Employment of polyacrylic acid beads in treatment of industrial water pollution with Pb (II) ions

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المستخلص :

تناولت الدراسة الحالية أزالة أيونات الرصاص من محاليلها المائية بأستخدام حبيبات البولي حامض الأكريليك . درست متغيرات عملية الأمتزاز وتضمنت زمن التماس؛ الدالة الحامضية؛ درجة الحرارة؛ التركيز الأولي للأيونات . سعة الأمتزاز وصل الى أعظم قيمة 565 mg/gm بعد مرور 24 ساعة . أثبت الدراسة تطابق نمذوج لانكماير للأمتزاز مع النتائج العملية ومن الدرجة الأولى الكاذبة مقارنة مع نوذج فرندلتش تحت نفس الظروف منحنيات الأمتزاز تتطابق بصورة جيدة مع الحرف S ومع منحنيات Giles . دراسة الديناميكا الحرارية أوضحت بأن عملية الأمتزاز هي ماصة للحرارة من خلال قيمة الأنثالبي الموجبة ΔH^o بينما قيمة الأنتروبي الموجبة تدل على زيادة الأنتظامية لعملية الأمتزاز .

Abstract:

The current study deals with the removal of Lead ions from its aqueous solution by using polyacrylic acid beads. The process variables have been studied where time of contact, pH of solution, temperature, initial concentration. The adsorption capacity reached a maximum value of 565 mg/gm. after 24 hours. The study proved the applicability of pseudo first order of Langmuir model comparing with Frundlich model using the same conditions. The adsorption isotherms correspond well with shape (S) and by Giles isotherms. The thermodynamic study showed that the adsorption is endothermic process from positive value of ΔH^o , while the positive value of entropy refers to the increased regularity of adsorption.

Keywords: Adsorption, Polyacrylic acid, Pb (II) ions, Langmuir model, Frundlich model

Introduction:

Due to the extensive use of lead in many industries which leads to pollution of the environment. Lead is heavy and does not decompose inside the body organism and thus become a threat to the environment in addition to the toxicity which is it possess, therefore many people are infected annually in urban areas also plant faced the same threat which reduces its effectiveness through entering within the tissue of plant fiber through dust in the air as well as through the effluent in the aquatic environment [1, 2]. At the present time the adsorption process is acceptable in reducing pollution to eliminate metal ions and organic materials in wastewater treatment in the whole world [3]. Many studies have recently been conducted to find out materials with high adsorption potential in addition to their low cost to remove metal ions in addition to developed adsorbent materials and testing it to determine their validity to use [4, 5, 6, and 7]. Many investigators have been employing activated carbon in removing heavy metals Co(II) , Cd(II) , Co(III) , Ni(II) , Cu(II) , Pb(II) , Cr(II). They studied the parameters which effect on adsorption rate time of contact , adsobent dosage , pH of the aqueous solution , temperature of adsorption process , initial metal ion concentration , and the extent of adsorption curves matching with both Langmuir isotherm and Freundlich model by using a comparison of correlation coefficient of linearity curves for experimental data obtained , however they found temperature , initial concentration , pH of solution and time affecting the whole adsorption capacity [8,9,10,11] . Several types polymeric hydrogel beads have been developed and tested by removing different types of heavy metal ions besides organic dyes meanwhile the kinetic and isotherm of adsorption and other effecting parameters have been thoroughly assessed recently [12,13,14,15,16] . Low cost materials used also to treat the heavy ion metals such as lignin [17], sawdust [18], clay [19], chitosan [20] have been employed. The polymers with flexible chains are suitable to adsorb effective the metal ions and other organics by penetrations inside the polymer and connect with its functional groups on backbone of polymer chains consequently the polymer swells [21].

Experimental and discussion:

Poly acrylic acid polymer beads have been used to remove Pb (II) ions from its aqueous solutions. For the experimental work 1000 ppm of Pb (II) was prepared dissolving Lead nitrite salt in distilled water then diluted to different concentration. the solution volume used in each experimental runs was 25 ml and by immersing a single bead of polymer with 0.04 gm. weight and 0.38 mm diameter in the aqueous solution of Pb (II) ions . The parameters are studied, contact time, pH of solution, temperature, and initial concentration of Pb (II) ions besides the kinetics and thermodynamics study also included in the this work. Atomic absorption spectrometry method was used to determine the remained concentration of Pb (II). The capacity of adsorption, Q in mg/gm. was

determined by using the following equation [22].

$Q = (Co – Ce) V / m$ ----- (1)

Where Co is initial concentration of Pb (II) ions in ppm, Ce is the equilibrium concentration of Pb (II) ions at time t in ppm, V is the volume of aqueous solution in ml, and m the mass of the bead in gm.

Effect of time of contact:

Table (1) shows the experimental results obtained from a series of runs of adsorption of Lead ions at (1, 3, 6, 9, 12, 24) hours, the initial concentration of Lead ion is 1000 ppm, pH equal to 5.84 and temperature $25C^{o}$. Figure (1) shows the pattern of the relationship between time and adsorption capacity, however the time to establish equilibrium was 12 hours and adsorption is carried out in two stages, the first stage if fairly rapid than second stage and consist of the adsorption the ions from its solution in the first 10 hours from the beginning of adsorption and the second stage which followed being slow and arrives equilibrium point with 24 hours from the beginning of adsorption. However, this can be explained by the fact that adsorption rate is high at the beginning on the surface of the polymer because of the active centers are free but when the sites are covered by Lead ions the adsorption starts to slow down and the rate of adsorption become dependent on the speed of ions transfer from the solution to the polymer surface. [23]

Table (1): Effect of contact time on adsorption of Pb (II)

Time , hr	Remained pb(II) ion ppm	Removal pb(II) ion ppm	% Removal	Capacity Q mg/gm
1	978.8	21.20	2.12	13.25
3	885.5	114.5	11.45	71.56
6	674.6	325.4	32.54	203.37
9	535.3	464.7	46.47	290.43
12	331.5	668.5	66.85	417.81
24	95.40	904.6	90.46	565.38
48	95.40	904.6	90.46	565.38

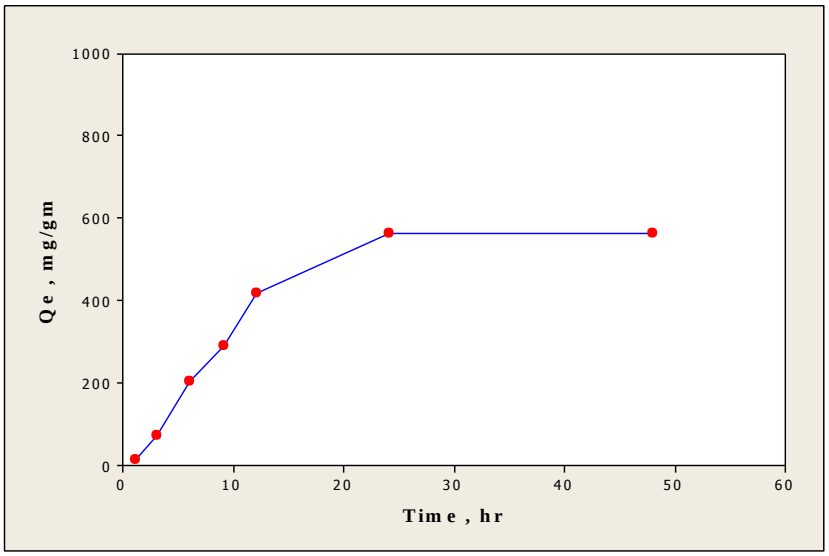

Figure (1): Effect of adsorption time on adsorption capacity

Effect of pH of solution:

Effect of pH of solution has been studied at different levels of pH at temperature of 25 C^{o} and time of adsorption 3 hours and initial concentration 1000 ppm; however the results are listed at Table (2). Figure (2) shows that the removal rate is increased with increasing of pH of the solution especially when solution becomes neutral. The competition of the ions on effective sites is greatly affected by the charge on which the ion adsorbed from solution. In low values of pH H_3O^+ ions will compete with Pb (II) ions on negative sites, while at higher values of pH the hydroxyl ions are predominant, thus reducing the competition of Pb (II) ions. The adsorption rate of Pb (II) on active sites of the polymer is inversely proportional to further increase in pH values, however there are two likely possibilities, first surface dissolves when the solution become highly basic which leads to braking the bonds of adsorbent surface and thus less adsorption rate at lower pH values, and the other possibility is due to ionic decomposition of Lead salt which leads to formation several negative and positive ions and formation negative Lead ions (complex or dimmers) and thus increasing of the volume of adsorbed ion and then it will be difficult to compete with hydrogen positive ions and become difficult to adsorb. Moreover the negative charge on Lead complex which is formed as negative dimmer which repellent with surface containing negative groups consequently adsorption rates declines [24] .

Table (2): Effect pH of solution on adsorption Pb (II) ion

pH of solution	Remained Pb(II) ion concentration ppm	Removal Pb(II) ion ppm	% Removal	Capacity Q mg/gm
5.84	885.5	114.5	11.45	71.560
6.35	770.0	230.0	23.00	143.75
6.83	606.3	393.7	39.37	246.06
7.57	641.7	358.3	35.83	223.93

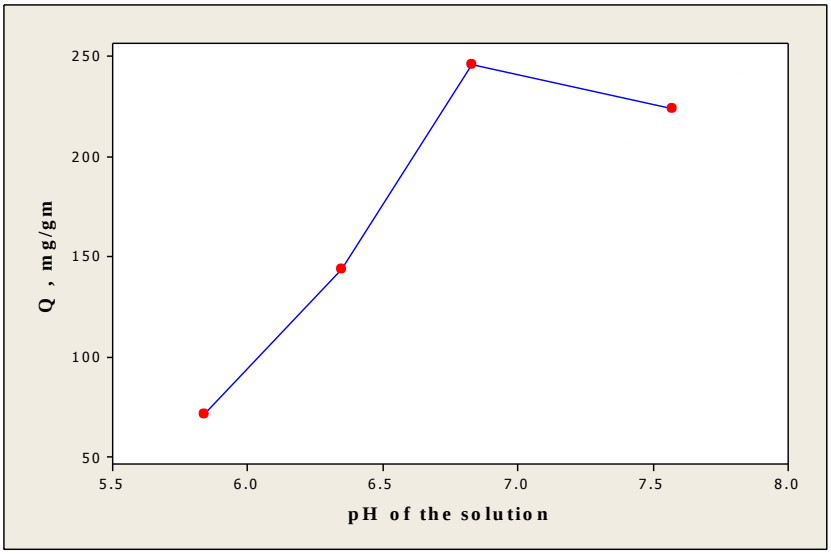

Figure (2): Effect of pH of the solution on adsorption capacity

Effect of adsorption temperature:

Four different temperatures used to study the adsorption process on Pb (II) ions on the surface and active sites of the polymer are (25,30,35,40 C^o) at initial concentration of 1000 ppm and contact time of 3 hours and pH of solution 5.84 . The experimental results are shown in Table (3) and Figure (3), however it can be noticed that the removal percentage of ions increases significantly with increasing temperature of adsorption process. The highest adsorption capacity was 238.46 mg/gm. at 40 C^o, however this is due to the increased kinetic energy of ions that are initially adsorbed from solution as it has the ability to contact the surface, on further increasing of temperature the adsorbed ions begins to require higher kinetic energy, thus the adsorption capacity changes its trends drastically and perhaps starts to decline, this is because of ions starts separating from the surface of polymer returning back to solution [25].

Table (3): Effect of solution temperature on adsorption of Pb (II) ion

Temperature C^o	Remained Pb(II) ion concentration ppm	Removal Pb(II) ion ppm	% Removal	Capacity Q , mg/gm
25	885.50	114.50	11.45	71.560
30	826.87	173.13	17.31	108.21
35	628.37	371.63	37.16	232.26
40	618.45	381.55	38.15	238.46

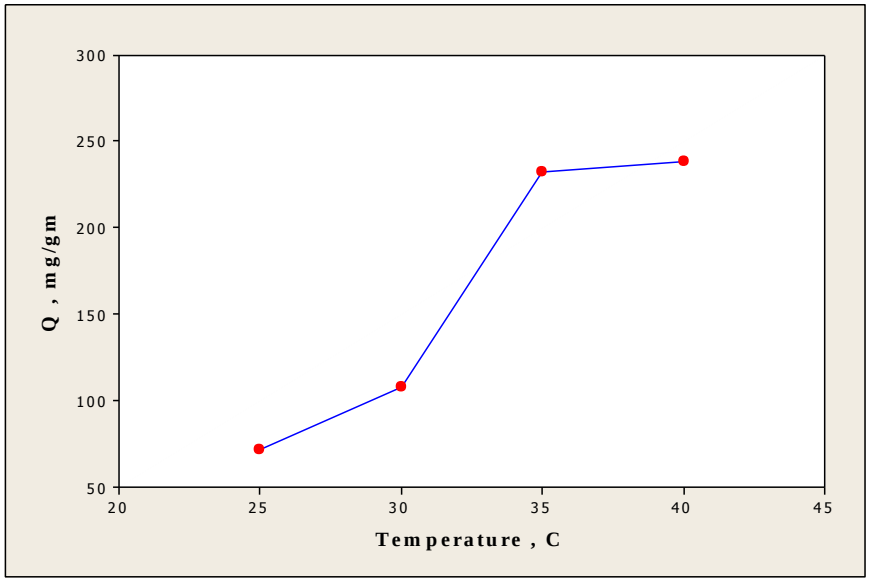

Figure (3): Effect of adsorption temperature on adsorption capacity

Effect of initial concentration of Pb (II) on adsorption process:

Different concentration of Pb (II) ions used (100, 200, 300, 1000 ppm) to study the effect of ion concentration with contact time of adsorption 3 hours and pH of solution 5.84. the results are tabulated at Table (4) and Figure (4) shows the effect of ion concentration on adsorption capacity, however it can be concluded that adsorption capacity increases with increasing initial concentration , this because of the adsorbing polymer surface is an electrostatic type in other words, increasing concentration or the number of Pb(II) adsorbed relation to the size of the solvent in the solution, thus increasing the probability of separation of ions from the solvent, thus increasing the magnitude of adsorption capacity [26] .

Table (4): Effect initial concentration of the solution on adsorption of Pb (II) ions

Initial Pb(II) ion concentration ppm	Remained Pb(II) ion concentration ppm	Removal Pb(II) ion ppm	% Removal	Capacity Q , mg/gm
100	10.000	90.00	90.00	56.25
200	96.300	103.7	51.85	64.81
300	187.76	112.2	37.40	70.12
1000	885.50	114.5	11.45	71.56

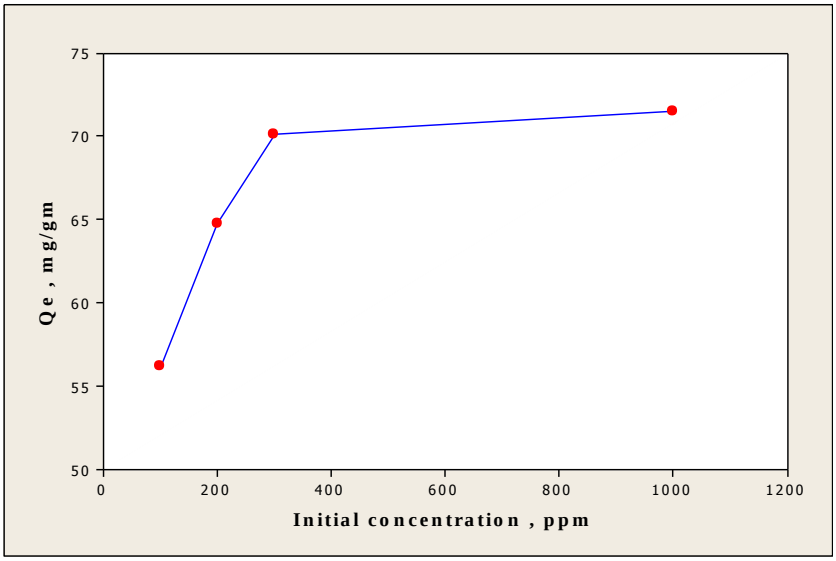

Figure (4): Effect of initial concentration of Pb (II) ions on adsorption capacity

Note that the adsorption strength of the adsorbent material increases whenever the solubility of the material is low in the solvent as proved by Giles isotherms [28]. Severe ions adsorption will take place on the surface of absorbent material in turn. This phenomena will reduce the adsorption of ions on the active sites since of pore blockage consequently the permitted surface area will reduce.

Kinetics of Pb (II) adsorption:

The kinetics of Pb (II) adsorption from its aqueous solution at adsorption time 3 hours, pH equal to 5.84, initial Pb (II) ions concentration 1000 ppm at 25 C^{o} can be assessed [27].

First pseudo order:

$$\log (Q_e - Q_t) = \log Q_e - (K1/2.303)\, t \quad \text{---- (2)}$$

Second pseudo order:

$$t/Q_t = (1/ K_2 Q_e^2) + (t/Q_e) \quad \text{---- (3)}$$

Where Q_e, Q_t is capacity of adsorption at equilibrium and at time of adsorption equal to (t) respectively. K_1, K_2 are adsorption rate constant for pseudo first order and second pseudo order respectively. By applying

equations (2) and (3) to experimental results in order to asses it, however the results showed the adsorption follows the first pseudo order since it fits the data with correlation factor R^2 = 99.20% as shown in Figure (5), while second pseudo order doesn't fit the experimental data well with correlation factor R^2 = 63.00% as shown in Figure (6).

Fitting equation for pseudo first order Y=2.793 - 0.03894X

Fitting equation for pseudo second order Y=0.06324 - 0.00345X

Table (5) shows the summary of results of pseudo first and second order kinetics of adsorption Pb (II) ions from its solution.

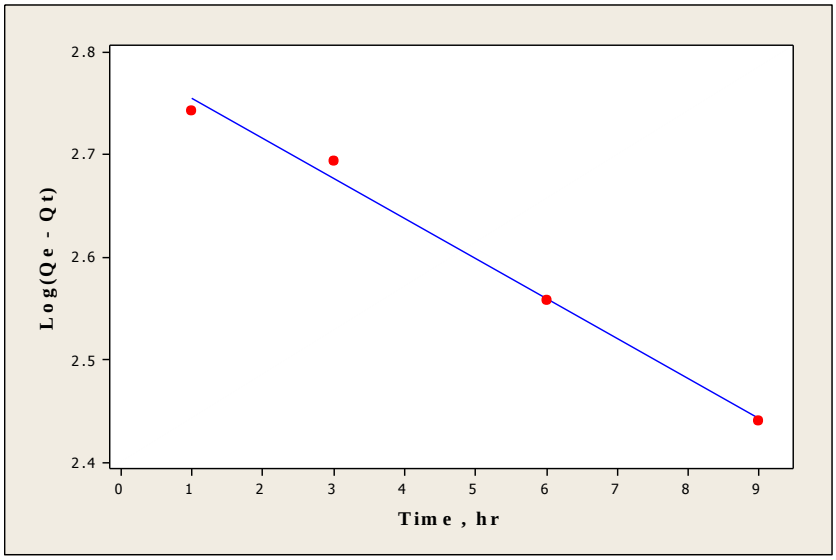

Figure (5): Adsorption with pseudo first order kinetics

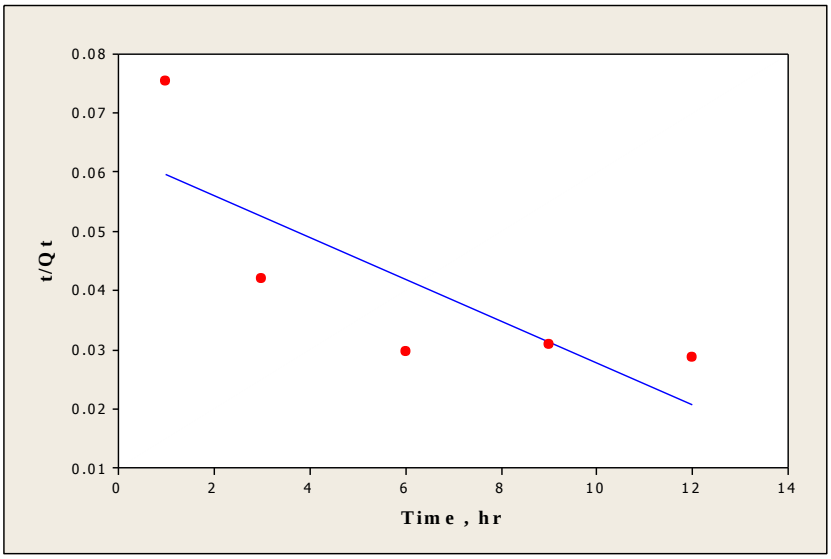

Figure (6): Adsorption with pseudo second order kinetic

Table (5): Kinetic parameters for Pb (II) ion removal by adsorption

Pb(II) ppm	Pseudo first order				Pseudo second order		
1000	Q estimated	Q experimental	K_1	R^2	Q estimated	K_2	R^2
	620.70	565.38	0.089	99.20%	282.32	0.00019	63.00%

Isotherms of the Pb (II) adsorption:

The isotherm of Pb (II) adsorption from its solution have been studied using poly acrylic acid beads at 25 C^o and 3 hours of contact time using 0.04 gm of adsorbent and different ion concentration (100, 200, 300, 1000) ppm and constant pH of solution 5.84. Figure (7) represents the relation between Qe and Ce. However the overall shapes of isotherm correspond well with shape (S) by Giles isotherms [28]. This indicates that the orientation of ions being adsorbed is either tilted or vertical, it also indicates an affinity for the molecules adsorbed toward the adsorption layer and that the solvent is highly adsorbed [25] .

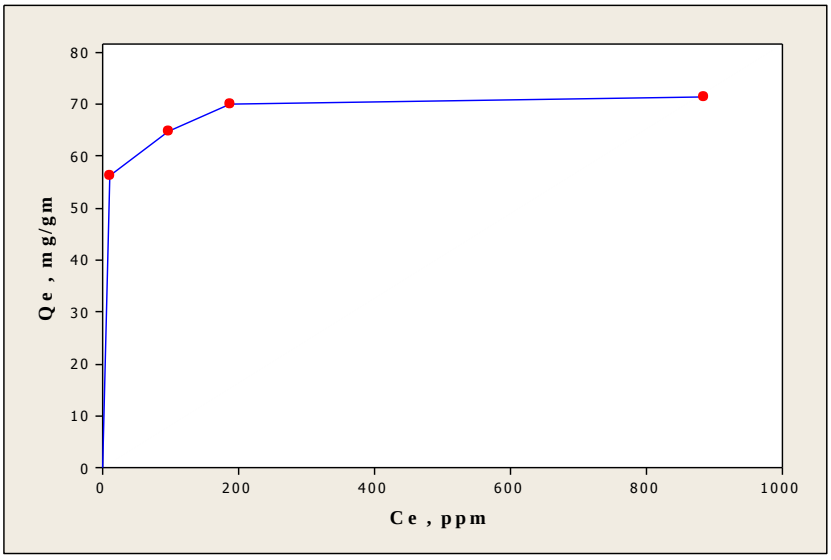

Figure (7): Langmuir isotherm of Pb (II) adsorption

In this work the data are tested by two well-known isotherms Langmuir and Freundlich isotherms, [29]:

Langmuir equation

Ce/Qe=(1/Qe K)+(Ce/Qmax) -----(4)

Freundlich equation:

$\ln Qe = \ln K_F + (1/n) \ln Ce$ -----(5)

Where Qmax is the maximum adsorption capacity, K_L is Langmuir constant, K_F and n are Freundlich constants.

Langmiuir and Freundlich parameter can be evaluated by from linear plot between Ce/Qe against Ce, and ln Qe against ln Ce respectively, as shown in Figure (8) and Figure (9)

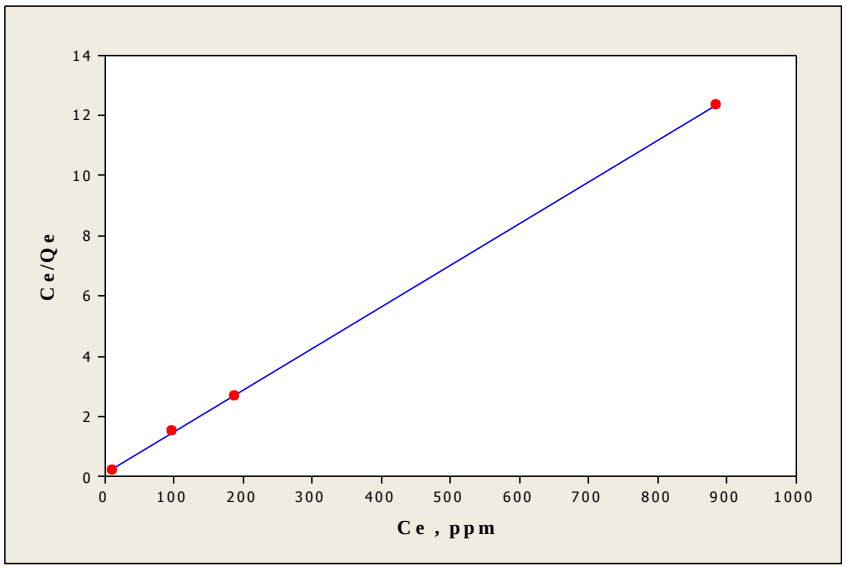

Figure (8): Langmuire adsorption plot for Pb (II) ions removal

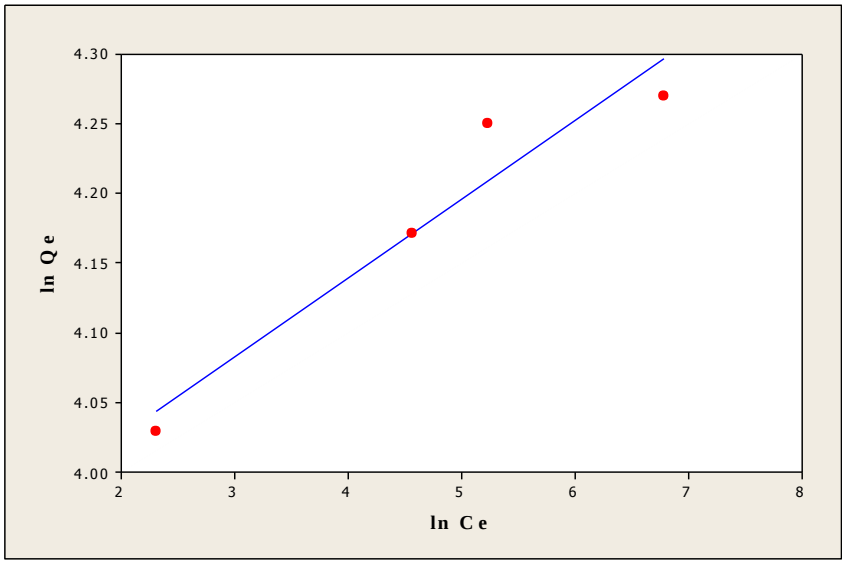

Figure (9): Freundlich asorption plot for Pb (II) ions removal

It was noticed from slope value and correlation coefficient R^2 of linear plot (Ce / Qe) against (Ce) (Figure (8)) Langmuir equation is most applicable than Freundlich equation Figure (9), in present work Langmuir equation is best suited for

existence of relationship between (Ce/Qe) against Ce at pH=5.84, time of contact 3 hours, and temperature 25 C^o . The value of R^2=99.5% and K_L=0.08296, Qmax=72.046 mg/gm. and the fitting equation is:

Y=0.08296 + 0.01388X

While using Freundlich equation Figure (9) which comes after Langmuir with R^2=92.8%, n=17.68 and K_F = 50.048 and the equation of fitting is:

Y=3.913 + 0.056569

Higher values of n in Freundlich were much preferred in adsorption because it relates to how Pb (II) ions bonded to the surface of the polymer when compared with other surfaces [29].

Thermodynamic of Pb (II) adsorption process:

The study of effect of temperature on the adsorption process enable us to assign the thermodynamic function (ΔG^o, ΔS^o, ΔH^o) to the significant of these values in understanding the adsorption process . The following relationships were employed for the evaluation:

$Kc = Qe/Ce$ ----(6)

$\ln Kc = \Delta S^o/R - \Delta H^o/ RT$ ----(7)

$\Delta G^o = \Delta H^o – T\Delta S^o$ ----(8)

Where ΔG^o is the free energy, R is the gas constant, and Kc is the thermodynamic equilibrium constant. These parameters can be obtained from slope and intercept of linear plot between Kc against 1/T Figure(10), and Table (6) shows the collected experimental thermodynamic results. However this data emphasizes that adsorption process is endothermic process.

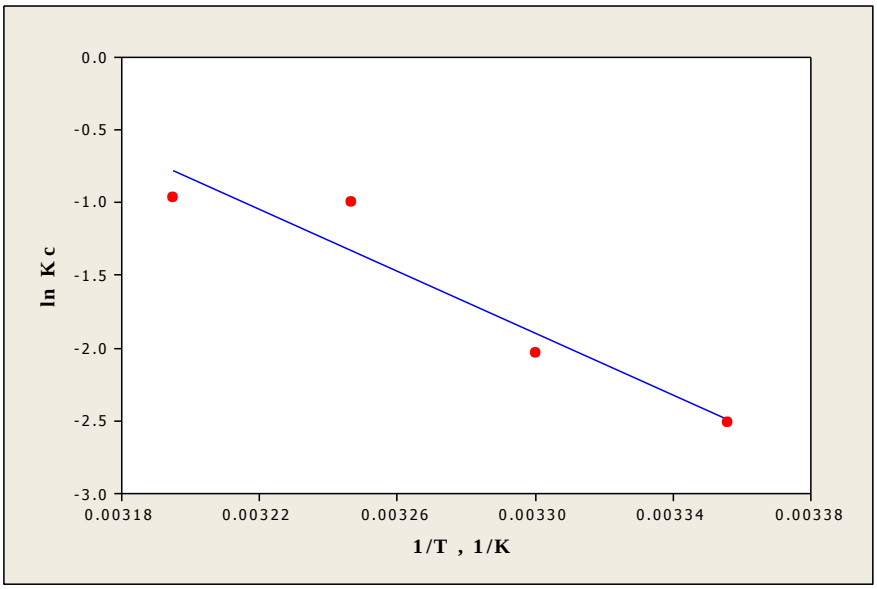

Figure (10): ln Kc plot against 1/T

Table (6): Thermodynamic properties for Pb (II) ion removal estimated at different temperature

Temperature , K	ΔG^o , Kj/mol.	ΔH^o Kj/mol.	ΔS^o , J/mol. K
298	6.19	88.535	276.357
303	4.81		
308	3.43		
313	2.05		

Conclusions:

The adsorption isotherm follows Langmuir isotherm with R^2 equal to 99.5% comparing with Freundlich R^2 equal to 92.8%, and its shape close to (S) and follows Giles isotherms. The adsorption process found to be following the first pseudo order since it fits the data with correlation factor R^2 equal to 99.20%, . Adsorption of Pb (II) on polymer surface was endothermic where ΔH value is positive. Capacity of adsorption increases with increasing of contact time, pH, and initial concentration of Pb (II).

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