Thermodynamics and Kinetics study of Lead Ions Adsorption on Iraqi Bentonite

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Abstract:

Evaluation of adsorption parameters of Iraqi bentonite for lead ions (Pb^{2+}) was investigated in a temperature range (10 – 50 ^{o}C) and pH values range (2-10). The method was based on the calculation of Langmuir adsorption maximum (b), and the bonding energy term (K_L). The parameters were the outcome of well – established linear relationships of C_e/Q versus C_e (C_e, 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 assess quantitatively and qualitatively the phenomena occurring at the interface aqueous – solid soil 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.

Experimantal:

Test chemicals and analysis (Instrumentation) :

Lead acetate stock solution (1000 mg/l Pb^{2+}) 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.

Analysis of Iraqi bentonite

Constituent	Wt %
SiO_2	56.77
Al_2O_3	15.67
CaO	4.48
MgO	3.42
K_2O	0.60
Na_2O	1.11
Fe_2O_3	5.12
L.O.I	12.49
Total	99.66

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:

$$Q = \frac{K_L C_e}{1 + aC_e} \quad \text{(1)}$$

Where (a and K_L) represents to Langmuir constant.

The amount of lead accumulated on bentonite was calculated by the following expression:

$$Q = \frac{(C_o - C_e)V}{M} \quad \text{(2)}$$

Where

Q (mg/g) is the amount of lead adsorbed

C_o (mg/l) represents initial lead concentration

C_e (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 mints to equilibrium times.

Lagergreen equation has the following formula:

$$\ln(q_e - q_t) = \ln q_e - k_{ad} t \quad \text{.....................} \quad (3)$$

where

q_e= the amount of lead ions removed at equilibrium

q_t= the amount of lead ions removed at (t) time

k_{ad}= rate constant of adsorption

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

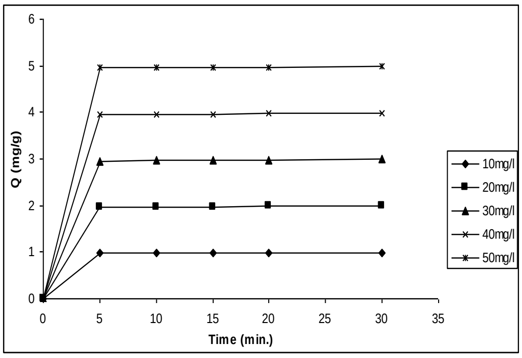


Fig 1: Effect of contact time on the adsorption amount.

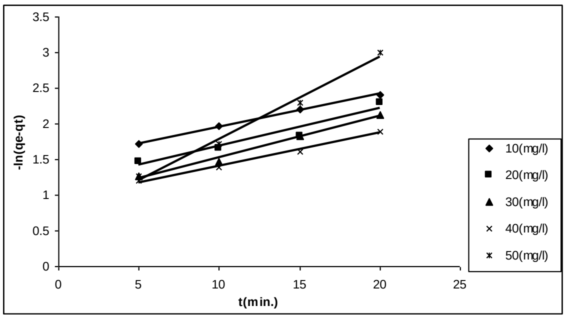


Fig. 2: The relation between ln(q_e – q_t) against (t).

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:

$$\frac{C_e}{Q} = \frac{1}{b} + C_e \quad \text{..................} \quad (4)$$

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.

Table (1): The value of C_e and Q at deferent temperatures.

Co (mg/l)	283 K		293 K		303 K		313 K		323 K	
	Ce	Q	Ce	Q	Ce	Q	Ce	Q	Ce	Q
100	0.8	9.92	0.65	9.935	0.55	9.945	0.52	9.948	0.5	9.95
200	24	17.6	13	18.7	6	19.4	4.9	19.15	2.5	19.75
300	25	27.5	26	27.4	12	28.8	1.2	29.88	1	29.9
400	38	36.2	26	37.4	21	37.9	4.5	39.55	3	39.7
500	42	45.8	25	47.5	16	48.4	4	49.6	1.5	49.85

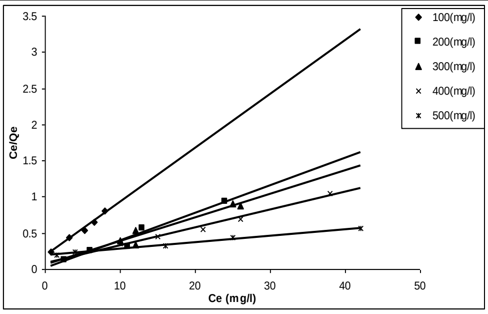


Fig 3: Langmuir isotherms of Pb^{2+} adsorption on bentonite .

The thermodynamic parameters (ΔG, ΔH, and ΔS) for lead adsorption can be calculated from the following equations:

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

$$a = \exp(\frac{\Delta S_a}{R}) \quad \text{.....................} \quad (6)$$

$$b = \exp(-\Delta H_a / RT).\exp(\Delta S_a / R) \quad \text{..} \quad (7)$$

$$\log b = \frac{-\Delta H_a}{2.303R} . \frac{1}{T} + \frac{\Delta S_a}{2.303R} \quad \text{.........} \quad (8)$$

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

The fig. 4 show the relation between(logb) and (1/T).

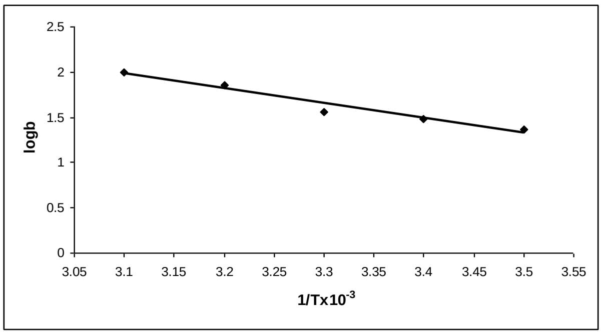


Fig. 4: shows the relation between logb and 1/T.

The value of ΔG, ΔS and ΔH 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 (ΔH_a 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 (2): The thermodynamics value of adsorption Pb^{2+} on bentonite.

T(K)	b	ΔG_a (kJ. mol^{-1})	ΔH_a (kJ. mol^{-1})	ΔS_a (J. mol . K $^{-1}$)
283	23.419	- 29.2763	+ 8.8313	+ 134.6561
293	30.769	- 30.3109	+ 8.8313	+ 134.6561
303	36.101	- 31.3453	+ 8.8313	+ 134.6561
313	71.942	- 32.3799	+ 8.8313	+ 134.6561
323	100	- 33.4144	+ 8.8313	+ 134.6561

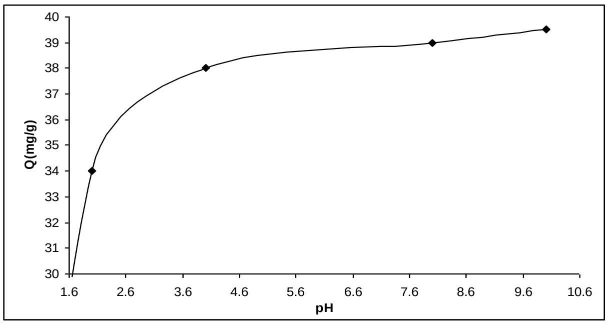
The adsorption of lead ions complexing with EDTA (Pb – EDTA) on bentonite was studied and table (3) show the adsorption parameters (Q and C_e). The results show a lowering on adsorption efficiency for the adsorption of (Pb – EDTA) than of free lead ions, which related to the larger molecular volume of (Pb – EDTA) complex than for free lead ions.

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

C_o (mg/l)	C_e (mg/l)	Q (mg/g)	C_e/Q
100	41	5.9	6.9491
200	90	11	8.1818
300	143	15.7	9.1082
400	190	21	9.0476
500	295	20.5	14.3902

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 Pb^{2+} on bentonite at (50 mg/L).



Conclusion:

The removal 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 (ΔG, ΔH and ΔS) for adsorption process, and positive ΔH 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.

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دراسة ديناميكية وحركية امتزاز ايونات الرصاص على البنتونايت العراقي

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الملخص:

تم تقدير دوال امتزاز ايونات الرصاص على البنتونايت العراقي عند المدى الحراري (10 – 50) درجة مئوية ومدى من الرقم الهيدروجيني (2– 10) . تعتمد الطريقة على حساب الامتزاز الأعظم من معادلة لنكماير المعروفة (b) ومن حساب ثابت (K_L) الخاص بطاقة الارتباط على السطح. وتم الحصول على هذه الدوال من العلاقة المستقيمة بين قيم C_e/Q مقابل C_e (حيث أن C_e هو التركيز عند الاتزان، Q كمية الرصاص الممتزة على البنتونايت) ، ووجد ان قيمة Q تزداد بزيادة درجة الحرارة والرقم الهيدروجيني. استخدمت معادلة لاگركرين الخاصة بقياس سرعة الامتزاز وكانت النتيجة الحصول على معادلة من المرتبة الأولى عند الفترة الزمنية بين خمس دقائق وزمن الاتزان ، ثم تم حساب ثابت سرعة للامتزاز. تم دراسة امتزاز الرصاص الموجود بشكل مرتبط مع EDTA أي بهيئة (Pb – EDTA) على سطح البنتونايت.

الكلمات الدالة: ايونات الرصاص ، الامتزاز ، البنتونايت.