Treatment of humic acid in drinking water by combining potassium manganate (Mn(VI)), ferrous sulphate and MIEX

Zhijun REN\textsuperscript{a,b} and Nigel GRAHAM\textsuperscript{a}

\textsuperscript{a}Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK (*Corresponding author: n.graham@imperial.ac.uk; tel: +44 2075946121; fax: +44 2075945934)

\textsuperscript{b}College of Aerospace and Civil Engineering, Harbin Engineering University, Harbin 150001, PR China (renzhijun2003@126.com; tel: +86 13115557461; fax: +8610 62327004)

Key words: potassium manganate; ferrous sulphate; MIEX; humic acid; oxidation; coagulation

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Abstract

This paper summarizes a preliminary investigation of the treatment of humic acid (HA) in drinking water by a novel combination of potassium manganate, ferrous sulphate and MIEX (magnetic ion exchange resin). Manganate (MnO$_4^{2-}$) is a stronger oxidant than permanganate which has received little attention to-date as a water treatment chemical, but in combination with ferrous sulphate (‘FeMnO’) can offer a potentially advantageous and more economical means of achieving pre-oxidation objectives and in-situ coagulation by Fe(III) species. To enhance the removal of organic substances, particularly the low molecular weight and more hydrophilic compounds, the subsequent treatment by MIEX was included as part of the overall process. Using model HA solutions of 5 mg·L$^{-1}$ DOC (dissolved organic carbon), a solution pH of 6.5 and a constant Fe:Mn molar ratio (2:1), the optimal FeMnO dose for organics (DOC) removal was 0.06 mmol·L$^{-1}$ (as K$_2$MnO$_4$). At this optimal dose, and with 10 mL·L$^{-1}$ MIEX, the DOC remaining after treatment was only 0.4 mg·L$^{-1}$, representing an overall organics removal of 92%. Synchronous fluorescence spectra of solutions during the treatment stages showed a corresponding major reduction in fluorophore peaks with a near-complete removal of fluorophore compounds in the ranges, 360 nm < λex < 420 nm, and λex > 420 nm.

Key words: potassium manganate; ferrous sulphate; MIEX; humic acid; oxidation; coagulation
Introduction

The presence of elevated natural organic matter (NOM) in surface waters presents treatment challenges relating to taste, odour, colour and disinfection by-products. Since both the quantity and nature of NOM, particularly humic material, in source waters are changing, there is continuing interest in new approaches to treating such material in more efficient and cost-effective ways. The potential use of anion exchange for separating humic substances has been proposed previously (Fu and Symons, 1990), and considerable interest has been focused on the MIEX® (magnetic ion exchange resin) process. This method of treatment is based on its strong base functionality capable of exchanging weak organic acid ions (phenolic and carboxylic acid groups) and the small particle size of the MIEX resin (150-180 μm) provides a high surface area for solute-resin interaction. The usual arrangement is for MIEX to be used as a pre-treatment for, or in combination with, coagulation. Considerable investigation of the process has been reported and the results have shown that MIEX is effective for the removal of a wide range of NOM, particularly the mid- to lower molecular weight (MW) fractions (Fearing et al., 2004).

As an intermediate in the industrial synthesis of potassium permanganate (Mn(VII)), potassium manganate (Mn(VI)) is an oxidant with high oxidation strength, as indicated in Table 1. Manganate, 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$_4^{2-}$. In addition, under conditions typical of water treatment manganate will disproportionate to permanganate and manganese dioxide, providing similar, complementary treatment mechanisms (Zhao et al., 2012). However, in practice the coagulation/adsorption
performance of manganese dioxide produced in-situ is not usually sufficient to achieve the
degree of treatment required, and the addition of a metal-ion coagulant is required.

As a pre-oxidant, manganate has received little attention in regard to water treatment, but
its application with ferrous sulphate offers a potentially economically favourable combination
of oxidant and coagulant (the latter produced from the in-situ conversion of Fe(II) to Fe(III)).
This paper summarizes a preliminary investigation of combining manganate, ferrous sulphate
and MIEX for the removal of humic acid. The principal objectives were to evaluate the
overall extent of organics removal and the relative contribution of MIEX.

Materials and Methods

Humic acid (HA) and potassium manganate were obtained as commercial reagent grade in
solid form from Sigma-Aldrich Company Ltd (UK). Ferrous sulphate was also obtained as
commercial reagent grade from BDH (UK). All other reagents and chemicals used in this
study were analytical grade, purchased from chemical suppliers in the UK, and used as
supplied. HA solutions were prepared in deionized water to the desired DOC concentration of
approximately 5 mgC·L\(^{-1}\), as determined by a laboratory TOC instrument (Shimadzu, Japan).
All treatment experiments were conducted using a Gator Jar, which is a calibrated 2 L square,
acrylic vessel with paddle stirring, built to a standard design recommended for coagulation
testing (AWWA, 2000).
MIEX resin was received in water from Orica Australia Pty Ltd and used either as
received or after washing and regeneration; the latter was carried out according to the
supplier’s recommended method. Adsorption kinetic tests with MIEX were conducted to
determine the effects of resin concentration and contact time on the removal of HA from the
test water. In these tests the Gator jar was filled with 1 L of test water, dosed with MIEX, and
mixed at 150 rpm (G = 216 s⁻¹) for 40 min. The volume of wet MIEX resin added was
quantified using a measuring cylinder. Samples were withdrawn from the Gator jar at
pre-determined time intervals and filtered (0.45 µm membrane) prior to DOC measurement.

Treatment of HA solutions was by the sequential addition of K₂MnO₄, FeSO₄ and MIEX.
Initially, K₂MnO₄ reacts with HA either directly, or indirectly by MnO₂⁻ and MnO₂ arising
from MnO₄²⁻ disproportionation. Subsequently, the addition of FeSO₄ enables reaction with
the remaining Mn-oxidants to produce Fe(III) hydrolysis species, such as insoluble Fe(OH)₃
by the reaction: MnO₄²⁻ + 2Fe²⁺ + 4H₂O = MnO₂ + 2Fe(OH)₃ + 2H⁺. For convenience, the
treatment combination of K₂MnO₄ and FeSO₄ is referred to as ‘FeMnO’, and the dosage of
FeMnO in the experiments is expressed as mmol·L⁻¹ as K₂MnO₄, and based on a theoretical
Fe:Mn molar ratio of 2:1 (as per the above reaction). For the treatment tests an appropriate
quantity of K₂MnO₄ (0.03 mol·L⁻¹) was added, with stirring (250 rpm; G = 439 s⁻¹), to the HA
model water in the Gator jar with HCl added for pH correction. After a reaction time of 40
min a stoichiometric amount of FeSO₄ (0.06 mol·L⁻¹, equivalent to Fe:Mn = 2:1) was added
to the solution in the Gator jar with stirring at 250 rpm for 1 min and at 150 rpm (G = 216 s⁻¹)
for 4 min, followed by 10 mL·L⁻¹ MIEX resin added under stirring at 150 rpm for 20 min.
The series of treatment tests described here were performed in duplicate at pH 6.5
(representative of typical water treatment), and under ambient conditions in an
environmentally controlled laboratory (room temperature 20±1 °C); the variation in duplicate
results was within 5%.
Synchronous fluorescence spectroscopy has been used widely for the characterization and identification of NOM from various origins (Matilainen et al., 2011). Selected samples were measured for fluorescence excitation emission matrices (F-EEM), using a JASCO FP-6500 fluorescence spectrometer at ambient pH and room temperature. A constant wavelength difference ($\Delta \lambda$) of 60 nm was maintained between excitation and emission wavelengths, over an excitation wavelength range of 200-600 nm. The fluorescence intensity (FI) is expressed in absorbance units.

Results and Discussion

HA removal by MIEX

An initial series of tests were undertaken to establish an optimal quantity of MIEX to use for the subsequent treatment tests. The results are summarized in Fig. 1 and show a systematic reduction in organic carbon with MIEX concentration, reflecting the increasing surface area (exchange sites) of the MIEX in solution. The DOC concentration followed non-linear kinetics with a decreasing rate of change with time, and the extent of adsorption was largely complete by 20 min (approximately 77-92% of ultimate DOC removal). Since there was relatively little additional benefit in increasing the contact time (an additional 5-15% DOC removal for a further 20 min) and increasing the MIEX concentration from 10 mL·L$^{-1}$ to 12 mL·L$^{-1}$, the subsequent tests employed a contact time of 20 min and a constant MIEX concentration of 10 mL·L$^{-1}$. These results are consistent with the findings of other studies, such as Humbert et al. (2007) (10 mL·L$^{-1}$ MIEX) and Singer and Bilyk (2002) (20-30 min contact time), and as used in practice (Slunjski et al., 2000).
A summary of the results showing the treatment performance of FeMnO and MIEX for DOC removal is given in Table 2. It was found that at FeMnO doses of 0.030 mmole·L$^{-1}$, there was little detectable change in the DOC by FeMnO treatment, indicating the absence of any significant coagulation by Fe species, and only a modest reduction in the DOC by the MIEX at 0.030 mmole·L$^{-1}$. However, at FeMnO doses of 0.06 mmol·L$^{-1}$ and greater, the reduction in DOC by FeMnO was consistently high, at about 70%, and corresponded to a Fe dose stoichiometry of approximately 1.6 mg Fe per mg C removed, which is less than with conventional Fe salts (~1.8; Eikebrokk, 1999) indicating a more efficient use of Fe for coagulation. Subsequent MIEX treatment following FeMnO treatment produced further DOC reduction. It was evident that the maximum overall reduction in DOC by the combined FeMnO-MIEX process was approximately 92%, corresponding to a final DOC concentration of only 0.4 mg·L$^{-1}$. This degree of HA treatment was greater than that found previously by the authors with conventional ferric chloride under more favourable pH conditions (pH 5; Graham et al., 2010).

The optimal FeMnO dose of 0.06 mmol·L$^{-1}$, corresponding to 11.8 mg·L$^{-1}$ K$_2$MnO$_4$ and 18.2 mg·L$^{-1}$ FeSO$_4$, is clearly evident in Table 2. Although higher FeMnO doses achieved approximately the same level of DOC removal, the subsequent removal by MIEX deteriorated with increasing FeMnO dose. The reason for the deteriorating MIEX performance is unclear but is believed to be related to the nature and extent of structural changes in the organics (e.g. MW distribution, hydrophilicity, charge densities) by the FeMnO treatment, which adversely...
affects the anionic exchange interactions.

Synchronous fluorescence spectral analysis

Synchronous fluorescence spectral analysis was carried out on samples of the HA solution subjected to combined FeMnO-MIEX treatment at the optimal dose of 0.06 mmol·L$^{-1}$, and the results are summarized in Fig. 2. The fluorescence spectrum for the HA solution at $\lambda_{\text{ex}} > 300$ nm corresponds to the pool of hydrophilic and hydrophobic, humic-type fluorophores, and four main peaks were observed: peak I ($\lambda_{\text{ex}} = 330\sim350$nm), peak II ($\lambda_{\text{ex}} = 400\sim420$nm), peak III ($\lambda_{\text{ex}} = 435\sim450$nm) and peak IV ($\lambda_{\text{ex}} = 500\sim525$nm); peak III had the greatest FI, and the general fluorescence spectrum was similar to those reported previously for soil humic acids (Trubetskaya et al., 2002).

The relative changes in the fluorescence spectra with the sequence of treatment, namely, manganate oxidation, Fe(III) coagulation following manganate oxidation, and subsequent MIEX treatment, provide an indication of overall changes to the matrix of organic substances that are sensitive to fluorescence (Fig.2). Firstly, manganate pretreatment appeared to increase the FI of all peaks (6%, 11%, 11% and 6%, respectively, for peak I to peak IV), indicating a modest degree of structural changes had occurred to a broad range of the organic macro-molecules. With subsequent coagulation (HA+FeMnO) the fluorescence intensities decreased greatly across the whole range of excitation wavelengths, with the FI values of the four peaks decreasing by 20.3%, 62.9%, 52.5%, 83.1% (relative to untreated HA). Further reduction in FI values was evident after MIEX treatment with the apparent loss of peaks II and IV. Overall, the total reduction in FI values by the combined FeMnO–MIEX process was
32.7%, 91.4%, 68.7%, 97.4% (relative to untreated HA), and the results indicated that both steps of the treatment were effective at removing a broad range of fluorophore compounds. Thus, for the fully treated water, with a DOC of ~0.4 mg·L⁻¹, there was a near-complete removal of fluorophore compounds in the ranges, 360 nm < λex < 420 nm, and λex > 420 nm.

Conclusions

The novel combination of manganate (MnO₄²⁻) and ferrous sulphate, ‘FeMnO’, provides treatment by oxidation and coagulation, and together with the MIEX process, as a subsequent polishing step, can achieve a high degree of humic acid removal. The results have shown that at pH 6.5 the removal of organics (as DOC) by FeMnO at an optimal dose (0.06 mmol·L⁻¹, as K₂MnO₄) was about 70%, and corresponded to a Fe dose stoichiometry of approximately 1.6 mg Fe per mg C removed; in both measures the performance of FeMnO was comparable or superior to conventional Fe coagulants. With subsequent treatment by 10 mL·L⁻¹ MIEX, the DOC was reduced further to only 0.4 mg·L⁻¹, representing an overall organics removal by FeMnO-MIEX of 92%. Associated with the major reductions in overall organic content were similar reductions in fluorophore compounds in general, and a near-complete removal of fluorophore compounds in the excitation wavelength ranges, 360 nm < λex < 420 nm, and λex > 420 nm.

Acknowledgements

The authors acknowledge the support of the China Scholarship Council.
Author Disclosure Statement

No competing financial interests exist.

References


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Figure Captions

Fig. 1. Effect of MIEX concentration and contact time on DOC removal (pH 6.5)

Fig. 2. Synchronous fluorescence spectra ($\Delta \lambda$=60 nm; F.I. - fluorescence intensity (AU – absorbance units)) at different stages of treatment
<table>
<thead>
<tr>
<th>Condition</th>
<th>Oxidation reaction</th>
<th>Electrode potential*, $E^o$(V)</th>
</tr>
</thead>
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<tr>
<td>MnO$_4^{2-}$ pH &lt; 7</td>
<td>MnO$_4^{2-}$ + 4H$^+$ + 2e$^-$ ⇌ MnO$_2$ + 2H$_2$O</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>MnO$_4^{2-}$ + 8H$^+$ + 4e$^-$ ⇌ Mn$^{2+}$ + 4H$_2$O</td>
<td>1.74</td>
</tr>
<tr>
<td>pH &gt; 7</td>
<td>MnO$_4^{2-}$ + 2H$_2$O + 2e$^-$ ⇌ MnO$_2$ + 4OH$^-$</td>
<td>0.62</td>
</tr>
<tr>
<td>MnO$_4^-$ pH &lt; 7</td>
<td>MnO$_4^-$ + 4H$^+$ + 3e$^-$ ⇌ MnO$_2$ + 2H$_2$O</td>
<td>1.70</td>
</tr>
<tr>
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<td>MnO$_4^-$ + 8H$^+$ + 5e$^-$ ⇌ Mn$^{2+}$ + 4H$_2$O</td>
<td>1.51</td>
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<tr>
<td>pH &gt; 7</td>
<td>MnO$_4^-$ + 2H$_2$O + 3e$^-$ ⇌ MnO$_2$ + 4OH$^-$</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*Standard state: 25 °C, 100 kPa
**TABLE 2.** Variation of humic acid concentration with FeMnO dose (and % DOC reduction) by FeMnO and FeMnO-MIEX treatments (initial HA = 5 mgC·L⁻¹)

<table>
<thead>
<tr>
<th>FeMnO Dose (mmol·L⁻¹)*</th>
<th>After FeMnO</th>
<th>After FeMnO-MIEX</th>
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<tr>
<td></td>
<td>DOC (mgC·L⁻¹)</td>
<td>% Reduction</td>
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<tr>
<td>0.06</td>
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</tr>
<tr>
<td>0.27</td>
<td>1.6</td>
<td>68</td>
</tr>
</tbody>
</table>

*as K₂MnO₄; where 1 mmol·L⁻¹ FeMnO = 2 mmol·L⁻¹ FeSO₄ + 1 mmol·L⁻¹ K₂MnO₄
Effect of MIEX concentration and contact time on DOC removal (pH 6.5)

254x190mm (96 x 96 DPI)
Synchronous fluorescence spectra ($\Delta \lambda = 60$ nm; F.I. - fluorescence intensity (AU - absorbance units)) at different stages of treatment

254x190mm (96 x 96 DPI)