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Removal characteristics of manganese-coated solid samples for Mn(II)

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ABSTRACT

Manganese-coated sand (MCS) and manganese-coated sericite (MCSe) were prepared at pH 4 and 9 (MCS4, MCS9, MCSe4 and MCSe9) and applied in the treatment of wastewater containing soluble Mn^{2+} in batch experiments under various pHs. The amount of Mn^{2+} adsorbed by manganese-coated solids increased as the solution pH increased from pH 4 to 11. In order to compare Mn^{2+} sorption onto manganese-coated solids in the presence of hypochlorite, 4 mg/L of NaClO was added into Mn^{2+} solution. It was observed that the presence of sodium hypochlorite dose significantly enhanced the uptake of Mn^{2+} from aqueous solutions for the entire pH range studied i.e., pH 4.0 to 11.0. In adsorption isotherm experiment, the results were fitted reasonably well for the Freundlich equation. Mn^{2+} breakthrough time in the effluent from both MCS and MCSe columns in the presence of hypochlorite was greatly enhanced. Among these manganese-coated solids, MCSe4 showed the highest adsorption capacity. Therefore, MCSe4 was identified as a better adsorbent and filter material for the treatment of wastewaters containing Mn^{2+}.

Keywords: Manganese-coated solid; Sand; Sericite; NaClO; Column experiment; Manganese removal

1. Introduction

Treatment of heavy metal contamination such as manganese in water is an important subject that has been of concern regarding environmental regulation and maintenance of human health. Manganese enters into our aquatic environment through the variety of applications viz., in ceramics, dry battery cells, electrical coils, manganese containing alloys etc. [1]. Typically, Mn concentrations from natural processes are low but can range up to 1.50 mg/L or higher [2]. Considerable progress has been made in treatment methods such as electrochemical treatment, coagulative precipitation, adsorption, ion exchange, reverse osmosis, and filtration. Among these water-treatment techniques, adsorption is generally preferred for the removal of heavy metal toxic ions due to its high efficiency, easy handling, availability and cost effectiveness. The adsorption of heavy metal cationic species onto synthetic oxides of Mn, Fe, Al, etc., has been studied extensively [3–8]. These multivalent hydrous oxides are amphoteric in nature, and the charge of the hydrous metal oxide depends on the pH of the medium.

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Mn^{2+} ions can gradually be oxidized to insoluble manganese dioxide causing several problems such as water discoloration, metallic taste, odour, turbidity, biofouling and corrosion, staining of laundry and plumbing fixture [2]. MnO_2 is one kind of surface acidic oxide whose pHpzc (point of zero charge value) is about 5.5 [9]. Generally, manganese oxide's surface charge is negative, and it can be used as an adsorbent to remove heavy metals from effluent or wastewater. However, most metal oxides are available only as fine powders or are generated in aqueous suspension as hydroxide floc or gel. In such forms, these oxides retain adsorptive properties for heavy metals, but a sedimentation basins or filtration unit is needed for solid/liquid separation.

Sands are widely used as filter media in the treatment of wastewater. However, the efficiency of the sand samples can be substantially enhanced for the removal of toxic heavy metal ions using the iron- or manganese-coated sands.

Sericite is a layered silicate mineral, generally recognized as white fine powders of muscovite in form, with nano-sized layer structure, interlayer spacing of (002) plane is 10Å. It has been reported that it is widely used in alkali flux and cosmetics; however, the application in wastewater treatment is yet to be explored [10,11]. Hence, in a quest of eco-friendly and cost-effective cleaner technologies, we attempted to exploit the abundantly available sericite for the removal of two important heavy metal toxic ions viz., Cu(II) and Pb(II) previously [12,13]. However, the removal capacity of sericite was found to be inadequate; hence we tried to coat it with manganese to enhance its applicability in the removal of heavy metal toxic ions.

Therefore, two different manganese-coated samples i.e., manganese-coated sand and manganese-coated sericite, were prepared and employed to assess their removal efficiency towards the Mn^{2+} from aqueous solutions over a wide pH range i.e., pH 4.0 to 11.0. Further, the nominal dose of sodium hypochlorite has also been evaluated for the additional removal of Mn^{2+} from aqueous solutions using these two solids.

2. Material and methods

2.1. Preparation of MCS samples

Manganese-coated sand/or sericite was prepared by taking the 100 g of sand/sericite (1.0 ± 0.2 mm in size; sand was obtained from the Joomoonjin, Kangwon Province, Korea; sericite was obtained from Samkyung Co, Korea) into 50 mL of $Mn(NO_3)_2$ solution (0.2 M) in a beaker and the solution pH was adjusted to 4 (MCS4, MCSe4) or pH 9 (MCS9, MCSe9). The mixture was heated and shaken, immersed in a water bath for 24 h to attain an equilibrium state at 105 °C in a rotary evaporator. When approximately 10% of water in the mixture remained, samples were washed with plenty of distilled water and dried at 105 °C for 1 h to allow stabilization of the coating process.

Table 1
Chemical composition of sericite

Metal oxides	% composition
SiO_2	70.12
Al_2O_3	17.97
Fe_2O_3	0.71
CaOMgO	0.27
K_2O	1.36
Na_2O	6.07
	0.14

The sericite sample contained various metal oxides; quantitatively it was analyzed and results are presented in Table 1. The content of the manganese was separately obtained for these two solid samples using the standard EPA method viz., EPA3050B. Manganese content was measured using AAS (Varian Spectra AA-300). All solutions were prepared with deionized distilled water (18 MΩ-cm) using the Millipore water purification system (Milli-Q+).

2.2. Effect of pH

Batch experiments were performed by taking 100.0 mL of 2.0 mg/L of Mn^{2+} (using $Mn(NO)_3{\cdot}6H_2O$; 97% solution, Extra Pure, Junsei Chemicals, Korea) solution in absence and presence of 4.0 mg/L NaClO (12% solution; Junsei Chemical, Japan). Solution pH was adjusted by the addition of small drops of concentrated HNO_3/NaOH solution; 0.5 g of solid (MCS4/or MCS9/or MCSe4/or MCSe9) was then added and the solution mixture was equilibrated for the period of 24 h in an automatic shaker at 25±2 °C. After equilibration the sample was taken out and was filtered with a 0.45 μm syringe filter, and the bulk metal concentration was measured using AAS (Varian Spectra AA-300). While doing the pH dependence study, the pH adjustment was made by the addition of drops of strong HNO_3/NaOH.

2.3. Sorption experiments

Sorption experiments were carried out by agitating manganese-coated solids (0.5 g/L) with different concentrations (1, 2, 3, 4, 6, 8, 10, and 12 ppm) of Mn^{2+} solution. These solutions were equilibrated in shaker at the 25±2 °C for 24 h. After agitation, the solid was removed by filtration through a 0.45 μm membrane filter. The final concentration of Mn^{2+} in the filtrate was analyzed using an atomic absorption spectrophotometer (Varian Spectr-300). Initial pH values of the solutions was adjusted to the desired value using 0.1M NaOH and 0.1M HNO_3, no efforts were made to maintain the solution pH while metal ions were being sorbed.

2.4. Column experiments

The Mn(II) removal was conducted in a 1.0 cm diameter glass column packed with 0.5 g of MCS4/or MCS9/or MCSe4/or MCSe9 along with 1.5 g of uncoated sand (kept below to the coated samples) at room temperature. The solution of Mn^{2+} (2.0 mg/L) with pH 6.5 (taken in the absence and presence of NaClO: 4.0 mg/L) was pumped upward from the bottom of the column using an Acuflow Series II, high-pressure liquid chromatograph, at a constant flow rate of 1.4 mL/min. Effluent samples were then collected using Spectra/Chrom CF-1 fraction collectors. Samples were filtered using 0.45 μm syringe filters, then subjected for the total bulk metal concentration using AAS (Varian Spectra AA-300). The pH of the influent solution and effluent solutions was also obtained.

3. Results and discussion

3.1. Stability and the amount of manganese coating

The amount of manganese coating on solids was evaluated usign the EPA3050B method. The amount of manganese was found to be 976.05, 866.2, 1056.22 and 928.3 mg/kg respectively for the MCS4, MCS9, MCSe4 and MCSe9 samples (cf. Fig. 1). In order to apply manganese-coated solids for the removal of manganese in the entire range of pH, the stability of coatings was obtained at different pH values i.e., from pH 2 to 7. The stability results were shown graphically in Fig. 2. It clearly showed that the manganese coating is fairly stable above the pH 3.5. However, it showed less stability below the pH 3.5. Hence, the most of the experiments were performed only at higher pH values i.e., pH 4.0 to 11.0. These results suggest that manganese-coated solids can be effectively employed in the treatment of wastewater with significant dissolution of the manganese.

3.2. Effect of the pH and removal behaviour of MCS and MCSe in presence of NaClO

The pH value is an important parameter controlling the adsorption of Mn^{2+} onto the surface of the manganese-coated solids. Fig. 3 shows the adsorption of manganese onto MCS and MCSe over a pH range of 4.0–11.0 keeping 2 mg/L of initial manganese concentration. The percentage of Mn^{2+}adsorbion was increased with increasing the pH value from pH 4.0 to 11.0. The removal efficiency of manganese was rapidly increased at pH 7 to 8 with nearly 80% of Mn^{2+} was removed at around this pH. This is perhaps due to the pH_{zpc}, which lies around pH 5.5. Hence, beyond this the surface becomes negatively charged and favors an enhanced uptake of Mn^{2+}. Tiwari et al. [12,13] obtained similar experimental results using manganese-coated sand for the removal of manganese. Moreover, in this pH region the manganese exists with manganese ion. Since manganese oxides on the surface of manganese-coated sand and sericite become negatively charged and promote the removal of metal ion, the possible mechanism and pathway of Mn^{2+} removal can be represented by the following reactions:

$$\equiv S\text{-}OH + Mn^{2+} \rightarrow \equiv S\text{-}O\text{-}Mn^{+} + H^{+} \quad (1)$$

$$\equiv S\text{-}O^{-} + Mn^{2+} \rightarrow \equiv S\text{-}O\text{-}Mn^{+} \quad (2)$$

These results demonstrate that manganese-coated sand and sericite prepared at low concentration of manganese can be used as cost-effective material for the removal of manganese.

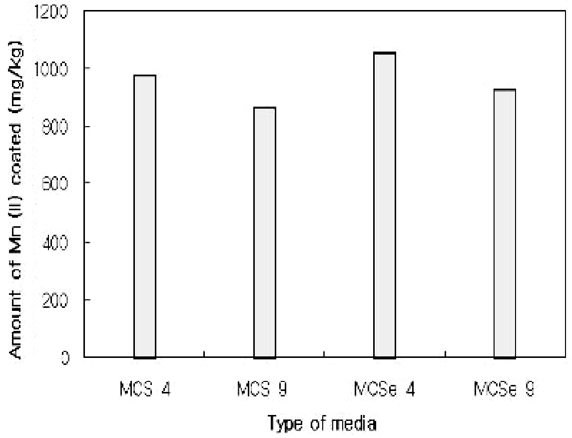

Fig. 1. Amount of manganese coating on solid material.

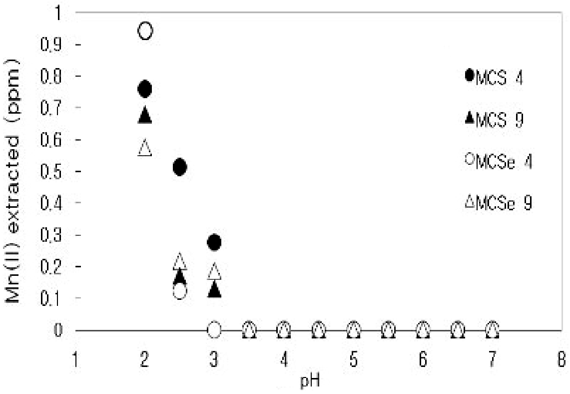

Fig. 2. Stability of manganese-coated solids.

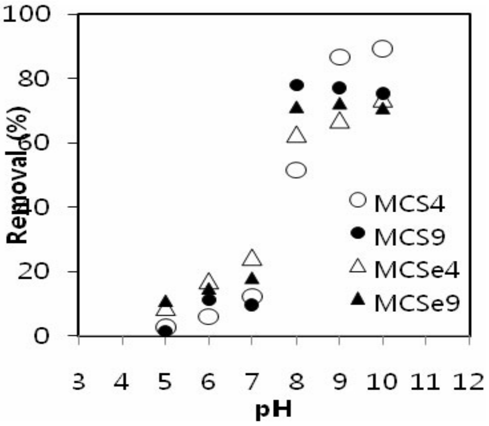

Fig. 3. Comparison of removal behaviour of MCS and MCSe without NaClO as a functionof pH.

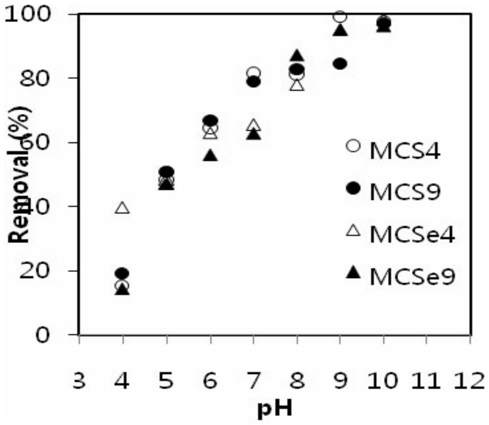

Fig. 4. Comparison of removal behaviour of MCS and MCSe in the presence of NaClO as a f unction of pH.

In order to compare Mn^{2+} sorption onto manganese-coated solids in the presence of hypochlorite, 4 mg/L of NaClO was added into Mn^{2+} solution at pH 4–11. After 24 h of contact time, equilibrium pH values were measured, as well as the bulk metal concentrations and the results are presented in Fig. 4. Removal efficiency of manganese was significantly increased in all manganese-coated solids at over pH 4.0 to11.0. The mechanism of manganese removal in the presence of NaClO can be explained by following reactions:

$$Mn^{2+} + MnO_2{\bullet}H_2O + H_2O \rightarrow MnO_2{\bullet}MnO{\bullet}H_2O + 2H^+ \quad (3)$$

$$MnO_2{\bullet}MnO{\bullet}H_2O + ClO^- \rightarrow 2MnO_2{\bullet}H_2O + 2Cl^- \quad (4)$$

3.3. Adsorption equilibrium of MCS and MCSe

Further, the concentration dependence data were used for the adsorption modelling using the Freundlich adsorption isotherm [Eq. (5)].

Table 2
Values of Freundlich coefficients

Sample	K (mg/g)	$1/n$	R^2
MCS4	0.185	0.724	0.971
MCS9	0.142	0.951	0.960
MCSe4	0.189	0.768	0.998
MCSe9	0.152	0.820	0.999

$$q_e = KC_e^{1/n} \quad (5)$$

where q_e is the mass of adsorbed solute per mass of adsorbent (mg/g), C_e is the equilibrium concentration of solute (mg/L), K and $1/n$ are the Freundlich constants. It is noted that the equilibrium adsorption data for the sorption of Mn^{2+} onto these solids fit well for the Freundlich adsorption isotherm [cf. Fig. 5(a)–(d)]. Moreover, the Freundlich constants were evaluated using these figures and are returned in Table 2. The closure scrutiny of these constants clearly indicate that the fractional values of $1/n$ for all these systems suggests the heterogeneous structure of the surface and exponential distribution of surface active sites [14]. Moreover, the adsorption capacity (i.e., K) shown for these solids for the removal of Mn^{2+} indicates that relatively MCSe4 possess the maximum adsorption capacity.

3.4. Column studies

The applicability of manganese-coated solids was assessed under the dynamic conditions in column experiments. In order to enhance the uptake of Mn^{2+} using these solids, an attempt has been made to perform the removal process in presence of sodium hypochlorite dose i.e., 4.0 mg/L in column experiments. A comparison of the presence and absence of sodium hypochlorite for the removal behaviour of these solids is presented separately in Figs. 6(a) and (b). These figures clearly indicate that the presence of sodium hypochlorite significantly enhanced the uptake of Mn^{2+} on the surface of MCS and MCSe samples. The increased uptake of Mn^{2+} in presence of sodium hypochlorite under the dynamic conditions again supports the hypothesis proposed earlier (vide equations 3 and 4) under the batch experiments. Fig. 7 illustrates the breakthrough curves for all manganese-coated solids in the presence of NaClO. The adsorption capacity of MCSe4 until the effluent concentration reached to initial concentration in the presence of NaClO was 13.83 g/kg at 550 pore volume while 6.62 g/kg at 250 pore volume without NaClO in the column experiment. The total amount of Mn^{2+} adsorbed on manganese-coated solids was calculated and is listed in Table 3. Among all these manganese-coated solids, MCSe4 possessed the highest adsorption

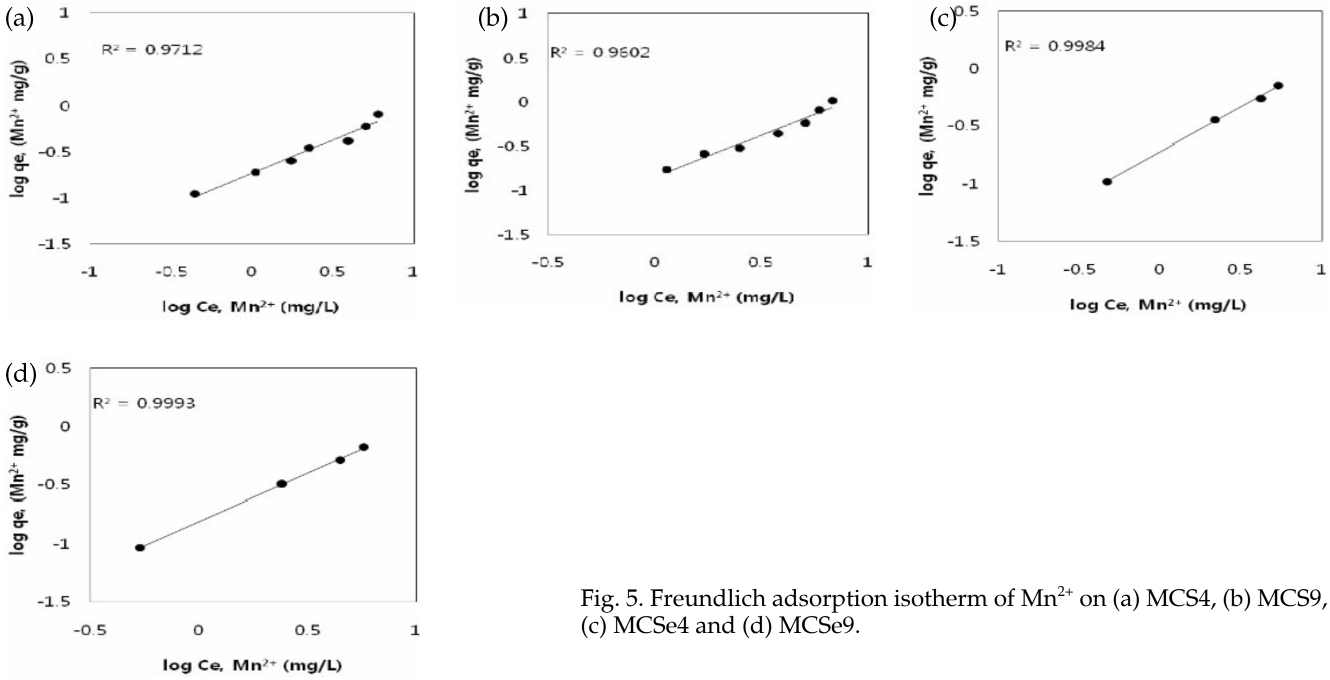

Fig. 5. Freundlich adsorption isotherm of Mn^{2+} on (a) MCS4, (b) MCS9, (c) MCSe4 and (d) MCSe9.

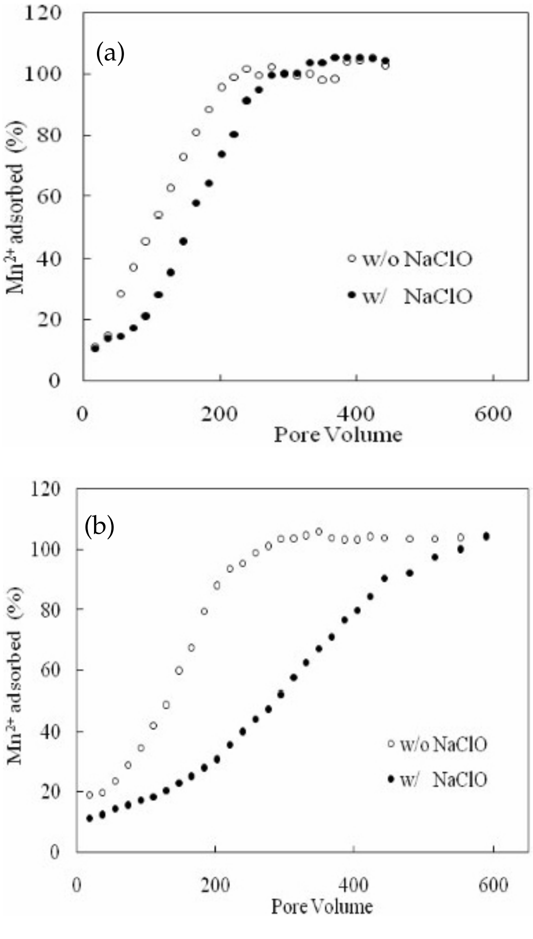

Fig. 6. Breakthrough curves for the removal of Mn^{2+} (a) MCS9, (b) MCSe4.

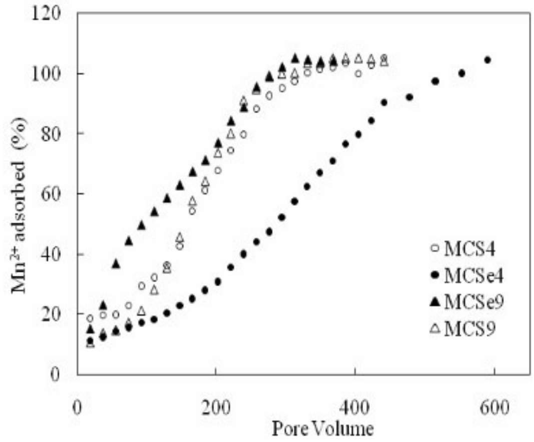

Fig. 7. Breakthrough curves for the removal of Mn^{2+} by manganese-coated solids in the presence of NaClO (4 mg/L).

Table 3
Total amount of Mn^{2+} adsorbed on manganese-coated solids in the column experiment

Adsorbent	Sorption capacity (g/kg)	
	Without NaClO	With NaClO
MCS4	7.64	8.06
MCS9	5.68	7.92
MCSe4	6.54	13.83
MCSe9	3.54	6.24

capacity. Therefore, MCSe4 was identified as a better adsorbent and filter material for the treatment of wastewaters containing Mn^{2+}.

4. Conclusions

The batch and column experiments were performed to assess the removal efficiency of manganese-coated solids viz., MCS and MCSe for the removal of Mn^{2+}. The percentage of Mn^{2+}adsorption increased with increasing the sorptive pH from pH 4.0 to 11.0. Moreover, the presence of minimal dose of sodium hypochlorite (4.0 mg/L) significantly increased the uptake of Mn^{2+} using all these manganese-coated solids. The results of adsorption isotherms fit reasonably well for the Freundlich equation. In the column study, the presence of sodium hypochlorite significantly enhanced the uptake of Mn^{2+} on the surface of MCS and MCSe samples. Among the manganese-coated solids, MCSe4 possessed the highest adsorption capacity. Therefore, MCSe can be used as cost-effective material for the removal of Mn^{2+} in water and wastewater treatment.

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