Desalination and Water Treatment
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11 (2009) 245–257

Removal of manganese from surface water with oxidants in supplement to natural manganese sand in Sinopec Shanghai Ltd.

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Received 11 June 2009; Accepted 25 August 2009

ABSTRACT

Sinopec waterworks in Shanghai has limitations on its current treatment process to effectively remove Mn(II) from its surface water source. Previous study used natural manganese sand together with quartz sand to intercept Mn(II) and demonstrated that natural manganese sand can not provide a stable Mn(II) removal when Mn(II) > 0.30 mg/L in the water source. In order to provide a more reliable Mn(II) removal strategy for Sinopec waterworks, this study applied chlorine dioxide, potassium permanganate, hydrogen peroxide, and aeration separately in supplement to natural manganese sand to remove Mn(II) within a pilot experiment system that simulates the current water treatment process in Sinopec waterworks. Experiment results indicated that chlorine dioxide and potassium permanganate both showed effective Mn(II) removal capabilities, with $KMnO_4$ more appropriate for Sinopec waterworks. Hydrogen peroxide showed a negative impact on Mn(II) removal by dissolving MnO_x(s). The improvement on Mn(II) removal from aeration was not promising neither. Final suggestion is to apply potassium permanganate as a pre-treatment process at about the stoichiometric Mn(II) oxidation requirement and keep filtration speed and coagulant dosage at Sinopec waterworks engineering convenience. Natural manganese sand still be used as a buffer for Mn(II) removal.

Keywords: Drinking water treatment; Manganese; Natural manganese sand; Oxidation; Potassium permanganate; Surface water

1. Introduction

The presence of manganese in natural andmunicipal water systems is of aesthetic, taste and health concerns. The World Health Organization has set a limit of 0.4 mg/L for Mn(II) in drinking water [1]. The China national drinking water standard for Mn(II) is 0.10 mg/L [2] and the US EPA regulation for secondary maximum contaminant level is 0.05 mg/L [3].

Sinopec waterworks in Shanghai is experiencing a seasonal variation of Mn(II), chemical oxygen demand (COD), and ammonia nitrogen (NH_3-N) (Figs. 1–3) in its water source since 2000. The current water treatment procedure of the Sinopec waterworks is a conventional coagulation–flocculation–sedimentation–filtration unit followed by chlorination, which could not maintain the overall water quality without significantly increasing the chlorine dosage in its effluent when Mn(II) is high in the receiving water. Sinopec waterworks also tried applying 0.5 mg Cl_2/L as a pre-treatment for Mn(II) removal, but still could not get a satisfied result. Increasing Cl_2 application in the pre-treatment might help reducing Mn(II), but it can also increase halogenated compounds occurrence when most organic substances are still in the water. A three-month

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doi: 10.5004/dwt.2009[illegible]

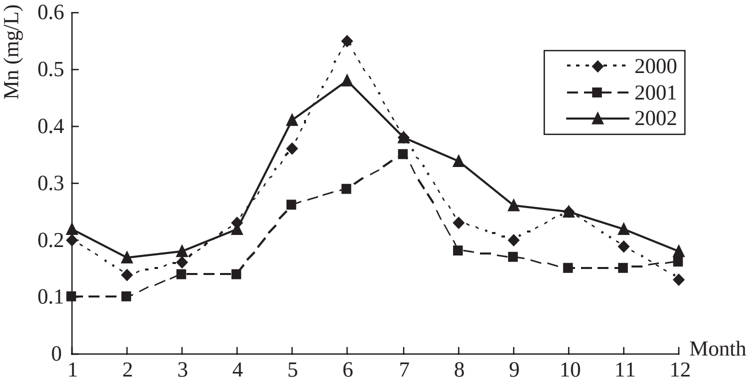

Fig. 1. Manganese variations in raw water during 2000–2002.

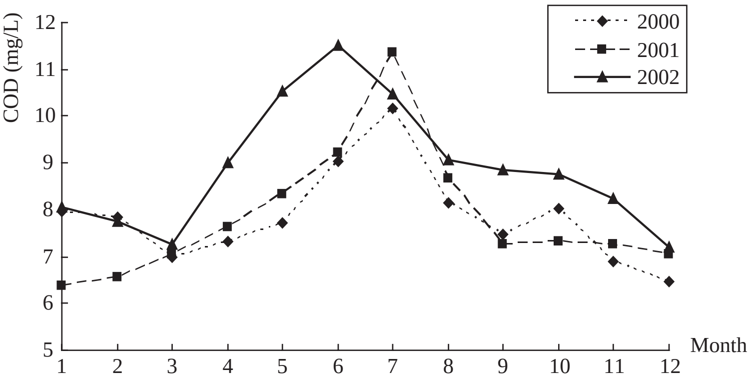

Fig. 2. COD variations in raw water during 2000–2002.

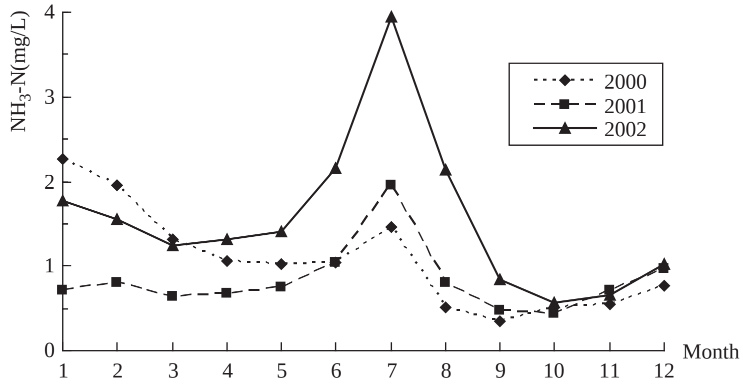

Fig. 3. NH3-N variations in raw water during 2000–2002.

pilot experiment was carried out previously in Sinopec waterworks by placing natural manganese sand together with quartz sand as a double-layer filter media for the final filtration to intercept Mn(II) [4]. The experiment results indicated that Mn(II) can be decreased to below 0.05 mg/L by controlling a 25–35 cm depth of natural manganese sand in the filtration bed, which corroborates an earlier finding that Mn(II) oxidation happened in the upper 25 cm of a fixed filtration bed that using anthracites with MnO_x(s) coating as the filter media [5]. However, when Mn(II) > 0.30 mg/L in the water source, the testing natural manganese sand could not guarantee the Mn(II) < 0.10 mg/L in its final filtration effluent even when the whole filtration column was filled with the natural manganese sand.

The Mn(II) removal by manganese oxide coated filter media is only sorption related when no oxidant is present [6], and the removal capacity is limited by available sorption sites in the filter media [6–8]. The adsorbed Mn(II) might be oxidized into MnO_x(s) by oxidants stronger than chlorine or by those coated manganese oxides through catalyzation [6,8]. Even manganese oxide coated filter media can effectively remove Mn(II) from water, its Mn(II) removal capability will be lost if those consumed adsorption sites can not be timely regenerated [6–8]. The Mn(II) removal capability of such a filtration bed can sustain for months to years depending on the water quality of the receiving water [6]. Previous pilot study in Sinopec waterworks showed no noticeable green-sand effects in the quartz sand filter, and that might be ascribed to the fact that manganese oxides were lost during daily backwash which is required by the drinking water treatment standard [4,5], or green-sand effect could not be formed under the testing water condition at all.

Scanning electrode microscope (SEM) and energy dispersive X-ray (EDAX) revealed that Mn(II) adsorption on manganese sand is single layer and oxidation happens on mineral surfaces [9]. The reported pseudo-equilibrium of Mn(II) adsorption is around 240 min, which is significantly longer than the 10-min filtration time used in Sinopec waterworks [4,9]. Based on these findings, the Mn(II) adsorption by natural manganese sand filter was not in equilibrium during the 10-min filtration. Those Mn(II) can not be timely adsorbed then percolated through the filtration bed. These findings suggest that the natural manganese sand is an unreliable Mn(II) removal process under the water condition of Sinopec waterworks.

Different engineering concepts and practices, other than natural manganese sand, have been tested for Mn(II) removal. Oxidants stronger than chlorine, such as potassium permanganate, ozone, and chlorine dioxide can oxidize Mn(II) into MnO_x(s) [9,10]. UV activated hydrogen peroxide also has been used to oxidize Mn(II) under alkalinity conditions [11,12]. It is reported that Mn(II) was controlled in a creek by automatic aeration triggered by a comparably lower water dissolved oxygen (DO) level, under which Mn(II) will leach from creek bottom sediments [13]. In another case, up to 95% Mn(II) removal from a groundwater source was achieved by using potassium permanganate to oxidize Mn(II), followed by flocculation, settling, and filtration [14]. Since every water type has its own peculiar characteristics, pilot scale studies are recommended and necessary to develop the most reliable and cost effective method of treatment [10].

In this study, the current water treatment process of Sinopec waterworks was simulated in a pilot experiment facility with the raw water directly supplied from the primary pump station of Sinopec waterworks.Chlorine dioxide (ClO_2), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and aeration (air) were applied separately into the system at different locations with changing dosage to study their impacts on Mn(II) removal within the water treatment process. The influence of coagulant dosage and filtration speed were also evaluated. Three parallel filtration columns with individual filter media (natural manganese sand, quartz sand, natural manganese sand and quartz sand 1:1 vol/vol) were used as the last step to intercept Mn(II) that was left from preceding treatment units. Columns containing natural manganese sand were used as the buffer for Mn(II) removal, while the quartz sand column was used to observe Mn(II) removal effectiveness of the testing oxidants without the help from natural manganese sand. The purpose of this experiment is to provide Sinopec waterworks a more reliable Mn(II) removal strategy with minimum change on the current water treatment process.

2. Materials and methods

2.1. Experiment apparatus

The natural manganese sand was collected from MaShan County (GuangXi, China), with a particle size of 0.6–1.2 mm. The quartz sand, with a particle size of 0.5–1.0 mm, was the same as those used in the filtration beds in Sinopec waterworks. Water was delivered to the pilot experiment facility directly from the primary pump station. Water first flowed into a pre-treatment column (as a potential oxidant dosing point), then gravitationally flowed into a circular clarifier, in which an alum salt (aluminum chlorhydroxide) was used as the coagulant. After flocculation and sedimentation, the clarifier effluent flowed into three parallel gravitational filtration columns by gravity (Fig. 4). With this setup, all three testing columns received the water with the same quality and water head. During the experiment, the three filtration columns were backwashed every 24 h with the filtration effluent stored in a water reservoir.

The specifics of the experiment units are shown in Fig. 5. The pre-treatment column was made of steel with an inside diameter of 0.6 m and a total height of 4.7 m. Water level was kept at 4.6 m and the flow rate can be kept between 1.0 and 2.2 m^3/h with a corresponding hydraulic retention time (HRT) of 0.6–1.3 h. The clarifier was made of steel with an inside diameter of 1.0 m and a total height of 3.2 m. Water level was kept at 3.0 m and the flow rate was kept at 1.5 m^3/h with a HRT of 1.5 h, corresponding to a hydraulic loading rate of 3.6 $m^3/m^2/h^{-1}$. The filtration columns were made of polymethyl methacrylate with a total height of 3.7 m and an inside diameter of 30 cm. The bottom 25 cm of each column was filled with gravels (diameter of 6–7 mm) as a supporting layer. During the experiment, natural manganese sand, quartz sand, and a 1:1 volumetric mixture (natural manganese sand on top of quartz sand) were filled into each column to a total depth of 70 cm. The inflow was put 0.5 m below

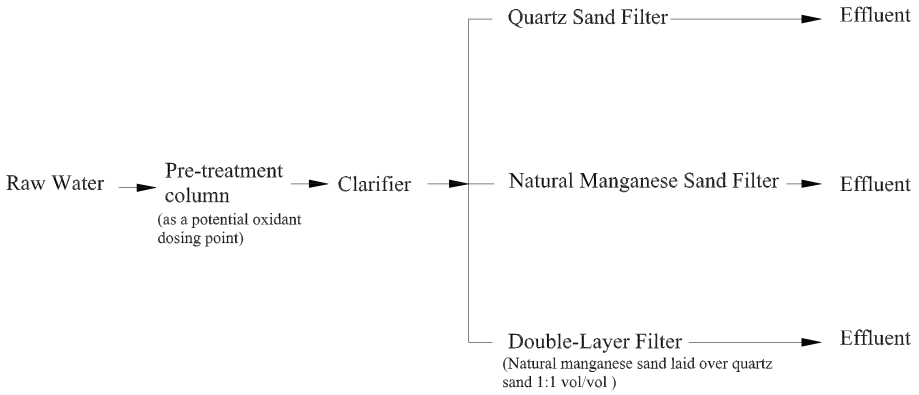

Fig. 4. The flow chart of the treatment process.

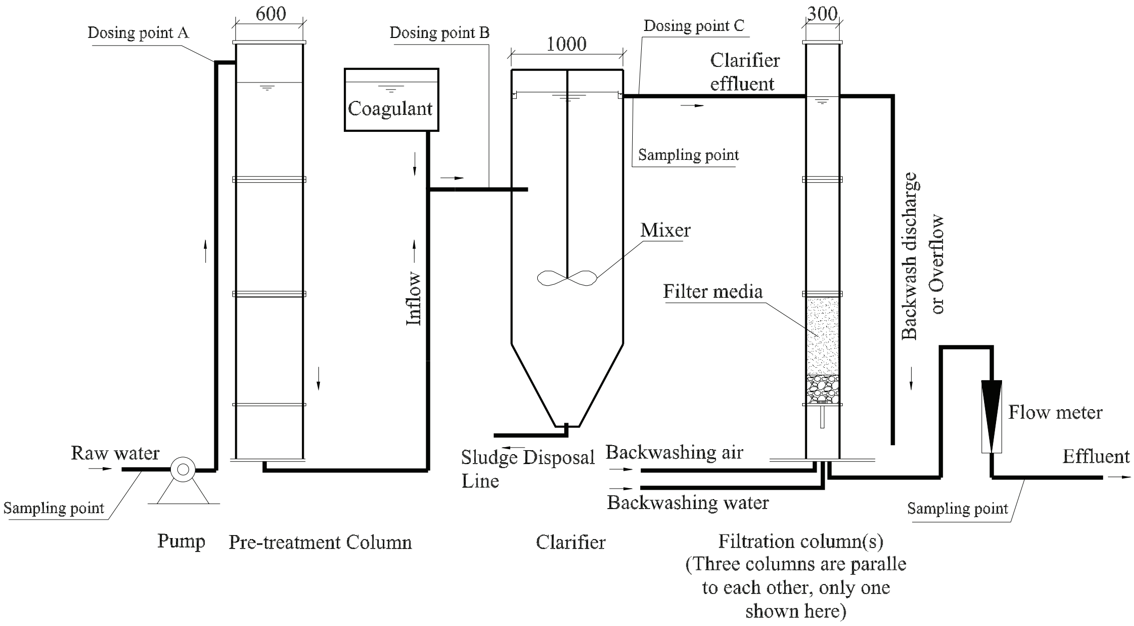

Fig. 5. Schematic drawing of the experiment facilities. (Unit: mm).

the top of the filtration column. The overflow outlet was set at the same height as the inflow, making the highest reachable water level above the filtration bed to be 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 outlet of each column to control the filtration speed. Water samples were taken at each sample point for Mn(II), color, turbidity, pH, DO, etc.

2.2. Testing scenarios

Four oxidants, ClO_2, $KMnO_4$, H_2O_2, and air were used with the purpose to assist natural manganese sand in Mn(II) removal. The involved Mn(II) removal mechanism is to oxidize Mn(II) into MnO_x(s) so as to be precipitated or intercepted by the coagulation–flocculation–sedimentation–filtration process. Natural manganese sand were used with the purpose to oxidize Mn(II) leftovers from pervious coagulation–flocculation–sedimentation process, and intercept the resulting MnO_x(s) and those leftovers from the proceeding sedimentation process.

For ClO_2 and $KMnO_4$, orthogonal experiment design was applied to evaluate the impacts on Mn(II) removal from their dosage, dosing point, coagulant dosage, and filtration speed. The tested factors and tested levels are listed in Table 1. The tested coagulant dosages and filtration speeds were within the current operation range of Sinopec waterworks. For the aeration tests, four aeration rates (1:4, 1:2, 3:4, 1:1 vol/vol air/water), realized by an air pump working with an air flow meter and a flow regulator, were applied on the clarifier effluent through air diffusers (30 μm) located at about 50 cm above the upper

Table 1
Tested factors and levels of the orthogonal experiments.

Levels	Factors									
	ClO_2 test				$KMnO_4$ added in the pre-treatment column			$KMnO_4$ added before water entering the clarifier		
	ClO_2 dosing point	ClO_2 dosage (mg/L)	Coagulant dosage (mg/L)	Filtration speed (m/h)	$KMnO_4$ dosage (mg/L)	Coagulant dosage (mg/L)	Filtration speed (m/h)	$KMnO_4$ dosage (mg/L)	Coagulant dosage (mg/L)	Filtration speed (m/h)
Level 1	A	5	20	6	0.5	20	6	0.5	20	6
Level 2	B	8	25	7	1.0	25	7	1.0	25	7
Level 3	C	10	30	8	3.0	30	8	3.0	30	8

surface of the filtration bed in each filtration column. There were at least three days for each treatment and each sampling point was sampled at least three times a day.

Manganese in the water was measured by persulfate method, and free chlorine was measure by colorimetric method as given in Standard Methods for Examination of Water and Wastewater [15]. A special notice should be given to the fact that the manganese measurement method used in this study will measure MnO_x(s) in the water sample by reducing it back to Mn(II). Therefore, MnO_x(s) that did not intercepted by filter will be measured, and even if the measured manganese is already in the form of MnO_x(s), it is still not taken as acceptable for drinking water [16]. DO was measured by an YSI DO meter (Model 52) and pH was measured by an Orion pH meter (Model 828). Chlorine dioxide was produced onsite by a commercial chlorine dioxide generator (Model OTH-20) provided by OTH company (Shenzhen, China) and the chlorine dioxide generation reaction is $NaClO_3 + 2HCl = ClO_2 + 0.5Cl_2 + NaCl + H_2O$. Sodium hyperchloride ($NaClO_3$) and hydrochloric acid (HCl) were reagent grade. Potassium permanganate ($KMnO_4$) was commercial grade, and hydrogen peroxide (H_2O_2) was 3% commercial grade.

3. Results and discussion

3.1. Chlorine dioxide

The experiment results of the orthogonal experiment $L_9(3^4)$ on ClO_2 application are tabulated in Table 2. Since the effluents of the columns containing naturalmanganese sand all maintained Mn(II) less than 0.01 mg/L when ClO_2 was applied, the Mn(II) removal effectiveness from the testing factors are calculated based on the quartz sand column effluents. The E_i value of each factor is the sum of the Mn(II) removal rates (based on the quartz sand column effluent) of those tests containing the tested level (*i*) of that factor. For example, E_1 of ClO_2 dosing point is the sum of the Mn(II) removal rates of the tests (test 1,2, and 3) containing A (level 1 of ClO_2 dosing point), and so $E_1 = 96 + 80 + 40 = 216$. A higher E_i value indicates a relatively higher Mn(II) removal efficiency from the tested level (*i*). The *R* value of each factor is the difference of the minimum and the maximum E_i values of that factor. Similar to *E* value, the *R* value indicates the response of Mn(II) removal as a result of the changing level of a given factor, with a higher value indicating a relatively higher impact on Mn(II) removal from that factor.

The *R* values (Table 2) of the tested four factors indicate that ClO_2 dosage has the highest impacts on Mn(II) removal, while the impacts from ClO_2 dosing point, coagulant dosage, and filtration speed are almost the same. During the experiment, the columns containing natural manganese sand maintained the Mn(II) lower than 0.01 mg/L in their effluent when ClO_2 was applied, but can only lower the Mn(II) to around 0.10–0.15 mg/L when ClO_2 was not applied. These observations indicate the addition of ClO_2 at the tested dosage can lower the Mn(II) before filtration to a level that can be effectively intercepted by the natural manganese sand. From the *E* values of each tested factor, applying ClO_2 at the pre-treatment column has the best result on Mn(II) removal than the other two dosing points, while coagulant dosage rate at 20 mg/L and filtration speed at 7 m/h are the optimum operation during the test.

As to the tests when ClO_2 was added in dosing point A (in the pre-treatment column) and B (right before water entering the clarifier), with the Mn(II) in the raw water maintained around 0.25 mg/L, the clarifier effluent had a lower Mn(II) level at the same ClO_2 dosage when ClO_2 was added in the pre-treatment column. The test (empty) without ClO_2 application showed the clarifier can barely lower the Mn(II) by about 0.05 mg/L, and the columns containing natural manganese sand can only lower Mn(II) to around 0.05–0.10 mg/L. When ClO_2 was applied, the Mn(II) removal by the clarifier was notably improved, suggesting the flocculation process worked effectively

Table 2
Orthogonal experiment $L_9(3^4)$ on ClO_2 application.

	Factors										
Test no	Dosing point	ClO_2 dosage (mg/L)	Coagulant dosage (mg/L)	Filtration speed (m/h)	Mn(II) in raw water (mg/L)	Mn(II) in clarifier effluent (mg/L)	Natural manganese sand column		Quartz sand column		Mixed sand column	
							Mn(II) (mg/L)	Removal rate (%)	Mn(II) (mg/L)	Removal rate (%)	Mn(II) (mg/L)	Removal rate (%)
1	A	10	20	6	0.25	<0.01	<0.01	>96	<0.01	>96	<0.01	>96
2	A	8	25	7	0.25	0.10	<0.01	>96	<0.05	>80	<0.01	>96
3	A	5	30	8	0.25	0.20	<0.01	>96	0.15	40	<0.01	>96
4	B	10	25	8	0.25	0.15	<0.01	>96	0.15	40	<0.01	>96
5	B	8	30	6	0.25	0.25	<0.01	>96	0.15	40	<0.01	>96
6	B	5	20	7	0.25	0.25	<0.01	>96	0.15	40	<0.01	>96
7	C	10	30	7	0.28	0.25	<0.01	>96	0.05	92	<0.01	>96
8	C	8	20	8	0.30	0.25	<0.01	>96	0.10	67	<0.01	>96
9	C	5	25	6	0.25	0.25	<0.01	>96	0.20	25	<0.01	>96
Empty	N/A	N/A	20–30	6–7	0.25	0.20–0.25	0.05–0.10	60–96	0.20–0.25	0–25	0.05–0.10	60–96
E1	216	105	203	161								
E2	120	187	145	212								
E3	184	228	172	147								
Optimum level	A	10	20	7								
R	96	123	58	65								

Note:

1. A is in the pre-treatment column, B is right before water entering the clarifier, C is in the clarifier effluent;
2. Water temperature during the experiment: 21–25ºC;
3. Raw water pH during the experiment: 6.59–7.79;
4. Raw water DO during the experiment: 4.0–6.0 mg/L.

for MnO_x(s) removal and had a very limited effectiveness for Mn(II) removal. These observations demonstrate the importance of oxidizing Mn(II) into MnO_x(s) and letting MnO_x(s) settled in the clarifier, which will lower the Mn(II) in the clarifier effluent and thus relief the Mn(II) burden on the natural manganese sand as well as the quartz sand.

Based on the *E* values, when ClO_2 was added in the clarifier effluent, the overall Mn(II) removal effectiveness is second to that when ClO_2 was added in the pre-treatment column, but higher than that when ClO_2 was added right before water entering the clarifier. The first result might be explained as an insufficient reaction time for ClO_2 to take effect and small MnO_x(s) particles that can not be effectively intercepted by the testing quartz sand filter [10,14]. In a study that using membrane to intercept MnO_x(s), either reducing the pore-size of the membrane or optimizing the flocculation process to increase the size of MnO_x(s) agglomerates can significantly help improving MnO_x(s) interception efficiency by the membrane [14]. In this study, the formed MnO_x(s) did not undergo a flocculation process when ClO_2 was added in the clarifier effluent. Therefore, the MnO_x(s) agglomerate growth did not get the help from the coagulant and was totally relying on the filter media for interception. However, the columns containing natural manganese sand can maintained Mn(II) < 0.01 mg/L in their effluents and this can be ascribed to the catalytic reaction from the manganese oxide coating [14,17].

On the other hand, the lowest efficiency on Mn(II) removal occurred when ClO_2 was added right before water entering the clarifier. This might be ascribed to the interference from ClO_2 to the flocculation process [17], which potentially led to a relatively smaller MnO_x(s) agglomerate size [10,14]. Hydrochloric acid as an ingredient for ClO_2 generation will inevitably be brought into the water and exerts adverse effects on the flocculation process since the coagulant is alum salt [17]. Also, ClO_2 has a disproportionate potential that consumes alkalinity [17], which will also reduce the flocculation effectiveness of the alum salt. Therefore, by adding ClO_2 too close to the alum salt coagulant adding point in the water treatment will have a tendency to decrease the flocculation efficiency, thus lower the growth of MnO_x(s) agglomerates and increase the burden on the next filtration process to remove Mn(II) and MnO_x(s).

3.2. Potassium permanganate

The orthogonal experiment $L_9(3^3)$ results of applying $KMnO_4$ in the pre-treatment column are tabulated in Table 3. The orthogonal experiment $L_9(3^3)$ results of applying $KMnO_4$ right before water entering the clarifier are tabulated in Table 4. Similar to ClO_2 application, the columns containing natural manganese sand maintained Mn(II) <0.01 mg/L in their effluents when $KMnO_4$ was applied, but can only maintain Mn(II) around 0.05–0.10 mg/L when $KMnO_4$ was not applied. These indicate that the addition of $KMnO_4$ at the tested dosage can also lower the Mn(II) before filtration to a level that can be effectively intercepted by the natural manganese sand. Same as the ClO_2 experiment, the *E* and *R* values are calculated based on the quartz sand column effluent.

When $KMnO_4$ was applied in the pre-treatment-column (Table 3), from the *R* values, $KMnO_4$ dosage demonstrates an impact on Mn(II) removal much higher than that of coagulant dosage and filtration speed. When $KMnO_4$ was added in the pre-treatment column at a dosage of 0.5 mg/L, the Mn(II) in the clarifier effluent dropped to less than 0.12 mg/L, and as a consequence, the Mn(II) in the quartz sand filtration effluent was able to be maintained at less than 0.10 mg/L. From the *E* values, the optimum coagulant dosage is 25 mg/L and the optimum filtration speed is 6 m/h.

When $KMnO_4$ was applied right before water entering the clarifier (Table 4), from the *R* values, $KMnO_4$ dosage still has the highest impact on Mn(II) removal. According to the *E* values, the optimum coagulant dosage is 25–30 mg/L and the optimum filtration speed is 7–8 m/h. It is observed that a $KMnO_4$ dosage between 1.0–3.0 mg/L might be sufficient to lower the Mn(II) to less than 0.10 mg/L in the effluent of the quartz sand column. However, a yellowish color was observed in the clarifier effluent when $KMnO_4$ dosage was 3.0 mg/L, indicating excess $KMnO_4$ were left from the Mn(II) oxidation process. Even $KMnO_4$ theoretically can regenerate the oxidation power of the natural manganese sand [10], there is still a pseudo-equilibrium issue during the 10-min filtration. Although the color was intercepted by all three filtration columns during this experiment, it is not certain that color will not penetrate the filtration columns under an even higher $KMnO_4$ level. Based on this observation, adding $KMnO_4$ in the clarifier effluent will be engineeringly in-appropriate since it will totally rely on the $KMnO_4$ and filtration media to remove Mn(II) within the 10-min filtration time, and thus increase the $KMnO_4$ breakthrough potential.

Comparing the Mn(II) removal effectiveness under the two $KMnO_4$ dosing points, a better Mn(II) removal result can be achieved by adding $KMnO_4$ in the pre-treatment column. Same $KMnO_4$ dosage has a higher overall Mn(II) removal when applied long before the flocculation process. Similar to the phenomenon when ClO_2 was applied right before water entering the clarifier, this observation might be ascribed to an insufficient reaction time between $KMnO_4$ and Mn(II) [17], and the pH decrease caused by $KMnO_4$ reaction that will interfere with the flocculation process of the alum salt [17].

Long reaction time is rated the main shortage of $KMnO_4$ [17]. The minimum reaction was from 30 min. to

Table 3
Orthogonal experiment $L_9(3^3)$ results of applying $KMnO_4$ in the pre-treatment column.

Test no	Factors										
	$KMnO_4$ dosage (mg/L)	Coagulant dosage (mg/L)	Filtration speed (m/h)	Mn(II) in raw water (mg/L)	Mn(II) in clarifier effluent (mg/L)	Natural manganese sand column		Quartz sand column		Mixed sand column	
						Mn(II) (mg/L)	Removal rate (%)	Mn(II) (mg/L)	Removal rate (%)	Mn(II) (mg/L)	Removal rate (%)
1	3.0	20	7	0.25	0.08	<0.01	>96	<0.01	>96	<0.01	>96
2	3.0	25	8	0.25	0.08	<0.01	>96	<0.01	>96	<0.01	>96
3	3.0	30	6	0.25	0.10	<0.01	>96	<0.01	>96	<0.01	>96
4	1.0	20	6	0.25	0.10	<0.01	>96	0.05	80	<0.01	>96
5	1.0	25	7	0.25	0.10	<0.01	>96	0.05	80	<0.01	>96
6	1.0	30	8	0.25	0.08	<0.01	>96	0.06	76	<0.01	>96
7	0.5	20	8	0.25	0.12	<0.01	>96	0.10	60	<0.01	>96
8	0.5	25	6	0.25	0.10	<0.01	>96	0.06	76	<0.01	>96
9	0.5	30	7	0.25	0.10	<0.01	>96	0.08	68	<0.01	>96
Empty	N/A	20–30	6–7	0.25	0.20–0.25	0.05–0.10	60–96	0.20–0.25	0–25	0.05–0.10	60–96
E1	204	236	252								
E2	236	252	244								
E3	288	240	232								
Optimum level	3.0	25	6								
R	84	16	20								

Note:
1. Water temperature during the experiment:14–20°C;
2. Raw water pH during the experiment: 7.2–7.6;
3. Raw water DO during the experiment: 4.0–6.0 mg/L.

Table 4
Orthogonal experiment $L_9(3^3)$ results of applying $KMnO_4$ right before water entering the clarifier.

Test no	Factors										
	$KMnO_4$ dosage (mg/L)	Coagulant dosage (mg/L)	Filtration speed (m/h)	Mn(II) in raw water (mg/L)	Mn(II) in clarifier effluent (mg/L)	Natural manganese sand column		Quartz sand column		Mixed sand column	
						Mn(II) (mg/L)	Removal rate (%)	Mn(II) (mg/L)	Removal rate (%)	Mn(II) (mg/L)	Removal rate (%)
1	3.0	20	7	0.25	<0.01	<0.01	>96	<0.02	92	<0.01	>96
2	3.0	25	8	0.25	0.10	<0.01	>96	<0.01	>96	<0.01	>96
3	3.0	30	6	0.25	0.20	<0.01	>96	<0.01	>96	<0.01	>96
4	1.0	20	6	0.25	0.15	<0.01	>96	<0.18	28	<0.01	>96
5	1.0	25	7	0.25	0.25	<0.01	>96	0.12	52	<0.01	>96
6	1.0	30	8	0.25	0.25	<0.01	>96	0.12	52	<0.01	>96
7	0.5	20	8	0.28	0.25	<0.01	>96	0.18	36	<0.01	>96
8	0.5	25	6	0.30	0.25	<0.01	>96	0.18	40	<0.01	>96
9	0.5	30	7	0.25	0.25	<0.01	>96	0.15	40	<0.01	>96
Empty	N/A	20–30	6–7	0.25	0.20–0.25	0.05–0.10	60–96	0.20–0.25	0–25	0.05–0.10	60–96
E1	116	156	164								
E2	132	188	184								
E3	284	188	184								
Optimum level	3.0	25–30	7–8								
R	168	32	20								

Note:
1. Water temperature during the experiment:14–20°C;
2. Raw water pH during the experiment: 7.2–7.6;
3. Raw water DO during the experiment: 4.0–6.0 mg/L.

90 depending on the type of filtration employed, and a minimum of 30 min. at pH 8.5 has been suggested necessary for MnO_4^- to fully oxidize Mn(II) in a lab study that simulated a drinking water treatment process [14]. During this experiment, by adding $KMnO_4$ in the pre-treatment column, there is at least 2.5 h HRT (1 h in the pre-treatment column and 1.5 h in the clarifier) be allocated for Mn(II) oxidation before water entering the filtration columns, while there is only about 1.5 h HRT when $KMnO_4$ was added right before water entering the clarifier. Furthermore, the optimum coagulant dosage was getting higher when $KMnO_4$ was added right before water entering the clarifier, suggesting an interfered flocculation process. The reduced reaction time together with the interfered flocculation process lowered the overall Mn(II) removal efficiency from $KMnO_4$ application. Consequently, an increased $KMnO_4$ dosage had to be applied for compensation and that might be the reason for the fact that no noticeable improvement on Mn(II) removal was observed as $KMnO_4$ dosage increased from 0.5 to 1.0 mg/L when $KMnO_4$ was added at this dosing point. The importance of letting the clarifier to achieve effective removals on Mn(II) and MnO_x(s) is demonstrated here again with this experiment observation.

The overall optimum operation for $KMnO_4$ application is to apply $KMnO_4$ in the pre-treatment column so as to leave enough reaction time for MnO_4^- to fullyoxidize Mn(II) and reduce the potential interference on the flocculation process. Meanwhile, the optimum coagulant dosage should be kept at 25 mg/L, suggesting a lowered coagulant dosage resulted from a less interfered flocculation process by putting $KMnO_4$ application point far from flocculation process. Also, the optimum filtration speed is 6 m/h, suggesting the desire for a prolonged contact time to improve Mn(II) and/or MnO_x(s) adsorption by the quartz sand as well as the natural manganese sand. Nevertheless, based on the *R* values, the impacts on Mn(II) removal from coagulant dosage and filtration speed are far less than that from $KMnO_4$, their operation can be kept at Sinopec waterworks' engineering convenience.

As to determine the effective $KMnO_4$ dosage, under the optimum operation when $KMnO_4$ was added in the pre-treatment column and the Mn(II) in the raw water was maintained around 0.25 mg/L, the effective $KMnO_4$ dosage was set at 0.5 mg/L. At this dosage, the Mn(II) in the quartz sand column effluent was maintained below 0.1 mg/L, and the Mn(II) in the columns containing the natural manganese sand were maintained below 0.01 mg/L. The advantages of choosing this 0.5 mg/L level over a higher dosage are that the buffer capacity of the natural manganese sand can be utilized, and the whole water treatment system can still satisfy the Mn(II) regulation when the natural manganese sand can not perform its function. This chosen $KMnO_4$ dosage is just about the stoichiometric requirement for a total Mn(II) oxidation. However, it is reported that a 0.5 stoichiometric dosage of $KMnO_4$ before flocculation can effectively remove Mn(II) at pH 8.5 [14] and that effect may be ascribed to the catalytic influence of MnO_2 on the reactions [14,17]. This discrepancy might be explained as the water type differences and the experiment scales, which indicate the necessity of carrying pilot studies before engineering applications [10].

Comparing the experiment results from ClO_2 and $KMnO_4$ applications, the ratio of the R value of $KMnO_4$ application to that of coagulant dosage and filtration speed is higher than the ratio of ClO_2 application, suggesting that $KMnO_4$ is more effective on Mn(II) removal under the fairly stable water condition during the experiment. For drinking water treatment, by-product production during ClO_2 generation is an important aspect that needs to be considered since they still have the potential of forming chlorinated compounds [17,18], while $KMnO_4$ does not have this kind of concern [17]. During the experiment when ClO_2 was added in the pre-treatment column, the residue chlorine in the quartz sand column effluent was at least 0.20 mg/L when Mn(II) can be effectively removed to below 0.10 mg/L, which is 4 times higher than the Sinopec waterworks allowance (< 0.05 mg Cl/L) (Fig. 6). Due to the experiment

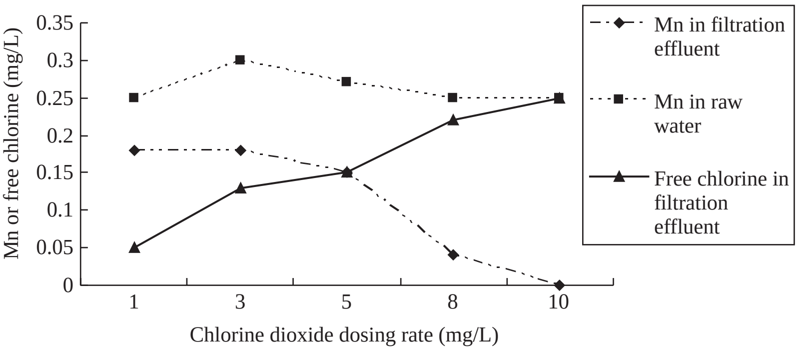

Fig. 6. Free chlorine level in the quartz sand column effluent versus ClO_2 dosage when ClO_2 was added in the pre-treatment column.

limitation, other by-products (such as ClO_2^-) during ClO_2 reaction were not measured. Furthermore, $KMnO_4$ is a commonly used chemical, while ClO_2 must be generated and used onsite. In general, $KMnO_4$ is more suitable than ClO_2 for Mn(II) removal based on the experiment results and engineering considerations of Sinopec waterworks.

3.3. Hydrogen peroxide

Hydrogen peroxide (H_2O_2) was directly added into the clarifier effluent, where only 10 min. left before filtration. H_2O_2 dosage was gradually increased to observe its impact on the Mn(II) in the filtration effluents of the three parallel filtration columns. The experiment results are listed in Table 5. Only very limited Mn(II) removal was observed from the quartz sand filtration column when H_2O_2 dosage was below 15 mg/L. Meanwhile, the columns containing natural manganese sand seems not affected by the H_2O_2 addition and maintained the Mn(II) around 0.05–0.10 mg/L in their effluents. These suggest H_2O_2 application was not able to lower Mn(II) at such dosage under the environment of the testing water.

However, as H_2O_2 dosage went above 15 mg/L, the columns containing natural manganese sand had air bubbles generated within their filter media and the Mn(II) in their filtration effluents varied around 3.0–4.0 mg/L. Meanwhile, the Mn(II) in the quartz sand column effluent was still maintained around 0.10–0.15 mg/L. After stop adding H_2O_2, the Mn(II) in the effluents of the columns containing natural manganese sand were maintained around 2.0–3.0 mg/L for days, indicating the natural manganese sand already lost its capability to adsorb Mn(II) and the manganese oxide coating was changed into water soluble forms. Due to the analysis limitation during the experiment, this phenomenon was not further investigated and the whole filter media was replaced.

It is reported that condition needed for an effective Mn(II) oxidation by H_2O_2 comprised of a 50-h reaction time and a pH of at least 9.3 [11,12], suggesting that H_2O_2 is not expected to have an effective Mn(II) removal in this experiment under a neutral pH with a maximum 3-h contact time (if applied in the pre-treatment column). Also, precipitated MnO_x(s) changed back to soluble forms by H_2O_2 at neutral pH have been observed [11,12] and the resulted conclusion is that H_2O_2 is effective to re-dissolve or wash the precipitated MnO_x(s) on the filters at neutral pH [12]. The H_2O_2 application in this pilot study also showed a negative effect on Mn(II) removal by dissolving the manganese oxide coating of the testing natural manganese sand. In general, based on this experiment and previous studies [11,12], H_2O_2 should not be used together with natural manganese sand for Mn(II) removal unless their oxidation process can be strictly separated. Nevertheless, further experiment that intends to apply H_2O_2 on the other possible dosing points was not proceeded since applying an ineffective Mn(II) removal oxidant with a potential to undermine the natural manganese sand is not engineeringly reliable.

3.4. Aeration

The DO levels within the treatment process under different aeration rates are listed in Table 6. As to the final filtration effluent, the natural manganese sand column had the highest DO level, followed by the mixed sand column, and the quartz sand column took the last. As to Mn(II) removal, the columns containing natural manganese sand could only reduce Mn(II) in their effluents to below 0.10 mg/L, and appeared not influenced by the aeration. The quartz sand column did not show a significant Mn(II) removal during aeration neither and the Mn(II) in its effluent was maintained 0.18–0.20 mg/L. A trend was observed that the quartz sand column consumed more oxygen, but removed less Mn(II) than the other two columns.

It was verified that natural manganese sand has mineral constituents of randomly stacked pyrolusite (MnO_2), γ-Mn_2O_3, and $Mn(OH)_4$ [9] and MnO_2 has the capability to assist degrading humic substances, ascorbate, and different types of catechols [19–21]. In this experiment, the fact that less oxygen was consumed in the columns containing natural manganese sand actually implies that manganese oxides can provide some water treatment that otherwise will rely on the DO in the water. This phenomenon also suggests that water quality will short the operational lifetime of the natural manganese sand [5–8].

In the previous pilot study [4] that only used natural manganese sand for Mn(II) removal, the high Mn(II) concentration was accompanied by a relatively lower DO in the raw water and the DO in the clarifier effluent was under 5.5 mg/L at most of the time. Furthermore, the tested natural manganese sand could maintained the Mn(II) less than 0.05 mg/L in its filtration effluent when the Mn(II) varied 0.25–0.30 mg/L in the raw water. However, in this study, the natural manganese sand can not lower Mn(II) to below 0.05 mg/L without extra oxidants, while the DO was above 7 mg/L in the clarifier effluent and the Mn(II) never went above 0.30 mg/L in the raw water. This implies that the DO sensitivity of Mn(II) during this experiment is different than that of the previous study.

The fact that ineffective Mn(II) removal from aeration on the clarifier effluent suggests that an even longer reaction time might be helpful in Mn(II) removal, such as putting aeration in the pre-treatment column. However, since the Cl_2 pre-treatment by Sinopec waterworks provided a limited effect on Mn(II) removal, and the literature also hold an opinion that it takes oxygen substantially longer reaction time to oxidize Mn(II)

Table 5
Manganese removal under H_2O_2 application.

H_2O_2 dosage (mg/L)	Mn(II) in clarifier effluent (mg/L)	pH in clarifier effluent	Mn(II) in effluent (mg/L)		
			Natural manganese sand column	Quartz sand column	Mixed sand column
0.5–5.0	0.22–0.26	7.34–7.51	0.05–0.10	0.20–0.25	0.05–0.10
5.0–15.0	0.23–0.26	7.34–7.51	0.05–0.10	0.10–0.15	0.05–0.10
15.0–20.0	0.22–0.27	7.34–7.51	3.0–4.0	0.10–0.15	3.0–4.0

Table 6
DO and Manganese levels (mg/L) of the three filtration columns at different aeration rates.

Air: water	DO of raw water	DO of clarifier effluent	DO of water right before filtration	Mn(II) in raw water	Mn(II) in clarifier effluent	Natural manganese sand column		Quartz sand column		Mixed sand column	
						DO	Mn(II)	DO	Mn(II)	DO	Mn(II)
1:4	5.68	7.86	9.36	0.25	0.22	7.38	0.05–0.10	7.10	0.18	7.26	0.05–0.10
1:2	5.10	7.34	9.95	0.28	0.23	7.32	0.05–0.10	7.03	0.20	7.25	0.05–0.10
3:4	5.36	7.24	10.45	0.25	0.21	7.89	0.05–0.10	7.22	0.18	7.38	0.05–0.10
1:1	5.88	7.56	10.95	0.26	0.20	7.95	0.05–0.10	7.64	0.17	7.86	0.05–0.10

Note:

1. Water temperature during the experiment: 14–20°C;
2. Saturate DO during the experiment: 10.4–11.8 mg/L.

than chlorine and potassium [22], then a significant improvement on Mn(II) removal was not anticipated for aeration on the raw water. In addition, $KMnO_4$ experiment illustrated a promising Mn(II) removal result. Therefore, no further tests on aeration were conducted.

4. Conclusion

Based on the experiment results, the optimum practice is to apply $KMnO_4$ at the pre-treatment column at a dosage of at least 0.5 mg/L, while coagulant dosage should be kept at 25 mg/L and filtration speed be controlled at 6 m/h. The final suggestion to Sinopec waterworks is to apply $KMnO_4$ as a pre-treatment, while natural manganese sand and quartz sand still be used as a double-layer filter media as a buffer for Mn(II) removal. The $KMnO_4$ dosage can be flexibly adjusted according to the Mn(II) in the raw water, while coagulant dosage and filtration speed can be kept at Sinopec waterworks engineering convenience. Since $KMnO_4$ can help to regenerate the Mn(II) adsorption sites of natural manganese sand, appropriate $KMnO_4$ overdose might be feasible under the condition that no $KMnO_4$ will penetrate the filtration bed. The result of this pilot experiment needs to be fine tuned for industry operation through full scale engineering tests. The result of this study should be considered valid under the condition that the natural manganese sand used in this study is in favor of Mn(II) removal. Nevertheless, it is necessary to emphasize that targeting the Mn(II) pollution source is equally important as removing Mn(II) within a waterworks facility, on which the stakes of public health and industry operation are held.

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