Thermodynamics and Kinetics study of Lead Ions
Adsorption on Iraqi Bentonite

Khulood A. S. AL – Saadi 1 Ghassan S. Dawood2

1Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.
2Department of Chemistry, College of Science, University of Tikrit, Tikrit, Iraq.

Abstract:
Evaluation of adsorption parameters of Iraqi bentonite for lead ions (Pb2+) was investigated in a temperature range (10 – 50 °C) and pH values range (2-10). The method was based on the calculation of Langmuir adsorption maximum (b), and the bonding energy term (Kb). The parameters were the outcome of well – established linear relationships of C/Q versus C (C, equilibrium concentration and Q, amount of lead adsorbed). The Q values increased with temperature and pH increasing. Kinetics study was conducted by using Lagergreen equation and a first order equation was obtained at time ranging from 5 mints to equilibrium time, and the rate constant of adsorption was calculated. The study included the adsorption of lead ions attached to EDTA as a complex (Pb – EDTA) on bentonite.

Keyword: Lead ion, Adsorption, Bentonite

Introduction:
The interaction of metal ions with soil body depends both on the physical and chemical nature of the adsorbing surface and properties of metals (1). Several studies have been conducted to quantitatively and qualitatively the phenomena occurring at the interface aqueous – solid phase (2-8). Bentonite is a clay which has the highest absorbent capacity than any of the mineral clays (9). Its advantages over other minerals (especially with regards to its low density and high specific surface) which have been accepted for a long time, and they account for most of the current uses of bentonite (10,11).

Thermodynamic data of adsorption, (standard free energy change, standard state enthalpies and the entropy changes) can be calculated using the surface partition coefficients (12). In this paper the sorption behavior of Iraqi bentonite toward lead ion was investigated in a batch type procedure using (AAS) to determination of lead concentration in solutions.

Experimental:
Test chemicals and analysis (Instrumentation) : Lead acetate stock solution (1000 mg/l Pb2+) was prepared by dissolving lead acetate in deionized water. The solution was further diluted before use. The lead acetate used was of analytical grade. Synthetic samples were prepared to give lead concentration of 10, 20, 30, 40, 50, 200 and 500 mg/l by adding appropriate amounts of lead acetate stock solution to distilled water.

The lead ions concentrations of the sample were determine by atomic absorption spectrometer (AAS) before and after adsorption process. Batch sorption isotherms were determined in 250 ml round bottom flasks. Weighed amounts (0.5 gm) of Iraqi bentonite (75µm particle size) were introduced into five flasks, into which 50 ml of the lead ions solution of concentrations between 10 and 500 mg/l were already present. The table below shows the Iraqi bentonite composition which supplied by Geological scanning company. The flasks were shaken for 30 minute and samples were taken periodically for measurement of aqueous – phase lead concentration. Preliminary test confirmed that a 30 min, contact time was enough to reached steady – state lead concentration.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>56.77</td>
</tr>
<tr>
<td>Al2O3</td>
<td>15.67</td>
</tr>
<tr>
<td>CaO</td>
<td>4.48</td>
</tr>
<tr>
<td>MgO</td>
<td>3.42</td>
</tr>
<tr>
<td>K2O</td>
<td>0.60</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.11</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>5.12</td>
</tr>
<tr>
<td>L.O.I</td>
<td>12.49</td>
</tr>
<tr>
<td>Total</td>
<td>99.66</td>
</tr>
</tbody>
</table>

Result and discussion:
Sorption isotherms
The Langmuir equation based on the Kinetic theory of gases is extensively used to describe gas adsorption on solids. The same equation often applies to the adsorption of liquids and ions from solution by solids although the same rigorous, theoretical basis is not as fully developed. As applied to liquids or ions, the following equation is used herein:

\[ Q = \frac{K_b C_e}{1 + a C_e} \]  

Where (a and K_b) represents to Langmuir constant.
The amount of lead accumulated on bentonite was calculated by the following expression:

\[ Q = \frac{(C_e - C_f)V}{M} \]

Where
- Q (mg/g) is the amount of lead adsorbed
- \(C_e\) (mg/l) represents initial lead concentration
- \(C_f\) (mg/l) represents equilibrium lead concentration
- V (L) is the volume of solution
- M (gm) is the mass of bentonite

Results determined by using Eq. (2) are plotted vs. time and show in fig. 1. The initial lead concentration provides the necessary driving force to overcome all mass – transfer resistances of lead between the aqueous and solid phases.

The removal of lead is high in the initial 5 min., but thereafter the rate significantly levels off and eventually approaches zero, i.e. when equilibrium is attained. These changes in the rate of removal is due to the fact that, initially, all adsorbent sites were vacant and the solute concentration gradient was high. Afterwards,
The lead uptake rate by bentonite decreased significantly, due to decrease in adsorption sites. A decreasing removal rate, particularly towards the end of experiment, indicated a possible monolayer of lead ions on the outer surface and pores of the bentonite and pore diffusion on to the inner surface of bentonite particles through the film due to continuous agitation maintained during the experiment. The adsorption rate of lead which calculated from Lagergreen equation (3) and a linear relation was obtained at time ranging from 5 mins to equilibrium times.

Lagergreen equation has the following formula:
\[
\ln(q_e - q_t) = \ln q_e - k_{ad} t \quad \text{…………………. (3)}
\]

where
\[
q_e = \text{the amount of lead ions removed at equilibrium}
\]
\[
q_t = \text{the amount of lead ions removed at (t) time}
\]
\[
k_{ad} = \text{rate constant of adsorption}
\]

The values of \(k_{ad} = 0.0464 \text{ min.}^{-1}\) at \(C_0 = 10 \text{ mg/l}\), \(k_{ad} = 0.0534 \text{ min.}^{-1}\) at \(C_0 = 20 \text{ mg/l}\), \(k_{ad} = 0.0581 \text{ min.}^{-1}\) at \(C_0 = 30 \text{ mg/l}\), \(k_{ad} = 0.0461 \text{ min.}^{-1}\) at \(C_0 = 40 \text{ mg/l}\), and \(k_{ad} = 0.1151 \text{ min.}^{-1}\) at \(C_0 = 50 \text{ mg/l}\). These values calculated for the slopes of the relation between \(\ln(q_e - q_t)\) against (t) as shown in fig. 2.

![Fig. 1: Effect of contact time on the adsorption amount.](image)

![Fig. 2: The relation between \(\ln(q_e - q_t)\) against (t).](image)

**Thermodynamic results:**

The values of (b) constant which related to the bonding energy of the bentonite with Pb (equilibrium constant) at initial concentration ranging from 10 to 50 mg/l are reported in table (1), and relation of another form of Langmuir equation (linear form) as:

\[
C_e = \frac{1}{Q} \left( \frac{b}{Ce} \right) \quad \text{…………………. (4)}
\]

was used by plotting the experimental data using equation (4) give good fit for the data as shown in fig. 3 for various temperature. First points for all lines due to 283K while seconds point due to 293K, the thirds to 303K, fourth to 313K and fifth to 323K.

![Fig. 3: Langmuir isotherms of Pb²⁺ adsorption on bentonite.](image)

The thermodynamic parameters (\(\Delta G\), \(\Delta H\), and \(\Delta S\)) for lead adsorption can be calculated from the following equations:

\[
b = a \exp(q/RT) \quad \text{………………. (5)}
\]

\[
a = \exp\left(\frac{\Delta S_u}{R}\right) \quad \text{………………. (6)}
\]

\[
b = \exp(-\Delta H_u / RT) \cdot \exp(\Delta S_u / R) \quad \text{…….. (7)}
\]

\[
\log b = \frac{-\Delta H_u}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S_u}{2.303R} \quad \text{…….. (8)}
\]

\[
\Delta G = \Delta H - T\Delta S \quad \text{………………. (9)}
\]

The fig. 4 show the relation between \(\log b\) and \((1/T)\).

![Fig. 4: shows the relation between \(\log b\) and \((1/T)\).](image)

The value of \(\Delta G\), \(\Delta S\) and \(\Delta H\) are reported in table (2) for different temperature. From the results, Q increase with temperature increase which related to the absorption processes occurred with adsorption process, and all sorption processes was endothermic (\(\Delta H\) positive values). A diffusion process for lead ions occurs inside the bentonite caverns and pores so endothermic process was occurred. Absorption processes follow special mechanism differs from langmuir adsorption isotherm mechanism.

![Table (1): The value of \(C_e\) and Q at deferent temperatures.](image)
The adsorption of lead ions complexing with EDTA (Pb – EDTA) on bentonite was studied and table (3) show the adsorption parameters (Q and C∞). The results show a lowering on adsorption efficiency for the adsorption of (Pb – EDTA) than of free lead ions, which related to the larger molecular volume of (Pb – EDTA) complex than for free lead ions.

Table (2): The thermodynamics value of adsorption Pb²⁺ on bentonite.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>b</th>
<th>∆G_a (kJ mol⁻¹)</th>
<th>∆H_a (kJ mol⁻¹)</th>
<th>∆S_a (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>23.419</td>
<td>-29.2763</td>
<td>+8.8313</td>
<td>+134.6561</td>
</tr>
<tr>
<td>293</td>
<td>30.769</td>
<td>-30.3109</td>
<td>+8.8313</td>
<td>+134.6561</td>
</tr>
<tr>
<td>303</td>
<td>36.101</td>
<td>-31.3453</td>
<td>+8.8313</td>
<td>+134.6561</td>
</tr>
<tr>
<td>313</td>
<td>71.942</td>
<td>-32.3799</td>
<td>+8.8313</td>
<td>+134.6561</td>
</tr>
<tr>
<td>323</td>
<td>100</td>
<td>-33.4144</td>
<td>+8.8313</td>
<td>+134.6561</td>
</tr>
</tbody>
</table>

The adsorption of lead ions from synthetic solution was demonstrated successfully on a laboratory scale with Iraqi bentonite. The following conclusions can be drawn from this study:

The data obtained from batch studies were applied to Langmuir isotherms. The Langmuir isotherm gives an adequate correlation coefficient value, led to thermodynamic parameters (∆G, ∆H and ∆S) for adsorption process, and positive AH values indicated to the endothermic sorption processes (adsorption + absorption) of lead ions inside the pores of bentonite. Adsorption efficiency of bentonite decrease where lead ions complexed with EDTA and increased with pH increased.

References:
9. Robertson, R. H. S., Cham. Ind. 5(1957) 1492.
10. Robertson, R. H. S., Silicates Ind. 38(1973) 33.

Conclusion:
The removal of lead ions from synthetic solution was demonstrated successfully on a laboratory scale with

Effect of the pH of the solutions on bentonite adsorption efficiency was determined and shown in fig. 5. the efficiency of bentonite increase with pH increase from pH=2 to pH=10. At low pH values, the hydrogen ion competes with heavy metals cations and percentage removals of metals decline. The lead adsorption was affected by the pH and temperature and at high pH values the degree of dispersion of bentonite increased considerably and permeability decreased.

Fig. 5: The pH effect on the adsorption of Pb²⁺ on bentonite at (50 mg/L).

Table (3): The value of C∞ and Q of adsorption (EDTA-Pb) on bentonite.

<table>
<thead>
<tr>
<th>C∞ (mg/l)</th>
<th>C (mg/l)</th>
<th>Q (mg/g)</th>
<th>C/Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>41</td>
<td>5.9</td>
<td>6.9491</td>
</tr>
<tr>
<td>200</td>
<td>90</td>
<td>11</td>
<td>8.1818</td>
</tr>
<tr>
<td>300</td>
<td>143</td>
<td>15.7</td>
<td>9.1082</td>
</tr>
<tr>
<td>400</td>
<td>190</td>
<td>21</td>
<td>9.0476</td>
</tr>
<tr>
<td>500</td>
<td>295</td>
<td>20.5</td>
<td>14.3902</td>
</tr>
</tbody>
</table>

Effect of the pH of the solutions on bentonite adsorption efficiency was determined and shown in fig. 5. the efficiency of bentonite increase with pH increase from pH=2 to pH=10. At low pH values, the hydrogen ion competes with heavy metals cations and percentage removals of metals decline. The lead adsorption was affected by the pH and temperature and at high pH values the degree of dispersion of bentonite increased considerably and permeability decreased.

Fig. 5: The pH effect on the adsorption of Pb²⁺ on bentonite at (50 mg/L).
دراسة ديناميكية وحركية امتزاز ايونات الرصاص على البنتونايت العراقي

خالد عبد صالح السعدي، غسان سعدون داود

قسم الكيمياء، كلية العلوم، جامعة بغداد، جمهورية العراق
قسم الكيمياء، كلية العلوم، جامعة تكريت، جمهورية العراق

الملخص:
تم تقدير دوال امتزاز ايونات الرصاص على البنتونايت العراقي عند المدى الحراري (10 – 50) درجة مئوية و middle (10 – 2) درجة مئوية. تستخدم الطريقة لحساب امتزازات الرصاص الموجودة بشكل مرتبط مع العدد الهيدروجيني. استخدمت معادلة لأتروكزين الخاصة بقياس سرعة الامتزاز و ذلك النتيجة الحصول على معادلة من المركبة الأولى عند الفترة الزمنية بين خمس دقائق زمن الإتزاز، ثم حساب ثابت سرعة للإتزاز. تم دراسة امتزاز الرصاص الموجود بشكل مرتبط مع Pb - EDTA على سطح البنتونايت. تتم تقدير دوال امتزاز ايونات الرصاص على البنتونايت العراقي عند المدى الحراري (10 – 50) درجة مئوية ومدى من الرصاص الهيدروجيني (10 – 2). تستخدم الطريقة لحساب امتزازات الرصاص الموجودة بشكل مرتبط مع Pb - EDTA على سطح البنتونايت.

الكلمات الدالة: ايونات الرصاص، الامتزاز، البنتونايت.