Sorption of Heavy Metal on Natural Clay

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Sorption of heavy metals on Na-montmorillonite was studied as a function of solution pH and different concentrations of background electrolyte and also a function of added metal ion at constant pH. Equilibrium isotherms have been measured and analyzed using a Langmuir isotherm model. The metal ions were predominantly adsorbed on the permanent charge sites in a easily replaceable state. There was also evident a substantial involvement of the hydroxyl groups on the edges of Na-montmorillonite in specific adsorption of the cations especially at higher pH.

Keywords: sorption, heavy metals, montmorillonite, Langmuir equation

The removal of heavy metals from water and industrial effluents is desired due to their extreme toxicity towards aquatic life and humans [1].

Sorption is an efficient method for the removal of metal ions from dilute aqueous solutions. Among the different sorptive materials that have been used to remove metal ions from aquatic solutions we can mention hydroxides and oxides [2], molecular sieves [3], fly ash [4], bone char [5], biomass [6, 7] and clays [8-13].

Clays are abundant and inexpensive layered aluminosilicate minerals with adsorbent properties due to their large surface areas and negative layer charge. In general, chemical species can interact with clays either by ion exchange [8] or physisorption [14], both being reversible processes.

Montmorillonite is a widespread mineral of weathering formation and sediment [15] that possesses a large specific surface area and a high structural charge (up to 1000 meq/kg).

The high surface reactivity of this mineral is a direct consequence of its lamellar and defective structure. Montmorillonite is built of layers made by the condensation of one central octahedral sheet and two tetrahedral sheets. Isomorphous substitution of Si^{4+} or Al^{3+} confers to montmorillonite a permanent negative structural charge, which is compensated by the sorption of cations on basal planes. Divalent cations sorbed on these planes form outer-sphere (OS) surface complexes [16, 17] and are easily exchanged with solution ions by varying the cationic composition of the solution. Besides these cation exchange properties, the montmorillonite also possesses pH-dependent sorption properties [18].

Experimental part

Materials

The montmorillonite used in this study was a Na-montmorillonite, with 99% of the clay particles < 10μm and with a cation exchange capacity (CEC) of about 0.92 meq/g. Specific surface area (SSA) of montmorillonite was determined by N_2 adsorption at 77 K using a Carlo Erba Sorptomatic SSA was calculated by applying the BET method as 72.4 m^2g^{-1}.

Mineral clay was used as supplied by I.C.P.M MINESA - S.A. Cluj Napoca.

Homoionic aqueous solutions of Pb^{2+}, Zn^{2+}, Cd^{2+} were prepared from the nitrate salts of the metals, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ (all p.a. Fluka). Exact concentrations of these stock solutions were determined by flame atomic absorption spectrometry. All metal solutions were diluted to the required concentrations with bidistilled water. As background electrolyte $NaNO_3$ solution has been used. In all the sorption experiments the concentration of montmorillonite was C_M= 1g/L.

Test of the adsorption of metals influenced by pH

Sorption of Zn, Cd and Pb species on Na-montmorillonite was determined in batch experiments. The experiments were performed at 20.0 ± 0.1 °C in glass vessels immersed in a thermostatic water bath.

Twenty milligrams of Na-montmorillonite were mixed with 10 mL of $2 \cdot 10^{-2}$ M $NaNO_3$ solution. Then, 10 mL of $2 \cdot 10^{-4}$ M Zn(II), Cd(II) or Pb(II) solutions were added and mixed well. The initial concentration of background electrolyte in solution was 10^{-2} M and that of metal species was 10^{-4} M. Solid/liquid ratio was 1 g/L. The *p*H value was adjusted by adding small volumes of 10^{-2} M NaOH or 10^{-2} M HNO_3 solutions and monitored by a pH electrode (Metrohm 6.0204.100) connected to a pH meter (Metrohm 713). This electrode was calibrated with buffers (Merck, titrisol). The *p*H was varied from about 4 to 7. A rotating magnetic bar ensured vigorous stirring of the suspension for equilibration with another interim adjustment of their *pH*. According to a previous kinetic study a 24-h reaction period was chosen. After equilibration, clays and solutions were separated by centrifugation (Beckman J-2-21) at 10000 rpm for 30 min.

The concentration of heavy metals in the supernatant was determined by atomic absorption spectroscopy (Perkin-Elmer 1100B atomic absorption spectrometer). The amount of adsorbed metal was calculated by difference between the initial and final solution concentration.

Partitioning of adsorbed metal species was done by a carefully controlled washing procedure [13] using 10^{-2} M $NaNO_3$ solution.

10 mL aliquot of the removed supernatant solution has been replaced by 10 mL of 10^{-2} M $NaNO_3$. The clays were then quickly suspended and immediately centrifuged. The resulted supernatant solution was taken for determination of metal concentration. The amount of adsorbed metal o species on the clay after this procedure was defined as

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strongly adsorbed. Weakly adsorbed (WA) metal was obtained from the difference of total adsorbed metal (TA) minus strongly adsorbed metal (SA).

Adsorption Experiments

Twenty milligrams of Na-montmorillonite were contacted for 24 h (until equilibrium is attainment) with 10 mL of $Zn(NO_3)_2$, $Cd(NO_3)_2$ or $Pb(NO_3)_2$ aqueous solutions with metal concentrations ranging from 0.1 to 1.1 mmol L^{-1}.

The *pH* of the Zn(II), Cd(II) and Pb(II) solutions was 5.50 ± 0.05. Isotherms for heavy metal sorption on Na-montmorillonite were determined at 20.0 ± 0.1 °C in glass vessels immersed in a thermostatic water bath, without exclusion of atmospheric CO_2.

The ionic strength of the solutions was about of 10^{-2} M. A rotating magnetic bar ensured vigorous stirring of the suspension. After equilibrium attainment, clays and solutions were separated by centrifugation at 10000 rpm for 30 min. The concentration of heavy metals in the supernatant was determined by atomic absorption spectroscopy. The amount of adsorbed metal was calculated considering the initial and final solution concentration.

Solutions containing metal ions without adsorbent were also stirred for 24 h and used as reference solutions. All measurements were run in duplicate.

Results and discussions

Chemical reactions such as montmorillonite dissolution or formation of pure or mixed Zn, Cd, Pb carbonates or hydroxides may strongly interfere with heavy metal cations sorption on mineral clay. Therefore, the sorption conditions (*pH*, ionic strength) for each metal sorption were carefully chosen to avoid the interferences.

The lower limit of the possible *pH* value for Zn, Cd or Pb species sorption was imposed by the dissolution of Na-montmorillonite (*pH* < 4). The upper *p*H limit was selected to avoid precipitation of pure or mixed Zn, Cd or Pb carbonates or hydroxides (*pH* > 6.5 for Pb^{2+}; *pH* > 7.9 for Zn^{2+}; *pH* > 7.5 for Cd^{2+})[19]. Zn, Cd and Pb adsorption isotherms are showed in figure1.

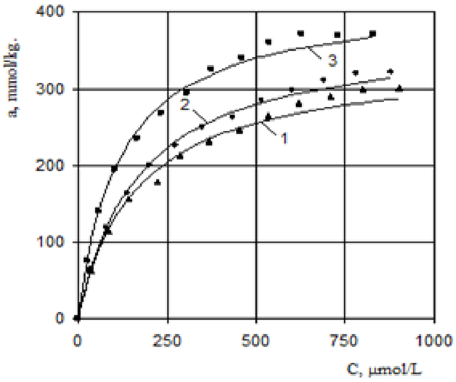

Fig. 1. Adsorption isotherms for 1- Pb; 2- Cd; 3 -Zn; Symbols are experimental data points, whereas lines are the Langmuir-fit adsorption curves

*p*H= 5.5 ± 0.05; T= 20.0 ± 0.1 °C; ionic strength = 10^{-2} M $NaNO_3$; C_M= 1 g·L^{-1}

The affinity of heavy metal sorbed onto clay varied in the following descending order: $Pb^{2+} > Cd^{2+} > Zn^{2+}$, respectively 369.6, 319.8 and 298.6 mol kg^{-1}.

The heavy metal sorption data were well described by the Langmuir equation:

$$a = a_m \frac{bC}{1 + bC} \qquad (1)$$

where: a -equilibrium concentration of adsorbed metal;
C - equilibrium concentration of metal species in solution;
a_m- the maximum concentration of adsorbed metal;
b - adsorption constant.

Langmuir equation can be also written as:

$$\frac{C}{a} = \frac{C}{a_m} + \frac{1}{a_m b} \qquad (2)$$

and, therefore, a plot of C/a vs. C will yield a straight line having slope $1/a_m$ and intercept $1/ba_m$.

Knowing values for the slope and the intercept allows one to easily calculate values of equilibrium sorption parameters, a_m and b. The straight line through the data is usually obtained by a linear least – square fitting procedure. Using this procedure the following equations (3), (4) and (5) for Zn, Cd and Pb adsorption on Na-montmorillonite were obtained:

$$\frac{C}{a} = 0.4881\ C + 2.9494 \qquad (3)$$

$$\frac{C}{a} = 0.4527\ C + 2.6804 \qquad (4)$$

$$\frac{C}{a} = 0.2837\ C + 2.3859 \qquad (5)$$

The equilibrium sorption parameters for heavy metal sorption on montmorillonite are shown in table 1.

Table 1

ADSORPTION PARAMETERS, a_m AND b, FOR Zn(II), Cd(II) AND Pb(II) ADSORPTION ON Na–MONTMORILLONITE

Cation	a_m [mmol kg^{-1}]	b [L $mmol^{-1}$]	Correlation coefficient, *r*
Zn^{2+}	339 ±	6 ± 1	0.998
Cd^{2+}	373 ±	6 ± 1	0.999
Pb^{2+}	419 ±	8 ± 2	0.999

Effect of pH on heavy metals sorption.

Adsorption of Zn^{2+}, Cd^{2+} and Pb^{2+} was studied by determination of adsorption degree (µ, %) solution *pH* at different concentrations of background electrolyte (figs. 2 and 3).

The obtained data showed clearly that the removal of Zn(II), Cd(II) or Pb(II) from their salt solutions by using mineral clay was *pH* dependent.

The minimum and maximum amounts of heavy metals adsorbed on Na-montmorillonite for different

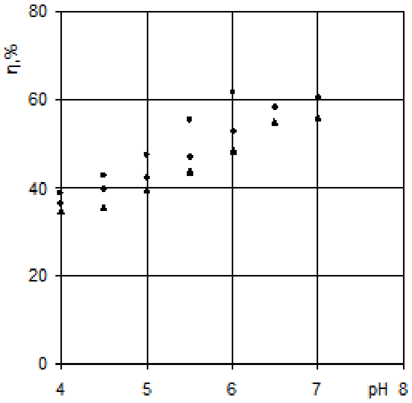

Fig. 2. The dependence of adsorption degree for •Pb; ♦ Cd; ▲ Zn on *p*H solution; C_i= 0.1 mmol/L; T= 20.0 ± 0.1 °C; ionic strength = 0.1M $NaNO_3$; C_M= 1g·L^{-1}

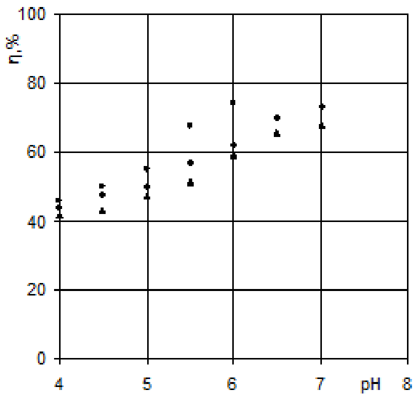

Fig. 3. The dependence of adsorption degree for •Pb; ♦ Cd; ▲ Zn on *p*H solution. C_i= 0.1 mmol/L; T= 20.0 ± 0.1 °C; ionic strength = 0.01M $NaNO_3$; C_M= 1g·L^{-1};

concentrations of background electrolyte are presented in table 2 and table 3, respectively.

Table 2

CONCENTRATION OF HEAVY METAL ADSORBED BY Na-MONTMORILLONITE AT A BACKGROUND ELECTROLYTE CONCENTRATION OF 10^{-2} M (INITIAL HEAVY METAL CONCENTRATION C_i=0.1 mmol·L^{-1})

Cation	Ionic strength (M)	*pH*	C (μmol g^{-1})
Zn^{2+}	0.01	4.02	41.8
		7.03	68.1
Cd^{2+}	0.01	4.01	43.9
		6.98	73.2
Pb^{2+}	0.01	4.04	45.9
		5.99	73.9

Table 3

CONCENTRATION OF HEAVY METAL ADSORBED BY Na-MONTMORILLONITE AT A BACKGROUND ELECTROLYTE CONCENTRATION OF 10^{-1} M (INITIAL HEAVY METAL CONCENTRATION C_i=0.1 mmol·L^{-1})

Cation	Ionic strength (M)	pH	C(μmol g^{-1})
Zn^{2+}	0.1	4.02	34.8
		7.03	56.2
Cd^{2+}	0.1	4.01	36.6
		6.98	60.5
Pb^{2+}	0.1	4.04	38.9
		5.99	61.7

The sorption behavior of the Na-montmorillonite can be explained by a combination of cation exchange at low *pH* and specific binding due to surface complexation at higher *pH*.

The *pH* dependent charge is located at the edge sites, where the surface hydroxyl groups can be either protonated or deprotonated, depending on the *pH* of solution. The adsorption of heavy metal cations by hydroxyl groups is governed by covalent binding and therefore is chemically specific [20, 21].

According to Bradbury and Baeyens [22], two types of surface hydroxyl groups (S^wOH with low affinity and S^sOH with strong affinity) were assumed for Na-montmorillonite. Cation exchange sites (X^-) were also taken into account.

The increase in metal adsorption on montmorillonite with increasing *pH* is modeled using the S^wOMe^+ and S^wOMeOH surface complexes [12, 22-24].

The model equations are given below:

$$\equiv S^SOH + H^+ \leftrightarrow \equiv S^SOH_2^+$$

$$\equiv S^SOH \leftrightarrow \equiv S^SO^- + H^+$$

$$\equiv S^SOH + Me^{2+} \leftrightarrow \equiv S^SOMe^+ + H^+$$

$$\equiv S^WOH + H^+ \leftrightarrow \equiv S^WOH_2^+$$

$$\equiv S^WOH \leftrightarrow \equiv S^WO^- + H^+$$

$$\equiv S^WOH + Me^{2+} \leftrightarrow \equiv S^WOMe^+ + H^+$$

$$\equiv S^WOH + Me^{2+} \leftrightarrow \equiv S^WOMeOH + 2H^+$$

$$\equiv 2XNa + Me^{2+} \leftrightarrow (\equiv X)_2Me + 2Na^+$$

Sorption experiments of Zn(II), Cd(II) and Pb(II) at different background electrolytes showed that the amounts of heavy metal adsorbed on Na-montmorillonite were higher at a lower ionic strength of the solution.

Partitioning of strong and weak adsorption

The adsorbed heavy metals were separated into strongly and weakly bound forms as described in Experimental part. The results are showed in figures 4, 5 and 6.

According to the experiments, the totally adsorbed (TA) and strongly adsorbed (SA) amounts of Zn, Cd and Pb increased with *p*H for the range studied. The ratio SA/TA increases with *p*H and depends on the kind of the metal.

Strong adsorption of Pb on montmorillonite is more pronounced than that of Cd and Zn. With increasing *pH*, the increasing difficulties in desorption of all heavy metals

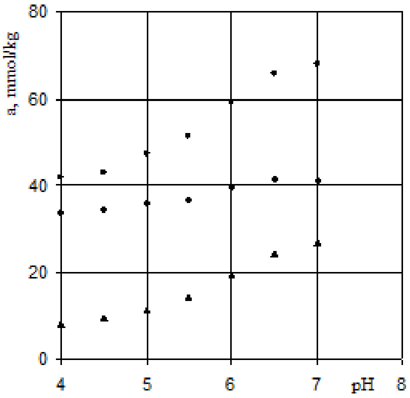

Fig. 4.The dependence of Zn solid phase concentration for • Zn total adsorbed; ♦ Zn weakly adsorbed; ▲Zn strongly adsorbed on *p*H solution. C_i = 0.1 mmol/L; T= 20.0 ± 0.1°C; ionic strength = 0.01M $NaNO_3$; C_M= 1g·L^{-1}

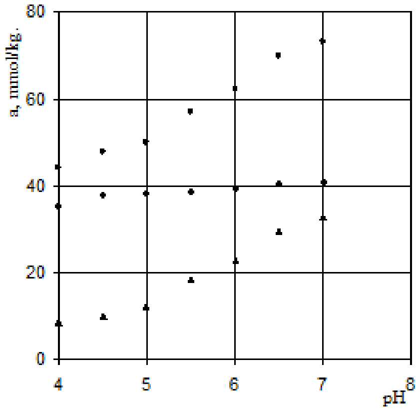

Fig. 5.The dependence of Cd solid phase concentration for • Cd total adsorbed; ♦ Cd weakly adsorbed; ▲ Cd strongly adsorbed on *p*H solution. C_i = 0.1 mmol/L; T= 20.0 ± 0.1°C; ionic strength = 0.01M $NaNO_3$; C_M= 1g·L^{-1}

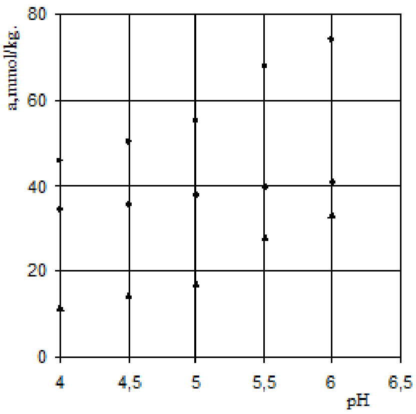

Fig. 6. The dependence of Pb solid phase concentration for ●Pb total adsorbed; ♦Pb weakly adsorbed; ▲Pb strongly adsorbed on *p*H solution. C_i = 0.1 mmol/L; T= 20.0 ± 0.1°C; ionic strength = 0.01M $NaNO_3$; C_M= $1 g·L^{-1}$;

could result in part due to the probable formation of complexes and precipitates.

Adsorption of all three metals on mineral clay was quite significant even at low *pH* values. This observation along with desorption data suggest that Cd and Zn adsorption in the low *pH* range could be concentrated on permanent charge sites where the protons could exert little competition. Desorption study of Pb^{2+} (fig. 6) suggests that even at low *pH,* in addition to being adsorbed on the permanent charge sites, Pb might have been adsorbed on the hydroxyl groups on the edges of Na-montmorillonite.

Conclusions

This study shows that Na-montmorillonite can be used for removing of zinc, cadmium and lead cations from dilute aqueous solutions. The Langmuir isotherm model was able to describe the sorption of metal cations on the mineral clay. The efficiency of this material in removing heavy metals would allow a new way to use commonly and economically available clay as an adsorbent. Soil minerals are often negatively charged and similar effects as observed for montmorillonite are expected, meaning that a mobilizing effect should occur for Zn, Cd and Pb only in soil with high *pH* values.

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