American Journal of Applied Sciences 4 (7): 502-507, 2007
ISSN 1546-9239

Removal of Pb^{+2} Ions from Aqueous Solutions by Adsorption on Kaolinite Clay

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Abstract: The adsorption potential of the kaolinite clay for the removal of lead ions from aqueous solutions was tested. The measured adsorption isotherms at the different temperatures 298.15 K, 308.15 K and 318.15 K were found to be perfectly fit to the Langmuir isotherm equation. A high adsorption capacity was calculated. An increase in the retention capacity with increasing temperature was measured. The adsorption process was found to be endothermic with an estimated mean enthalpy change of 135.2 kJ/mol. The measured adsorption kinetic data at different temperatures proved that not only intraparticle diffusion controls the adsorption process but also surface adsorption contributes to the control of rate of adsorption. The influence of pH in the acidic range was investigated. The measured increase in the adsorption rate at higher pH values (4.9) was explained through the influence of H^+ ions on the complex ion formation.

Key words: Adsorption, Kaolinite, Clay, Lead, Aqueous Solution, pH

INTRODUCTION

Contamination of water with lead heavy metal ions is a large environmental concern associated with the increasing of industrial processes which discharge aqueous effluents containing lead ions. Lead ions are not biodegradable and tend to accumulate in living organisms, causing various health problems. According to the World Health Organisation, the accepted range of Pb^{+2} in water is 0.01 ppm.

There are many conventional processes for the removal of lead and the different heavy metals from industrial wastewater streams such as precipitation, coagulation, ion exchange etc. [1]. These processes have many disadvantages such as incomplete removal, high energy and reagents costs and disposal of toxic sludge.

Adsorption methods were found to be more effective and attractive due to its lower costs and the higher efficiency of heavy metal ions removal from wastewater. Activated carbon is a potential adsorbent for the removal of several organic and inorganic pollutants [2]. Zeolites were used for the purification of wastewater from heavy metals [3]. Removal of lead from water by adsorption on a kaolinite clay was investigated [4].

In this work, the kaolinite clay which was obtained from Petra location in Jordan will be investigated as a potential and low cost adsorbent for Pb^{+2} ions from aqueous solutions. The thermodynamic and kinetic parameters involved in the adsorption process will be estimated. Also the role of pH and temperature will be tested.

MATERIALS AND METHODS

All the experiments were conducted with artificial wastewater stock solution prepared by dissolving analytical grade $PbCl_2$ to distilled water. The stock solution was diluted to a specific concentrations and stored at 25 °C in a dark place. The initial pH of the solution was adjusted using a 1.0 M HCl solution.

Clay samples obtained from Petra area were used as adsorbent material. The collected raw samples have been subjected to beneficiation process using hydro cyclone to reduce the quartz ratio as described by Gougazeh [5]. Hence, a high grade kaolinite was implemented for the adsorption experiments. The mineralogical and chemical composition of the clay before and after beneficiation are displayed in tables 1and 2, respectively.

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Table 1: Mineralogical composition (XRD, Qualitative) ordered from the higher ratio, given the number 1, to lower ratio, given the number 5.

Ratio Order	Raw Clay Mineral Components	Ratio Order	Beneficiated Clay Mineral Components
1	Quartz (SiO_2)	1	Kaolinite ($Al_2Si_2O_5(OH)_4$
2	Kaolinite ($Al_2Si_2O_5(OH)_4$	2	Quartz (SiO_2)
3	K-Feldspar ($KAlSi_2O_8$) [Traces]	3	K-Feldspar ($KAlSi_2O_8$)
4	Muscovite [Traces]	4	Illite [Traces]
5	Hematite (Fe_2O_3) [Traces]	5	Hematite (Fe_2O_3) [Traces]

Table 2: Chemical Composition (XRF)

Compound	Ratio (Wt.%) Raw Clay	Ratio(Wt.%) Beneficiated Clay
SiO_2	67.4	55.29
TiO_2	0.84	1.25
Al_2O_3	15.73	26.43
Fe_2O_3	4.65	2.1
MgO	1.4	0.72
MnO	0.02	0.02
CaO	0.09	0.23
Na_2O_3	0.01	0.4
K_2O	2.7	3.59

Before the experiment, the clay samples were washed with deionised water several times with a constant stirring, to remove the soluble inorganic salts and any adhering materials. The samples were then left to settle, separated from liquid by filtration and then dried at 80 °C for 24 hours. The samples were afterwards subjected to sieve analysis. The average size of kaolinite used in all experiments was 53 µm.

The adsorption isotherms were determined by allowing a lead ions solution of known initial concentration to be mixed with accurately weighed amount of kaolinite in a tightly closed flask at a certain temperature. The amount of kaolinite in the slurry was 1 g/250 mL solution. A constant mixing at a constant temperature was achieved using a water bath shaker. The kaolinite-solution were then equilibrated for 50 hours. The clay suspensions were then filtered and the supernatant solution was subjected to analysis using Atomic Absorption Spectrophotometer (AAS). The amount of lead ions retained by kaolinite were calculated from the difference between the initial concentration and the equilibrium concentration. The same experiment was repeated at different initial concentrations and different temperatures.

The adsorption rate data at different initial pH values and different temperatures were obtained by allowing the kaolinite-solution (1g clay/ 250 mL solution) to be mixed in a water bath shaker. The initial concentration of lead ions was 200 mg/L. During the experiments, samples of the solution were periodically withdrawn each defined period of time, filtered and then subjected to concentration analysis using AAS method.

RESULTS AND DISCUSSIONS

Adsorption isotherms: The obtained experimental equilibrium data for the adsorption of Pb^{+2} ions by kaolinite at the different temperatures 298.15 K, 308.15 K and 318.15 K are presented in figure 1. The adsorption isotherms were measured at a constant initial pH value of 4.5.

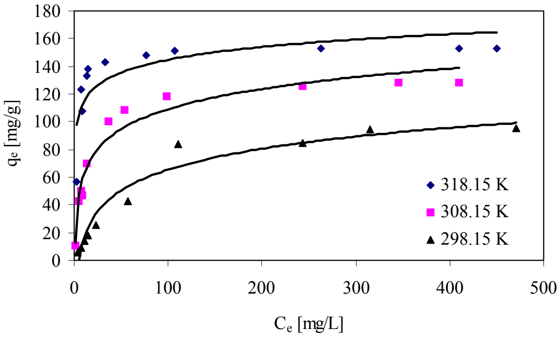

Fig. 1: Adsorption isotherms of Pb^{+2} ions by kaolinite at different temperatures. Initial pH 4.5

The experimentally obtained equilibrium data for the adsorption of lead ions from aqueous solutions by kaolinite at different temperatures were analysed according to the Langmuir adsorption isotherm equation:

$$\frac{C_e}{q_e} = \frac{1}{a_l.k_l} + \frac{C_e}{a_l} \qquad (1)$$

where C_e is the equilibrium concentration of Pb^{+2} ions remaining in the solution and q_e is the amount of Pb^{+2} ions adsorbed per unit mass of kaolinite. The Langmuir equilibrium constants a_l and k_l in equation 1 are quantities describing the adsorption process, where a_l is related to the retention capacity of the adsorbent and k_l is related to the binding energy between the adsorbent and the adsorbate.

The results presented in figure 1 indicate a high retention capacity for the Pb^{+2} metal ions by kaolinite particles. The retention capacity of kaolinite increases with increasing the temperature over the temperature range studied. Figure 2 shows the straight line fitting of the measured adsorption isotherms according to Langmuir equation.

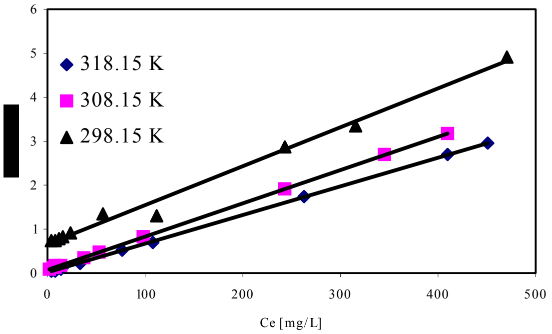

Fig. 2: Straight line fitting of the experimental equilibrium data for the adsorption of Pb^{+2} according to Langmuir isotherm, equation 1.

As Fig. 2 displays, the measured adsorption isotherms fit very well to the Langmuir equation with a high correlation coefficients. The Langmuir constants a_l and k_l are evaluated from the slopes and intercepts of the straight lines using the method of least squares linear regression analysis. The Langmuir constants as well as the correlation coefficients of the Langmuir isotherm (equation 1) at the temperatures studies are listed in table 3.

Table 3: Langmuir equilibrium constants evaluated from the linear regression analysis shown in figure 2

T [k]	a_l [mg/g]	k_l [L/mg]	R^2[-]
298.15	113.63	0.01320	0.9915
308.15	131.58	0.08482	1
318.15	153.84	0.40625	0.9999

The calculated values of a_l are relatively high indicating a higher retention capacity of the kaolinite. The higher retention capacity might be attributed to the implemented beneficiated kaolinite. Referring to tables 1 and 2, the beneficiated kaolinite includes illite which has a great retention capacity of lead ions. Moreover, the decrease in the quartz ratio and the increase in kaolite ratioin the clay due to the beneficiation processes might be another reason standing behind the reported high adsorption capacity. The retention capacity increases strongly with increasing temperature o the increased diffusion rate of the adsorbent in the bulk solution as well as the increase in intra-particle diffusion. The high values of k_l which are listed in table 1 indicates a higher ability of kaolinite to adsorb lead ions and to form a stable complexes. The increased values of k_l with increasing temperature represents an evidence that a chemical interaction between lead ions and kaolinite occurs.

The higher adsorption capacity of kaolinite is attributed to its molecular structure. It consists of micelles with each micelle is constructed of a layer of silicon tetrahedral units and a layer of aluminum octahedral in a 1:1 ratio. The availability silanols and aluminols which are the proton bearing surface functional group of kaolinite layers facilitates the adsorption of lead ions to take place effectively. This is resulted from the formation of stable complexes between lead ions and the silanol and aluminol groups.

Thermodynamic parameters: The thermodynamic parameters for the adsorption of lead ions by kaolinite such as the enthalpy change (ΔH^o), the Gibbs free energy change (ΔG^o) and the entropy change (ΔS^o) can be calculated from the variation of Langmuir constant (k_l) with temperature (T) using the following basic thermodynamic relations [6]:

$$\ln k_l = A - \frac{\Delta H^o}{RT} \tag{2}$$

$$\ln k_l = -\frac{\Delta G^o}{RT} \tag{3}$$

$$\Delta S^o = \frac{\left(\Delta H^o - \Delta G^o\right)}{T} \tag{4}$$

According to equation 2, the mean value of the enthalpy change due do the adsorption of lead ions by kaolinite over the temperature range studied can be determined graphically by the linear plotting of ln k_l against 1/T using the least squares analysis, see figure 3.

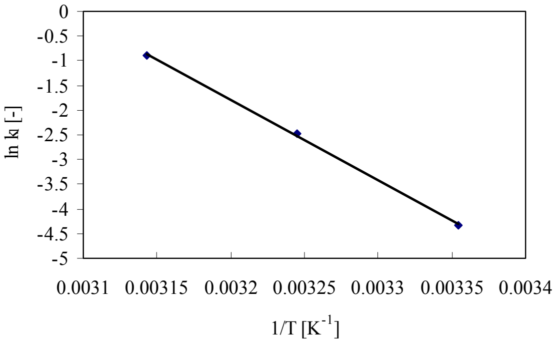

Fig. 3: The variation of Langmuir constant with temperature according to equation 2

The mean enthalpy change can be determined from the slope of the straight line. The variation of Gibbs free energy and entropy change with temperature can be calculated using equations 3 and 4, respectively. The results are arranged in table 4.

Table 4: The thermodynamic parameters for the adsorption of lead ions on the kaolinite

T [k]	ΔH^o [kJ/mol] Mean value	ΔG^o [kJ/mol]	ΔS^o [kJ/mol.K]
298.15	135.2	10.7	0.417
308.15	135.2	6.3	0.418
318.15	135.2	2.4	0.417

An important result can be obtained from table 4 is that the Gibbs free energy (ΔG^o) is small and positive with its value decreases with increasing temperature. This indicates that the adsorption processes of lead ions by kaolinite can be enhanced by increasing temperature. The values of entropy change (ΔS^o) are positive and remain almost constant with temperature. This gives an evidence that structural changes in lead ions and kaolinite occur during the adsorption process. The positive values of enthalpy change (ΔH^o) show the endothermic nature of the adsorption process of lead ions by kaolinite.

Adsorption Kinetics: The kinetics of adsorption and the steps controlling the rate of adsorption process of lead ions by kaolinite particles are determined by obtaining measurements of adsorption rate with time. The measurements of variation of lead ions concentration as a function of time at different temperatures are shown in figure 4. The data presented heir are for a solution with an initial pH value of 4.5 and initial lead ions concentration of 200 mg/L. The adsorbent amount in the mixture is 1g/250 mL solution.

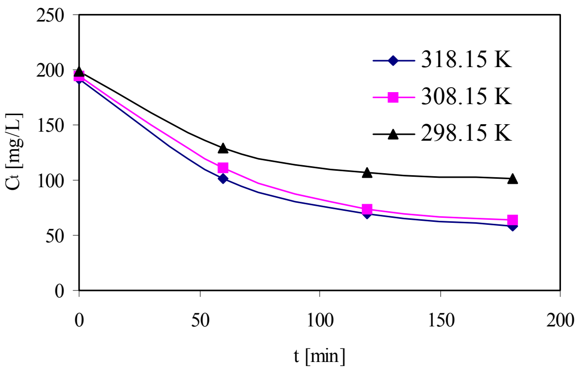

Fig. 4: Effect of temperature on the lead ions adsorption rate

The measured increase in adsorption with increasing temperature is explained previously through the thermodynamic parameters. The boundary layer mass transfer across the liquid film surrounding each particle is enhanced with increasing temperature. Since the adsorption experiments were conducted in a shaker water bath which was continuously agitated and mixed, it can be assumed that the mass transfer step of lead ions from the bulk liquid to the external surface of kaolinite particles does not limit the rate of adsorption process.

In the present context, the results shown in figure 4 will be examined in terms of the step of intraparticle diffusion of lead ions within the pores of kaolinite. It has been proven in previous adsorption studies [7,8] that if intraparticle diffusion is assumed to be the rate controlling step, the rate of adsorption process is normally expressed in terms of the square root of time ($t^{0.5}$). From the data presented in figure 4, the fraction of lead ions adsorbed is plotted against the square root of time at different temperatures in figure 5.

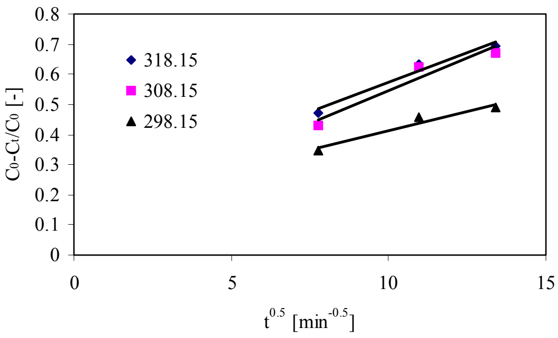

Fig. 5: The fraction of lead ions adsorbed against the square root of time at different temperatures

As shown in figure 5, the plot can be approximated to be linear over the range of adsorption times but does not pass through the origin. This indicates that not only intraparticle diffusion controls the adsorption process but also surface adsorption contributes to the control of rate of adsorption [9].

However, kaolinite is a clay the interlayer space of which is tight and therefore is not susceptible to intraparticle diffusion on the molecular structural level, thus it is valid for diffusion into the voids created by collections of grains of the clay.

Effect of initial pH of the lead solution: The experimental measurements for the change in lead ions concentration as a function of time at different initial pH values are depicted in figure 6. The adsorption experiments were conducted at 25 °C and initial lead ions concentration of 200 mg/L. The adsorbent amount used is 1g/250 mL solution. As shown in figure 6, increasing the pH value of the solution from 2.8 to 4.9 leads to an acceleration in the adsorption rate especially in the earlier stages. This dependence of adsorption rate on pH was reported in the literature [10]. Also it has been reported that better adsorption of lead ions by kaolinite takes place at higher pH values within the acidic range [4].

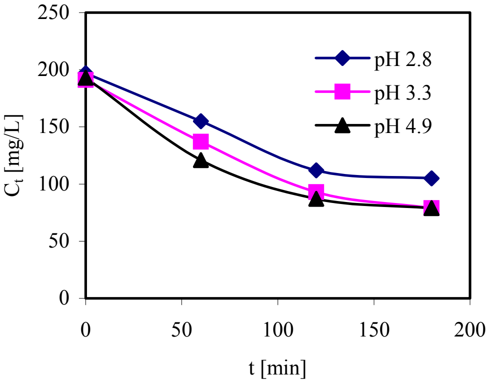

Fig. 6: Variation of lead ions concentration with time during its adsorption by kaolinite particles at different pH values in the acidic medium.

The influence of pH on the adsorption process of lead ions on kaolinite can be explained through the influence of H^+ ions on the complex ion formation process. The formation of complexes during the adsorption process is occurred by the interaction between the lead ions and the kaolinite negative charged sites (SiO^-) as well as the lattice hydroxyl groups (Si-OH) according to the equations [6]:

$$2SiO^- + Pb^{2+} \rightarrow (Si-O)_2 - Pb \qquad (5)$$

$$2Si-OH+Pb^{+2} \Leftrightarrow (Si-O)_2 - Pb + 2H^+ \qquad (6)$$

Decreasing the pH value results in increasing the a mount of H^+ ions in the solution. H^+ ions can compete with Pb^{+2} ions and bond to the SiO^- site of kaolinite according to equation 5. As a result the number of free SiO^- free sites available for Pb^{+2} ions to form a stable complexes will decrease, therefore the adsorption rate will consequently decrease. Moreover, increasing the amount of H^+ ions due to the decreasing in the pH value will lead to shifting of the equilibrium described by equation 6 to the lift side leading to a decrease of the adsorption rate of lead ions.

Because protons H^+ ions can adsorb into and desorb from surface charge sites, the pH value of the solution contacting the surface of the clay affects its net surface charge, and thus its ion exchange capacity. The pH at which a surface has an overall charge zero is known as its zero point of charge (ZPC). For clays dominated by kaolinite the reported ZPC values lies in the pH range from 1 to 3. Accordingly, the shown in figure 6 increasing adsorption rate at pH values greater than 3 can be attributed to the possible formation of negative charges on the clay surface, hence increasing of the ion exchange capacity of the clay.

CONCLUSION

Natural beneficiated clay kaolinite collected from Petra location in Jordan was investigated as a low cost and potential adsorbents for the removal of toxic lead ions from wastewater and industrial solutions. Results obtained indicates that a very fast and efficient removal of lead ions can be achieved using kaolinite as adsorbent. In this study, experiments were conducted with low kaolinite to solution ratio (1 g/250 mL solution) aiming to understand the kinetics and the effect of pH and temperature. However, a complete removal can be achieved by increasing the kaolinite to solution ratio. A faster removal of lead ions can be achieved by increasing the temperature up to 45 °C and increasing the pH in the acidic medium to 4.9.

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