Enhanced coagulation with in situ manganese dioxide on removal of humic acid in micro-polluted water
Yubin Zeng, Ziyang Zeng and Junlin Wang

ABSTRACT
The morphology and surface characteristics of manganese dioxide (MnO₂) formed in situ, which was prepared through the oxidation of MnSO₄ using KMnO₄, were studied. The effects of factors including the form of MnO₂, dosage, pH, dosing sequence of in situ MnO₂ on the enhanced coagulation were systematically evaluated. The results of analysis by the UV254 and permanganate index CODMn methods indicated that humic acid removal increased from 9.2 and 2.5% to 55.0 and 38.9%, when 10 mg/L of the in situ MnO₂ was added in the presence of 2 mg/L of polyaluminum sulfate. The studies of orthogonal experiment revealed that coagulation was most affected by the pH, whereas the dosage of in situ MnO₂ and slow stirring duration exhibited a weaker effect. At a pH value of 4.0, in situ MnO₂ dosage of 10 mg/L, slow stir over 40 min, and the total solids content was 20 mg/L, the humic acid removal by UV254 and CODMn methods reached 71.2 and 61.2%. These results indicated that the presence of in situ MnO₂ enhanced the coagulation and removal of humic acid from water.

Key words | enhanced coagulation, humic acid, in situ MnO₂, online dosing method

INTRODUCTION
Humic acid, which is a main organic constituent, accounts for 60–90% of the total organic content of natural waters (Traversa et al. 2014; Wang et al. 2014). The functional groups of humic acid, such as the carboxyl group, hydroxyl group, quinone, and ether, can react with various types of cations or organic reactive groups in water, particularly polar organic compounds to form complexes. These reactions can increase the solubility of insoluble toxic compounds in water; therefore, the existence of humic acid is one of the primary factors that create potential safety hazards in water (El-Rehaili & Weber 1999). Fenton’s peroxidation was used as an advanced oxidation technique to treat high concentrations of humic acid in simulated wastewater, and the mechanism consists of both oxidation and coagulation simultaneously (Wu et al. 2010).

Enhanced coagulation is a method that is based on conventional coagulation. By adjusting the pH and increasing the coagulant dosage, the efficacy of the coagulation effect is enhanced. The development of MnO₂ originates from the use of potassium permanganate for pre-treatment of wastewater. During the reduction of potassium permanganate, in situ-state MnO₂ is formed; this compound possesses greater reactivity, specific surface area, and absorption capacity than aged MnO₂ (Liang et al. 2005; Fan et al. 2010). At present, the use of in situ MnO₂ in research is primarily focused on its role as both an oxidant and absorbent; more specifically, the latter use is removal of heavy metals, such as cadmium, strontium, and lead, from water (Xu et al. 2013; Wan et al. 2014). In contrast, relatively few studies have reported using in situ MnO₂ as an enhanced coagulant to remove natural organic matter.
from waters. This paper reports the enhanced coagulation effect of in situ-state MnO₂ formed by reacting potassium permanganate and manganese sulphate, which has value for removal of organic pollutants from water.

**METHODS**

Reagents and water sources

All the reagents used were analytical grade. The concentration of stock solution KMnO₄ and MnSO₄ was 4.6 mmol/L and 6.9 mmol/L, respectively. Commercial polyaluminium sulfate (PAS) was purchased from a purification-reactent company in Henan province, China, and used in the experiment as the coagulant. The flocculant polyacrylamide (PAM) used in jar tests were provided from other companies. The raw water from East Lake of Wuhan, China was used in this investigation. The initial concentration of humic acid in micro-polluted water by the UV254 and permanganate index CODMn methods was in the range of 0.20–0.80 and 4 mg/L–20 mg/L, respectively.

Experimental methods

Jar tests: the enhanced coagulation test was conducted in a jar filled with 1 L of micro-polluted lake water, and a programmable jar testing apparatus was used with the following procedure: addition of coagulant PAS following 1 min of rapid mixing at 250 rpm, followed by addition of MnO₂ in different forms, rapid mixing at 250 rpm for 1 min. Then, 1 mg/L of PAM was added to the solution, which was subsequently stirred at 150 rpm for 30 min and settling. After settling for 30 min was completed, the samples (1 cm below) were collected and filtered with 0.45 μm cellulose acetate membrane for measurement of CODMn and UV254.

The effects of different factors on enhanced coagulation were systematically studied. These tests included the comparison between PAS and PAS+MnO₂, the comparison between in situ MnO₂ and commercial MnO₂; the effects of pH of the water, temperature, dosage of in situ MnO₂, and ratio of KMnO₄/MnSO₄, dosing sequence, dosing methods, and mixing time.

Orthogonal experiments: to obtain the optimal enhanced coagulation parameters, a standard orthogonal array matrix L₉ (3⁴) was constructed with four major factors and three levels. The four factors and three levels are as follows: (1) pH: 4, 6, 8; (2) dosage of in situ MnO₂: 6, 10, 15 mg/L; (3) slow stirring time: 20, 30, 40 min; (4) particulate concentration: 10, 20, 30 mg/L. Results of humic acid removal were analyzed and optimized statistically to identify significant factors and to evaluate optimal values.

The percentage of humic acid removal (%) by UV254 and CODMn measurements was considered as

\[
\text{Removal (%) } = 100 - \frac{100C_t}{C_0}.
\]

where \(C_0\) is the initial concentration of humic acid by UV254 and CODMn methods, and \(C_t\) is the concentration of humic acid by UV254 and CODMn methods after completing coagulation.

The Brunauer Emmett Teller (BET) specific surface area of in situ MnO₂ was determined using nitrogen adsorption-desorption analysis (Ladavos et al. 2012). A total of 0.0443 g of sample was used, with nitrogen gas as the adsorbate, in the adsorption measurement under liquid nitrogen at 77.31 K. The specific surface areas of the samples were determined by applying the BET equation to the data.

The zero point of charge (pHzPC) of the in situ MnO₂ was determined using a Malvern Zetasizer at 25 °C. The same mole ratio of KMnO₄ and MnSO₄ were added into 100 mL of deionized water. 1 M NaOH and 1 M HCl solution was used to adjust the pH values to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0. The zeta potential at different pH conditions was measured.

The permanganate index was calculated as the chemical oxygen consumption using potassium permanganate solution as the oxidant, which is denoted as CODMn, in accordance with the standards (Standard Methods for the Examination of Water and Wastewater 1998). The UV254 absorbance was defined as the absorbance of some organic matter in water in the presence of ultraviolet light with a wavelength of 254 nm. UV254 can reflect the content of natural organic matter such as humic acid, molecules that consists of conjugated double bonds, and aromatic compounds with \(C=O\) functional groups.

**Instruments**

X-ray diffraction (XRD) was performed to confirm the crystal structure and identity using X-ray diffractometer (Rigaku D/MAX-RB, Japan) with Cu Kα radiation in the 2θ ranges of 5–80° at a scan rate of 1°/min. The surface structure of samples was determined using scanning electron microscopy (SEM, JSM-5610LV, Japan). The characterizations of the samples were carried out at their optimal working conditions. A glass pH electrode (PHS-25, China)
was used for pH measurement. The instrument used in BET specific surface area was a Micromeritics (Shanghai) automated ASAP 2020 accelerated specific surface area and porosimetry analyzer. The UV$_{254}$ absorbance was measured using a UV-1600 UV/Vis spectrophotometer.

**RESULTS AND DISCUSSION**

**XRD and SEM**

The XRD pattern of the *in situ* MnO$_2$ is shown in Figure 1. The diffraction peak of the *in situ* MnO$_2$ is relatively weak and wide, which indicates low crystalline structure. Analyzing the XRD pattern as a whole, only one peak is apparent, which suggests that the purity of the *in situ* MnO$_2$ was relatively high. Given that the diffraction peak is at $2\theta = 37.17^\circ$, a comparison with powder diffraction patterns indicates that the nature of the manganese dioxide is $\gamma$-MnO$_2$ (Fathy et al. 2015).

The SEM image of the *in situ* MnO$_2$ is shown in Figure 2. It can be observed that the *in situ* MnO$_2$ particles are amorphous in nature, with a maximum diameter of approximately 120 nm. With an aging time of 30 min, the *in situ* MnO$_2$ is observed to coagulate into clusters. There is a tendency of increasing aggregation with increasing concentration of the *in situ* MnO$_2$.

**BET specific surface area and pH$_{ZPC}$**

The specific surface area directly governs the contact interfacial area that is available for adsorption. Generally speaking, the adsorption capacity increases with increasing specific surface area. The N$_2$ adsorption/desorption isotherm of MnO$_2$ and the fitted curve of the BET equation are shown in Figures 3(a) and 3(b). According to the classification of gas adsorption isotherms, the nitrogen adsorption isotherm of MnO$_2$ exhibits a steep straight line at low pressures, whereas at high pressures, the adsorption isotherm plateaus at a fixed value. The calculated specific surface area of the MnO$_2$ is 99.31 m$^2$/g. The specific surface area of *in situ* MnO$_2$ is dependent on the preparation method and conditions: Zhang & Ma (2008) used equivalents of KMnO$_4$ to oxidize MnSO$_4$ (small amounts of NaCO$_3$ were added to neutralize the H$^+$ produced during the reaction), and the specific surface area of the produced *in situ* MnO$_2$ was 184 m$^2$/g.

It can be observed from Figure 4 that the zeta potential of *in situ* MnO$_2$ varies within the tested pH range of 2.0–10.0. The pH$_{ZPC}$ of *in situ* MnO$_2$ is in the pH range of 2.5–5.0. When the pH of the solution is greater than this value, the surface of the *in situ* MnO$_2$ is negatively charged, i.e., the zeta potential is negative on the surface of *in situ* MnO$_2$. Conversely, when the pH is less than the isoelectric point, the zeta potential of the *in situ* MnO$_2$ is positive (Savaji et al. 2014; Kosmulski 2014).

**Effect of the form of the manganese dioxide on enhanced coagulation**

Figures 5(a) and 5(b) show a comparison between the effects of *in situ* MnO$_2$ and commercial MnO$_2$ on the efficiency of enhanced coagulation. It was observed that with increasing coagulant dosage, both UV$_{254}$ removal and COD$_{Mn}$ removal increased dramatically with *in situ* MnO$_2$. This enhanced coagulation effect was even more apparent at low coagulant dosage. When the dosage of PAS was 2 mg/L, the removal of UV$_{254}$ and COD$_{Mn}$ were 9.2% and 2.5%, respectively. When 10 mg/L of *in situ* MnO$_2$ was added, the removal of UV$_{254}$ and COD$_{Mn}$ increased to 55.0% and 38.9%, respectively. In contrast, the UV$_{254}$ removal remained unchanged.
and the COD$_{\text{Mn}}$ removal increased to a far lesser extent when commercially available MnO$_2$ particles were used. The reason for this difference is that in situ MnO$_2$ has strong adsorption capacity at low coagulant dosage. Therefore, adding a certain amount of in situ MnO$_2$ can effectively enhance the removal of organic matter from water. In contrast, commercially available MnO$_2$ has weak adsorption capacity, and its enhanced coagulation efficacy is not significant.

**Effect of pH value on enhanced coagulation**

The pH value is an important factor that affects the coagulation efficiency. The pH value can impact both the reaction and the product of coagulant in water, and it also influences the amount of organic matter in water (Xie et al. 2014).

As shown in Figures 6(a) and 6(b), at pH ≤ 4.0, humic acid removal was higher than under alkaline conditions. Specifically, the humic acid removal by UV$_{254}$ method reached 65.9% at pH ≤ 4.0, whereas the humic acid removal by COD$_{\text{Mn}}$ method was 32.2%. In alkaline conditions,
humic acid removal by UV$_{254}$ and COD$_{Mn}$ methods were 40.0% and 25.0%, respectively. This difference can be attributed to the following: at pH = 4.0, PAS hydrolyses in water, forming Al$_8$(OH)$_{20}^{4+}$. pH 4.0 is close to pH$_{ZPC}$ of in situ MnO$_2$, which causes MnO$_2$ to aggregate with hydrolysate of PAS through electrostatic attraction. This generates a manganese-dioxide aluminum network that precipitates readily and facilitates the removal of humic acid molecules by adsorption from the aqueous solution. At pH = 2.0, the hydrolysate of PAS is present in the form [Al(H$_2$O)$_n$]$^{3+}$ ($n = 6–10$). The degree of polymerization is less than that for pH = 4.0. At pH > 8.0, PAS takes the forms of Al(OH)$^-_{n}$ and Al(OH)$_{26}^{2-}$, and the zeta potential of the in situ MnO$_2$ is less than $-8.0$ mV; this results in an electrostatic repulsion that negatively impacts adsorption and bridging, so resulting in less of an coagulation enhancement.

**Effect of in situ manganese dioxide dosage on the enhanced coagulation**

As shown in Figure 7, humic acid removal by UV$_{254}$ and COD$_{Mn}$ methods increased rapidly when the dosage of in situ MnO$_2$ was increased from 2 to 10 mg/L; the UV$_{254}$ removal increased from 5.8 to 26.0%, whereas the COD$_{Mn}$ removal increased from 6.1 to 25.9%. When the dosage of in situ MnO$_2$ was continuously increased from 10 to 20 mg/L, both the UV$_{254}$ and COD$_{Mn}$ removal decreased slightly. Because this study used micro-polluted water, which exhibits low turbidity, this decrease resulted in an increased interparticle distance within the aqueous environment. The addition of in situ MnO$_2$ causes high efficiency of adsorbing organic contaminants and concomitantly increases the probability of interparticle collision, thus way causing large aggregates that precipitate out of the water. Consequently, both the UV$_{254}$ and COD$_{Mn}$ removal increased with increasing dosage of in situ MnO$_2$. With a further increase in the dosage of in situ MnO$_2$, the resultant increase in concentration caused auto-aggregation between MnO$_2$ species, accordingly reducing its total adsorption capacity. In addition, aggregated MnO$_2$ clusters reduced the interparticle collision frequency, thereby causing a reduction in coagulation effects.

**Effect of the KMnO$_4$/MnSO$_4$ dosing ratio on enhanced coagulation**

The effect of the KMnO$_4$/MnSO$_4$ dosing ratio on the enhanced coagulation is shown in Figure 8. As the
KMnO4/MnSO4 dosing ratio was decreased from 5 to 0.33, the UV254 removal first exhibited an increase, which was followed by a decrease. When the KMnO4/MnSO4 dosing ratio was greater than 1, the UV254 removal increased with decreasing KMnO4/MnSO4 ratio. This result occurred because as the KMnO4/MnSO4 dosing ratio became greater than 1, the concentration of KMnO4 was 10 mg/L, whereas that of MnSO4 was less than 10 mg/L. As a result, when the KMnO4/MnSO4 dosing ratio was greater than 1, MnSO4 became the limiting reagent in the production of in situ MnO2. The concentration of in situ MnO2 increased with decreasing KMnO4/MnSO4 concentration, hence increasing the enhanced coagulation effect. When the KMnO4/MnSO4 dosing ratio was less than 1, MnSO4 became the limiting reagent in the production of in situ MnO2. The concentration of in situ MnO2 increased with decreasing KMnO4/MnSO4 dosing ratio (increasing MnSO4 concentration), hence increasing the enhanced coagulation effect. When the KMnO4/MnSO4 dosing ratio was less than 1, the concentration of in situ MnO2 was 10 mg/L, with an excess of MnSO4 in solution. The concentration of excess MnSO4 increased with decreasing KMnO4/MnSO4 dosing ratio, resulting in an increase of Mn2+ species in solution, which hindered the adsorption of small organic molecules, thus reducing the UV254 removal efficiency.

**Effect of dosing sequence and dosing methods on enhanced coagulation**

Six types of dosing method were used: (1) in situ MnO2 (online) + PAS + PAM; (2) PAS + in situ MnO2 (online) + PAM; (3) MnO2 (commercial source) + PAS + PAM; (4) in situ MnO2 (mixed first then added) + PAS + PAM; (5) PAS + MnO2 (commercial source) + PAM; and (6) PAS + PAM.

The effect of the dosing sequence and methods on coagulation is shown in Figure 9. The UV254 removal was consistent among all methods, with a value of approximately 40%, which indicates that the differences in dosing methods and sequence had little effect on the UV254 removal. However, method 2 resulted in the optimal CODMn removal of 21.6%. In comparison with method 6, the CODMn removal was double in method 2. The addition of in situ MnO2 resulted in better CODMn removal compared with commercially available MnO2. In addition, the removal efficiency was greater when the in situ MnO2 was added after the addition of PAS compared with that when the in situ MnO2 was added before the addition of PAS. This result can be attributed to the fact that in situ MnO2 is not yet aggregated, in contrast with commercially available MnO2. Therefore, in situ MnO2 possesses a greater adsorption capacity. Furthermore, addition of in situ MnO2 can enhance coagulation through adsorption bridging, which leads to a stronger coagulation effect. Addition of in situ MnO2 after the coagulant facilitates the formation of aggregates of PAS with stronger coagulation efficiency and [Al(OH)3]m precipitate, thus enhancing humic acid adsorption in water.

**Orthogonal array analysis of the enhanced coagulation parameters**

The results of orthogonal test are summarized in Tables 1 and 2. In Table 2, $K_i$ ($i = 1, 2, 3$) is the sum of humic acid removal by UV254 and CODMn methods at the same codified factor 1; $k_i$ ($i = 1, 2, 3$) is the average value of humic acid removal at the same codified factor i; $R$ is the difference value between the maximum of $k_i$ and the minimum $k_i$,

$$R = \max (k_i) - \min (k_i),$$

which can identify the order of significant factors.
### Table 1 | A standard L₉ (3⁴) matrix

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<th>In situ MnO₂ dosage (mg/L)</th>
<th>Slow stirring time (min)</th>
<th>Particulate concentration (mg/L)</th>
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### Table 2 | A standard L₉ (3⁴) matrix analysis and humic acid removal

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Sum of $K_i$ and average of $k_i$ by UV₂₅₄ method

| $K_1$ | 209.6 | 118.4 | 116.4 | 119.2 |
| $K_2$ | 58.4  | 125.2 | 119.2 | 121.6 |
| $K_3$ | 94.0  | 118.4 | 126.4 | 121.6 |
| $k_1$ | 69.9  | 39.5  | 38.8  | 39.7  |
| $k_2$ | 19.5  | 41.7  | 39.7  | 40.5  |
| $k_3$ | 31.3  | 39.5  | 42.1  | 40.5  |
| R     | 50.4  | 2.3   | 3.3   | 0.8   |

Sum of $K_i$ and average of $k_i$ by CODₘ₃₀ method

| $K_1$ | 181.6 | 128.5 | 134.6 | 126.4 |
| $K_2$ | 73.4  | 128.5 | 120.3 | 134.6 |
| $K_3$ | 126.4 | 124.4 | 126.4 | 120.3 |
| $k_1$ | 60.5  | 42.8  | 44.9  | 42.2  |
| $k_2$ | 24.5  | 42.8  | 40.1  | 44.9  |
| $k_3$ | 42.2  | 41.5  | 42.2  | 40.1  |
| R     | 36.1  | 1.4   | 4.8   | 4.8   |
It can be found from Table 2 that for the UV254 removal, the pH of the water was the greatest contributing factor, followed by the slow stirring time, then the in situ MnO2 dosage, and finally the concentration of particulates. The R value was 50.4 for the pH factor, which is significantly greater than the R values for the factors of in situ MnO2 dosage, slow speed stirring time, and concentration of particulates. This result indicates that pH is the dominant determinant of the UV254 removal efficiency. For the CODMn removal, the pH was also found to be the dominant factor, and the rest of the parameters are ranked in order of decreasing significance as follows: slow stirring time > particulate concentration > manganese dioxide dosage. Comparing the R values for each parameter, the R value for pH factor is high for both UV254 and CODMn removal. Furthermore, at pH = 4, the removal of UV254 and CODMn was far greater than at pH = 6.0 and pH = 8.0. This result is consistent with the results obtained through single-factor analysis. By comparing the K values of the orthogonal test, the following can be deduced: for maximal UV254 and CODMn removal, a pH of 4.0, in situ MnO2 dosage of 10 mg/L, slow stirring time of 20 or 40 min, and particulate concentration at 20 or 30 mg/L should be used.

CONCLUSIONS

In situ MnO2-enhanced coagulation can significantly improve humic acid removal efficiencies of PAS. At pH = 4, the enhancement of coagulation was most apparent when the dosage of PAS was 2 mg/L and the dosage of in situ MnO2 was 10 mg/L. Humic acid removal by UV254 and CODMn methods increased from 9.2% and 2.5% to 55.0% and 38.9%, respectively, upon the addition of in situ MnO2.

The effect of in situ MnO2 on coagulation enhancement is most affected by pH, whereas the effects of the other parameters rank in order of decreasing significance as follows: slow stirring time > particulate concentration > MnO2 dosage.

The use of in situ MnO2 as a coagulant additive enhances the coagulation effect of PAS, which can effectively improve the removal of humic acid. The dissolved aluminum and manganese content after treatment met the corresponding water standards, and there was no secondary pollution. This method is easy to use and economically sound. This work provides a scientific basis and reference for the removal of humic acid through enhanced coagulation.

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