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

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

Running Title: Treatment of humic acid by Mn(VI), Fe(II) and MIEX

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 $5 \text{ mg}\cdot\text{L}^{-1}$ 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 $0.06 \text{ mmol}\cdot\text{L}^{-1}$ (as K_2MnO_4). At this optimal dose, and with $10 \text{ mL}\cdot\text{L}^{-1}$ MIEX, the DOC remaining after treatment was only $0.4 \text{ mg}\cdot\text{L}^{-1}$, 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, $360 \text{ nm} < \lambda_{\text{ex}} < 420 \text{ nm}$, and $\lambda_{\text{ex}} > 420 \text{ nm}$.

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

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41 **Introduction**

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

56 As an intermediate in the industrial synthesis of potassium permanganate (Mn(VII)),
57 potassium manganate (Mn(VI)) is an oxidant with high oxidation strength, as indicated in
58 Table 1. Manganate, like permanganate, can act as both an oxidant and a coagulant/adsorbent
59 arising from the formation of insoluble manganese dioxide (Mn(IV)) from the chemical
60 reduction of MnO_4^{2-} . In addition, under conditions typical of water treatment manganate will
61 disproportionate to permanganate and manganese dioxide, providing similar, complementary
62 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 $5 \text{ mgC} \cdot \text{L}^{-1}$, 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

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85 determine the effects of resin concentration and contact time on the removal of HA from the
86 test water. In these tests the Gator jar was filled with 1 L of test water, dosed with MIEX, and
87 mixed at 150 rpm ($G = 216 \text{ s}^{-1}$) for 40 min. The volume of wet MIEX resin added was
88 quantified using a measuring cylinder. Samples were withdrawn from the Gator jar at
89 pre-determined time intervals and filtered (0.45 μm membrane) prior to DOC measurement.

90 Treatment of HA solutions was by the sequential addition of K_2MnO_4 , FeSO_4 and MIEX.
91 Initially, K_2MnO_4 reacts with HA either directly, or indirectly by MnO_4^- and MnO_2 arising
92 from MnO_4^{2-} disproportionation. Subsequently, the addition of FeSO_4 enables reaction with
93 the remaining Mn-oxidants to produce Fe(III) hydrolysis species, such as insoluble $\text{Fe}(\text{OH})_3$
94 by the reaction: $\text{MnO}_4^{2-} + 2\text{Fe}^{2+} + 4\text{H}_2\text{O} = \text{MnO}_2 + 2\text{Fe}(\text{OH})_3 + 2\text{H}^+$. For convenience, the
95 treatment combination of K_2MnO_4 and FeSO_4 is referred to as ‘FeMnO’, and the dosage of
96 FeMnO in the experiments is expressed as $\text{mmol}\cdot\text{L}^{-1}$ as K_2MnO_4 , and based on a theoretical
97 Fe:Mn molar ratio of 2:1 (as per the above reaction). For the treatment tests an appropriate
98 quantity of K_2MnO_4 ($0.03 \text{ mol}\cdot\text{L}^{-1}$) was added, with stirring (250 rpm; $G = 439 \text{ s}^{-1}$), to the HA
99 model water in the Gator jar with HCl added for pH correction. After a reaction time of 40
100 min a stoichiometric amount of FeSO_4 ($0.06 \text{ mol}\cdot\text{L}^{-1}$, equivalent to Fe:Mn = 2:1) was added
101 to the solution in the Gator jar with stirring at 250 rpm for 1 min and at 150 rpm ($G = 216 \text{ s}^{-1}$)
102 for 4 min, followed by $10 \text{ mL}\cdot\text{L}^{-1}$ MIEX resin added under stirring at 150 rpm for 20 min.
103 The series of treatment tests described here were performed in duplicate at pH 6.5
104 (representative of typical water treatment), and under ambient conditions in an
105 environmentally controlled laboratory (room temperature $20\pm 1 \text{ }^\circ\text{C}$); the variation in duplicate
106 results was within 5%.

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4 107 Synchronous fluorescence spectroscopy has been used widely for the characterization and
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6 108 identification of NOM from various origins (Matilainen *et al.*, 2011). Selected samples were
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9 109 measured for fluorescence excitation emission matrices (F-EEM), using a JASCO FP-6500
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11 110 fluorescence spectrometer at ambient pH and room temperature. A constant wavelength
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13 111 difference ($\Delta\lambda$) of 60 nm was maintained between excitation and emission wavelengths, over
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16 112 an excitation wavelength range of 200-600 nm. The fluorescence intensity (FI) is expressed in
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19 113 absorbance units.
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23 24 115 **Results and Discussion**

25 26 116 *HA removal by MIEX*

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29 117 An initial series of tests were undertaken to establish an optimal quantity of MIEX to use
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31 118 for the subsequent treatment tests. The results are summarized in Fig. 1 and show a systematic
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33 119 reduction in organic carbon with MIEX concentration, reflecting the increasing surface area
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36 120 (exchange sites) of the MIEX in solution. The DOC concentration followed non-linear
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39 121 kinetics with a decreasing rate of change with time, and the extent of adsorption was largely
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41 122 complete by 20 min (approximately 77-92% of ultimate DOC removal). Since there was
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44 123 relatively little additional benefit in increasing the contact time (an additional 5-15% DOC
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46 124 removal for a further 20 min) and increasing the MIEX concentration from 10 mL·L⁻¹ to 12
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49 125 mL·L⁻¹, the subsequent tests employed a contact time of 20 min and a constant MIEX
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51 126 concentration of 10 mL·L⁻¹. These results are consistent with the findings of other studies,
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54 127 such as Humbert *et al.* (2007) (10 mL·L⁻¹ MIEX) and Singer and Bilyk (2002) (20-30 min
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56 128 contact time), and as used in practice (Slunjski *et al.*, 2000).
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130 *Combined FeMnO and MIEX treatment*

131 A summary of the results showing the treatment performance of FeMnO and MIEX for
132 DOC removal is given in Table 2. It was found that at FeMnO doses of $< 0.030 \text{ mmole}\cdot\text{L}^{-1}$,
133 there was little detectable change in the DOC by FeMnO treatment, indicating the absence of
134 any significant coagulation by Fe species, and only a modest reduction in the DOC by the
135 MIEX at $0.030 \text{ mmole}\cdot\text{L}^{-1}$. However, at FeMnO doses of $0.06 \text{ mmol}\cdot\text{L}^{-1}$ and greater, the
136 reduction in DOC by FeMnO was consistently high, at about 70%, and corresponded to a Fe
137 dose stoichiometry of approximately 1.6 mg Fe per mg C removed, which is less than with
138 conventional Fe salts (~ 1.8 ; Eikebrokk, 1999) indicating a more efficient use of Fe for
139 coagulation. Subsequent MIEX treatment following FeMnO treatment produced further DOC
140 reduction. It was evident that the maximum overall reduction in DOC by the combined
141 FeMnO-MIEX process was approximately 92%, corresponding to a final DOC concentration
142 of only $0.4 \text{ mg}\cdot\text{L}^{-1}$. This degree of HA treatment was greater than that found previously by the
143 authors with conventional ferric chloride under more favourable pH conditions (pH 5;
144 Graham *et al.*, 2010).

145 The optimal FeMnO dose of $0.06 \text{ mmol}\cdot\text{L}^{-1}$, corresponding to $11.8 \text{ mg}\cdot\text{l}^{-1} \text{ K}_2\text{MnO}_4$ and
146 $18.2 \text{ mg}\cdot\text{l}^{-1} \text{ FeSO}_4$, is clearly evident in Table 2. Although higher FeMnO doses achieved
147 approximately the same level of DOC removal, the subsequent removal by MIEX deteriorated
148 with increasing FeMnO dose. The reason for the deteriorating MIEX performance is unclear
149 but is believed to be related to the nature and extent of structural changes in the organics (e.g
150 MW distribution, hydrophilicity, charge densities) by the FeMnO treatment, which adversely

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Synchronous fluorescence spectral analysis

154 Synchronous fluorescence spectral analysis was carried out on samples of the HA solution
155 subjected to combined FeMnO-MIEX treatment at the optimal dose of $0.06 \text{ mmol}\cdot\text{L}^{-1}$, and the
156 results are summarized in Fig. 2. The fluorescence spectrum for the HA solution at $\lambda_{\text{ex}} > 300$
157 nm corresponds to the pool of hydrophilic and hydrophobic, humic-type fluorophores, and
158 four main peaks were observed: peak I ($\lambda_{\text{ex}} = 330\sim 350\text{nm}$), peak II ($\lambda_{\text{ex}} = 400\sim 420\text{nm}$), peak
159 III ($\lambda_{\text{ex}} = 435\sim 450\text{nm}$) and peak IV ($\lambda_{\text{ex}} = 500\sim 525\text{nm}$); peak III had the greatest FI, and the
160 general fluorescence spectrum was similar to those reported previously for soil humic acids
161 (Trubetskaya *et al.*, 2002).

162 The relative changes in the fluorescence spectra with the sequence of treatment, namely,
163 manganate oxidation, Fe(III) coagulation following manganate oxidation, and subsequent
164 MIEX treatment, provide an indication of overall changes to the matrix of organic substances
165 that are sensitive to fluorescence (Fig.2). Firstly, manganate pretreatment appeared to increase
166 the FI of all peaks (6%, 11%, 11% and 6%, respectively, for peak I to peak IV), indicating a
167 modest degree of structural changes had occurred to a broad range of the organic
168 macro-molecules. With subsequent coagulation (HA+FeMnO) the fluorescence intensities
169 decreased greatly across the whole range of excitation wavelengths, with the FI values of the
170 four peaks decreasing by 20.3%, 62.9%, 52.5%, 83.1% (relative to untreated HA). Further
171 reduction in FI values was evident after MIEX treatment with the apparent loss of peaks II
172 and IV. Overall, the total reduction in FI values by the combined FeMnO-MIEX process was

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173 32.7%, 91.4%, 68.7%, 97.4% (relative to untreated HA), and the results indicated that both
174 steps of the treatment were effective at removing a broad range of fluorophore compounds.
175 Thus, for the fully treated water, with a DOC of $\sim 0.4 \text{ mg}\cdot\text{L}^{-1}$, there was a near-complete
176 removal of fluorophore compounds in the ranges, $360 \text{ nm} < \lambda_{\text{ex}} < 420 \text{ nm}$, and $\lambda_{\text{ex}} > 420 \text{ nm}$.
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178 **Conclusions**

179 The novel combination of manganate (MnO_4^{2-}) and ferrous sulphate, ‘FeMnO’, provides
180 treatment by oxidation and coagulation, and together with the MIEX process, as a subsequent
181 polishing step, can achieve a high degree of humic acid removal. The results have shown that
182 at pH 6.5 the removal of organics (as DOC) by FeMnO at an optimal dose ($0.06 \text{ mmol}\cdot\text{L}^{-1}$, as
183 K_2MnO_4) was about 70%, and corresponded to a Fe dose stoichiometry of approximately 1.6
184 mg Fe per mg C removed; in both measures the performance of FeMnO was comparable or
185 superior to conventional Fe coagulants. With subsequent treatment by $10 \text{ mL}\cdot\text{L}^{-1}$ MIEX, the
186 DOC was reduced further to only $0.4 \text{ mg}\cdot\text{L}^{-1}$, representing an overall organics removal by
187 FeMnO-MIEX of 92%. Associated with the major reductions in overall organic content were
188 similar reductions in fluorophore compounds in general, and a near-complete removal of
189 fluorophore compounds in the excitation wavelength ranges, $360 \text{ nm} < \lambda_{\text{ex}} < 420 \text{ nm}$, and
190 $\lambda_{\text{ex}} > 420 \text{ nm}$.

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Author Disclosure Statement

No competing financial interests exist.

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231 **List of Tables**

232 **Table 1.** Oxidation reactions of MnO_4^{2-} and MnO_4^- anions (Bard *et al.*, 1985)

233 **Table 2.** Variation of humic acid concentration with FeMnO dose (and % DOC reduction) by
234 FeMnO and FeMnO-MIEX treatments (initial HA = 5 $\text{mgC}\cdot\text{L}^{-1}$)

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237 **Figure Captions**

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

239 **Fig. 2.** Synchronous fluorescence spectra ($\Delta\lambda=60$ nm; F.I. - fluorescence intensity (AU –
240 absorbance units)) at different stages of treatment

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TABLE 1. Oxidation reactions of MnO_4^{2-} and MnO_4^- anions (Bard *et al.*, 1985)

Condition	Oxidation reaction	Electrode potential*, $E^{\circ}(\text{V})$
MnO_4^{2-} $\text{pH} < 7$	$\text{MnO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	2.27
	$\text{MnO}_4^{2-} + 8\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.74
	$\text{pH} > 7$ $\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	0.62
MnO_4^- $\text{pH} < 7$	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	1.70
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
	$\text{pH} > 7$ $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	0.60

*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)

FeMnO Dose (mmol·L ⁻¹)*	After FeMnO		After FeMnO-MIEX	
	DOC (mgC·L ⁻¹)	% Reduction	DOC (mgC·L ⁻¹)	% Reduction
0.03	~ 5	0	3.2	36
0.06	1.4	72	0.4	92
0.18	1.5	70	0.8	84
0.27	1.6	68	1.1	78

*as K₂MnO₄; where 1 mmol·L⁻¹ FeMnO $\equiv$ 2 mmol·L⁻¹ FeSO₄ + 1 mmol·L⁻¹ K₂MnO₄

Fig. 1

Effect of MIEX concentration and contact time on DOC removal (pH 6.5)
254x190mm (96 x 96 DPI)

Fig. 2

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