RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Enhanced removal of manganese in organic-rich surface water by combined sodium hypochlorite and potassium permanganate during drinking water treatment

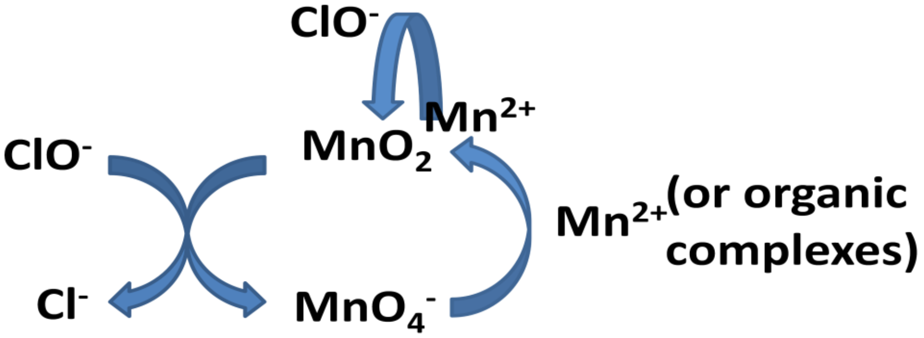
Wenzheng Yu[a,b], Luiza Campos[c],Tong Shi[d], Guibai Li[b], Nigel Graham[a*]*
[a] Department of Civil and Environmental Engineering, Imperial College London,
South Kensington Campus, London SW7 2AZ, UK.
w.yu@imperial.ac.uk, *n.graham@imperial.ac.uk*

[b] State Key Laboratory of Urban Water Resource and Environment (SKLUWRE),
School of Municipal & Environmental Engineering, Harbin Institute of Technology,
PO 73, Huanghe Road, Nangang District, Harbin, 150090, China

[c] Department of Civil, Environmental and Geomatic Engineering, University College
London, Gower Street, London WC1E 6BT, UK
l.campos.@ucl.ac.uk

[d] Department of Civil and Environmental Engineering, Zhejiang Gongshang
University, Hangzhou,310018, China.

**Corresponding author: Tel: +44 2075946121, Fax: +44 2075945934*



Combination of $KMnO_4$ and NaClO is beneficial and synergistic for removing Mn^{2+} in water with high concentration of organic matter

Abstract: High levels of manganese (Mn) are known to occur in ground waters and some organic-rich surface waters, and are sometimes in a form (e.g. organically-bound) that is difficult to remove during conventional drinking water treatment. In this study the potential benefits of combining permanganate and chlorine prior to coagulation for Mn removal have been investigated, with particular reference to an organic-rich surface water (river Bajiang, China). The respective roles and potential synergy of permanganate and chlorine when applied together were considered by comparing the removal of Mn with the chemicals together and separately, using samples of river water and model organic-Mn solutions (humic acid and EDTA). In addition, the significance of the order of NaClO and $KMnO_4$ dosing, and the influence of coagulant dose have been evaluated. The results have shown that the combination of the two chemicals is beneficial and synergistic. For river water containing 0.22 mg/L Mn, a dose of 1.76 mg/L NaClO reduced half dose of the permanganate required to achieve the drinking water target concentration of 0.05 mg/L Mn. The addition of chlorine appears to enhance the release of bound-Mn and the subsequent conversion of Mn(II) to insoluble Mn(IV). The mechanisms responsible are believed to involve chlorine-assisted autocatalytic Mn oxidation and MnO_4^- recycling.

Keywords: drinking water treatment; manganese removal; oxidation; potassium permanganate; sodium hypochlorite; coagulation

1 Introduction

Manganese concentrations in drinking water that exceed the current recommended maximum value of 0.05 mg/L (EU and USEPA Secondary Maximum Contaminant Level) can create problems for consumers leading to complaints about plumbing fixtures and laundry staining, discoloured water, and taste and odour [1]. Also manganese exposure produces dopamine neuron degeneration and movement abnormalities [2]. High levels of manganese are known to occur in ground waters and organic-rich surface waters, such as the river Bajiang (Huadu District, Guangzhou, China), where the Mn concentration is typically 0.2-0.3 mg/L, and sometimes higher. The form of the Mn in such waters, whether inorganic or organically-bound, depends on its origin and the general water quality. Thus, in surface waters with a high concentration of organic matter the Mn may be organically-complexed and its behaviour depends on the type and concentration of the associated organic substances [3]. Organically-complexed Mn is very stable, and difficult to remove during conventional drinking water treatment. The high concentration of Mn in the river Bajiang at near pH 8 is a good example, which is the basis for the research study reported here.

In general, the literature describes various methods for removing Mn during drinking water treatment that have been studied and applied based on adsorption/filtration, biological treatment and chemical oxidation. With the former, some materials have been found to have a significant capability for Mn-adsorption such as Moringaoleifera seeds [4] and oxidized multiwalled carbon nanotubes

(MWCNTs) [5]. Also, Mn(II) ions can be removed effectively by filtration with modified clinoptilolite (nearly 100%) [6] and with low cost crushed dolomite [7]. Recently, the use of synthesized polyvinyl alcohol/ 3-mercaptopropyltriethoxysilane/ tetraethoxysilane hybrid materials has been shown to be effective for the removal of Mn ions by adsorption [8].

Biological Mn(II) removal has been the subject of a number of studies in recent years [9], and particularly by bio-filtration processes [10]. Soluble manganese can be removed from water by biological processes involving manganese-oxidizing bacteria, either in situ, or in sand filters [11]. A variety of full- and pilot-scale biological filters have been used for combined or simultaneous biological removal of Mn, Fe and NH_4^+ [12]. The bio-filtration can achieve Mn removal without the use of chemical agents and under natural pH conditions [13]. The fungus on the media can accumulate the oxidized Mn species [14], and backwash process may remove fungus and decrease the transformation of Mn(II) to MnO_2.

In comparison to the previous methods, chemical oxidation provides a rapid and practically convenient method (without changing the structure of water plant) for manganese removal and the application of potassium permanganate oxidation (at $6.5 < pH < 8.5$) followed by flocculation, settling and filtration is a common treatment scheme [15], especially for large-scale water treatment plants [16]. The insoluble products of permanganate reduction and Mn(II) oxidation are Mn(III) and Mn(IV) oxides, $MnO_x(s)$[17], and these can have a catalytic effect on the adsorption and removal of soluble Mn(II) from influent waters [18]. Also the manganese can be removed by ozonation [19] and by impregnated activated carbon coated by permanganate [20]. However, where Mn(II) is present in relatively high concentrations, and/or in a complexed form, large doses of permanganate may be required which may lead to residual Mn concentrations that exceed the regulated level in treated waters. Alternatively, the use of chlorine combined with the catalytic action of $MnO_x(s)$ oxides can assist Mn(II) removal by oxidizing adsorbed Mn(II) to more stable $MnO_x(s)$ [21]. While the removal of various levels of iron and manganese (higher than 80%) from lake water has been reported to be high using an in-line pre-chlorination step [22]. Various studies (e.g. [23]) have shown that the oxidation of dissolved manganese (Mn(II)) during chlorination is a relatively slow process which may lead to high residual Mn(II) in treated drinking waters (although the rate may be enhanced in bromide-containing waters).

To-date, no previously reported studies have considered the potential advantages of combining permanganate and chlorine to enhance the removal efficiency of Mn. Thus, in this study the performance and mechanisms of combining permanganate oxidation with pre-chlorination for Mn removal are investigated, with particular focus on the problem of Mn in organic-rich surface water sources, as represented by the case of the river Bajiang. Pre-chlorination of surface waters is often used as a means of reducing ammonia and for other treatment benefits at doses that do not cause significant halogenated by-product formation, but by itself chlorination is unable to oxidize Mn effectively at pH<9 [24]. Thus, the respective roles and potential synergy of permanganate and chlorine are considered in this study by comparing the removal of

Mn with the chemicals together and separately, focusing on samples of river Bajiang and model organic-Mn solutions (humic acid and EDTA). The results have shown that the combination of the two chemicals is beneficial and synergistic and this is described in detail as follows.

2 Materials and methods

2.1 Chemicals and test solutions

Polyaluminum chloride (PACl, 1.5 basicity) was used as the coagulant in this study, purchased from Guangzhou Jiequan, China. Stock $KMnO_4$ was prepared as 1000 mg/L; stock NaClO was prepared as 1000 mg/L every day and was considered stable for one day.

A bulk sample of raw water (as experimental water here) was obtained from the river Bajiang, Guangzhou, China, and stored at 4 ^{o}C during the period of laboratory testing. Samples were allowed to come to room temperature prior to experiments. Relevant values of the raw water quality are as follows: Mn 0.22±0.03 mg/L, Fe 0.03±0.01 mg/L, TOC 6.5±0.4 mg/L, Trihalomethanes (THMs) formation potential 1.54±0.28 mg/L, Turbidity 14.3±1.5 NTU, colour 30±2 ^{o}H, pH 7.84±0.13, NH_4^+-N 1.15±0.12 mg/L, alkalinity 148±23 mg/L (calculated as $CaCO_3$). There was little bromide in the water (below 10 μg/L, the detection limit of bromide concentration by Ion Chromatography).

For the tests involving the preparation of solutions of EDTA-Mn and humic acid-Mn, an appropriate quantity of either EDTA (Ethylenediaminetetraacetic acid, Sigma, USA) or humic acid (HA, sodium salt, Aldrich, USA) was added to deionised (DI) water to give a concentration of 5 mg/L to represent the complexion of Mn(II) with EDTA and humic acid (it is confirmed in section 3.5 that there is little complex between HA and Mn^{2+} and there is complex between EDTA and Mn^{2+}); neutral pH was obtained by the addition of 5 mM $NaHCO_3$ and by adding NaOH or HCl. Subsequently, 1 mg/L Mn^{2+} (as $MnCl_2$) was added to the respective solutions and mixed continuously for 24 h, which was used as model waters for exploring mechanism (the molar ratio of EDTA and Mn^{2+} was near 1:1, which is stoichiometry of the EDTA-Mn complexes). EDTA was chosen here as it had been found in raw water supplies [25], and it can represent the organic matter, which can complex with the Mn in the water. The model water was used in section 3.5 only.

2.2 Treatment experiments

The treatment process for Mn, as well as other contaminants, employed *two* 0.5 L/h mini-pilot scale water plants *in parallel* (Figure S1, only one was demonstrated), which comprised mixing tanks, flocculation tanks, a sedimentation tank, and a sand filtration column, in order to simulate the real water treatment plant. NaClO (0~4.4 mg/L), $KMnO_4$ (0~5 mg/L) and PACl (dosed at 7.2 mg/L, except where otherwise stated) were continuously added to the raw water via the mixing tanks, and the mode of addition of oxidants (together or separately) was varied as part of the study. The rapid mix speed was 200 rpm (180 s^{-1}) in the mixing tanks each with a hydraulic retention time (HRT) of 1 min, and 50 rpm (23 s^{-1}) in the three flocculation tanks, each with a HRT of 5 min. Subsequently the coagulated water passed into the sedimentation tank for flocs to settle (HRT 15 min) and then to the sand filtration column (sand size: 0.5 mm-0.8 mm) with a 5 min real HRT (pore volume in the sand tank divided by the flow rate). The total HRT of the system was 40 min, and each experiment was conducted for 2 h to ensure the results were representative of the process performance.

Following the tests with the raw water additional tests were carried out with solutions of EDTA-Mn and humic acid-Mn using the same mini-pilot scale system (Section 3.5). Each solution was prepared as described in section 2.1. All treatment tests were carried out for three replicates at 25 ± 2 ℃.

2.3 Analytical methods

Turbidity was determined by a WTW TURB555IR turbidimeter. Residual manganese and aluminum after sand filtration were measured by inductivity coupled plasma optical emission spectrometry (ICP-OES, Optima 7300 DV, PerkinElmer, USA). Dissolved organic carbon (DOC) was determined with a total organic carbon (TOC) analyzer (TOC-V_{CPH}, Shimadzu, Japan). The colour in the water was measured by the chromium - cobalt colorimetry method, and the UV-visible absorbance (between 190 nm and 800 nm, by pre-experiment) of 0.45 μm filtered solutions was determined by spectrophotometry (U-3010, Hitachi High Technologies Co., Japan). Active chlorine was determined by spectrophotometry using N,N-diethyl-1,4-phenylenediamine (DPD). The concentration of $KMnO_4$ was measured through visible absorbance at 535 nm [26].

3 Results

A first series of tests were undertaken to establish the effect of permanganate treatment on Mn removal, with and without the addition of NaClO, for a range of NaClO and $KMnO_4$ doses. For these tests the coagulation dosage of PACl, 7.2 mg/L, was chosen to be the same as the dosage used at the Bajiang water treatment plant (and confirmed in the mini-pilot scale tests – section 3.4). No pH correction was made, so the solution pH decreased slightly from 7.9 to 7.5 after PACl addition. Subsequent tests were carried out to consider the significance of the order of NaClO and $KMnO_4$ addition, and the influence of coagulant dose. In order to provide further insight into the reaction mechanism, further tests were conducted using model Mn-organic solutions corresponding to weak and strong ligands in section 3.5 (Mn-humic acid and Mn-EDTA respectively).

3.1 Effect of NaClO dose on the removal of Mn

The effect of different dosages of NaClO (0~4.4 mg/L) on the removal of Mn was explored with an applied $KMnO_4$ dosage of either 0 or 1.5 mg/L (Figure 1). In these tests, after NaClO and $KMnO_4$ were added simultaneously, PACl was added to the solution 1 min later. In the absence of both NaClO and $KMnO_4$ there was no measurable change in the Mn concentration indicating that coagulation had no impact on the inorganic and organic species of Mn presenting, although part of organic matter was removed (35%). This is consistent with other work which reported that Mn-bound organic matter was of low molecular (MW) weight substances (MW<2000) [27], as larger MW organic matter was much easier to be removed by coagulation process. With the addition of NaClO alone (no $KMnO_4$) there was a minor (0~15%), increasing reduction in Mn with increasing NaClO dose (Figure 1) indicating some release and oxidation of organically-bound Mn. However, with the addition of 1.5 mg/L $KMnO_4$ the effluent Mn concentration (0.035 ~ 0.115 mg/L) was much lower than without $KMnO_4$ (0.18 ~ 0.22 mg/L) for all NaClO doses. When NaClO doses equal or lower than 0.44 mg/L, no synergistic effect is observed at these conditions and the reduction of dissolved Mn(II) being mainly due to $KMnO_4$. This result may be because of the reaction of NH_4^+-N and NaClO ($k \sim 10^4$ M^{-1} s^{-1} [28] at pH 7). After that, it can be seen that the reduction in effluent Mn concentration increased substantially up to a NaClO dose of 1.76 mg/L (50% higher removal) with 1.5 mg/L $KMnO_4$, which meant that there was synergetic effect for NaClO and $KMnO_4$.

Figure 1

3.2 Effect of $KMnO_4$ dose on the removal of Mn

The influence of $KMnO_4$ dose on the removal of Mn was investigated both without, and with, NaClO (0 mg/L or 1.76 mg/L, respectively) (Figure 2). For the former case, the theoretical, stoichiometric molar ratio for the oxidation of free Mn^{2+} to MnO_2 by permanganate is 3: 2 (Mn^{2+}: $KMnO_4$), which means that a minimum

$KMnO_4$ dose of 0.42 mg/L would be required to remove all Mn^{2+} in the raw water if the Mn(II) was freely available (unbound). It can be seen in Figure 2 that the reduction in Mn(II) concentration was only about 10% for a $KMnO_4$ dose of 0.42 mg/L with nearly 0 mg/L residual $KMnO_4$. Since the reactivity of non-complex Mn^{2+} with permanganate is much greater ($k \sim 10^5\ M^{-1}\ s^{-1}$[29]) than permanganate with organic substrates ($k < 10^2\ M^{-1}\ s^{-1}$ [30]), the low Mn removal from the raw water at a low, but stoichiometric, $KMnO_4$ dose (~ 0.5 mg/L) is consistent with the Mn being present in an *organically-bound form*. No detected residual $KMnO_4$ further confirmed this result. At higher doses of $KMnO_4$ it is assumed that there is greater reactivity with the organic matter, some of which is related to the severing of Mn-organic bonds, thereby leading to a greater removal of Mn. Thus, a $KMnO_4$ dose of 3 mg/L achieved a residual Mn concentration (after coagulation/filtration) of 0.05 mg/L, representing a reduction of ~77%.

For the tests with NaClO the dose of 1.76 mg/L was chosen since this corresponded to the practical optimal concentration found in the previous tests that achieved a low level of Mn with 1.5 mg/L $KMnO_4$ (see Figure 1). This is illustrated by the much higher dosage of $KMnO_4$ needed to meet the current water quality regulation for Mn of 0.05 mg/L, if no NaClO is added, compared to that with NaClO (nearly two times). Whether NaClO was present or not, the effluent concentration of Mn decreased to lower than 0.05 mg/L as the dosage of $KMnO_4$ increased up to 5 mg/L. However, the effluent Mn concentration was much lower (0.02 ~0.05 mg/L less) for the combination of $KMnO_4$ with 1.76 mg/L NaClO than without NaClO. Clearly, these results show the benefit of combining NaClO with $KMnO_4$ on the overall reduction of Mn, and there appeared to be a synergistic effect between the two chemicals (maximum at approximately 1.5 mg/L $KMnO_4$ /1.76 mg/L NaClO doses) which will be discussed in section 4. Furthermore, although there was little further reduction in Mn at $KMnO_4$ doses > 3 mg/L, indicating that a fraction of the organic-complexed Mn cannot be removed (or because of the presence of unfiltered colloidal MnO_x), the effluent concentration of Mn was lower at all $KMnO_4$ doses with the combined NaClO/$KMnO_4$ compared to $KMnO_4$ alone.

Figure 2

3.3 Effect of chemical dosing sequence on the removal of Mn

In these tests a comparison was made between the dosing arrangement used previously (i.e. NaClO was added before, together and later than $KMnO_4$, followed by PACl added 1 min later) (Table S1), on the removal of Mn. The results showed that when NaClO and $KMnO_4$ were added together before PACl, the effluent Mn concentration for all $KMnO_4$ dosages was much lower (around 50%) than the other two arrangements of adding two oxidants separately, especially delaying the $KMnO_4$ addition (after NaClO) (Figure 3a). It can be seen from Figure 3a that the mixed dosing arrangement enabled the required Mn maximum concentration (0.05 mg/L) to be achieved with 1.5 mg/L $KMnO_4$, whereas for the $KMnO_4$-NaClO arrangement it needs 2.0 mg/L and for NaClO-$KMnO_4$ arrangement even the highest $KMnO_4$ dose of

2.5 mg/L could not achieve an effluent Mn concentration≤0.05 mg/L.

A similar trend of behavior was found for solution colour (Figure 3b). The colour arises from the presence of dissolved organic substances, some of which are associated with Mn. It was clear that the co-addition of NaClO and $KMnO_4$ prior to coagulation was much more effective (10%~30%) in reducing the colour than adding two oxidants separately before PACl coagulation, suggesting a greater oxidation effect. However, the removal by adding $KMnO_4$ and then NaClO was much close to the one by adding $KMnO_4$ and NaClO together, as the residual Mn concentration of these two arrangements was same. Nano-MnO_x particles formed after adding $KMnO_4$ to the raw water and aggregation between these nanoparticles may occur, which would decrease the catalysis of NaClO when NaClO was added later. This will be discussed subsequently.

Figure 3

3.4 Effect of PACl dosage on the removal of Mn

The coagulation process is of major importance for the separation and removal of colloidal MnO_x(s) particles formed by the pre-oxidation. The influence of PACl dose on the treatment performance, in terms of the effluent Mn concentration and turbidity after settling and filtration, is shown in Figure 4. As expected, dose regions corresponding to no-, low- and high-coagulation were evident which are characteristic of ‘sweep flocculation’ by insoluble Al-hydrolysis species. High coagulation efficiency was observed for PACl doses >4.8 mg/L and high dose of PACl induced higher removal of Mn, such as 7.2 mg/L, which is applied at full-scale water plant. The result meant the addition of permanganate could form nano-colloidal particles with Mn(II) in the water [31], and the coagulation process is of great importance on the removal of these new formed MnO_x particles. A close relationship was evident between residual Mn and turbidity which confirmed that the residual Mn was in the form of colloidal particles.

Figure 4

3.5 Model Mn-organic solutions

In order to further examine the nature of the reactions between $KMnO_4$ and organically-bound Mn, with and without NaClO, model Mn-organic solutions corresponding to weak and strong complexes (Mn-humic acid and Mn-EDTA respectively) were considered. For the case of Mn-humic acid, Figure 5a shows the removal of Mn by $KMnO_4$ oxidation and PACl coagulation. The dose of $KMnO_4$ was varied from 0 to 3.84 mg/L and the PACl dose was maintained at an optimal value of 2.7 mg/L (see Figure 5b). In the absence of $KMnO_4$ (0 mg/L) there was no measurable change in the Mn concentration (1 mg/L) despite good coagulation of the humic material (great decrease of UV_{254} value, which is in line with humic concentration), indicating that the humic acid had little complexed Mn(II) during the preparation of the model water. With the addition of $KMnO_4$ the concentration of residual Mn reduced systematically with increasing $KMnO_4$ dose and was almost zero at a $KMnO_4$ dose of 1.92 mg/L (Figure 5a), corresponding almost exactly with the theoretical dose required for the oxidation of free Mn^{2+} to MnO_2 by permanganate. This is consistent with the much faster reaction of permanganate with Mn^{2+} than with organic substrates, as mentioned previously. Coagulation is needed to separate the MnO_2 formed by the permanganate, as shown in Figure 5b (i.e. no Mn removal at 0 mg/L PACl), and a PACl dose of 2.70 mg/L was found to be the optimal dose.

At $KMnO_4$ doses greater than 1.92 mg/L, the excess permanganate (i.e. $[KMnO_4]$– 1.92 mg/L) is unavailable to react with the humic acid in solution quickly. This leads to high residual Mn concentration with increasing $KMnO_4$ dose, when it was higher than 1.92 mg/L. The equivalent of ~40% of the Mn from the excess permanganate was not removed at a $KMnO_4$ dose of 3.84 mg/L (Figure 5a).

In contrast, free Mn(II) ions readily complex with EDTA [32], and the respective reactions of Mn-EDTA with 1 mg/L NaClO and 1.92 mg/L $KMnO_4$, separately and together, and with coagulation (at different PACl dosages) are shown in Figure 5c. With NaClO alone (1 mg/L), there was virtually no removal of Mn. $KMnO_4$ can oxidize/react with EDTA, but the kinetics are very slow [33] and no significant oxidation was detectible in 60 min (Figure S2a). A significant reaction was evident with $KMnO_4$ which achieved a reduction in Mn that was approximately 65% of the total Mn in solution (2 mg/L; from 1 mg/L Mn as EDTA-complexed Mn and 1 mg/L Mn as added $KMnO_4$) with around 7 mg/L PACl (Figure 5c). Thus, the results indicate the capability of $KMnO_4$ to attack the EDTA-Mn bond and release the Mn from the

EDTA complex. However, the combination of NaClO and $KMnO_4$ produced a degree of Mn removal that was much greater than with $KMnO_4$ alone (Figure 5c). From the relative changes in residual Mn it is clear that the addition of NaClO provides a synergistic benefit to the $KMnO_4$ reaction. Since the addition of NaClO had no significant impact on the oxidation of EDTA by $KMnO_4$ (See Figure S2b), it can be concluded that the synergistic effect must be related to the severing of the Mn-EDTA bond.

Figure 5

Information of the variation of $KMnO_4$ and MnO_x was obtained from UV-visible spectroscopy of the reactions, as summarized in Figure 6. Changes in the UV-visible light absorbance of solutions were followed for reaction times up to 1h. As indicated previously, there was no evidence of any reaction between EDTA-Mn and NaClO alone over 1 h (Figure 6a). However, for the reaction between EDTA-Mn and $KMnO_4$ alone, or $KMnO_4$ with NaClO, broad spectra (200 – 600 nm) were evident representing the combined absorbance of $KMnO_4$ (around 535 nm) and colloidal MnO_x (around 330 nm) (Figures 6b and 6c, respectively) [34]. As a reference, the spectrum for MnO_2 was produced by the Mn^{2+}/$KMnO_4$ reaction which indicated an absorbance peak at 300-400 nm, as shown in Figure 6d; this peak is consistent with other studies of MnO_2 [9, 35]. It is clear that the extent of MnO_2 produced and $KMnO_4$ decreased in the reactions with $KMnO_4$ alone or NaClO and $KMnO_4$ together, which were time dependent (Figures 6b and 6c) and rapid, with significant changes occurring after only 1 min. However, the relative rate of reaction in the two cases was different. This can be seen by comparing Figure 6b with Figure 6c, which shows that the absorbance spectrum for the NaClO and $KMnO_4$ together at 10 min was the same as that for the $KMnO_4$ alone at 30 min, and similarly at 15 min and 60 min, respectively. These results demonstrate that the reaction was much faster for NaClO and $KMnO_4$ together than $KMnO_4$ alone, and Figure 6d clearly shows the relative superiority of NaClO and $KMnO_4$ after 15 min oxidation, particularly in terms of the MnO_2 peak.

Figure 6

4 Discussions

The removal of manganese from surface and ground waters is often a requirement during drinking water treatment in order to meet national water quality regulations. In cases where the manganese speciation is either inorganic or bound to low molecular weight organic matter, the Mn is poorly removed by conventional coagulation and filtration processes, and for the river Bajiang this has led to a long period of non-compliance with the water treatment objective of achieving Mn< 0.05 mg/L. Pre-treatment with chlorine is capable of oxidizing Mn(II) but is not efficient at pH<9 ($k \sim 6.4 \times 10^{-4}$ M^{-1} s^{-1} at pH 8 [36]) and elevated chloride doses may lead to undesirable levels of halogenated by-product compounds. In contrast, permanganate has been shown to be an effective oxidant in circumneutral conditions and in this study a relatively high $KMnO_4$ dose of 3 mg/L, prior to coagulation and filtration, was able to achieve 0.05 mg/L Mn in the treated water from the original river water concentration of 0.22 mg/L Mn. However, with a simultaneous dose of chlorine (1.76 mg/L) the permanganate dose required was approximately halved (1.5 mg/L) and the combination of the two chemicals appeared to be synergistic. A similar behavior was found for the model solution containing the Mn-EDTA complex. The results showed that the combination of chlorine and permanganate was more effective than permanganate alone in separating the Mn from the complex.

Three possible reasons for the advantageous and synergistic combination of chlorine and permanganate in the treatment of organically-bound Mn are proposed as follows:

(i) Reduction in permanganate oxidation demand by chlorine;
(ii) Recycling of permanganate by chlorine oxidation of MnO_2;
(iii) Enhanced autocatalytic process of Mn oxidation/precipitation [37].

The first of these effects is that chlorine, as a co-oxidant, can lower the permanganate oxidation demand of the water leading to a relatively greater $KMnO_4$ concentration available to react with the Mn species, both for releasing the bound Mn and for oxidizing the Mn to solid phase MnO_x. Given the estimated oxidation strength (reduction potential) of chlorine under the test conditions (E_{OCl^-/Cl^-} ~ +1.27V, pH 7.8), it is expected that some degree of general solute oxidation occurs, including the release of bound Mn as indicated in Figure 1. Thus, the two chemical oxidants (chloride and $KMnO_4$) can be considered as complementary. However, the marked difference in treatment performance observed in this study when the chlorine was added either together with, or prior to, the $KMnO_4$ (Figure 3) showed that other reaction phenomena are also involved.

The second reason for the beneficial effect of chlorine is the possible in-situ recycling of MnO_4^- ions by the chlorine oxidation of MnO_2 (viz. $MnO_2(s) + 4OH^- \rightarrow MnO_4^- + 2H_2O + 3e^-$), with the latter formed by $KMnO_4$ reduction via solute oxidation reactions ($MnO_4^- \rightarrow MnO_2$). Thermodynamically, this is feasible since the reduction potential of hypochlorite in the solution conditions (E_{OCl^-/Cl^-} ~ +1.27V, pH 7.8) exceeds the oxidation potential of MnO_2 ($E_{MnO2\ /\ MnO4^-}$ ~ -0.99V, pH 7.8), but the kinetics of the reaction are unclear. If the kinetics of the recycling of MnO_4^- ions were favourable then this would enhance the MnO_4^- concentration during the reaction period (while sufficient chlorine is present) giving two benefits: a greater release of bound-Mn and conversion of the released Mn^{2+} to $MnO_x(s)$.

The third effect relates to the Mn autocatalysis process whereby Mn^{2+} ions released from organo-Mn compounds readily adsorb on the surfaces of in-situ formed Mn oxide surfaces ($MnO_x(s)$) where they subsequently oxidize to MnO_2. The presence of chlorine in solution greatly enhances the rate at which the adsorbed Mn(II) can be oxidized to Mn(IV) (‘heterogeneous oxidation’), and this in turn accelerates the further adsorption of Mn(II) [36-37] because of the increased quantity, and surface area of MnO_2. Therefore, the new formed MnO_2 nanoparticles with NaClO can remove more Mn(II) in the raw water as it had greater surface area when $KMnO_4$ was added together with NaClO (Figure 3).

Both the second and third effects correspond to the observed synergistic behavior since they depend on the formation of MnO_x(s), which is only poorly formed by chlorine alone. The magnitude of the synergy will be dependent on the concentration and duration of chlorine present during the reactions, as demonstrated by the poorer performance observed when chlorine was added in advance of permanganate (Figure 3), where chlorine consumption by reactive substrates in solution leads to a lower chlorine concentration than when it is added simultaneously with permanganate. The greater reduction of solution colour when permanganate and chlorine were added simultaneously may be explained by a greater oxidation because of the maintenance of higher permanganate concentrations through the effect of in-situ recycling of MnO_4^- ions by the chlorine. In addition, the greater reduction of colour may be due to enhanced adsorption of organic chromophores on to MnO_x(s), and the more efficient removal of the MnO_x(s) by the coagulation/filtration.

5 Conclusions

In this study the potential benefits of combining permanganate and chlorine prior to coagulation for Mn removal have been investigated, with particular focus on the problem of organically-bound Mn. The principal conclusions care as follows:

- The simultaneous addition of NaClO and $KMnO_4$ enhanced the overall removal of Mn compared to $KMnO_4$ alone.

- The sequence of NaClO and $KMnO_4$ addition was found to affect overall the Mn reduction; simultaneous addition of the chemicals was superior to adding NaClO before $KMnO_4$.

- Whilst $KMnO_4$ is able to break Mn-organic bonds, the combination of NaClO and $KMnO_4$ was found to enhance this effect synergistically.

- The greater performance of combined NaClO and $KMnO_4$ is believed to occur via mechanisms involving chlorine-assisted autocatalytic Mn oxidation and MnO_4^- recycling.

Acknowledgements

The authors wish to acknowledge the assistance of the Guangzhou-Huadu Water Company, China. This research was supported by a Marie Curie International Incoming Fellowship within the 7th European Community Framework Programme for Dr Wenzheng Yu (FP7-PEOPLE-2012-IIF-328867).

References

1. P. Kohl and S. Medlar, *Awwarf Report 91147*, **2007**.

2. T. R. Guilarte, *Cienc Saude Coletiva*, **2011,** *16*.

3. E. O. Sommerfeld, *Denver, CO: AWWA*, **1999**.

4. T. L. Marques, V. N. Alves, L. M. Coelho and N. M. M. Coelho, *Bioresources*, **2013,** *8*, 2738.

5. P. Ganesan, R. Kamaraj, G. Sozhan and S. Vasudevan, *Environ Sci Pollut R*, **2013,** *20*, 987.

6. Y. I. Tarasevich, V. V. Goncharuk, V. E. Polyakov, D. A. Krysenko, Z. G. Ivanova, E. V. Aksenenko and M. Y. Tryfonova, *J Ind Eng Chem*, **2012,** *18*, 1438.

7. H. A. Aziz and P. G. Smith, *Water Res*, **1996,** *30*, 489.

8. N. Georgieva, R. Bryaskova, N. Lazarova and R. Racheva, *Biotechnol Biotec Eq*, **2013,** *27*, 4078.

9. C. N. Butterfield, A. V. Soldatova, S. W. Lee, T. G. Spiro and B. M. Tebo, *P Natl Acad Sci USA*, **2013,** *110*, 11731.

10. (a) M. S. Burger, S. S. Mercer, G. D. Shupe and G. A. Gagnon, *Water Res*, **2008,** *42*, 4733,(b) I. A. Katsoyiannis and A. I. Zouboulis, *Water Res*, **2004,** *38*, 1922,(c) S. Y. Qin, F. Ma, P. Huang and J. X. Yang, *Desalination*, **2009,** *245*, 183.

11. (a) A. M. Gounot, *Fems Microbiol Rev*, **1994,** *14*, 339,(b) B. M. Tebo, J. R. Bargar, B. G. Clement, G. J. Dick, K. J. Murray, D. Parker, R. Verity and S. M. Webb, *Annu Rev Earth Pl Sc*, **2004,** *32*, 287,(c) V. W. Hoyland, W. R. Knocke, J. O. Falkinham, A. Pruden and G. Singh, *Water Res*, **2014,** *66*, 31,(d) J. R. Bargar, B. M.

Tebo and J. E. Villinski, *Geochim Cosmochim Ac*, **2000,** *64*, 2775.

12. (a) A. G. Tekerlekopoulou, S. Pavlou and D. V. Vayenas, *J Chem Technol Biot*, **2013,** *88*, 751,(b) M. Han, Z. W. Zhao, W. Gao and F. Y. Cui, *Bioresource Technol*, **2013,** *145*, 17,(c) J. Vandenabeele, M. Vandewoestyne, F. Houwen, R. Germonpre, D. Vandesande and W. Verstraete, *Microbial Ecol*, **1995,** *29*, 83.

13. (a) V. A. Pacini, A. M. Ingallinella and G. Sanguinetti, *Water Res*, **2005,** *39*, 4463,(b) A. G. Tekerlekopoulou and D. V. Vayenas, *Biochem Eng J*, **2008,** *39*, 215,(c) P. Berbenni, A. Pollice, R. Canziani, L. Stabile and F. Nobili, *Bioresource Technol*, **2000,** *74*, 109.

14. K. Sasaki, H. Konno, M. Endo and K. Takano, *Biotechnol Bioeng*, **2004,** *85*, 489.

15. (a) P. Roccaro, C. Barone, G. Mancini and F. G. A. Vagliasindi, *Desalination*, **2007,** *210*, 205,(b) J. E. Vanbenschoten, L. Wei and W. R. Knocke, *Environ Sci Technol*, **1992,** *26*, 1327.

16. R. Raveendran, B. Chatelier and K. Williams, *Water Science and Technology: Water Supply*, **2002,** *2*, 173.

17. Q. W. Li, G. Luo, J. Li and X. Xia, *J Mater Process Tech*, **2003,** *137*, 25.

18. (a) G. Hamilton, B. Chiswell, J. Terry, D. Dixon and L. Sly, *J Water Supply Res T*, **2013,** *62*, 417,(b) M. M. Michel and L. Kiedrynska, *Przem Chem*, **2012,** *91*, 1416,(c) J. Jez-Walkowiak and Z. Dymaczewski, *J Water Supply Res T*, **2012,** *61*, 364,(d) T. Ormanci, G. T. Demirkol, I. M. Aydin and N. Tufekci, *Desalin Water Treat*, **2013,** *51*, 2225.

19. K. F. Mcknight, M. Carlson, P. Fortin and C. Ziesemer, *Ozone-Sci Eng,* **1993,** *15*, 331.

20. E. Okoniewska, J. Lach, M. Kacprzak and E. Neczaj, *Desalination,* **2007,** *206*, 251.

21. (a) J. M. Cerrato, W. R. Knocke, M. F. Hochella, A. M. Dietrich, A. Jones and T. F. Cromer, *Environ Sci Technol,* **2011,** *45*, 10068,(b) W. R. Knocke, L. Zuravnsky, J. C. Little and J. E. Tobiason, *J Am Water Works Ass,* **2010,** *102*, 64.

22. K. H. Choo, H. Lee and S. J. Choi, *J Membrane Sci,* **2005,** *267*, 18.

23. S. Allard, L. Fouche, J. Dick, A. Heitz and U. von Gunten, *Environ Sci Technol,* **2013,** *47*, 8716.

24. W. Stumm and J. J. Morgan, *New York, NY: Wiley,* **1996**.

25. E. Gilbert and S. Hoffmannglewe, *Water Res,* **1990,** *24*, 39.

26. J. F. Perez-Benito and J. Ferrando, *J Phys Chem B,* **2014,** *118*, 14949.

27. R. Munter, P. Overbeck and J. Sutt, *Ozone-Sci Eng,* **2008,** *30*, 73.

28. M. Deborde and U. von Gunten, *Water Res,* **2008,** *42*, 13.

29. J. E. Vanbenschoten, L. Wei and W. R. Knocke, *Environ Sci Technol,* **1992,** *26*, 1327.

30. R. H. Waldemer and P. G. Tratnyek, *Environ Sci Technol,* **2006,** *40*, 1055.

31. F. Freeman and J. C. Kappos, *J Am Chem Soc,* **1985,** *107*, 6628.

32. R. N. Collins, B. C. Onisko, M. J. McLaughlin and G. Merrington, *Environ Sci Technol,* **2001,** *35*, 2589.

33. R. N. Bose, C. Keane, A. Xidis, J. W. Reed, R. M. Li, H. Tu and P. L. Hamlet,

Inorg Chem, **1991,** *30*, 2638.

34. J. Jiang, S. Y. Pang and J. Ma, *Environ Sci Technol*, **2010,** *44*, 4270.

35. M. Altaf and D. Jaganyi, *J Disper Sci Technol*, **2013,** *34*, 1481.

36. O. J. Hao, A. P. Davis and P. H. Chang, *J Environ Eng-Asce*, **1991,** *117*, 359.

37. M. A. Kessick and J. J. Morgan, *Environ Sci Technol*, **1975,** *9*, 157.

Captions

Figure 1 The effect of sodium hypochlorite dosage on the effluent manganese concentration in Bajiang river water (NaClO and $KMnO_4$ were added simultaneously 1 min prior to 7.2 mg/L PACl).

Figure 2 The effect of potassium permanganate dosage on the effluent concentration of manganese with and without sodium hypochlorite (1.76 mg/L) in Bajiang river water (NaClO and $KMnO_4$ were added simultaneously 1 min prior to 7.2 mg/L PACl).

Figure 3 The effect of changing the point of potassium permanganate and sodium hypochlorite addition on the removal of manganese (a) and solution colour (b) in Bajiang river water (The dosage of NaClO was 1.76 mg/L and PACl was 7.2 mg/L; $KMnO_4$ was added before, together or later than NaClO).

Figure 4 Effect of PACl dosage on the effluent concentration of manganese and turbidity in Bajiang river water (1.76 mg/L NaClO and 1.5 mg/L $KMnO_4$ were added simultaneously 1 min prior to PACl).

Figure 5 Effect of $KMnO_4$ oxidation and coagulation process on the removal of 1 mg/L Mn^{2+} associated with either humic acid or EDTA at pH 7 in model waters: a) humic-Mn oxidized by different $KMnO_4$ dosages and coagulated by 2.7 mg/L PACl; b) humic-Mn oxidized by 1.92 mg/L $KMnO_4$ and coagulated by different PACl dosages;

c) EDTA-Mn oxidized by 1 mg/L NaClO and 1.92 mg/L $KMnO_4$ separately and together, and coagulated by different PACl dosages (humic acid and EDTA were both 5 mg/L).

Figure 6 Effect of different oxidant combinations on the EDTA-Mn solution as indicated by UV/visible absorption in model waters (same reaction conditions as Figure 5, but without coagulant and finished in bottled experiment): a) NaClO; b) $KMnO_4$; c) NaClO+$KMnO_4$; d) EDTA-Mn or $Mn^{2+}$with different oxidant combinations after 15 min.

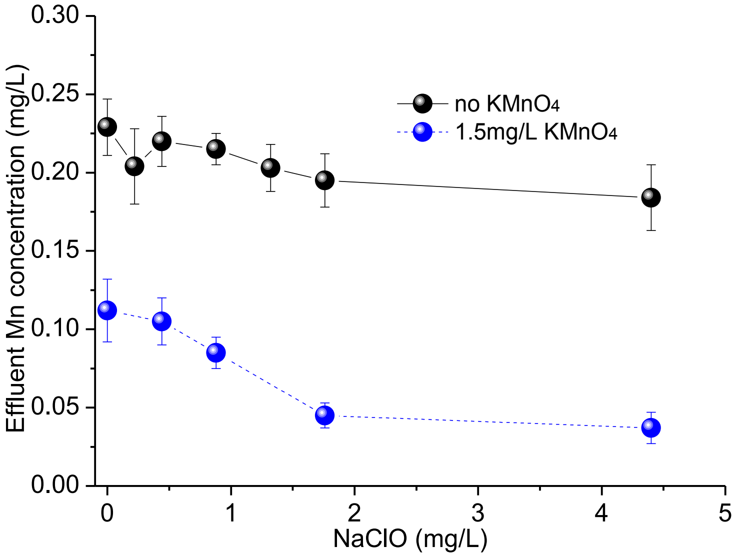


Figure 1 The effect of sodium hypochlorite dosage on the effluent manganese concentration in Bajiang river water (NaClO and $KMnO_4$ were added simultaneously 1 min prior to 7.2 mg/L PACl).

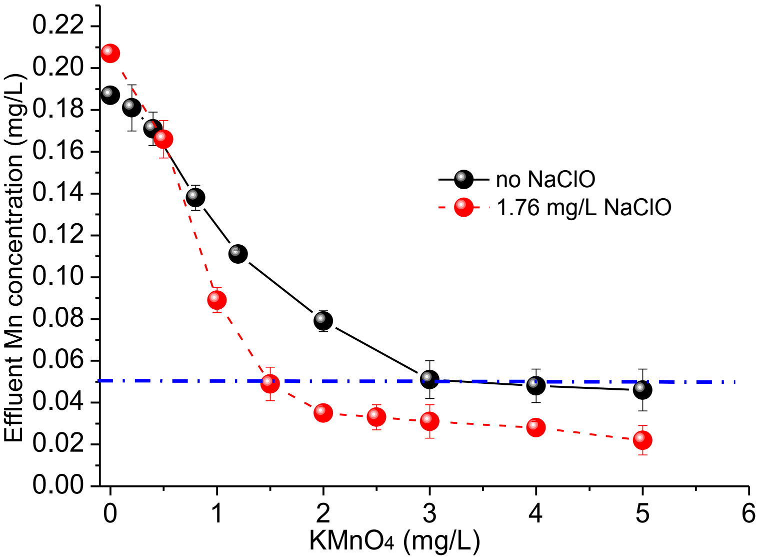


Figure 2 The effect of potassium permanganate dosage on the effluent concentration of manganese with and without sodium hypochlorite (1.76 mg/L) in Bajiang river water (NaClO and $KMnO_4$ were added simultaneously 1 min prior to 7.2 mg/L PACl).

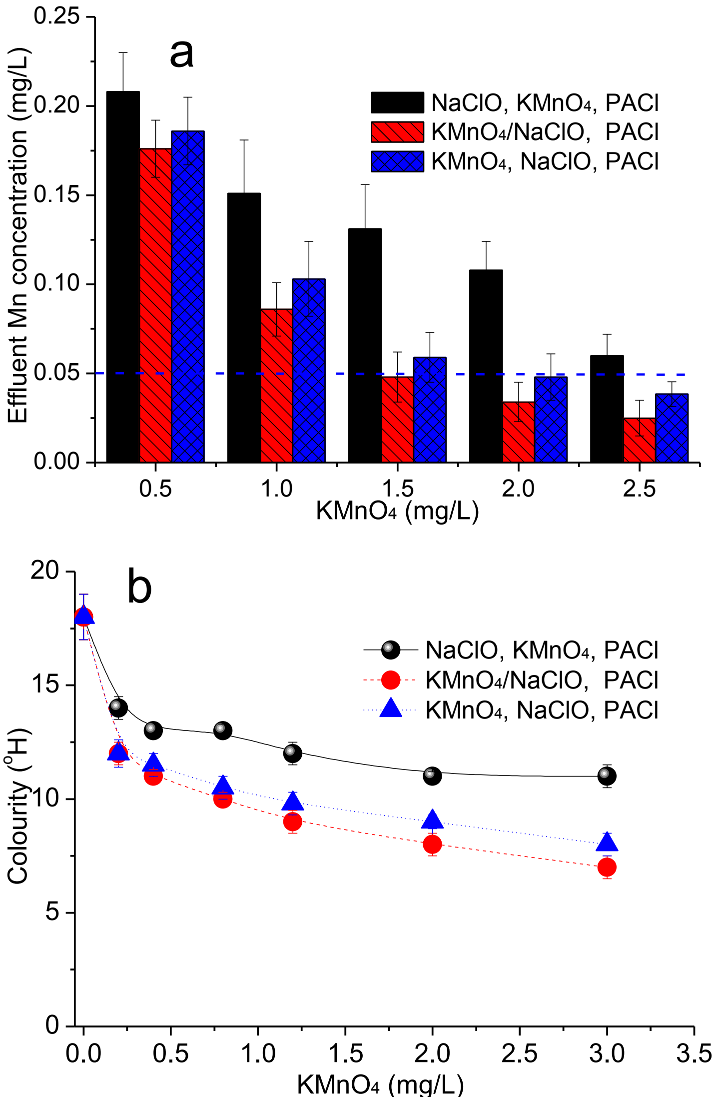


Figure 3 The effect of changing the point of potassium permanganate and sodium hypochlorite addition on the removal of manganese (a) and solution colour (b) in Bajiang river water (The dosage of NaClO was 1.76 mg/L and PACl was 7.2 mg/L; $KMnO_4$ was added before, together or later than NaClO).

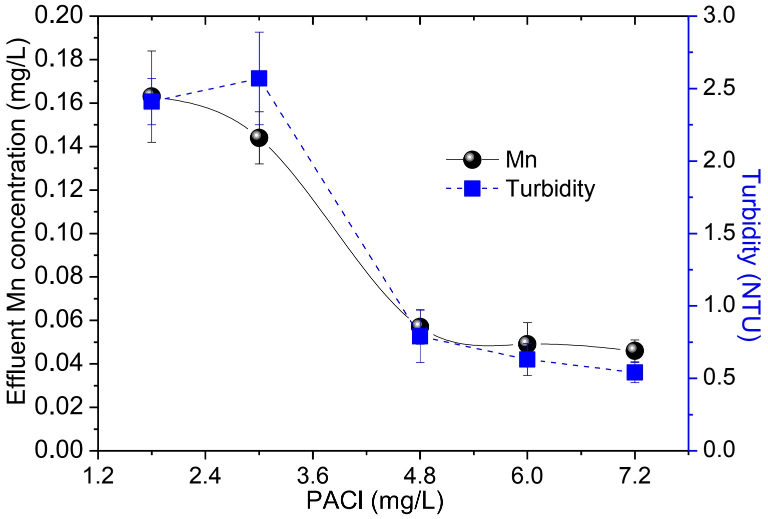


Figure 4 Effect of PACl dosage on the effluent concentration of manganese and turbidity in Bajiang river water (1.76 mg/L NaClO and 1.5 mg/L $KMnO_4$ were added simultaneously 1 min prior to PACl).

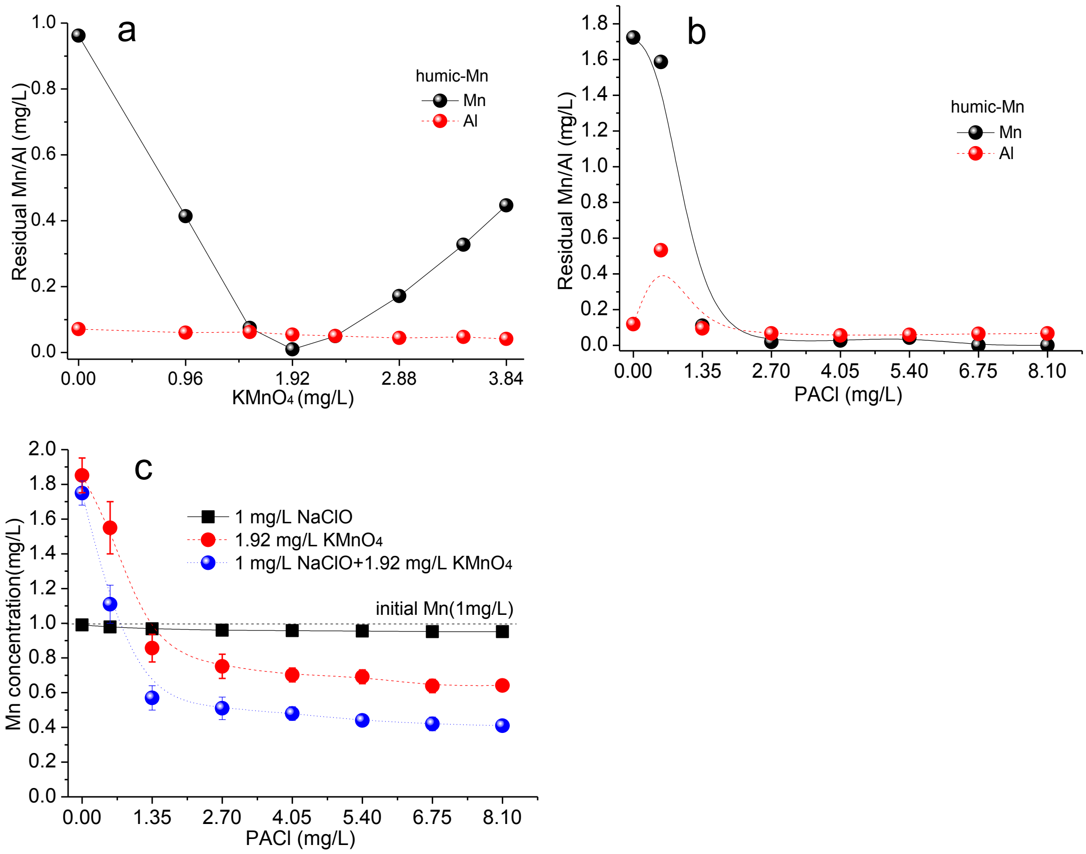


Figure 5 Effect of $KMnO_4$ oxidation and coagulation process on the removal of 1 mg/L Mn^{2+} associated with either humic acid or EDTA at pH 7 in model waters: a) humic-Mn oxidized by different $KMnO_4$ dosages and coagulated by 2.7 mg/L PACl; b) humic-Mn oxidized by 1.92 mg/L $KMnO_4$ and coagulated by different PACl dosages; c) EDTA-Mn oxidized by 1 mg/L NaClO and 1.92 mg/L $KMnO_4$ separately and together, and coagulated by different PACl dosages (humic acid and EDTA were both 5 mg/L).

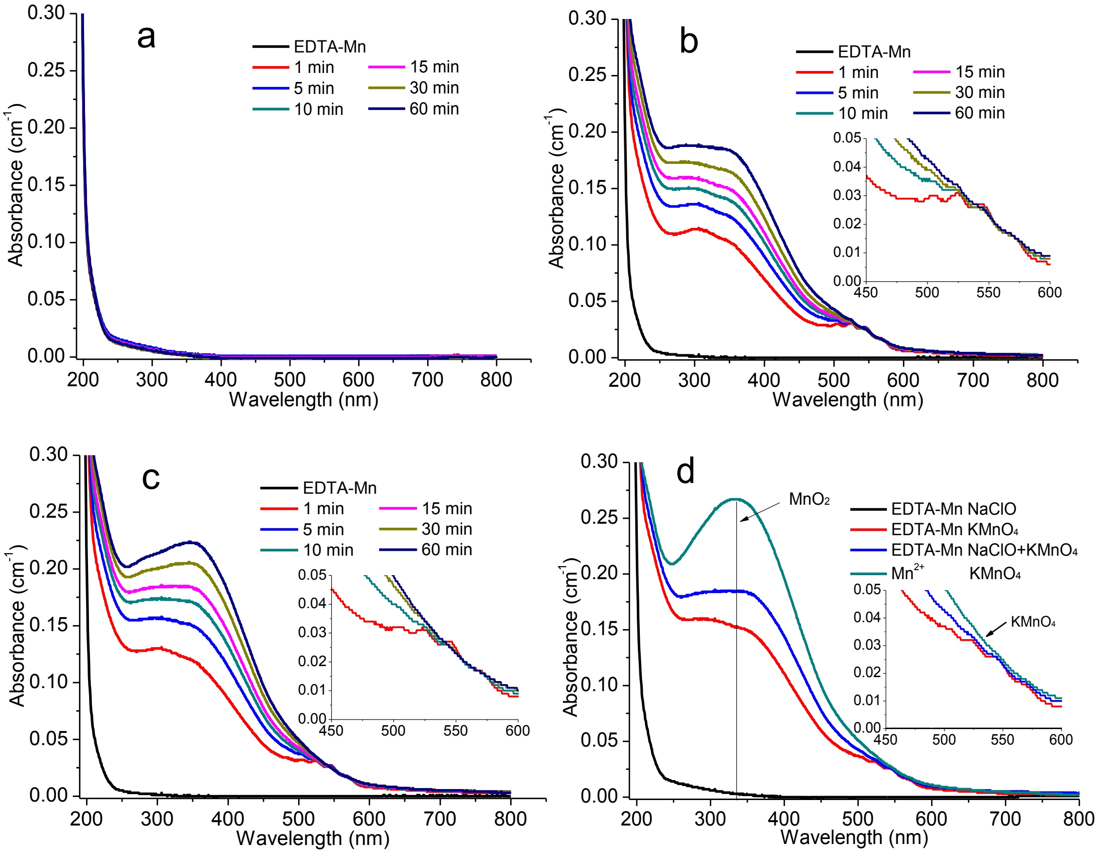


Figure 6 Effect of different oxidant combinations on the EDTA-Mn solution as indicated by UV/visible absorption in model waters (same reaction conditions as Figure 5, but without coagulant and finished in bottled experiment): a) NaClO; b) $KMnO_4$; c) NaClO+$KMnO_4$; d) EDTA-Mn or Mn^{2+} with different oxidant combinations after 15 min.