SCIENCE CHINA
Technological Sciences

• Article •

June 2014 Vol.57 No.6: 1160–1164
doi: 10.1007/s11431-014-5515-3

# Effect and mechanism of manganate preoxidation for organics removal

REN ZhiJun[1,2*] & NIGEL Graham[2]

[1] *College of Aerospace and Civil Engineering, Harbin Engineering University, Harbin 150001, China;*
[2] *Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW72AZ, UK*

Received November 5, 2013; accepted January 9, 2014

The performance and mechanism of manganate preoxidation process for organics removal were investigated in the present paper. The results showed that manganate was a potentially powerful oxidizing agent and could make the natural organic matter (NOM) concentration of sample solution increase. The process of manganate in combination with ferrous sulphate (FeMnO) was effective for organics removal and with the highest removal rate of 89% when the FeMnO dose was 0.18 mmol/L. The fluorescence analysis showed that the fluorescence intensity values related to hydrophobic acids and model humic acid polymers were the highest and the relative position of the main peak fluorescence intensity was shifted towards lower emission wavelengths, which indicated the reduction in the degree of aromaticity of residual organic matter fraction.

**potassium manganate, femno process, oxidation, organic matters**

**Citation:** Ren Z J, Nigel G. Effect and mechanism of manganate preoxidation for organics removal. Sci China Tech Sci, 2014, 57: 1160–1164, doi: 10.1007/s11431-014-5515-3

## 1 Introduction

Removal of natural organic matter (NOM) in surface water has been paid more and more attention to in recent years. These dissolved organics in drinking water treatment are common impediment responsible for coagulant increasing, formation of disinfection by-products (DBPs) and microbial regrowth in distribution system and are hardly removed by traditional treatment processes [1]. Considerable efforts have been made in drinking water treatment to develop methods which can improve NOM removal [2,3]. Chemical oxidation has been proved to be one of the effective methods to enhance coagulation and improve NOM removal [4]. Permanganate preoxidation has been widely used for organics removal, especially for high organic content [5,6]. It was speculated that $KMnO_4$ oxidized the organics and made them easier to be absorbed by the hydrolysis products of coagulant. Some of the organics with higher molecular weight may be adsorbed on the surface of newly formed manganese dioxide, thus causing the reduction of organics of higher molecular weight when the water was subjected to permanganate preoxidation. Furthermore, permanganate might destroy some unsaturated organic bonds and result in either the reduction in ultraviolet (UV) absorbance or the formation of some products with lower molecular weights, and so the disinfection by-products can be controlled correspondingly [7].

As an intermediate in the industrial synthesis of $KMnO_4$, potassium manganate is an oxidant with high oxidation capacity and the electrode potentials of manganate is 1.43 at pH of 7 compared with permanganate (1.14 at pH of 7). Some previous studies have been undertaken in China concerned with the role of preoxidation by manganate as a coagulation-enhancing reagent to remove turbidity, and the results showed that potassium manganate had good coagu-

*Corresponding author (email: renzhijun2003@126.com)

lation-supporting effect on treating water of high turbidity and under the best potassium manganate dosage, the turbidity removal efficiency of sedimentation water exceeded 90% [8,9].

Manganate (Mn(VI)), like permanganate, can act as both an oxidant and a coagulant/adsorbent arising from the formation of insoluble manganese dioxide (Mn(IV)) from the chemical reduction of $MnO_4^{2-}$. Organics can react with manganate directly as well as with its disproportionation products. However, until now, there has not been any reported information related to the variation of molecular weight distribution of natural organic matter after they are subjected to manganate oxidation.

In order to gain an insight into the more complex interaction between manganate as a water treatment chemical and NOM, the reaction between manganate and organics was investigated in the present paper. The results provide further information for assessing the potential advantages of using potassium manganate in drinking water treatment in comparison to conventional alternative chemicals.

## 2 Materials and methods

All the reagents and chemicals used in this study were purchased from chemical suppliers in the UK. These reagents and chemicals were all analytical grade and used as supplied. The paper and membranes of all kinds used in this study were bought from Whatman (Germany). Humic acid (HA) (sodium salts, 4.2% carbon content) and potassium manganate were obtained as commercial reagent grade in solid from Sigma-Aldrich Company Ltd. (UK). Ferrous sulphate was also obtained as commercial reagent grade (BDH, UK).

### 2.1 Preparation of feed water

Test (model) solutions were obtained by diluting HA stock solution to demonized water to the desired concentration (5 mg/L). Humic acid stock solution was prepared by dissolving 1 g of dry humic acid into 1 L of demonized water and the solution was vigorously mixed for 12 h and then filtered through a 0.45 μm pore size filter membrane. The concentration of humic acid after filtration was approximately 1 g/L. 25 mL of this solution was further diluted to 1 L solution thereby reaching an effective concentration of 5 mg/L. The color of the solution was brown due to the humic acid added to the water.

### 2.2 Gator jar setup

All of the experiments were conducted by using Gator Jar Setup, which is a 2 L square, acrylic vessel of 21 cm height and 11.5 cm square side built with a standard design recommended by AWWA (AWWA, 2000).

### 2.3 Manganate preoxidation for organics removal

Model solution was treated by manganate in combination with ferrous sulphate. An appropriate quantity of $K_2MnO_4$ (0.03 mol/L, with 0.5 mol/L NaOH as solvent) was added to the HA model water in the Gator jar with HCl for pH correction. After peroxidation for 40 min, a certain amount of $FeSO_4$ (0.06 mol/L) was added to the solution in the Gator jar with stirring at 250 r/m for 1 min and at 150 r/m for 4 min. In this process, $K_2MnO_4$ was added to the HA model solution, allowing HA to be oxidized directly by $K_2MnO_4$ or indirectly by $KMnO_4$ arising from potassium manganate disproportionation. Then, with the addition of $FeSO_4$, the remaining oxidants were able to produce higher state Fe species, such as insoluble $Fe(OH)_3$ by the reaction equation: $MnO_4^{2-}+2Fe^{2+}+4H_2O=MnO_2+2Fe(OH)_3+2H^+$. For convenience, the treatment combination of manganate and $FeSO_4$ is referred to as 'FeMnO', and the dosage of FeMnO in the experiments is expressed as mmol/L (as $K_2MnO_4$).

### 2.4 Samples analysis

All the samples were filtered through a 0.45 μm membrane filter prior to simulating distribution system tests and analyses used to characterize the treated waters.

Nonpurgeable organic carbon (NPOC) was measured using the TOC-Vws (Shimadzo, Japan) instrument. The selected samples were measured by fluorescence excitation emission matrices (F-EEM), using an FP-6500 spectrofluorometer (Jasco) at ambient pH. Samples were diluted to a dissolved organic carbon (DOC) concentration of 1 mg/L prior to measurements. EEMs were generated for each sample by scanning over excitation wavelengths between 220 and 400 nm at intervals of 5 nm and emission wavelengths between 280 and 480 nm at intervals of 2 nm.

## 3 Result and discussion

### 3.1 Effect of manganate preoxidation on NOM removal

The reduction in HA concentrations with potassium manganate was studied with different doses of $K_2MnO_4$. Manganate with different dosages from 0.006 to 0.27 mmol/L was added to the HA solution for 40 min and $Na_2S_2O_3$ was added to the solution to end the reaction.

Figure 1 shows the results of HA treatment by manganate preoxidation, expressed as NPDOC removal. In Figure 1, it can be seen that the concentration of sample water increased as manganate dose increasing. The concentration of HA solution was 5.2 mg/L. Even little dose of manganate (0.006 mmol/L) could make the concentration of HA solution increase by 0.3 mg/L. And when the manganate dose was higher than 0.018 mmol/L, the concentration of HA solution appeared to increase slightly.

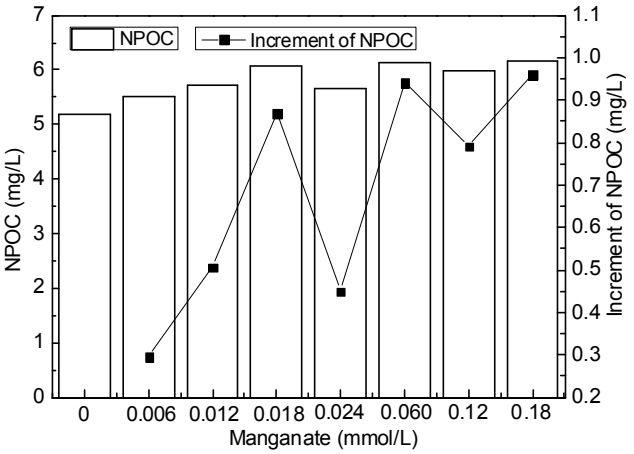


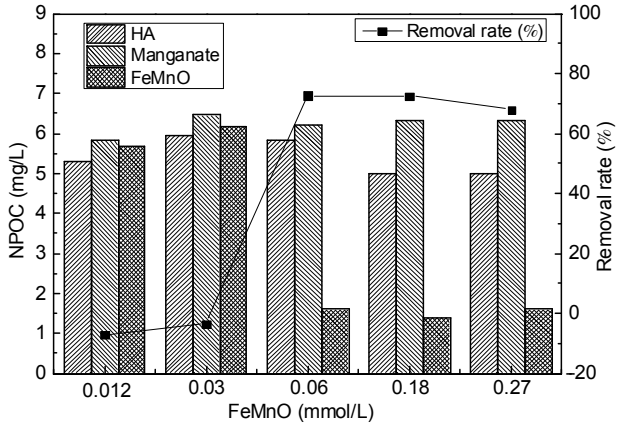

**Figure 1** Effect of dosage of manganate on NOM removal.

After manganate preoxidation, the organics concentration increased. The main reasons for this might be that the macromolecules were degradated into less recalcitrant and lower MW reaction products due to the effect of manganate oxidation on HA. Now, there have been no reported studies in literature about the impact of manganate on humic substances.

### 3.2 Effect of FeMnO process on NOM removal

The effect of different doses of FeMnO process for organic matters removal was studied and the result was shown in Fiugre 2.

In Fiugre 2, it can be seen that at lower FeMnO dose of 0.012 and 0.03 mmol/L of manganate, the concentration of HA increased compared with sample HA solution. Taking 0.03 mmol/L FeMnO process for example, after manganate preoxidation for 40 mins, the organics concentration increased by 21%, then $FeSO_4$ was added into the HA solution, the HA concentration increased by 16% compared with the model HA solution. When the FeMnO dose was more than 0.06 mmol/L, the HA removal rate was consistently high. The highest removal rate was 89% when the FeMnO dose was 0.18 mmol/L, then with the FeMnO dose increased, the removal efficiency systematically decreased. This result was similar to Zhao's [10] research work, which showed that increasing the FeMnO dose could get the higher HA removal rate.




**Fiugre 2** Effect of FeMnO process on organic removal.

In FeMnO process, $K_2MnO_4$ was added to the HA model solution, allowing the HA to be oxidized directly by $K_2MnO_4$ or indirectly by $KMnO_4$ arising from potassium manganate disproportionation. Then, with the addition of $FeSO_4$, the remaining oxidants were able to produce higher state Fe species, such as insoluble $Fe(OH)_3$. The solid phase $MnO_2$ and $Fe(OH)_3$ formed during the reaction can remove the intermediates of HA oxidation and the remaining HA by charge interaction, enmeshment and adsorption. As discussed above, the HA removal rate was very lower at a lower FeMnO dose, which is believed to be due to the effects of oxidation of the organic macromolecules creating smaller, more hydrophilic fractions which are more difficult to remove by coagulation, and require greater amounts of Fe and Mn species for achieving their removal; increasing FeMnO dose will cause greater amounts of $Fe(OH)_3$ and $MnO_2$ and have a higher HA removal rate.

### 3.3 Mechanism analysis of manganate process for organics removal

In order to reveal the relative change of organic matters, the experiment of organic matter removal in manganate process was carried out. In this experiment, 0.06 mmol/L manganate was first added to the sample water, after peroxidation for 40 mins, a certain amount of $FeSO_4$ (0.06 mmol/L) was added to the solution in the Gator jar with stirring at 250 r/m for 1 min and at 150 r/m for 4 min. TOC analyses, UV scan and fluorescence spectroscopy measurements were carried out on samples of raw, manganate preoxidation and FeMnO process.

The UV and NPOC values of different water samples were shown in Table 1. The results in Table 1 were consistent with the above discussed results and showed that $UV_{254}$, NPOC and SUVA values were increased by 46.0%, 4.48% and39.8% respectively after manganate preoxidation, and in FeMnO process, $UV_{254}$, NPOC and SUVA values were decreased greatly and decreased by 84.4%, 70.0% and 48.2% respectively compared with raw sample water.

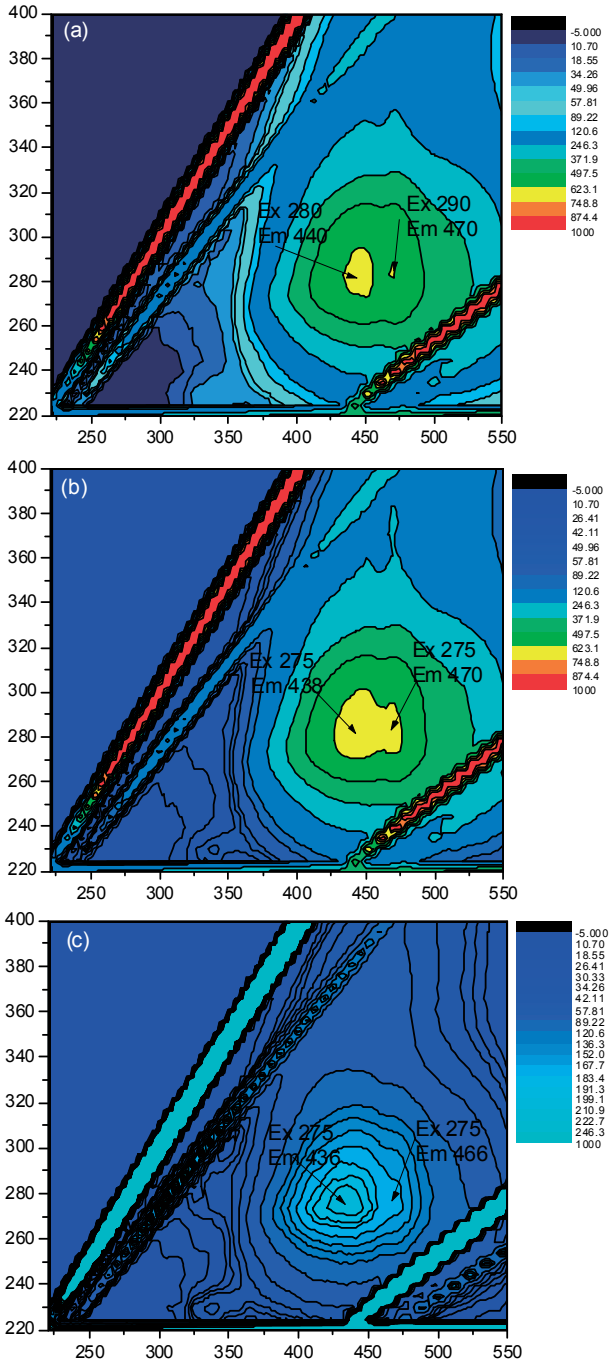
The relative change in quantitative and qualitative properties for different water samples can provide useful information on the degree of NOM removal with relation to

**Table 1** UV and NPOC value of different water samples

| Process | Raw water | Manganate | FeMnO |
|---|---|---|---|
| $UV_{254}$ (m) | 61.7 | 90.1 | 9.6 |
| TOC (mg/L) | 6.03 | 6.3 | 1.81 |
| SUVA (L/mg/m) | 10.23 | 14.3 | 5.3 |

physicochemical properties of the removed fractions. The water samples of raw, manganate preoxidated and MnFeO were analyzed by fluorescence spectra analysis and the results were shown in Fiugre 3 and Table 2.

According to the results of fluorescence excitation emission matrix spectroscopy (EEMs) of different water treatments, the presence of four main fluorescence peak regions was observed: peak I belonged to aromatic protein (fluorescence excited between 220 and 250 nm, and emitted between 330 and 380 nm), peak II belonged to suluble microbial by-product (fluorescence excited between 250 and 280 nm, and emitted between 290 and 380 nm), peak III belonged to the related hydrophobic acids (fluorescence excited longer than 250 nm and emitted between 380 and 480 nm) and peak IV belonged to model humic acid polymers (fluorescence excited between 220 and 250 nm and emitted between 330 and 380 nm) [11], in which the fluorescence intensity values of peak III and peak IV were the highest.




**Fiugre 3** Fluorescence EEMs of raw water (a), manganate preoxidation (b), and FeMnO process (c).

**Table 2** Excitation-emission matrices of raw water (a), manganate preoxidation (b), and FeMnO process (c)

| Sample | | | a | b | c |
|---|---|---|---|---|---|
| | EM | nm | 230 | 220 | 225 |
| Peak I | EX | nm | 340 | 338 | 336 |
| | Intensity | au | 44.1 | 44.9 | 45.7 |
| | EM | nm | 285 | 275 | 275 |
| Peak II | EX | nm | 338 | 326 | 342 |
| | Intensity | au | 48.9 | 34.7 | 34 |
| | EM | nm | 280 | 275 | 275 |
| Peak III | EX | nm | 440 | 438 | 436 |
| | Intensity | au | 640.8 | 662.7 | 205.3 |
| | EM | nm | 290 | 275 | 275 |
| Peak IV | EX | nm | 470 | 470 | 466 |
| | Intensity | au | 613.6 | 645.7 | 180.2 |

Take the fluorescence intensity (FI) changes of peak III for an example, the FI of peak III was increased firstly after manganate preoxidation, then decreased in FeMnO process. The relative changes in HA measured as peak III intensity between raw water and subsequent treatment stages increased by 3.4% for manganate pretreatment, and then decreased by 67.9% for final water. Similar pattern of changes was observed for Peak IV.

On the other hand, the relative position of the maximum peak III and peak IV fluorescence intensity was shifted towards lower emission wavelengths for 15 nm (Table 2), which indicated the reduction in the degree of aromaticity of residual organic matter fraction.

## 4 Conclusions

The overall goal of this work is to evaluate manganate oxidation process for NOM removal. The major conclusions of this work are summarized as follows:

1) Manganate is a potentially powerful oxidizing agent and even a little dose of manganate (0.006 mmol/L) will cause the HA concentration increasing.

2) FeMnO process produced by $K_2MnO_4$ and $FeSO_4$ has a better performance for organics removal when the dose of FeMnO is higher than 0.06 mmol/L and the highest removal rate is 89% when the FeMnO dose is 0.18 mmol/L.

3) The fluorescence analysis enables qualitative characterization of the organic matter fractions preferentially removed by manganate treatment processes. The results show that the FI related to hydrophobic acids and model humic acid polymers is the highest and the relative position of the main peak fluorescence intensity is shifted towards lower emission wavelengths, indicating the reduction in the degree of aromaticity of residual organic matter fraction.

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