Case study: reducing manganese (Mn++) level in surface water with natural manganese-coated sand in Sinopec Shanghai Ltd

Kai Yang, Yingwen Xue, Jiajie He and Xiaojun Yang

ABSTRACT

Sinopec Shanghai Ltd has been experiencing an increased manganese (Mn++) level in its water source since 2000. The purpose of this research is to reduce Mn++ in conventional gravitational filtration effluent to below the national standard and provide suggestions for Sinopec waterworks to carry out full-scale industrial tests. A pilot experiment, using natural manganese sand, quartz sand and their mixtures as the filtration medium, was conducted from 20 September 2003 to 26 December 2003 in Sinopec waterworks. The results indicated that the tested natural manganese sand has a stronger adsorption for Mn++ than the quartz sand within the hydraulic retention time of the filtration bed ($<$ 30 min.). Water redox status was found to be vital in Mn++ adsorption by the tested natural manganese sand. A dual-medium with a volumetric mix ratio between 1:1 and 1:2 (natural manganese sand: quartz sand) was suggested for engineering application in Sinopec waterworks. Meanwhile, the filtration loading rates should be kept within $6-8\,m^3\,h^{-1}\,m^2$ and the suggested backwashing loading rate should be $15-16\,l\,s^{-1}\,m^{-2}$ for 5–6 min.

Key words | dual-medium filter, manganese removal, natural manganese sand, quartz sand, surface water

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INTRODUCTION

Soluble manganese (Mn++) levels in natural surface water sources are mainly controlled by the activity of metal-reducing bacteria under different dissolved oxygen (DO) levels in the water (Nealson & Saffarini 1994; Cerrato et al. 2006). The presence of manganese in natural and municipal water systems is of aesthetic, taste and health concerns. Takeda (2003) showed that manganese tends to accumulate in human brains and causes neurological disorders (Donaldson 1987). The World Health Organization has set a limit of $0.4\,mg\,l^{-1}$ for Mn++ (World Health Organization 1998) in drinking water. The China national drinking water standard for Mn++ is $0.1\,mg\,l^{-1}$ (China Environment Protection Bureau 1988) and the US EPA level for secondary maximum contaminant level is $0.05\,mg\,l^{-1}$ (United States Environmental Protection Agency 1979).

Recent researches have focused on manganese fate, transport and reactions in engineering and natural ecosystems. Edenborn & Brickett (2002) observed a highly seasonal and spatial variation of manganese in a wetland receiving coal mine drainage. Delgadillo-Hinojosa et al. (2006) studied manganese distribution in the Gulf of California, USA. Their researches showed a profile of manganese variation with water redox conditions. Dellwig et al. (2007) concluded that microbial activity is the main culprit for seasonal manganese variation in a tidal basin in Germany.

Tournassat et al. (2002) mentioned that even though Mn++ is theoretically easy to oxidize, it still takes oxygen several years to finish the conversion. A so-called 'natural greensand effect' has been documented (Merkle & Knocke 1997), in which mineral deposits form oxides on the filter

medium over weeks to months of operation and can provide strong adsorption and oxidation for the metals in the water. Oxide coated filter mediums have been used successfully to remove copper, lead (Han *et al.* 2006) and caesium (Mishra & Vijaya 2007) from aqueous solutions in lab scale experiments.

Researchers in North China have used manganese (coated by manganese oxides) sand to remove ferric ion and manganese ion from underground water with notable removal efficiencies (Li & Liu 1989; Liu *et al.* 1996; Zhang & Dai 1996, 1997). In South China, manganese pollution is mainly in surface water systems. Mn^{++} concentration in the Yizheng segment, part of the Yangtze River, accounts for 77% of all the detectable pollutants in the river (Xu & Zhao 1997); the annual average concentration of Mn^{++} in Le'An River system, located in Jiangxi Province, is $0.3–0.4\,mg\,l^{-1}$ (Zhu 2001).

Sinopec waterworks in Shanghai is the only water treatment plant that provides industrial water to Sinopec Shanghai Ltd. The current treatment procedure is a conventional flocculation–sedimentation–filtration unit followed by chlorination. Since 2000, manganese (Mn^{++}) levels started to increase in the river water source. A seasonal variation of manganese (Mn^{++}), chemical oxygen demand (COD) and ammoniacal nitrogen (NH$_3$—N) has been observed (Figures 1–3, respectively). Sinopec waterworks could not maintain the overall water quality without greatly increasing the chlorine dosage in its effluent. After an extensive field survey that failed to find any potential point source pollution for manganese in the upstream area, Sinopec waterworks was compelled to modify its water treatment facilities in order to lower the Mn^{++} level in its filtration effluents.
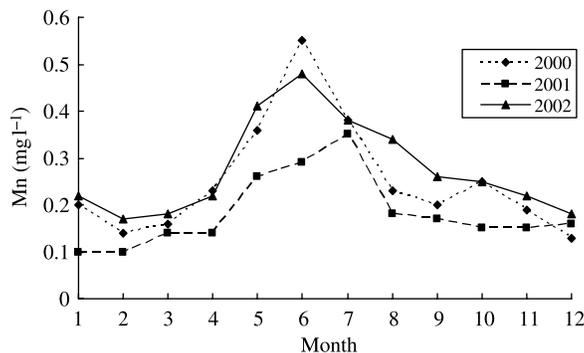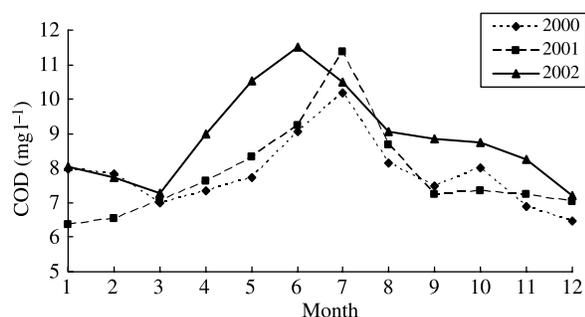

Figure 2 | COD variations in raw water during 2000–2002.

This research focused on using natural manganese sand as a filter medium in a fixed filtration bed to reduce the manganese (Mn^{++}) level in the receiving water and provide preliminary suggestions to Sinopec waterworks for further engineering applications. A pilot water treatment system was set up in Sinopec waterworks in Shanghai. Natural manganese sand, quartz sand and their mixtures were tested through column experiments from September 2003 to December 2003, when manganese (Mn^{++}) levels in the river water source varied between 0.20 and $0.35\,mg\,l^{-1}$. The experiment comprised two phases to serve different purposes. Phase one focused on the comparison between natural manganese sand, quartz sand and a 1:1 (natural manganese sand: quartz sand, volumetric based) mixture in their manganese removal efficiencies and hydraulic performance. In phase two, different ratios of natural manganese sand and quartz sand mixtures were tested to determine an optimum mix ratio that is operationally feasible for Sinopec waterworks. Besides manganese removal, routine water quality parameters, such as colour, DO, pH and turbidity were also monitored.
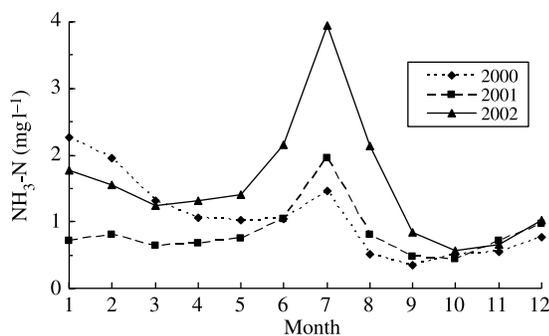

Figure 1 | Mn^{++} variations in raw water during 2000–2002.

Figure 3 | NH$_3$-N variations in raw water during 2000–2002.

MATERIALS AND METHODS

The natural manganese sand was collected from Mashan County, Guangxi Province, with a particle size 0.6–1.2 mm. The quartz sand was supplied by Sinopec waterworks. Water was delivered to the pilot experiment facility by connecting a branch water line to the primary delivery pump station. Continuous flow first entered a circular clarifier. After flocculation and sedimentation, the clarifier effluent flowed into three parallel gravitational filtration columns by gravity (Figure 4). With this set-up, all the testing columns received water with the same quality and water head.

The specifics of each experimental unit are shown in Figure 5. The clarifier was made of steel with an inside diameter of 1.0 m and a total height of 3.2 m. The water level was kept at 3.0 m and the flow rate was kept at 1.5 m^{3}h^{-1} with a hydraulic retention time of 1.5 hours, equal to a hydraulic loading rate of 3.6 m^{3}m^{-2}h^{-1}. Aluminium chlorhydroxide was used as coagulant in the clarifier. During the whole experiment, the coagulant dosing rate ranged from 20 to 30 mg l^{-1} and the turbidity in the clarifier effluent was kept below 5 NTU. The filtration columns were made of polymethyl methacrylate with a total height of 3.75 m and an inside diameter of 30 cm. The bottom 25 cm of each column was filled with gravel (diameter of 6–7 mm) as a supporting layer. In phase one, the natural manganese sand, quartz sand and a 1:1 volumetric mixture (natural manganese sand on top of quartz sand) were put in each column to a depth of 70 cm. In phase two, three volumetric mix ratios (1:1, 1:2 and 1:3, natural manganese sand on top of quartz sand) were tested with the overall filtration bed depth kept at 70 cm. The inlet was put 0.5 m below the top of the filtration column. The overflow outlet was set at the same height as the inlet, making the highest water level above the filtration bed at 1.8 m. A 0.5 m space under the supporting layer was used as an effluent distribution zone. The flow rate
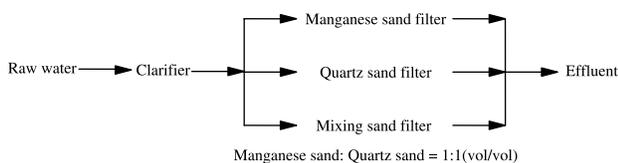
of each column was monitored by a rotameter mounted on the discharge line. PVC ball valves were used on both the inlet and the outlet of each column to control the flow rate. Water samples were taken at least three times a day at sample points for manganese (Mn^{++}), colour, turbidity, pH, DO and so on.

Manganese (Mn^{++}) was measured using US Standard Method 3500-Mn (*Standard Methods* 1998). Colour was measured with US Standard Method 2120B. Dissolved oxygen was measured with an YSI52 DO meter and pH was measured with a PH-1 pH meter. Turbidity was measured with a HACH 2001P turbidity meter.

RESULTS AND DISCUSSION

Phase one

The filtration columns started to receive water on 20 September 2003, when the turbidity of the clarifier effluent stabilized below 5 NTU. The water temperature was 20–26°C during the experiment. The manganese (Mn^{++}) level entering the filtration column was 0.25–0.30 mg l^{-1}, and the filtration velocity was controlled between 6 and 8 m h^{-1}.

Manganese levels at all sampling points are shown in Figure 6. It was observed that the manganese sand column and the mixture column showed an apparently higher Mn^{++} removal over the quartz sand column. The average Mn^{++} removal rate of each filtration column during this phase is shown in Table 1. The data show that the columns containing manganese sand had a 96% Mn^{++} removal rate, with effluent manganese (Mn^{++}) concentrations less than 0.1 mg l^{-1}. Meanwhile, the quartz sand column only had a 20% Mn^{++} removal rate, and Mn^{++} in its effluent fluctuated between 0.15 and 0.25 mg l^{-1}. Hu *et al.* (2004) studied the characteristics of manganese sand and reported an adsorption equilibrium time of less than 4 hours. Take into account that the water ran through the filtration bed within 30 minutes under the tested hydraulic loading rate, and the columns went through backwash every 24 hours, this indicated a strong selective adsorption for manganese (Mn^{++}) by the tested natural manganese sand compared with the quartz sand. The quartz sand column could not intercept Mn^{++} effectively to reduce it to below 1.0 mg l^{-1} in the effluent during the experiment.

Raw water ⟶ Clarifier ⟶ Manganese sand filter ⟶ Effluent
                          Quartz sand filter
                          Mixing sand filter

Manganese sand: Quartz sand = 1:1(vol/vol)

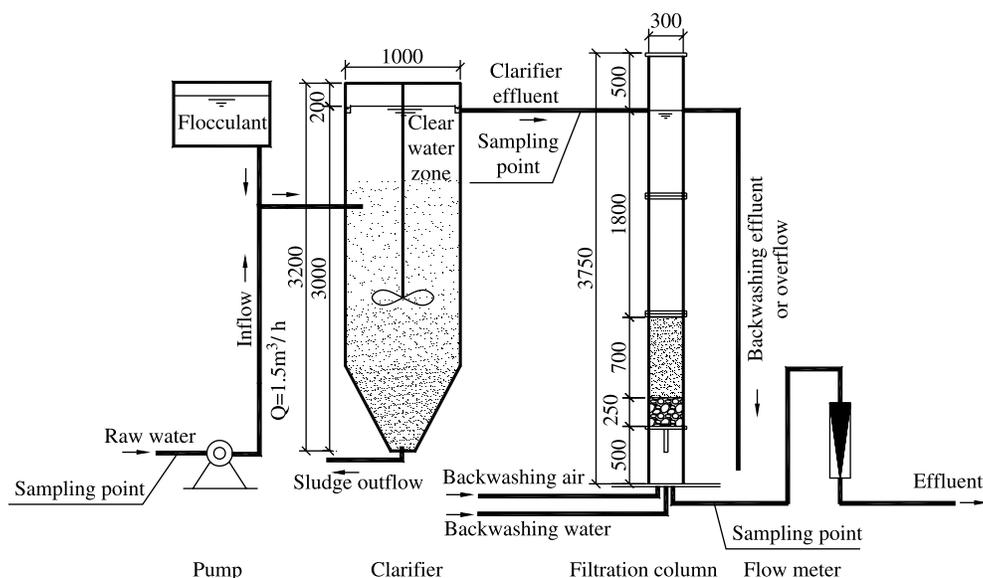**Figure 4** │ Flow chart of the treatment process.

Figure 5 | Schematic drawing of the experiment facilities (unit: mm).

An increase in manganese in the filtration effluents can also be observed in Figure 6, corresponding to a sudden manganese surge in raw water from 26 September to 8 October. This indicated that the adsorption capacity of the manganese sand was depleted within 24 hours under the manganese surge. The DO data (Figure 7) during the manganese surge showed a drop from $6\,mg\,l^{-1}$ to $4\,mg\,l^{-1}$ in clarifier effluents, while pH levels (Figure 8) remained fairly stable. This indicated that DO levels in the water were vital for manganese status in the raw water of Sinopec waterworks and that Mn^{++} adsorption capacity and adsorption kinetics of the tested natural manganese sand were also DO dependent under the experimental environment. These findings correspond to the argument
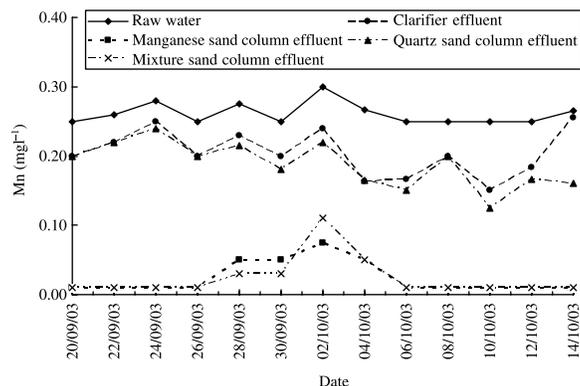

Figure 6 | Mn^{++} levels at different sampling points during the experiment (phase one).

that manganese status is highly variable in nature, controlled by DO and pH (Edenborn & Brickett 2002; Delgadillo-Hinojosa *et al.* 2006). The oxidation process after Mn^{++} adsorption was not investigated in this research, but Hu *et al.* (2004), with a scanning electron microscope analysis, revealed that manganese (Mn^{++}) adsorption on manganese sand is single layer and oxidation happens on mineral surfaces. This suggests that the redox status in the solid–aqueous interface is decisive in manganese sand adsorption capacity. With regard to engineering applications for Sinopec waterworks, a certain method is required to increase the DO level (no less than $6\,mg\,l^{-1}$ in this case) in the influent of filtration beds. Otherwise, the tested natural manganese sand might not provide satisfactory Mn^{++} removal efficiencies to keep Mn^{++} below $1.0\,mg\,l^{-1}$ in filtration effluent.

There was no significant difference in turbidity removal between the three columns (Table 2) during the test, which indicated that the tested manganese sand was close to quartz sand in its ability to intercept particles. With regard to colour removal (Figure 9), although the adsorption ability for most common chromatic compounds was fairly the same among the columns, there were still differences between them and the addition of the natural manganese sand will potentially weaken the colour removal ability of the filtration columns.

Table 1 | Manganese removal in different columns during the experiment (phase one)

| Raw water Mn^{++} $(mg\,l^{-1})$	Column	Filtration velocity $(m\,h^{-1})$	Effluent Mn^{++} $(mg\,l^{-1})$	Removal efficiency (%)
0.25–0.30	Manganese sand filter	6–8	N/A	96
	Quartz sand filter		0.15–0.25	20
	Mixture sand filter		N/A	96

N/A indicates that the manganese level is below the detection limit of $0.01\,mg\,l^{-1}$.

Hydraulic performance of the natural manganese sand cannot be ignored when using the manganese sand as a filter medium in a fixed filtration bed. Theis *et al.* (1992) indicated that metal oxides have a poor hydraulic conductivity. Therefore, a column breakthrough test with regard to turbidity and water head losses, and a backwash test in respect of backwash flow rate and effluent turbidity were performed on the three columns.

Two filtration velocities ($6\,m\,h^{-1}$ and $8\,m\,h^{-1}$) were applied to the columns in the breakthrough test. Water head losses and turbidity in the filtration effluents were monitored for 24 hours. Figure 10 and Figure 11 show the water head losses and the effluent turbidity of each column under the tested filtration velocities. It can be observed that the manganese sand column and the mixture column showed a gradually increased divergence from the quartz sand column with respect to water head losses and turbidity under a filtration velocity of $6\,m\,h^{-1}$, while the differences are not that significant under a filtration velocity of $8\,m\,h^{-1}$. After the first four hours, it took the quartz sand column at least two hours to reach the same levels of water head loss and effluent turbidity as that of the manganese sand column and the mixture sand column. Sinopec requires the turbidity in the filtration effluent to be kept below 1.0 NTU. Under

such a criterion, the quartz sand column could keep the turbidity below 1.0 NTU for at least 17 hours under a filtration velocity of $8\,m\,h^{-1}$, while the manganese sand column could only maintain that level for less than 15 hours. At the filtration velocity of $6\,m\,h^{-1}$, the above differences between the manganese sand column and the quartz sand column increased to around 5 hours. Under both tests, the mixture sand column data lay between the manganese sand column and the quartz sand column in terms of water head losses and effluent turbidity. The mixture sand column performed more closely to the quartz sand column than to the manganese sand column. It was also observed that the performance differences between the mixture sand column and the quartz sand column tend to decrease as the filtration velocity increased. But high filtration velocity did deplete the filtration columns' ability to intercept the particles in the receiving water more quickly, which means a shortened filtration cycle.

Backwash tests were performed on each column after 24 hours' filtration. Table 3 lists the test results of each column under different backwashing loading rates. It showed that the quartz sand column had a higher expansion rate than the manganese sand column under the same backwash loading rate, indicating that the tested natural manganese sand is of a higher particle density than
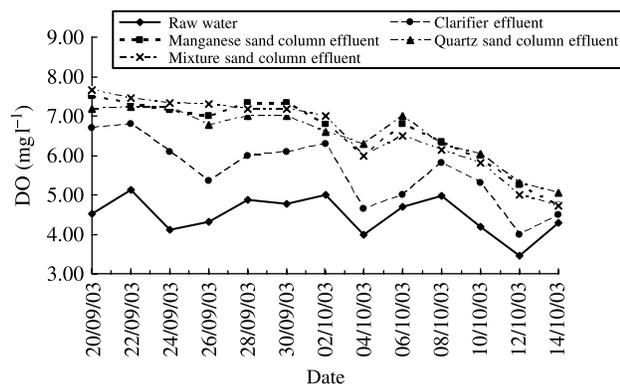
Figure 7 | DO levels at different sampling points during the experiment (phase one).
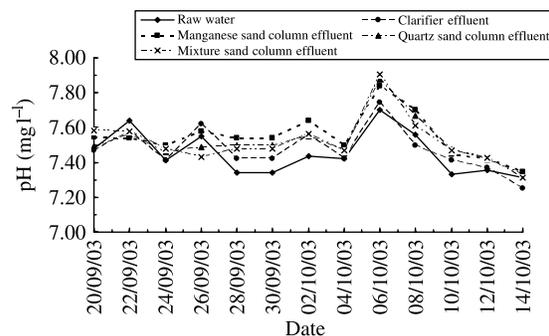
**Figure 8** | pH levels at different sampling points during the experiment (phase one).

Table 2 │ Turbidity removal rate by different testing columns during the experiment (phase one)

Clarifier effluent (NTU)	Manganese sand column		Quartz sand column		Mixture sand column	
	Turbidity (NTU)	Removal rate (%)	Turbidity (NTU)	Removal rate (%)	Turbidity (NTU)	Removal rate (%)
4.2	0.42	90*	0.43	89.8	0.40	90.5

*Average of at least 50 observations.
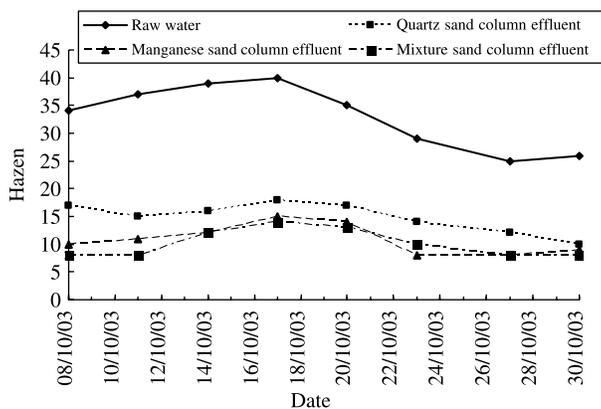
Figure 9 │ Colour levels at different sampling points during the experiment (phase one).
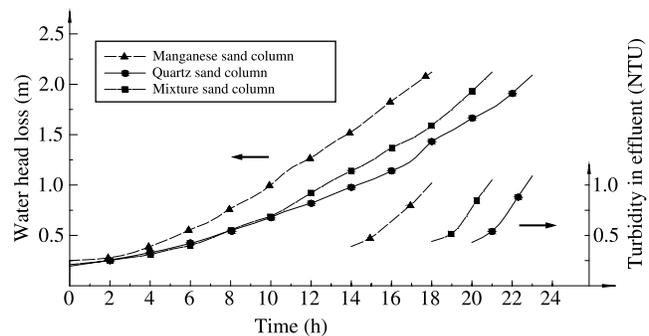
the quartz sand. On the other hand, the manganese sand column showed signs of losing its filter material by having an extremely high turbidity in its backwash effluent. A similar situation occurred with the mixture sand column, but not at a comparable level to that presented by the manganese sand column. In order to obtain a thorough clean for the manganese sand column, filter medium losses seemed unavoidable. Meanwhile, the data for the mixture
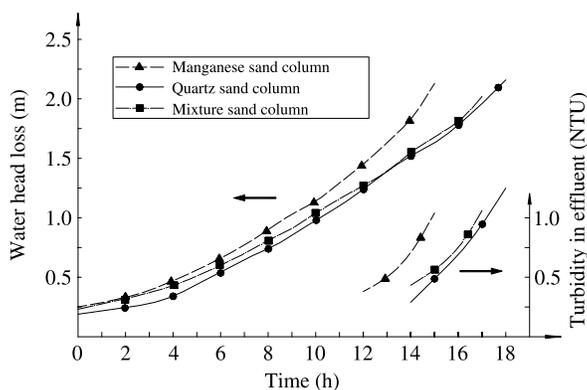
sand column and the quartz sand column showed that a backflow loading rate of $15-16 \, l \, s^{-1} \, m^{-2}$ could finish the filter cleaning within 5–6 minutes and the expansion rate of the filtration beds could be at least 29%. A higher backwash flow rate could only increase the expansion rate, but showed no advantage in saving the backwash time or reducing the turbidity in backwash effluents.

After every backwash, the initial filtration effluent was sampled at 1-minute intervals for turbidity. Figure 12 shows the results observed from each column based on at least 13 observations. It was noticed that the manganese sand column had a turbidity surge that went up to 6.5 NTU and took more than 30 minutes to drop back to 1.0 NTU. Meanwhile, the quartz sand column effluent remained fairly stable at under 1.0 NTU. The mixture sand column showed a similar tend to that of the manganese sand column, but the peak was below 2.0 NTU and the turbidity dropped back to 1.0 NTU in less than 9 minutes.

The results of phase one indicated that manganese sand does provide manganese removal in surface water, but that DO is vital in manganese (Mn++) adsorption onto the tested natural manganese sand. The manganese sand column did not show a comparable hydraulic performance to that of the quartz sand column, while the mixture sand column performed more closely to the quartz sand column. These results suggest that neither the natural manganese sand nor the quartz sand could satisfy Mn++ removal and hydraulic requirements by itself; a dual-medium that combines the advantages of both types might be a practical alternative for engineering purposes.

Figure 10 │ Hydraulic performances of different filters under the filtration velocity of $8 \, m \, h^{-1}$ (phase one).

Figure 11 │ Hydraulic performances of different filters under the filtration velocity of $6 \, m \, h^{-1}$ (phase one).

Table 3 | Backwash test on different columns in the experiment (phase one)

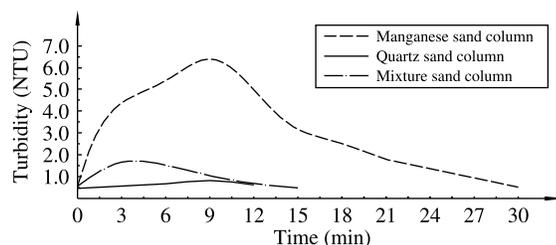| Column	Backwash loading rate (l s^{-1}m^{-2})	Backwash flow rate (m^3 h^{-1})	Backwash time* (min)	Expansion rate of filtration bed (%)	Turbidity in backwash effluent† (NTU)
Manganese sand column	15	3.7	6–8	19.6	118
	16	4.0	5–6	21.0	110
	18	4.5	5–6	32.4	108
	23	5.9	5–6	41.5	112
Quartz sand column	12	3.1	5–6	23.9	4.25
	15	3.7	5–6	35.7	2.47
	16	4.0	5–6	41.9	2.15
	18	4.5	5–6	47.3	2.03
Mixture sand column	12	3.1	5–6	21.4	20.5
	15	3.7	5–6	29.3	10.4
	16	4.0	5–6	37.1	8.86
	18	4.5	5–6	42.9	7.83

*The time required for the backwash effluent to show no visible turbidity.
†The average of all samples sampled at 1-minute intervals during the backwash.

Phase two

All three filtration columns were empted after phase one was concluded. On 17 November 2003, the three columns were filled with three different volumetric ratios (1:1, 1:2 and 1:3, natural manganese sand on top of quartz sand) of sand mixtures. The water levels and flow rates in all experimental units were kept the same as those in phase one. The filtration columns began to receive water on 20 November 2003, after the clarifier effluent stabilized its turbidity under 5 NTU. Water temperature during this period ranged between 10 and 15°C, water pH was between 7.4 and 7.6, dissolved oxygen varied between 4 and 6 mg l^{-1}, and the manganese (Mn^{++}) level in the raw water ranged between 0.25 and 0.35 mg l^{-1}.

Manganese (Mn^{++}) levels at the sampling points are presented in Figure 13. As shown, the manganese (Mn^{++})

variation in the filtration effluents responded to that in the receiving water. A manganese (Mn^{++}) surge occurred from 26 November to 14 December, while the DO levels in the receiving water varied in the range 4–4.5 mg l^{-1} (Figure 14) with pH 7.4–7.6 (Figure 15). The 1:1 column showed a Mn^{++} increase earlier than the 1:2 column, followed by the 1:3 column. This implied that the natural manganese coating might be reduced back to Mn^{++} under low DO levels in the water, and the phenomenon would become more apparent with more natural manganese sand present in the filtration columns. After the manganese surge, the 1:1 and 1:2 columns

Figure 12 | Turbidity in initial filtration effluents from the tested columns (phase one).
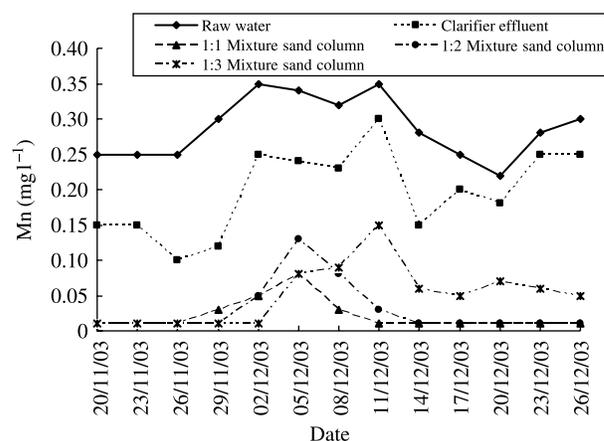
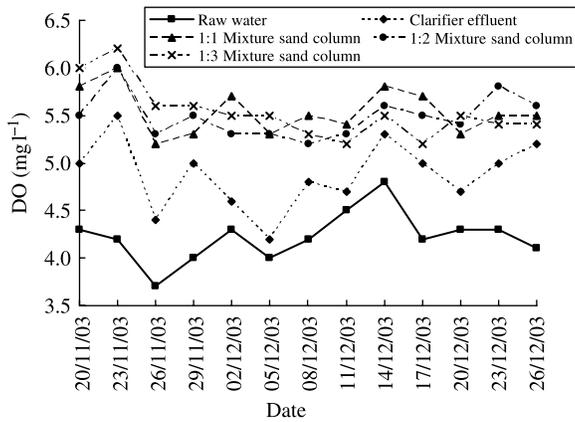**Figure 13** | Mn^{++} levels at different sampling points during the experiment (phase two).

Figure 14 │ DO levels at different sampling points during the experiment (phase two).

kept manganese (Mn^{++}) levels lower than $0.05\,\mathrm{mg\,l^{-1}}$ in their effluents, while the 1:3 column had a manganese (Mn^{++}) level between 0.05 and $0.1\,\mathrm{mg\,l^{-1}}$. Although the effluent from all three columns met the national standard, the 1:1 and 1:2 columns showed a more stable performance in Mn^{++} removal, while the 1:3 column presented a distinct difference and might be unstable if applied in full-scale tests.

The same column breakthrough tests in phase one were carried out on each column at the filtration velocity of $6\,\mathrm{m\,h^{-1}}$, and the results are presented in Figure 16. The data show a similar trend to that in the breakthrough tests in phase one. The higher the proportion of natural manganese sand in the column, the more rapid the increase in effluent turbidity and water head loss. This clearly shows that the addition of the natural manganese sand will weaken the quartz sand's ability for particle interception. These results
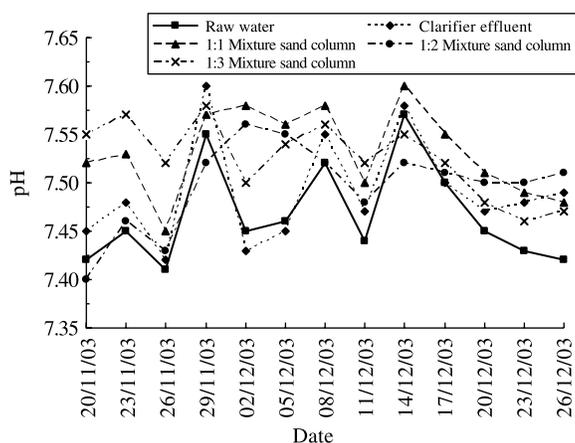

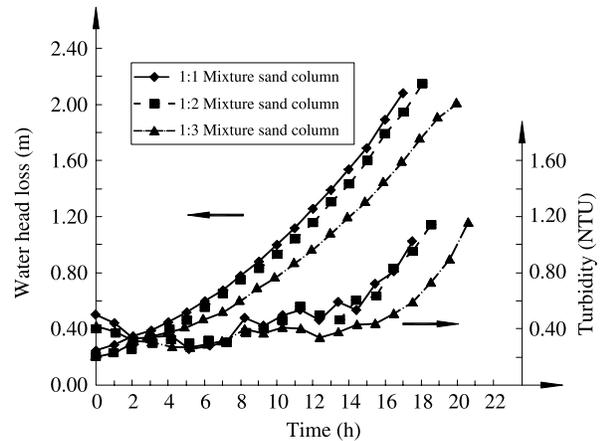**Figure 15** │ pH levels at different sampling points during the experiment (phase two).

Figure 16 │ Hydraulic performances of dual-medium filters under the filtration velocity of $6\,\mathrm{m\,h^{-1}}$ (phase two).

indicate that the filtration cycle was shortened because of the elevated rate of water head loss and filtration effluent turbidity increase due to the natural manganese sand present.

The results in this phase indicated that, under the experimental environment, there was a minimum percentage of manganese sand that should be maintained in the filtration columns to keep Mn^{++} below $1.0\,\mathrm{mg\,l^{-1}}$ in the filtration effluent; at the same time, the hydraulic performance of the dual-medium can stay within the concurrent operation capability of Sinopec waterworks. The tested natural manganese sand showed some adverse effects, such as a reduced filtration cycle, an observable filter medium loss during backwash, and an unacceptable turbidity surge during the initial filtration period. An optimum volumetric mixture ratio of natural manganese sand and quartz sand of between 1:1 and 1:2 was suggested based on the experimental results. Hargette & Knocke (2001) found that the oxidation of Mn^{++} occurred in the upper 25 cm of a fixed filter bed using anthracite with MnO$_x$(s) coating as the filter media. Regarding the depth of the filtration bed tested in the experiment, the optimum depth of the natural manganese sand that should be kept in the filtration bed was suggested to be 25–35 cm, which was close to Hargette's lab − scale test.

Full-scale experiments in the industrial facilities in Sinopec waterworks are still needed to further justify the engineering application of natural manganese sand. Filter medium losses and filter medium mixing effects should be observed and studied through long-term engineering operations.

The observed manganese (Mn^{++}) surges in the water source during the experiment indicated that there might be large-scale land developments happening at that time in the upstream areas. For long-term purposes, the manganese pollution in the water source might be better solved through upstream water protection and soil conservation.

CONCLUSIONS

This study showed that the tested manganese sand has strong adsorption ability for Mn^{++}, but the adsorption capacity and adsorption kinetics were influenced by water DO levels. The strategy suggested to Sinopec waterworks was to keep 33–50% (volumetric) manganese sand in its filtration mediums, corresponding to a manganese sand depth of 25–35 cm. The filtration loading rates should be kept between 6 and $8\,m^3\,h^{-1}\,m^2$ and the backwashing loading rate was $15–16\,l\,s^{-1}\,m^{-2}$ for 5–6 min. Manganese sand losses should also be monitored. DO should be kept above $6\,mg\,l^{-1}$ for water entering the dual-medium filtration bed, otherwise the natural manganese sand might lose its manganese removal effect by presenting a decreased adsorption capacity, reduced adsorption kinetics and a potential manganese coating loss.

ACKNOWLEDGEMENTS

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