

Evaluation of Poly Acrylic Acid(PAA) Hydrogel Beads as Adsorbent for The Removal of Lead(II)ion from Water

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Abstract

Laboratory studies reported earlier, have been showed a very promising result in the selective removal of heavy toxic metals from aqueous solution by a commercially available super absorbent polymer (SAP). In this study one of these super absorbent hydrogels (Poly acrylic acid) beads was used to remove Pb (II)ion from aqueous solutions. The effect of time on adsorption was studied. Kinetic experiments showed that the rate of Pb (II) adsorption on the hydrogel bead was quite good. More than, 90% of the equilibrium adsorption capacity occurs within (10hr) and the adsorption equilibrium could be achieved within (24hr), with adsorption equilibrium capacity (113.40 mg/g). The adsorption kinetic fit well with a pseudo-first-order equation. The effect of the initial metal concentration on the removal percentage of Pb (II) ion was studied. Freundlich and Langmuir isotherm constants and correlation coefficients were calculated. The thermodynamic parameters ΔG° , ΔH° , ΔS° and ΔH_{ads} were also calculated .

Introduction

The water is an essential matter to human and other living organism. Water may be polluted from the effluent of several industries such as chemical industrial, electroplating industrial, dye industrial and battery industrial [1]. The heavy metal ions were found to be one of the main pollutants in water. The pollutants heavy metals were intensively studied due to their significance from the point of view of persistence and toxicity. The toxic metals can cause accumulative poisoning cancer and brain damage when found above the tolerance levels [2]. The agencies for the environmental monitoring have set permissible limits for heavy metals levels in drinking water because of their harmful effects. The removal and tepid decontamination of heavy metals (Cd, Pb, Cu, Hg) become very important for the environmental remediation. Many processes have been used for the removal of heavy metals from waste water, such as chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange and adsorption[3]. For dilute metal concentration, ion exchange, reverse osmosis and adsorption can be applied [4]. However, the common use of ion exchange and reverse osmosis is restricted by the high operating cost. As an alternative to chemical precipitation membrane filtration, or ion exchange, adsorption processes with wide variety of adsorbents have been used. The adsorbents

used should have some specific properties, such as a high ability to reduce the concentration of heavy metals below the acceptable limited, high adsorption capacity, high swelling ratio, and long life time [5]. Many materials have been used as adsorbents including chitosan[6], clay[7], zeolite[8], sawdust[9], bark[10], lignin[11], and other[12]. However, low adsorption capacity and rate for heavy metal ions are the main problems for these low-cost adsorbents [13]. Recently hydrogel bead was used as adsorbent for the removal of heavy metal ion [14]. The flexible polymer chains which is convenient for the penetration of solute molecules with water into the hydrogel. The solute molecules then bind with functional group inside the bead [15]. Polyacrylic acid (PAA) is another water-swelling polymer that can be bound to many cations [16]. In this study the adsorption behavior and adsorption kinetic of Pb (II) adsorption onto polyacrylic acid (PAA) hydrogel bead were studied, the effects of initial concentration and temperature were also studied. Thermodynamic parameters were calculated and a pseudo-first-order and a pseudo-second-order were applied.

Experiments and Materials

Materials and Apparatus

All the reagents were of analytical grade and were used without further purification. Commercial polyacrylic acid (PAA) was used; lead acetate was purchased by Riedel-Dehaen AG. and was used to prepare stock solution ($1000 \text{ mg.L}^{-1} \text{ Pb}^{2+}$) by accurately weighing (1.5592) g of lead acetate and dissolving in 1 L of distilled water. Solutions of desired concentration of Pb(II) were prepared from the stock solution by appropriate dilution. Shimadzu Atomic Absorption (model GBC 933 plus) was used to determine the remained Pb(II) in solution. Ametrohm E.632 PH meter (Switzerland) with glass combination electrode was used throughout this study. Fourier transform infrared (FTIR) spectrophotometer (model shimadzu pretige 21 Japan) was also used.

Batch Experiment

The adsorption of Pb (II) from aqueous solution into PAA was performed using batch equilibrium technique. A 25 ml of solution containing Pb (II) ion with different initial known concentration 100,200,300, and 400 mg.L^{-1} were used. The hydro gel beads with 0.0382 g weight and 3.67 mm diameter were used for removal of Pb(II) from aqueous solution at different time (1-24 hr) and the residual Pb(II) concentration was determined using atomic absorption spectrophotometer. The adsorption tests were continued until the equilibrium concentration was achieved. The effect of contact time on the amount of Pb(II) adsorbed was investigated as a function of initial concentration of Pb(II), pH and temperature. The adsorption capacity Q_e (mg/g) of adsorbent was calculated by a mass balance relationship which represents the amount of adsorbed Pb(II) per the amount of dry adsorbent:

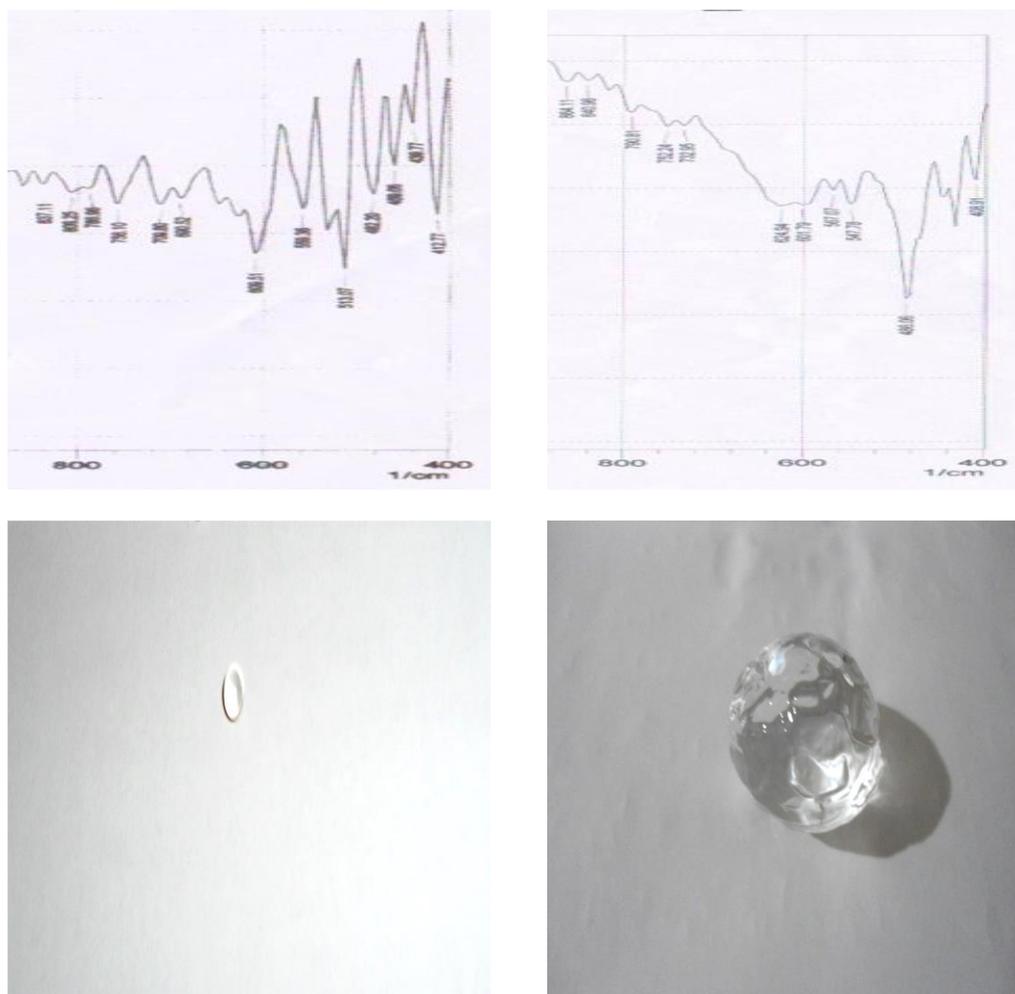
$$Q_e = (C_0 - C_e) V / m \dots\dots\dots(1)$$

Where Q_e is the adsorption capacity at equilibrium (mg/g) C_0 , C_e are the initial and equilibrium Pb (II) concentration in solution (mg.L^{-1}). V is the volume of Pb (II) solution used (L) and m is the mass of hydrogel (g) used. All of the experimental results were the average of triplicate experiments.

Results and Discussion

Effect of Contact Time

The effect of contact time on the rate of the removal of Pb (II).(Fig.(2)) was investigated at initial Pb (II) concentration of 100, 200, 300 and 400 mg.L^{-1} using a constant weight of hydrogel bead 0.0382 g. The rate of removal of Pb (II) by hydrogel bead was rapid at the beginning (1-8 hr), but it gradually be slow with time until it reached equilibrium (maximum capacity with constant value).



Gel bead before metal ion adsorption.

Gel bead after metal ion adsorption.

Fig.(1) This figure shows the profile and size of gel bead before and after entrapment of Lead(II) ion, with IR spectrum of loaded and original gel bead at 400-800 nm, which was shown that there is a clear difference in profile, size, and spectrum.

The plots in Fig.(2). Reveals that maximum percent removal is higher at the beginning due to a larger surface area available of the adsorbent. After adsorption,

the rate of Pb (II) uptake is controlled by the rate of Pb (II) transported from the exterior to the interior sites of the adsorbent.

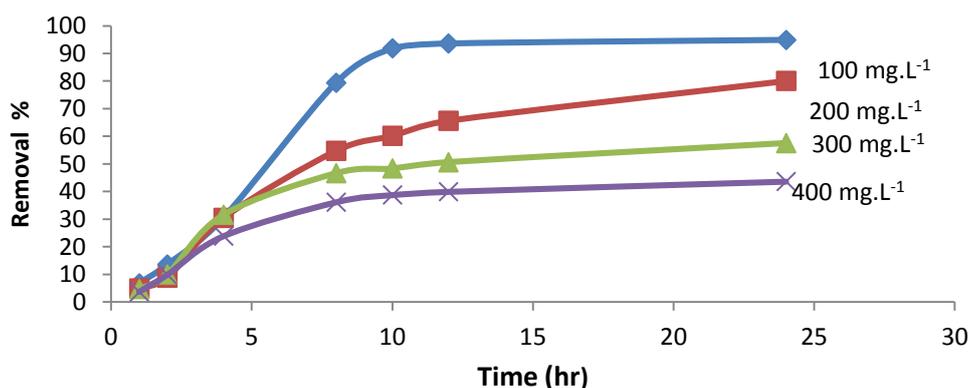


Fig. (2) Effect of the time variation on the %removal of Pb(II)ion.

Effect of pH.

The influence of pH on the removal of Pb (II) by hydrogel bead was studied to gain further insight into the adsorption process. The effect of pH was checked over the pH range (1-6.3) using 100 mg.L^{-1} of Pb (II). pH values were adjusted by adding (0.5) M HCl. The samples were left for (20hr) contact time (for reach maximum removal of ion) with 0.0382 g hydrogel. The results obtained

(Fig.(3)) showed that the optimized pH for the removal of Pb (II) was at 6.3. The adsorption process happens mainly because of static attraction between the carboxyl groups in adsorbents. At lower pH values, protons were available to protonate the carboxyl groups of PAA, therefore, the attraction to cationic Pb (II) ions decreases, while near the basic condition the cations will begin to precipitate from the solution and the removal percentage decreases.

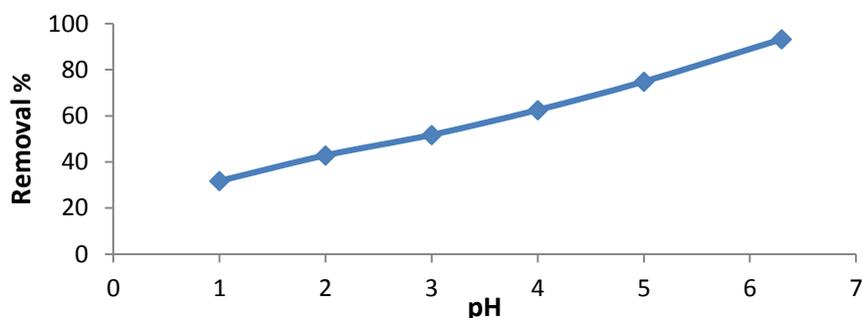


Fig.(3) Effect of pH on the removal of Pb(II).

Effect of Temperature

The adsorption studies were carried out to five different temperatures (10, 20, 25, and 30 °C). Results obtained (Fig.(4)) showed that, at the range of studied temperature, the adsorption increases with increasing temperature, this may be as a result of increase

in the mobility of the Pb(II) ions with the increasing of the temperature, which may also produce a swelling effect within the internal structure of the PAAc enabling more Pb(II) to penetrate further [17,18].

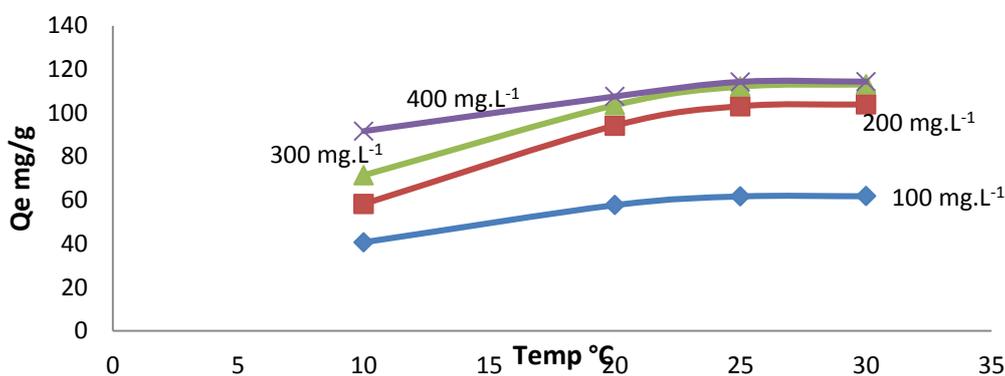


Fig.(4) Effect of temperature on the adsorption capacity.

Adsorption Isotherm

To identify the mechanism of the adsorption process, the adsorption of Pb (II) into PAA was determined as a function of equilibrium (residual) Pb (II) concentration C_e and the corresponding adsorption isotherm was plotted as shown in (Fig.(5)).

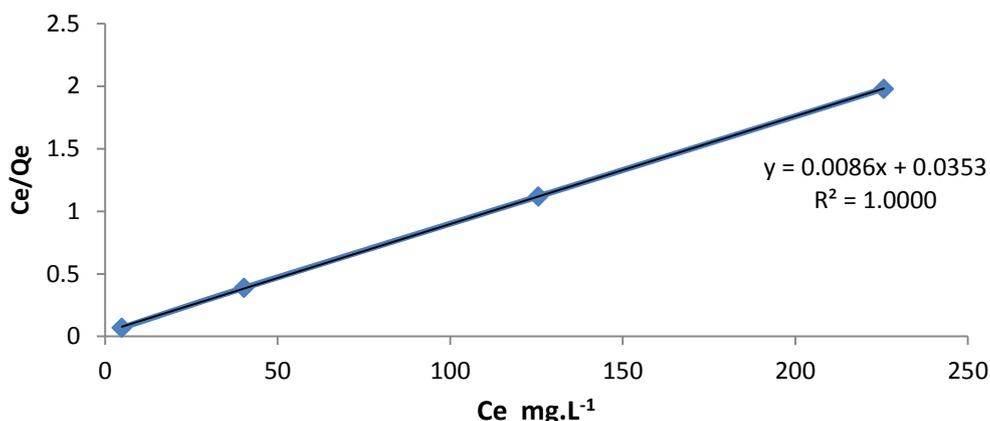


Fig. (5) langmuir plots for the adsorption of Pb (II).

The data can then be correlated with a suitable isotherm the Langmuir adsorption isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorption. The Langmuir equation is given in the following equation:[19]

$$C_e/Q_e = 1/K_L Q_{max} + C_e/Q_{max} \dots \dots \dots (2)$$

Where Q_e is the adsorption capacity at equilibrium (mg/g), Q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), C_e is the concentration of adsorbate at equilibrium (mg.L⁻¹) and K_L is the Langmuir constant (L/mg), which can be evaluated from the intercepts of the linear plots of C_e/Q_e vs C_e , the slope of the straight line equal to $1/Q_{max}$. It was found from this study that the equilibrium adsorption data of Pb (II) adsorption was followed Langmuir's isotherm. Langmuir parameters calculated from Eq. (2) are listed in Table (1). The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separate factor, R_L , which can be defined as:[20]

$$R_L = \frac{1}{1 + K_L C_0} \dots \dots \dots (3)$$

Where C_0 is the highest initial solute concentration (400 mg.L⁻¹) at which the maximum capacity was achieved, and K_L is the Langmuir adsorption constant (L.mg). Table (1). shows the values of R_L equal to

(0.011) which was in the range of 0-1 at 25 °C studied and this confirm that a favorable uptake of Pb (II) .Freundlich equation which is given in the following equation:[21]

$$\text{Log } Q_e = \text{Log } K_F + 1/n \text{ Log } C_e \dots \dots \dots (4)$$

Was applied for fitting the experimental data and calculated Freundlich constant K_F , and n , which can be obtained from the intercept and slopes of the plotting of the $\text{log } Q_e$ vs $\text{Log } C_e$ (Fig.(6)). The Freundlich isotherm describes a small value of reversible adsorption, and the Pb(II) concentration on the adsorption will increase so long as there is an increased in the Pb(II) concentration in the liquid, it is clear from Table (1). That the values of the Freundlich exponents, n , were greater than one ($n > 1$) which represents a favorable adsorption condition[22]. Examination of the linear isotherm plots suggested that the Langmuir model yielded a much better fit than the Freundlich model.

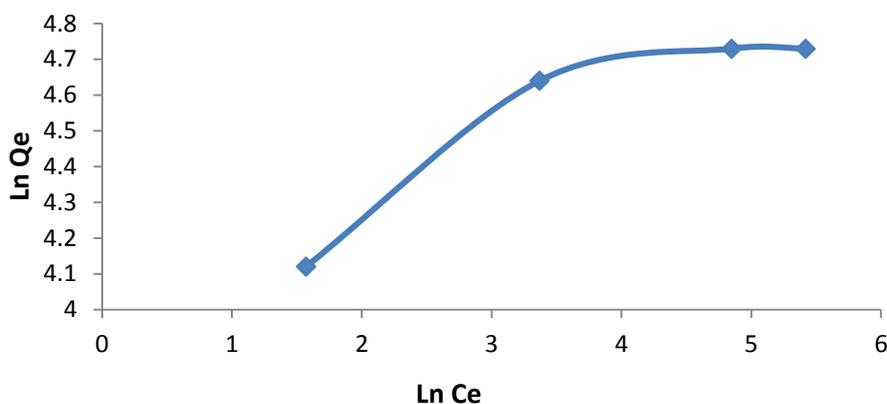


Fig.(6) Freundlich plots for the adsorption of Pb(II).

Table (1)

Isotherm parameters obtained from the two models for the adsorption of Pb(II) ion.

Freundlich isotherm			Langmuir isotherm			
$K_F(mg^{1-n} \cdot L^n \cdot g^{-1})$	n	R^2	$Q_{max}(mg \cdot g^{-1})$	$K_L(L \cdot mg^{-1})$	R_L	R^2
51.85	6.32	0.8570	113.40	0.23	0.011	1.0000

Adsorption Kinetics

The kinetics of the adsorption data was processed to understand the dynamic of the adsorption process in terms of the order and rate constant. Two kinetic models were applied to the adsorption kinetic data in order to investigate the behavior of the adsorption process of Pb (II) into PAA beads. These models were the pseudo- first-order and pseudo-second-order models.[23]

Pseudo-first-order kinetic model

The adsorption kinetic data were described by the Lagergren pseudo-first-order model, which is the earliest known equation describing the adsorption rate based on the

adsorption capacity. The general equation can be expressed as below after definite integration by applying the initial condition:

$$\text{Log}(Q_e - Q_t) = \text{Log} Q_e - \frac{k_1}{2.303} t \dots\dots\dots(5)$$

Where Q_e and Q_t are the amounts of Pb (II) adsorbed (mg/g) at equilibrium and at any time t . k_1 is the rate constant (hr^{-1}). The plot of $\log(Q_e - Q_t)$ vs t gives a straight line for the pseudo-first-order adsorption kinetic (Fig.(7)). The value of k_1 was obtained from the slopes of the straight lines. The k_1 , correlation coefficients (R^2), and $Q_{e,cal}$, $Q_{e,exp}$ values are given in Table (2).

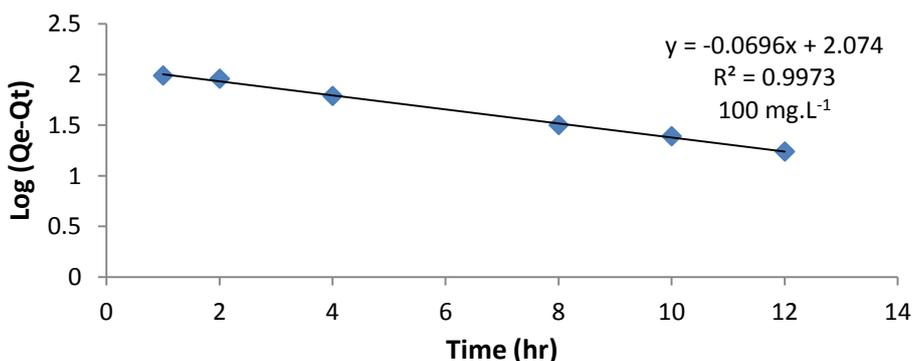


Fig.(7) Pseudo- first - order kinetic plot.

Pseudo – second – order model

Adsorption kinetic was explained by the pseudo – second – order model developed

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \dots\dots\dots(6)$$

Where k_2 is the second order rate constant ($g.mg^{-1} h^{-1}$). The values of k_2 at different initial

Pb (II) concentration were calculated from the slopes of the linear plot of t/Q_t vs t (Fig.(8).) The values of k_2 , R^2 , $Q_{e cal}$ and $Q_{e exp}$ are listed in Table (2).

Table (2)
Comparison of the pseudo–first–order and pseudo–second–order adsorption rate constant for Pb (II) ion adsorption.

Pb(II) ion Conc. mg.L ⁻¹	Pseudo-first-order				Pseudo-second-order		
	Q _{exp} mg/g	k ₁ h ⁻¹	Q _{e cal.} mg/g	R ²	Q _{e cal.} mg/g	k ₂ g.mg ⁻¹ h ⁻¹	R ²
100	113.40	0.1600	118.58	0.9973	66.23	0.009	0.9869

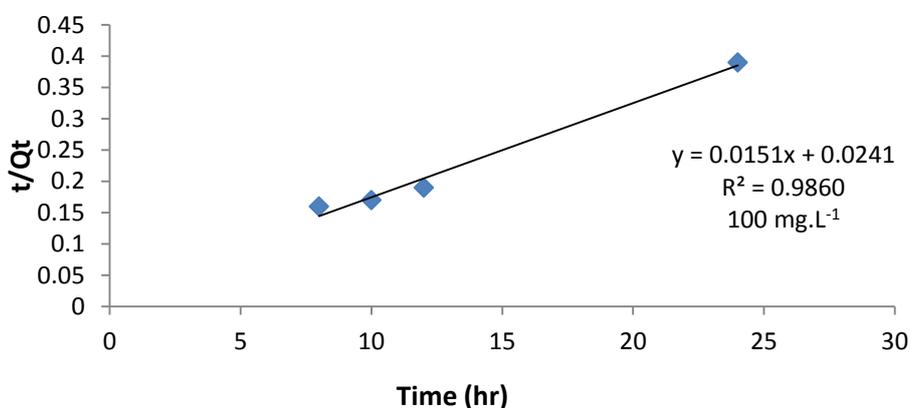


Fig.(8) Pseudo- second - order kinetic plot.

Thermodynamic Studies

The thermodynamic parameter of the adsorption of Pb(II) on PAAC can be obtained using the following relations:

$$K_c = Q_e / C_e \dots\dots\dots(7)$$

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \dots\dots\dots(8)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \dots\dots\dots(9)$$

Where $R = 8.314 J/mol K$ is the universal gas constant, (T) is the absolute temperature and $K_c(L/g)$ is the standard thermodynamic equilibrium constant. By plotting of $\ln K_c$ vs $1/T$ the values ΔH° and ΔS° can be estimated from the slope and intercept (Fig.(9)). The results obtained are shown in Table (3). The

negative values of ΔG° and positive ΔH° and ΔS° obtained indicated that the Pb^{2+} adsorption process is a spontaneous and an endothermic with increasing of randomness at the solid / solution interface occur in the internal structure of the adsorption of Pb(II) onto PAA.

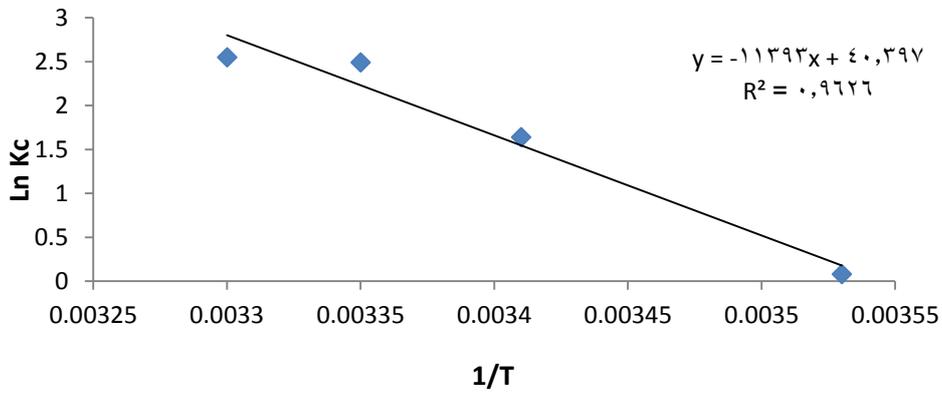


Fig.(9) Ln Kc Versus 1/T plot.

Table (3)
Thermodynamic parameter of adsorption process at different temperature.

Temp K	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)
283	-0.38		
293	-3.73	94.72	336
298	-5.41		
303	-7.09		

The values of ΔH_{ads} can be calculated from the slop of the plot of Ln Ce vs 1/T, (Fig.(10)) according to Chaperon equation:

$$\Delta H_{ads} = R \left[\frac{d(\ln C_e)}{d\left(\frac{1}{T}\right)} \right]$$

Where ΔH_{ads} . is the heat of adsorption (kJ/mol.). The resulting values are given in Table (4).

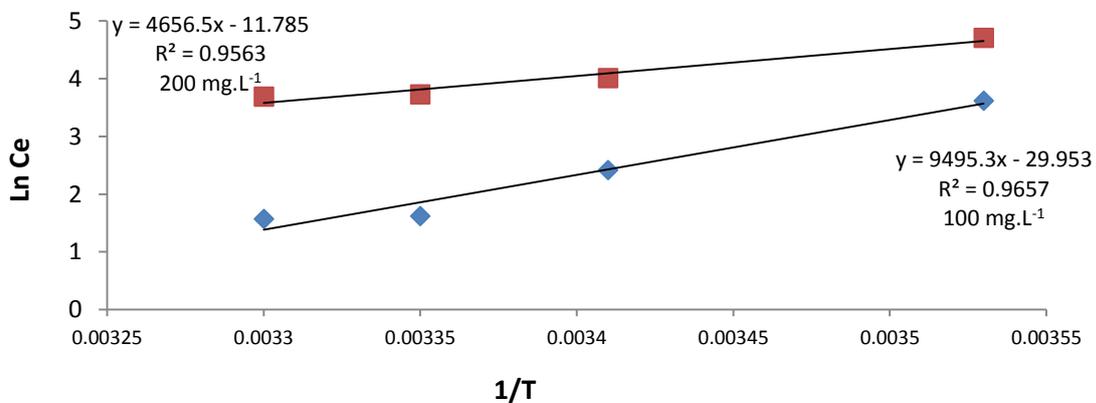


Fig.(10) Ln Ce versus 1/T.

Table (4)
The estimated values of ΔH_{ads} .

<i>Initial concentration</i>	
<i>Pb (II) mg. L⁻¹</i>	<i>ΔH_{ads} kJ/mol</i>
100	78.94
200	38.71
300	1585
400	5.37

Conclusions

In this study, a hydrogel bead of polyacrylic acid (PAA) was used for adsorbed Pb(II) from aqueous solution. The results indicate that the adsorption of Pb(II) was increase with increasing of temperature and time. The maximum capacity was reached at 24 hr with 113.43 mg/g value. The adsorption kinetic data can be described by the pseudo – first – order kinetic model and the adsorption isotherm agree well with the Langmuir model.

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معادلة الدرجة الأولى الكاذبة.تم دراسة تأثير التركيز الابتدائي على نسبة السحب لايون العنصر.تم حساب ثوابت لانكمور وفراندلج والمعطيات الترموداينميكية (الانتالبي، الانتروبي، الطاقة الحرة وانتالبي الامتزاز).

الخلاصة

بينت الدراسات الاولية ألمختبريه نتائج جيده وواعده في مجال سحب وإزالة العناصر الثقيلة السامة من المحاليل المائية باستخدام أصناف تجاريه من المواد البوليمريه ذات الكفاءة العاليه للامتزاز.في هذه الدراسة تم استخدام احد هذه الأنواع وهو حبيبات الجل (متعدد حامض الاكريلك) لسحب ايون الرصاص الثنائي من المحاليل المائية. لقد تم دراسة تأثير الزمن على السحب، أظهرت التجارب الحركية بان سرعة امتزاز الرصاص في حبيبات الجل جيده. أكثر من ٩٠% من سعة الامتزاز عند حالة التوازن حصلت خلال ١٠ ساعة، والوصول إلى حالة التوازن التامة يحتاج إلى ٢٤ ساعة. بلغت سعة الامتزاز عند التوازن ١١٣,٤ ملغ/غم، حركيات الامتزاز متطابقة بشكل جيد مع