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Removal of manganese(II) and iron(II) from synthetic groundwater using potassium permanganate

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ABSTRACT

The removal of Mn^{2+} and Fe^{2+} from synthetic groundwater via oxidation using potassium permanganate was investigated. Batch jar tests were carried out under a constant pH of 8.0, where the effect of parameters such as the oxidant dose, presence of co-ions (Ca^{2+}, Mg^{2+}) and alum addition on the removal of Mn^{2+} and Fe^{2+} was examined. The partial removal of Mn^{2+} using aeration in single and dual metal system was 30.6% and 37.2%, respectively. The oxidant dose of 0.603 mg/L $KMnO_4$ was the minimum amount needed to reduce Mn^{2+} below its maximum contaminant level. The presence of Fe^{2+} improved the removal of Mn^{2+} due to the autocatalytic effect of hydrous manganese-iron oxide, where its presence was confirmed by digital microscopy and EDX. The presence of Ca^{2+} and Mg^{2+} as well as the alum addition after oxidation has a negative effect on the removal of Mn^{2+}. The removal mechanism of Mn^{2+} and Fe^{2+} was a combination of oxidation and adsorption or co-precipitation between the hydrous oxide and the dissolved metal ions.

Keywords: Iron; Manganese; Groundwater; Oxidation; Potassium permanganate

1. Introduction

Groundwater is one of the major sources of drinking water. Generally, it is characterized by high carbon dioxide concentration, low temperature, high alkalinity and hardness, and has a low content of suspended solids [1]. Manganese (Mn^{2+}) and iron (Fe^{2+}) are naturally found in groundwater, where the concentration of Fe^{2+} exceeds that of Mn^{2+} [2,3]. In Taiwan, the maximum contaminant level (MCL) of Mn^{2+} and Fe^{2+} in drinking water is 0.05 and 0.30 mg/L, respectively [4], whereas the international standards are set at 0.10 mg/L Mn^{2+} and 0.30 mg/L Fe^{2+} [5]. The presence of Mn^{2+} and Fe^{2+} at elevated levels in

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groundwater is considered to be undesirable. Upon exposure to oxygen, Mn^{2+} and Fe^{2+} are oxidized into MnO_2 and $Fe(OH)_3$. The precipitates could stain household utensils and clothes, and could impart a bitter, metallic taste to the water [6]. Therefore, it is important to remove Mn^{2+} and Fe^{2+} from groundwater.

Current technologies used in removing Mn^{2+} and Fe^{2+} from groundwater include biological, physical, and chemical processes. A common removal method is through chemical means where a strong oxidizing agent such as chlorine, hypochlorite, ozone or potassium permanganate ($KMnO_4$) is used. In this study, $KMnO_4$ was selected as the oxidizing agent of Mn^{2+} and Fe^{2+} because it is neither toxic nor expensive. In addition, it removes undesirable taste and odor caused by manganese, iron, bacteria, and hydrogen sulfide [7].

Oxidation of Mn^{2+} and Fe^{2+} using $KMnO_4$ is illustrated in Eqs. (1) and (2), respectively [8].

$$3Mn^{2+}_{(aq)} + 2KMnO_{4(aq)} + 2H_2O_{(l)} \rightarrow 5MnO_{2(s)} + 2K^{+}_{(aq)} + 4H^{+}_{(aq)} \quad (1)$$

$$3Fe^{2+}_{(aq)} + KMnO_{4(aq)} + 7H_2O_{(l)} \rightarrow 3Fe(OH)_{3(s)} + K^{+}_{(aq)} + MnO_{2(s)} + 5H^{+}_{(aq)} \quad (2)$$

$$KMnO_{4(aq)} + 8H^{+}_{(aq)} + 5e^{-}_{(eq)} \leftrightarrow Mn^{2+}_{(aq)} + K^{+}_{(aq)} + 4H_2O_{(l)} \quad (3)$$

A stoichiometric quantity of 1.92 mg (1.21×10^{-5} mol) and 0.94 mg (5.95×10^{-6} mol) of $KMnO_4$ could be used to oxidize 1 mg of Mn^{2+} (1.82×10^{-5} mol) and Fe^{2+} (1.79×10^{-5} mol), respectively. Any excess amount of $KMnO_4$ may deter the removal of Mn^{2+} because MnO_4^- produces Mn^{2+} as well (Eq. (3)). Therefore, an optimum amount of $KMnO_4$ is determined in order to reduce Mn^{2+} and Fe^{2+} to a concentration below the MCL. The optimum conditions such as pH and stirring speed obtained from the previous study [9] would be utilized in the removal of Fe^{2+} and Mn^{2+} in this study.

Among the pretreatment technologies, coagulation is widely used in the pre-treatment of wastewater and industrial streams [11]. Its main application is the removal of humic substances and colloidal particles such as aluminum, silt and clay minerals, colloidal sulfur, and silica [12]. In this process, a coagulant is added to water that contains a low concentration of particles to form nucleating sites for the formation of larger flocs. In drinking water and wastewater treatment, aluminum sulfate ($Al_2(SO_4)_3$), polyferric sulfate (PFS) and ferric chloride ($FeCl_3$) are commonly used as coagulants. According to El Araby et al. (2009), addition of alum after ozonation can improve the removal of iron and manganese [13].

The main purpose of this study is to investigate the removal of Mn^{2+} and Fe^{2+} from synthetic groundwater using a combined method of pre-aeration and oxidation using $KMnO_4$. The removal of Mn^{2+} and Fe^{2+} in single and dual metal system was studied in order to understand the influence of Fe^{2+} on the oxidation of Mn^{2+}. The effect of operating parameters such as oxidant dose, effect of co-ions (Ca^{2+} and Mg^{2+}), and alum addition on the removal of Mn^{2+} and Fe^{2+} was determined. The particle charge was determined using a zeta potentiometer, whereas the morphology and composition of the precipitates were analyzed using a digital microscope and energy dispersive X-ray (EDX) analysis, respectively.

2. Materials and methods

2.1. Chemicals

Reagents such as $MnCl_2{\cdot}4H_2O$, $FeSO_4{\cdot}7H_2O$, $CaCl_2{\cdot}4H_2O$, $MgCl_2{\cdot}4H_2O$, $NaHCO_3$, $NaSO_4$, HNO_3, HCl (37% fuming), KCl, and NaOH were procured from Merck (Germany) while $Al_2(SO_4)_3{\cdot}16\text{-}18H_2O$ was obtained from Nihon Shiyaku (Japan). Deionized water (DI) with a resistivity of 18.9 MΩ was used in the preparation of all samples and standards. The chemicals were of analytical grade and were used without further purification.

2.2. Experimental methods

Stock solutions of Mn^{2+} or Fe^{2+} with a concentration of 1,000 mg/L were prepared from $MnCl_2{\cdot}4H_2O$ and $FeSO_4{\cdot}7H_2O$, respectively. A stock solution of alum with a concentration of 6,000 mg/L was prepared from $Al_2(SO_4)_3{\cdot}16\text{-}18H_2O$. Stock solutions of Ca^{2+} and Mg^{2+} with a concentration of 4,000 mg/L (100 mM) and 2,430 mg/L (100 mM) were prepared from $CaCl_2{\cdot}4H_2O$ and $MgCl_2{\cdot}4H_2O$, respectively.

2.3. Batch study

Experiments were carried out using a standard jar test system, similar to those reported in Phatai et al. [9]. Jar tests were done in triplicate and the average was obtained. The control parameters include oxidant dose (0.603 and 0.648 mg/L), effect of co-ions like Ca^{2+} (4.0, 40.0, and 400.0 mg/L) and Mg^{2+} (2.4, 24.3, and 243.0 mg/L), and alum addition after oxidation

(10, 20, and 30 mg/L). The mixture was initially aerated for 20 min. A sample was obtained after pre-aeration and was referred to as 0 min of oxidation reaction time. Upon addition of $KMnO_4$, the samples were taken at 15 min time interval for a total duration of 1 h.

2.4. Effect of Ca^{2+} and Mg^{2+}

The effect of co-ions such as Ca^{2+} (4.0, 40.0, and 400.0 mg/L) and Mg^{2+} (2.4, 24.3, and 243.0 mg/L) on the removal of Mn^{2+} and Fe^{2+} was examined under a varying concentration range. The wide concentration range was selected since the amount of Ca^{2+} and Mg^{2+} normally fluctuates, which is caused by the changing conditions of natural groundwater.

2.5. Effect of alum addition after oxidation

After the oxidation stage, addition of alum (10, 20 and 30 mg/L) was done and its effect on the removal performance of Mn^{2+} was studied. The values of alum dosage applied are for the coagulation of typically low turbid water [7]. Upon addition of alum to the mixture, the stirring speed was decreased to 50 rpm and the total duration of coagulation-flocculation time was 1 h. Samples were taken at 15-min time intervals and were referred to as 75, 90, 105, and 120 min of the reaction time, respectively.

To investigate the effect of alum when combined with aeration, alum with a dosage of 30 mg/L was added into the mixture instead of $KMnO_4$ after the pre-aeration step of 20 min. The stirring speed was maintained at 120 rpm for 1 h and was decreased to 50 rpm during the coagulation-flocculation process. The sampling was done at a 15 min time interval for a total duration of 2 h.

2.6. Analytical method

The residual ions including Mn^{2+}, Fe^{2+}, Ca^{2+}, and Mg^{2+} were analyzed by using inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer DV 2000). The samples were nitrified and filtered using a membrane micro filter with a nominal pore size of 0.45 µm. A blank solution containing synthetic groundwater without the ions was analyzed as well.

2.7. Characterization

The oxide precipitates were collected after 1 h at the end of the run. The precipitates were dehydrated in a freeze dryer for 2 days in order to remove free water and were kept in a desiccator before analyses. A digital microscope (Hirox, KH-7700) with a magnification of 700× equipped with EDX (Hariba Emax 400) was used in analyzing the precipitates.

The colloidal solution from the dual Mn^{2+}–Fe^{2+} system at pH 6.0–9.0 was collected after 1 h of oxidation run. A zeta potentiometer (Zetasizer Nano-ZS, Malvern) was used to determine the surface charge of the precipitates.

3. Results and discussion

3.1. Effect of aeration in single and metal dual system

The effect of pre-aeration on the removal of Mn^{2+} and Fe^{2+} from synthetic groundwater was investigated. The average removal in the single and dual oxidation system is presented in Fig. 1. In the single metal system (Fig. 1(a)), a maximum Mn^{2+} removal of 30.6% was achieved after 15 min, where residual Mn^{2+} of 0.347 mg/L was still higher than the MCL. The oxidation efficiency using aeration was low because the reaction requires an ORP higher than 400 mV [10]. In contrast, Fe^{2+} in single metal system provided high removal efficiency of 90.0% for an oxidation time of 15 min and its residual concentration was lower than the permitted level. The removal of Fe^{2+} and Mn^{2+} is given by the reactions below [8]:

$$3Fe^{2+} + MnO_4^- + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + 5H^+$$

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

The removal efficiency of Fe^{2+} was higher because it is easily oxidized in comparison to Mn^{2+}. From the reaction below, Mn^{4+} is more strongly electronegative over Fe^{3+} due to its higher redox potential of +1.23 V. Therefore, Mn^{4+} (as MnO_2) is more likely to be reduced to Mn^{2+} in comparison to Fe^{3+} (as $Fe(OH)_3$) being reduced to Fe^{2+}.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^\circ = +0.77V$$

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+} \qquad E^\circ = +1.23V$$

In the pre-aeration of the dual oxidation system (Fig. 1(b)), the remaining concentration of Mn^{2+} and Fe^{2+} was 0.314 mg/L (37.2% conversion) and 0.048 mg/L (90.4% conversion), respectively. In comparison to the single oxidation system, the

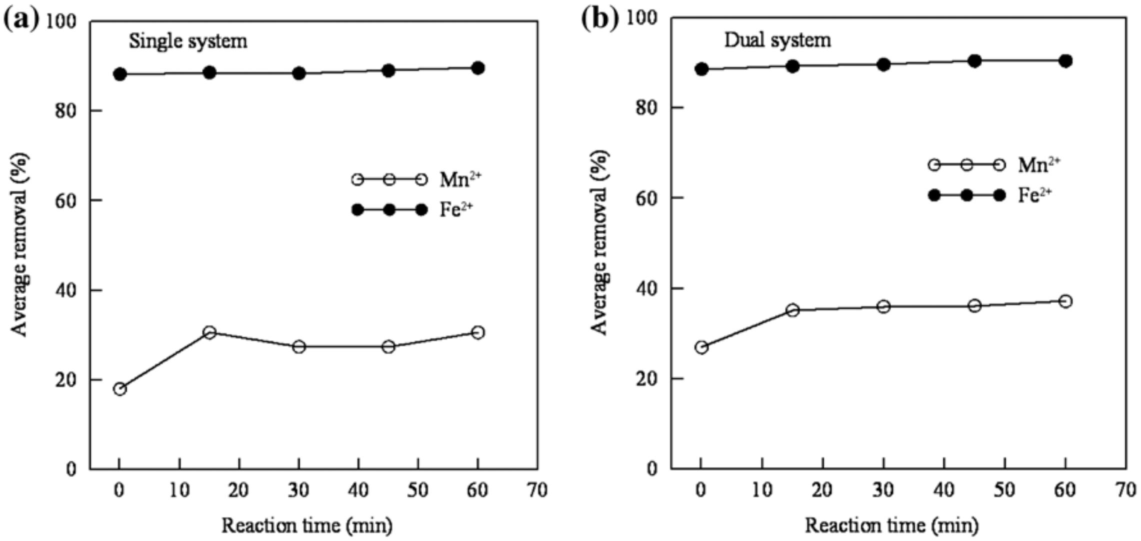


Fig. 1. Average removal using aeration from synthetic groundwater (pH 8.0 and stirring speed 120 rpm) in (a) single and (b) dual metal oxidation system.

removal efficiency of Mn^{2+} increased by 6.6% due to the presence of Fe^{2+}. During the pre-aeration step, precipitates of $Fe(OH)_3$ were formed that provided surface for the autocatalytic oxidation of soluble Mn^{2+} and Fe^{2+} [15]. The removal of Fe^{2+} was observed to be less effective in the presence of Mn^{2+} in groundwater. However, only the residual concentration of Mn^{2+} did not meet the MCL. Therefore, addition of an oxidizing agent is required to improve the removal efficiency of Mn^{2+} in both single and dual metal system.

3.2. *Effect of oxidant dose in the removal of Mn^{2+} in single and dual metal systems*

After the pre-aeration step, the oxidation of the remaining Mn^{2+} using $KMnO_4$ was investigated. Jar tests were carried out using low-level aeration combined with oxidation under different doses of $KMnO_4$. Based from Eqs. (1) and (2), the stoichiometric dose of $KMnO_4$ should be 0.603 and 0.648 mg/L in order to remove the residual Mn^{2+} in single (0.314 mg/L) and dual (0.314 mg/L) metal systems, respectively.

Fig. 2 illustrates the percent removal of Mn^{2+} in single and dual metal systems. In a single metal system (Fig. 2(a)), the soluble Mn^{2+} was rapidly oxidized within 15 min. At a dose of 0.603 mg/L $KMnO_4$, the efficiency was 84.6% at 15 min and increased to 92.2% in 1 h, where the residual Mn^{2+} was below the MCL. In the dual system, a dose of 0.648 mg/L $KMnO_4$ produced a higher percent removal of 92.2% at 15 min. It is observed that 92.2% removal was attained in shorter reaction times for dual Fe^{2+}-Mn^{2+} system at 15 min, while it was obtained in 1 h for single Mn^{2+} system. This is due to the higher dose of oxidant, which led to an increase in the conversion of Mn^{2+} into MnO_2 precipitates, which would provide more autocatalytic activity in the removal of Mn^{2+} and enhanced co-precipitation on the produced oxide [14–18]. A two-reaction mechanism has been proposed, where relatively rapid adsorption of Mn^{2+} is followed by a slower oxidation step:

$$Mn^{2+}_{(aq)} + MnO_{2(s)} \rightarrow MnO_2Mn^{2+}_{(s)} \quad (4)$$

$$O_{2(g)} + MnO_2Mn^{2+}_{(s)} \rightarrow 2MnO_{2(s)} \quad (5)$$

The main mechanisms in the removal of Mn^{2+} are oxidation using $KMnO_4$ that forms MnO_2, adsorption of Mn^{2+} onto MnO_2, and slow oxidation of solid MnO_2Mn^{2+} into MnO_2. The pH and ORP of the single and dual metal oxidation system were measured with values falling within the range of pH 6.0–9.0 and + 598 to + 825 mV. Based on the Eh-pH diagram, the main Mn species present in the system is MnO_2 [12].

In Fig. 2, the removal of Mn^{2+} and Fe^{2+} in single and dual metals system has a similar trend. In both systems, the Mn^{2+} level was reduced below its MCL within 15 min where the percent removal in a dual metal system was higher than in a single metal system. In addition, Fe^{2+} removal is greater than 94.0% at 15 min, where no further increase in the removal was observed as the oxidant dose was increased. Soluble Fe^{2+} oxidizes into $Fe(OH)_3$, which could combine with MnO_2 and further enhance the co-precipitation of Mn^{2+} [18]. Results show that

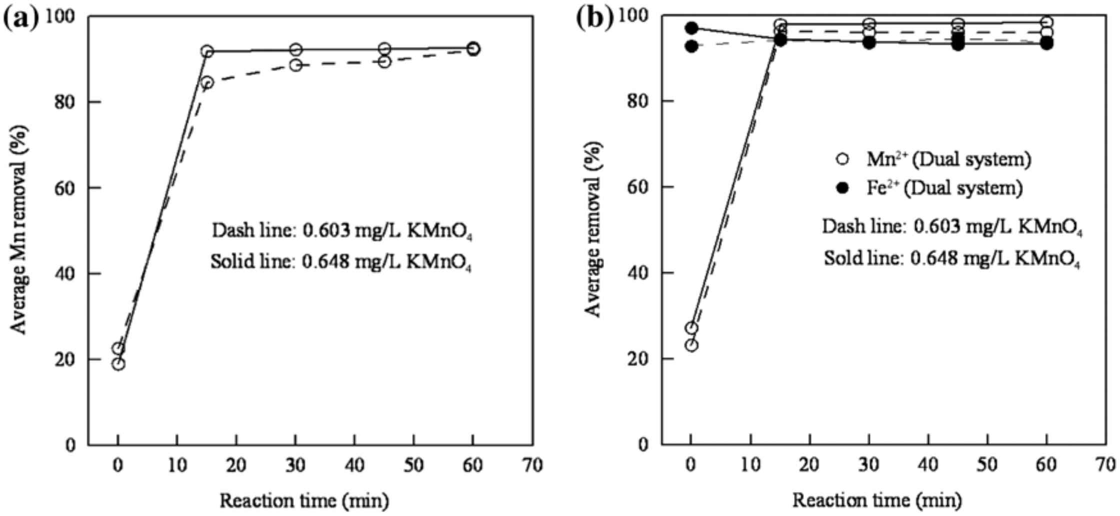


Fig. 2. Average removal of Mn^{2+} from synthetic groundwater by oxidation; (a) single Mn^{2+}, (b) dual Mn^{2+} and Fe^{2+} (oxidant doses, 0.603 (dash line) and 0.648 mg/L (solid line); pH was 8.0; stirring speed was 120 rpm).

pre-aeration and oxidation of single and dual metal systems provided satisfactory (below the MCL) removal of Mn^{2+} and Fe^{2+} using pH 8.0, 0.603 mg/L of $KMnO_4$, and 15 min of oxidation time. Therefore, the oxidant dose of 0.603 mg/L was utilized throughout the entire study.

3.3. *Effect of Ca^{2+} and Mg^{2+} on removal of Mn^{2+} in dual system*

The effect of co-ions like Ca^{2+} and Mg^{2+} on the removal of Mn^{2+} and Fe^{2+} was investigated using an oxidant dose of 0.603 mg/L and a pH of 8.0. The removal of Mn^{2+} under different concentrations of Ca^{2+} and Mg^{2+} is shown in Fig. 3.

It was observed that increasing the Ca^{2+} concentration from 4.0 to 400.0 mg/L causes a corresponding decrease in the percent removal of Mn^{2+} from 88.34% to 86.10%. Under the presence of Ca^{2+} in the solution, the residual Mn^{2+} concentration still met the permitted level.

Precipitates of MnO_2 and $Fe(OH)_3$ have a point of zero charge (PZC) of around 3 and 8, respectively [19]. When the pH is less than pH_{PZC}, the surface

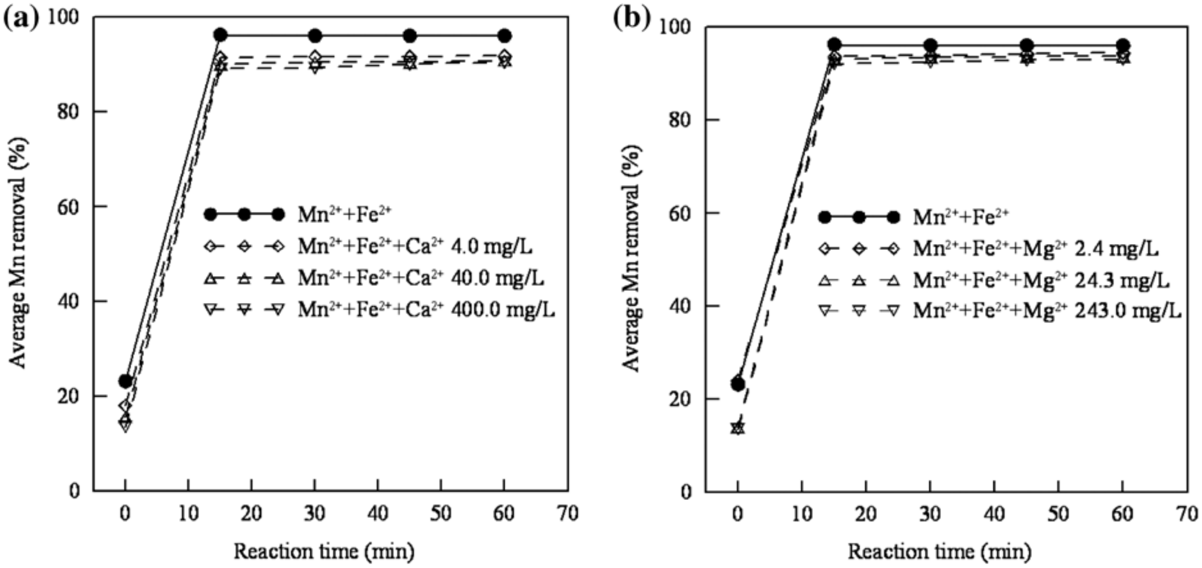


Fig. 3. Effect of co-ions (a) Ca^{2+} and (b) Mg^{2+} in the synthetic groundwater on the removal efficiency of Mn^{2+} (oxidant dose 0.603 mg/L; pH 8.0; stirring speed 120 rpm).

charge is positive and vice versa, and the reactions are as follows [20]:

$$\equiv \text{Mn-OH}_{(s)} + \text{H}_2\text{O}_{(1)} \rightarrow \equiv \text{Mn-OH}^{+}(\text{s}) + \text{OH}^{-}_{(aq)} \quad (\text{pH} < \text{pH}_{\text{PZC}}) \tag{6}$$

$$\equiv \text{Mn-OH}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \equiv \text{Mn-OH}^{-}_{(s)} + \text{OH}^{-}_{(aq)} \quad (\text{pH} > \text{pH}_{\text{PZC}}) \tag{7}$$

where $\equiv$Mn–OH$_2^+$, $\equiv$Mn–OH and $\equiv$Mn–O$^-$ represent positively charged, neutral and negatively charged surface hydroxyl, respectively.

As shown in Fig. 4, the net charge of the Mn–Fe precipitate was negative from pH 6.0 to 9.0 and becomes more negatively charged as the solution's pH becomes more basic. The net negative charge was mainly due to the reduction of MnO_4^- under alkaline condition ($pH > pH_{PZC}$) [20]. In this study, the Mn–Fe precipitate had a surface charge of −6.0 mV under a pH of 8.0. In the presence of 4.0 mg/L Ca^{2+}, the surface charge becomes more positive and increased to −1.54 mV. The decrease in the removal of Mn^{2+} when Ca^{2+} is present could be attributed to the decrease in the negative surface charge of the Fe–Mn oxide precipitates. This is due to Ca^{2+} surrounding the surface of the Fe–Mn oxide precipitates, which results in more positive surface charge.

The effect of Mg^{2+} on the removal of Mn^{2+} is presented in Fig. 3(b). The percent removal slightly decreased from 90.20 to 88.15% as the Mg^{2+} concentration was increased from 2.4 to 243.0 mg/L, respectively. This is attributed to the more positive mean surface charge of the precipitate, consisting of Mn^{2+}, Fe^{2+}, and Mg^{2+}, hence the presence of Mg^{2+} inhibited the removal of Mn^{2+}.

Based on the results, the presence of Ca^{2+} and Mg^{2+} slightly inhibited the removal of Mn^{2+} but still met the MCL. This may be due to the sufficient amount of $KMnO_4$ used in the oxidation step, which produced Mn-Fe precipitates to enhance the removal of Mn^{2+} and Fe^{2+}. In addition, Ca^{2+} and Mg^{2+} could precipitate to form calcium and magnesium carbonate, which could capture residual Mn^{2+} [21,22]. Table 1 shows the *p*-values and standard deviation of Mn^{2+} removal under different concentrations of Ca^{2+} and Mg^{2+}. The values were derived using a two-tailed *t*-test. The *p-values* were determined to be 0.16873, 0.10843, and 0.74681for 4.0, 40.0, and 400.0 mg/L Ca^{2+} and 0.48364, 0.29603, and 0.83162 for 2.4, 24.3, and 243.0 mg/L Mg^{2+} in relation to the Mn^{2+} removal. Based on these results ($p\text{-values} > 0.05$), it implies that the effect of Ca^{2+} and Mg^{2+} in decreasing Mn^{2+} removal is statistically insignificant.

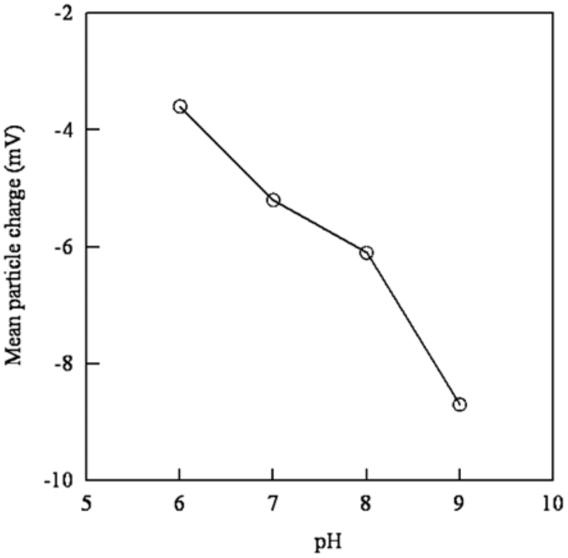


Fig. 4. Mean particle charge of precipitates after 60 min of Mn^{2+} and Fe^{2+} oxidation (without Ca^{2+} and/or Mg^{2+}); oxidant dose 0.603 mg/L; pH 8.0; stirring speed 120 rpm.

3.4. Effect of coagulation after oxidation

After combined aeration and oxidation was carried out, alum was added and its effect on the removal of Mn^{2+} was studied. From Fig. 5, the addition of alum after pre-aeration has no effect on the removal of Mn^{2+} (dash line). The maximum Mn^{2+} removal was 30.0%, which is of similar value to the removal by aeration alone. Therefore, the removal of Mn^{2+} using pre-aeration and coagulants was not sufficient and the addition of $KMnO_4$ was further studied.

Table 1
Statistical analysis of the effect of Ca^{2+} and Mg^{2+} on Mn^{2+} removal using *t*-test analysis

	Mn^{2+} alone	Mg^{2+} (mg/L)			Ca^{2+} (mg/L)		
		2.4	24.3	243.0	4.0	40.0	400.0
Mean value	93.20	90.20	88.62	88.15	86.10	87.64	88.34
Standard deviation	23.5796	34.375	34.5271	35.3096	33.9375	34.4842	34.0154
p-value		0.48364	0.29603	0.83162	0.16873	0.10843	0.74681

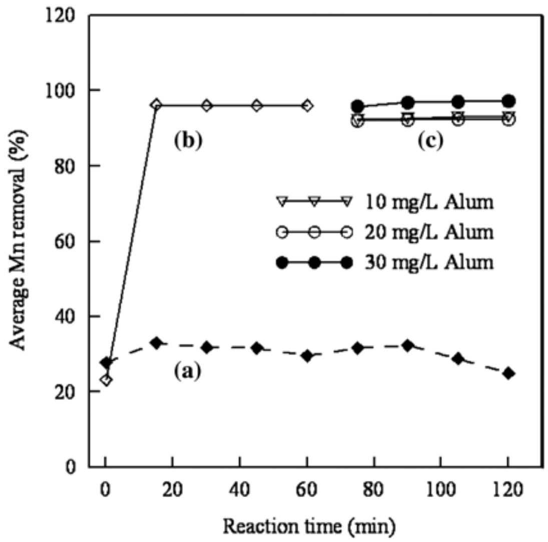


Fig. 5. Effect of coagulation on average Mn removal over time, (a) combined aeration and 30 mg/L alum, (b) combined aeration and 0.603 mg/L $KMnO_4$, (c) coagulation after 60 min of the oxidation; pH was 8.0; stirring speed 120 rpm.

Using pre-aeration and oxidation methods for 0.603 mg/L $KMnO_4$, the percent removal of Mn^{2+} slightly decreased to 87.00%, 88.00%, and 91.20% as the dosage of alum added increased from 10, 20 to 30 mg/L, respectively. The negative effect on the Mn^{2+} removal is due to alum causing the pH to drop, converting MnO_2 back to Mn^{2+} [23]. Addition of alum in water would yield the following reaction:

$$KAl(SO_4)_2 + 12H_2O \rightarrow Al(OH)_3 + 2H_2SO_4 + KOH + 8H_2O$$

Thus, gel-like precipitates of $Al(OH)_3$ are produced. In addition, 2 mol of H_2SO_4 are produced for every mole of alum added, which causes the pH of the system to be more acidic. The excess H^+ ions would cause MnO_2 to be converted into Mn^{2+}, as shown in the reaction below:

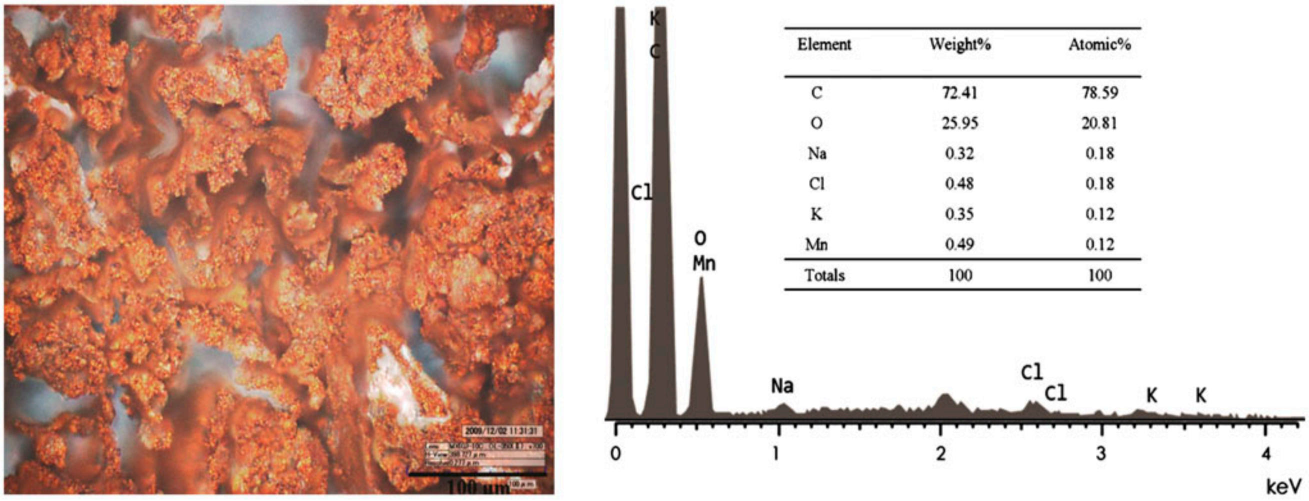
$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

However, despite the decrease in the removal of Mn^{2+} caused by the addition of alum, the residual amount of Mn^{2+} was still below the permitted level.

3.5. Characterization of oxide precipitates

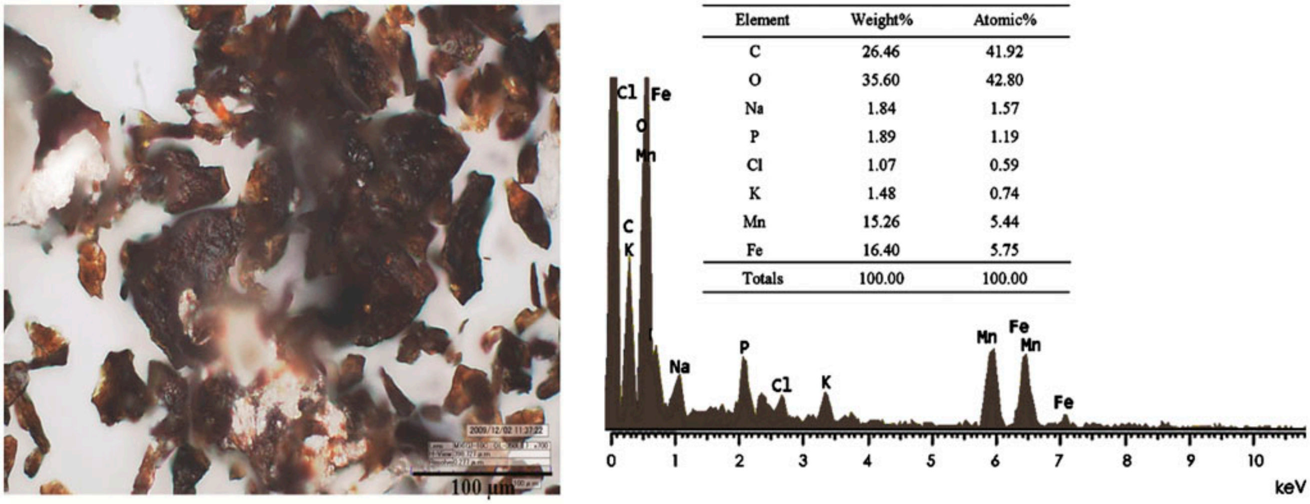
The morphology and composition of the precipitates obtained from single and dual metal system were examined using a digital microscope and EDX. In single metal system, light brown particles were observed (Fig. 6) due to the precipitation of the electrolytes present in the synthetic groundwater solution.

The corresponding amount of Na, Cl, and K is 0.32, 0.48, and 0.35% by weight, respectively. The presence of C at 72.41% by weight was due to the composition of the cellulose acetate membrane. The existence of O at 35.60% by weight indicates that the brown precipitate was in the oxide form with a 0.49% by weight of Mn.



Element	Weight%	Atomic%
C	72.41	78.59
O	25.95	20.81
Na	0.32	0.18
Cl	0.48	0.18
K	0.35	0.12
Mn	0.49	0.12
Totals	100	100

Fig. 6. Image from a digital camera and elemental composition of the precipitates from single Mn^{2+} oxidation; oxidant dose 0.603 mg/L; pH 8.0; stirring speed 120 rpm; reaction time 60 min.



Element	Weight%	Atomic%
C	26.46	41.92
O	35.60	42.80
Na	1.84	1.57
P	1.89	1.19
Cl	1.07	0.59
K	1.48	0.74
Mn	15.26	5.44
Fe	16.40	5.75
Totals	100.00	100.00

Fig. 7. Image from a digital camera and elemental composition of the precipitates from dual oxidation of Mn^{2+} and Fe^{2+}; oxidant dose 0.603 mg/L; pH 8.0; stirring speed 120 rpm; reaction time 60 min.

In the dual system, the formation of dark brown particles of crystalline nature was observed (Fig. 7). The particles were composed of manganese oxide (15.26% by weight) and iron oxide (16.40% by weight). An increase in MnO_2 formed in the dual system was due to the oxidation of Mn^{2+} and reduction of MnO_4^-.

3.6. Possible mechanisms on removal of Mn^{2+} and Fe^{2+}

The possible mechanisms of the removal of Mn^{2+} and Fe^{2+} using 0.603 mg/L $KMnO_4$ were examined under a solution pH of 8.0. The experimental design simulated the conditions during remediation of contaminated water, where pH control is not necessary. Variations of solution pH, average removal of Mn^{2+}, and concentration of the co-ions were recorded as shown in Figs. 8 and 9, respectively.

In the absence of Ca^{2+} and Mg^{2+}, the pH of synthetic groundwater containing soluble Mn^{2+} and Fe^{2+} did not change after 1 h (Fig. 9), indicating that oxidation did not take place in the system. However, the pH decreased from 8.0 to 7.94 within 1 min after the addition of $KMnO_4$ that reduced the concentration of Mn^{2+} and Fe^{2+} below their MCLs. The possible removal mechanism includes oxidation of Mn^{2+} and Fe^{2+} and adsorption or co-precipitation of the dissolved metal ions (Mn^{2+} and Fe^{2+}) by the hydrous oxide precipitate [14,20,24].

In the first mechanism, MnO_4^- reacts rapidly with Mn^{2+} and Fe^{2+} that produces MnO_2, $Fe(OH)_3$, and H^+, which caused the pH to drop. The percent removal of Mn^{2+} increased quickly and reached 98% within 1 min and became constant after 5 min. The result indicates that oxidation using aeration and 0.603 mg/L $KMnO_4$ effectively removed Mn^{2+} to the level below the MCL in shorter time and with less amount of $KMnO_4$ compared to other studies. A previous study obtained 95% removal of Mn^{2+} in 90 min after oxidation with $KMnO_4$ at a pH of 8.5 and an initial Mn concentration of 1.80 mg/L [24]. Another study achieved complete removal of Mn^{2+} and Fe^{2+}, after 24 h sampling using an alum dose of 40 mg/L at a pH of 6.5 and a $KMnO_4$ dose of 2.5 mg/L at a pH of 8.5 [25].

The second mechanism involves adsorption or co-precipitation of metal ions with hydrous metal oxide. As illustrated in Eq. (8), a bond is formed between Mn^{2+} and surface oxygen atoms of the hydrous Mn–Fe oxide, resulting in the release of protons and a drop in pH [2]. In this study, the experiment was done in alkaline condition, where the oxide surface is negatively charged, which makes it more attractive to cations as shown in Eq. (9):

$$\equiv (\mathrm{Mn-Fe})\text{-}\mathrm{OH_{(s)}} + \mathrm{Me^{2+}_{(aq)}} \rightarrow \equiv (\mathrm{Mn-Fe}) - \mathrm{O\text{-}Me^{+}_{(s)}} + \mathrm{H^{+}_{(aq)}} \tag{8}$$

$$\equiv (\mathrm{Mn-Fe}) - \mathrm{OH_{(s)}} + \mathrm{Me^{2+}_{(aq)}} + \mathrm{H_2O_{(l)}} \rightarrow \equiv (\mathrm{Mn-Fe}) - \mathrm{O} - \mathrm{MeO^{-}_{(s)}} + 3\mathrm{H^{+}_{(aq)}} \tag{9}$$

where Me is denoted as divalent ions, Mn^{2+}, Fe^{2+}, Ca^{2+}, and Mg^{2+}.

Both Mn^{2+} and Fe^{2+} could be removed predominantly by oxidation, where adsorption or co-precipitation is the secondary removal mechanism.

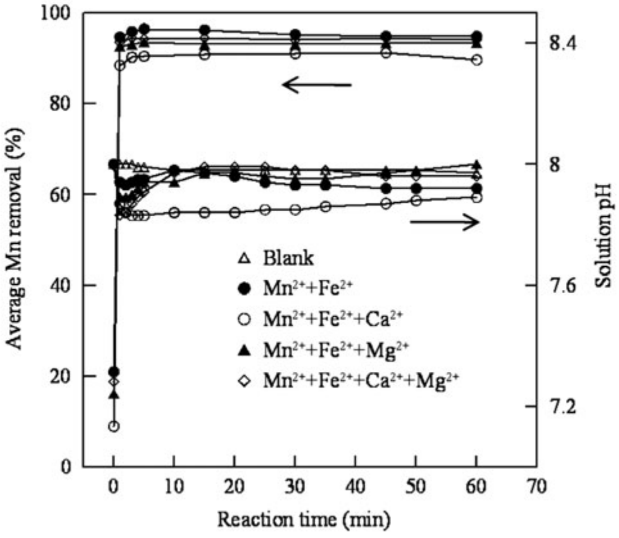


Fig. 8. Variations of average Mn removal (%) and solution pH in different compositions in uncontrolled pH; oxidant dose 0.603 mg/L; stirring speed 120 rpm.

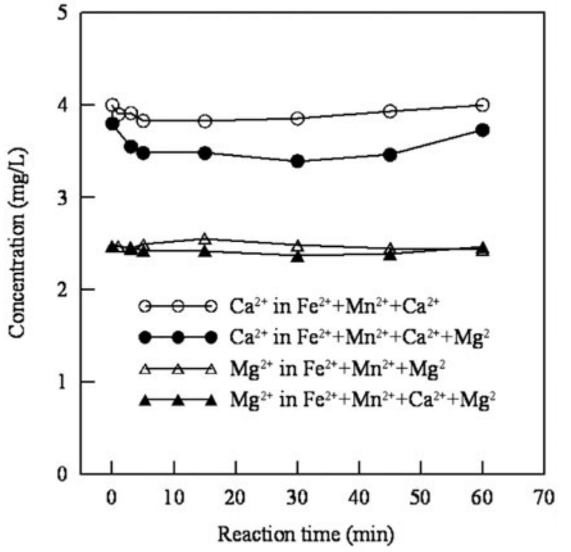


Fig. 9. Variations of Mg^{2+} and Ca^{2+} concentrations in different compositions in uncontrolled pH; oxidant dose 0.603 mg/L; stirring speed 120 rpm.

In the presence of co-ions like Ca^{2+} and Mg^{2+} ions (Fig. 8), the average Mn^{2+} removal has similar values in all the systems. However, the solution's pH was most basic in the absence of Ca^{2+} and Mg^{2+}. This indicates that either Ca^{2+} or Mg^{2+} could have exchanged places with H^+ attached on the Mn-Fe precipitate, releasing H^+ back into the solution. However, this did not affect the removal of Mn^{2+} and Fe^{2+} as their residual concentrations are still below the MCL (Fig. 8). The solution pH in the presence of Ca^{2+} was greatly reduced in comparison to that in the presence of Mg^{2+}. This implied that Ca^{2+} increased the surface charge of the precipitate more than Mg^{2+}, therefore inhibiting the removal efficiency of Mn^{2+}.

As illustrated in Figs. 8 and 9, the concentration of Ca^{2+} and Mg^{2+} as well as the solution pH decreased immediately upon the addition of $KMnO_4$. However, their concentration slightly increased within 1 h. These results validate the mechanism of adsorption or co-precipitation of Ca^{2+} and Mg^{2+} onto hydrous oxide in exchange with the bound H^+. However, Ca^{2+} and Mg^{2+} could be released back into the solution since they are weakly held by the oxygen groups of the oxide precipitate [18]. In addition, the result could be attributed to the reversible formation of $CaCO_3$ and $MgCO_3$ under these conditions.

In this study, the oxidation reaction using $KMnO_4$ is a major mechanism in the removal of Mn^{2+} and Fe^{2+}. However, the mechanism of adsorption or co-precipitation of metal ions like Ca^{2+} on the hydrous Mn-Fe oxide should be investigated further.

4. Conclusions

The dual removal of Mn^{2+} and Fe^{2+} from synthetic groundwater using pre-aeration and oxidation ($KMnO_4$) was investigated. The partial removal of Mn^{2+} using aeration was 30.6 and 37.2% for the single and dual metal systems, respectively. The minimum concentration of $KMnO_4$ was 0.603 mg/L, which can quickly oxidize Mn^{2+} below its MCL. The presence of Fe^{2+} improved the removal of Mn^{2+} due to the autocatalytic effect of iron oxide. Characterization using a digital microscope and EDX proved the formation of the hydrous Mn-Fe oxide. The presence of Ca^{2+} and Mg^{2+} as well as alum addition slightly inhibited the removal of Mn^{2+}. The possible removal mechanism of Mn^{2+} and Fe^{2+} are oxidation and adsorption onto the oxide precipitate.

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