Application of biological process to treat the groundwater with high concentration of iron and manganese

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ABSTRACT

A biological process was adopted in a groundwater plant for iron and manganese removal. The process included low-level aeration and single stage biological filtration. The separated native iron and manganese oxidizing bacteria were inoculated to the filter bed alongside raw water containing high concentrations of iron and manganese after multiplication (Fe^{2+} 10–14 mg l^{-1}, Mn^{2+} 0.65–1.1 mg l^{-1}). The predominance of iron and manganese oxidizing bacteria were maintained in the filter by appropriately monitoring the operational parameters (filtration rate, backwash intensity, backwash duration and backwash period). Then the filter had a significant and stable ability for iron and manganese removal. The quality of the filtrate met the Chinese National Standard for Drinking Water with concentrations of 0.05–0.1 mg l^{-1} Total-Fe (T-Fe) and 0.05 mg l^{-1} Total-Mn (T-Mn) under the condition of the normal filtration rate (5–7 m h^{-1}). The process reduced investment costs by 6 million yuans (¥) and power costs by 250 thousand yuans (¥) per year compared with the traditional process (chemistry-contact oxidation including two-stage aeration and two-stage filtration).

Key words | biological filtering bed, groundwater, iron and manganese oxidizing bacteria, simultaneous removal

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INTRODUCTION

It is known that groundwater is the only water resource in many countries (Li & Liu 1989; Gao 2004; Zhang *et al.* 2005). It is a common phenomenon for the groundwater to contain iron and manganese (Fe^{2+}, Mn^{2+}) (Zhou & Zhu 1997; Murdoch & Smith 2000). The removal of iron and manganese has not been a neglected problem because excessive iron and manganese can affect human health and industry production (Liu 1988; Conrad & Umbreit 2002; Liu *et al.* 2002; Zhang *et al.* 2003). A lot of treatment processes have been developed since the end of the 19th century (Wong 1984; Thornton 1995; Aziz & Smith 1996; Gouzinis & Kosmidis 1998; Suzuki *et al.* 1998; Ellis *et al.* 2000). The discovery of iron and manganese oxidizing bacteria in filters has promoted the great progress in the field since the 1990 s (Zhang *et al.* 1996, 1997; Hedberg & Wahlberg 1998). Following the studies on iron and manganese oxidizing bacteria, biological filters came into birth for iron and manganese removal from groundwater (Seppanen 1992; Piao *et al.* 1998; Tamura *et al.* 1999). In 2001, a groundwater treatment plant was built in Shenyang, Liaoning province China, which adopted the novel biological process for iron and manganese removal. The satisfactory removal of iron and manganese and the low operation/maintenance costs have been reported (Li *et al.* 2005). The excellent quality of filtrate (Fe < 0.05 mg l^{-1}, Mn < 0.05 mg l^{-1}) proved the validity of the biological process for iron and manganese removal from groundwater (Fe^{2+}: 0.01–0.5 mg l^{-1}, T-Mn: 0.575–3.05 mg l^{-1}). In some areas, high concentrations of iron and manganese ($Fe^{2+} > 10$ mg l^{-1}, Mn > 0.65 mg l^{-1})were detected in groundwater. For this water, the cost and filtrate quality were not satisfactory using traditional processes such as strong oxidants oxidation, chemistry–contact oxidation

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and so on. After a lot of research, the biological process was adopted in the water treatment plant. The operational performance of the water treatment plant is presented in this paper in detail.

Groundwater characteristics

Lanxi, a small town lies in the north-west of Harbin which is the capital city of the Heilongjiang province. The average temperature is below −30 °C in winter because of its latitude. The town has a population of 80 thousand. Groundwater became the necessary water source because of the pollution of the river, and is pumped from open wells with depths of 10 m and diameters of 6 m. The output is 2500 $m^3\,day^{-1}$. The concentrations of Fe^{2+} and T-Mn were 10–14 $mg\,l^{-1}$ and 0.65–1.1 $mg\,l^{-1}$, respectively. The groundwater characteristics during the monitoring period (Oct 22, 2003-Sep 10, 2004) are shown in Table 1.

The design of the water treatment plant

The total treatment capacity of the groundwater treatment plant is $1.5 \times 10^4\,m^3\,day^{-1}$ including filters, cascade aeration tanks, clean water reservoir, backwash pump house, pump house, office building, furnace and laboratory. Silica sand was adopted as the filter medium with the diameter of 0.5–1.2 mm. The depth of the filter bed is designed to be 1000 mm. A plan of this water treatment plant is shown in Figure 1. The main treatment units and their parameters are shown in Table 2. The adopted flow chart is shown in Figure 2. The main advantage of the process is the simultaneous removal of iron and manganese in one filter without any additional strong oxidants.

MATERIALS AND METHODS

Iron and manganese assays were performed using an atomic absorption spectrophotometer (Jena Vario 6, Analytik Jena A G, Germany). Prior to atomic absorption spectrophotometry, all samples were quickly acidified ($pH < 2$) with hydrochloric acid to avoid oxidation of iron when exposed to air. Before assay, the water samples do not need to be acid-decomposed.

Detection of the bacteria was performed using a microscope (Olympus BX-41TF, Olympus Optical Co. Ltd, Japan). The population of the bacteria was detected using the method of most probable number (MPN). The sand (5 g wet sand) was sampled at different depths along the filter bed at the same time. Each sample was dipped in 10 ml sterilized distilled water and shook vigorously for 30 min. The suspension was diluted to 10^1–10^7 fold, then 0.1 ml of the diluted suspension was added to test tubes containing special culture medium for iron and manganese oxidizing bacteria, and incubated at 25 °C for 15 days.

The components of the special culture medium for iron and manganese oxidizing bacteria were 0.5 g NH_4NO_3, 10 g Ferric Ammonium Citrate, 0.1 g $CaCl_2$, 0.2 g $MnSO_4 \bullet H_2O$, 0.5 g K_2HPO_4, 0.5 g $MgSO_4 \bullet 7H_2O$, 0.5 g $NaNO_3$, 1,000 ml H_2O, pH 6.8–7.2.

Table 1 | Characteristics of the groundwater

Parameter	Value	Parameter	Value
Temperature (°C)	10.0–11.0	NO_3^- ($mg\,l^{-1}$)	0.04–1.36
pH	6.5–6.8	HCO_3^{2-} ($mg\,l^{-1}$)	97.63–573.59
Fe^{2+} ($mg\,l^{-1}$)	10–14	T-Mn ($mg\,l^{-1}$)	0.65–1.1
NH_4^+ ($mg\,l^{-1}$)	0.04–1.36	Ca^{2+} ($mg\,l^{-1}$)	15.9–103.37
Fe^{3+} ($mg\,l^{-1}$)	0.1–1	Mg^{2+} ($mg\,l^{-1}$)	4.83–33.78

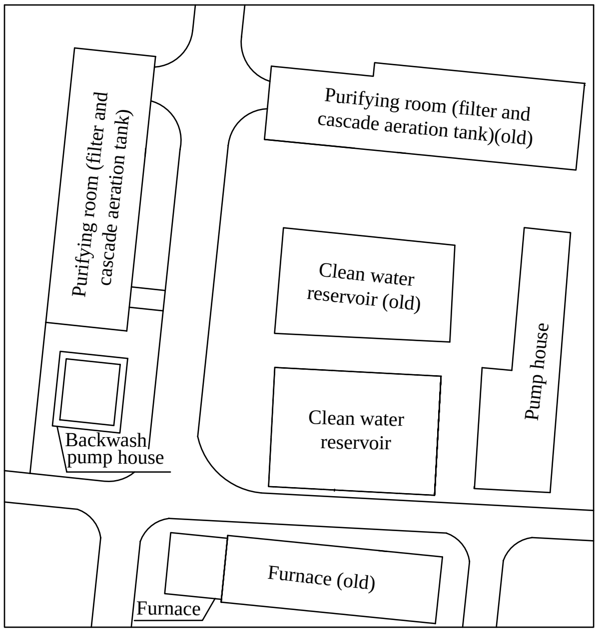

Figure 1 | Plan of Lanxi water treatment plant.

RESULTS AND DISCUSSION

The native iron and manganese oxidizing bacteria were inoculated to the filter on October 22, 2003 after collecting, culturing, domestication and multiplication. The detailed procedure can be obtained from the earlier paper (Li *et al.* 2005). Low filtration rate (less than 2.5 m h^{-1}), low intensity of backwash (10 l m^{-2} s^{-1}), long backwash period (72 hours) and short backwash duration (3 minutes) were adopted in the culture period.

Concentrations of iron and manganese in raw water and filtrate were measured daily. Step by step, the filter had significant and stable removal ability for iron but slight removal ability for manganese after several days (Figure 3). The data shown in Figure 3 are averaged values. The concentration of Fe in filtrate had been less than 0.5 mg l^{-1} since October 28, 2003 and 0.01 mg l^{-1} since January 13, 2004, which was far below the required concentration for iron by the Chinese National Standard for Drinking Water (T-Fe < 0.3 mg l^{-1}) (*Analytical Method* 1998). So the curve of iron removal will not be present anymore in other figures below. The population of iron and manganese oxidizing bacteria is shown in Figure 4. At the end of December, manganese removal rates decreased from 40 percent to 28 percent, and much mud pie was found in the filters (Figure 4). It was considered that the mud pie embedded the bacteria, which led to a decrease in the contact chance between raw water and bacteria, as well as the lessening of the activity and population increase of the bacteria. It is clear that the appearance of mud pie is the result of unsuitable backwash parameters for such water in the initial operation. The backwash intensity had been increased to 14 l m^{-2} s^{-1} with short backwash period of 24 hours and long backwash duration of 6 minutes since January 1, 2004. Much mud pie was washed out of the filter and the manganese removal rate recovered step by step. Taking into consideration of the slow increase of manganese removal activity of the bacteria, the depth of the filter bed was increased to 1300 mm from 1000 mm on March 6, 2004 in order to shorten the culture time. It is obvious that the manganese removal rate increased sharply after March 13, 2004 (Figure 5). Although the population of bacteria will be increased to a certain degree with the proper increasing of the filter bed depth, it is not reasonable to think that

Table 2 | Main treatment units in the water treatment plant

Units	Materials	Size (m)	Number
Cascade aeration tank	Reinforced concrete	$10 \times 10 \times 0.60$	1
Biological filter	Reinforced concrete	4..5 $\times$ 5 $\times$ 3.5	4
Clean water reservoir	Reinforced concrete	$25 \times 20 \times 3.5$	1
Backwash pump house	Reinforced concrete	V = 300 m^3 Height: 10.5 m	1
Pump house	Reinforced concrete	30×9	1

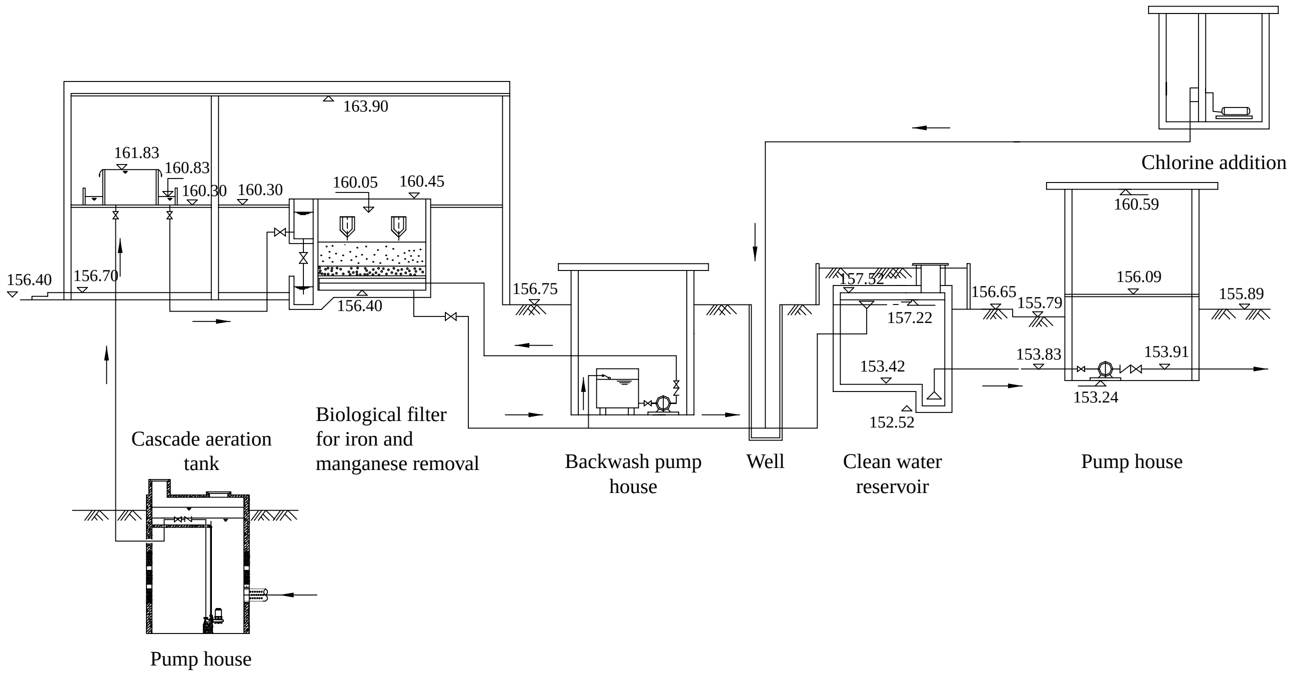

Figure 2 | Flow chart of Lanxi water treatment plant.

the deeper filter bed leads to the higher removal rate, which was also proved in Shenyang water treatment plant with respect to the distribution of the bacteria in mature filter (Figure 6). The population of bacteria decreased with the increasing of the filter depth because of the nutrient conditions along the filter bed. Many problems will be encountered when developing the filter bed depth including the choice of backwash equipment and the design of the filter structure. The most important is that more water and power will be used which leads to greatly increasing costs.

The manganese removal rate increased rapidly from May to June, especially during June. The detailed data of four filters are shown in Figures 7 and 8. Manganese concentration in filtrate of the four filters (Figure 7) decreased sharply from June 1 to June 15. The manganese concentration of filter 1 increased from June 15 with the increase of manganese concentration in raw water, while other filters still had good filtrate. This phenomenon may be the result of the different filtration rates. It had been noted above that operational parameters were the same except

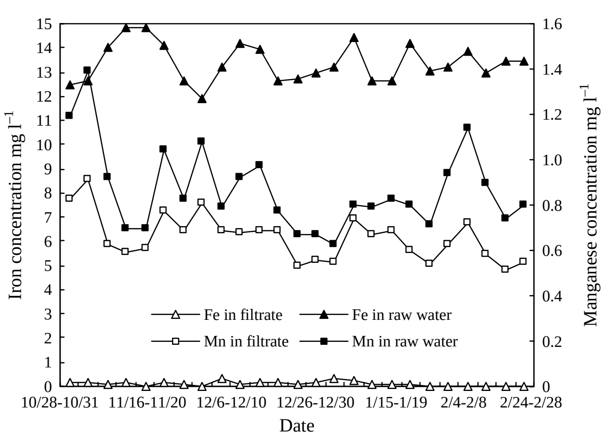

Figure 3 | Raw water and filtrate quality in the initial 4 months.

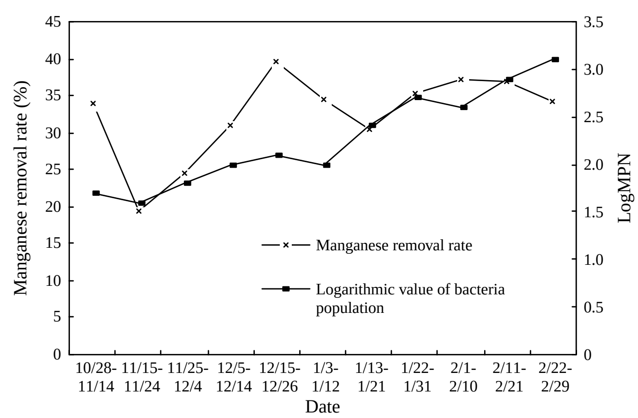

Figure 4 | Manganese removal rate and population of iron and manganese oxidizing bacteria.

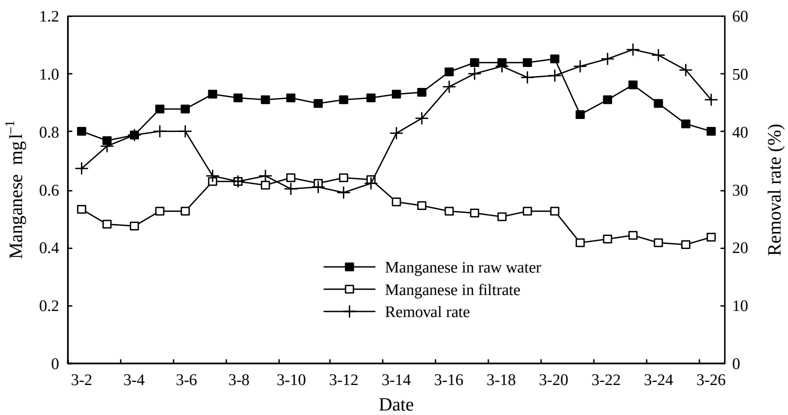

Figure 5 | Variation of Mn in raw water and filtrate of the plant.

the filtration rate (filtration rate of filter 1 to 4 were $2.3\,m\,h^{-1}$, $1.9\,m\,h^{-1}$, $1.4\,m\,h^{-1}$, $1.0\,m\,h^{-1}$, respectively). Manganese removal ability will not be stable under a relativity high filtration rate ($2.3\,m\,h^{-1}$) and the filter cannot resist the quality fluctuation of raw water.

The operational performance in July proved the analysis above. Filter 4 had failed to operate from July because of strobe malfunction, so there is no data for filter 4 shown in Figure 8. The manganese removal rate increased with the decreasing filtration rate from filter 1 to filter 3, which showed that low-level filtration rates promoted the maturity of the filter in the culture period. The contact time between water and filter media can be prolonged under the low-level filtration rate, accordingly, the reproducibility of bacteria can be increased. On the other hand, the shearing strength can be decreased under low-level filtration rate. After August 20, all the filters had a stable and powerful ability

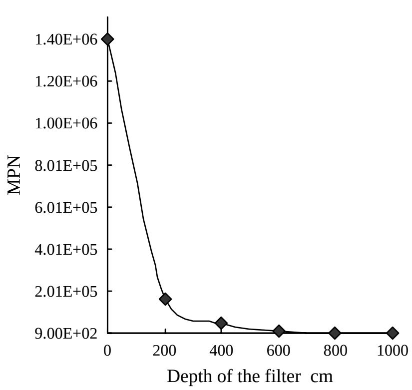

Figure 6 | Distribution of the bacteria along the filter bed in Shenyang water treatment plant.

for manganese removal, and the average concentration of manganese in filtrate was less than $0.05\,mg\,l^{-1}$. Then the filtration rate was increased to $5\,m\,h^{-1}$ little by little under the condition of the satisfactory filtrate quality(Fe $< 0.1\,mg\,l^{-1}$, Mn $< 0.1\,mg\,l^{-1}$).

The bio-film on the filter media formed by iron and manganese oxidizing bacteria in a mature filter in the water treatment plant is shown in Figure 9. The large black part is silica sand coated with iron and manganese oxides which looks like manganese sand in Figure 9a. The protonema on the surface of the silica sand is iron and manganese oxidizing bacteria. The original silica sand and that coated with iron and manganese oxide are shown in Figure 9b. During one-year operation, no deterioration of filtrate quality had happened. Up to now, iron and manganese concentration in the filtrate has been all less than $0.05\,mg\,l^{-1}$.

The operational performance during the whole culture period is shown in Figure 10. Several reasons can be considered to lead to the long culture period. Firstly, the quality of raw water is the most important reason. Li *et al.* (2005) reported that the culture period is only 2–3 months in another water treatment plant with low concentrations of iron and manganese (Fe^{2+}: $0.01–0.5\,mg\,l^{-1}$ and Mn: $0.575–3.05\,mg\,l^{-1}$). Secondly, the operational parameters have great influence on the length of the culture period. In the initial time of operation, low intensity of backwash ($10\,l\,m^{-2}\,s^{-1}$), long backwash period (72 hours) and short backwash duration (3 minutes) were adopted which led to the appearance of much mud pie. Finally, the depth of the filter bed can also influence the maturity of the filter. A suitably deeper filter

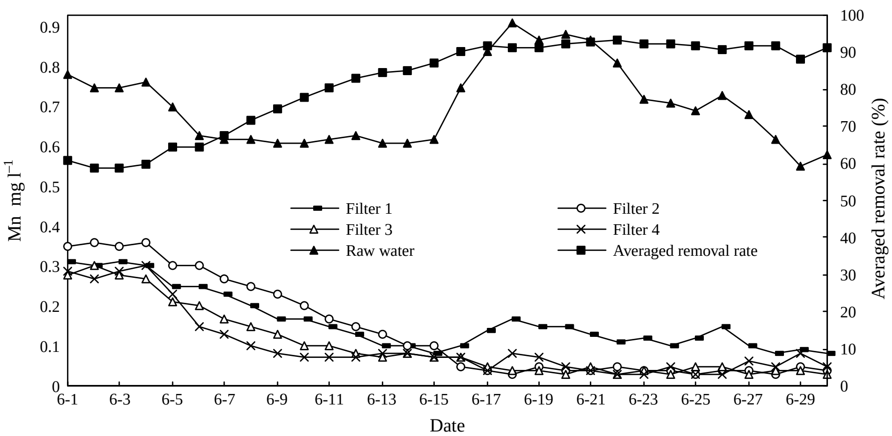

Figure 7 | Manganese in filtrate of each filter in June.

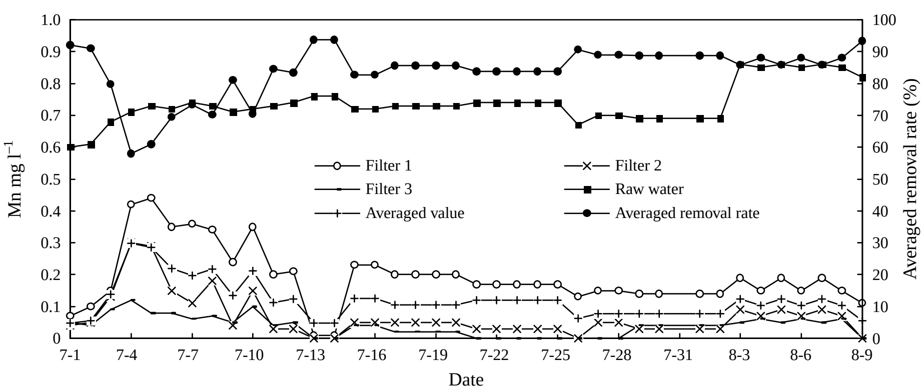

Figure 8 | Manganese in filtrate of each filter in July.

can promote the maturity of the filter for groundwater containing high iron and manganese.

Compared with iron removal, much more time was required for manganese removal (Figure 10). The satisfactory quality of filtrate ($Fe < 0.3\,mg\,l^{-1}$, $Mn < 0.1\,mg\,l^{-1}$) had not been obtained until the end of July 2004. The population of iron and manganese oxidizing bacteria in the filter and the manganese removal rate during the whole culture period are shown in Figure 11. There is a good correlation between the population of iron and manganese

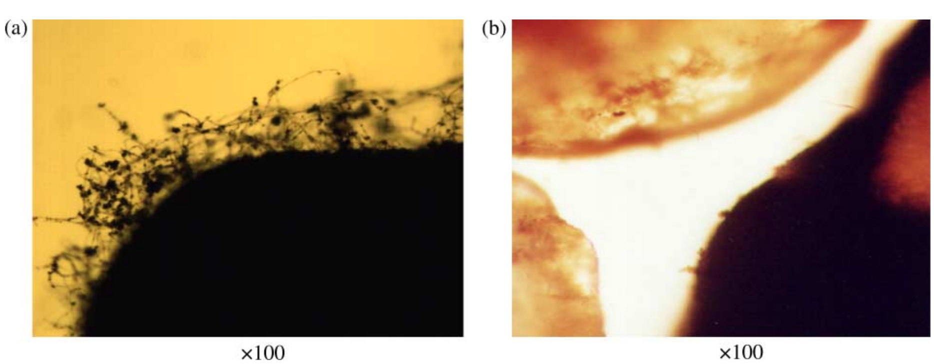

Figure 9 | Silica sand in filter at different time in Lanxi water plant. (a) Silica sand coated by bio-film consisting of iron and manganese oxidizing bacteria in the mature filter. (b) Silica sand without bio-film in the initial time of culture period in immature filter.

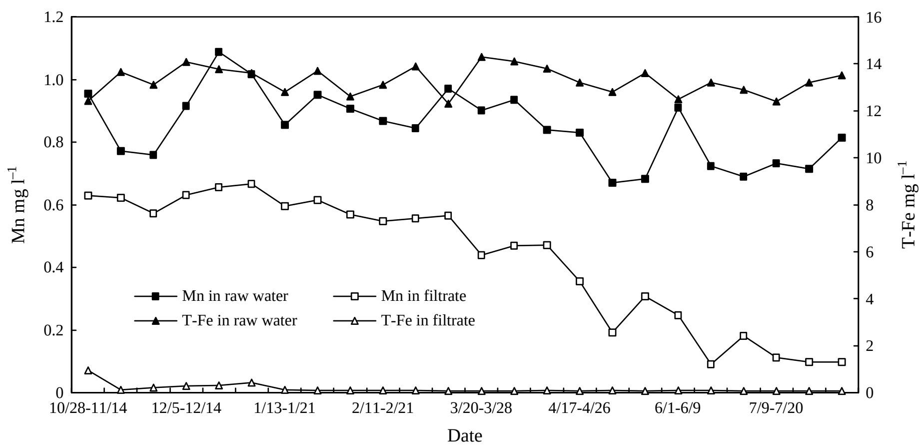

Figure 10 | Variation of T-Fe and Mn in raw water and filtrate of the plant during the whole culture period.

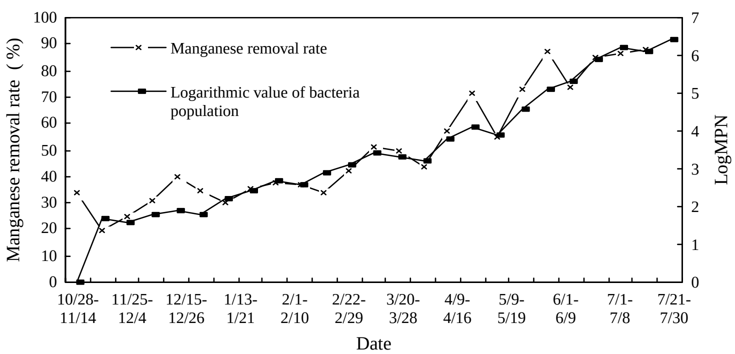

Figure 11 | Variation of manganese removal rate with the increasing of the bacteria population.

oxidizing bacteria and manganese removal rates which proved that manganese removal depended to a large degree on bio-oxidation of iron and manganese oxidizing bacteria surviving in the filter. In contrast, iron concentration had decreased rapidly to $1\,mg\,l^{-1}$ by November 14 (Figure 10) while the population of iron and manganese oxidizing bacteria was very small at that time, which proved that the population of bacteria was not the key point for iron removal. Some studies reported that iron was an indispensable nutrient for iron and manganese oxidizing bacteria surviving in the filter (Zhang *et al.* 2001). So iron removal may be the integrated result of chemical and biological oxidation. However, the relationship between chemical oxidation and bio-oxidation of iron is not clear in the biological filter for iron and manganese removal.

Compared with the traditional chemistry-contact process including two-stage aeration and two-stage filtration, 6 million yuans (¥), which amounts to 30% of the total investment cost was saved, and 250 thousand yuans (¥) per year, which amounts to 20% of the total aeration cost was saved also.

CONCLUSIONS

The biological process was successfully applied in a groundwater treatment plant for iron and manganese removal. The operational parameters should be determined by considering many factors including groundwater quality. The satisfactory operational performance can be obtained by selecting suitable parameters. The debugging of the plant is essential to the operational performance. Although the quality of filtrate is satisfactory ($Fe < 0.05\,mg\,l^{-1}$, $Mn < 0.05\,mg\,l^{-1}$), the long culture time that the biological filter needs is still an important problem to be solved.

Otherwise, the application in engineering will be greatly affected. So far, little is known about the specific iron and manganese oxidizing bacteria surviving in the filter. Further control of the bacteria themselves can not be realized. The corresponding research and development will greatly promote the wider application of this biological process for iron and manganese removal from groundwater. Thus, the future study should focus on the start-up of the plant in a short time and the micro-ecosystem in the filter.

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