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The Feasibility of Using Diatomite and Mn–Diatomite for Remediation of Pb^{2+} , Cu^{2+} , and Cd^{2+} from Water

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ABSTRACT

Diatomite and manganese-oxide-modified-diatomite (Mn–diatomite) were tested as adsorbents for Pb^{2+} , Cu^{2+} , and Cd^{2+} removal from water. Impregnating the surface of diatomite with 0.38 g of manganese oxide per gram diatomite shows an increase of 2.4-fold in the surface area of the modified diatomite. The adsorption capacities were 99, 51, and 26 mg/g Mn–diatomite for Pb^{2+} , Cu^{2+} , and Cd^{2+} , respectively, obtained at solution pH 4, while values of 24, 21, and 16 mg/g diatomite were obtained at the same conditions and for the same metals. The obtained adsorption kinetics experimental data display that 95% of the original Pb^{2+} concentrated was adsorbed by Mn–diatomite within 10 min, while kinetic data for diatomite showed a lower rate for Pb^{2+} uptake. The filtration quality of diatomite was significantly enhanced with the surface modification by manganese oxide.

Key Words. Adsorption; Metal ions; Diatomite

INTRODUCTION

Elimination of heavy metals from water is an important public health issue. Proposed methods for the removal of heavy metals include chemical precipitation, membrane filtration, ion exchange, alum coagulation, and adsorption. Adsorption is considered a reliable process that can be used to remediate a mixture of contaminants with low concentration (1). Several synthesized and nat-

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urally occurring materials could be employed as adsorbents. Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of trace quantities of heavy metals (2). However, the use of activated carbon is not suitable for developing countries because of its high manufacturing cost (3). An alternative material that can be used efficiently and at a low cost is diatomaceous earth (4). Diatomite or diatomaceous earth is a pale, soft, lightweight rock composed principally of the silica microfossils of aquatic unicellular algae. It has a unique combination of physical and chemical properties such as high porosity, high permeability, small particle size, and large surface area, which makes diatomite suitable for a wide range of industrial applications, such as use as a filter aid or filler (5). Recently, many attempts have been made to increase sorption capacity of natural adsorbents toward heavy metals by chemical modification of their surface (6). Karthikeyan and Malay studied the removal of Hg^{2+} by coal treated with nitric acid, hydrogen peroxide, carbon disulfide, and manganese oxide impregnation (7). Moore and Reid showed manganese-impregnated acrylic fibers to be effective for removing radium from natural water (8). Brandao and Galembeck reported that manganese dioxide-impregnated cellulose acetate has a high efficiency toward Cu^{2+} , Pb^{2+} , and Zn^{2+} from aqueous solutions (9). Sagara et al. prepared a selective ion-exchanger material for Li^+ and Na^+ by dispersion of MnO_2 in cellulose gel beads (10). Despite the efforts made to utilize diatomite as an adsorbent, more studies on increasing its adsorption capacity are needed. In Jordan, diatomaceous earth and manganese exist in large quantities. It is shown here that Jordan's diatomite can be employed for removing Pb^{2+} , Cu^{2+} , and Cd^{2+} from water by impregnating its surface with manganese oxides.

EXPERIMENTAL

Adsorbent and Adsorbate

Diatomite samples were obtained through the Natural Resources Authority (NRA), Amman, Jordan. These samples were washed with distilled water to remove particles less than $2\text{ }\mu\text{m}$ in diameter and other adhered impurities, dried at 100°C , desiccated, and stored in tightly stoppered glass bottles for use in sorption experiments. Surface modification and characterization of manganese-oxide-modified diatomite was accomplished by treating diatomite with manganese chloride and sodium hydroxide (8). A sample of 15 g of diatomite was immersed in sufficient 6 M sodium hydroxide at $90 \pm 1^\circ\text{C}$ and stored for 2 h. The mixture was placed in 100 mL of 2.5 M manganese chloride (pH adjusted to 1–2 with hydrochloric acid) at room temperature ($23 \pm 1^\circ\text{C}$) for 10 h. The manganese-soaked diatomite was filtrated and separated from the supernatant. Then it was immersed in 6 M sodium hydroxide at room temperature for 10 h to precipitate manganese hydroxide. The excess was decanted and diatomite

was left exposed to air to facilitate oxidation of manganese hydroxide to a mixture of hydrated manganese oxides. Then the sample was washed with water, dried at $100 \pm 1^\circ\text{C}$, desiccated, and stored in tightly stoppered glass bottles for use. The amount of manganese oxides on diatomite was determined by dissolving the oxides in 4 M hydrochloric acid at $40 \pm 1^\circ\text{C}$ in a hot-water bath, in which manganese ions were determined by atomic absorption (Pye Unicam SP9). Different loaded manganese-oxide diatomites were prepared following the forgoing procedure in which 0.20, 1.50, and 3.50 M MnCl_2 were used as initial concentration. The effect of chemical modification on adsorbent was characterized by determination of the surface area and Zn^{2+} adsorption method. The surface area for the diatomite was estimated according to Sears' method by weighing 1.5 g of diatomite, and acidifying with dilute hydrochloric acid to pH of 3–3.5 (11). Then 30 g of sodium chloride was added, with stirring, and the volume was brought to 150 mL with distilled water. The solution was titrated with 0.10 N sodium hydroxide. The volume, V , needed to raise the pH from 4 to 9 was recorded. The surface area was estimated from the equation.

$$S (\text{m}^2/\text{g}) = 32 V - 25 \quad (1)$$

The surface area for Mn-diatomite was estimated according to a Zn^{2+} adsorption method in which a 2-g sample was mixed with 25 mL of Zn^{2+} solution (2M NH_4Cl , 0.1073 M ZnCl_2) in a 100-mL flask (12). The mixture was shaken for 24 h and allowed to settle overnight. The supernatant solution was analyzed for Zn^{2+} by using atomic absorption spectroscopy.

All chemicals were Fisher Scientific grade and the glassware was Pyrex type. Laboratory deionized water was used throughout the experiment.

Adsorption Isotherms

Isotherm experiments were conducted by adding 50 mg of adsorbent into a varied concentration of metal ions under investigation [$\text{Pb}(\text{NO}_3)_2$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and CdCl_2] in a cleaned stoppered glass bottle, and shaking in an isothermal shaker at $23 \pm 1^\circ\text{C}$ for 24 h. The volume of these adsorbate solutions was fixed at 50 mL and the particle size of the adsorbent was 45 μm . Blank samples containing adsorbate solution were also prepared. The pH of the adsorbate solution was buffered to 4 by using $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ solution (0.1 M). After equilibrium time, residual Pb^{2+} and Cd^{2+} ions were analyzed by using differential pulse polarography (626 polarecord, model E 505, Metrohm Herisau). Residual Cu^{2+} ions were analyzed by using an atomic absorption spectrophotometer (Pye Unicam SP9).

Adsorption Kinetics

The rate of Pb^{2+} adsorption by diatomite and Mn-diatomite was evaluated to determine the kinetics of adsorption. Samples of diatomite and Mn-di-

atomite (45 μm) of 1.700 g each were agitated separately at 380 rpm with 50 mg/L Pb^{2+} in a batch adsorber (13). The volume of lead solution was 1.7 L and the temperature was $15 \pm 1^\circ\text{C}$. The amount of adsorbent was introduced to the solution, and 5 mL samples were withdrawn using a pipette at specified time intervals. The solution pH was kept at 4.0. Concentrations of the removed Pb^{2+} samples were measured using differential pulse polarography.

Filtration Rate

The effect of chemical modification by manganese oxides on diatomite filtration quality was investigated by using a simple suction-filtration technique. Samples of 3 g each were shaken with 50 mL of water and added to a filtration funnel (6-cm diameter) and allowed to filtrate. An additional 100 mL of water was then added to the funnel and the time needed for filtration was recorded.

RESULTS AND DISCUSSION

The chemical composition of Jordan's diatomite determined by an x-ray diffraction technique is shown in Table 1. It appears that the main constituent of diatomite samples is SiO_2 (72%). The high content of silica in diatomite makes it a good adsorbent for metal ions. This silica structure was impregnated with MnO_2 . The amount of manganese oxides loaded on the surface was 0.38 g/g diatomite, which simulates a birnessite type crystal ($\text{Na}_4\text{Mn}_{14}\text{O}_{27}\cdot 9\text{H}_2\text{O}$) (14). This loading value was calculated from desorbing of Mn^{2+} ion from the Mn-diatomite surface. Moore and Reid, and Sagara et al. reported a value of 0.18 g/g support while other modifications give a value

TABLE I
Typical Spectrographic Analysis of
Jordanian Diatomite

Oxide	Composition (%)
SiO_2	72.50
TiO_2	—
Al_2O_3	11.42
Fe_2O_3	5.81
MnO	—
MgO	0.25
CaO	1.48
Na_2O	7.21
K_2O	0.69
P_2O_5	—

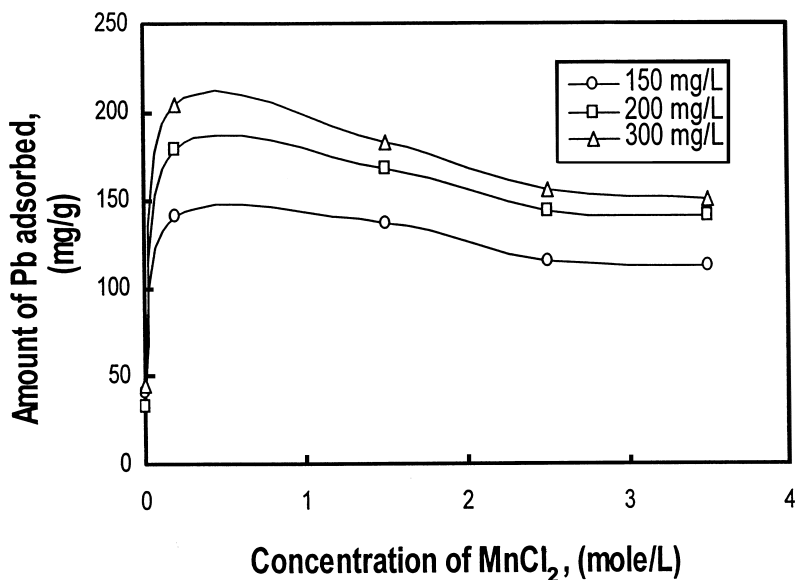


FIG. 1 Effect of MnCl_2 loading on the adsorption of Pb^{2+} onto Mn-diatomite.

of 0.71-g MnO_2 per gram support (8, 10). The amount of manganese oxide loaded on the surface depends on the nature of the surface of the diatomite and on solution acidity and duration of treatment (15). Moore's method has been adopted since this method can achieve high loading and good chemical strength between the support and manganese oxide. Figure 1 shows the effect of the concentration of MnCl_2 on the adsorption of Pb^{2+} onto the Mn-diatomite surface. The maximum amounts of Pb^{2+} adsorbed at different initial concentrations of 150, 200, and 300 mg/L were 148, 188, and 212 mg/g Mn-diatomite, respectively, obtained at the optimum value of 0.2 mole/L MnCl_2 .

The surface area of diatomite and Mn-diatomite calculated from Sears' and Zn^{2+} adsorption methods were 33 and 80 m^2/g , respectively. These methods are developed for silica-based material and manganese oxide surfaces, which depend on surface hydroxyl groups ($-\text{OH}$) for estimating surface area. As observed from these values, Mn-diatomite manifested a high surface area compared with diatomite.

Batch isotherm studies for Pb^{2+} , Cu^{2+} , and Cd^{2+} were conducted at pH 4 for 24 h. Sorption capacity of diatomite and Mn-diatomite are shown in Figs. 2–4 which show that adsorption of Pb^{2+} onto the surface of diatomite and Mn-diatomite has a monolayer of adsorption, while Cu^{2+} and Cd^{2+} have multilayers of adsorption. The equilibrium data were fitted to the best linear form

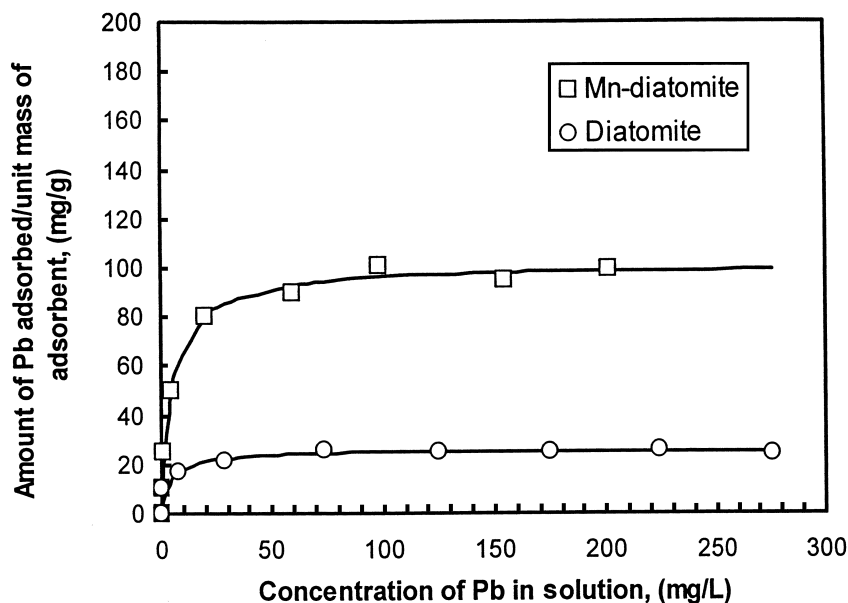


FIG. 2 Adsorption isotherm of Pb^{2+} onto diatomite and Mn-diatomite.

of the Langmuir, Freundlich, Redlich-Peterson's, and BET equations to evaluate the adsorption isotherm parameters

$$\text{Langmuir equation; } \frac{Ce}{qe} = \frac{1}{K} + \frac{a}{K} Ce \quad (2)$$

$$\text{Freundlich equation; } \log qe = \log K + \frac{1}{n} \log Ce \quad (3)$$

$$\text{Redlich-Peterson equation; } \log \left\{ \frac{KCe}{qe} - 1 \right\} = \log a + \beta \log Ce \quad (4)$$

$$\text{BET equation; } \frac{Ce}{(Cs - Ce)qe} = \frac{1}{BQ^0} + \left(\frac{B - 1}{BQ^0} \right) \frac{Ce}{Cs} \quad (5)$$

where Ce is the equilibrium concentration for the adsorbate (mg/L), Cs is the saturation concentration (mg/L), qe is the surface concentration for the adsorbate on adsorbent (mg/g), and a , B , β , K , Q^0 , and n are constants. Figures 5–7 and Table 2 show the best isotherm models and parameters that fit these data.

Using the Langmuir model, the maximum adsorption capacity for diatomite and Mn-diatomite were found to be 24 mg/g diatomite and 99 mg/g Mn-diatomite for Pb^{2+} . Adsorption capacity for Cu^{2+} and Cd^{2+} calculated from the

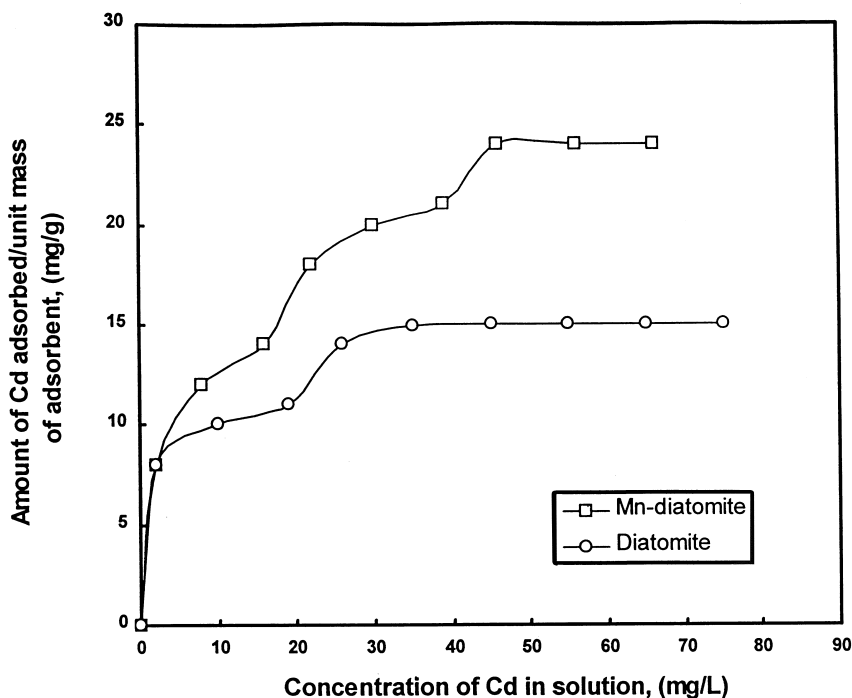


FIG. 3 Adsorption isotherms of Cd^{2+} onto diatomite and Mn-diatomite.

BET model was 21 mg/g diatomite and 51 mg/g Mn-diatomite for Cu^{2+} , and 16 mg/g diatomite and 26 mg/g Mn-diatomite for Cd^{2+} . This enhancement in sorption capacity for Mn-diatomite is due to an increase in the surface area of the modified surface, and to the surface charge of manganese oxides on the diatomite surface. The manganese oxides surface charge in solution was high enough compared with other oxides like SiO_2 , TiO_2 , Al_2O_3 , and FeOOH . This is due to the larger acidity constant of the manganese oxides surface, in which the surface ionizes at low pH and carries a net negative charge larger than for other oxides (16). If it is assumed that SiO_2 is the main active center for adsorption in diatomite, then the surface charges for diatomite and Mn-diatomite at pH 4 were zero and $-40 \mu\text{col}/\text{cm}^2$, respectively (17). This high negative surface charge makes the adsorption process a type of chemisorption or adsorption as reported by James and Stanl (14). The presence of acetate buffer solution could decrease the amount of metal ions adsorbed onto the diatomite and Mn-diatomite surfaces, perhaps because of the competition between the hydrogen ions from the buffer solution and the target metal ions (2).

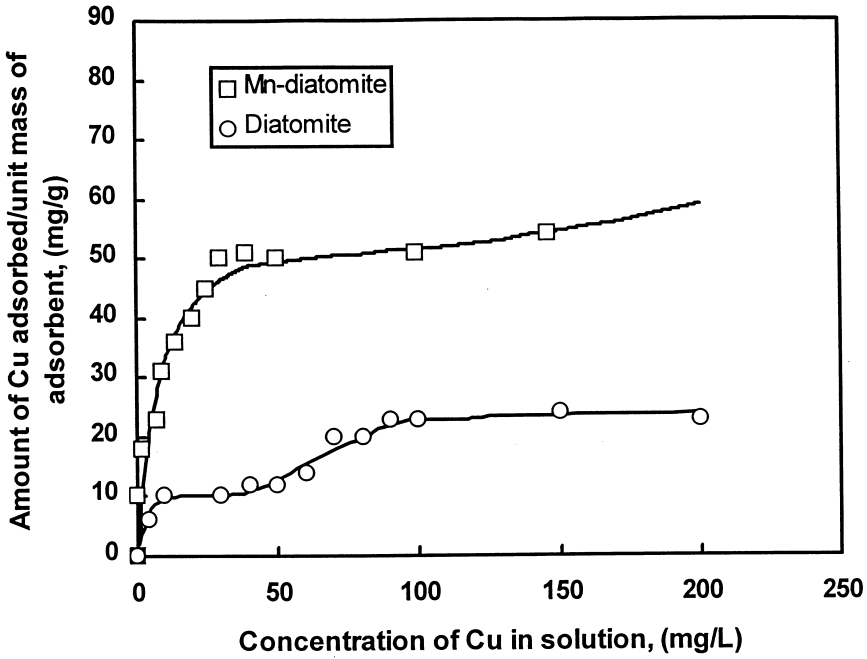


FIG. 4 Adsorption isotherms of Cu^{2+} onto diatomite and Mn-diatomite.

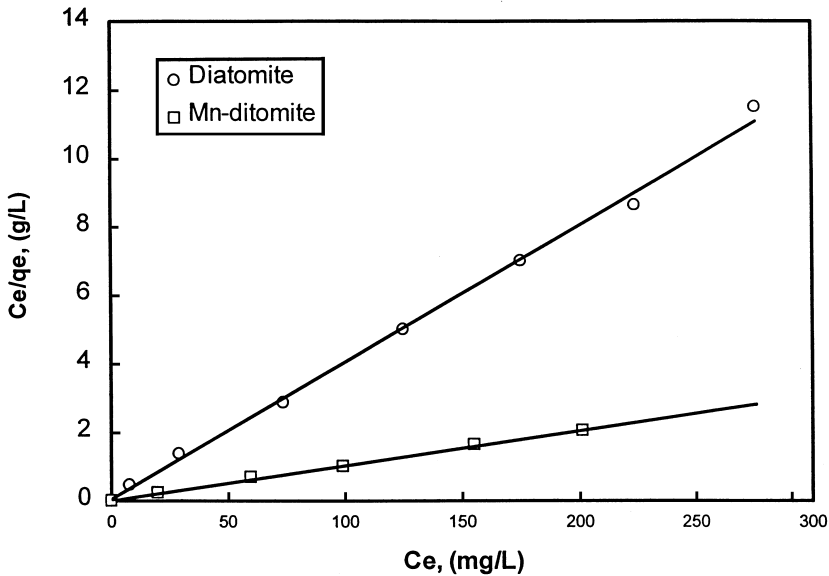


FIG. 5 Linearized form of Langmuir equation for adsorption isotherm of Pb^{2+} onto diatomite and Mn-diatomite.

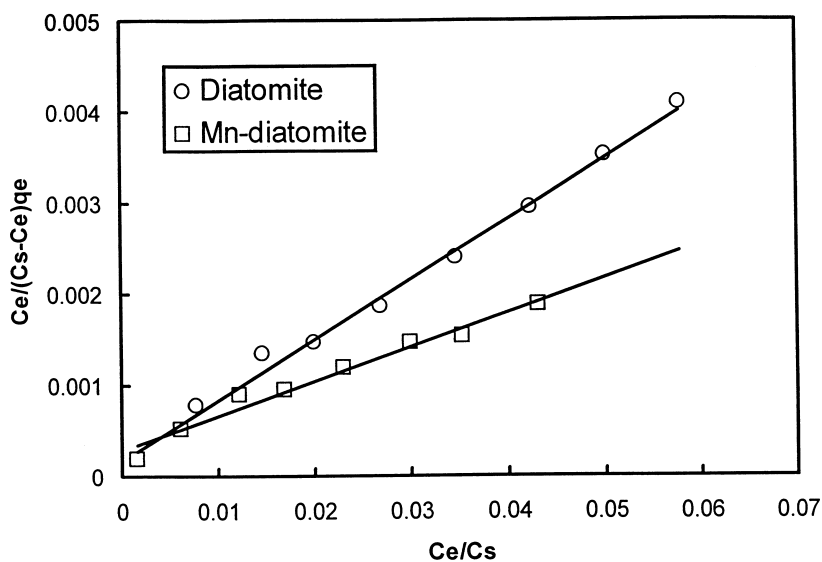


FIG. 6 Linearized form of BET equation for adsorption isotherm of Cd^{2+} onto diatomite and Mn-diatomite.

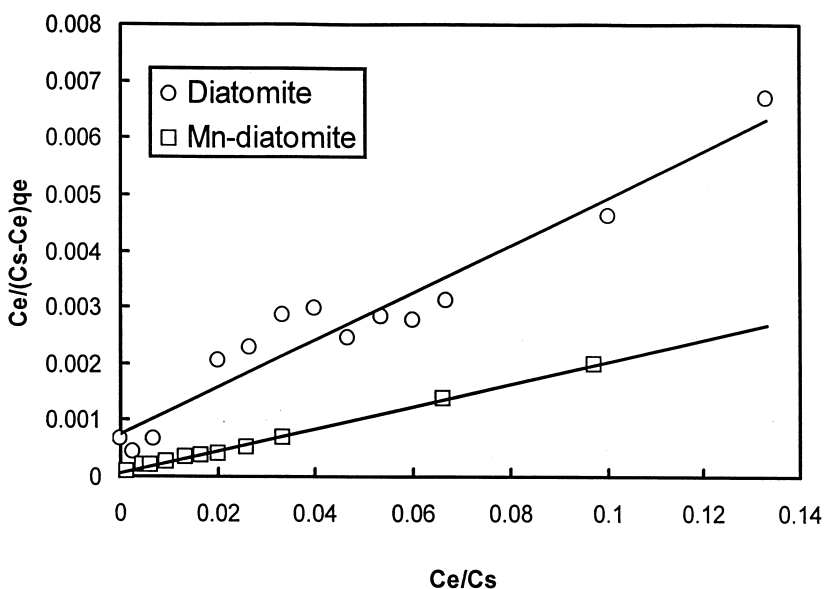


FIG. 7 Linearized form of BET equation for adsorption isotherm of Cu^{2+} onto diatomite and Mn-diatomite.

TABLE 2
Parameters of Isotherm Model that Best Fit the Experimental Data

Metal ion	Isotherm model	Adsorbent	Parameters
Lead	Langmuir	Diatomite	$K = 27.17 \text{ (L/g)}$ $a = 1.09 \text{ (L/mg)}$
		Mn-diatomite	$K = 64.93 \text{ (L/g)}$ $a = 0.66 \text{ (L/mg)}$
Copper	BET	Diatomite	$Q^0 = 21.00 \text{ (mg/g)}$ $C_s = 950.00 \text{ (mg/L)}$ $B = 43.00$
		Mn-diatomite	$Q^0 = 51.00 \text{ (mg/g)}$ $C_s = 1500.00 \text{ (mg/L)}$ $B = 325.00$
Cadmium	BET	Diatomite	$Q^0 = 16.00 \text{ (mg/g)}$ $C_s = 1300.00 \text{ (mg/L)}$ $B = 300.00$
		Mn-diatomite	$Q^0 = 26.00 \text{ (mg/g)}$ $C_s = 1300.00 \text{ (mg/L)}$ $B = 120.00$

However, these metal ions will precipitate as Pb(OH)_2 , Cu(OH)_2 , and Cd(OH)_2 at high pH (18).

Sorption kinetics of lead onto diatomite and Mn-diatomite is shown in Fig. 8. The concentration of the lead in solution declined from 50 mg/L to 2 mg/L

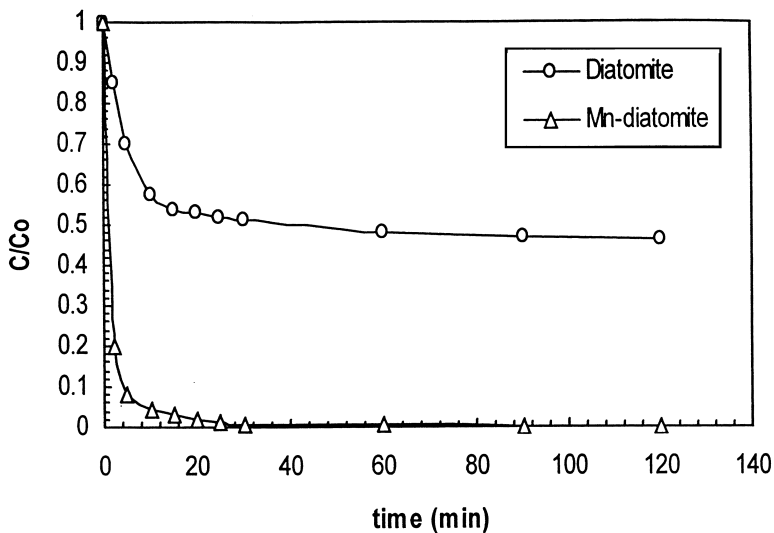


FIG. 8 Adsorption kinetics of Pb^{2+} onto diatomite and Mn-diatomite.

within 10 min when using Mn-diatomite as an adsorbent. The time required to attain equilibrium adsorption was 30 min. It takes more than 3 h to attain equilibrium with diatomite. After 30 min, the concentration of lead in solution reached zero. At this value, the amount of lead adsorbed on the surface of Mn-diatomite was calculated to be 50 mg/g Mn-diatomite. However, this value is expected to be 99 mg/g Mn-diatomite. This is attributed to the Pb^{2+} -free surface of Mn-diatomite, and to the fact that not all of the surface is exposed to Pb^{2+} , as a result of small quantity of initial Pb^{2+} concentration in solution. Also changing the kinetics parameters such as solution temperature, adsorbent quantity, particle size, and stirring speed can significantly change the adsorption equilibrium (2).

The filtration rate of diatomite and Mn-diatomite were measured at 1.53 and 68.57 mL/m²·s, respectively. This high increase in filtration rate could be attributed to the changing of the colloid-chemical properties of diatomite, and as a result, increasing the aggregation of the particle (19).

CONCLUSION

Diatomite and manganese-oxides-modified-diatomite are effective adsorbents for removing Pb^{2+} , Cu^{2+} , and Cd^{2+} ions. The sorption capacity of Mn-diatomite was considerably increased compared to the original material for removing the studied metals. The improved performance for adsorption was attributed to high negative surface charge on the modified surface; furthermore, the increment of surface area is assumed to play a significant role in the overall removal process. It was observed that diatomite with lower loading has a better performance over higher loading adsorbents. A 0.20 M MnCl_2 initial concentration showed the best removal efficiency for Pb^{2+} . The filtration quality of diatomite was significantly increased after modification with Mn-oxides. This treatment was lengthy, and additional studies on preparation time are planned.

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