Removal of manganese ions from artificial groundwater by oxidation using $KMnO_4$ and characterization of produced MnO_2 particles

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Annotation
The aim of this research is to investigate conditions for the removal of manganese ions from artificial groundwater by oxidation with $KMnO_4$ to keep their concentration below the allowed levels (0.05 mg/L). The process includes low-level aeration and $KMnO_4$ combination in a Jar test system. The manganese oxide (MnO_2) particles produced from oxidation were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The particles were in amorphous phase and were active adsorption sites for the removal of manganese ions. Parameters in the oxidation were solution pH, oxidant dosage, and stirring speed. The optimum solution pH was 8.0 which gave a complete Mn removal within 15 min. An increase of stirring speed diminished the rate of oxygen transfer and the proper speed was 120 rpm. Conversely, the adsorption activity of the particles at pH 9.0 complemented the oxidation of manganese ions exhibiting analogous effect with less consumption of $KMnO_4$ than the required theoretical amount to complete the reaction.

Keywords
Manganese removal, MnO_2 particle, Adsorption behavior, Groundwater,

INTRODUCTION

Soluble manganese ions in divalent form (Mn^{2+}) are found in groundwater particularly in deeper wells where the groundwater sparsely contains or no oxygen and in the areas where the groundwater flows through soil reach organic matters [1]. Mn^{2+} can be changed to an oxidized form whenever it exposes to oxygen. The problems of these ions in groundwater are global and many countries are aware of the issues [2]. The European Commission (98/83/1998) recommends an upper limit of 0.05 mg/L for manganese in drinking water. Although ingestion of manganese ions at the concentration above 0.5 mg/L has no harmful effects on human health [3], its presence in drinking water at concentrations above 0.1 mg/L is undesirable to customers. The excess amount of manganese ions in groundwater may become serious impact whenever they are vulnerable to air or oxygenic substances. The precipitation can stain household utensils and clothes and may impart a metallic, bitter, astringent or medicinal taste to the water.

Several treatment methods are employed for heavy metal removal from contaminated groundwater including physical and chemical treatment processes (e.g. coagulation, flocculation, membrane system, filtration, sorption, and ion-exchange). Those methods have high operating cost, or are not effective in the heavy metal removal, especially for groundwater polluted at low concentration. Chemical oxidation technology is a common treatment method for such water. It is a nonselective treatment and effective in treating wastes contaminated with halogenated and non-halogenated volatile, volatile and nonvolatile metals [4]. In this work $KMnO_4$ is used as an oxidant for manganese ions.

The oxidation of manganese (II) by $KMnO_4$ can be further enhanced by the formation of hydrous manganese dioxide flocs (MnO_2) which act as catalyst for further oxidation [5] and also could be preferably cation exchanger for multivalent cations such as Mn^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+} [6]. Those hydrous oxide could exchange the cations with H^+ ions on the particle surface, thus, increasing the overall adsorption capacities of Mn^{2+} and Zn^{2+} and higher than those of Ca^{2+}, Mg^{2+}. According to their high specific surface area (290 m^3/g) [7], a large amount of hydrous oxides of manganese can be strongly adsorbed in the interface. As a result, less amount of $KMnO_4$ is needed to complete the oxidation reaction than is theoretically required [8]. Besides, MnO_2 has been shown to be a relatively strong oxidants in the environment to remove high level of heavy metals such as Pb, Ni, Zn, Cd [9-11], however, there is scarce information concentrating on surface morphology of active particle like MnO_2 produced during in situ oxidation for manganese adsorption.

The purpose of this lab-scale experiment was to investigate the efficiency of manganese removals from artificial groundwater by in situ oxidation with $KMnO_4$ to determine appropriate conditions to decrease the manganese concentration below the maximum contaminant level (MCL). Therefore, artificial groundwater was prepared to obtain similar contamination to natural groundwater in Taiwan. Manganese levels were similarly adjusted to 0.5 mg/L. Moreover, analytical measurements were essential to confirm the actual compositions in artificial groundwater. Studied parameters included solution pH, oxidant dose, and stirring speed for metal removals. Active particles of precipitated MnO_2 were scrutinized to understand the adsorption behavior. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and particle size analyzer were used to determine the morphology, cystallinity and particle size of the oxide particles. An oxidation reduction potential (ORP) was also determined.

MATERIALS AND METHODS

Deionized water with 18.9 MΩ resistivity was produced by Ruda Ultrapure Water system, and used for the preparation of all samples, standards and feed waters. The stock solution containing 1000 mg/L of Mn(II) in water was prepared from manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, Merck, Germany). 0.5 mg/L sodium bicarbonate solution ($NaHCO_3$, Merck, Germany) was prepared and used to adjust alkalinity value. 1000 mg/L potassium permanganate ($KMnO_4$, J. T. Baker, USA) solution was prepared as a strong oxidizing agent. The desired solution pH was adjusted by using 0.1 M of hydrochloric acid (HCl 37%, Merck, Germany) and sodium hydroxide (NaOH, Merck, Germany). The following salts were used: sodium sulfate (Na_2SO_4, Merck, Germany), sodium chloride (NaCl, Taiyen Biotech, Taiwan) and potassium chloride (KCl, Merck, Germany) to regulate salinity of solution. A concentrated nitric acid (HNO_3, Merck, Germany) was also applied to dissolve any manganese oxide suspension before ICP analysis.

Batch experiment tests were performed using a standard Jar test system equipped with six mixing paddles, timer and automatic regulator of mixing paddles. Six prismatic beakers with squared cross section (L x W x H, 11.5 cm x 11.5 cm x 21.0 cm) were utilized. The volume of each sample solution was adjusted to 2L, and aerated by air pump (Elite 802, China) for 20 min in order to determine the partial oxidation of Mn^{2+}. This procedure was carried out to minimize the consumption of $KMnO_4$ which is somewhat an expensive oxidant when it is used continuously with a large flow [12]. After that the solution pH was controlled to an acceptable range (± 0.1 pH unit) and air bubble was continuously fed throughout the reaction. Subsequently, the stock solution of $KMnO_4$ was introduced to the mixed solution. The reaction was investigated entirely for 1 hr and sampling was done every 15 min. The quantity of the oxidant depends upon the amount of Mn^{2+} in the solution. The detail of oxidant applied for each parameter would be explained for each section.

ANALYTICAL METHODS

Residual manganese concentration was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, ICP-OES Perkin Elmer DV 2000). The particles were separated from the solution by 0.45 μm membrane filtration and concentrate HNO_3 was added to ensure the solubility of all manganese particles. A blank solution, without manganese was also prepared from the artificial groundwater. The morphology and elemental analysis of the oxide were analyzed by scanning electron microscope (SEM, Hitashi S-4800) and energy dispersive X-ray analysis (EDX, Horiba Emax 400), respectively. The particle size analyzer (N5 Submicron particle size analyzer, Beckman Coulter) was applied for particle size measurement. The X-ray diffraction (XRD) patterns were recorded on a Bruker D5005 using Cu Kα radiation. An oxidation reduction potential (ORP) was monitored using ORP meter (ORP 5041, Rocker).

RESULTS AND DISCUSSION

1. Effect of pH

The solution pH plays a key role for the oxidation reaction since it influences directly to the formation of manganese dioxide particles. The results from aeration at different pH are shown in Figure 1a. Concentration of Mn^{2+} ions below the secondary MCL (0.05 mg/L) could not be achieved under these experimental conditions unless the pH was raised above 7.0. Even though ORP value was as high as 400-600 mV at low pH, manganese ions still can not be removed. The decrease in the residual manganese levels clearly shows that the enhance oxidation of manganese and increased formation of manganese dioxide particles occurred with the increasing of solution pH according to the oxygenation rate dependence of Mn^{2+} as a function of pH. The oxidation rate of Mn^{2+} is somewhat low for pH values less than 9.0. However, manganese typically required chemical oxidation and in the absence of a strong oxidant it is not able to diminish remaining manganese concentrations to trace levels with aeration only. Nevertheless, too high pH adjustments (near 10) lead to high filtration resistance. Therefore, we chose the solution pH of 8.0 as the minimum pH throughout this study.
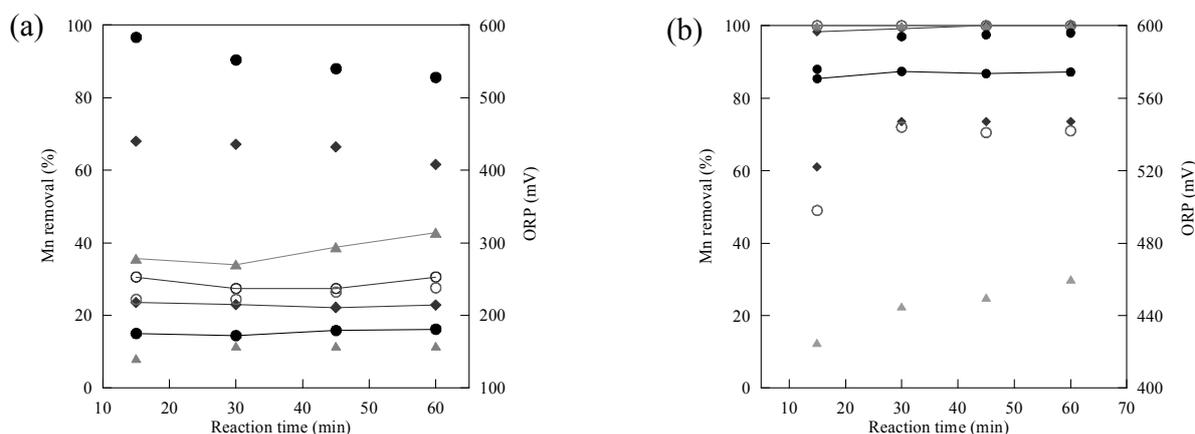

Figure 1 Removal efficiency of manganese over time; (a) aeration, (b) KMnO₄, KMnO₄ dosage = 1.0 mg/L, stirring speed = 120 rpm; (●) pH 6.0, (♦) pH 7.0, (○) pH 8.0, (▲) pH 9.0; Scatter = ORP.

When KMnO₄ was added to enhance the removal efficiency of manganese ions in artificial groundwater, the results are shown in Figure 1b. Residual manganese levels at solution pH higher than 6.0 was well below secondary MCL within 15 min. At pH of 6.0, manganese removal was persistently

limited at 85%. It was not efficiently oxidized even through the contact time was extended to 1 hr. At neutral pH manganese can be removed almost 100%. Besides, when considering to ORP value it can be noticed that manganese removal requires theoretically ORP value higher than 400 mV. This is consistent with results reported by Mouchet [13] that the redox potential increase the oxidation and manganese oxidation requires appropriately controlled conditions than iron with ORP in the range of 300-500 mV [14].
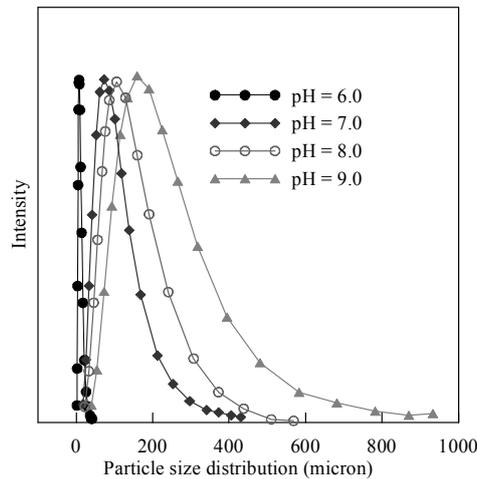

Figure 2 Particle size distribution at different solution pH; KMnO$_4$ dosage = 1.0 mg/L, stirring speed = 120 rpm; (●) pH 6.0, (♦) pH 7.0, (○) pH 8.0, (▲) pH 9.0.

The evaluation of the particle size distribution after oxidation is shown in Figure 2. This result indicated that when the pH of the solution increase from 6.0 to 9.0, mean particle sizes increased from 1.0 to 500 μm. Manganese particle sizes increased with enhancing the solution pH and can be separated using 0.45 μm filters.

2. Effect of oxidant dose

The result of manganese removal by different concentration of KMnO$_4$ is shown in Figure 3a. To investigate the influence of oxidant dosages, the different concentrations of KMnO$_4$ were used including 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L for half, equal to and above stoichiometric values, respectively. The study was primarily conducted at a basic pH (8.0) with different oxidant doses as well as oxidation time. The manganese removal was not satisfied when KMnO$_4$ dosage was half of the stoichiometric value possibly owing to the curtailed oxidation of manganese. The amount of KMnO$_4$ may not be sufficient for decreasing manganese concentration below MCL. However, manganese removal increased quickly with the stoichiometric value at 1.0 mg/L KMnO$_4$ and reached 100% within 15 min. In contrast, when the concentration of KMnO$_4$ was overdosed (2.0 mg/L), manganese removal was gradually improved from 85% to 100% at 15 min to 1 hr.

Besides, the residual manganese concentrations increased with KMnO$_4$ dose at pH 9.0 as seen in Figure 3b. The concentration of 2.0 mg/L was very high for the removal of 1.0 mg/L manganese. The KMnO$_4$ addition actually increased the residual manganese levels. The actual amount of KMnO$_4$ used for the oxidation is less than the dosage calculated probably due to the adsorption influence of MnO$_2$ on the reaction.
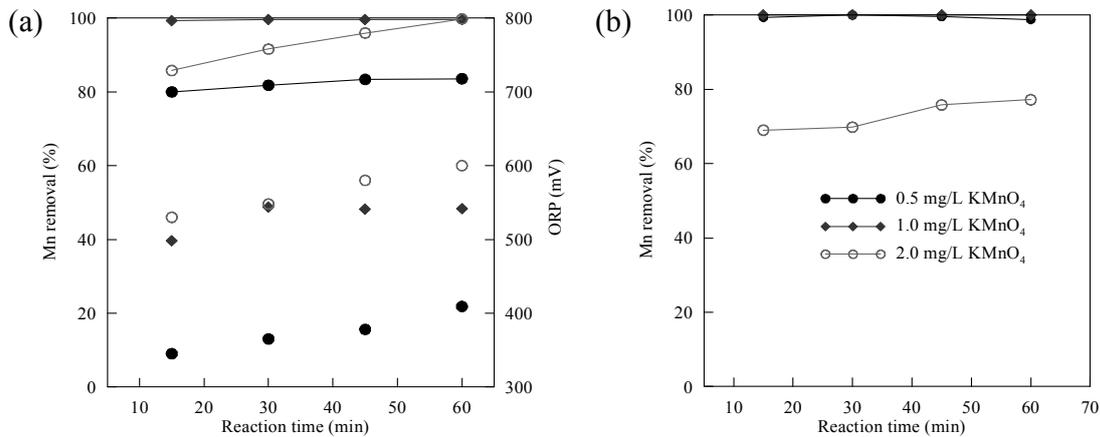
Figure 3 Removal efficiency of manganese over time at different KMnO₄ dosages;
(a) pH = 8.0, (b) pH = 9.0; stirring speed = 120 rpm; (●) 0.5 mg/L KMnO₄,
(♦) 1.0 mg/L KMnO₄, (○) 2.0 mg/L KMnO₄; Scatter = ORP.

3. Effect of stirring speed

The effect of stirring speed in the oxidation of manganese ions could be related to the transfer of the oxygen atoms and hydroxyl radicals of KMnO₄ to the inorganic compounds. As seen in Figure 4, the higher removal efficiency was observed at low stirring speed between 50 to 120 rpm, reaching 100% within 15 min. ORP ranges between 400-600 mV. The manganese efficiency was consistently removed at 80% at the entire of reaction time when the stirring speed was raised to 200 rpm. The growth of MnO₂ particles was also a key role and related to the diffusion rate of manganese ions to the MnO₂ particles. Not all the Mn^{2+} ions were converted to MnO₂ but some adsorbed on MnO₂ particles. The increases of stirring speed disturbed the formation of MnO₂ particles, and subsequently decelerated to the adsorption process because the MnO₂ particles formed during the oxidation could serve as adsorption sites for Mn^{2+} [15]. The sorption also increased the conversion of Mn^{2+} to MnO₂.
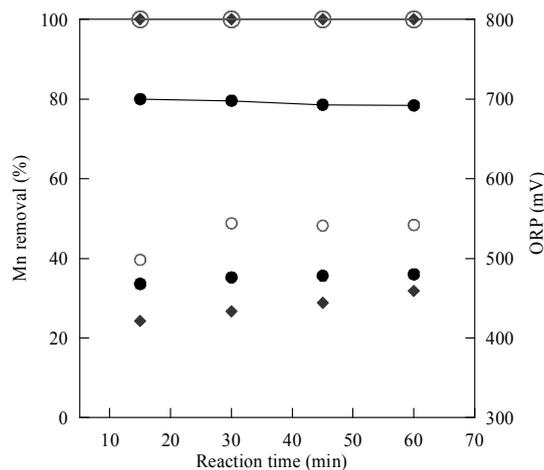

Figure 4 Removal efficiency of manganese over time at different stirring speeds; pH = 8.0;
1.0 mg/L KMnO₄; stirring speed ; (○) 50 rpm, (♦) 120 rpm, (●) 200 rpm; Scatter = ORP.

4. Characterization of precipitated particles

The SEM-EDX results of the membrane filter used to study the morphology of precipitated particles are shown in Figure 5. There are many clusters of particles on the filter surface. The small particles were loosely aggregated on filter plane, which led to a rough surface and the presence of porous structure. The composition of manganese oxide was observed which was crucial for sorption of Mn^{2+} ions.

The powder XRD patterns of the products are shown in Figure 6. The spectrum inluded broad peaks appeared at 2θ = 12.4, 24.8, and 36.3° that were attributed to layered manganese dioxide (δ-MnO_2). These broad diffraction peaks indicated amorphous phase of precipitated MnO_2 existed mainly in amorphous form, which may be responsible for the high surface area.
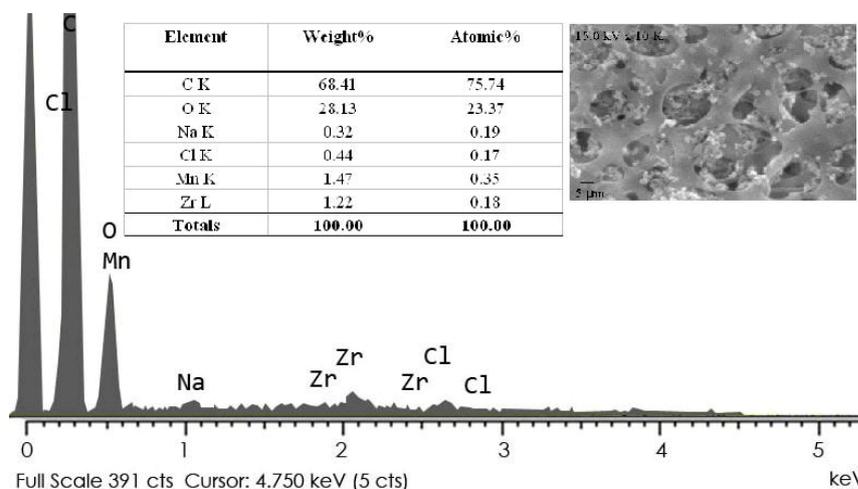

Element	Weight%	Atomic%
C K	68.41	75.74
O K	28.13	23.37
Na K	0.32	0.19
Cl K	0.44	0.17
Mn K	1.47	0.35
Zr L	1.22	0.13
Totals	100.00	100.00

Full Scale 391 cts Cursor: 4.750 keV (5 cts)

Figure 5 SEM-EDX images of the filtered oxide on filter surface; pH = 8.0, stirring speed = 120 rpm; 1.0 mg/L KMnO₄.
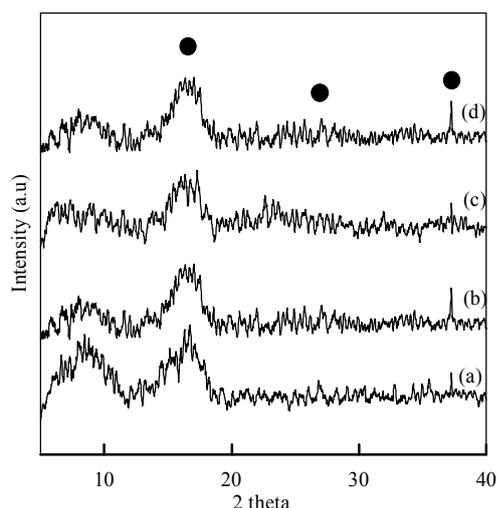

Figure 6 Powder XRD patterns of the filtered oxide on filter surface at different solution pH (a) pH 6.0, (b) pH 7.0, (c) pH 8.0 (c) pH 9.0; stirring speed = 120 rpm; 1.0 mg/L KMnO₄. ● = δ-MnO₂.

CONCLUSIONS

The study investigated the conditions on the removal of Mn^{2+} from artificial groundwater via oxidation using $KMnO_4$ as a strong oxidant. The results revealed that the solution pH, oxidant dose and stirring speed were the important parameters. The solution pH of 8.0 and stirring speed of 120 rpm were the optimum condition that decreased the concentration of Mn^{2+} to the value below acceptable level with the oxidant dosage of 1.0 mg/L. The main composition of the precipitated particles was manganese oxide which was crucial particle for other ions sorption. The active sorption on MnO_2 particles took place at the solution pH of 9.0 using $KMnO_4$ less than the theoretical amount. However, the oxidation at high pH (9.0) would be affected adversely to filtration process. The increase of stirring speed diminished the rate of oxygen transfer and the proper speed was 120 rpm.

ACKNOWLEDGMENTS

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