

# Occurance and control of manganese in a large scale water treatment plant

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**Abstract** The continuous variations of dissolved oxygen (DO), manganese (Mn), pH, and their effect on manganese removal by different water treatment processes are investigated. The results show that the declined DO concentration and pH value in the bottom of reservoir results in the increasing release of Mn from sediment to source water. Manganese concentration increased from 0.1 to 0.4 mg·L<sup>-1</sup> under the condition that DO concentration decreased from 12.0 to 2.0 mg·L<sup>-1</sup> in raw water. The different water treatment processes exhibited different efficiency on manganese removal. The processes with recycling of the suspended sludge, low elevation velocity in settling tank and slow filter rate, will benefit the manganese removal. During a high release of manganese in raw water, traditional coagulation-sedimentation and filtration could not completely remove Mn, although granular activated carbon filtration (GAC) had been applied. At that case, preoxidation with chlorine or potassium permanganate (KMnO<sub>4</sub>) was necessary to address the high manganese concentration.

**Keywords** manganese release, dissolved oxygen, settling filtration, pre-oxidation

## 1 Introduction

Manganese (Mn) exists widely in nature. Low level of Mn is necessary for humans to survive. However, it is toxic if its concentration is above certain degree in a human body. Manganese can transform among the various morphology in the environment, but it can not be biodegraded.

Therefore, the pollution caused by Mn was difficult to eliminate [1,2]. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage [3–5]. Mn can also cause Parkinson, lung embolism and bronchitis [6,7]. Considering its toxicity, Chinese government addresses more attention on it and regulates that the maximum manganese concentration can not be above 0.1 mg·L<sup>-1</sup> in the “Standards for drinking water” (GB5749-2006).

To effectively remove Mn from water, lots of studies are addressed on this topic. Some researchers investigated the manganese distribution and valence conversions in water [6–8]. Some studied the removal methods, such as aeration and filtration, chemical oxidation and manganese oxidizing bacteria and so on [1,2,9]. Manganese in water can be oxidized by chlorine, converting them to manganese dioxide [10]. Then coagulation process can remove manganese by charge neutralization, adsorption and so on [11–13]. Finally Mn would be dispatched by sedimentation and filtration [14–17]. Apparently, these technologies have been successful applied into manganese removal in water treatment plants [18–21]. However, studies on manganese concentration variation in raw water and its removal efficiency in water treatment plants with existing processes are more plausible. Moreover, little information is published regarding how those common water pretreatment technologies works in manganese removal.

In this study, we chose one of the largest surface water treatment plants in north China as a research object, which takes reservoir as the main raw water. The plant mainly has two different water treatment processes. One is traditional method with coagulation-sedimentation; the other is coagulation-sedimentation with micro-sand [22,23]. Mn exceeded the regulation during this plant in the past. Therefore, it is a great worth to analyze the quality data of the raw water and effluent from 2005 to 2011, especially

the relationship between Mn with pH and dissolved oxygen (DO). The comparison of manganese removal by these two different processes was conducted. Additionally, effects of preoxidation were also evaluated. Finally, we hope to thoroughly understand the function of various stages of water treatment processes in manganese removal, and provide helpful advices for waterworks.

## 2 Experimental methods and water treatment processes

### 2.1 Experimental methods

The analytical methods of all data in this paper are followed with the “Standard examination methods for drinking water” (GB/T5750.1~5750.13-2006) issued by China Ministry of health [24]. Ammonium persulfate differentiation photometric method is used to test Mn, and iodine quantity method is used to test DO.

### 2.2 Water treatment process

The raw water flows into the water plant by the gravity via the tunnel in the reservoir bottom and 75 km sealed pipes. The flow rate can be adjusted by valves installed between the tunnel and pipe. And the sampling point for the raw water is located at the upstream 1 m of valves. The depth between tunnel and reservoir surface is about 20 m, and about 10 m between tunnel and reservoir bottom. The reservoir storage is about  $1.2 \times 10^9 \text{ m}^3$  in recent 10 years. Except for supplying residents and lakes in this city, this reservoir has not discharged any flood and mud for many years.  $\text{Cl}_2$ ,  $\text{KMnO}_4$  and powdered activated carbon (PAC) can be dosed at the downstream 5–10 m of valves. Normally,  $\text{Cl}_2$  dosage is between 1.0 and  $1.5 \text{ mg}\cdot\text{L}^{-1}$ , only when the odor appears. PAC or  $\text{KMnO}_4$  could be dosed instead of chlorine. The date of chemical dosing is listed in Table 1. There are two different water treatment processes in this waterworks. The treatment capacities are  $5 \times 10^5 \text{ m}^3\cdot\text{d}^{-1}$  and  $6.6 \times 10^5 \text{ m}^3\cdot\text{d}^{-1}$  for process 1 and process 2 respectively. Process 1 used the traditional coagulation and sedimentation by adding polymeric aluminum chloride (PACl) and  $\text{FeCl}_3$  as the coagulant. The retention time is 96 min. But the process 2 used Actiflo by adding PACl and polyacrylamide (PAM) with a hydraulic retention time (HRT) 27 min. For process1, the filtration used double layer filters (40 cm thickness anthracite and 40 com thickness quartz and sands). The filtration rate is about  $7.5 \text{ m}\cdot\text{h}^{-1}$ . While, in process 2, monolayer anthracite with 150 cm thickness was applied. Its filtration rate is about  $10 \text{ m}\cdot\text{h}^{-1}$ . For advanced treatment, both processes used monolayer granular activated carbon (GAC). However, the filtration rate is different. One is  $10 \text{ m}\cdot\text{h}^{-1}$  and the other is  $12 \text{ m}\cdot\text{h}^{-1}$ .

**Table 1** Date of chemicals dosing in raw water

chemical	dosage /( $\text{mg}\cdot\text{L}^{-1}$ )	date(dd/mm/year)
$\text{KMnO}_4$	0.6	1/1/2005 – 21/4/2005; 16/11/2005 – 6/3/2006
	0.8	5/9/2005 – 21/9/2005
	0.7	13/4/2006 – 30/9/2006; 10/10/2006 – 6/12/2006
$\text{Cl}_2$	1.2	21/4/2005 – 5/9/2005
	1.1	6/3/2006 – 13/4/2006
	1.5	26/3/2007 – 5/9/2007; 10/10/2009 – 23/9/2010; 14/10/2010 – 31/12/2010
	1.0	29/9/2007 – 24/9/2008; 27/10/2008 – 21/9/2009
PAC	15	21/9/2005 – 16/11/2005; 30/9/2006 – 10/10/2006;
	5	5/9/2007 – 29/9/2007
	8	24/9/2008 – 27/10/2008; 21/9/2009 – 10/10/2009; 23/9/2010 – 14/10/2010

## 3 Results and discussion

### 3.1 DO and Manganese concentration variation in raw water

Figures 1 and 2 respectively depicted the variation of DO and manganese concentration of raw water in a 6-year continued observation. It can be noted that DO concentration began to decline in May of each year, and reached its minimum value of below  $2.0 \text{ mg}\cdot\text{L}^{-1}$ , then rose to the normal concentration up to  $8.0 \text{ mg}\cdot\text{L}^{-1}$  in November. Interestingly, the variation of manganese concentration was another situation compared to the DO. During January to July, the concentration of Mn was always less than  $0.1 \text{ mg}\cdot\text{L}^{-1}$ . However, the concentration of manganese began to rise in August, and reached the concentration up to  $0.45 \text{ mg}\cdot\text{L}^{-1}$  in September, then again decreased to below  $0.1 \text{ mg}\cdot\text{L}^{-1}$ . To further reveal the reason of manganese concentration increasing, the pH variations in different months are presented in Fig. 3. Apparently, pH value was a little bit higher in winter as an average of 8.3, while it became lower when summer came. The lowest pH value is between 7.4–7.7. Higher pH value would lead to a lower manganese concentration since  $\text{OH}^-$  would react with manganese to settle down.

To correlate the pH, DO and Mn, further investigation among Mn, DO and pH was carried out during August to November in 2011 (Fig. 4). The results identified the reverse relationship between Mn and DO. Although DO concentration returned to normal  $8.0 \text{ mg}\cdot\text{L}^{-1}$  and pH returned to 8.0 in the beginning of October, manganese release was increasing continuously while the concentration decreased slowly.

DO concentration in reservoir reduced gradually from water surface to reservoir bottom [1]. The changes of DO concentration is closely related with the algae growth or death [22]. As the definition of pH, reductant and oxidant

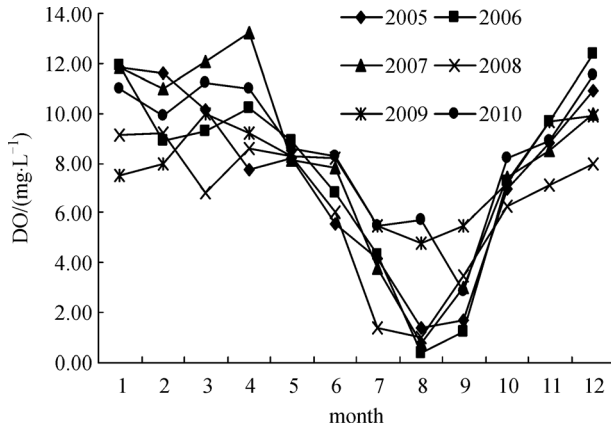


Fig. 1 DO concentration of raw water

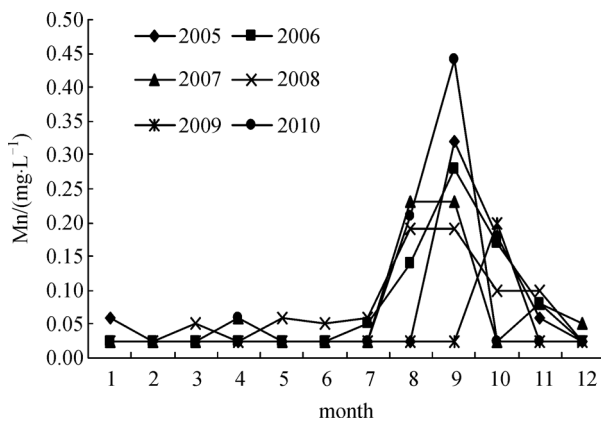


Fig. 2 Manganese concentration of raw water

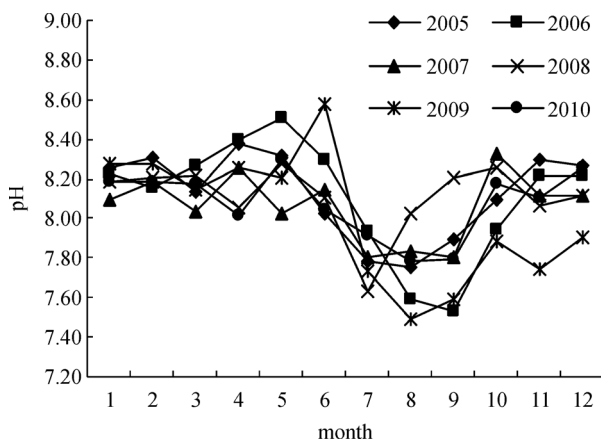


Fig. 3 pH value of raw water

can be also defined as the electron donor and electron acceptor. So we can use Eq. (1) to define pE.

$$\text{pE} = -\lg(\alpha_e), \quad (1)$$

where  $\alpha_e$  is electron activity in the aqueous solution. From

Fig. 5, we can find pE is a key factor in manganese conversion, when pE in reservoir is enhanced, manganese ions will be oxidized into  $\text{MnO}_2$  particles [11]. Because the distance between sampling point for raw water and reservoir bottom is about 10 m, when the sampling points of DO concentration is reduced to be below  $2.0 \text{ mg}\cdot\text{L}^{-1}$ , the reservoir bottom might have been in an extremely anoxic conditions. The solid manganese particles in reservoir bottom sediments will be deoxidized to dissolve manganese ion, and diffused into water. With DO diffused to the bottom of the reservoir, oxygen demand by algae could slow down. Therefore, DO concentration will increase gradually, and manganese ion is oxidized to manganese solid, such as manganese (IV) dioxide, then settled into the reservoir bottom again. Therefore, increasing and keeping a certain DO concentration, or controlling the sediments in the reservoir bottom, would be possible ways to avoid high manganese concentration.

Besides that, pH is another key factor in the manganese conversion. The changes of pH will bring about the pE of manganese conversion decline or rise directly. From Fig. 5, we find that the PE of manganese ions converted to  $\text{MnO}_2$  decrease with the pH of raw water is increased. We can infer that in an alkaline environment, manganese ions is more easily oxidized into  $\text{MnO}_2$  particles and removed from the water.

### 3.2 Mn removal in each treatment stage

Normally chemicals will be dosed into raw water in reservoir intake (Table 1), then raw water flows into the process inlet with 15–40 h, manganese concentration in process inlet are shown in Figs. 6 and 7.

From Figs. 6 and 7, the variation of the inlet concentration of Mn in the different processes is similar with the raw water. The maximum manganese concentration happened during August to October. In addition, the inlet concentrations of Mn in the treatment processes are higher than that in raw water in all months of 2005 and 2006, highly due to the dosage of  $\text{KMnO}_4$  or powder activated carbon (PAC) in raw water intake. Moreover, the inlet concentration of manganese in process 1 are slightly higher than process 2 in some time owing to the filter backwash water flowing back to process 1 since manganese concentration in filter backwash water are obviously higher than the raw water, and ever reached  $1.15 \text{ mg}\cdot\text{L}^{-1}$ . Because of the chlorine dosage of  $1.5 \text{ mg}\cdot\text{L}^{-1}$  in 2009, the inlet concentrations of manganese in the treatment processes are obviously slower than the raw water.

Due to the addition of  $\text{Cl}_2$  or  $\text{KMnO}_4$  in raw water and oxygen supplement by water contacting with air in the process inlet, the manganese ion will be transferred into solid manganese dioxide, and suspended in water, which will be possible to be removed by coagulation and sedimentation. The efficiency of manganese oxidation is

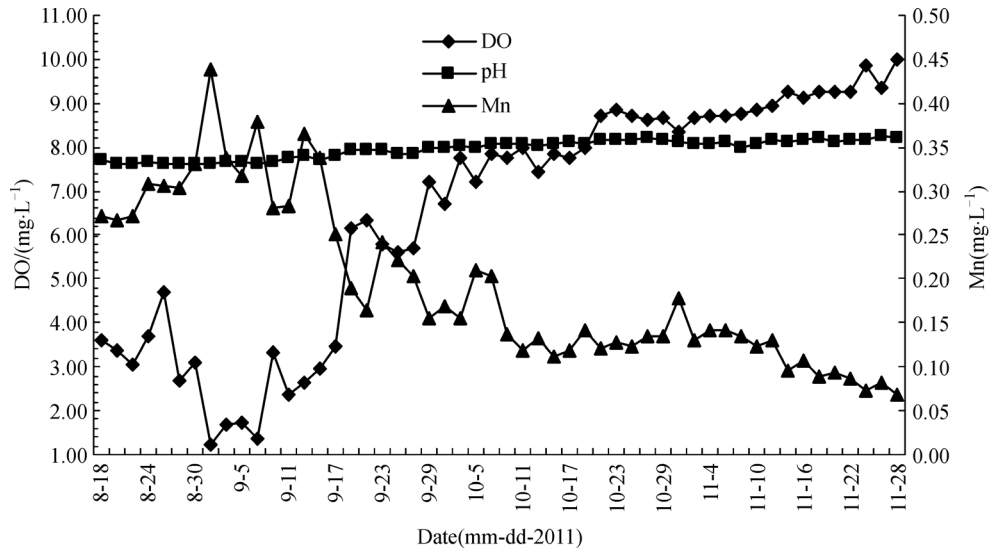


Fig. 4 DO, pH and Mn concentration of raw water between August and November, 2011

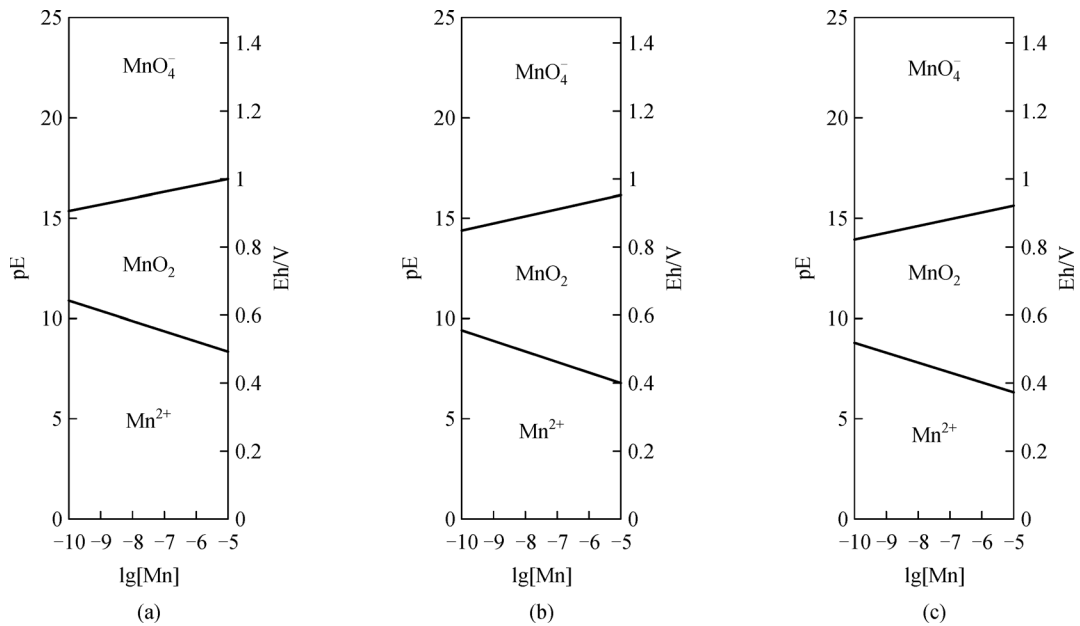


Fig. 5 pE-lg[Mn] in water: (a) pH = 7.5; (b) pH = 8.2; (c) pH = 8.5

normally linked with the dosage and the pH. As shown in Fig. 8, in the region  $E > 0.5$  and  $pH > 7.0$ , precipitated forms of manganese dioxide ( $MnO_2$ ) are possible. In water treatment plant, it is necessary either very often to raise the pH or redox potential (E). As the setting of the oxidant that increases the potential is tricky, so as not to exceed a threshold that causes the manganese to remain soluble form highly oxidized ( $MnO_4^-$  or  $Mn^{7+}$ ), that is, with  $E(v) > 0.7$  for  $pH = 6$ . It is preferred to control the pH to be above 7.2 to obtain a rapid reaction. The higher the pH is, the faster the oxidation kinetics is, even in the range of pH 8.5–9.0.

Manganese concentration in Clarification and Actiflo outlet are shown in Figs. 9 and 10. Although the inlet concentration of Mn in process 1 is higher than process 2, manganese concentration in clarification outlet are lower than Actiflo outlet in most period. And manganese removal rate in clarification reached about 50%. There are mainly two reasons for this phenomenon. One is that more suspended sludge is included in clarification process. The other is the rising velocity in clarification is only 10% of actiflo. The corresponding hydraulic retention time is 10 times higher than high speed clarifier. Moreover, traditional clarifier contains a lot of suspended sludge which is

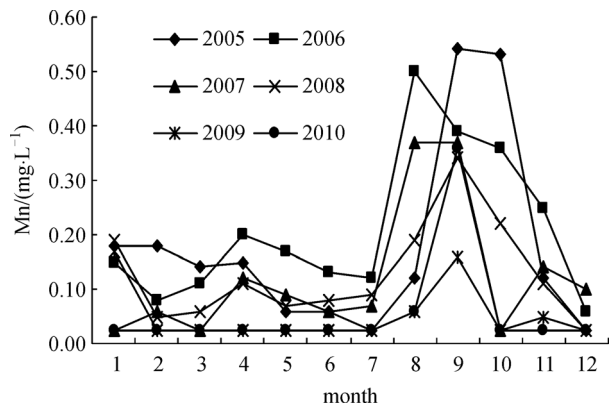


Fig. 6 Mn concentration of inlet in process 1

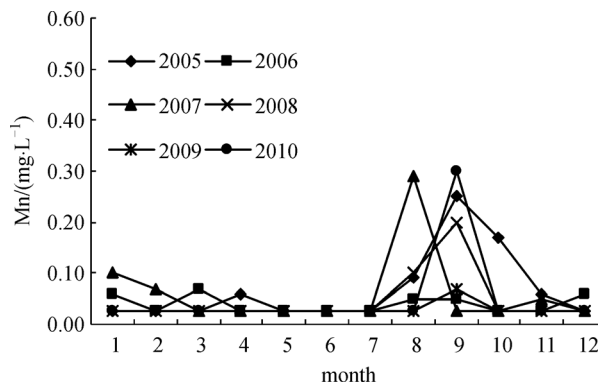


Fig. 9 Mn concentration in Clarification outlet of process 1

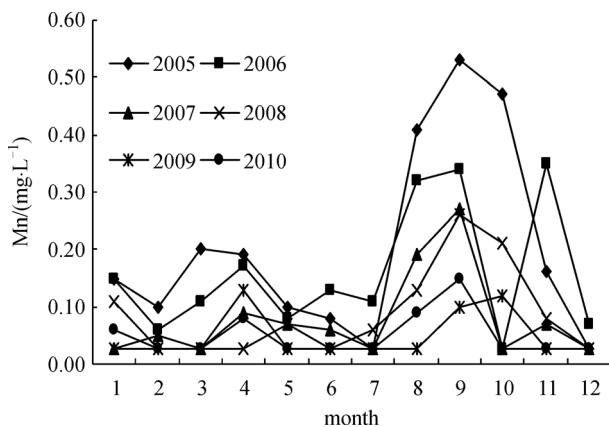


Fig. 7 Mn concentration of inlet in process 2

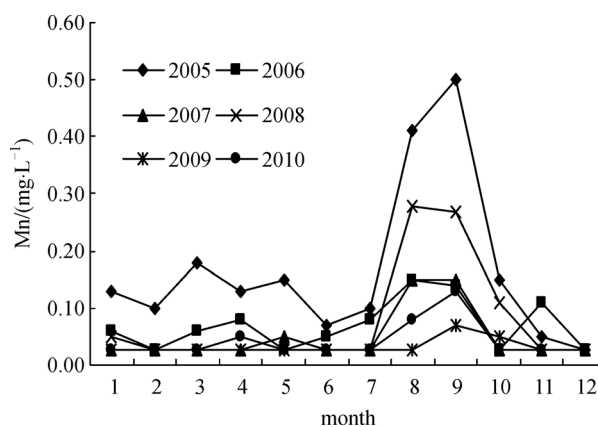


Fig. 10 Mn concentration in Actiflo outlet of process 2

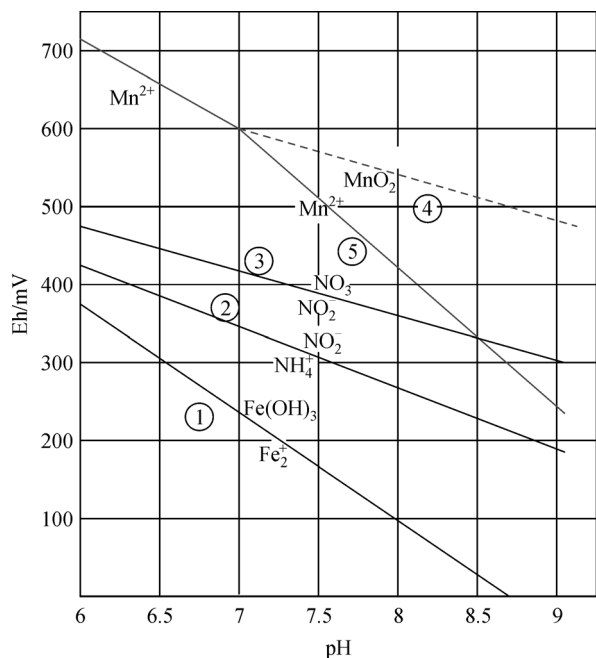


Fig. 8 Relationship between Manganese precipitation and pH

discharged regularly. In contrast, Actiflo contains micro-sand which is recirculated with constant sludge discharge. Apparently, with the classical clarifier, sufficient contact time is provided. Thus, these two points are favorable in coagulation and sedimentation. Therefore, process 1 is more helpful for manganese removal.

Mn will be further removed during filtration, however over  $0.1 \text{ mg} \cdot \text{L}^{-1}$  manganese concentration still appeared in the outlet of process 1 and process 2 (Figs. 11 and 12), indicating that settling and filtration is not enough for manganese removal. It can be found that the removal rate of manganese in process 1 can reach about 60%, more effective than that in process 2, although the filter thickness of process 2 (1.5 m) is bigger than process 1 (0.8 m). It can be explained that process 2 with a thinner quartz sand diameter has a higher filtration rate of  $12.0 \text{ m} \cdot \text{h}^{-1}$ .

From Figs. 13 and 14, it can be noticed that the outlet concentration of manganese was measured as  $0.3 \text{ mg} \cdot \text{L}^{-1}$  manganese in Process 2 which exceeds the Chinese standard in September 2005. Generally, manganese concentrations after GAC in Process 1 and process 2 are all below  $0.1 \text{ mg} \cdot \text{L}^{-1}$  or detection limit, showing that GAC filter have considerable effect on manganese removal [3].

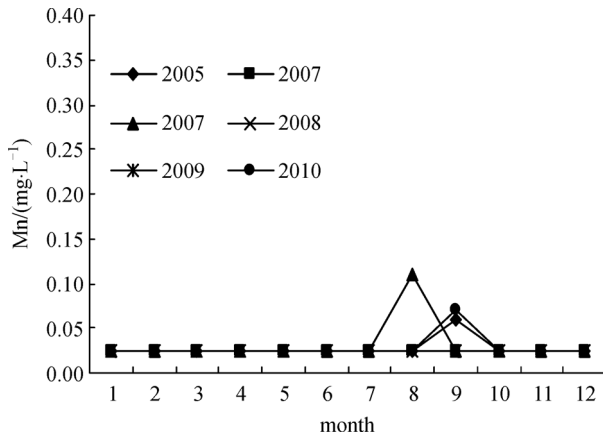


Fig. 11 Mn concentration in Anthracite sand Filter outlet of process 1

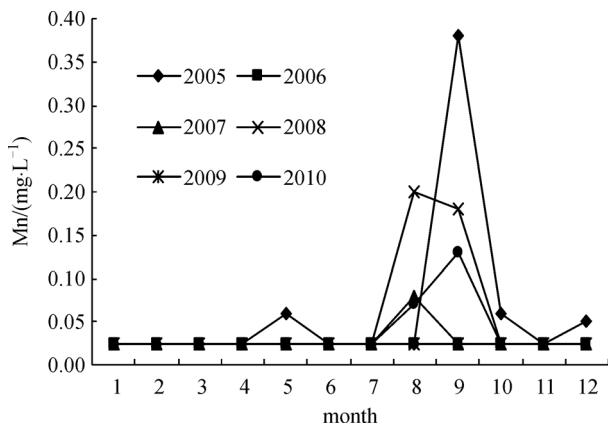


Fig. 12 Mn concentration in Anthracite Filter outlet of process 2

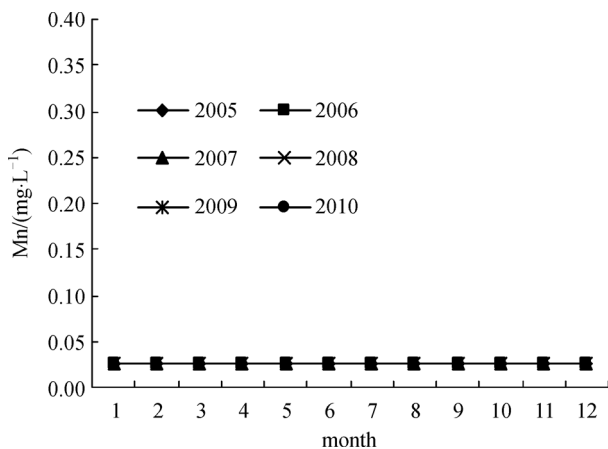


Fig. 13 Mn concentration in GAC Filter outlet of process 1

In September 2005, the odor was happened, PAC, instead of chlorine, was dosed. However, it is not effective for manganese ion oxidation, resulting in high manganese concentration in the outlet of sedimentation, anthracite filter and GAC filter. It also can be found the similar

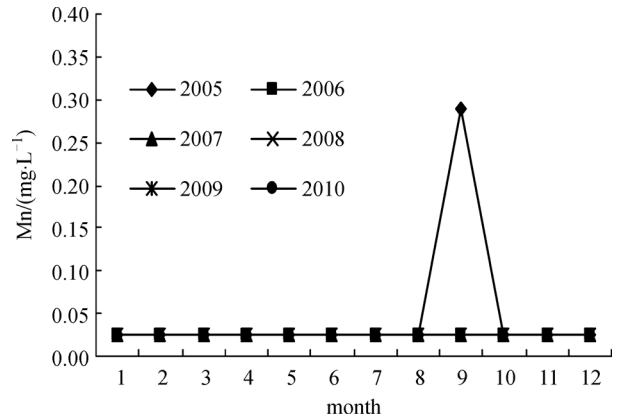


Fig. 14 Mn concentration in GAC Filter outlet of process 2

phenomenon happened in September 2008 and 2010. Another reason which caused manganese above the national standard of process 2 in September 2005 is that the load concentration of manganese reached the maximum value. Under these circumstances, a high rising velocity in settling tank and a high flirtation rate are all unfavorable for manganese removal. By contrast, in 2006, the manganese concentration of inlet was increased after dosing  $0.7 \text{ mg} \cdot \text{L}^{-1} \text{ KMnO}_4$ , manganese can be easily removed by sedimentation and filtration. Thus, the addition of chlorination or  $\text{KMnO}_4$  in the pretreatment should be a better method to control the manganese [5].

## 4 Conclusions

By six-years investigation on water quality change, the correlation between Mn, DO, and pH is analyzed in this paper. The effect of preoxidation and different treatment process on manganese removal was investigated. The results were concluded as below:

1) During August to October of each year, the declined DO concentration and pH promotes the reduction of manganese-solid particles in reservoir bottom and its transformation into dissolved  $\text{Mn}^{2+}$ , which leads to the increase of manganese concentration in raw water.

2) Both lower elevation velocity in settling tank and longer filtration time in process benefit higher manganese removal.

3) Apparently, traditional method, such coagulation and sedimentation and filtration, can not sufficiently remove Mn to meet the national standard ( $0.1 \text{ mg} \cdot \text{L}^{-1}$ ) under the condition that manganese concentration in raw water is over  $0.5 \text{ mg} \cdot \text{L}^{-1}$ . Therefore, GAC should be used as an important supplement way for manganese removal.

4) The addition of  $\text{Cl}_2$  or  $\text{KMnO}_4$  as a pretreatment is necessary under the condition of manganese concentration of  $0.5 \text{ mg} \cdot \text{L}^{-1}$  in raw water, which will oxidize the soluble  $\text{Mn}^{2+}$  into nonsoluble  $\text{MnO}_2$  and further promote the manganese removal by conventional treatment processes.

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