which can basically guarantee the dissolved oxygen needed for the water purification. And after the cascaded aeration added in the filter, DO was generally around 10 mg/L, and DO concentration of effluent was about 2 mg/L, had a slight surplus and could cope with certain water quality fluctuations. (*Note*: the determination time was after parallel operation.)

3.1.3. Optimization of filter layer

The key structure of biological manganese fixation and removal technology is biofilter. The main function body of biofilter is the manganese removal biofilm on the surface of filter material. The formation and maintenance of this film directly affects the start-up and daily operation of groundwater treatment plant for iron and manganese removal. The film is composed of iron-manganese oxidizing sediment, IOB-MOB and their secretion and metabolites. The sediments and metabolites secreted by bacteria were taken as the main structures to provide space for the survival and reproduction of

Table 2
DO of each section of process

Parameter	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#
DO of raw water after the sparger (mg/L)	8.60					8.80				
DO of influent before the filter (mg/L)	10.10	9.60	9.63	10.10	10.18	10.28	10.35	9.90	10.31	10.25
DO of effluent after the filter (mg/L)	2.57	2.18	2.02	1.36	3.23	3.48	3.67	3.05	3.21	2.80

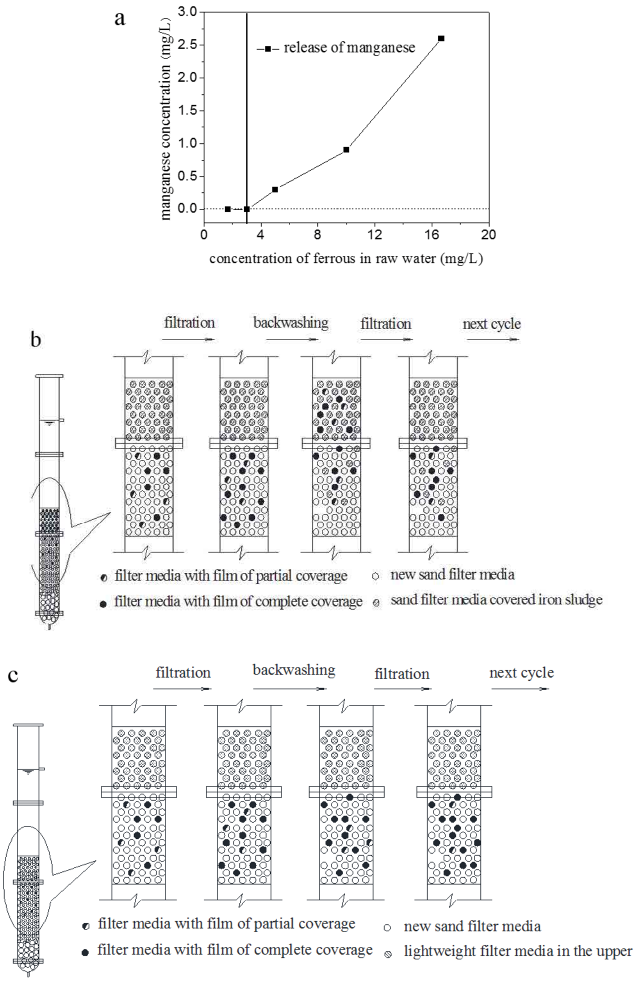

Fig. 3. Release of manganese and its countermeasure: (a) dissolution of manganese under different ferrous concentrations, (b) model of biofilter using mono-media and (c) model of biofilter using dual-media.

IOB-MOB [25]. Previous studies showed that the start-up of biological manganese removal filter was prolonged sharply when the iron ion concentration of raw water is high, and the stability of mature filter was affected. Many researchers attributed it to the high concentration of ferrous in the raw water, which resulted in the formation of a large number of iron oxides and was intercepted by the filter, resulting in easy blockage of the filter, increased backwash frequency, which was not conducive to the cultivation of microorganisms for manganese removal [28]. However, according to the early data in this experiment, the concentration of manganese ion in the effluent was often higher than that in the influent, which indicated the release of reductive manganese. Therefore, 1.0 g of biofilm-mature filter media obtained from the secondary filter was used for immersion test (25 min) with raw water (diluted with distilled water to 50 ml with different ferrous ion concentration of 1.7, 3.0, 5, 10 and 16.7 mg/L). It was found that the reduction and release of manganese ions did exist, as shown in Fig. 3a. The release of manganese ion is positively correlated with the concentration of ferrous ion. Therefore, it can be inferred that when the raw water contains high concentration of ferrous ions, start-up or stable operation will be great impacted, because the biological manganese removal filter may be destroyed by high concentration of ferrous ions.

This course could be described as Fig. 3b: for the Mn-removal filter, the biogenic manganese oxides and the extracellular polymeric substances (EPS) structure the living space for the MOB, around the surface of filter media, forming the biofilm. This efficient Mn-removing biofilm was always located in the middle and lower part of the filter [29]. But some of the filter media will often be involved to the upper part of the filter after the backwashing in the mono-media filter, especially under the malfeasance operation, when the biogenic manganese oxides meet the Fe^{2+} in the raw water, the reaction: $Fe^{2+} + Mn^{4+} \rightarrow Fe^{3+} + Mn^{2+}$ will take place. In this situation, the living space for the MOB will collapse while the Mn^{4+} reduced into the water, which could always increase the manganese concentration in the effluent of biofilter. And the MOB will be washed out of the filter in the next backwashing. So in order to relax the admixture of the filter media during the backwashing process and protect the Mn-removing biofilm from damage caused by Fe^{2+}, the dual-media filter was recommended as shown in Fig. 3c. The lower layer is ordinary filter material (such as quartz sand) and the upper layer is lightweight filter material (such as anthracite) [16]. The dual-media filter can effectively prevent the filter material of lower layer from mixing into the upper layer, thus prevent the manganese removal biofilm accumulated in the lower layer from being destroyed when entering the upper layer after backwashing, which is conducive to the cultivation and stable operation of the manganese removal biological filter layer.

So before the operation in parallel for the waterworks, a height of 20 cm anthracite in the top of all the filters was added to structure dual-media filters. Previous studies have shown that inoculation with mature biofilter media could accelerate the maturation of biofilter. So a height of 15 cm mature filter media from the second purification filters was added into the first purification filters below the layer of anthracite, in order to accelerate the start-up process of the first purification filters and solve the growing contradiction of water supply and public requirements.

3.1.4. Maturation of biofilter layer for manganese removal

As shown in Figs. 4a and b, using filter 3# and 5# for example, after the accomplishment of the aeration enhancement in March, the manganese removal ability increased step by step, and great progress had been made from May to June, reducing the manganese concentration in the filtrate near to the national standards of China 0.1 mg/L. In order to operate the waterworks in parallel to expand the water supply capacity as soon as possible, the filter layers were adjusted as described ahead in July, it cost about 10 d for all the 10 filters. After that the first purification filters were immediately able to remove the Mn^{2+} below 0.1 mg/L under the filtration velocity of 4 m/h, and it is increased to 5 m/h later.

It could be found that the whole culture period cost about 4 months from mid-March to mid-July, after the aeration enhancement. Compared with the previous studies [17], where it cost almost 8 months for the maturity of the biofilter with the high concentration of iron (10~14 mg/L) and manganese (0.65~1.1 mg/L) in the influent, this study greatly shortened the start-up process, actually with the higher concentration. Although it couldn't be directly proved that the dual-media filter has played a key role, it could be inferred that there was a certain relationship. And it deserves more in-depth study in the future.

After the adjustment of aeration and filter bed, the removal ability of manganese and ammonia nitrogen in the first-stage filter became stronger, and the concentration of effluent became lower, which directly led to the operation of the second-stage filter for about one month with low concentration of manganese and ammonia nitrogen in influent. However, after parallel operation with the raw water as influent, the concentration of iron, manganese and ammonia nitrogen increased sharply, but the effluent of the filter basically reached the standard, indicating that the microbial system in the former second-stage filter, including MOB and ammonia nitrifying bacteria, had strong adaptability to the fluctuation of the influent water quality.

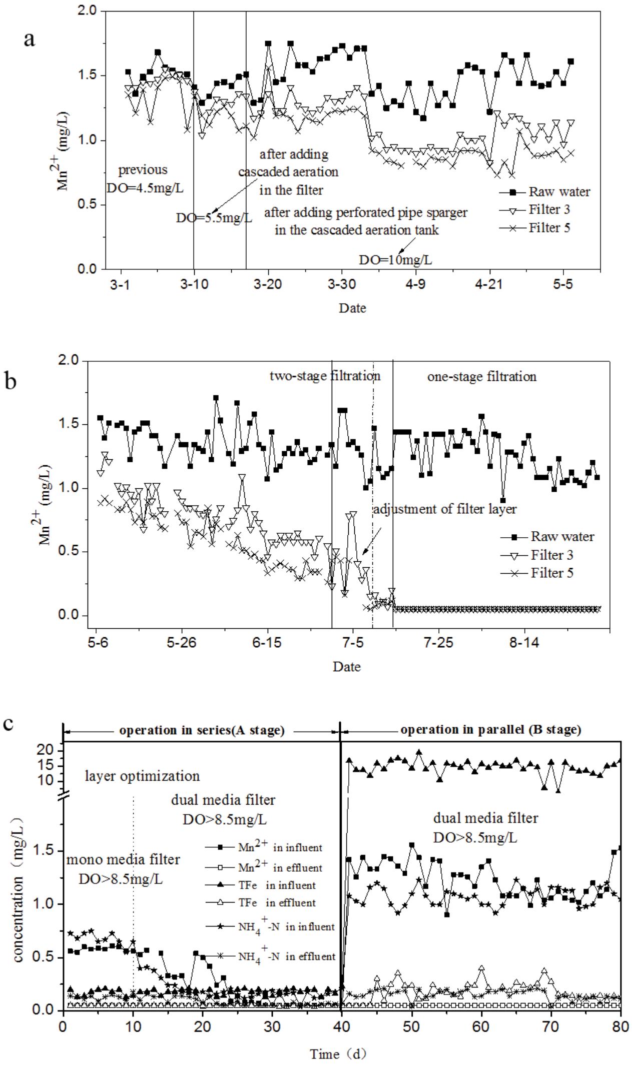

Fig. 4. Culture process of Biofilter: Variation of water quality in raw water and filtrate of the filters after the aeration enhancement and layer optimization (a) initial phase of first-stage biofilter, (b) later phase of first-stage biofilter and (c) second-stage biofilter (average of 6#–10#).

3.2. Removal of ammonium and its impact on manganese removal

Many previous studies have shown that it was difficult to remove NH_4^+–N and Mn^{2+} at the same time, owing to the different oxidation-reduction potentials(ORPs), it is proposed that ammonia nitrogen should be removed before manganese with a two-stage process [12]. However, with an upgrading of knowledge and technology, simultaneous NH_4^+–N and Mn^{2+} removal has been reported in a single-stage treatment [19,20].

As revealed in this study, the simultaneous removal of NH_4^+–N and Mn^{2+} indeed be achieved in a single-stage treatment. During the culture course of the biofilters, the removal of ammonium in the raw water was paid more attention to, so was the impact of ammonium upon the manganese removal. Filter 5# was fetched and studied, the experiment data is shown in Fig. 5. The ammonium removal ability of the filter 5# increased swiftly day by day after the accomplishment of the aeration enhancement, and one month later the ammonium in effluent remained at about 0.2 mg/L stably. It showed that even in the low temperature 7°C, the biological activity for the removal of ammonium was strong. The contact time was less than 15 min, but the removal rate could arrive at 80%, and after the waterworks operated in parallel,

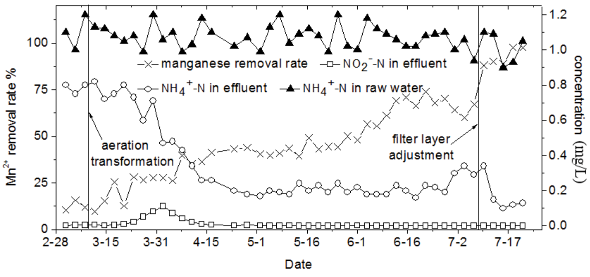

Fig. 5. Removal of ammonium and its impact on manganese removal for filter 5#.

it increased to nearly 90%, due to the decrease of the filtration velocity in the biofilters.

However, it was found that ammonia nitrogen had some effects on manganese removal in the following two aspects, including inhibition of manganese oxidation by the formation of nitrate and the competition of dissolved oxygen between manganese oxidation and nitrification.

First, biological ammonium removal includes two-stage nitrification processes: the ammonium into nitrites and the nitrites into nitrates. Vandenabeele et al. [30,31] found that NO_2^- had a marked inhibitory effect on the removal of Mn^{2+}. The concentration of NO_2^- accumulated along with the enhancement of the nitrification ability of the filters. For filter 5# the accumulation of NO_2^-–N persisted for about 3 weeks, the highest value was 0.112 mg/L, and the manganese removal efficiency halted about half a month.

Second, in the biofilter for the simultaneous removal of Mn^{2+} and NH_4^+–N, due to the influence of ferrous ions, the removal space of manganese is located in the middle and lower part of the filter after the removal of iron band in the upper part, while ammonia nitrogen can begin to oxidize in the upper part of the filter layer [28]. Therefore, if there is insufficient dissolved oxygen in the influent, oxygen will be exhausted in the upper part of the filter layer due to iron oxidation, nitrification of ammonia nitrogen and oxidation of other reducing substances. The MOB in the lower part of the filter cannot get any dissolved oxygen for the oxidation of manganese ions in water. Of course, the residual ammonia nitrogen in water also cannot be oxidized by the nitrifying bacteria in the lower filter layer because of the lack of dissolved oxygen. Finally, the Mn^{2+} and NH_4^+–N in the effluent exceed the standard, this situation has been validated in the culture process of first-stage biofilter mentioned above. But there were also different situations [32]. For the simultaneous removal of iron, manganese and ammonium in the approximately similar influent, when the dissolved oxygen in influent was 4 mg/L, the MOB won the competition of dissolved oxygen, with the concentration of manganese ion in the effluent below 0.1 mg/L and NH_4^+–N more than 0.8 mg/L. The reasons may be as follows: the size of filter material (1 mm) in this biological filter column was smaller, and the filtration speed was lower (2 m/h), the removal of iron was accomplished quickly, so the removal space of manganese was not compressed to a too low position. Therefore, there was an opportunity to use the residual dissolved oxygen in the filter to complete the biological oxidation of manganese. Finally, it could be infered that the competition for dissolved oxygen between the two biological oxidation processes mainly depends on the location.

3.3. Impact of high concentration iron on the second purification biofilters

For the waterworks' operation in parallel, the former second purification biofilters faced the high concentration of ferrous ions, and the adaptability of biological manganese removal filter layer got tested. Actually the biofilters lived up to the expectations, as mentioned above (Fig. 4c). After the waterworks' operation in parallel, the iron concentration in the filtrate was controlled at about 0.25 mg/L, and the ability of manganese removal in the biofilters wasn't affected. The reasons are as follows: Iron oxidation was proved to include physicochemical and biological oxidation [24], and physicochemical oxidation was more dominant than the other, the bio-oxidation improved the oxidation efficiency by only about 5%–6%. Early studies also told that chemical oxidation of Fe^{2+} to FeOOH was an autocatalystic reaction [25] and the start-up of filters for the iron removal needed only 7~10 d [27]. So in the first few days after the operation in parallel, under the condition of the adsorption capacity of the new anthracite and the oxidation capacity of biogenic manganese oxides, the iron concentration in the filtrate could be controlled in a low level, then the autocatalystic filter layer for the oxidation of Fe^{2+} would have grown quickly. At the beginning, according to the reaction law between ferrous ions and manganese oxides mentioned above, high concentration ferrous ions in the influent would inevitably contact the biological manganese removal filter layer, which would lead to the reduction and dissolution of manganese ions to a large extent. However, due to the strong manganese removal ability in the middle and lower parts of the filter layer, the reduced manganese ions would be oxidized and intercepted again, so it was not reflected in the effluent.

Yet in the first days, the iron concentration in the filtrate fluctuated after the backwashing of the filters, sometimes it could exceed 0.3 mg/L. The filtrate of the filter 6# and 9# were

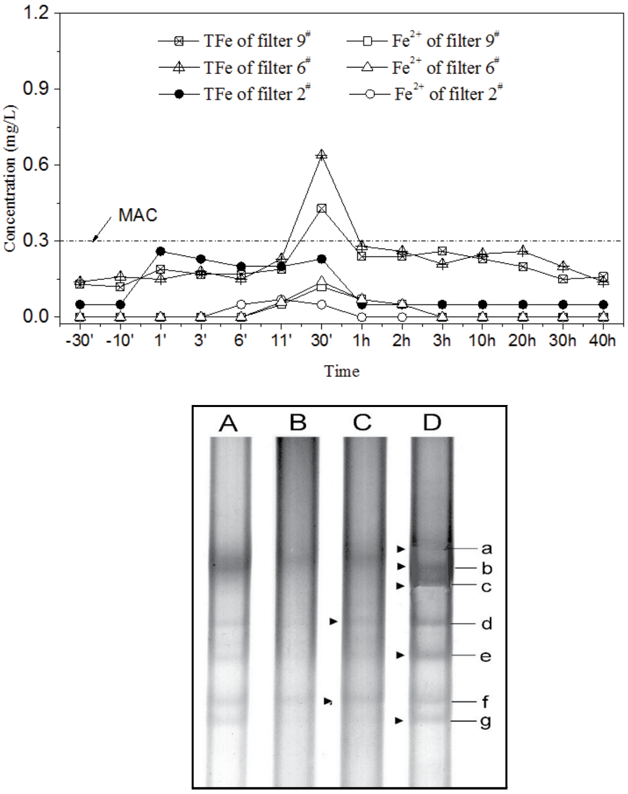

Fig. 6. (a) Concentration of TFe and Fe^{2+} in the filtrate before and after the backwashing (′ = min, h = hour), (b) SSCP profile of microbial communities in biofilter, depth of biofilter (*A* = 0 cm, *B* = 20 cm, *C* = 40 cm and *D* = 80 cm); ('σ' represents sequencing strip).

Table 3
Retrieve results of 8OTUs of Eubacteria by BLAST

Strip	Most similar sequence, sequence number	Similarity degree	Most similar genera
a	Uncultured bacterium, EU340160.1	98%	Uncultured bacterium
b-1	Uncultured bacterium, EU242876.1	99%	Uncultured bacterium
b-2	*Flavobacterium* sp. RI02, DQ530115.1	97%	*Flavobacterium*
c	*Clonothrix* fusca strain AW-b, DQ984190.1	94%	*Clonothrix*
d	Uncultured bacterium, DQ452498.1	96%	*Gallionella*
e	Uncultured *Ferribacterium* sp.,AJ890202.1	96%	*Ferribacterium*
f	Uncultured bacterium, AB240483.1	98%	*Zoogloea*
g	*Crenothrix* polyspora, DQ295890.1	97%	*Crenothrix*

monitored before and after the backwashing, compared with the filter 2# (Fig. 6a). For filter 6# and 9# the iron concentration increased after the backwashing and achieved the greatest value about 30 min later, subsequently it recovered to the initial situation through about 1 d. Fe^{3+} comprised the main iron species in the filtrate, the proportion was as high as about 80%. It would be concluded that after the backwashing the oxidation ability of Fe^{2+} in the filters was not affected, but was the filtration ability for Fe^{3+}. And it recovered along with the filters' operation.

3.4. Analysis of IOB and MOB

SSCP atlas showed that the microbial community structure change at different depth of the filter layer were not too obvious. The microbes represented by strips of d, e, and f existed at different depths of the filter (Fig. 6b). Microbial species in surface and filter depth of 80 cm were relatively increased, but microbes represented by strip g were almost extinct both at depth of 20 and 40 cm. After the 16S rDNA sequencing analysis of the dominant bands, 8 OTUs were obtained, of which Gallionella, Ferribacterium and other ferric bacteria existed at different depths in the whole filter (Table 3). It was due to the high concentration of ferrous ions in the influent quality: the higher the concentration of the ferrous ion, the greater the thickness of the filter layer required for ferrous ion oxidation and removal. With the influent of 14~18 mg/L ferrous ion, it needed about 60 cm~80 cm depth of filter layer for IOB distribution. Zoogloea, easy to form bacteria micelles and with strong adaptability, was the dominant bacteria in the filter, which was also the main functional group for manganese redox and played an important role in the stability of the system.

3.5. Long-term operation after upgrading

In the case of limited land occupation, only by replacing some pipes, valves and adjusting the aeration and filter layer partly, the potential of the primary filter was fully excavated. And the implementation of parallel operation has increased the purification capacity of waterworks from 1 × 10^4 m^3/d to 2 × 10^4 m^3/d. It cost only 3 million RMB, saving 20 million RMB in construction cost and 250 thousand RMB in electricity charges per year, compared with two stage process flow. And what's more, the water quality of the effluent was stable as shown in Fig. 7 by monthly average value.

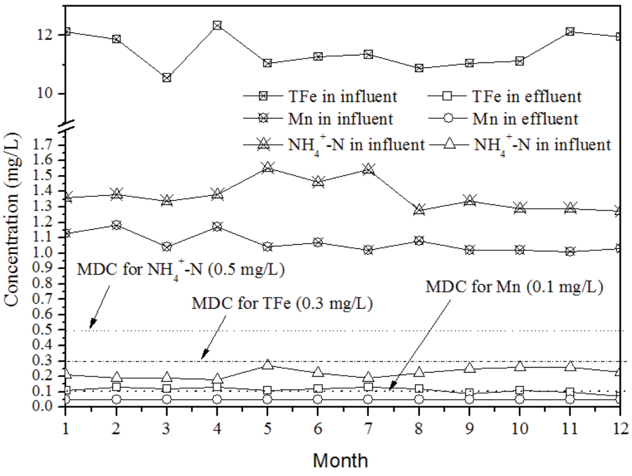

Fig. 7. Water quality of effluent after long-term operation (monthly average value during one year).

4. Conclusion

By the simultaneous removal of iron, manganese and NH_4^+–N, the waterworks accomplished the upgrading from operation in series to operation in parallel. It doubled the waterworks' production capacity and saved millions of dollars for the capital construction. And the following outlines were confirmed: (1) Biological removal of manganese and nitrification of NH_4^+–N could take place at the same time. (2) Dissolved oxygen was the key factor for the biological removal of manganese from the groundwater when containing NH_4^+–N. (3) Dual-media filter might maintain the efficiency for the simultaneous removal of high concentration of iron and manganese.

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