Research Article

Removal of Pb^{2+} and Fe^{2+} from Aqueos Solutions by Adsorbtion on "Kosovo" Clay

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ABSTRACT

The use of clay in its natural and treated form obtained from Kamenica, state Kosovo, as adsorbent to remove Pb^{2+} and Fe^{2+} from aqueous solution was investigated using batch experiments. Adsorption experiments were carried out for various initial concentrations of ions and contact times while the amount of adsorbent was kept unchanged. From the results obtained, it was found that the removal of ions depends on initial concentrations and contact times, the amount of metal ions adsorbed was increased with increasing of initial concentration and contact time. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherms. The Freundlich isotherm model gave a better fit to the adsorption data than the Langmuir isotherm. Therefore, this study demonstrates that our clay could be used to adsorb heavy metals from aqua solutions.

Keywords: Adsorption, clay, isotherm, metal ion.

INTRODUCTION

The pollution by heavy metals currently it is becoming a big challenge and a concern for the water quality and also for the environment in general[1]. Some metal ions are toxic even if their concentration is very low, and their toxicity increases with accumulation in water and soils[2].

Metals found to be of great environmental concern by the World Health Organization (WHO) are lead, mercury, chromium, zinc and iron.

Lead is one of the most toxic among these metals, is widely distributed in water and soil with recognized accumulative and persistent characteristics[3].

When accumulated in the human body, Pb(II) causes damage to organs and other systems (especially in young children)[4-6]. The assimilation of relatively small amount of lead over a long period of time in humans can cause malfunctioning of the organs and central nervous system, high concentration of lead can damage the brain, liver and kidney[7].

Several treatment methods have been suggested for heavy metals mitigation, nevertheless, the search for cost effective, alternative technologies or sorbents for metals treatment from contaminated wastewater streams is needed. Natural materials that are available in large quantities or even certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents[8].

Physiochemical methods such as coagulation, flocculation, ion exchange, membrane separation, photodegradation, and electrochemical oxidation have been used for the treatment of contaminated water. Among them, adsorption is the most efficient, promising, and widely used in wastewater treatment because of its simplicity, economic viability, technical feasibility, and social acceptability[9].

Clay has typical properties (larg surface area, high cation exchange capacity chemical and mechanical stability and a layered structure) that predispose them to be good adsorbents. Bentonite belongs to the group of clay minerals. A number of studies have shown their effectiveness for the removal of metal ions[10].

Keeping this in mind, the main purpose of the present work was to evaluate the feasibility of Kamenica's clay to operate as sorbents to capture heavy metals from wastewater in order to propose other roles for these materials than its use as soil amendment.

MATERIALS AND METHODS

Reagents and Solutions

All the reagents used were of analytical grade and distilled de-ionized water was used in preparation of all solutions.

Solution of heavy metals, with different concentration was prepared by dissolving required quantity of their salts ($PbCl_2$ and $FeCl_2$) in water. Freshly prepared solution was used for each experiment.

Preparation of Acid-Ativated Bentonite

Kamenica's (Kosovo) clay was obtained from Kamenica, Kosovo. The clay was dried and after that the clay was treated with 1M sulphuric acid in water bath in relation 1g bentonite with 5ml acid. The composition was shaken for 1h. The acid treated clay was centrifuged, air dried and ground to fine powder (< 0.12 mesh).

Adsorption Experiments

Adsorbtion tests were performed by batch experiments, under stirring at room temperature (20 °C). Each adsorption study was performed by adding 1g of the adsorbent to 5 ml of a given concentration of the adsorbate.

At the end of the given contact time, the solid and liquid phases were separated by centrifugation. The initial (C_0) and equilibrium (C_e) concentrations of Pb^{2+} and Fe^{2+} in the solutions were determined by flame atomic absorbtion spectrometer (Parkin Elmer 370A). All measurements were carried out in air/acetylene flame. Each experiment was repeated and the mean value was calculated in order to minimize errors. The uptake capacity of the clay for Pb^{2+} and Fe^{2+} ions was calculated from the mass balance equation given in equation 1.

$$q_e = V * [C_0 - C_e] / m \qquad (1)$$

Percent removal of Pb^{2+} and Fe^{2+} ions was calculated according to equation 2.

$$R\% = [(C_0 - C_e) / C_0] * 100 \qquad (2)$$

Where q_e is the uptake capacity (mg/g), C_0 is the initial ion concentration (mg/dm^3), C_e is the concentration of ions remaining in solution at equilibrium (mg/dm^3), **V** is the volume of ion solution used (dm^3) and m is the mass of adsorbent.

RESULTS AND DISCUSSION

The chemical composition of Kamenica's (Kosovo) clay is shown in Table 1.

Table 1: Chemical Composition of Clay.

Composition	% by Weight
SiO_2	45.75
Al_2O_3	13.61
K_2O	8.01
MgO	7.70
Fe_2O_3	10.76
CaO	4.84
Na_2O	4.43

It is observed that silica and alumina are the major constituents.

In Table 2 and 3 heavy metal ion adsorption capacities of clay are presented as a function of the initial metal ions concentration. The initial metal ion concentration is an important factor to be considered in adsorption studies, since the rate of adsorption is dependent on the initial concentration of metal ion present in solution.

It is seen that the uptake capacity of the clay increased with increase in initial concentration of ions.

This increase is simply due to the presence of more metal ions in solution available for sorption and higher interaction between ions and adsorbent.

This is obvious also from the fact that this increase in the initial ions concentration provides an important driving force to overcome all of mass transfer resistance[11].

Table 2: Adsorption Parameters for the Adsorption of Pb^{2+} on Clays at Different Initial Ions Concentration.

Pb	C_o (mg/dm^3)	C_e (mg/dm^3)	q_e (mg/g)	R %	C_e / q_e	ln C_e	ln q_e	R_L
Natural Clay	47.54	0.15	0.24	99.68	0.63	-1.90	-1.44	0.0141
	93.84	2.50	0.46	97.34	5.47	0.92	-0.78	0.0072
	137.63	9.15	0.64	93.35	14.24	2.21	-0.44	0.0049
Treated Clay	49.61	7.00	0.21	85.89	32.86	1.95	-1.55	0.0839
	93.22	35.00	0.29	62.45	120.23	3.56	-1.23	0.0465
	135.11	71.40	0.32	47.15	224.13	4.27	-1.14	0.0325

Table 3: Adsorption Parameters for the Adsorption of Fe^{2+} on Clays at Different Initial Ions Concentration.

Fe	C_o (mg/dm^3)	C_e (mg/dm^3)	q_e (mg/g)	R %	C_e / q_e	ln C_e	ln q_e	R_L
Natural Clay	34.97	0.50	0.17	98.57	2.90	-0.69	-1.76	0.0387
	69.94	6.08	0.32	91.31	19.04	1.81	-1.14	0.0197
	100.00	16.84	0.42	83.16	40.50	2.82	-0.88	0.0138
Treated Clay	33.41	0.80	0.16	97.61	4.91	-0.22	-1.81	0.0748
	64.85	3.50	0.31	94.60	11.41	1.25	-1.18	0.0400
	99.17	7.00	0.46	92.94	15.19	1.95	-0.77	0.0265

Table 4: Langmuir and Freundlich Constants for the Adsorption of Pb^{2+} and Fe^{2+} Ions on Clay.

Langmuir Isotherm					
Clay	**Metal ion**	**q_m**	**B**	**R^2**	**R_L**
Natural	Pb^{2+}	0.68	1.47	0.9892	$0 < R_L < 1$
Treated	Pb^{2+}	0.34	0.22	0.9994	$0 < R_L < 1$
Natural	Fe^{2+}	0.44	0.71	0.9901	$0 < R_L < 1$
Treated	Fe^{2+}	0.61	0.37	0.9497	$0 < R_L < 1$
Freundlich Isotherm					
Clay	Metal ion	N	K_f	R^2	
Natural	Pb^{2+}	4.15	0.37	0.9991	
Treated	Pb^{2+}	5.66	0.15	0.9921	
Natural	Fe^{2+}	4.00	0.21	0.9999	
Treated	Fe^{2+}	2.12	0.18	0.9934	

The Langmuir and Freundlich adsorption isotherms were applied to the data obtained on the effect of initial metal ion concentration.

Each isotherm was assessed based on the closeness of the value of the regression coefficient (R^2) to 1.

The linearized form of the Langmuir and Freundlich isotherms are given in equations 3 and 4 and in Figures 1, 2, 3 and 4, respectively.

Ce/qe = Ce/qm + 1/qmb (3)

Ce (mg/dm^3) is the concentration of heavy metal ions in equilibrium, **qe** (mg/g) is the equilibrium uptake capacity, **qm** (mg/g) is the maximum adsorption capacity corresponding to a complete monolayer coverage and **b** (dm^3/mg) is the Langmuir isotherm constant which quantitatively reflects the affinity between the adsorbent and the adsorbate.

lnqe = lnKf + [1/n]lnCe (4)

n is a dimensionless constant describing the adsorption intensity and **Kf** (dm^3/g) is the Freundlich isotherm constant describing the adsorption capacity of the adsorbent.

The experimental adsorption isotherms were fitted to Langmuir and Freundlich models to describe the adsorption characteristics of natural and treated clay with a correlation coefficient of 0.9497-0.9999 (Tables 4).

A linear plot of Ce/qe against Ce confirms the Langmuir isotherms and are shown in Figure 1 and 2. qm and b were calculated from the slope and intercept respectively.

The Langmuir isotherm parameters are given in Table 4. The value of b (Langmuir constant) obtained is low which implies that the sorption of Pb^{2+} and Fe^{2+} ions onto our clay is a favorable one.

The Langmuir constant ranged between 1.47 and 0.71 for natural clay and 0.22 and 0.37 for treated clay shows that the adsorption was more favorable for the treated clay.

The dimensionless separation factor (R_L), as a measure of the adsorption favorability, was calculated ($0 < R_L < 1$, the smaller is the more favorable) by using the following equation:

$R_L = 1/(1+bCo)$ where b is the Langmuir constant[9].

The Freundlich isotherms were confirmed by the plot of lnqe against lnCe shown in Figure 3 and 4.

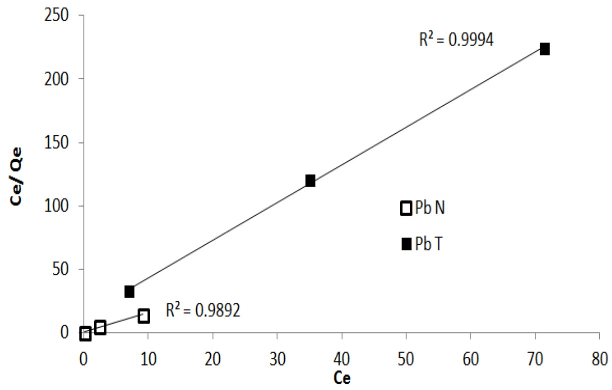

Figure 1: Langmuir's linear isotherms related to adsorption of Pb^{2+} from aqueous solution on natural (Pb N) and treated clay (Pb T).

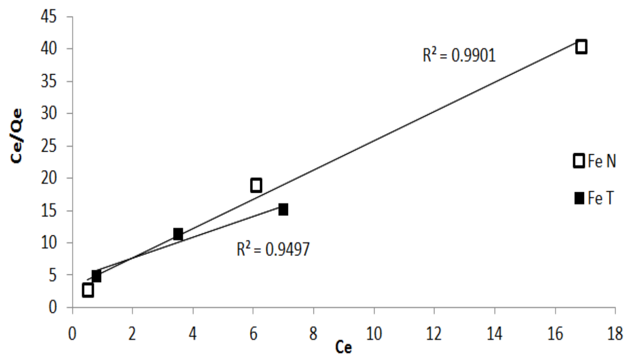

Figure 2: Langmuir's linear isotherms related to adsorption of Fe^{2+} from aqueous solution on natural (Fe N) and treated clay (Fe T).

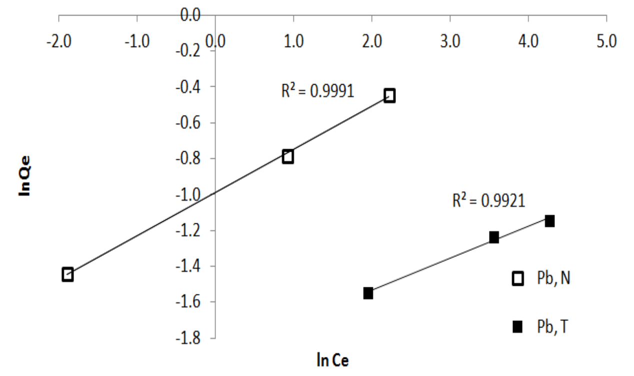

Figure 3: Freundlich's linear isotherms related to adsorption of Pb^{2+} from aqueous solution on natural (Pb, N) and treated clay (Pb, T).

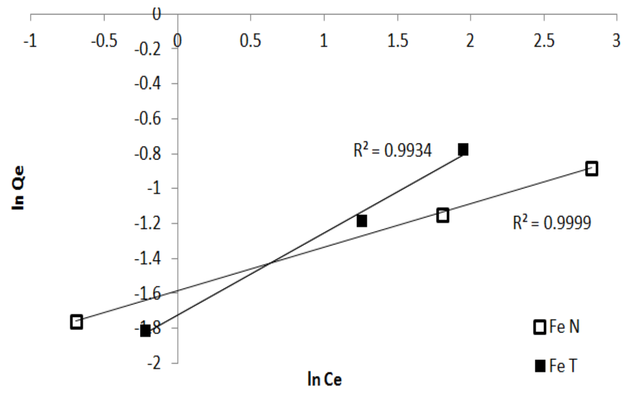

Figure 4: Freundlich's linear isotherms related to adsorption of Fe^{2+} from aqueous solution on natural (Fe N) and treated clay (Fe T).

The constants n and Kf were obtained from the slope and intercept respectively. The freundlich isotherm parameters are presented in Table 4. The n value in Freundlich equation was found to be 2.12–5.66. A value of n above unity indicates a favourable adsorption[12].

The situation n > 1 is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent adsorbate interaction with increasing surface density and the values of n within the range of 1–10 represent good adsorption[13]. Increasingly large Kf value indicates greater adsorption capacity[14].

In the present study, since n lies between 1 and 10 it indicates the physical adsorption of metal ions onto clay.

Langmuir and Freundlich adsorption constants and correlation coefficients (R^2) are presented in Table 4. The value of the regression coefficient (R^2) of both models are close to the value of 1, but correlation coefficients for the Freundlich isotherm are closer to 1 and this shows that Freundlich adsorption isotherm was the better model for the metal ions adsorption onto our clay.

CONCLUSION

The removal efficiency of Pb^{2+} and Fe^{2+} by Kosovo clay was investigated. The results of the adsorption studies revealed that the removal of Pb^{2+} and Fe^{2+} on the Kosovo clay adsorbent may be described by the Freundlich isotherm and Langmuir isotherms but Freundlich adsorption isotherm was the better model for the metal ions adsorption onto our clay.

The percentage of adsorption of Pb^{2+} and Fe^{2+} from aqueous solution onto Kosovo clay goes up to the value 99.68%.

It was found that the Kosovo clay were an effective adsorbent for removal Pb^{2+} and Fe^{2+} from the aqueous solutions.

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