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Thermodynamic and Kinetic Study of the Adsorption of Pb (II) from Aqueous Solution Using Bentonite and Activated Carbon

Bassim Hameed Graimed* **Ziad T. Abd Ali****

**University of Baghdad*

***Department of Environmental Engineering/ University of Baghdad*

*E-mail: bassim.hameed@yahoo.com

**E-mail:Z.teach2000@ yahoo.com

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Abstract

The adsorption of Pb(II) ions onto bentonite and activated carbon was investigated. The effects of pH, initial adsorbent dosage, contact time and temperature were studied in batch experiments. The maximum adsorption capacities for bentonite and activated carbon were 0.0364 and 0.015 mg/mg, respectively. Thermodynamic parameters such as Gibbs free energy change, Enthalpy change and Entropy change have been calculated. These thermodynamic parameters indicated that the adsorption process was thermodynamically spontaneous under natural conditions and the adsorption was endothermic in nature. Experimental data were also tested in terms of adsorption kinetics, the results showed that the adsorption processes followed well pseudo second- order kinetics.

Keywords: *Bentonite, Activated carbon, lead ions, Adsorption, Kinetic.*

1. Introduction

According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. In particular, lead is one of the important toxic elements found in industrial effluents causing water pollution.

Lead is one of the industrial pollutants; possibly enters to the ecosystem through soil, air and water. Inorganic lead causes disturbance in the central nervous system by changing the characteristics of the early organism [9,6]. According to WHO, the maximum permissible limit of lead in drinking water is 0.1 mg/l [16]. Hence, the appropriate treatment of industrial wastewater which releases lead into the aquatic and terrestrial systems is very important.

At present, a number of technologies can be used to remove heavy metals from the contaminated wastewater such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation, and electro-remediation methods [5,11]. However, most of these methods might not be efficient in removing heavy metal at very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment. Hence, the simple, effective, low cost and eco-friendly techniques are required for the fine tuning of effluent wastewater treatment. The search for low cost, and easily available adsorbents has led to the investigation of materials of agricultural and biological origin, alongside those of industrial by-products as adsorbents for removal of heavy metals [8,13]. Examples of such low cost adsorbents are clay [2], cotton [12], wool fiber [1], tea leaves [14] and other materials. The main aim of this study is the presence of heavy metals in water is a major concern due to their toxic effects since they cause severe health

problems to animals and human beings. Many industrial processes produce aqueous effluents containing toxic metal contaminants.

2. Experimental Work and Methods

2.1. Preparation of Adsorbents

Bentonite and activated carbon used were as the adsorbents in this study. Bentonite was supplied by the State Company of Geological Survey and Mining (Baghdad) as pieces of rocks, these rocks were destructed to granules of different sizes, using sieves to produce granules of sizes (0.5 - 0.6) mm, (D_e= 0.00054) m. The granules of bentonite were dried at (100) °C for (1) hour before used. Granulated activated carbon (GAC) was supplied by Unicarbo, Italians to the Iraqi local markets. The granulated activated carbon was crushed, sieved into (0.5- 0.6) mm, (De = 0.00054) m. The require sieve fraction was washed many times by distilled water to remove fines from the crushed GAC and dried in an oven maintained at (100) °C for (2) hours, after which the GAC was kept in a desiccators for experimental use.

2.2. Preparation of Simulated Wastewater

Stock solutions (1000 mg/l) of lead ions were prepared by dissolving an appropriate weight of pure salt $Pb(N0_3)_2$ in the desired volume of de-ionized water. The stock solution was successively diluted with de-ionized water to obtain the desired test concentration (800 mg/l) of metal ions. Concentration of lead ion was measured using atomic adsorption spectrophotometer (type: ACCUSYS 211 ,UK- SCIENTIFIC Ltd.).

2.3. Adsorption Experiments

The batch experiments were performed by adding the desired amount (100 ml) of the dilute stock solution (800 mg/l) in 250 ml of volumetric flasks at the designated adsorbent dose, pH, and temperature. The solution was shaken using shaker at 200 rpm for a definite period (5, 10, 20, 40, 80, 120, 150) min. Adsorbent dose, contact time, temperature and pH were optimized by continuous variation method (studying one, while keeping the other parameters constant). After equilibrium, the solution was allowed to settle for 20-30 min, filtered by filter paper (Whatman 542, England) and analyzed for lead. The difference in the lead content before and after adsorption experiments represents the amount of lead adsorbed by the adsorbent. All experiments were performed at room temperature (20 °C), pH 4 by the addition of HNO_3 or NaOH solution. The percent removal of metal ions can be calculated by using the following equation:

$$\%Removal = [(C_0-C_e)/C_0] \times 100 \qquad \ldots(1)$$

Where, C_0 = initial concentration of the metal ion in mg/l, Ce = metal ion concentration at equilibrium in mg/l.

2.4. Contact Time

Batch adsorption tests were carried out at different contact time intervals (5 - 150 min) at initial Pb (II) concentration of 800 mg/l. This was done by contacting 2 g of each adsorbent with 100 ml of Pb (II) solution at the pH 4.

The residual Pb (II) concentration in each solution was then filtered using filter paper (type: Whatman 542, England) and analyzed using Atomic Absorption Spectrophotometer.

2.5. Adsorbent Dosage

100 ml of the metal ion solution of (800 mg/l) was added to various amount of the several adsorbents (0.2-3 g) in 250 ml volumetric flasks and agitated for 2hr on a shaker. The content of the glass bottles were filtered and analyzed by the same procedure mentioned above.

2.6. pH Variation

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH, which influences both the adsorbent surface metal binding sites and the metal chemistry in water [15]. The effect of pH on the adsorption of Pb (II) using bentonite and activated carbon (each one separately) was carried out within the range that would not be influenced by the metal precipitated [10]. It was reported that the suitable pH range for the adsorption of Pb(II) was (2 - 8). This experiment was conducted at 20 °C to study the effect of initial solution pH on the adsorption of Pb(II) by contacting 2 g of the adsorbent (bentonite or activated carbon) with 100 ml of 800 mg/l Pb(II) solution in a volumetric flasks. The pH of each solution was

adjusted to the desired value with adding 0.1M HNO_3 and/or 0.1M NaOH. The volumetric flasks containing the mixture were left in a shaker for 2h. Solution was filtrated using filter paper and the Pb(II) concentration in the solution was analyzed by means of Atomic Absorption Spectrophotometer.

2.7. Agitation Speed

The effect of agitation of the sorbent/sorbate system for lead adsorption was monitored at (0, 100, 200, 300 and 400 rpm).

2.8. Temperature Variation

The batch adsorption process was studied at different temperatures of 20, 30, 40, 50 and 60 °C in order to investigate the effect of temperature on the adsorption process using bentonite and activated carbon. This was done by contacting 2 g of adsorbents with 100 ml of 800 mg/l Pb(II) solution at pH 4 for 120 min with agitation speed of 200 rpm by using shaker incubator. The results were used to investigate the thermodynamics of the adsorption process.

3. Kinetic Equations

The kinetics of lead adsorption on bentonite and activated carbon were analyzed using pseudo-first-order [4] and Pseudo-second-order models [3], The pseudo-first order kinetic rate equation is:

$$(dq_t/dt)=k_1(q_e-q_t) \quad \ldots(2)$$

Where k_1 is the rate constant of pseudo first order adsorption (min^{-1}), q_e is the amount of lead sorbed at equilibrium (mg/mg) and q_t the amount of lead sorbed at time t (mg/mg). Integrating equation (2) for the boundary conditions $t=0$ to $t=t$ and $qt=0$ to $qt= q_e$ and rearranging yields the linear time-dependent function.

$$Log(q_e-q_t) = Logq_e-(kt/2.303) \quad \ldots(3)$$

The intercept of the straight-line plots of log (q_e-q_t) against t equal log q_e , However, if the intercept does not equal q_e, then the reaction is not likely to be first-order, irrespective of the magnitude of the correlation coefficient. The pseudo- second- order kinetic rate equation is:

$$(dq_t/dt)=k_2(q_e-q_t)^2 \quad \ldots(4)$$

Where k_2 is the rate constant of pseudo second order adsorption ($mg.mg^{-1}.min^{-1}$).Taking into account, the boundary conditions t=0 to t=t and $q_t=0$ to $q_t=q_t$ .The integrated form of Equation (4) can be rearranged to obtain Equation (5):

$$(t/ q_t)= (1/k_2q_e^2)+ (t/q_e) \quad \ldots(5)$$

The plot of (t/q_t) and t of Equation (5) gives a linear relationship, q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

4. Result and Discussion

4.1. Effect of Contact Time

The effect of contact time on the adsorption of Pb(II) from the solution is shown in Figure (1).

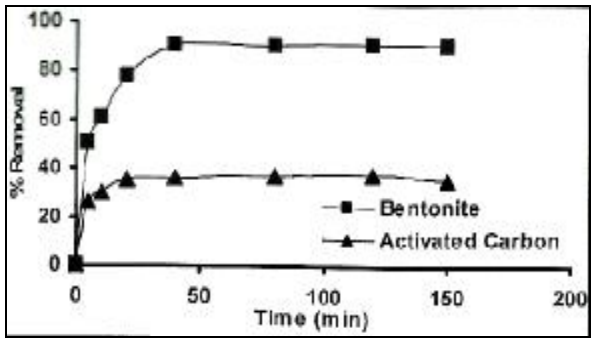

Fig. 1. Time Effect of the Adsorption of Pb(II) onto Bentonite and Activated Carbon at 20°C, pH 4, Co=800 mg/l, rpm=200.

It is observed that the removal of Pb(II) increased with increase in contact time. The adsorption of Pb(II) by the bentonite was rapid for the first 20 min as a result of available binding sites on the bentonite, while the adsorption by activated carbon was less rapid than bentonite.

The adsorption reached equilibrium within 120 min as the binding sites on the bentonite and activated carbon were used up. The period of 120 min was therefore used for the adsorption of Pb(II) by bentonite and activated carbon. The initial fast removal occurs due to surface adsorption on the adsorbent. The subsequent slow phase occurs due to diffusion of the metal ions into the inner part of the adsorbent.

4.2. Effect of Adsorbent Dosage

The adsorption of lead ions was observed to increase as the amount of adsorbent is increased gradually from 0.2 to 3.0 g, (Figure 2).

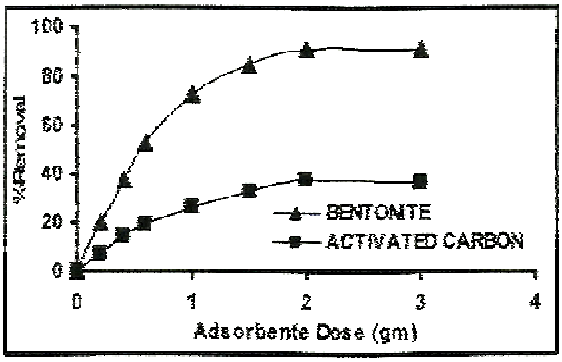

Fig. 2. Effect of Adsorbent Dose (pH =4, Co = 800mg/l, rpm=200, time=2 h).

The maximum removal is obtained at the adsorbent dose of 2.0 g where a further increase in the quantity of the adsorbent up to 2 g has no more effect to the adsorption rate. Therefore, 2.0 g of the adsorbent is sufficient to adsorb the maximum ions and that the percent removal by bentonite was more than that of activated carbon. Also the removal efficiency is associated with the adsorbent dose increases which are due to the availability of more adsorbing sites at higher doses.

4.3. Effect of pH on Adsorption

The pH of solution was examined at different pH values, covering a range of 2.0-8.0. In the case of Pb(II) the maximum adsorption was obtained at pH 4.0 for both adsorbents. Removal of Pb(II) onto bentonite and activated carbon is pH dependent as shown in Figure (3).

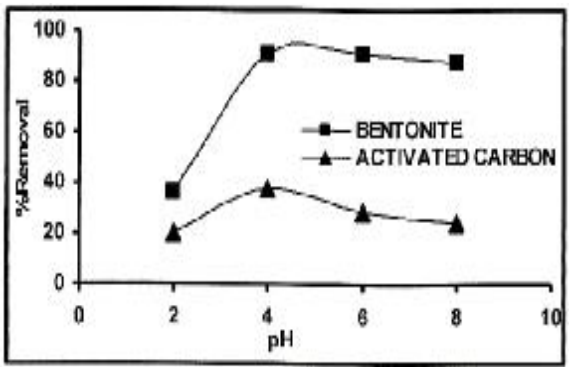

Fig. 3. Effect of pH on the Adsorption of Pb(II) by Bentonite and Activated Carbon, at 20°C , Co= 800 mg /l, rpm=200.

At pH < 3.0, H^+ ions compete with Pb(II) ions for the surface of the adsorbent which would hinder Pb(II) ions from reaching the binding sites of the sorbet caused by the repulsive forces. At pH > 5.5, the Pb(II) will precipitate due to hydroxide anions forming a lead hydroxide precipitate. For this reason the maximum pH value was selected to be 4.0. The highest efficiency was observed 91.1 % at pH of 4.0 for bentonite and 37.5 % for activated carbon.

Change in pH of the solution after adsorption was observed in this study for example, the pH value changes from 4 to 3 for bentonite dose of 1.0 g, to pH value of 2.65 for bentonite dose of 2.0 g and to pH values of 2.1 for adsorbent dose of 3.0 g. In all cases, pH of the solution decreases after equilibrium was reached. Therefore the study indicated that a change in pH value is dependent on the amount of adsorbent dose. Thus higher the adsorbent dose the larger the change in pH until the equilibrium is attained. The study further alluded that adsorption of the metal ions on the surface could result in the release of more H^+ ions from the surface, indicating ion exchange mechanism as shown from the decrease of the pH from the initial pH value.

4.4. Effect of Agitation Speed

Experimental results of the effect of agitation speed (0,100, 200, 300, and 400) are presented in Figure (4). It is obvious that agitation is found to be appropriate for maximum adsorption of lead from minerals. The removal of Pb (II) is reaching 99.3% and 42.5% using bentonite and activated carbon respectively at 400 rpm, Figures (4 and 5).

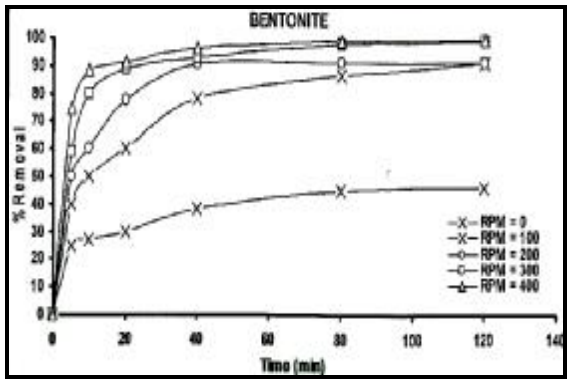

Fig. 4. Percentage Removal of Lead with Various Agitation Speeds for Bentonite.

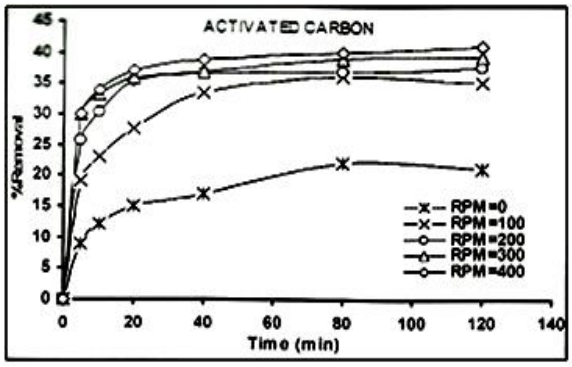

Fig .5. Percentage Removal of Lead with Various Agitation Speeds for Activated Carbon.

It can be seen that the removal percent increases with increasing agitation speed because increasing of agitation speed will decrease the boundary layer resistance, furthermore this experiment shows that the higher removal level reached by bentonite.

4.5. Effect of Temperature

The extent of lead ion adsorption on the bentonite and activated carbon at various temperatures is shown in Figures (6 and 7).

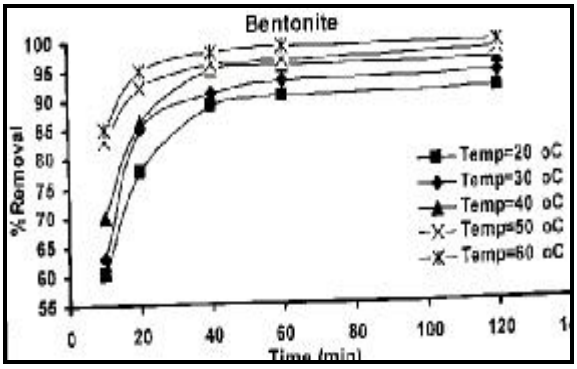

Fig. 6. Effect of Temperature (pH=4, Adsorbent Dose = 2 g, rpm=200, Time = 2h).

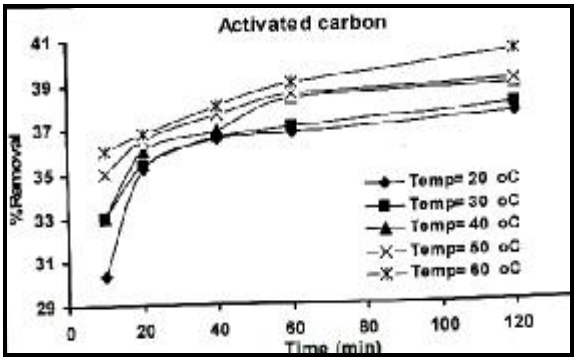

Fig. 7. Effect of Temperature (pH = 4, Adsorbent Dose = 2 g, rpm=200, Time = 2 h).

As observed from the figures, temperature rises therein resulted in an increase in the removal a percentage of the metal. The enhancement of the adsorption capacity when temperature is increased could be due to increased mobility and diffusion of ionic species

The adsorption experiment could be regarded as a heterogeneous and reversible process at equilibrium. The apparent equilibrium constant for the process is shown to be:

$$Kc = C_{ad}/C_e \quad ...(6)$$

The Gibbs free energy of the adsorption process [7] is:

$$AG° = - RT \ln K_r \quad ...(7)$$

AG° is the standard Gibbs free energy change for the adsorption process(J mol^{-1}); R, the universal gas constant (8.314 J $mol^{-1}K^{-1}$) while T is the temperature (K). The effect of temperature on the adsorption of Pb(II) by bentonite and activated carbon is listed in Table (1) and shown in Figures (8 and 9).

Table 1,
Gibbs Free Energy Values Obtained from the Adsorption of Pb (II) Using Bentonite and Activated Carbon at Different Temperatures.

Temperature (K)	AG° (KJ mor'K^{-1})	
	Bentonite	**Activated Carbon**
293	-5.66	1.244
303	-6.93	1.245
313	-8.44	1.202
323	-10.45	1.198
333	-11.58	1.108

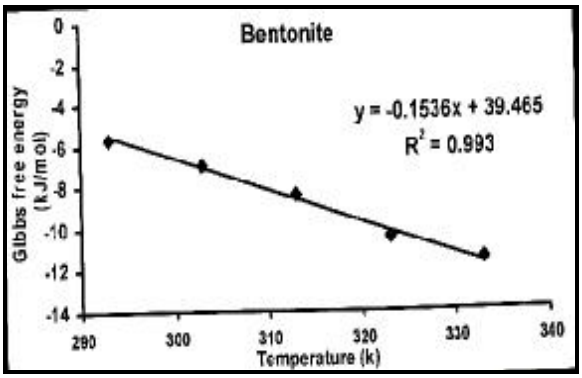

Fig. 8. The Gibbs Free Energy Plot for the Adsorption of Pb(II) Using Activated Carbon at pH 4 , Co= 800 mg/L, rpm=200.

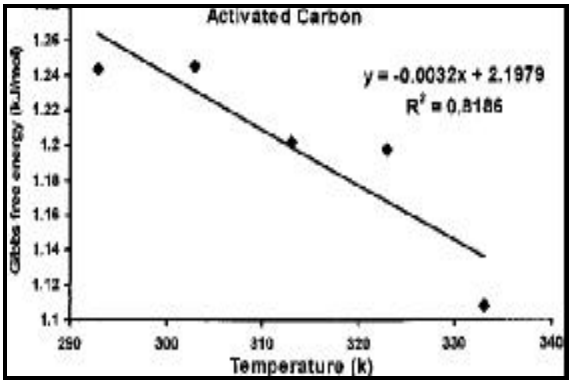

Fig. 9. The Gibbs Free Energy Plot for the Adsorption of Pb(II) using Activated Carbon at pH 4 , Co= 800 mg/L, rpm=200.

The free energy change (AG°) obtained for the adsorption of Pb(II) at 293 K, initial concentration of 800 mg/L, and pH 4 is (-5.66 and 1.244)kJ mol^{-1} for bentonite and activated carbon respectively. The negative value of AG° obtained for the adsorption of Pb(II) onto bentonite shows spontaneity of the adsorption process at that temperature, opposite for activated carbon. However, the result in Table (1) shows that the free energy values for bentomte and activated carbon decreases with increasing temperature. This implies that the spontaneity of the adsorption process increases with increasing in temperature. Consequently, the adsorption of the Pb(II) using bentonite and activated carbon as adsorbents is endothermic hence the process is better carried out at kindly high temperature.

From thermodynamics,

$$\Delta G° = \Delta H - T\Delta S \qquad \ldots(8)$$

Or

$$\Delta G° = -\Delta S\,(T) + \Delta H \qquad \ldots(9)$$

A plot of temperature against AG° gives a straight line with slope AS^0 and an intercept of ΔH. In (Figures 7 and 8) the slopes are (0.1536 and 0.0035) kJ/mol while the intercepts are (39.465 and 2.197) kJ/mol for bentonite and activated carbon respectively. Therefore, the values of the entropy are (0.1536 and 0.0035) kJ/mol and enthalpy are (39.465 and 2.197) kJ/mol for bentonite and activated carbon, respectively. The decrease in the value of the free energy with increase in temperature indicates that the adsorption process is endothermic and it is thereby favored with kindly increase in temperature.

4.6. Kinetic Study

It is clear from Figures (10, 11, 12 and 13) and Table (2) that the reactions for bentonite and activated carbon are not likely to be first-order because of the value of q_e (experimental) does not equal to the value of q_e(theoretical), irrespective of the magnitude of the correlation coefficient, while the values of q_e (experimental) and q_e(theoretical) are very close with higher value of correlation coefficient in case of second - order, therefore the adsorption processes followed well pseudo second- order kinetics for the two adsorbents.

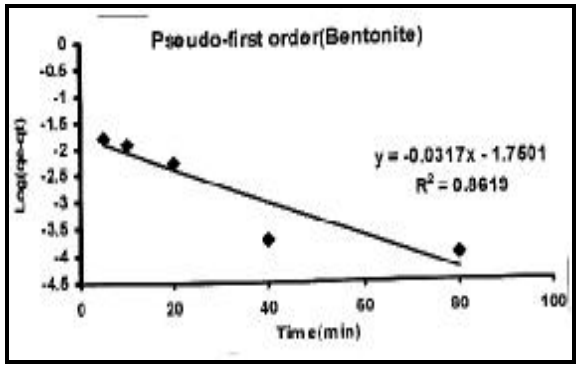

Fig. 10. Pseudo- First Order for Bentonite.

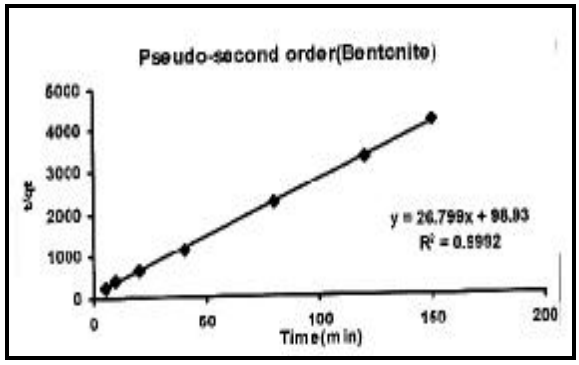

Fig. 11. Pseudo- Second Order for Bentonite.

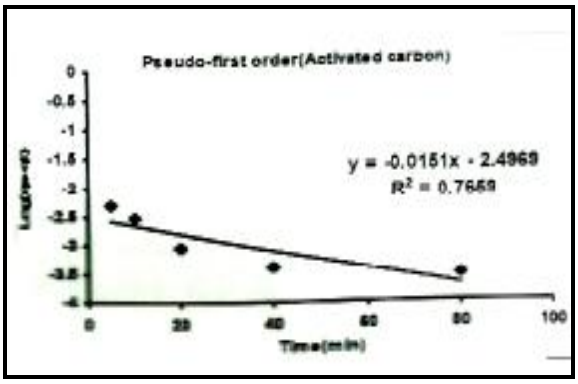

Fig. 12. Pseudo- First Order for Activated Carbon.

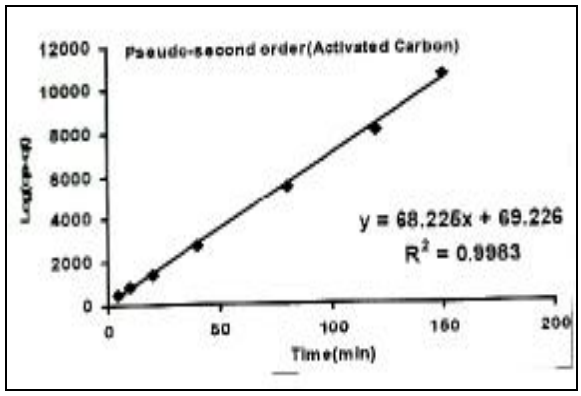

Fig. 13. Pseudo- Second Order for Activated Carbon.

Table 2,
Constants of PSEUDO- FIRST and Second Order.

Adsorbent	q_e(mg/mg) Experimental	Pseudo- first – order	Pseudo – second- order
Bentonite	0.0364	K_1,(min)$^{-1}$ 0.073 q_e, (mg/mg) 0.0177 R^2 0.8619	K_2, (mg.mg^{-1}min^{-1}) 7.2653 q_e, (mg/mg) 0.037 R^2 0.9992
Activated Carbon	0.015	K_1,(min)$^{-1}$ 0.0347 q_e, (mg/mg) 0.0031 R^2 0.7659	K_2, (mg.mg^{-1}min^{-1}) 67.768 q_e, (mg/mg) 0.014 R^2 0.9983

5. Conclusion

The potential use of bentonite and activated carbon as an adsorbents for lead(II) was studied. It was found that bentonite is more effective than activated carbon for removal high concentration of Pb(II) from aqueous solution, the maximum adsorption capacities for bentonite and activated carbon were 0.0364 and 0.015mg/mg, respectively. The percentage removal was strongly dependent on the adsorbent dosage, contact time, agitation speed and initial pH. The study of the thermodynamic parameters indicated that the adsorption process was thermodynamically spontaneous under natural conditions and the adsorption is endothermic in nature. The process kinetics was found to follow the pseudo-second order rate equation.

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دراسة الخواص الديناميكية الحرارية والحركية لامتزاز الرصاص (II) من محلول مائي باستخدام البنتونايت والكاربون الفعال

باسم حميد جريمد* **زياد طارق عبد علي****

**جامعة بغداد*

*** قسم الهندسة البيئية/ جامعة بغداد*

*البريد الالكتروني: bassim.hameed@yahoo.com

**البريد الالكتروني: Z.teach2000@ yahoo.com

الخلاصة

تم التحري عن امتزاز ايونات الرصاص (II) باستخدام البنتونايت و الكاربون الفعال كمواد مازه. كما تم دراسة تأثير كل من الحامضية pH ، وكمية المادة المازة، وفترة التماس، ودرجة الحرارة باستخدام تجارب الامتزاز الكتلي. بلغت اعلى نسبة امتزاز للبنتونايت و الكاربون الفعال و ٠.٠٣٦٤ و٠.٠١٥ ملغم/ ملغم مادة مازة على التوالي. وكذلك تم دراسة الخواص الحرارية الحركية لعملية الامتزاز كالتغير في طاقة جبس الحرة، والتغير في الأنثالبية والانتروبية وقد تبين عند دراسة الخواص الحرارية الحركية اعلاه بان عملية الامتزاز هي عملية حرارية حركية تلقائية تحت الظروف الاعتيادية وإنها ممتصة للحرارة. وأخيرا تم دراسة الطاقة الحركية للامتزاز وبعد تحليل النتائج تبين ان حركية الامتزاز تتوافق مع الحركية الامتزازية من الدرجة الثانية.