Thermodynamics and Kinetics of Pb(II) and Hg(II) Ions Removal from Aqueous Solution by Romanian Clays

CLAUDIA HRISTODOR, VIOLETA COPCIA, DOINA LUTIC , EVELINE POPOVICI*
Al. I. Cuza University of Iasi, Faculty of Chemistry, 11 Bd. Carol I , 700506, Iasi, Romania

Heavy metals cations are released to the environment by natural phenomena and human activities, such as agricultural practices, transport, industrial activities and waste disposal. Because of their high negative impact as environmental contaminants, in this study the removal of Pb(II) and Hg(II) from wastewaters was studied. Clays from Valea Chioarului and Razoare areas - Romania as well as Na-clays were investigated as sorbents.

The effect of initial concentration of metal ions - Pb(II) and Hg(II), temperature and time on removal efficiency was studied. The equilibrium data were fitted with two standard isotherms, the Langmuir and Freundlich models. The Langmuir model was more suitable for these systems. The highest ion exchange capacity based on Langmuir constants was displayed by the Na-exchanged clay: 0.696 mmoles/g for lead and 0.71 mmoles/g for mercury. These amounts of lead and mercury immobilized on solids are high enough to foresee their convenient possibility of separation from wastewaters. A future study concerning the toxic ions form real wastewaters will be necessary in this respect. The kinetic studies showed that the sorption rates could be described by a second-order Lagergren equation.

Keywords: ion exchange, raw clay, Na-clay, Pb(II) and Hg(II) removal

The presence of heavy metals in the waste streams of many industrial activities cause serious pollution problems in aquatic environment. These heavy metals are toxic and not biodegradable pollutants. They have the tendency to accumulate in living organisms, causing serious diseases and disorders, threatening the human and animal health [1-3]. Lead is known to have toxic effect on neuronal system and on the function of brain cells [4]; health hazards related to the toxicity of lead in waters have been reported [5]. Also, mercury and most of its compounds are well known poisons which attack the central nervous system and cause irreversible damages [6].

The concentration of these metals' ions in many natural and industrial waste streams must be controlled to be below the acceptable level, according to the environmental regulation worldwide, in always increasing severity.

In this work the sorption features of the native and sodium-exchanged form of clay samples from Valea Chioarului and Razoare areas towards Pb(II) and Hg(II) ions were studied.

Experimental part

Materials

The minerals used in this study were two natural clays, from Valea Chiuoarului and Răzoare areas. Both samples were used in the raw form as well as in the Na-exchanged form. The samples involved in this study were denominated as: raw clay from Valea Chioarului, Ci and Na-clay from Valea Chioarului, C-Na, with 64% smectite (SiO_2/Al_2O_3 = 8.95 mol/mol, 59m^2/g); raw clay from Răzoare, Ri and Na-clay from Răzoare, R-Na (SiO_2/Al_2O_3 = 7.42 mol/mol, 39m^2/g), with significant amounts of clinoptilolite zeolite joining the illite clay and quartz. Details about these clays composition and structure can be found in our previous work [2,3,7].

The Na-forms of the raw clays from Valea Chioarului and Răzoare were prepared by treating the raw forms with 1M solutions of NaCl in a solid/liquid ratio of 10, at room temperature, under magnetic slow stirring for 12 h, followed by centrifugation, water washing and air drying at 80°C for 5 h [8].

The Pb(II) şi Hg(II) nitrate solutions (0.1M) were prepared by dissolution in distilled water. Nitric acid was added to reach a pH value of 2. The solutions for the tests of ion exchange were obtained by appropriate dilution.

Methods

The sorption experiments were performed in batch technique, mixing samples of about 0.2 g clay with 25 mL of salt solutions in glass tubes with lids. The exchange was performed at three constant temperature values (293, 313 and 333 K), by placing the tubes in a thermostatic bath and occasional stirring. After a preset time, the heavy metals content from the liquid phases were analyzed by the complexometric method [9]. The exchange equilibrium sampling was done after 24 h.

The uptake of metal ion was expressed as the amount of metal ions (mmoles) retained per gram of solid or by calculating the percent of heavy metal removed from the solution, using by the following relations:

$$q = (c_0 - c) \cdot V \cdot 10^{-3} / m \,.\, A, \text{ mg/g} \quad (1)$$

$$R = (c_0 - c) \cdot 100 / c_{0,} \% \quad (2)$$

where c_0 and c are the initial and the actual concentration of heavy ions (mg/L), m is the amount of sorbent (grams), A is the atomic mass of the ions (Pb = 207.2 and Hg = 200.59) and V is volume of exchange solution (mL).

Results and discussions

In order to evaluate the sorption performances of the different clay samples, they were contacted with solutions of different initial concentrations in metal ions, Pb (II) and Hg (II). The retention degrees were determined. The results presented in table 1 were obtained at 293 K, after 24 h of contact between solution and solid, at a solid/liquid ratio of 8 g/L.

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* *email: eveline@uaic.ro; Tel. 0232 201135*

Table 1
DEGREE (%) OF METAL IONS RETAINED ON NATURAL AND MODIFIED CLAY

Ions	$C_0 \cdot 10^3$, moli M(II)/ L	C -Na	R-Na	Ci	Ri
Pb(II)	0.79	84.3	78.9	63.0	84.4
	7.90	9.7	25.2	9.0	14.7
	15.81	5.6	13.0	4.8	8.4
	23.71	4.6	8.8	3.4	5.9
	31.62	3.7	6.7	2.8	4.8
	55.34	2.5	4.2	1.6	3.0
Hg(II)	2.01	21.1	68.9	52.2	40.4
	4.02	11.5	57.2	37.1	20.8
	8.05	7.1	31.8	18.8	11.4
	16.10	4.5	16.7	9.6	6.9
	24.15	3.1	11.8	6.5	4.9
	40.26	2.2	7.18	4.4	3.1

The results from table 1 show that the degree of metal removal from aqueous solution decreases steeply with the increase of the initial metal ion concentration. This is due to the saturation of the solid in ions. On another hand, these experiments indicate that the removal of heavy metals such as Pb (II) and Hg (II) from very diluted aqueous solutions is possible using these class as sorbents. Since the heavy metals concentrations in wastewaters are situated in mmoles/liter range, our removal method has a good application potential in wastewaters remediation. At low heavy metal concentrations, the retention degree is quite high, indicating the good affinity of the solid for these ions. At both low and medium concentration values, there is a net superior behaviour of the sample R – Na as regarded to the other solids. The sodium form of the clay behaves better than the native one, probably due to the obtaining of a higher void fraction or higher structure ordering associated to the sodium exchange step [10]. The steep decrease of the retention degree with the concentration of the heavy metal ions can be related either to the low exchangeable ions concentration in the clay, either to the quite limited void volume in the structure where the ions can accommodate in adsorption sites. We believe that contribution of adsorption is higher than that of ionic exchange on the overall ion uptake.

The influence of temperature on the metal ions (Pb (II) and Hg (II)) sorption on original and Na-exchanged clays is presented in figure 1. The increase of temperature is beneficial on the amount of ion metal retained from the solution, as expected, since the ions diffusion is favoured by higher temperatures.

The results in figure 1 above can be commented from two points of view: comparison between the two solids and comparison between the ions adsorbed.

On one hand, the results show much higher values of the ions (PbII and HgII) amount uptake in the case of the clay from Razoare, in both native (Ri) and Na-exchanged (R - Na)forms. It is quite unexpected, since the value of the specific surface area is bigger for the other clay from Valea Chioarului. It is a clear indication that the inner pore structure of the pores of the R clay is more appropriate to accommodate the exchange ions. The ionic radiuses for the two ions are, respectively, Hg (II): 1.02 Å and Pb (II) 1.19 Å [11]. The smaller radius of the Hg (II) determines a much higher amount adsorbed as regarded to Pb (II), on the R series samples.

On another hand, it is also interesting to note that on the C – Na and Ci samples, the temperature scarcely influences the Hg II retention while its effect on Pb II retention is quite strong. It is an indication that the bigger ion radius of Pb can diffuse to the sorption sites easier when thermal agitation is stronger. The sites on Ci and C-Na are improper for the Hg II retention.

The distribution between the amount of metal ions kept per unit mass of adsorbent and its equilibrium concentration in solution of ions is displayed in figures 2

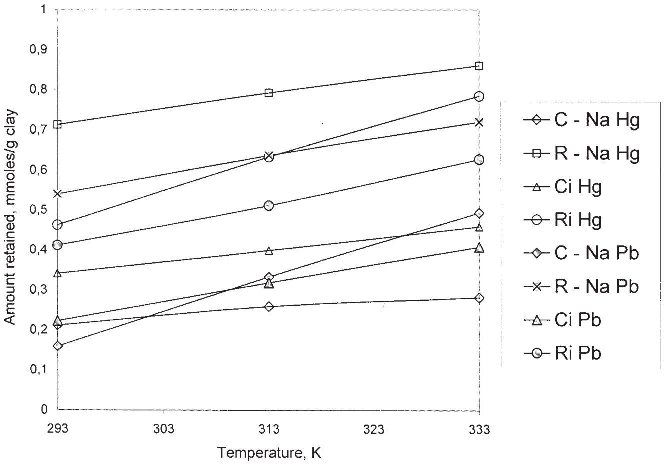

Fig. 1.Influence of temperature on the metal ions sorption

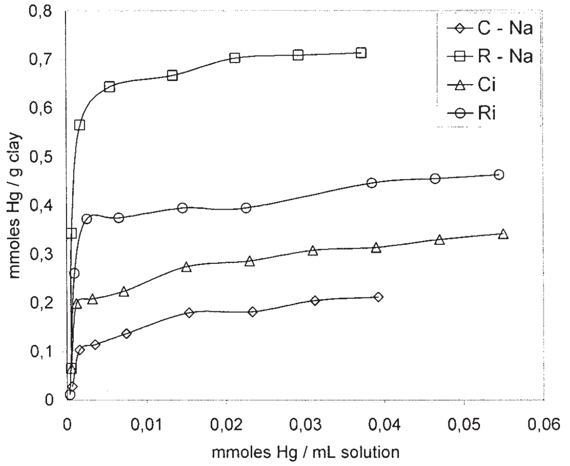

Fig. 2. Hg (II) ions distribution between aqueous solution and clay

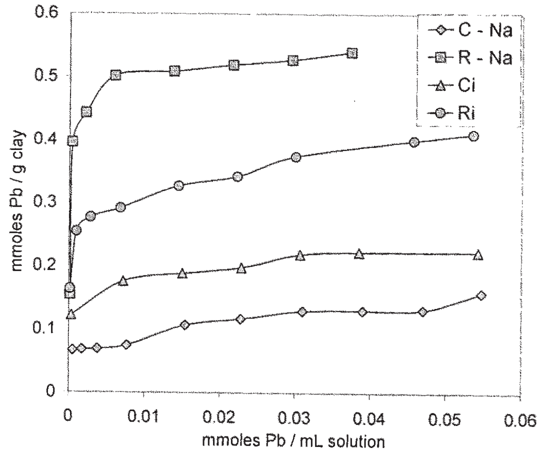

Fig. 3. Pb (II) ions distribution between aqueous solution and clay

and 3. The exchange was performed at 293 K on original and modified clays.

For both sample series, the affinity of the solid for the two ions decreases in the following order: R – Na > Ri > Ci > C – Na. It is worthy to note that the sodium initial exchange is crucial for the improvement of the sorption capacity of the clay from Razoare, while the reverse occurred for the Valea Chioarului clay. For both ionic adsorbed species, the increase in the retention capacity of the solid is more significant only up to 0.01-0.02 mmoles/mL, showing that the sorption is effective only for low toxic ions concentration values.

We tried further to fit the equilibrium sorption data with the Langmuir and Freundlich models (Goswami and Ghosh [12]).

The Langmuir isotherm in liquid phase is given by the following equation:

$$\frac{c}{q} = \frac{1}{q_0 K_L} + \frac{c}{q_0} \qquad (3)$$

where c is the residual concentration of ions in solution at equilibrium, q and q_0 are the amounts of ions incorporated in the solid in a given moment and at equilibrium, respectively, and K_L is the Langmuir constant, being the ratio between the adsorption and desorption rates.

The Freundlich isotherm for aqueous phase is described by the equation:

$$\ln q_c = \ln K_F + \frac{1}{n} \ln C_c \qquad (4)$$

where q_c is the amount adsorbed, C_c is the equilibrium ion concentration and K_F and n are the Freundlich constants indicating the favourableness and capacity of the sorbent.

The sorption isotherm constants determined from intercepts and slopes of linear plots of these equations for Pb (II) and Hg (II) sorption on natural and modified clays and their correlation coefficients (R^2) are presented in table 2.

From the q_0 values it can be concluded that the affinity order for metal sorption under the same conditions is Hg (II) > Pb (II), as observed before from the equilibrium sorption data. The values of R^2 from table 2 show that the ion exchange isotherms data for both Pb (II) and Hg(II) ions can be better described by the Langmuir than by the Freundlich model. It allows us to calculate some thermodynamic parameters of the sorption process.

The thermodynamic parameters ΔG, ΔH and ΔS for the metal sorption studied on Na-clays were calculated (table 3) from the temperature dependence of Langmuir constant, using the following equations:

$$\Delta G = -R\,T \ln K_L \qquad (5)$$

$$\ln K_L = -\frac{\Delta H}{R \cdot T} + const \qquad (6)$$

$$T\,\Delta S = \Delta H - \Delta G \qquad (7)$$

Table 2
CONSTANTS OF LANGMUIR AND FREUNDLICH ISOTHERMS AND CORRELATION COEFFICIENTS (R^2)

Ions	**Sample**	**Langmuir constants**			**Freundlich constants**		
		q_0 (mg/g)	**$K_L.10^3$ (L/g)**	**R^2**	**n**	**K_F**	**R^2**
Pb (II)	C-Na	51.55	5.47	0.9877	12.22	25.45	0.8983
	R-Na	112.99	4.86	0.9963	14.20	60.48	0.9613
	Ci	47.17	4.36	0.9910	8.34	15.37	0.9884
	Ri	129.87	7.62	0.9984	12.48	61.46	0.9806
Hg (II)	C-Na	45.45	1.36	0.9920	4.26	5.12	0.9856
	R-Na	151.55	2.47	0.9865	13.32	74.28	0.9650
	Ci	69.44	1.69	0.9951	5.54	12.67	0.9828
	Ri	93.46	3.06	0.9970	7.35	26.37	0.9609

Sample	Metal ions	T, K	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, kJ/mol K
C-Na	Pb	293	-16.888	-42.255	-0.0865
		313	-14.325		-0.0892
		333	-13.448		-0.0865
	Hg^{2+}	293	-13.132	-2.295	-0.0335
		313	-13.206		-0.0348
		333	-14.618		-0.0370
R-Na	Pb	293	-16.812	23.037	0.1360
		313	-20.094		0.1377
		333	-22.063		0.1354
	Hg^{2+}	293	-17.792	4.388	0.0756
		313	-19.197		0.0753
		333	-20.825		0.0757
Ci	Pb	293	-14.032	23.531	0.1282
		313	-17.163		0.1300
		333	-19.137		0.1281
	Hg^{2+}	293	-12.797	19.152	0.1090
		313	-11.870		0.0991
		333	-11.939		0.0933
Ri	Pb	293	-14.770	24.884	0.1353
		313	-18.252		0.1378
		333	-19.634		0.1336
	Hg^{2+}	293	-15.884	5.657	0.0735
		313	-16.985		0.0723
		333	-17.447		0.0693

Table 3
THERMODYNAMIC PARAMETERS OF THE STUDIED METAL SORPTION ON RAW AND Na - EXCHANGED CLAYS

where R is the gas constant of gases and T is absolute temperature, K.

The negative values of free energy changes (ΔG) show that the adsorption process occurs spontaneously for both Pb(II) and Hg(II) species on the tested modified clays over the whole range of working temperatures. For most samples, there is a slight increase of the absolute value of ΔG, suggesting that the temperature increase is favourable for the ions removal from the solutions. There is a different behaviour between the sample C-Na and the other ones. The enthalpy variation is negative for this sample, indicating an exothermal process, while for the other samples, the process is endothermic. It suggests that the uptake mechanism is predominantly adsorption for the sample C-Na, while ionic exchange seems to predominate in the other samples. This hypothesis is also confirmed by the much lower ionic exchange capacity of this sample (see fig. 3). This is further confirmed by the values of the entropy variation. The release of sodium ions to the aqueous solution during the ionic exchange increases the entropy, while the adsorption decreases the ions moving freedom and the entropy also decreases.

Another parameter displaying the efficiency of a sorbent in heavy metal removal/recovery is the equilibration time. The data presented in figure 4 show that the equilibrium is reached in about 25 - 30 min. It suggests that the intra particle exchange ions diffusion is the limiting factor in the process.

The reaction order of sorption in metal ion clays systems was determined using two kinetic models, namely pseudo-

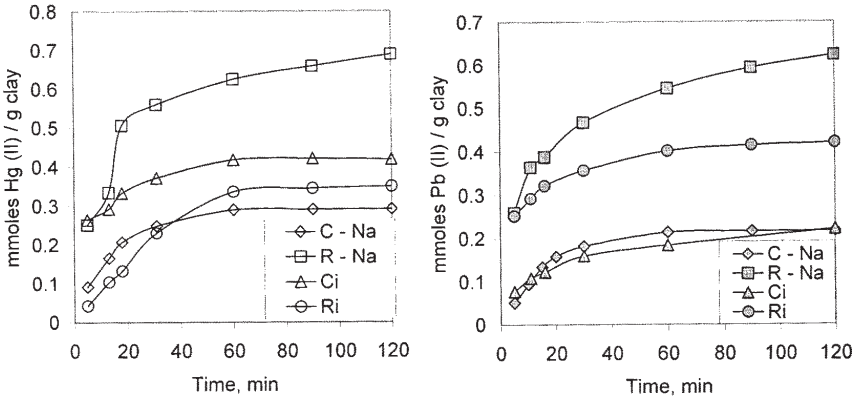

Fig. 4. Evolution with time of the removal degree of Pb (II) and Hg (II) on natural and modified clays

Table.4
KINETICS PARAMETERS OF SORPTION PROCESS Of Pb (II) AND Hg (II) ON CLAYS

Ions	Sample	Pseudo-first kinetic model (eq. 8)		Pseudo-second kinetic model (eq. 9)		
		$K_1 . 10^3$ [mg/g·min]	R^2	K_2 [g/mg·min]	H [mg/g·min]	R^2
Pb (II)	C-Na	-24.8	0,9956	2.96	0.169	0.9969
	R-Na	-12.1	0,9939	0.78	0.004	0.9958
	Ci	-10.2	0,9923	3.22	0.226	0.9991
	Ri	-17.2	0,9998	0.39	0.0016	0.9980
Hg(II)	C-Na	- 40	0,9956	2.19	0.0707	0.9972
	R-Na	-13.7	0,9987	1.26	0.0105	0.9943
	Ci	-25.2	0,9691	54.39	16.567	0.9985
	Ri	-34.5	0,9776	0.35	0.0014	0.9955

first order model (Lagergren equation) and pseudo-second order model, described by the following equations [12, 13]:

$$\ln (q_0 - q_t) = \ln q_0 - K_l \cdot t \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_0^2} + \frac{t}{q_0} \tag{9}$$

where q_0 is the initial amount of metal in the solution, q_t the amount of sorbed ions at time t, K_l is the Langergren rate constant of the first order sorbtion and K_2 is the rate constant of second order sorption.

The kinetic parameters calculated from the slope and intercept of corresponding plots as well as the correlation coefficients are presented in table 4.

The results show that the sorption process of both divalent metals on original and modified clays can be described by a pseudo second order model and the intra-particle diffusion is the rate – controlling step.

Conclusions

The sorption of Pb (II) and Hg (II) from aqueous solutions on original and modified clays depends on the initial ion metal concentration, temperature and contact time. The uptake of metal ions in diluted solutions is quite high especially for lead ions.

The equilibrium sorption data for both metal ions in the clay samples fitted well to the Langmuir model. The thermodynamic parameters deduced form this model showed that there are differences between the mechanisms of sorption, i.e., both adsorption and ionic change can occur.

The kinetic sorption data fitted well to the second-order kinetic model, indicating an intra particle diffusion limiting step.

The obtained data are promising for the application of toxic ions removal from industrial wastewaters on modified clays, since these solids are easyly available and cheap. However, the long term stockage of the solids used as adsorbents and ion exchangers is still a problem which needs to be solved before applying the ions removal at large scale, since they are a hazardous material for the environment.

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