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Competitive adsorption of Ag^+, Pb^{2+}, Ni^{2+}, and Cd^2 ions on vermiuculite in a binary, ternary, and quaternary mixture was investigated in batch experiments. The effects of the presence of Ag^+, Ni^{2+}, and Cd^{2+} ions on the adsorption of Pb^{2+} ions were investigated in terms of the equilibrium isotherm. Experimental results indicated that Pb^{2+} ions always favorably adsorbed on vermiculite over Ag^+, Ni^{2+}, and Cd^{2+} ions. The adsorption equilibrium data of Pb^{2+} ions better fitted the Langmuir model than the Freundlich model. The results showed that the pseudo-second-order kinetics model was in good agreement with the experimental results for all metal ions, and the adsorption rate among the metal ions followed $Ag^+ > Pb^{2+} > Ni^{2+} > Cd^{2+}$. The desorption and regenration study indicated that vermiculite can be used repeatedly and be suitable for the design of a continuous process.

Keywords competitive adsorption; metal ion; vermiculite

INTRODUCTION

Heavy metals such as lead, nickel, and cadmium are released into aquatic environments largely from various anthropogenic activities and may cause a range of health problems. Silver is widely used in the electroplating, coinage, photographic, and imaging industry. The pollution caused by silver-bearing wastewater has been increasingly serious, leading to the possible exposure of aquatic organisms (1), and then would do harm to humans. So, the removal of heavy metal pollutants from aqueous systems has received a considerable amount of attention. Although some conventional methods can remove heavy metals from their effluents, they are practically not economical (2,3). Numerous approaches have been studied for the development of cheaper and environmentally friendly metal adsorbents such as fly ash (4,5), peat (6,7), microbial biomass (8), biosorbents (9), clays, and related minerals (10–12). Vermiculite is relatively cheap and easily available in China. It consists of unit layers composed from two silica tetrahedral sheets attached to a central magnesium octahedral sheet. Al^{3+} substitution for Si^{4+} in tetrahedral layers, and Al^{3+} and/or Fe^{3+} substitutions for Mg^{2+} in octahedral layers are responsible for the negative charge of the structure. It has characteristics of a permanent negative charge, large surface area, and profound reactive surface sites and has high ability for cation sorption, e.g., a large cation exchange capacity (CEC). Such unique properties enable vermiculite to be a promising ion exchanger for metal ions. The use of vermiculite in wastewater treatment has been studied in recent years and experimental results have shown vermiculite to be a suitable adsorbent for the removal of heavy metals from wastewaters. Bandyopadhyay et al. (13) studied Cu (II) removal by vermiculite from Bihar, India, under conditions of constant ionic strength. They reported 80% Cu (II) removal at pH 6 with an equilibrium time of 12 hours, and that the adsorption followed the Freundlich isotherm. Bors et al. (14) studied iodide, cesium, and strontium adsorption by untreated and a treated-organophilic vermiculite. They concluded that the cation adsorption was substantially reduced for the organophilic vermiculite. Mathialagan et al. (15) used natural vermiculite to achieve 96% removal of Cd (II) from aqueous solutions. They found that the optimum pH for adsorption was 6. The adsorption reached equilibrium in about four hours following Ho's pseudo-second-order model, and the adsorption followed the Freundlich isotherm model. In a recent study (16,17), we have examined the adsorption behaviors of single metal ions like Ag^+, Pb^{2+}, Ni^{2+}, and Cd^{2+} ions on vermiculite and the possible adsorption mechanisms. It was found that vermiculite displayed a strong adsorption capacity toward those metal ions, especially to Pb^{2+} ions.

In general, contaminated water contains more than one heavy metal. It is thus of more industrial interest to study the adsorption equilibria and kinetics of multi heavy metal ions. As a continuation of our effort on developing vermiculite as an adsorbent for metals removal from wastewater and drinking water, we attempted to examine the competitive adsorption properties of metals like Ag^+, Pb^{2+}, Ni^{2+},

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and Cd^{2+} on vermiculite in binary, ternary, and quaternary systems in this work.

EXPERIMENTAL PROCEDURE

Adsorbent

Vermiculite used in this work was supplied by the Xinjiang Yuli Xinlong Vermiculite Company, China. Vermiculite was initially rinsed with deionzed water several times, and dried in an oven at 80°C. The X-ray diffraction pattern for Mg-saturated vermiculite (Fig. 1) shows strong peaks at 1.45 and 1.28 nm, the former corresponding to vermiculite and the latter to a mica-type mineral, indicating that the sample was a mixture of clay minerals. The peak heights under the (001) basal reflections of the identified clay minerals were used to quantitative analysis (18), and the vermiculite component was 62%. Previous authors also observed these peaks in ethyleneglycolated vermiculite from Vali (19) interpreting the peak at 1.43 nm as vermiculite and the peak at 1.2 nm as a biotite–vermiculite mixed layer mineral with 50–70% biotite component. The chemical composition of the vermiculite was performed by X-ray fluorescence (XRF, ARL 9800 XP, Switzerland), the result is SiO_2, 37.01%; Al_2O_3, 10.63%; MgO, 22.82%; K_2O, 4.81%; CaO, 2.00%; Na_2O, 1.34%; TiO_2, 1.39%; Fe_2O_3, FeO, 6.45%; Cr_2O_3, 0.34%; MnO, 0.05%; BaO, 0.23%; loss on ignition, 12.92 wt%. The pH was determined in 1% vermiculite using a pH glass electrode. The surface area of the vermiculite was determined with the Nova 2200 apparatus (Quantachrome Corp.) according to the BET method. The cation exchange capacity (CEC) was determined by the method of ammonium acetate (20). The selected physicochemical properties of the vermiculite are given in Table 1.

Apparatus

The X-Ray diffraction experiments were performed with X'Pert Pro MPD X-ray diffractometer (Philips, Netherlands). The voltage and anode current were 40 kV and 40 mA, respectively. The Cu $K_\alpha = 0.15405$ nm and continuous scanning mode were 0.01 step size. An atomic absorption spectrometer (AAS, Spectr AA 220FS, Varian, USA) was used for the determination of metal ion concentration.

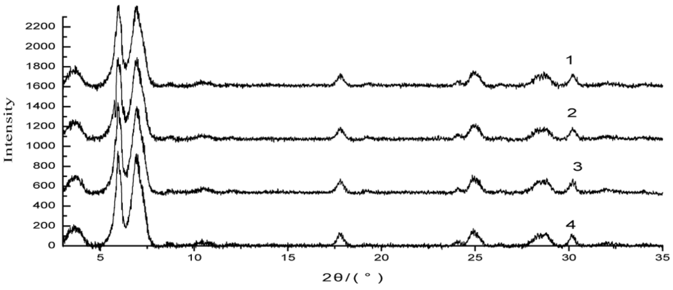


FIG. 1. Four XRD patterns of Mg-saturated vermiculite.

TABLE 1
Physical and chemical characteristics of vermiculite

Parameter	Value
pH (1% solution)	5.5
Density ($g\,cm^{-3}$)	2.3
Hardness	1.5
Particle size (μm)	160
S_{BET} ($m^2\,g^{-1}$)	12.8
cation exchange capacity (mmol/100 g)	73.30

Adsorption of Metal Ions

Ag^+, Pb^{2+}, Ni^{2+}, and Cd^{2+} solutions were prepared from analytical grade $AgNO_3$, $Pb(NO_3)_2$, $Ni(NO_3) \cdot 6H_2O$, and $Cd(NO_3) \cdot 4H_2O$. All other chemicals were of analytical grade.

The adsorption equilibrium measurements of binary, ternary, and quaternary metal ion systems were carried out at 20°C by agitating 50 ml metal ions solution of different initial concentration with $4.0\,g\,l^{-1}$ vermiculite. Table 2 shows the initial concentration of the metals in the binary, ternary, and quaternary systems that have been investigated. To avoid metal precipitation at high pH and the competition by hydrogen ions at low pH, the pH value of the solution was maintained at 5.0 by nitric acid. The mixture was agitated for 60 minute, which was found to be sufficient to attain adsorption equilibrium, and the stirring rate was 1200 r/min during the experiments. The equilibrium concentration of the metal ions was measured by using an atomic absorption spectrometer. The amount of metal adsorbed, Q_e was calculated with

$$Q_e = \frac{V_L(C_0 - C_e)}{1000\,m} \tag{1}$$

where C_0 is the initial concentration of metal ions ($mg\,l^{-1}$), C_e is the concentration of metal ions at equilibrium ($mg\,l^{-1}$), V_L refers to the volume of solution (ml), and m is the mass of vermiculite sample (g).

Batch kinetic measurements were studied by agitating 50 ml solution containing multiple metal ions of different initial concentration (Ag^+: $90\,mg\,l^{-1}$, Pb^{2+}: $80\,mg\,l^{-1}$, Ni^{2+}: $92\,mg\,l^{-1}$, Cd^{2+}: $90\,mg\,l^{-1}$) with $4.0\,g\,l^{-1}$ vermiculite at pH 5.0. The stirring rate was 1200 r/min during the experiments. Samples were collected at 1st, 5th, 10th, 20th, 30th, and 60th minute. The amount of metal ions adsorbed at time t, Q_t, was calculated from the mass balance between C_0 and the concentration at time t, C_t.

Adsorption of metal ions on the walls of glass flasks and plastic bottles was found to be negligible by running blank

TABLE 2
Initial concentration ranges of the metals in the multiple-metal systems

System	Metal's Ratio	Initial concentration (mmol l^{-1})				
		1	2	3	4	5
Pb^{2+}/Ag^{+}	1:1.2	0.13(Pb) + 0.16(Ag)	0.33(Pb) + 0.39(Ag)	0.65(Pb) + 0.78(Ag)	0.98(Pb) + 1.17(Ag)	1.3(Pb) + 1.6(Ag)
Pb^{2+}/Ni^{2+}	1:2.4	0.13(Pb) + 0.31(Ni)	0.33(Pb) + 0.76(Ni)	0.65(Pb) + 1.53(Ni)	0.98(Pb) + 2.29(Ni)	1.3(Pb) + 3.1(Ni)
Pb^{2+}/Cd^{2+}	1:1.1	0.13(Pb) + 0.14(Cd)	0.33(Pb) + 0.36(Cd)	0.65(Pb) + 0.72(Cd)	0.98(Pb) + 1.08(Cd)	1.3(Pb) + 1.4(Cd)
$Pb^{2+}/Ag^{+}/Ni^{2+}$	1:1.2:2.4	0.13(Pb) + 0.16(Ag) + 0.31(Ni)	0.33(Pb) + 0.39(Ag) + 0.76(Ni)	0.65(Pb) + 0.78(Ag) + 1.53(Ni)	0.98(Pb) + 1.17(Ag) + 2.29(Ni)	1.3(Pb) + 1.6(Ag) + 3.1(Ni)
$Pb^{2+}/Ag^{+}/Cd^{2+}$	1:1.2:1.1	0.13(Pb) + 0.16(Ag) + 0.14(Cd)	0.33(Pb) + 0.39(Ag) + 0.36(Cd)	0.65(Pb) + 0.78(Ag) + 0.72(Cd)	0.98(Pb) + 1.17(Ag) + 1.08(Cd)	1.3(Pb) + 1.6(Ag) + 1.4(Cd)
$Pb^{2+}/Ni^{2+}/Cd^{2+}$	1:2.4:1.1	0.13(Pb) + 0.31(Ni) + 0.14(Cd)	0.33(Pb) + 0.76(Ni) + 0.36(Cd)	0.65(Pb) + 1.53(Ni) + 0.72(Cd)	0.98(Pb) + 2.29(Ni) + 1.08(Cd)	1.3(Pb) + 3.1(Ni) + 1.4(Cd)
$Pb^{2+}/Ag^{+}/Ni^{2+}/Cd^{2+}$	1:1.2:2.4:1.1	0.13(Pb) + 0.16(Ag) 0.31(Ni) + 0.14(Cd)	0.33(Pb) + 0.39(Ag) + 0.76(Ni) + 0.36(Cd)	0.65(Pb) + 0.78(Ag) + 1.53(Ni) + 0.72(Cd)	0.98(Pb) + 1.17(Ag) + 2.29(Ni) + 1.08(Cd)	1.3(Pb) + 1.6(Ag) + 3.1(Ni) + 1.4(Cd)

experiments. Each experiment was carried out in duplicate and the average results were presented in this work.

Desorption and Regeneration Experiments

The adsorption experiment was carried out by agitating 50 ml metal ions of different initial concentration (Ag^{+}: 16.87 mg l^{-1}, Pb^{2+}: 26.97 mg l^{-1}, Ni^{2+}: 17.91 mg l^{-1}, Cd^{2+}: 16.21 mg l^{-1}) with 4.0 g l^{-1} vermiculite at pH 5.0 for 60 min. Then, vermiculite adsorbed Ag^{+}, Pb^{2+}, Ni^{2+}, and Cd^{2+} were separated out by filtration and dried at 60°C for 24 h. In our previous experiments for the single metal desorption (17), HNO_3 has been proved to be the optimum desorbing agent. So the desorption test was conducted by using HNO_3 in the present experiment. The vermiculite adsorbed heavy metal ions were stirred at 1200 r/min in 1 mol l^{-1} HNO_3 solutions at 4.0 g l^{-1} for 60 min at room temperature. For regeneration studies, HNO_3-desorbed vermiculites were rinsed with deionized water several times to neutral pH. Then, the vermiculite were dried at 60°C for 24 h and re-used in the subsequent adsorption-desorption cycles for five times.

RESULTS AND DISCUSSION

Speciation of Aqueous Metals Ions

The speciation of metal ions in an aqueous solution significantly affects their interaction with a solid adsorbent. So the speciation of metals as a function of pH was studied using the computer program Visual MINTEQ, Version 2.30 (21). Figure 2 shows the speciation of lead, silver, nickel, and cadmium as a function of pH at the metal ionic concentration of 0.5 mmol l^{-1}. As depicted in Fig. 2, lead appears predominantly as Pb^{2+} species at $pH < 6.0$, after which its concentration decreases. Concentrations of various Pb hydroxyl species such as $Pb(OH)_2$ (aq), $Pb(OH)_3^{-}$, $Pb_3(OH)_4^{2+}$, and $PbOH^{+}$, increases at $pH > 6.0$ in the solutions. Silver appears predominantly as Ag^{+} species at $pH < 10.0$. Concentrations of Ag(OH) (aq) and $Ag(OH))_2^{-}$ increases at $pH > 10.0$. Similarly, Nickel and Cadmium appear predominantly as Ni^{2+} and Cd^{2+} at $pH < 8$. Therefore, under the experimental conditions used in this study, Pb^{2+}, Ag^{+}, Ni^{2+}, Cd^{2+} are believed to be the major species at pH 5.0 in the multi-component systems.

Adsorption Isotherms of Pb^{2+} in the Presence of Ni^{2+}, Cd^{2+}, and/or Ag^{+}

The effects of the presence of Ni^{2+}, Cd^{2+}, and/or Ag^{+} on the adsorption of Pb^{2+} is quantitatively demonstrated in Fig. 3. It can be seen that Pb^{2+} ions always favorably adsorb on vermiculite over Ag^{+}, Ni^{2+}, and Cd^{2+} ions in Pb^{2+}/Ag^{+}, Pb^{2+}/Ni^{2+}, and Pb^{2+}/Cd^{2+} binary mixture systems. It is also seen from Figs. 3a and 3b that at low equilibrium concentrations of Pb^{2+}, the adsorption amounts of Ag^{+} and Ni^{2+} reach a maximum and then level off with the increase in equilibrium concentration,

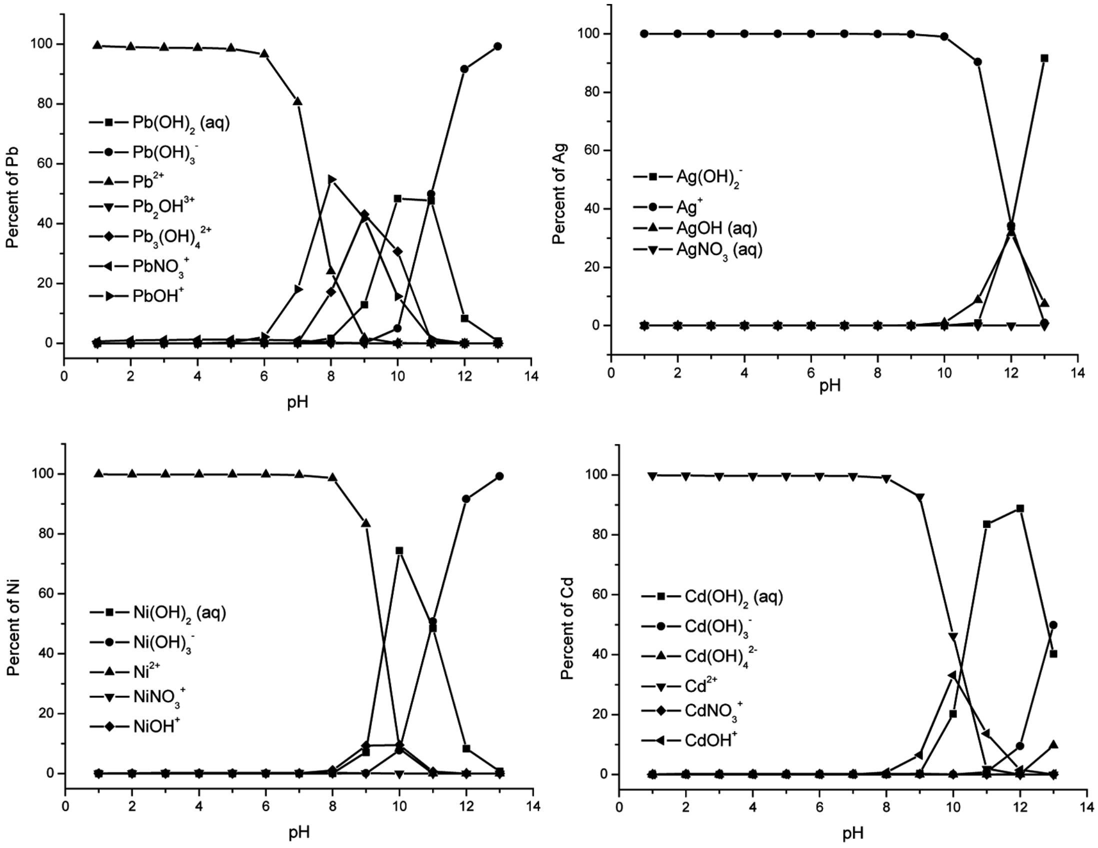


FIG. 2. Aqueous speciation of Pb, Ag, Ni, and Cd as a function of pH.

while the adsorption amount of Pb^{2+} increased as the equilibrium concentration of Pb^{2+} was increased. This phenomenon can be explained by two kinds of binding sites onto vermiculite: ion exchange at the permanently charged sites on the silanol faces, and complexation to −Al−OH, −Si−OH, which occur at the crystal edges. Because of the high cation exchange capacity (see Table 1), the vermiculite has strong ion exchange ability. At low concentrations of the metal ions, Pb^{2+} species occupies parts of the ion-exchange sites and complexation sites of vermiculite so that some Ag^{+} or Ni^{2+} ions are able to adsorb on vermiculite. With increasing concentration, Pb^{2+} ions in solution compete with the other metal ions and displace those Ag^{+} or Ni^{2+} ions having adsorbed on vermiculite, resulting in a decrease of the amount adsorbed of Ag^{+} or Ni^{2+}. This characterized the competitive adsorption between Pb^{2+} and Ag^{+} or Ni^{2+}, where Ag^{+} and Ni^{2+} are weaker competitive species. Figure 3c shows that in the Pb^{2+}/Cd^{2+} binary systems, Pb^{2+} favorably adsorbed on vermiculite over Cd^{2+}. In the ternary and quaternary systems (see Figs. 3d, 3e, 3f, and 3 g), the competitive adsorption isotherms of Pb^{2+} with Ag^{+}, Ni^{2+}, and Cd^{2+} ions exactly duplicate those in the binary Pb^{2+}/Ag^{+}, Pb^{2+}/Ni^{2+}, and Pb^{2+}/Cd^{2+} systems.

The preferential adsorption of Pb^{2+} to other metals is in agreement with the results of Li et al. (22) who found that simultaneous competition onto carbon nanotubes favors Pb^{2+} in compared to Cu^{2+} and Cd^{2+}. The observed competitive adsorption ability differences from one metal to another and from one system to another are related to many factors, such as ion charges, hydrated ionic radius and hydration energy of the metals (23,24). In the multicomponent systems, Ag^{+}, Pb^{2+}, Ni^{2+}, Cd^{2+} are the major species at pH 5.0. The major preference of divalent ions over monovalent ones can be explained by an increased electrostatic contribution to the Gibbs free energy of adsorption for the former. At the same ionic charge, Pb^{2+} species with the lowest hydration energy (1481 kJ/mol (25)) among the three metals assayed, followed by Cd^{2+} (1807 kJ/mol (25)) and Ni^{2+}(2106 kJ/mol (26)), may facilitate the hydrated Pb^{2+} ions more easily entering the channel of vermiculite than the other two metals. On the other hand, a preferential adsorption of Pb^{2+} (hydrated ionic radius is 0.2655 nm (25)) in comparison to Cd^{2+} (hydrated ionic radius is 0.2305 nm (25)) and Ni^{2+} (hydrated ionic radius is 0.2025 nm (26)) can be attributed to the fact that the hydrated ionic radius of both Cd^{2+} and Ni^{2+} are smaller than the hydrated ionic radius of Pb^{2+} by

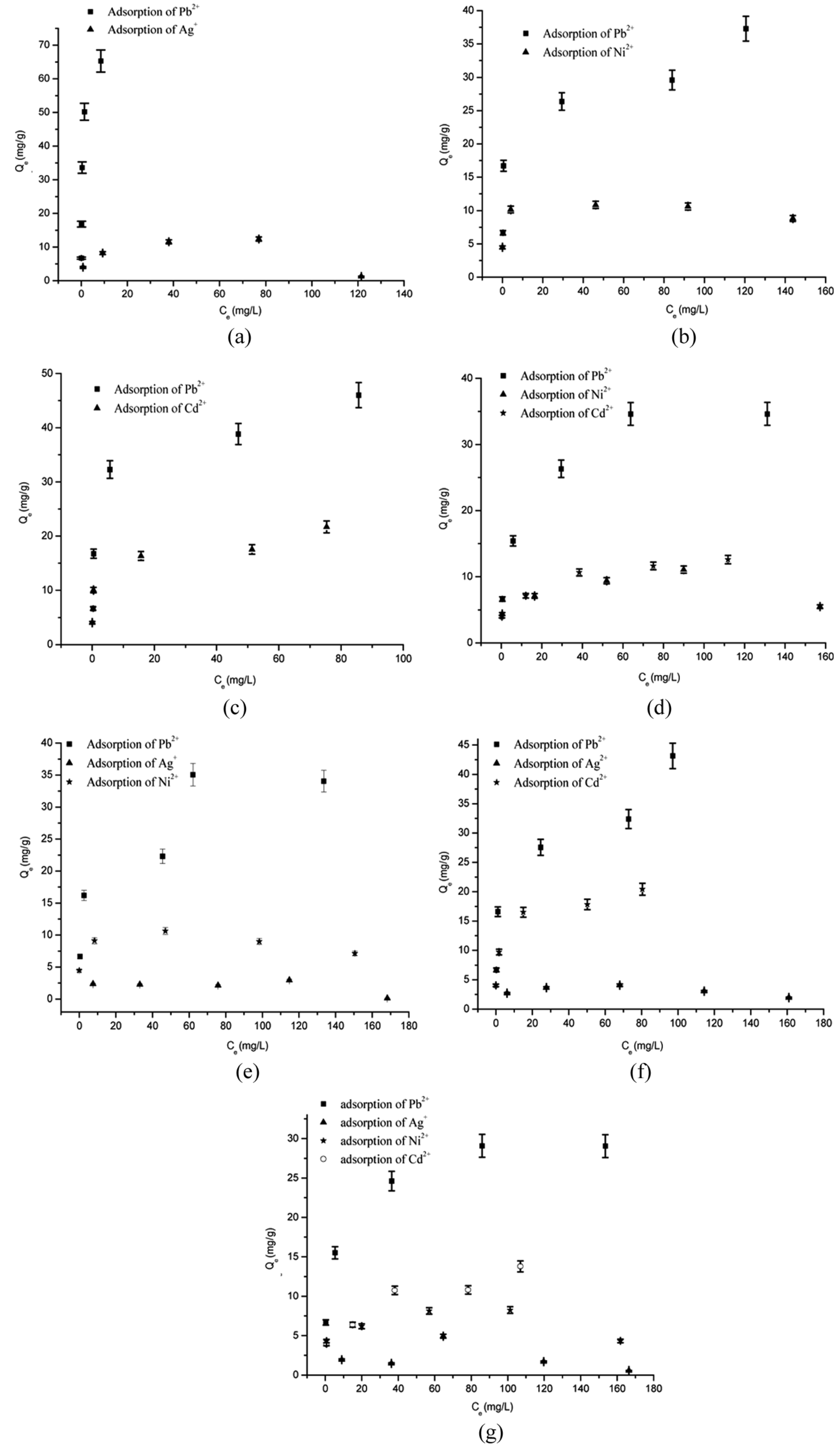


FIG. 3. Adsorption isotherms of lead on vermiculite in the presence of other metals from binary, ternary and quaternary systems. (a) Pb^{2+}/Ag^{+}, (b) Pb^{2+}/Ni^{2+}, (c) Pb^{2+}/Cd^{2+}, (d) $Pb^{2+}/Ni^{2+}/Cd^{2+}$, (e) $Pb^{2+}/Ag^{+}/Ni^{2+}$, (f) $Pb^{2+}/Ag^{+}/Cd^{2+}$, and (g) $Pb^{2+}/Ag^{+}/Ni^{2+}/Cd^{2+}$.

TABLE 3
Langmuir and Freundlich parameters for Pb^{2+} in binary, ternary and quaternary system

Metal species	Langmuir			Freundlich		
	Q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	K_F	N	R^2
Pb^{2+} in Pb^{2+}/Ag^{+}	68.35	2.414	0.9995	35.81	2.427	0.8628
Pb^{2+} in Pb^{2+}/Ni^{2+}	36.32	0.2051	0.9728	12.69	4.647	0.8386
Pb^{2+} in Pb^{2+}/Cd^{2+}	45.68	0.3931	0.9919	14.66	3.597	0.8182
Pb^{2+} in $Pb^{2+}/Ag^{+}/Ni^{2+}$	34.98	0.1467	0.9626	9.840	3.745	0.9157
Pb^{2+} in $Pb^{2+}/Ag^{+}/Cd^{2+}$	40.52	0.1880	0.9546	12.13	3.831	0.9190
Pb^{2+} in $Pb^{2+}/Ni^{2+}/Cd^{2+}$	35.70	0.1612	0.9954	8.610	3.195	0.9826
Pb^{2+} in $Pb^{2+}/Ag^{+}/Ni^{2+}/Cd^{2+}$	29.82	0.2496	0.9984	9.528	4.098	0.9810

the cation exchange theory. Many studies (27–29), considering the sorption of heavy metals (i.e., Pb, Cu, Zn, Cd, and Ni) added to pure minerals, have inferred a higher Pb selectivity relative to other heavy metals.

In the present study, the Langmuir and Freundlich adsorption model were used to predict Pb^{2+} adsorption isotherms in the presence of Ag^{+}, Ni^{2+}, Cd^{2+}. The Langmuir adsorption model is valid for monolayer sorption due to a surface of a finite number of identical sites and is expressed in the linear form as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \tag{2}$$

where Q_{max} is the maximum adsorbed material in mg per g of the adsorbent and b is the Langmuir isotherm constant.

The Freundlich adsorption isotherm describes the heterogeneous surface energies by multiplayer adsorption and is expressed in linear form as:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \tag{3}$$

where K_F and $1/n$ are Freundlich constants related to the adsorption capacity and the adsorption efficiency, respectively.

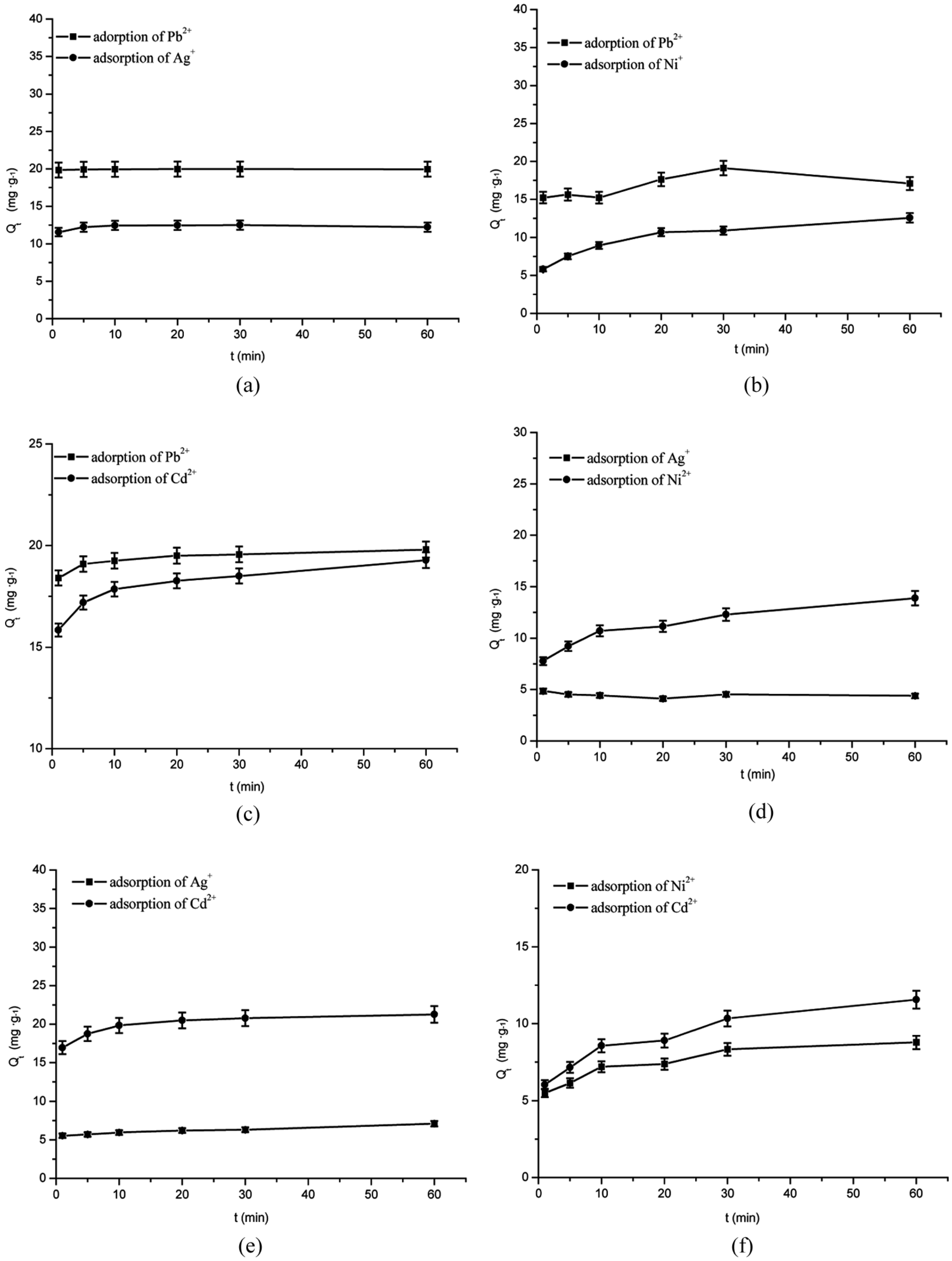
The Langmuir and Freundlich model parameters of Pb^{2+} adsorption on vermiculite in the binary, ternary and quaternary systems are tabulated in Table 3. As shown in Table 3, the results indicated that the adsorptions follow both the Langmuir model and Freundlich model. Yet, the correlation coefficient of the Langmuir curve was distinctly higher than that of the Freundlich curve. This observation implies that monolayer sorption, as well as heterogeneous surface conditions, may coexist under the applied experimental conditions. Hence, the overall sorptions of Pb^{2+} on the vermiculite in the presence of Ag^{+}, Ni^{2+}, Cd^{2+} are complex, involving more than one mechanism, such as ion exchange, surface complexation, and so on. The adsorpton capacity (Q_{max}) of different adsorbents to adsorb Pb^{2+} ion in multi-component solutions under different environmental conditions as reported in the literature is compared in Table 4. It may be seen that the Q_{max} value differs widely for different adsorbents. A comparison of Q_{max} values shows that the vermiculite exhibits a reasonable capacity for Pb^{2+} ion adsorption from multi-component solutions.

Adsorption Kinetics

The competitive adsorption kinetics of the metal ions in binary mixtures Pb^{2+}/Ag^{+}, Pb^{2+}/Ni^{2+}, Pb^{2+}/Cd^{2+}, Ag^{+}/Ni^{2+}, Ag^{+}/Cd^{2+}, and Ni^{2+}/Cd^{2+}, in ternary mixtures $Pb^{2+}/Ag^{+}/Ni^{2+}$, $Pb^{2+}/Ag^{+}/Cd^{2+}$, $Pb^{2+}/Ni^{2+}/Cd^{2+}$, and $Ag^{+}/Ni^{2+}/Cd^{2+}$ and in a quaternary mixture $Pb^{2+}/Ag^{+}/Ni^{2+}/Cd^{2+}$ on vermiculite are shown in Figs. 4 and 5. It can be seen that the adsorption of Ag^{+} is rapid, essentially attaining equilibrium within 10 min. On the other hand, the adsorption of Ag^{+} behaves strangely – reaching a

TABLE 4
Adsorption capacity of various adsorbents for the adsorption Pb^{2+} as reported in literature

Adsorbent	System	Pb Q_{max} (mg g^{-1})	References
Carbon aeroger	Pb/Hg	23.31	30
Carbon aeroger	Pb/Cd	12.38	30
Carbon aeroger	Pb/Hg/Cd	8.40	30
Danish peat	Pb/Cd	78.66	31
Danish peat	Pb/Cu	58.79	31
Danish peat	Pb/Cu/Cd	26.60	31
Heilongjiang peat	Pb/Cd	48.44	31
Heilongjiang peat	Pb/Cu	20.02	31
Heilongjiang Peat	Pb/Cu/Cd	26.5	31
Multiwalled carbon nanotubes	Pb/Cu/Cd	34.01	22



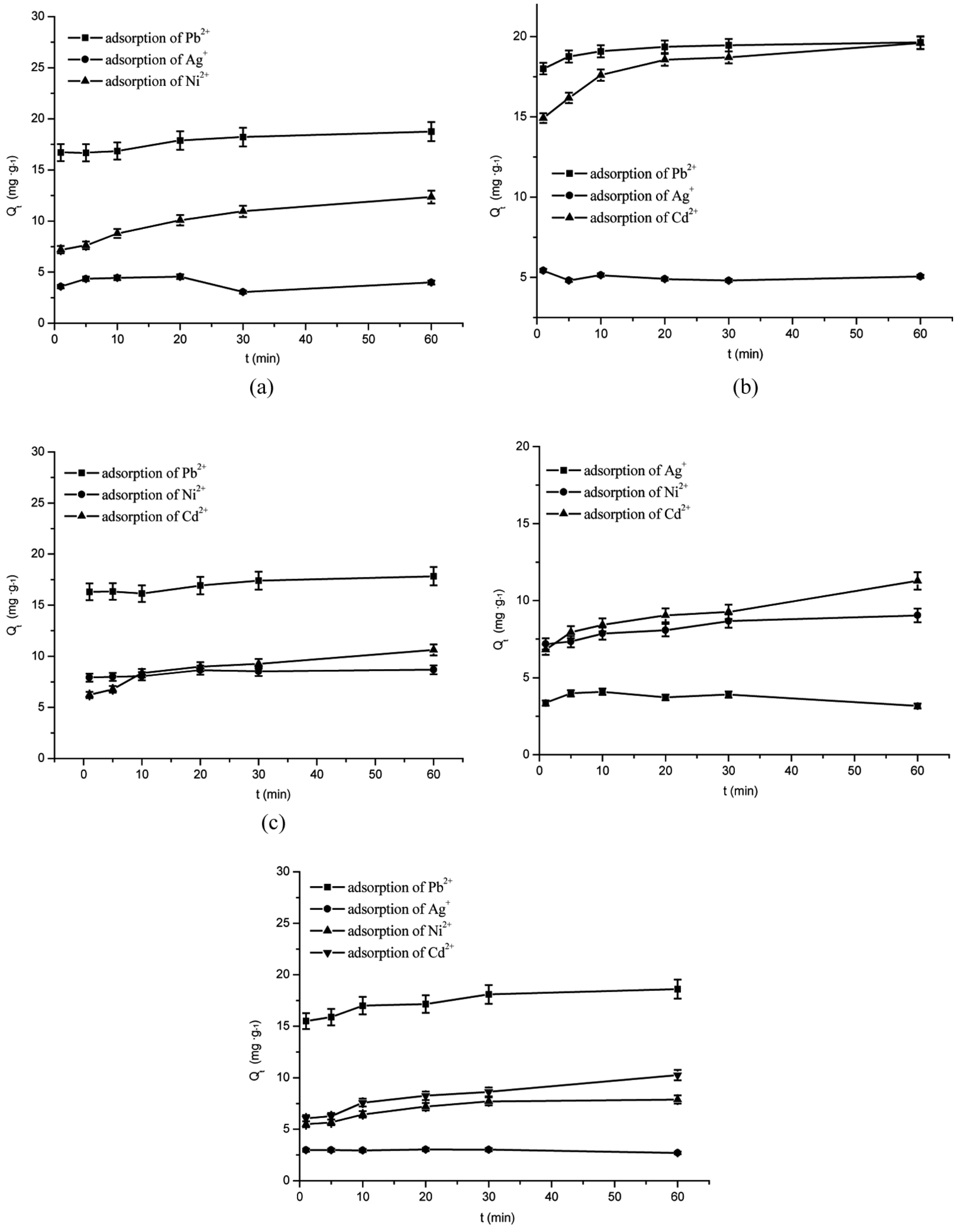
(a) (b)

(c) (d)

(e) (f)

FIG. 4. Competitive adsorption kinetics of binary metal ions on vermiculite: (a) Pb^{2+}/Ag^{+}, (b) Pb^{2+}/ Ni^{2+}, (c) Pb^{2+}/ Cd^{2+}, (d) Ag^{+}/Ni^{2+}, (e) Ag^{+}/ Cd^{2+}, and (f) Ni^{2+}/Cd^{2+}.

maximum at the early stage and then decreasing as the adsorption time is prolonged, see Fig. 5a. Such an adsorption behavior indicates the possible underlying adsorption mechanism: upon contact of the liquid with the solid, Pb^{2+}, Ag^{+}, and Ni^{2+} ions all adsorb on the surface of vermiculite. Because of the stronger affinity of vermiculite toward Pb^{2+} and Ni^{2+} over Ag^{+}, the former competitively replace Ag^{+} ions that has previously adsorbed onto vermiculite, resulting in the desorption of Ag^{+} ions into the solution. Similar adsorption profiles are observed in the other binary systems, Fig. 4b and 4d. From Fig. 5e, it indicates that the adsorption affinity of Pb^{2+} to vermiculite is the highest among the four metals studied, followed by that of Cd^{2+}, then Ni^{2+}, and then Ag^{+}.



(a) (b)

(c)

(e)

FIG. 5. Competitive adsorption kinetics of ternary and quaternary metal ions on vermiculite: (a) $Pb^{2+}/Ag^{+}/Ni^{2+}$, (b) $Pb^{2+}/Ag^{+}/Cd^{2+}$, (c) $Pb^{2+}/Ni^{2+}/Cd^{2+}$, (d) $Ag^{+}/Ni^{2+}/Cd^{2+}$, and (e) $Pb^{2+}/Ag^{+}/Ni^{2+}/ Cd^{2+}$.

In a mixed metals system, competition among H^+, Na^+, K^+, and the heavy metal ions for the ion exchange and adsorption sites of vermiculite may be cooperative, which can be described by the following three general equations, where S are the ion exchange sites and $S-OH$ are the surface functionalities of vermiculite, such as −Al,OH, −Ri,OH. M^*, M^{2+} refers to the ion-changeable metal ions, i.e., Na^+, K^+, and Ca^{2+}, Mg^{2+}. A^+ represents Ag^+, and B^{2+} represents heavy metal species with a stronger affinity to vermiculite than Ag^+.

Various models can describe the kinetic data. Most of these have been reported as pseudo-first-order and some as pseudo-second-order, and Elovich models.

The pseudo-first-order kinetic model known as the Lagergren equation (32):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \tag{4}$$

where Q_t and Q_e are the amounts of metal ions adsorbed at time t and equilibrium (mg g^{-1}), respectively, and k_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}).

The pseudo-second-order kinetic model: (7)

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{e,2}^2} + \frac{t}{Q_{e,2}} \tag{5}$$

where k_2 is the equilibrium rate constant of pseudo-second-order sorption (g mg^{-1} min^{-1}).

The sorption data may also be analyzed using the Elovich equation, which has the linear form (33):

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{6}$$

where α is the initial sorption rate constant (mg g^{-1} min^{-1}), and β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}).

The kinetics constants for the competitive adsorption of metal ions on vermiculite are tabulated in Table 5. It can be seen that the pseudo-second-order kinetic model fits the experimental data better than the other kinetic models, and the correlation coefficients obtained for the pseudo-second-order kinetic model are greater than 0.99 for all metals. Lu Lv et al. (24) reported that the k_2 for Pb^{2+}

TABLE 5
The kinetics constants for metal species adsorption on vermiculite in multi-component systems

		Pseudo-first-order equation		Pseudo-second-order equation			Elovich equation		
Mixed metal system	Metal species	k_1 (min^{-1})	R^2	$Q_{e,2}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	α (mg g^{-1} min^{-1})	β(g min^{-1})	R^2
Pb^{2+}/Ag^{+}	Pb^{2+}	0.04461	0.3995	19.96	11.51	0.9999	/	32.31	0.1249
	Ag^{+}	0.00373	0.0044	12.24	33.35	0.9998	4.645×10^{26}	5.350	0.3953
Pb^{2+}/ Ni^{2+}	Pb^{2+}	0.01124	0.3793	20.06	0.02859	0.9977	1.947×10^{8}	1.305	0.5052
	Ni^{2+}	0.05012	0.9379	13.04	0.02095	0.9940	41.66	0.5967	0.8729
Pb^{2+}/Cd2+	Pb^{2+}	0.05763	0.9062	19.84	0.2032	0.9999	2.908×10^{23}	2.986	0.1867
	Cd^{2+}	0.04727	0.9049	19.38	0.06586	0.9995	2.274×10^{8}	1.226	0.5944
Ag^{+}/Ni^{2+}	Ag^{+}	/	0.01601	4.398	0.4241	0.9989	/	/	0.0036
	Ni^{2+}	0.04259	0.9522	14.23	0.02259	0.9931	228.8	0.6887	0.8549
Ag^{+}/ Cd^{2+}	Ag^{+}	0.02432	0.9642	7.147	0.07632	0.9955	1.512×10^{6}	2.885	0.5146
	Cd^{2+}	0.07601	0.9570	21.43	0.06828	0.9998	7.182×10^{6}	0.9200	0.4858
Ni^{2+}/Cd^{2+}	Ni^{2+}	0.06286	0.9269	9.009	0.04775	0.9967	430.7	1.198	0.8405
	Cd^{2+}	0.04797	0.9434	11.96	0.02277	0.9911	83.04	0.7452	0.9359
$Pb^{2+}/Ag^{+}/Ni^{2+}$	Pb^{2+}	0.05048	0.9457	18.90	0.06672	0.9996	1.453×10^{7}	1.101	0.5588
	Ag^{+}	/	0.0926	3.830	33.41	0.9692	/	206.2	0.0349
	Ni^{2+}	0.04619	0.9917	12.77	0.03337	0.9932	184.0	0.7752	0.8878
$Pb^{2+}/Ag^{+}/Cd^{2+}$	Pb^{2+}	0.07535	0.9616	19.80	0.2036	0.9999	7.706×10^{18}	2.456	0.4845
	Ag^{+}	0.00300	0.03449	5.036	0.7231	0.9991	/	/	0.1578
	Cd^{2+}	0.05891	0.9286	19.68	0.04731	0.9994	2.934×10^{5}	0.8425	0.6778
$Pb^{2+}/Ni^{2+}/Cd^{2+}$	Pb^{2+}	0.04433	0.8592	17.96	0.07783	0.9996	4.322×10^{17}	2.614	0.2574
	Ni^{2+}	0.08136	0.5206	8.727	0.06587	0.9998	2.556×10^{15}	4.742	0.5762
	Cd^{2+}	0.04195	0.9162	10.86	0.03157	0.9942	225.9	0.9251	0.8272
$Ag^{+}/Ni^{2+}/Cd^{2+}$	Ag^{+}	/	0.1791	3.169	187.5	0.9994	/	/	0.0025
	Ni^{2+}	0.05298	0.9350	9.157	0.07873	0.9986	1.201×10^{6}	2.138	0.4768
	Cd^{2+}	0.02570	0.9025	11.43	0.02700	0.9867	767.2	1.032	0.8876
$Pb^{2+}/Ag^{+}/Ni^{2+}/Cd^{2+}$	Pb^{2+}	0.05812	0.9258	18.79	0.05532	0.9993	1.734×10^{8}	1.268	0.5092
	Ag^{+}	/	0.2522	2.709	136.3	0.9999	/	/	0.1866
	Ni^{2+}	0.03416	0.9634	8.094	0.05263	0.9987	1444	1.499	0.7921
	Cd^{2+}	0.09051	0.9487	10.52	0.02642	0.9895	220.1	0.9950	0.8669

TABLE 6
Regeneration of the vermiculite

Cycle no.	Adsorption percentage (%)			
	Ag^+	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	46.25	98.90	96.37	96.38
2	46.20	98.90	96.30	96.30
3	46.10	98.50	96.20	96.35
4	46.12	98.80	96.20	96.30
5	46.10	98.70	96.10	96.15

obtained by pesudo-second-order equation in ternary $Pb^{2+}/Cu^{2+}/Cd^{2+}$ system is $0.016\,g\,mmol^{-1}\,s^{-1}$, which were smaller than the results obtained by the present study. This may be due to the difference in the adsorbent employed in the experiments. When comparing the obtained values k_2 by pesudo-second-order equation, Ag^+ presented the highest value, followed by the other metals in the following order: $Ag^+ > Pb^{2+} > Ni^{2+} > Cd^{2+}$. Several authors that studied the competitive adsorpton of divalent metals on heterogeneous sorbents reported that most of the metal sorption kinetics follows pseudo-second-order mechanism (24,33).

Desorption and Regeneration

The reusability of vermiculite was examined based on the desorption ability and regeneration of the sorption ability. The adsorption-desorption data of Ag^+, Pb^{2+}, Ni^{2+}, and Cd^{2+} after five cycles of consecutive adsorption and desorption procedure were listed in Table 6. As seen, no significant loss of adsoption percentages for all metal ions during five cycles of adsorption-desorption, demonstrating that vermiculite was very suitable for the design of a continuous process.

CONCLUSIONS

The aim of this work was to find the possible use of vermiculite as a new sobent for the removal of Ag^+, Pb^{2+}, Ni^{2+}, and Cd^{2+} from binary, ternary, and quaternary systems. Pb^{2+} ions always favorably adsorbed on vermiculite over Ag^+, Ni^{2+}, and Cd^{2+} ions in the multi-component systems. Such behaviors are determined by the ion charge, hydrated ionic radius, and the hydration energies of the metal species. The adsorption equilibrium data of Pb^{2+} were correlated with the Langmuir and the Freundlich isotherms, and Langmuir model were found to be better fitted for the experimental data. The suitability of the pseudo-first-order, pseudo-second-order, and Elovich model for the adsorption of metals onto vermiculite in the multi-component systems was also discussed. The results showed that the pseudo-second-order kinetics model was in good agreement with the experimental results for every metal ions, and the adsorption rate among the metal ions for the adsorption onto vermiculite followed $Ag^+ > Pb^{2+} > Ni^{2+} > Cd^{2+}$. The desorption and regenration study indicated that vermiculite can be used repeatedly and be suitable for the design of a continuous process.

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