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Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral

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Abstract

Vermiculite, a 2:1 clay mineral, was applied as adsorbent for removal of cadmium, zinc, manganese, and chromium from aqueous solutions. Parameters such as time of reaction, effect of pH and cation concentration were investigated. All isotherms were L type of the Gilles classification, except zinc (type S). The adsorbent showed good sorption potential for these cations. The experimental data was analyzed by Langmuir isotherm model showing reasonable adjustment. The quantity of adsorbed cations was 0.50, 0.52, 0.60, and 0.48 mmol g^{-1} of Cd^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+}, respectively.
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Keywords: Adsorption; Clay mineral; Cadmium; Chromium; Manganese; Zinc

1. Introduction

The presence of heavy metals in environment is a potential problem to water and soil quality due to their high toxicity to plant, animal, and human life. Moreover, heavy metals cannot be destroyed chemically as organic pollutants. Therefore, several treatment technologies have been developed for eliminating heavy metal from solution such as chemical precipitation, ultra filtration, adsorption and ion exchange [1]. Among these methods, adsorption and ion exchange using natural, synthetic and modified inorganic and organic solids have been explored [2–9]. In this group, clay minerals act as potential ionic exchangers for heavy metals due to their low cost, high abundance, easy manipulation, and harmlessness to the environment. Crystalline structures of most clay minerals are generated by a combination of octahedral and tetrahedral sheets normally classified in two groups of hydrous phyllosilicates that have the inorganic structural arrangement in 1:1 or 2:1 layers. The first layered structure consists of a single tetrahedral coordinated $[Si_2O_5](OH)_2$ layer which is connected to an edge-shared octahedral $M(OH)_6$ sheet, where M is Mg^{2+}, Al^{3+} [10,11]. The 2:1 layered material contains one octahedral sandwiched by two tetrahedral layers and in both cases the oxygen atoms are responsible to connect the sheets. However, the main inorganic layered can have the cation substituted either in the tetrahedral or octahedral sites for cations of comparable radii. Such substitution causes residual negative charges which are neutralized by the electrostatic adsorption of alkali and alkali earth cations (typically sodium, calcium, and magnesium). Thus, the ions present in the interlayer space of clay minerals can be exchanged by other cationic ion. This quantity is defined as the cation exchange capacity (CEC) of solid, which depends on many factors like origin and formation of clay. CEC is an important parameter of clay mineral classification. Vermiculite was the clay mineral chosen for heavy metal adsorption. It is classified as 2:1 type and it has been explored with the aim of evaluating structural changes, adsorptive, catalytic and electrochemical properties [12–16]. Several works have applied vermiculite as ion exchanger for hazardous cations [17–21]. Among other advantages, vermiculite is widely available, easily handled, low-costly adsorbent, and quite selective over other solids.

In this work, we show the application of a Brazilian vermiculite in the removal of specific toxic metal as zinc, cadmium, chromium and manganese from aqueous solution.

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2. Experimental

2.1. Chemicals

Natural vermiculite was supplied by the Companhia União Brasileira de Mineração from the municipally of Santa Rita, State of Paraiba, Brazil. Chemical analyses of the sample were performed by AAS, by using a Perkin-Elmer 5100 Model instrument with an air-acetylene flame. For analyses, samples were digested with a mixture of (HF-HCl). The CEC was measured by using the ammonium acetate method buffered at pH 7.0 [22] in which nitrogen content was determined on a Perkin-Elmer model 2400 analyzer.

Inorganic salts of zinc(II), cadmium(II) and chromium(III) nitrates (Merck) and manganese(II) sulphate (Nuclear), all with analytical grade were used without previous purification. Deionized water was used in all experimental measurements.

2.2. Other characterizations

The original vermiculite sample was characterized by X-ray diffraction patterns by using a nickel-filtered Cu Kα radiation on a Shimadzu model XD3A diffractometric apparatus in the range $2\theta = 1.5$–70° and at a scan rate of $0.67^\circ\ s^{-1}$.

Infrared spectra were recorded on a Bomem MB-Series spectrophotometer, by dispersing the solid sample in KBr, with resolution of $4\ cm^{-1}$ and 30 accumulation scans in the range of 4000–400 cm^{-1}.

2.3. Construction of exchange isotherms

The isotherms of ion exchange were obtained by using the batchwise method, which consisted in suspending a series of samples of about 50 mg of the solid in 20.0 mL of aqueous solutions, containing each cation in concentration near 0.01 mol L^{-1}, for a sequence of time of reaction varying from 12, 24, 48, 72, and 96 h. The solutions were mechanically stirred at 298 ± 1 K and after each time established the solid was separated by filtration. The amount of cation content in the supernatant was measured in triplicates by using a GBC absorption atomic apparatus, 808 AA model.

Control experiments, processed without the addition of vermiculite, confirmed that the adsorption of cations on the polyethylene bottom or in the filtration systems was negligible.

2.4. Influence of cation concentration on exchange process

For such study the isotherms were obtained as in the preceding section, by using a variation in cation concentration from 10^{-3} to 0.010 mol L^{-1}. As established before, the plateau of saturation was determined after analysing the supernatant samples to give 12.0, 48.0, 48.0, and 72.0 h for $Cr^{3+} < Zn^{2+} = Mn^{2+} < Cd^{2+}$, respectively.

2.5. Influence of pH

The pH was measured as above-mentioned by suspending near 50.0 mg of solid in systems containing 10.0 mmol L^{-1} of each cation. The pH was adjusted by using a series of buffer solutions with well-established pH values of 1.15 $C_8H_5KO_4$/HCl; 3.53 $C_8H_5KO_4$/HCl; 5.20 Hac/NaAc and 9.0 THAM/HC [23]. Each cation was mechanically stirred as time required and the supernatant analyzed as above-mentioned.

3. Results and discussion

3.1. Original properties of vermiculite

The chemical composition of vermiculite in weight percentage of oxides was: SiO_2 (44.62); Al_2O_3 (9.18) Fe_2O_3 (5.46); CaO (0.78); MgO (20.44); Na_2O (0.11); and K_2O 0.48. The loss of weight after heating at 1273 K was 18.93%. Based on the data, the structural formulae of the sample studied (calculated on the basis of $O_{20}(OH)_4$ per formula unit) is $Mg_{4.68}Ca_{0.128}Na_{0.032}K_{0.094}Fe_{0.63}Al_{1.66}Si_{6.85}$ where Fe^{3+} is equal to total Fe on the basis of wet chemical analysis. The CEC is 135 mequiv./100 g and BET surface area is 16.0 $m^2\ g^{-1}$.

The main infrared absorption bands for support were located at 3450, 997, 814 and 680 cm^{-1}, and were attributed respectively to water stretching vibration, symmetric deformation of Si–O–Si and Si–O–Al groups, Al–OH deformation, and Al–O deformation [24,25]. The X-ray patterns for the original vermiculite are in agreement with high purity and crystallinity without impurities of SiO_2 as quartz and hematite.

3.2. Exchange isotherms

The first parameter investigated for this exchange process was to establish the time necessary for the sorption equilibrium. For the set of cations the experiments were realized in systems containing 0.01 mol L^{-1} of each cation. The changes of cation concentration as a function of time are shown in Fig. 1. The kinetic of exchange enables ordering them as $Cr^{3+} < Zn^{2+} = Mn^{2+} < Cd^{2+}$, whose maximum equilibrium were 12.0, 48.0, 48.0, and 72.0 h, respectively. Chromium is a trivalent cation and its high ionic charge favors the exchange over the other cations.

Another important parameter to be considered in exchange processes was the pH of the medium which varied from 1.0 to

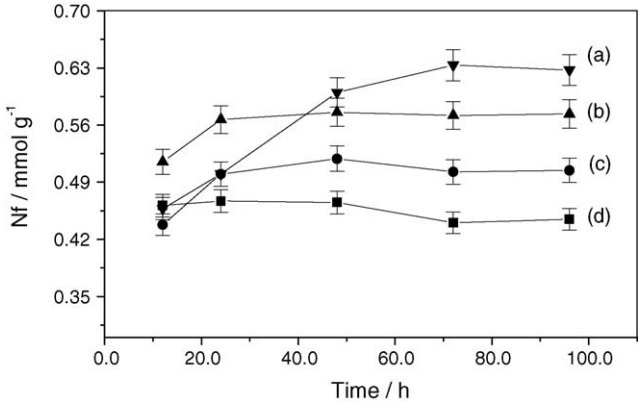

Fig. 1. Effect of contact time on adsorption of (a) Cd^{2+}, (b) Zn^{2+}, (c) Mn^{2+}, and (d) Cr^{3+} when exchanged in vermiculite at 298 ± 1 K with cation initial concentration of 0.01 mol L^{-1}.

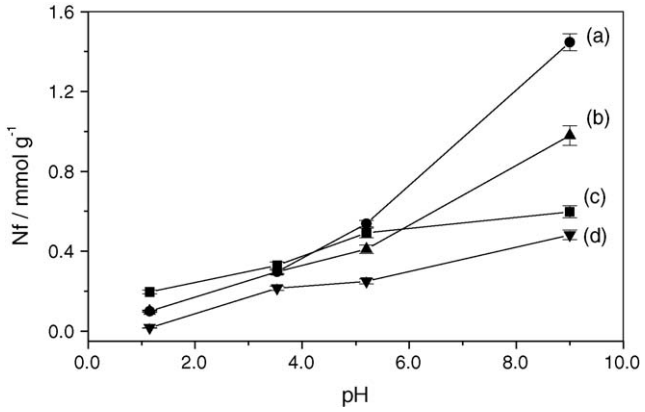

Fig. 2. Effect of pH on adsorption of cations (a) Mn^{2+}, (b) Cr^{3+}, (c) Zn^{2+}, and (d) Cd^{2+} by vermiculite at 298 ± 1 K with cation initial concentration of 0.01 mol L^{-1}.

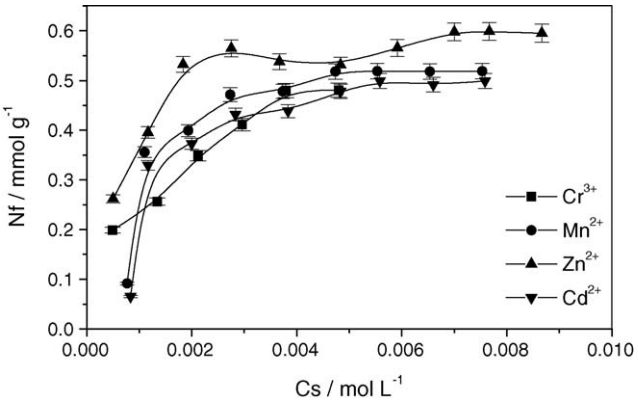

Fig. 3. Adsorption isotherms of cations on vermiculite at 298 ± 1 K.

9.0. For the four chosen buffered pH values the ion-exchange were performed as represented in Fig. 2. For Cd^{2+}, Mn^{2+} and Zn^{2+} at pH 1.15, 3.5 and 5.20, respectively, and for Cr^{3+} at pH 1.15 the predominant species in solutions were free cations according to the predictions obtained by MINEQL software, as illustrated in Table 1. Thus, the principal metal-retention mechanism was due to ion exchange. Under low pH conditions, the ions H_3O^+ in high concentration compete by the negative sites of clay and the observed exchange was lower for heavy cations. For pH 9.0 the formation of cationic hidroxo complexes and precipitation of $M^{n+}(OH)_n$ are favorable and two mechanisms of retention are suggested: adsorption on surface of solid and ion exchange involving the cationic complexes. For chromium the formations of hidroxo complexes and $Cr(OH)_3$ occur at pH 3.5, 5.20 and 9.0. At pH 3.5, for example, the species $Cr(OH)_2{}^+$ and Cr^{3+} are 24.57 and 60.44%, respectively. At pH 5.2, the cationic complexes $Cr(OH)^{2+}$ and $Cr_2(OH)_2{}^{4+}$ are 35.14 and 62.78% while Cr^{3+} 0.064%. All species compete among each other for exchange sites in interlayer space.

Table 1
Principal species of cations at several pH

Cation	Species	pH/% species			
		1.15 (%)	3.50 (%)	5.20 (%)	9.00 (%)
Cd^{2+}	Cd^{2+}	99.997	99.997	99.997	93.92
	$Cd(OH)^+$	<0.001	<0.001	<0.001	0.811
	$Cd_2(OH)^{3+}$	<0.001	<0.001	<0.001	4.988
	$Cd(OH)_{2(aq)}$	<0.001	<0.001	<0.001	0.275
Zn^{2+}	Zn^{2+}	99.997	99.997	99.989	8.088
	$Zn(OH)^+$	<0.001	<0.001	0.011	7.017
	$Zn_2(OH)^{3+}$	<0.001	<0.001	<0.001	0.014
	$Zn(OH)_{2(aq)}$	<0.001	<0.001	<0.001	84.60
Mn^{2+}	Mn^{2+}	99.997	99.997	99.989	23.286
	$Mn(OH)^+$	<0.001	<0.001	0.011	0.455
	$Mn_2(OH)^{3+}$	<0.001	<0.001	<0.001	76.256
	$Mn(OH)_{2(aq)}$	<0.001	<0.001	<0.001	<0.001
Cr^{3+}	Cr^{3+}	99.810	60.448	0.064	<0.001
	$Cr(OH)_2{}^+$	<0.001	0.0250	35.140	0.219
	$Cr(OH)^{2+}$	<0.124	24.570	62.780	<0.001
	$Cr_2(OH)_2{}^{4+}$	<0.001	14.189	0.143	<0.001
	$Cr_2(OH)_4{}^{5+}$	<0.001	0.796	0.015	<0.001
	$Cr(OH)_{3(aq)}$	<0.001	<0.001	1.853	99.790

The initial cation concentration affecting the interaction processes for all cations are shown in Fig. 3. For this set of isotherms the maximum concentration of cation in initial solution was 0.01 mol L^{-1} showing pH of 6.2, 6.4, 5.6, and 2.6 for cadmium, manganese, zinc and chromium nitrates, respectively. In this condition, a percentage of 99.9% of cadmium, manganese, and zinc cations and 95.0% of chromium were in free form. Thus, the principal mechanism of interaction is ionic exchange which can be represented by general equation:

$$VMg_n^{2+}(s) + M^{n+}(aq) \leftrightarrow VM^{n+}(s) + nMg^{2+}(aq)$$

Where V is the vermiculite, Mg^{2+} the magnesium, n is the charges of the cation M in aqueous solution or exchange in solid. This equation shows that for each mol of exchanged magnesium, the same quantity of a cation entries in solid.

A classification of the interactive phenomenum for solid/liquid interface was suggested by Gilles [26], who showed four classes of isotherms: high-affinity (H), Langmuir (L), constant-partition (C), and sigmoidal-shaped (S). Based on their shapes, the isotherms were classified as type 2L for Cd^{2+} and Mn^{2+}, 4S for Zn^{2+} and 1L for Cr^{3+}.

The quantity of exchanged cations was 0.50, 0.52, 0.60, and 0.48 mmol g^{-1}, for Cd^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+}, respectively. Taking into account the maximum values, the order of the capacity increased as follows: $Cd^{2+} < Mn^{2+} < Zn^{2+} < Cr^{3+}$.

Although these isotherms can be differently classified, all have a normal tendency on saturating the exchange into the interlamellar space at the solid/liquid interface, during this process. Thus, in an attempt to have more information on the cation/vermiculite equilibrium, the data were adjusted to a modified Langmuir equation [27] in the form 1:

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \quad (1)$$

Where C_s is the concentration of cation in the supernatant (mol dm^{-3}) at equilibrium, N_s the maximum amount of the cation exchanged per gram of the solid, and b is a constant which

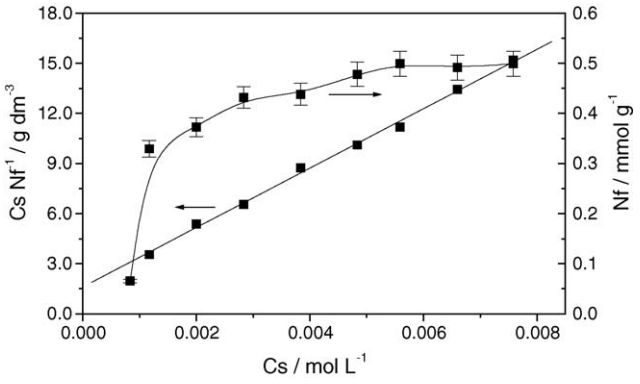

Fig. 4. Isotherm of exchange of cadmium in vermiculite, at various concentrations, at 298 ± 1 K and its linearized form.

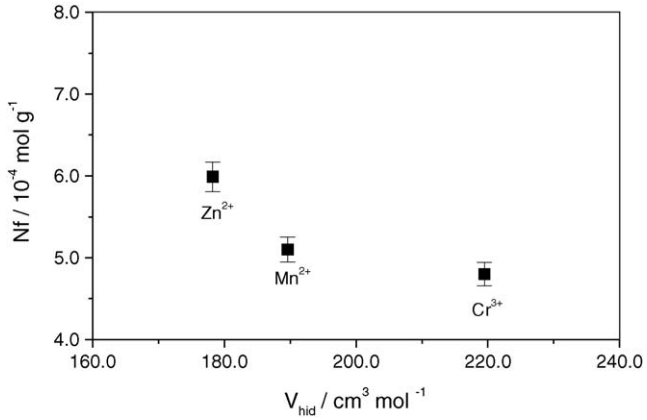

Fig. 5. Correlation between the maximum ion-exchange of heavy cations in vermiculite and the hydration volume of ions at 298 ± 1 K.

depends on solvent properties such as density (d), molar mass (MM) and the constant of equilibrium of the process, defined by the expression $b = \mathrm{MM}\,K/d$. Thus, N_s and b can be obtained from the angular and linear coefficients, respectively, of the linearized form of the adsorption isotherms, by considering C_s/N_f as function of C_s values. This procedure is illustrated for cadmium as shown in Fig. 4. In Table 2 the results for all cations are shown. By using b value, that is associated with equilibrium constant (K) of the ion-exchange process, the free energy ΔG° was calculated through the Gibbs equation $\Delta G^\circ = -RT \ln K$, where T is absolute temperature and R the ideal gas constant, 8.314 J mol^{-1} K^{-1}. For all cases the negative values are in agreement with the spontaneity of this general exchange reaction. R_L, a dimensionless constant separation factor or equilibrium parameter, that is an important characteristic of the Langmuir isotherm defined as $R_L = 1/(1 + bC_0)$, where C_0 is the initial concentration of cation [28]. For zinc, cadmium, manganese and chromium, the R_L values were between 0 and 1.0, indicating that adsorption of these heavy metals by vermiculite is favorable in agreement with ΔG° values.

The exchange data were related to properties of cations such as hydration volume and hydration enthalpy of cation. Results obtained formerly from other heavy metals adsorbed on vermiculite in the same experimental conditions showed same tendency [29].

The first correlation between the exchange capacity and hydration volume of cations showed the preference of exchange for ions with lower hydration volume (Fig. 5). This fact can be related to diffusion of ion through the interlayer space of vermiculite. Cadmium(II) with the same hydration volume of cobalt(II) was omitted because the same trend was not observed.

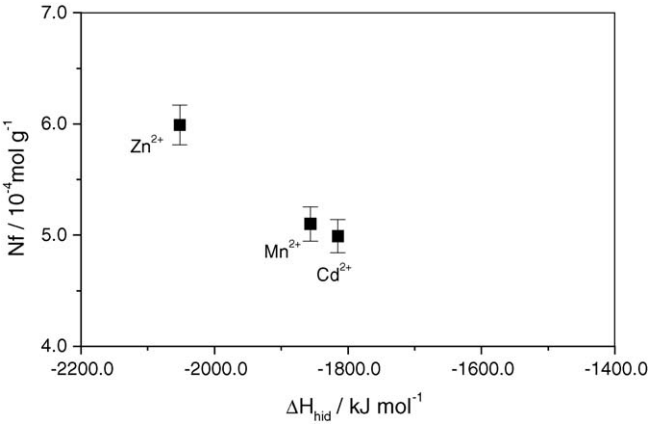

Fig. 6. Correlation between the maximum number of moles of divalent cations exchanged and the enthalpy of hydration (ΔH_{hid}) for heavy cations in vermiculite at 298 ± 1 K.

The enthalpy of hydration of divalent cations was also correlated to the amount of exchanged ions [30,31], as shown in Fig. 6. The outlined curve resembles clearly an exponential decay in ion-exchanging from zinc to cadmium. Thus, the decrease in the sequence of the enthalpy of hydration values for all cations follows the capacity of exchanging as observed by the N_f value. Therefore, the smallest enthalpic value for cadmium gave the least ion-exchange value. This behavior suggested that some of the water molecules involved in cation hydration can be removed in order to accommodate the cation within the interlayer space.

Table 2
Constants of Langmuir model applied in the adsorption of heavy cations onto vermiculite showing the hypothetical maximum amount exchanged (N_s), b constant, the constant of equilibrium (K), free Gibbs energy (ΔG°), R_L parameter and the coefficient of correlation (r) for the linearized form of the isotherm

Cation	N_s (mmol g^{-1})	b (L g^{-1})	ln K	ΔG° (kJ mol^{-1})	r	R_L
Cr^{3+}	0.751 ± 0.05	406 ± 45	10.02	−24.85 ± 0.01	0.9800	0.045
Zn^{2+}	0.639 ± 0.015	1607 ± 144	11.40	−28.26 ± 0.01	0.9969	0.009
Cd^{2+}	0.563 ± 0.012	1100 ± 77	10.02	−27.32 ± 0.01	0.9987	0.008
Mn^{2+}	0.574 ± 0.010	1456 ± 87	11.30	−28.01 ± 0.01	0.9988	0.012

4. Conclusion

This study indicated that vermiculite could be used as an effective adsorbent for the sequestration of heavy ions in aqueous solution. The exchange processes showed depend on many factors, like the physicochemical characteristics of solid and cation, and experimental conditions involving time of reaction, concentration of ions and pH of the medium.

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