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Removal of Mn(II) from Aqueous Solutions Using Manganese-Coated Sand Samples

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Two different manganese-coated samples, that is, manganese-coated sand (MCS1) (laboratory preparation) and a Birm sample (Birm, a commercial product; MCS2), were employed to assess their removal efficiencies for Mn(II) from aqueous solutions over a wide pH range (i.e., pH 5.0 to 10.5). The study was performed in both the absence and presence of sodium hypochlorite. The pH dependence data obtained through batch tests showed that the removal of Mn(II) by these solids significantly increased with increasing solution pH from 5.0 to 10.0. Moreover, the removal efficiency was more favored in the presence of sodium hypochlorite (4.0 $\text{mg}\cdot\text{L}^{-1}$). This suggested that the presence of NaClO caused the oxidation of Mn(II) to Mn(IV); hence, the formation of MnO_2 at the surface of the manganese-coated samples further enhanced the removal efficiency of the solids. Moreover, the removal of Mn(II) was also performed under dynamic conditions in column experiments. The data from the column experiments also showed that the presence of NaClO significantly enhanced the removal capacity of MCS1, that is, from (10.93 to 20.21) $\text{mg}\cdot\text{g}^{-1}$, but only slightly increased that for MCS2, that is, from (59.34 to 65.44) $\text{mg}\cdot\text{g}^{-1}$ in the absence and presence of sodium hypochlorite, respectively.

Introduction

Manganese occurs in natural waters in both its most reduced and soluble form, the manganese(II) ion, and the oxidized form, MnO_2 (pyrolusite). If not oxidized, Mn(II) ions can easily pass through water treatment processes, and once they are within the distribution system, they can gradually oxidize to insoluble manganese dioxide, causing several problems, such as water discoloration, a metallic taste, odor, turbidity, biofouling, and corrosion as well as staining of laundry and plumbing fixtures.[1] Moreover, acid mine drainage (AMD) from abandoned mines is a natural source of manganese contamination of water bodies. The cessation of pumping following the closure of many underground mines has been reported to result in a rebound of the groundwater table. Leachates emanating from old mines often contain higher concentrations of dissolved metals (Fe, Mn, Al, and Zn) and SO_4^{2-}, which could also contain high acidity.[2−4] In addition, manganese enters our aquatic environment via a variety of applications, namely, ceramics, dry battery cells, electrical coils, manganese-containing alloys, and so on.[5] Burning of coal and oil is also a major source of manganese contamination.[6] The concentration of manganese in raw water has been found to be higher than the standards for drinking water in at least two multiregional water treatment plants (WTPs), on the basis of a survey of 31 such WTPs in Korea.[7] The levels of manganese in groundwater due to natural leaching processes have been reported to vary widely depending on the types of rock and minerals present at the water table. Typically, Mn concentrations from natural processes are low but can range up to 1.50 $\text{mg}\cdot\text{L}^{-1}$ or higher.[8]

Although manganese has been reported to be an essential trace ion, the enhanced intake of manganese causes several adverse effects in human beings, such as problems in the respiratory tract and brain. Symptoms of manganese poisoning include hallucinations, forgetfulness, and nerve damage.[9] Similarly, a high intake of manganese caused manganese psychosis, an irreversible neurological disorder characterized by uncontrollable laughter, sexual excitement, and impotence,[10] and may also cause manganese pneumonia.[5] Therefore, the current U.K. and U.S. legislation for soluble manganese states that fresh water should have $< 30\ \mu\text{g}\cdot\text{L}^{-1}$ (EQS) and $< 0.05\ \text{mg}\cdot\text{L}^{-1}$ (EPA), respectively.[2]

Kaolinite has been used for the removal of Mn(II), possessing a removal capacity of 0.446 $\text{mg}\cdot\text{g}^{-1}$ for Mn(II), as obtained from batch test data using Langmuir fitting. Moreover, the uptake of Mn(II) onto the surface of kaolinite is endothermic in nature and thus is favored by increasing temperature.[11] Fly ash has also been used for the removal of Mn(II) from aqueous solutions,[5] which is conversely exothermic in nature. Granular activated carbon[12] and some biological processes are also reported to be effective for Mn(II) removal.[13−16] The Kahrizak (southern part of Tehran, Iran) landfill, which receives municipal solid wastes and emanates high levels of Mn(II) and Zn(II) in the leachates, was effectively treated using soil and various doses of lime.[17] An in situ study revealed that the presence of lime was effective for the daily treatment of the leachates because it was able to remove Mn(II) effectively through chemical precipitation. Lignite has been employed for the removal and recovery of metal ions from AMD[18] as an attempt for a cost-

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Table 1. Physical Properties of Birm (MCS2)

color	black
bulk density	(40 to 45) lb·ft^{-3}
mesh size	10·40
specific gravity	2.0 g·cm^{-3}
effective size	0.88 mm
uniformity coefficient	2.7

Table 2. Amount of Manganese Coated on the Surface of Solids Samples

sample	Mn content (mg·kg^{-1})
MCS1[a]	674.7
MCS2[b]	55 066.0

[a] Effective coated manganese content obtained by subtracting from the Mn content of the sand. [b] Total manganese content in the sample.

effective treatment strategy. Clinoptilolite (Clin), a natural zeolite, and Clinoptilolite modified with iron (Clin-Fe) were used for the removal of Mn^{2+} from drinking water. Clin possessed a 7.69 mg·g^{-1} sorption capacity for Mn(II); whereas, Clin-Fe possessed a 27.12 mg·g^{-1} capacity.[8] Sand is widely used as a filter medium for various waste WTPs because of its availability and cost effectiveness. However, sand shows a very low removal capacity for heavy metal cations.[19] Therefore, various attempts have been taken to modify the surface properties of the sand by coating with manganese or iron, which can significantly enhance the removal efficiency. Conversely, pure manganese oxide or iron oxides as filter media are not favorable for economic reasons or because of their physical and chemical properties. The fine particle size of these metal oxides makes their separation from the water phase or for material to infiltrate through very difficult. However, coating these oxides onto the surface of sand or other minerals may overcome the difficulties of using these materials and at the same time can enhance their efficiencies.[20−25] This enhanced capacity results from the increased surface and amphoteric surface charge possessed by the coating materials, that is, manganese or iron oxide.[26] Therefore, a manganese-coated sand (MCS) was prepared in the laboratory as well on a pilot plant level[9] and was applied for the removal of Mn(II) from aqueous solutions. Furthermore, the removal efficiencies of these MCS samples for Mn(II) were greatly enhanced by appropriate dosing with sodium hypochlorite. The present investigation, an extension of our previous study, compares the removal efficiencies of manganese-coated samples, that is, MCS1 and MCS2, in the presence and absence of sodium hypochlorite. Moreover, a critical examination of the removal efficiency of MCS1 with the commercial product MCS2 is also undertaken.

Experimental Section

Materials. Preparation of MCS1 Sample. We prepared MCS by adding 100 g of sand of (0.8 to 1.2) mm in size (sand obtained from the Joomoonjin, Gangwon province, Korea) and 100.0 mL of 0.05 mol·L^{-1} manganese nitrate solution to a beaker heated to 100 °C with regular manual stirring until dryness. Dried samples were washed with plenty of distilled water and dried again at 100 °C. These dried samples were used for the entire investigation. We note that a relatively very low dose of Mn(II) (i.e., 0.05 mol·L^{-1}) along with the abundantly available sand may significantly reduce the cost of the samples prepared and thus may provide a good cost-effective treatment technology for the treatment of waste/effluent waters containing Mn(II).

A commercial sample, Birm (MCS2), obtained from the Clark Corporation (Windsor, WI), was also employed in the present investigation. It was reported that Birm is a granular filter media that is commonly used for the reduction of iron, manganese, or both from water supplies. The physical properties of the Birm sample are given in Table 1 as provided by the supplier.

Furthermore, the manganese content was separately obtained for these two solid samples using the standard EPA method, namely, EPA3050B; the results of which are shown in Table 2. From Table 2, the MCS2 sample clearly contains a very high (ca. 81 times higher) manganese content compared with that of MCS1. This infers a higher initial cost of the MCS2, that is, the Birm sample.

The pH of zero-point charge (pH_{ZPC}) was determined using a titration method. Briefly, 1.0 g of the MCS1 was suspended in 500 mL of a solution of known ionic strength at 25 °C. The suspension was then titrated with 0.1 M HNO_3, with the pH recorded after it was stabilized. Following titration with HNO_3, 0.1 M NaOH was used to take the pH to 10. The pH_{ZPC} was found to be 6.0 for the MCS1 sample.

The other chemicals used were of either GR or AR grade and were used without any prior purification.

Methodology. Batch Experiments. We performed batch experiments by taking 100.0 mL of 2.0 mg·L^{-1} Mn(II) (using $Mn(NO)_3 \cdot 6H_2O$; 97 % solution, Extra Pure, Junsei Chemical, Japan) solution in both the absence and presence of 4.0 mg·L^{-1} NaClO (12 % solution; Junsei Chemical, Japan) with the pH adjusted by the addition of small drops of concentrated HNO_3/NaOH solution. 0.5 g of solid (MCS1 or MCS2) was then added, and the solution mixture was shaken in an automatic shaker at (25 ± 2) °C for ca. 24 h to complete the adsorption process, and an apparent equilibrium was likely to be achieved between the solid/solution interface. After equilibrium was attained, the samples were removed from the shaker and filtered through a 0.45 μm syringe filter, and the pH was again checked and given as the final pH. These filtered samples were further subjected for bulk Mn(II) concentration analysis using AAS (Varian AA-300).

Column Experiments. Column experiments were performed using a glass column (1.0 cm inner diameter) packed with 1.5 g of uncoated sand followed by 0.5 g of MCS1 or MCS2 samples. A sorptive solution of Mn(II) (2.0 mg·L^{-1}), pH 7.5 (taken in the absence and presence of NaClO: 4.0 mg·L^{-1}), was pumped upward from the bottom of the column using an Acuflow Series II high-pressure liquid chromatograph at a constant flow rate of 1.42 mL·min^{-1}. Effluent samples were then collected using Spectra/Chrom CF-1 fraction collectors. Furthermore, these collected samples were filtered using a 0.45 μm syringe filter, and the bulk Mn(II) concentration was measured using AAS.

Results and Discussion

Speciation of Mn(II). Speciation of the manganese in the aqueous medium was evaluated using MINEQL+ (version 4.5), a geochemical simulation program, at an initial Mn(II) concentration of 2.0 mg·L^{-1}, and the results of which are shown as a function of pH in Figure 1. Figure 1 clearly demonstrates that almost 100 % of the Mn(II) is in the ionic form, that is, Mn^{2+}, up to pH 8.5, but pyrochroite ($Mn(OH)_2$) precipitates at higher pH. Beyond pH 11.0, 99 % of the Mn(II) is in the form of pyrochroite. In between these two, a maximum of 13.7 % of the soluble $Mn(OH)^+$ species occurs at pH 9.8.

Batch Experiments. Removal Behavior of MCS1 and MCS2 for Mn(II) in the Absence of NaClO. The removal behavior of these two solids was studied using a 2.0 mg·L^{-1} Mn(II) solution at a constant temperature of (25 ± 2) °C for various pH values and is shown in Figure 2 (that is, from 5.0

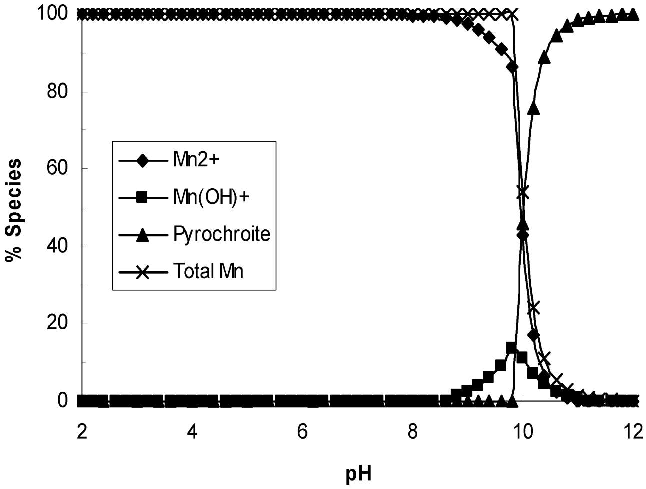

Figure 1. Percentage distribution of various Mn(II) species as a function of pH (Mn(II): 2 mg·L^{-1}).

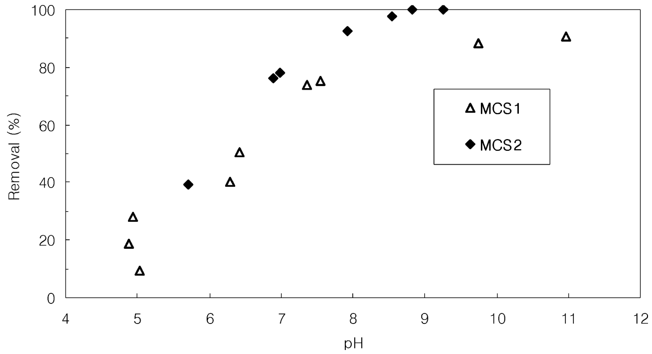

Figure 2. Removal behavior of MCS1 and MCS2 as a function of pH (Mn(II) concentration: 2.0 mg·L^{-1}; solid dose: 5.0 g·L^{-1}; NaClO dose: 0.0 mg·L^{-1}).

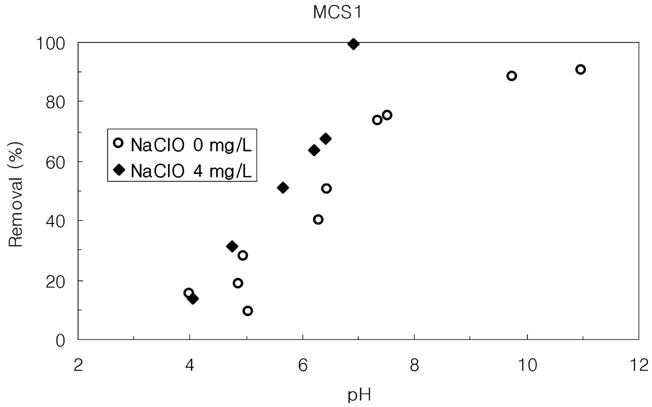

Figure 3. Comparison of the removal behavior of MCS1 in the presence and absence of NaClO as a function of pH (Mn(II) concentration: 2.0 mg·L^{-1}; MCS1 dose: 5 g·L^{-1}).

to 10.5; the pH given in Figures 2, 3, and 4 is the final pH). The results obtained are presented as the percent removal as a function of pH and are shown graphically in Figure 2. This Figure clearly indicates that near neutral pH (i.e., pH 7.0 to 8.0), very comparable results for the removal of Mn(II) are observed for these two samples, that is, the laboratory prepared and commercial product samples, MCS1 and MCS2, respectively. Therefore, it may be concluded that the samples prepared in the laboratory, with a minimal dose of Mn(II), that is, MCS1, can be used to substitute the commercial product, MCS2, at least for the removal of Mn(II). Also, this laboratory-prepared sample, that is, MCS1, is also supposed to be cost-effective.

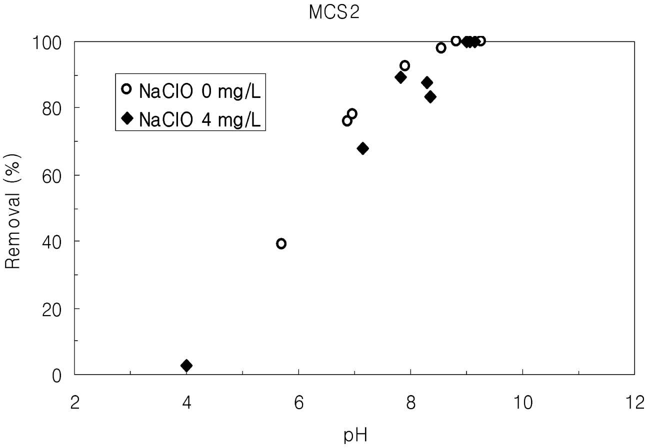

Figure 4. Comparison of the removal behavior of MCS2 in the presence and absence of NaClO as a function of pH (Mn(II) concentration: 2.0 mg·L^{-1}; MCS2 dose: 5 g·L^{-1}).

Figure 2 also indicates that increasing the pH from 5.0 to 8.0 causes a relatively sharp increase in the uptake of Mn(II) by these two solids and at higher pH attains a constant value, that is, ca. 90 % at pH 10.0 for the MCS1 and ca. 100 % at pH 9.0 for the MCS2 samples. This increase in the uptake may be explained on the basis of the surface properties of the solids and those of the sorbing species. In the pH range of 5.0 to 8.0, most of the Mn(II) exists as Mn^{2+} ions,[27] which is also shown by the MINEQL data (Figure 1). On the other hand, the solids primarily contain layers of manganese, possibly in the form of manganese dioxide, which is supposed to facilitate the sorption of sorbing species. Moreover, the surface of the solids may likely become negatively charged at around pH 6.0 because the pH_{ZPC} for MCS1 was measured to be 6.0, with that of manganese dioxide reported to be 5.5.[28] Therefore, the complex reactions of Mn^{2+} with manganese dioxide may be written as follows[29,30]

$$\equiv MnOH + Mn^{2+} \leftrightarrow \equiv MnO^{-}Mn^{2+} + H^{+} \qquad (1)$$

$$\equiv MnO^{-} + Mn^{2+} \leftrightarrow \equiv MnO^{-}Mn^{2+} \qquad (2)$$

$$2(\equiv MnOH) + Mn^{2+} \leftrightarrow (\equiv MnO^{-})_2Mn^{2+} + 2H^{+} \qquad (3)$$

$$2(\equiv MnO^{-}) + Mn^{2+} \leftrightarrow (\equiv MnO^{-})_2Mn^{2+} \qquad (4)$$

Furthermore, beyond the pH_{ZPC} value, in addition to specific sorption of Mn(II) onto the solid surface, some kind of electrostatic attraction could presumably take place with the negatively charged solid surface. A similar observation was reported for the sorption of Mn(II) onto the surface of kaolinite.[31] However, at lower pH values, that is, below pH 6, the sorption of Mn(II) onto the solid surface is greatly inhibited because in this pH region, H^{+} ions in solution may compete for the MCS surface and render a decreased removal of Mn(II).[23,30]

Previously, it was reported that MCS possesses both the +3 and +4 oxidation states of manganese on the sand surface, as evidenced by XPS analysis.[30] Moreover, this solid removes Cu(II) and Pb(II) with a mechanism similar to that proposed for Mn(II), that is, exchange and surface complexation uptake.[19] Beyond pH 8.0, a mixed effect of adsorption and precipitation could possibly take place, causing an apparently very high uptake, that is, ca. 100 % removal.[32]

Removal Behavior of MCS1 and MCS2 for Mn(II) in the Presence of NaClO. The presence of oxidizing agents in these manganese-coated solids acts as an insoluble catalyst to enhance the reaction between dissolved oxygen (DO) and the soluble manganese compounds, that is, Mn(II). The oxidation of these soluble manganese compounds to Mn(IV) as manganese oxide is then aggregated on the solid surface and hence further enhances the applicability of these solids. Therefore, to enhance the uptake of Mn(II) using these two solids, an attempt has been made to perform the removal process in the presence of sodium hypochlorite, that is, 4.0 $\mathrm{mg \cdot L^{-1}}$, in batch experiments. The results obtained are shown graphically in Figures 3 and 4, respectively, for MCS1 and MCS2 as a function of pH (final pH). It is clear from these Figures that comparable removal efficiencies are achieved by these two solids in the presence of NaClO.

Moreover, a comparison of the removal behavior of these solids in the presence and absence of sodium hypochlorite (cf. Figures 3 and 4) for MCS1 and MCS2 clearly indicates that the presence of sodium hypochlorite significantly enhances the uptake of Mn(II) onto the surface of the MCS1 sample (cf. Figure 3). However, the presence of sodium hypochlorite could not show a pronounced effect on the MCS2 sample (cf. Figure 4). This may have been due to the saturation of the manganese dioxide on the surface of the MCS2 samples because it contained a very high manganese content (cf. Table 1); whereas, the significant increase in the Mn(II) uptake onto the surface of MCS1 may be explained on the basis of the redox reactions, which perhaps take place on the surface of the solid. The oxidation process, that is, the conversion of Mn(II) to Mn(IV), may be greatly facilitated by the surface of the solids, hence allowing the formation of MnO_2. This MnO_2 may be aggregated on the surface of the solids. The possible mechanism and pathway of Mn(II) aggregation on the surface of manganese-coated solids in the presence of NaClO may be represented by the following insoluble catalytic mechanisms

$$Mn^{2+} + MnO_2 \cdot H_2O + H_2O \rightarrow MnO_2 \cdot MnO \cdot H_2O + 2H^+ \tag{5}$$

$$MnO_2 \cdot MnO \cdot H_2O + ClO^- \rightarrow 2MnO_2 \cdot H_2O + 2Cl^- \tag{6}$$

Similar results are also reported for the oxidation of Mn(II) to Mn(IV) in the presence of Cl_2 gas.[7] An alternative approach was proposed for removing the soluble manganese from mine waters using fixed bed bioreactors. Ferromanganese nodules (about 2 cm diameter) collected from an abandoned mine adit in north Wales, U.K. were used to inoculate the bioreactors (working volume ca. 700 mL). Following colonization by manganese-oxidizing microbes, the aerated bioreactor catalyzed the removal of solute manganese via oxidation of Mn(II) and precipitation of the resultant Mn(IV) in the bioreactor in synthetic media and mine water from the Wheal Jane PPTP (pilot passive treatment plant).[33]

Column Experiments. In recent times, the fluidized bed reactor (FBR) technique has been widely applied as an alternative treatment method for the removal of several metal cations.[34−39] The process of crystallizing $CaCO_3$ in an FBR was also applied in the softening of drinking water.[34] Nielson et al.[36] tested the fluidized bed technique at a coal-fired power station with wastewater from a flue gas desulphurisation unit for the removal of heavy metals from wastewater. In this technique, manganese or ferrous ions and an oxidizing agent (e.g., O_2, H_2O_2, $KMnO_4$) are continuously added to the wastewater. Adsorptive granules of either FeOOH (ferric oxyhydroxide) or manganese dioxide are generated as a coating on the surface of the carrier material. Furthermore, heavy metal removal[37−39] by means of the crystallization of carbonates in an FBR is employed to reduce the disposal of hydroxide sludge and to reduce the cost of the metal involved. Therefore, the applicability of these two solids under dynamic conditions is assessed in column studies. For this purpose, column experiments were performed by taking 0.50 g of solid (i.e., MCS1 or MCS2) packed into a column with the influent solution, that is, 2.0 $\mathrm{mg \cdot L^{-1}}$ Mn(II) solution at pH 7.5 (in the presence and absence of NaClO: 4.0 $\mathrm{mg \cdot L^{-1}}$), pumped through from the bottom of the column at a flow rate of 1.42 $\mathrm{mL \cdot min^{-1}}$. The results obtained are presented in Figures 5 and 6 for MCS1 and MCS2, respectively. Furthermore, the breakthrough curves obtained are also analyzed using the Thomas equation[40] in its standard form

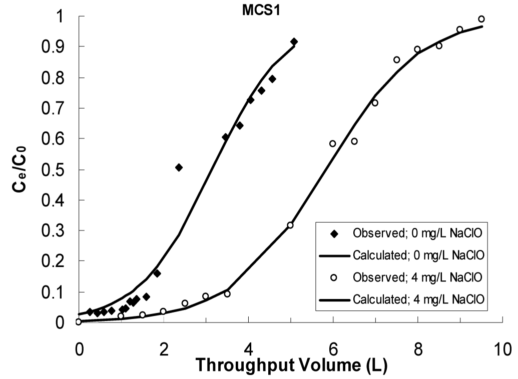

Figure 5. Breakthrough curves for the removal of Mn(II) using MCS1 for the Thomas model (influent Mn(II) concentration: 2 $\mathrm{mg \cdot L^{-1}}$; MCS1 dose: 0.5 g; flow rate: $1.42 \cdot 10^{-3}$ $\mathrm{L \cdot min^{-1}}$).

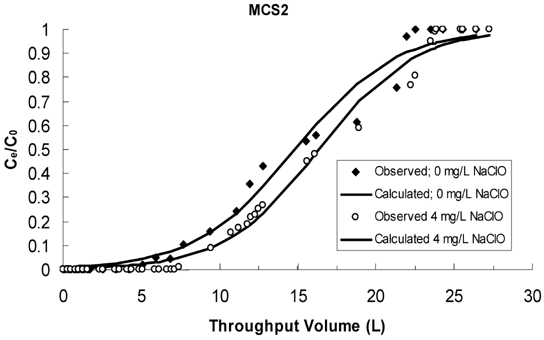

Figure 6. Breakthrough curves for the removal of Mn(II) using MCS2 for the Thomas model (influent Mn(II) concentration: 2 $\mathrm{mg \cdot L^{-1}}$; MCS2 dose: 0.5 g; flow rate: $1.42 \cdot 10^{-3}$ $\mathrm{L \cdot min^{-1}}$).

$$\frac{C_e}{C_0} = \frac{1}{1 + e^{(K_T(q_0 \cdot m - C_0 \cdot V))/Q}}$$

where C_e and C_0 stand, respectively, for the concentration of effluent and feed of Mn(II) solution ($\mathrm{mg \cdot L^{-1}}$), K_T refers to the Thomas rate constant ($\mathrm{L \cdot min^{-1} \cdot mg^{-1}}$), and q_0 stands for the maximum amount of Mn(II) that can be loaded ($\mathrm{mg \cdot g^{-1}}$) under the specified conditions. m is the mass of the adsorbent loaded (g), V is the throughput volume (L), and Q is the flow rate ($\mathrm{L \cdot min^{-1}}$).

A nonlinear regression of the break-through curves using the Thomas equation is also presented in Figures 5 and 6 for MCS1 and MCS2, respectively. The Thomas constants for fitting of the curves, that is, K_T ($L \cdot min^{-1} \cdot mg^{-1}$) and q_0 ($mg \cdot g^{-1}$), for the removal of Mn(II) by these solids are found to be, respectively, $9.43 \cdot 10^{-3}$ and 10.93 (without NaClO) and $7.42 \cdot 10^{-3}$ and 20.21 (with NaClO) for MCS1, and $2.23 \cdot 10^{-4}$ and 59.34 (without NaClO) and $2.37 \cdot 10^{-4}$ and 65.44 (with NaClO) for MCS2. It is noted that the presence of sodium hypochlorite greatly enhances the removal efficiency of the MCS1 sample (cf. Figure 5); however, it is slightly increased for the MCS2 sample (cf. Figure 6). Moreover, the breakthrough curves are found to be more diffused in presence of the hypochlorite dose. This may be due to the slow oxidation of Mn(II) onto the surface of these manganese-coated solids. The practical sorption capacity obtained under the dynamic conditions is reported to be similar to previous reports obtained for the removal of Cu(II) and Pb(II) using MCZ (manganese-coated zeolite) employing the Thomas equation.[41] These results are again in accordance with the independently obtained batch data. In addition, the increase in the uptake of Mn(II) in the presence of sodium hypochlorite may be ascribed because of the thermodynamic explanation proposed earlier. Mn(II) should spontaneously oxidize to Mn(IV) in aerated, neutral pH waters, but the activation energy required is relatively high, and this greatly slows down the process, causing Mn(II) to be far more stable in most acidic waters than is ferrous ion. In contrast, the adsorption of Mn(II) onto MnO_2 is much more rapid. The "activation energy barrier" for Mn oxidation can be overcome biologically/chemically. Many microorganisms, oxidizing agents, or both are known to be able to catalyze the oxidation of Mn(II), and at least some of these are known to utilize the energy available from the reaction.[27,42]

Moreover, the column results also showed that MCS2 possesses a relatively higher removal capacity for Mn(II) compared with MCS1. This higher uptake is contrary to the batch data because very comparable uptakes are observed at around pH 7.0 (final pH) in the batch experiments. Therefore, the pH of the effluent solutions in the column experiments was also checked, and an effluent pH ca. 7.0 was found for MCS1; however, this increased to pH 9.8 for MCS2, which may likely be the cause of the higher uptake of Mn(II) by MCS2. Therefore, it may be concluded that the samples prepared in the laboratory with a low manganese(II) dose ($0.05 \ mol \cdot L^{-1}$), that is, MCS1, show very comparable removal efficiency, at least for the removal of Mn(II), under dynamic conditions (i.e., in the column experiments). Therefore, MCS1 could be a potential alternative material for the removal of Mn(II) from aqueous solutions and would likely be cost-effective.

Conclusions

Both batch and column experiments were performed to assess the removal efficiencies of two different samples, that is, MCS1 (prepared in the laboratory with a low dose of Mn(II); $0.05 \ mol \cdot L^{-1}$) and MCS2 (i.e., Birm, a commercial product) for Mn(II). It was found that these two solids showed very comparable removal efficiencies in both the presence and absence of NaClO in the batch experiments. However, the presence of NaClO apparently enhanced the uptake of Mn(II), especially in the case of MCS1. Moreover, column experiments showed MCS2 to have a very high removal capacity compared with MCS1 for the influent Mn(II) at pH 7.5; however, the effluent pH increased to 9.8 for MCS2; whereas, this was ca. 7.0 for MCS1. It may be concluded that the increase in pH favored only the removal of Mn(II) by MCS2. Therefore, the present study may enable the samples obtained in the laboratory, that is, MCS1, with a lower dose of manganese ($0.05 \ mol \cdot L^{-1}$) to be a good cost-effective alternative to the commercial MCS2 sample, at least for the removal of Mn(II) from aqueous solutions.

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