Catalytic assistance of ultrasound for manganese removal by waste oyster shells

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A R T I C L E  I N F O

Article history:
Received 30 April 2012
Received in revised form 25 September 2012
Accepted 25 October 2012
Available online

Keywords:
Manganese
Ultrasound
Waste oyster shell
Kinetics
Mechanism

A B S T R A C T

The catalytic assistance of ultrasound (designated as US) for the removal of Mn(II) by oyster shells (designated as OS) was investigated with respect to major parameters such as pH, initial Mn(II) concentration, and US power density. The kinetic data of Mn(II) removal by the combination of oyster shells and ultrasound (OS/US) was fitted by the first-order kinetic model. Results show that the rate constant of the OS/US system was in the range 3.1 – 54.3 × 10−2 min−1, which is about 130 times higher than that of the homogeneous oxidation of Mn(II) by O2, and was about two times higher than that of commercial surrogate materials (CaO and CaCO3) associated with US under the same operational condition. The US power densities for the OS/US system and the log-scale of the first-order rate constants showed a linear positive correlation with a slope of 0.042. X-ray diffraction, and Fourier transform infrared analyses revealed that the dissolved Mn(II) was oxidized into MnO2 or MnO2, as well as precipitated in the form of MnCO3 by OS/US.

1. Introduction

Soluble manganese can often be detected at considerably higher concentrations in mine drainage water than in polluted streams and groundwater (Banks et al., 1997). Even though there exist uncertainties regarding the toxicity of manganese, recent research has shown that a high level of manganese is correlated with the toxicity of pore water in lake sediment (Boucher and Watzin, 1999; Doyle et al., 2003). The U.S Environmental Protection Agency has established guidelines to limit the concentration of manganese in the lake sediment (Boucher and Watzin, 1999; Kostka et al., 1995). Although manganese exists in a number of oxidation states, Mn(II) is the most stable species (Van Benschoten et al., 1992). In oxygenated water, Mn(III) and Mn(IV) are stable oxidation states and exist in scarcely soluble oxide and hydroxide solid phases such as MnO2 and MnO2(s). In the highly oxidizing and alkaline environment of the ocean, manganese is found predominantly in the form of particulate MnO2 (Stumm and Morgan, 1981). Although recent work by Kostka et al. (1995) suggested that there exist some soluble Mn(III) complexes in natural water, most Mn(III) complexes are present as metastable particulate oxides. The primary dissolved form of manganese is Mn(II). As a thermodynamic model representing the equilibrium forms of chemical species, the Eh-pH diagram of the Mn/oxygen/water system shows the solubilities and stabilities of manganese ions in response to oxidation (Bricker, 1965). Manganese is stable under reducing conditions, which are typical in mine drainage, up to pH 10. Raising the pH under reducing conditions converts manganese ions into their hydroxide form. The oxidation of manganese is very slow among the various reactions taking place in mine drainage. An important fact is that Mn(II) can not be converted directly into oxides in water without transforming it into hydroxide (Coughlin and Matsui, 1976; Hem, 1981). In fact, the rate of oxidation depends on the oxygen concentration and the square of the hydroxide concentration, implying that manganese hydroxide is an intermediate. Therefore, the formation of the hydroxide plays an important role in the creation of oxides.

With respect to autocatalysis, manganese removal is catalyzed by Mn(II) oxides (Kessick and Morgan, 1975; Coughlin and Matsui, 1976). The Mn/oxygen/water system shows the solubilities and stabilities of manganese ions in response to oxidation (Bricker, 1965). Manganese is stable under reducing conditions, which are typical in mine drainage, up to pH 10. Raising the pH under reducing conditions converts manganese ions into their hydroxide form. The oxidation of manganese is very slow among the various reactions taking place in mine drainage. An important fact is that Mn(II) can not be converted directly into oxides in water without transforming it into hydroxide (Coughlin and Matsui, 1976; Hem, 1981). In fact, the rate of oxidation depends on the oxygen concentration and the square of the hydroxide concentration, implying that manganese hydroxide is an intermediate. Therefore, the formation of the hydroxide plays an important role in the creation of oxides.
The rate of Mn(II) oxidation can be enhanced by recycling sludge that is produced from the oxidation of Mn(II). Owing to the acidic nature and low oxygen content of mine water, the resulting slow oxidation kinetics make the removal of Mn(II) a great challenge. In addition, because parallel reactions such as those involving organic matter and Fe(II) oxidation result in the excessive consumption of oxidants, the chemical oxidation of Mn(II) is kinetically slow (Katsoyiannis and Zouboulis, 2004). Therefore, iron needs to be removed prior to manganese oxidation (Bamforth et al., 2006). Currently, in the field of study of Mn(II) oxidation, homogeneous oxidation has been studied using ClO₂, O₃, O₂, and H₂SO₄ (Lawrance and Ward, 1983; Van Benschoten et al., 1992; Bamforth et al., 2006) whereas KMnO₄, hematite, goethite, and albite have been used to study its heterogeneous oxidation (Van Benschoten et al., 1992; Junta and Hochella, 1994). Carbonate-based media such as calcite (CaCO₃), dolomite [(CaMg)CO₃]₂, and limestone (CaCO₃) have also been used as materials for precipitating oxidized manganese products (Silva et al., 2010). The chemical composition of precipitated manganese material has been identified as phyllosilicates such as (MnCa)MnO₂·H₂O and (CaMn)MnO₂·3H₂O (Lind and Hem, 1993; Bilinski et al., 1996). Manganese-bearing carbonate minerals such as (MnCO₃) and (CaMn)CO₃ have been identified in mine water-impacted environments (Lind and Hem, 1993; Hem and Lind, 1994). In addition, a study on Mn(II) removal by a biological method was also reported (Hallberg and Johnson, 2005). Because the global cycling of manganese is affected by bacteria, microbial activity can play a major role in the oxidation of Mn(II). In the search for biological catalysts, the dominant mechanisms of Mn(II) oxidation in circumneutral freshwater (Nealson et al., 1988) and marine environments (Moffett, 1997) have been extensively documented.

Because US can be used to produce a strong oxidant, the hydroxyl radical (·OH) having a redox potential of 2.7 V, it has great potential for rapidly oxidizing manganese. Through reducing the energy barrier of oxidation (Rokhina et al., 2010), US could have a catalytic effect on the oxidation of Mn(II). In this study, waste oyster shells (designated as WOS), a waste material that is produced by oyster farms, was selected for use as an alkaline material for promoting the oxidation of Mn(II) in conjunction with US. Among the industries that are located by the sea, oyster farms produce massive volumes of WOS. Accordingly, a poor management of WOS can contaminate fish grounds, and cause trouble in terms of the maintenance of public seawater, resulting in the damage of seaside scenery. About 360,000 tons of WOS are produced yearly in South Korea and only 10% is recycled in the form of stabilizers. Considering these facts, the treatment and recycling of WOS should be promoted to protect the marine environment. As the main element, WOS has a high CaCO₃ content. Although CaCO₃ has a limited solubility product ($K_{sp}$ = 4.8 x 10⁻⁹), it could be used to precipitate or co-precipitate Mn(II) in the form of MnCO₃. However, when WOS is calcined, most of the CaCO₃ can be transformed into CaO. Accordingly, calcined WOS (CWOS) has the capacity to promote the oxidation of Mn(II) because it contains a high level of CaO, which can be completely dissolved in water and can raise the pH by releasing hydroxyl ions (OH⁻). In South Korea, the cost for obtaining CaO through calcining WOS is about $80 per ton, whereas the price of synthetic CaO is $75 per ton. In terms of recycling waste material, it is economically feasible to use WOS and CWOS (Ok et al., 2010).

Until now, with respect to the kinetics and mechanism, no study has been conducted in the field of heterogeneous oxidation of Mn(II) using WOS and the catalytic effects of US. The objectives of this study were (1) to investigate the removal kinetics of Mn(II) and the capacity of WOS assisted by US, and (2) to elucidate the mechanism of Mn(II) oxidative removal.

### 2. Experimental

#### 2.1. Materials and methods

All the chemicals employed in this study were of analytical grade and were used without further purification. Manganese chloride (MnCl₂·4H₂O, Sigma–Aldrich, purity > 98%) was used to make a stock solution of Mn(II). All the solutions were prepared using deionized water. A stock solution was prepared and diluted to the required initial concentration of Mn(II). The commercial surrogate materials (CM), calcium oxide (CaO), and calcium carbonate (CaCO₃) were purchased from Sigma–Aldrich. The purity of each chemical was greater than 99%.

##### 2.2. Reactor setup

A sonoreactor was made up of a 1 L capacity horn-type glass cup equipped with a horn-type ultrasonic transducer (Mira Ultrasonic MEGA-100). The applied frequency was 450 kHz and the maximum power (100 W) was provided by a single piezoelectric transducer (Tamura). The diameter of each transducer was 10 cm, and 500 mL of the solution was applied. The temperature of the solution was measured using a thermometer (Tecpel DTM-318) at several locations during US irradiation, and the ultrasonic power was varied using the calorimetric method:

**Calorimetric power (W) =** 

\[
mc_p(dT/dt)
\]

where $c_p$ is the heat capacity of the solvent (J kg⁻¹ K⁻¹), $m$ is the mass of the solvent (kg), and $dT$ is the temperature difference between the initial and final temperature after a specific time interval dt (s).

For the kinetic tests, 0.3 g of a mixture of CWOS (0.2 g) and WOS (0.1 g) was added to 0.5 L of the Mn(II) solution and then the Mn(II) concentration was measured over time. The operating temperature was 20 ± 2 °C. The first-order rate constant ($k_1$) was obtained by applying the following first-order kinetic model:

**Ln [Mn(II)₀/Mn(II)ₜ] = k₁t**

Here, Mn(II)₀ and Mn(II)ₜ are the concentration of manganese at the initial time and time t, and $k_1$ is the first-order rate constant.

The power density was calculated using the following equation, in which the calorimetric power and liquid volume were applied.

**Power density = $P_c/V_L$**

Here, $P_c$ and $V_L$ are the calorimetric power and the liquid volume, respectively.

#### 2.3. Analysis

Spectroscopic analyses were conducted to characterize the surface involved with and the precipitates formed as a result of oxidation. The elemental compositions of the WOS and CWOS were determined using an XRF spectrometer (XRF-1700, Shimadzu). Using a PANalytical XRD instrument (X'Pert PRO MPD) with a CuKα radiation at a scan speed of 2.5° min⁻¹ in the 10–90° range of 2θ, the XRD analyses were conducted for the freeze-dried powdered samples selected. Phase identification was also carried out by means of the X'Pert accompanying software program High Score Plus and the reference intensity ratio method ICDD PDF-4+ database. The FT-IR absorption spectra of the samples in the spectral range 400–4000 cm⁻¹ were also obtained with an FT-IR spectrometer (FT-IR 6200, JASCO). The IR absorption measurements were carried out using the KBr pellet technique. To obtain good
quality spectra, the samples were crushed in an agate mortar, and microsize particles were obtained. The Mn(II) concentrations were measured using an inductively coupled plasma atomic emission spectrometer (5300DV ICP-AES, Perkin-Elmer). The minimum detection limit of ICP-AES for manganese ions was 0.005 mg L\(^{-1}\). The redox potentials were measured using an ORP meter (Model D52, Horiba) coupled with a reference electrode.

3. Results and discussion

3.1. Characterization of waste and calcined oyster shells

In this study, a mixture of WOS and CWOS was used for the heterogeneous oxidation and precipitation for Mn(II) removal. As shown in the XRD results, the main compounds for the WOS and CWOS were CaCO\(_3\) and CaO, respectively (Supplementary Material, Fig. 1). The XRF analysis also showed that the weight percentages of calcium oxide were 87.7% and 88.1% for the CWOS and WOS, respectively (Supplementary Material, Table 1). Except for the difference in the species of calcium oxide, the quantities of other elements were similar to both of these materials.

3.2. Kinetics of Mn(II) removal

Fig. 1(A) and (B) shows the variation in pH and potential over time, respectively, during Mn(II) removal using a mixture of WOS and CWOS. During the kinetics, US (power density: 17.1 W L\(^{-1}\)) was applied to the suspension. The applied concentration and the ratio of CWOS to WOS were 0.15 g L\(^{-1}\) and 2:1, respectively. At 51 mg L\(^{-1}\) Mn(II), the pH increased from 6.17 to 11.57 within 10 min and then reached equilibrium. In contrast, as the pH increased, the potential decreased from 286 mV to -5 mV within 20 min prior to reaching equilibrium. When Mn(II) was added up to 95 mg L\(^{-1}\), the pH slowly increased from 5.91 and reached 10.87 at 60 min, whereas the potential declined from 253 mV to 18 mV at 40 min. For 189 mg L\(^{-1}\) Mn(II), the pH increased from 6.11 to 8.13 at 10 min before reaching equilibrium and the potential decreased from 249 mV to 162 mV within 20 min. In another trial, a mixture of CaO and CaCO\(_3\) (CaO:CaCO\(_3\) = 2:1, 0.15 g L\(^{-1}\)) was applied to 0.5 L of solution containing 98 mg L\(^{-1}\) Mn(II). The initial pH was 6.41 and increased to 11.52 at 40 min, whereas the potential decreased from 272 mV to -48 mV at 20 min. Accordingly, as the pH increased during the oxidation reaction, the potential simultaneously decreased owing to the reduction of dissolved oxygen. With a higher Mn(II) concentration, the potential decreased even more. To summarize, Mn(II) removal can be promoted by raising the pH as the main components of OS (CaO and CaCO\(_3\)) are dissolved out. In this study, along with OH\(^{-}\) released by the alkaline materials, OH produced by US (Eqs. (4) and (5)) can be used to further promote the hydrolysis of Mn(II) through the reaction shown in Eq. (6). Here, "\(\bullet\)" is used to denote US.

\[
\text{H}_2\text{O(\text{US})} = \text{OH}^- + \bullet\text{H} \tag{4}
\]

\[
2\text{H}_2\text{O(\text{US})} = 2\text{OH}^- + \text{H}_2 \tag{5}
\]

\[
\text{Mn}^{2+} + \text{OH}^- + \text{OH}^- \rightarrow \text{Mn(OH)}_2^{2(aq)} \tag{6}
\]
The oxidation of Mn(OH)_2 formed can be achieved by homogeneous and heterogeneous processes (Eqs. (7) and (8)) (Morgan, 2001; Rivas et al., 2001).

4Mn(OH)_2 + O_2 + 4H^+ → 4Mn(III)(OH)_2^+ + 2H_2O (homogeneous)  

4[Mn(II)•MOH] + O_2 + 4 H^+ → 4[Mn(III)•MOH] + 2H_2O (heterogeneous)  

Here, [MOH] represents a multivalent oxide surface site. Compared to homogeneous oxidation, however, oxidation and precipitation by heterogeneous oxidation can occur more quickly owing to the heterogeneous reactivity of mineral surfaces. As shown in other references (Table 1), the first-order rate constants of heterogeneous oxidation by TiO_2 or Fe_2O_4 (0.02–2 min^-1) are much higher than those for homogeneous oxidation by O_2 or O_3 (1.67 × 10^6 to 4.2 × 10^-3 min^-1). In the case of homogeneous oxidation by O_2, Diem and Stumm (1984) showed that various species of soluble manganese (total of 1 mg L^-1) were not fully oxidized at pH 8.4 for several years even in the presence of dissolved O_2. In our study, at the US frequency of 450 kHz and power density of 17.1 W L^-1, heterogeneous oxidation using a mixture of OS (WOS:CWOS = 2:1, 0.15 g OS L^-1) had a first-order rate constant (k_1) of 0.545, 0.222, and 0.031 min^-1 at the initial Mn(II) concentrations of 51, 95, and 189 mg L^-1, respectively. Accordingly, it can be deduced that the pH had a significant effect on the first-order rate constants, compared to the initial concentration of Mn(II). The removal of Mn(II) was completed within 30 min for all cases except for the case when the initial concentration was 189 mg L^-1. The removal capacity of Mn(II) for OS was found to be 228 mg g^-1 at 60 min of operation. When only OS was applied without US, the first-order rate constant was 0.085 min^-1. Therefore, the removal rate of OS/US was about 2.6 times higher than that of the system without US. The Mn(II) removal rate might be strongly linked with the pH and the physical effects of US such as microjets (100 ms^-1) and microstreaming, which might increase the dissolution rate of CaCO_3 or CaO in OS.

At 98 mg L^-1 Mn(II), the CM/US (CaO:CaCO_3 = 2:1, 0.15 g CM L^-1) had a first-order rate constant of 0.116 min^-1 (R^2: 0.983). Although the increase in pH of the OS/US system was less than that of the CM/US system at a similar initial concentration of Mn(II), the oxidation rate of OS/US was two times higher than that of CM/US. When the values of pH and Eh obtained at equilibrium in the kinetic study were substituted into the Eh-pH diagram, it was found that Mn(II) was oxidized to become Mn_3O_4 or MnOOH in heterogeneous oxidation systems such as those for OS/US and CM/US (Fig. 1(D)). Interestingly, the oxidation number of manganese species at the equilibrium resulting from the kinetics by CM/US was lower than those by OS/US, of which all data were located at the border of MnOOH and Mn_3O_4.

3.3. Kinetics of Mn(II) removal by different US power densities

The power density needed for the application of US should be optimized to reduce energy costs and find the appropriate treatment capacity because it can be controlled by the applied power and volume of the reaction system. A plot of the first-order rate constant according to the power density was constructed using the results of kinetics (Fig. 2). For this testing, both CWOS and WOS were applied at a ratio of 2:1 and at a fixed concentration was 0.15 g L^-1. To compare the results with those for OS, a mixture of CaO and CaCO_3 (CaO:CaCO_3 = 2:1, 0.15 g L^-1) was applied at a power density of 34.23 W L^-1.

As the power density in the OS/US system increased from 0 to 34.23 W L^-1, the first-order rate constant linearly increased from

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Kinetic comparison of Mn(II) removal by homogeneous and heterogeneous oxidation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Manganese (mg L^-1)</td>
</tr>
<tr>
<td>O_2</td>
<td>0.412</td>
</tr>
<tr>
<td>O_2</td>
<td>—</td>
</tr>
<tr>
<td>O_2</td>
<td>88</td>
</tr>
<tr>
<td>137.5</td>
<td>8.95</td>
</tr>
<tr>
<td>9.25</td>
<td>25</td>
</tr>
<tr>
<td>TiO_2</td>
<td>190</td>
</tr>
<tr>
<td>Fe_2O_4</td>
<td>190</td>
</tr>
<tr>
<td>OS/US</td>
<td>51</td>
</tr>
<tr>
<td>95</td>
<td>10.87</td>
</tr>
<tr>
<td>189</td>
<td>8.13</td>
</tr>
<tr>
<td>CM/US</td>
<td>98</td>
</tr>
<tr>
<td>95</td>
<td>9.25</td>
</tr>
</tbody>
</table>

OS (CWOS:WOS = 2:1, 0.15 g OS L^-1); CM (CaO:CaCO_3 = 2:1, 0.15 g CM L^-1).

Fig. 2. Effect of US power density on kinetics of Mn(II). (A) Mn(II) concentration and (B) ln(k_1) vs. power density. Experimental conditions: frequency of 450 kHz, CWOS:WOS = 2:1 (0.15 g OS L^-1), 104.3 ± 3.5 mg L^-1 of initial Mn(II), temperature of 20 ± 2 °C, and reaction time of 60 min.
0.085 to 0.37 min⁻¹. For the CM/US system at a power density of 34.23 W L⁻¹, the first-order rate constant was 0.24 min⁻¹. Therefore, as shown in the previous results, the treatment using OS had a higher rate constant than that using CM. With the same power density (17.1 W L⁻¹) and Mn(II) concentration (95 mg L⁻¹), the first-order rate constant (0.22 min⁻¹) obtained in the second experiment was similar to that obtained for the previous test (0.27 min⁻¹). This result represents a good reliability in kinetic experiments.

The following mathematical equation was obtained to express the correlation between the first-order rate constant and the power density.

\[
\ln(k_1) = 0.042(P_c/V_L) - 2.49
\]

where \(P_c\) is the calorimetric power (W), \(V_L\) is the solution volume (L), and \(P_c/V_L\) is the calorimetric power density in W L⁻¹ (power density range: 0–40 W L⁻¹).

Owing to the high determination coefficient \(R^2: 0.968\), it can be inferred that the applied power density was well-correlated with the kinetics of the Mn(II) removal. This was because of the intensification of the violent collapse of microbubbles caused by increasing the acoustic pressure, which was accomplished by increasing the applied power (Sirotyuk, 1961).

3.4. Mechanism

Fig. 3 shows the XRD pattern of the dried solid obtained from the OS/US test that was conducted under the following experimental conditions: frequency of 450 kHz, CWOS:WOS = 2:1 (0.15 g OS L⁻¹, 95 mg L⁻¹ of initial Mn(II)), temperature of 20 ± 2 °C, and reaction time of 60 min. At the plane (104) of CaCO₃, a strong peak is present at 29.4° (Kim et al., 2010). Without the crystalline phase of CaO, several peaks of calcite were also shown at various 2θ values. From this, it can be deduced that CaCO₃ was the only chemical that remained owing to its limited solubility. The peaks at 31.4° and 51.7° were identified as the planes (104) and (116) of the MnCO₃ reflection (Zhu et al., 2005). However, only the highest peak at 31.4° was shown. The peak shown at 32.9° was also identified as the planes of Mn₂O₃ (222) (Zhu et al., 2005).

Fig. 4 shows the results of FT-IR analysis for the same media that was analyzed in the XRD tests. Characteristic absorption bands ascribed to CaCO₃ and CaO were observed over the range 711.6–712.4 cm⁻¹ in all samples, irrespective of the presence of manganese. Mn₂O₃ presents as bands in the range 665.3–667.2 cm⁻¹, whereas MnCO₃ has an absorption band over the range 724.9–725.1 cm⁻¹. The absorption band over the range 1031.7–1042.8 cm⁻¹ is attributed to the presence of hydrogen bonding and/or MnO₂ stretching modes. The FT-IR spectrum peaks at 662 and 1032 cm⁻¹ are characteristic peaks of MnO₂, whereas the peaks at 660 and 724 cm⁻¹ are attributed to the phase γ-MnO₂ (Van Benschoten et al., 1992; Morgan, 2001) and to MnCO₃ (Junta and Hochella, 1994), respectively.

As deduced from the XRD and FT-IR results, Mn(II) was mainly oxidized into MnO₂ or Mn₂O₃ and partly precipitated as MnCO₃ by the reaction with carbonate ions dissolved from OS. The balanced half reaction for the Mn(II) precipitation is as follows:

\[
\text{Mn}^{2+} + \text{HCO}_3^- \rightarrow \text{MnCO}_3 + \text{H}^+ 
\]  

4. Conclusions

In this study, the catalytic effect of ultrasound on the heterogeneous oxidation of Mn(II) by waste oyster shells were studied. Through kinetic studies on Mn(II) removal, we found that the first-order rate constants of the OS/US system were in the range of 3.1–54.5 × 10⁻² min⁻¹, which were much higher than the homogeneous oxidation rates for O₂. Under the same operational conditions, the OS/US system had about a two times higher Mn(II) removal rate than that of the CM/US system. The first-order rate constants increased logarithmically as the US power density increased, representing the catalytic effect of US on the Mn(II) removal. Spectroscopic analyses such as XRD and FT-IR revealed that the dissolved Mn(II) was oxidized into MnO₂ or Mn₂O₃, and that it was also partly precipitated as a form of MnCO₃. As an alkaline material, OS can be effective and economically used to remove Mn(II) in acid mine drainage (AMD). Based on the results of kinetics according to the power density of US, the physico-chemical
catalytic effects of US enhance the rates of Mn(II) removal by OS. If OS is not wasted and instead recycled, we can not only protect the marine environment but also achieve the environmentally-friendly application of a waste to water treatment.

Acknowledgment

This work was supported by the Basic Science Research Program through a National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (KRF-2009-0092799) and supported by a Korea University Grant.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2012.10.033.

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