Lead Uptake by Natural Clay

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Abstract: A local clay from Baha Region Southwest of Saudi Arabia was characterized and tested for its ability to adsorb lead ions from aqueous solutions. The adsorption capacity of the acid treated clay did not increase as compared to the untreated clay due to significant reduction in peak intensities at 2θ = 12 for the acid treated clays as shown from XRD characterization. The increase in temperature caused an increase in the lead adsorption capacity of clay. The maximum adsorption capacity of clay was 29.25 mg g⁻¹ at 80°C. It was observed that the adsorption system is endothermic. Also, the randomness of the system increased during the adsorption of lead ions on Baha clay. A comparison between Langmuir and Freundlich models at different temperatures showed that the Langmuir model described the experimental data better than the Freundlich model.

Key words: Adsorption, lead ions, acid (HCl), temperature, Baha clay, Langmuir, Freundlich

INTRODUCTION

Removal of heavy metals from aqueous solutions can be achieved by applying several physical and chemical methods such as ion exchange, extraction, flocculation, electro-deposition, coagulation, and precipitation. However, most of these methods are considered non-viable due to the cost factor. Clay, a naturally occurring material, can be used as an alternative cost-effective adsorbent for the removal of heavy metals such as lead ions from wastewater.

Previously, many researchers reported the adsorption of lead ions by clay minerals. Servidoto and Estes (1975) used various types of clays (kaolinite, illite, montmorillonite) for the adsorption of lead ions from wastewater in a pH range of 2.5 to 11. They found that montmorillonite has a maximum adsorption capacity at pH = 7.5 and kaolinite has a maximum adsorption capacity at pH = 4.5. Kaolinite and gilu clays from Nigeria were used for adsorption of lead ions from wastewater by Orumwenso (1996), who concluded that adsorption of lead ions is favorable at low pH, low concentration and at high temperature. Utilizing phosphatic clay to adsorb lead ions from aqueous solution, Singh et al. (2006) found that adsorption of lead ions enhanced in the presence of oxalic acid due to the formation of lead oxalate. Okitosho et al. (2006) investigated the effect of salt on adsorption of lead ions on marine clay. They found that lead ions retention is affected by carbonate and hydroxide phases. Adebowale et al. (2006) used kaolinite clay modified by orthophosphate to adsorb lead ions from wastewater. They found that lead adsorption increased by increasing the initial concentrations, pH and adsorbent dose. Unuabonah et al. (2007a) used kaolinite clay modified by tripolyphosphate for lead adsorption from aqueous solution. They reported that lead adsorption capacity was as high as 126.58 mg g⁻¹. The adsorption isotherm experimental data was correlated using different types of isotherm models and concluded that Toth and Freundlich models described the experimental data very well. Unuabonah et al. (2007b) studied the influence of initial concentration and temperatures on adsorption rate of lead ions on phosphate clay from Nigeria. They found that increasing the initial concentration and temperature caused an increase in the adsorption rate. They also observed that the process of lead adsorption on Nigerian phosphatic clay was endothermic and spontaneous. Ayari et al. (2007) studied the effect of treating bentonite clay by hydrochloric acid (HCl) on the adsorption isotherm of lead ions from aqueous solutions. They concluded that increasing the time of treatment caused a decrease in the cation exchange capacity. Chari et al. (2008) investigated the effect of acid treatment on the adsorption capacity of lead ions on clay. They reported that clay treated by sulphuric acid adsorbed more lead ions than that treated by hydrochloric acid. They attributed the discrepancy in adsorption performance to different kinds of acids (sulphuric acid, hydrochloric acid).

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Because, the ability of sulphuric acid to dissolve clay minerals is more than hydrochloric acid. Chen and Wang (2007) reported that the kinetics of lead adsorption on the Polygorskite clay followed pseudo-second-order with a maximum adsorption capacity of 104.28 mg g⁻¹. The kinetics of lead adsorption on smectite-bearing clay was also reported by Guerra and Airoldi (2008). They observed that the internal diffusion model described the experimental data well. Clay-carbon composite was suggested as a good adsorbent for lead ions in aqueous solution by Ake et al. (2001).

Recently, Al-Jill and Alsewailim (2009) tested the ability of some local clay materials from different regions of Saudi Arabia to adsorb lead ions from water. They reported that raw clays without treatment showed high adsorption capacities (mass of lead removed as mg·g⁻¹ mass of clay). At the same time, the acid treated clays exhibited lower adsorption capacities than the untreated clays.

The main objective of this investigation was to determine the influence of acid (HCl) treatment and the experimental temperature on the lead adsorption capability of Baha clay. Also to perform the compositional, crystallographic and topographical characterization of clay with and without treatment by hydrochloric acid (HCl).

**MATERIALS AND METHODS**

**Collection of experimental materials:** The clay soil was collected from Baha Region, Southwest of Saudi Arabia. Lead ions solutions were prepared from lead nitrate purified LR (Pb(NO₃)₂) supplied by S. define-chemicals limited (Laboratory Rasayan). Hydrochloric acid (HCl), a Laboratory Reagent Grade was used to activate the adsorption sites within the clay particles.

**Preparation of acid-treated clay samples:** The clay samples were activated by 1 M HCl at 90°C for two time intervals namely 1 and 3 h. In addition to above, the clay samples were also activated by 3 M HCl at 90°C for 1 h. Eight grams of clay samples were mixed with 25 mL of 1 M HCl solution and stirred thoroughly for homogeneity. Then the clay material was separated by filtration by washing several times with distilled water. Finally, the acid treated clay samples were air-dried for 24 h.

**Characterization of clay samples:** Clay samples (untreated and acid-treated Baha) were characterized by X-ray fluorescence (XRF) for compositional analysis and X-ray diffraction (XRD) for crystallography of the clay platelets.

**Equilibrium experiments:** Stock lead solutions of 1000 mg L⁻¹ concentration were diluted to required concentrations ranging from 50-1000 mg L⁻¹. Equilibrium isotherms were obtained by placing 1 g mass of clay in 50 mL lead solution in glass bottles and placed on a shaker for constant agitation. In each isotherm experiment, the solution concentrations ranged from 50-1000 mg L⁻¹ in the temperature range of 20-80°C. The duration for the equilibrium experiments was 3 h to assure that the adsorption process achieved state of equilibrium according to Al-Jill and Alsewailim (2009). Later on, the mixture was filtered using filter papers, then diluted and the absorbance was measured using atomic absorption spectroscopy both for the treated and untreated clay samples. The absorbance values for the unknown samples were compared with the calibration curve to determine the concentrations of lead. The amount of lead ions adsorbed on the clay was calculated from the mass balance equation on the batch reactor as follows:

\[ q_e = \frac{V(C_i - C_e)}{M} \]  

where, M is the adsorbent mass in g, V is the solution volume in liter, qₑ is the adsorbed lead ions concentration in mg·g⁻¹ and Cᵢ, and Cₑ are the initial concentration of lead ions and lead ions concentration in bulk solution at equilibrium in mg·L⁻¹, respectively.

The amount of lead ions adsorbed onto the adsorbent material versus the lead ions equilibrium concentration in the solution was plotted to obtain the equilibrium adsorption isotherm curves and the maximum adsorption capacity of lead ions on Baha clay.

**RESULTS AND DISCUSSION**

The adsorption capacity of clay, when treated with 1 M HCl and kept for 3 h, showed slight increase as compared to the untreated clay but the adsorption capacity decreased with increasing acid concentration (Fig. 1). The concentration of some major elements increased due to acid treatment, while other elements decreased. The chlorine was detected in the acid (3 M HCl) treated clay samples.

The slight increase in the adsorption capacity of the acid treated clay by HCl (1 M, 3 h) is presented in Table 1 and 2 and Fig. 2. It is quite evident that H⁺ ions might have released the interlayer cations such as Fe³⁺ (Table 1) thus causing a decrease in the cation sites and partly disrupted the clay structure as evident from XRD results (Fig. 2). Where the crystal structure has changed as shown from the XRD pattern for the acid treated clay at 20 = 12. Also,
the pore size of treated clay decreased from 329.75 Å to 125.673 Å (Table 2), suggesting that the adsorption of lead ions decreased with decreasing ion exchange process between the lead ions and the interlayer cations. On the other hand, the surface area of clay increased from 0.786 to 29.309 m² g⁻¹ (Table 2). It is well known that the ion adsorption increases with increasing surface area. This could be attributed to the acid activation process which increased the surface area and simultaneously decreased the number of cation sites in the interlayer of the clay. Hence, the adsorption capacity of the treated clay for adsorption of lead ions showed slight increases. Similar results were reported by Kara et al. (2003), Taylor and Jenkins (1988), Morgan et al. (1985) and Kheok and Lim (1982).

The reduction in adsorption capacity of clay at high concentration of acid (3 M, 1 h) might be due to the collapse of the structure or the formation of amorphous layers which decreased the lead ions capability to exchange with cationic ions in the interlayer space of the clay (Kara et al., 2003; Hernandez et al., 1986). This was also noticed in the present investigation from the intensity of XRD peaks at 2θ = 12 which diminished at high acid concentration (Fig. 2).

In conclusion, the ion adsorption depends on the interlayer space of the clay because of the ion exchange between lead ions in the solution and the cationic ions inside the space of the clay layers. In addition, the adsorption of lead ions slightly depends on the clay surface area, but the major effect on the adsorption of lead ions is the interlayer space of the clay. The XRD showed a decrease in the interlayer space of the clay which could be attributed to acid treatment of clay by HCl. Because the collapses of the interlayer space of the clay were high especially at high concentration of acid treatment.
Fig. 3: Effect of temperature on the adsorption capacity of Baha clay

Fig. 4: Langmuir model fit of the adsorption of lead ions on Baha clay at different temperatures

The ion adsorption capacity of clay increased with an increase in the experimental temperatures (Fig. 3). This behavior indicated that the adsorption system is endothermic.

Langmuir and Freundlich models were applied in the linear forms to explain the experimental data for untreated clay samples at different temperatures. The mathematical forms of Langmuir and Freundlich models, respectively in the linear form are given below:

\[ \frac{C_i}{q_i} = \frac{1}{K} + \left( \frac{n}{K} \right) C_e \] (2)

\[ \log q_e = \log K_f + \left( \frac{1}{n} \right) \log C_e \] (3)

A plot of \( \frac{C_i}{q_i} \) versus \( C_e \) (Fig. 4) provided the constants \( n \) and \( K \) for the system. Constants \( K \) and \( a \) for lead ions are tabulated in Table 3.

A plot of \( \log q_e \) versus \( \log C_e \) (Fig. 5) provided the constants \( K_f \) and \( n_f \) for the system. The constants, \( K_f \) and \( n_f \), for lead ions are tabulated in Table 4.

As shown from the values of \( R^2 \) (Table 3, 4), the Langmuir model describes the experimental data for the lead ions adsorption on Baha clay very well and better than Freundlich model.

Table 3: Langmuir constants for lead ions adsorption on Baha clay at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K (m^2 kg^{-1})</th>
<th>a (m^2 kg^{-1})</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>29.24</td>
<td>1167</td>
<td>0.999</td>
</tr>
<tr>
<td>40</td>
<td>22.27</td>
<td>833</td>
<td>0.997</td>
</tr>
<tr>
<td>60</td>
<td>29.41</td>
<td>1041</td>
<td>0.998</td>
</tr>
<tr>
<td>80</td>
<td>40.62</td>
<td>1364</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 4: Freundlich constants for lead ions adsorption on Baha clay at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K_f (m^2 kg^{-1})</th>
<th>n (-)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.63</td>
<td>3.799</td>
<td>0.805</td>
</tr>
<tr>
<td>40</td>
<td>2.66</td>
<td>3.59</td>
<td>0.833</td>
</tr>
<tr>
<td>60</td>
<td>2.87</td>
<td>3.67</td>
<td>0.643</td>
</tr>
<tr>
<td>80</td>
<td>3.21</td>
<td>2.85</td>
<td>0.748</td>
</tr>
</tbody>
</table>

Fig. 5: Freundlich model fit of the adsorption of lead ions on Baha clay at different temperatures

**Thermodynamic parameters calculations:** The thermodynamic parameters are enthalpy change (\( \Delta H \)) standard free energy change (\( \Delta G \)) and entropy change (\( \Delta S \)). The enthalpy and entropy can be calculated from Van't Hoff equation as follows:

\[
\ln K_\ell = \left( \frac{-\Delta H}{R} \right) + \left( \frac{\Delta S}{R} \right) (4)
\]

The value of enthalpy was obtained from the slope of the plot of \( \ln K_\ell \) Vs. \( 1/T \), where \( K_\ell = C_s/C_e \), \( C_s \) is the lead ions adsorption on clay per liters of solution at equilibrium (mg L^{-1}), \( C_e \) is the lead ions concentration in the solution at equilibrium (mg L^{-1}), \( R \) is a gas constant and \( T \) is absolute temperature. The value of the entropy was obtained from the intercept of the plot. The standard free energy can be calculated from:

\[
\Delta G = -R T \ln K_\ell (5)
\]

The values of the thermodynamic parameters were recorded (Table 5). It was observed that the adsorption process is endothermic due to the positive value of the enthalpy. Since, the increasing temperatures decreased
Table 5: Thermodynamic parameters calculations for lead ions/Bahia clay system.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T</th>
<th>ln K (KJ mol⁻¹ K)</th>
<th>ΔH (KJ mol⁻¹)</th>
<th>ΔS (KJ mol⁻¹ K)</th>
<th>ΔG (KJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>3.458</td>
<td>0.003413</td>
<td>1.260846</td>
<td>-3.08591</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>4.25</td>
<td>0.003195</td>
<td>1.487270</td>
<td>6.124</td>
<td>0.0317</td>
</tr>
<tr>
<td>333</td>
<td>5.0389</td>
<td>0.003003</td>
<td>1.617188</td>
<td>-4.47728</td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>5.4355</td>
<td>0.002833</td>
<td>1.692952</td>
<td>-4.96555</td>
<td></td>
</tr>
</tbody>
</table>

the values of standard free energy (Table 5), therefore, the adsorption becomes favorable at high temperatures. Also, the adsorption process turned out to be more random between the adsorbent and the adsorbate through the adsorption process because the value of the entropy was positive. These results agree with those of Qadeer and Khalid (2005).

CONCLUSION

The adsorption capacity decreased with increasing acid treatment dose partly due to disruption of the interlayer space of the clay. The adsorption capacity of Bahia clay increased with an increase in experimental temperature. According to Langmuir model, the maximum adsorption capacity of Bahia clay was 29.25 mg g⁻¹ at 80°C. It was found that the adsorption system is endothermic and the randomness of the adsorption increased during the adsorption of lead ions on the Bahia clay. Among the two models tested at different temperatures, the Langmuir model described the experimental data better than the Freundlich model.

ACKNOWLEDGMENT

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NOMENCLATURE

The following nomenclature were used to describe various abbreviations in the experimental results.

M : Bahia clay mass
V : Volume of the solution
q : The amount of adsorption
C₀ : Initial solution concentration
Cₑ : Concentration at equilibrium
Kₑ : Equilibrium constant of Langmuir model
aₑ : Equilibrium constant of Freundlich model
nₑ : Equilibrium parameter of Freundlich model
R : The gas constant
T : The absolute temperature
Kₑ : Dimensionless constant

REFERENCES


