



Removal of Iron (Iii) Ion from Aqueous Solution using Polyacrylic Acid Hydorgel Beads as Adsorbent

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Abstract:

This research focuses on the removal and adsorption of Fe (III) ion using a low cost commercial polyacrylic acid hydrogel beads as adsorbent. The effects of time, initial concentration and pH on the metal ion adsorption capacity were investigated. The regeneration of the hydrogel bead and recovery of the metal ion adsorbed were study. The adsorption isotherm models were applied on experimental data and it is shown that the Langmuir model was the best one for Fe (III) ion removal. The maximum capacity was calculated. First-order and second- order kinetic models were used and it is shown that the experimental data was in reliable compliance with the first- order model with R² value of (0.9935, 0.9011, 0.9695, 0.9912) for all concentrations which were used in this study (100, 200, 300, 400) mg.L⁻¹ respectively.

Keyword: Removal, Polyacrylic acid, Hydrogel

إزالة ايون الحديد الثلاثي من المحاليل المائية باستخدام حبيبات الجل المائية لمتعدد حامض الاكريلك كمادة مازة

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الخلاصة:

هذا البحث يتضمن دراسة عملية إزالة و امتزاز ايون الحديد الثلاثي من محاليله المائية باستخدام متعدد حامض الاكريلك كمادة مازة. لقد تم دراسة تأثير الزمن، التركيز الابتدائي و الدالة الحامضية. كما تم تطبيق الموديلات الايزوثيرمية للامتزاز على النتائج المستحصلة وبينت ان موديل لانكماير هو الأفضل لايون الحديد الثلاثي. لقد تم حساب السعة القصوى، كما تمت دراسة عملية استرجاع ايون الفلز الممتز داخل حبيبة الجل المائية وتهيئة الحبيبة للاستخدام لمرة أخرى. طبقت معادلتى الدرجة الأولى و الثانية على النتائج المستحصلة وبتبين إنها تتفق مع الدرجة الأولى وحسب قيمة معامل الخطية العالية 0.9935, 0.9011, 0.9695, 0.9912) للتراكز المستخدمة في الدراسة (100,200,300,400) ملغ لتر على التعاقب.

1. Introduction:

Water pollution by toxic metals remains a serious environmental problem and can be detrimental to living organisms. Metals can be toxic pollutants that are nonbiodegradable,

undergo transformation, and have great environmental, public health and economic impacts [1]. In the environment, one element can be present in different chemical forms, which differ in their chemical behavior,

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bioavailability and toxicity. Some elements such as iron [2], arsenic [3], manganese [4] and chromium [5] are mainly present in natural water as different oxidation states. For instance Cr (VI), As (III), and As (V) are known carcinogens, while Fe (II), Fe (III), Mn (II), Mn (VII) and Cr (III) are essential micronutrients for organisms and plants. However they become toxic at higher levels. Effective removal of heavy metal ions from aqueous solution is important in the protection of environmental quality and public health [6].

Several treatment processes such as adsorption [7], coagulation and precipitation [8], ion exchange [9] and co-precipitation/adsorption [10], etc. have been developed over the years to remove heavy metal ions from aqueous solution. The adsorption method is the most frequently used because of its flexibility in design and operation as well as easy regeneration of the adsorbent [11].

It has been gradually recognized that using low-cost and environmentally friendly adsorbents to remove pollutants is an effective and economical method of water decontamination. Many materials have been used as adsorbent including clay [12], zeolite [13], sawdust [14], bark [15], lignin [16] and others [17]. However, low adsorption capacity and rate for heavy metal ions are the main problems for these low-cost adsorbents [18]. Recently hydrogel bead was used as adsorbent for the removal of heavy metal ion [19]. The flexible polymer chains which are convenient for the penetration of solute molecules with water into the hydrogel. Iron plays important roles in both biological and environmental media [20]. Fe (III) is important in the biosphere, serving as an active centre of a wide range of proteins such as oxidases, reductases and dehydrases. The present study focused on the use of the polyacrylic acid PAA with carboxylic acid functional group for removal of Fe (III) from aqueous solution.

2. Experimental

Materials:

All reagents used in this study were of analytical reagent grade and were used as received. Commercial polyacrylic acid (PAA) and FeCl_3 was purchased from Riedel-Dehaen. Working solution of $1000 \text{ mg}\cdot\text{L}^{-1}$ Fe (III) ions was prepared as a stock, and then different solutions were prepared from this stock solution, by simple dilution with distilled water.

Instrumentation:

Flow injection analysis system with (homemade) spectrophotometer was used for the determination of the remained metal ion in solution according to the method suggested by Shaker, et al [21] and Vogel [22]. Ametronm E.632 PH meter (Switzerland) with glass combination electrode was used throughout this study. A Shimadzu FTIR spectrometer model (Pretiges 21) with KBr pellets was used. Figure 1 shows the FTIR of loaded and non loaded sorbent spectrum.

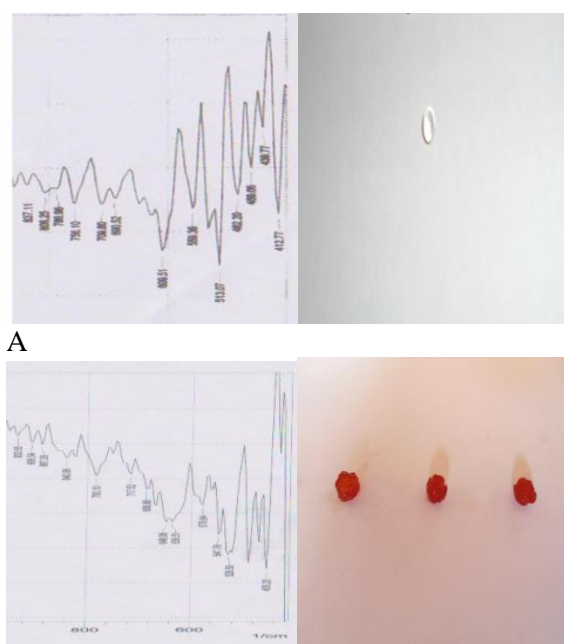


Figure 1- The profile and size of gel bead before (A) and after (B) entrapment of Fe (III) ion, with IR spectra of loaded and original gel bead at 400-800 nm.

Batch Experiment:

Each adsorption experiment was conducted with the PAA hydrogel beads for removal of Fe (III) ion from aqueous solution. A 25 mL of solution containing Fe(III) ion with different initial known concentration 100, 200, 300, and 400 $\text{mg}\cdot\text{L}^{-1}$ were used. The hydrogel beads with 0.0382 g weight and 3.67 mm diameter were used for removal of Fe (III) from aqueous solution at different time (1-48 hr) and the residual Fe (III) concentration was determined using flow injection analysis. The adsorption tests were continued until the equilibrium concentration was achieved. The effect of contact time on the amount of Fe (III) adsorbed was investigated as a function of initial concentration of Fe (III), 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 Fe (III) per the amount of dry adsorbent:

$$Q_e = (C_o - C_e) V / m \quad (1)$$

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

3. Results and discussion:

All the results obtained are tabulated in Tables (1-8).

Ferric (III) ion determination:

This study was carried out by using the preliminary experimental concentration for Fe (III), 50 mg.L^{-1} 5% NH_4SCN - H_3O^+ , and Ayah-3Sx3 - 3D - solar (homemade) which is showed in Figure.2.

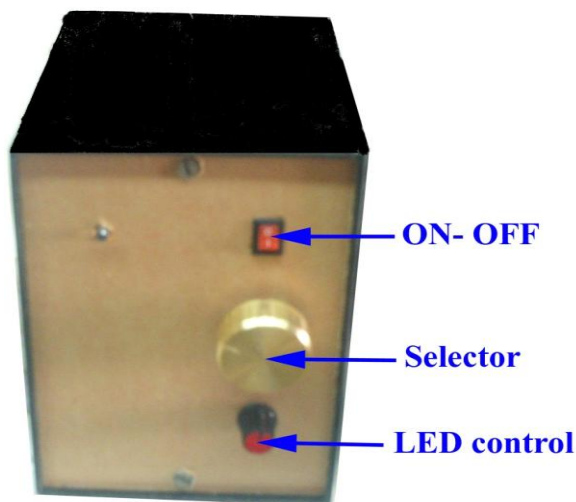


Figure 2-AYAH-3Sx3-3D-SOLAR microphotometer used for determination of Fe (III) ion.

Variations of the response with concentration of Fe (III) and detection limit of Fe (III)-5% NH_4SCN - H_3O^+ system were studied (Figure.3.) by preparing a series of solutions of Fe (III) ion, with concentration range of 0.5 - 150 mg.L^{-1} and measured by FIA using the conditions which are listed in Table 1.

Table 1- Summary of optimum parameters used.

parameters	Fe (III) ion
Type of chemical system	Fe(III)- H_3O^+ - NH_4SCN
Number of line	2
Number of coil	1 60 μL 30 Cm
Flow rate of carrier (mL.min^{-1})	1.8
Flow rate of reagent (mL.min^{-1})	2.0
Concentration of H_3O^+ (mol.L^{-1})	0.5
Concentration of NH_4SCN (w/v)	5 %
Volume of injection valve (μL)	80
LOD ($\text{ng}/80 \mu\text{L}$)	40

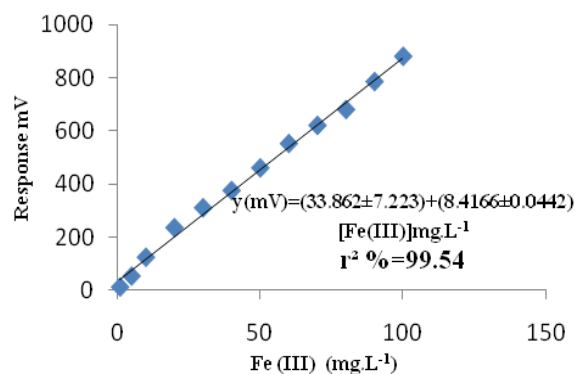


Figure 3- Variation response for Fe(III) ion determination using 5% NH_4SCN .

Effect of Contact Time:

The effect of contact time on the rate of the removing of Fe (III) (Figure.4) was investigated at initial Fe (III) concentration 400 mg.L^{-1} using a constant weight of hydrogel bead 0.0382 g .

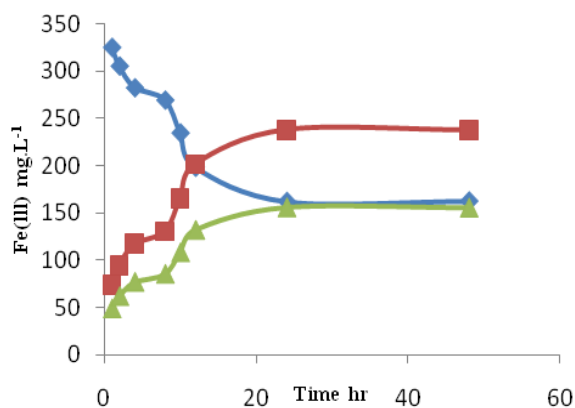


Figure 4- Effect of time variation on remaine \blacksquare , removal \blacksquare , Fe(III) and capacity \blacktriangle mg/g

The results indicate that there is proportional relation between time and removal Fe (III) ion. The time at which the maximum removal of Fe (III) ion was occurred at the first hour, and the minimum removal was occurred at 6-24 hr. The symmetry point (the hour at which the remained and removal Fe (III) ion was at the same value) is at 1-2 hr, as shown in Figure.4 and Table 2.

Table 2- Summary of the results of time variation effect on the removal of Fe (III) ion initial concentration 400 mg.L⁻¹.

Time hr	Remained [Fe(III)] in solution mg.L ⁻¹	removal [Fe(III)] in bead mg.L ⁻¹	Capacity mg/g
1	325.6	74.4	48.7
2	305.7	94.3	61.8
4	282.6	117.4	76.8
8	269.4	130.4	85.4
10	234.8	165.2	108.1
12	198.4	201.6	131.9
24	162.1	237.9	155.7
48	162.5	237.5	155.4

Effect of pH:

The influence of pH on the removal of Fe (III) by hydrogel bead was studied to gain further insight in to the removal process. The effect of pH was checked over the pH range (1-6.3) using 100 mg.L⁻¹ of Fe (III). pH values were adjusted by adding (0.5) M HCl. The samples were left for (20hr) contact time (for reach maximum removal of ion). The results obtained (Figure .5) showed that the optimized pH for the removal of Fe (III) was at 6.3 as shown in Table 3.

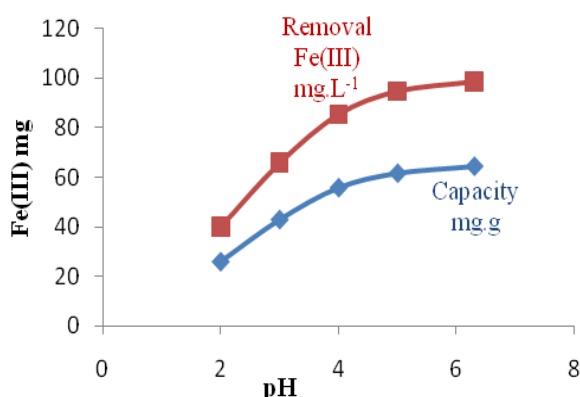


Figure 5- The relation between pH and removal Fe(III) ion and capacity using 100mg/L

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 Fe(III) cations will begin to precipitate from the solution and the removal percentage decrease. ions decrease, while near the basic condition the

Table 3- Effect of pH on the gel bead entrapment.

pH	Remained Fe(III) mg.L ⁻¹	Removal Fe(III) mg.L ⁻¹	Capacity mg/g
1	71.3	29.7	19.4
2	60	40	26.2
3	34.2	65.8	43.1
4	14.6	85.4	55.9
5	5.3	94.7	62
6.3	1.4	98.6	64.5

Adsorption Kinetic For Fe (III):

In order to examine the controlling mechanism of the adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equation were used to test the experimental data[23,24]:

$$\text{Log}(Q_e - Q_t) = \text{Log} Q_e - k_1 / 2.303 t \quad (2)$$

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \quad (3)$$

Where Q_e , Q_t are the amount of Fe (III) adsorbed into hydrogel (mg/g) at equilibrium and at time t , respectively, k_1 and k_2 are the rate constants of pseudo-first-order (hr^{-1}) and pseudo-second-order (g/mg hr) adsorption. The straight line plots of $\text{log}(Q_e - Q_t)$ against t , and t/Q_t against t Tables.4, and 5.

Table 4- The results of $\text{Log}(Q_e - Q_t)$ values.

Time hr	Concentration of Fe(III) ion mg.L ⁻¹			
	100	200	300	400
1	1.54	1.95	2.02	2.03
2	1.43	1.88	1.94	1.97
4	1.19	1.76	1.89	1.89
8	0.59	1.68	1.80	1.85
10	0.15	1.46	1.61	1.68
12	-0.07	1.15	1.30	1.38

Table 5- The results of t/Q_t values.

Time hr	Concentration of Fe (III) ion mg.L ⁻¹			
	100	200	300	400
1	0.033	0.030	0.025	0.021
2	0.052	0.043	0.034	0.032
4	0.081	0.062	0.058	0.052
8	0.131	0.109	0.096	0.093
10	0.157	0.109	0.095	0.092
12	0.187	0.112	0.095	0.091
24	0.369	0.198	0.164	0.154

were used to determine the rate constant k_1 and k_2 and correlation coefficient R values (Figure.6 and 7) These parameters were calculated and

summarized in Table .6, which was shown that the process follow a pseudo-first-order in concentration ranged between 100-400 mg.L^{-1} .

Table 6- Estimated adsorption kinetic parameters for Fe (III) adsorption.

Initial Conc.of [Fe(III)] (mg.L^{-1})	Pseudo – first – order				Pseudo – second – order			
	$Q_e \text{ exp}$ (mg/g)	$Q_e \text{ cal}$ (mg/g)	$K_1(\text{h}^{-1})$	R^2	$Q_e \text{ exp}$ (mg/g)	$Q_e \text{ cal}$ (mg/g)	$K_2(\text{g.mg}^{-1}.\text{h}^{-1})$	R^2
100	65	54.60	0.3482	0.9935	65	69.40	0.0110	0.9984
200	121.28	107.90	0.1446	0.9011	121.28	140.80	0.0015	0.9699
300	146.20	125.90	0.1268	0.9695	146.20	172.40	0.0015	0.9494
400	155.70	184.93	0.1122	0.9912	155.70	178.50	0.0015	0.9377

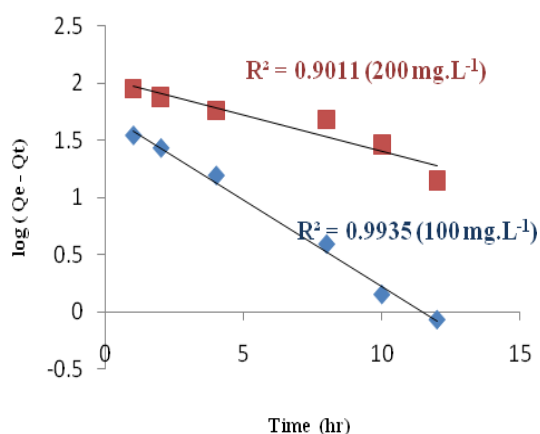


Figure 6- pseudo – first order kinetic plot

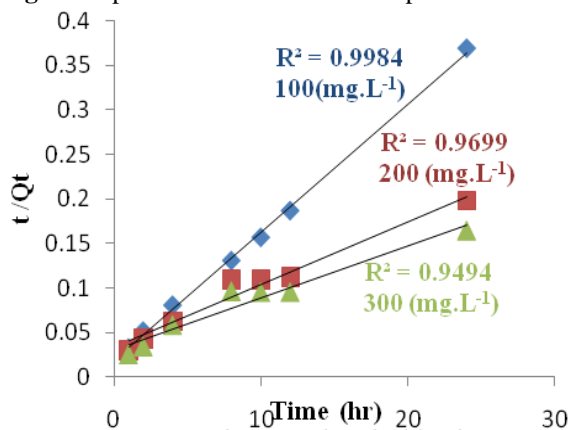


Figure 7- second order kinetic plot

Adsorption Isotherm:

To identify the mechanism of the adsorption process, the adsorption of Fe (III) in to PAA was determined as a function of equilibrium (residual) Fe (III) concentration C_e and the corresponding adsorption isotherm was plotted as shown in(Figure.8.) 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:[25]

$$C_e/Q_e = 1/K_L Q_{\max} + C_e/Q_{\max} \quad (4)$$

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 Fe (III) adsorption is followed Langmuir's isotherm. Langmuir parameters calculated from Eq. (4) are listed in Table 7.

Freundlich equation which is given in the following equation:[26]

$$\text{Log} Q_e = \text{Log} K_F + 1/n \text{Log} C_e \quad (5)$$

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 $\text{Log } C_e$ (Figure .9.). It is clear from Table 7, that the values of the freundlich exponents, n , were greater than one ($n > 1$) which represents a favorable adsorption condition[27]. Examination of the linear isotherm plots suggested that the Langmuir model yielded a much better fit than the freundlich model.

Table 7- Estimated adsorption isotherm parameters of Fe (III) ion.

Langmuir model			Freundlich model		
Q_{\max} (mg/g)	K_L (L/mg)	R^2	K_f (mg/g) (L/mg)	n	R^2
158.73	0.2165	0.9982	70.96	6.26	0.9723

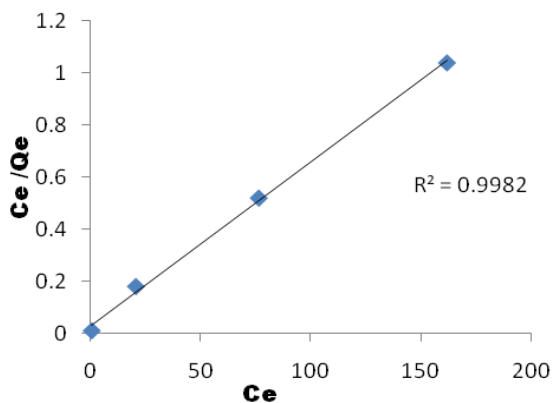


Figure 8- Langmuir plots for the adsorption of Fe(III)

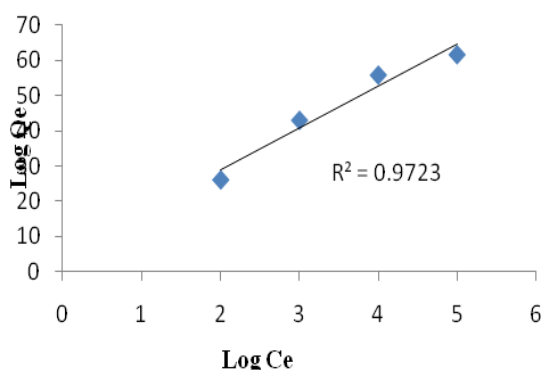


Figure 9- Freundlich plots for the adsorption of Fe(III)

Regeneration of beads:

For practical use, the metal ion adsorbed by a polymeric bead must be desorbed easily and the polymer can be reused again after repeated regeneration. Desorption of PAA polymer are investigated with batch experimental technique. The amount of adsorbed and desorbed metal ions was determined. This study was carried out by using hydrochloric acid of concentration of 0.5 M for the desorption of the metal ion from PAA polymer.

Table 8-Results of the recovery of the Fe (III) ion.

Time (hr)	Recoverd Fe(III) mg.L ⁻¹	Recovery %	Capacity mg.g
1	18	18.2	11.8
2	20.1	20.4	13.2
3	21.3	21.5	13.9
4	22.1	22.4	14.5
5	27.5	27.8	18.0
6	35.5	35.9	23.2
8	47.7	48.2	31.2
10	62.4	63.6	40.8

The results obtained (Table 8) indicated that the recovery% and the capacity were increased with the increase of the contact time with 0.5 M HCl solution. It has also been observed that a highest recovery% (63.6%) was occurred at 10 hr, as shown in Figure.10.

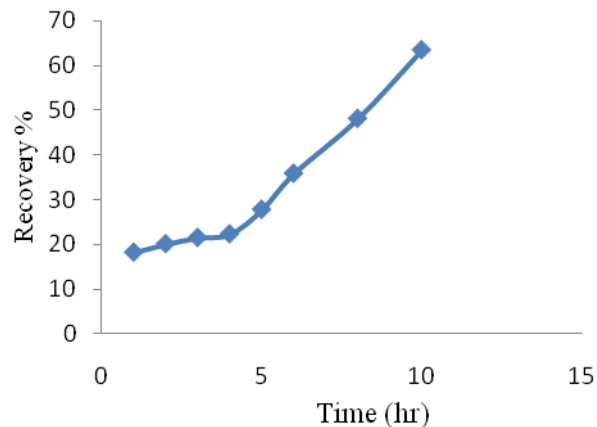


Figure 10- The relation between time and recovery of Fe(III)

It was observed that the percentage recovery of Fe (III) ion from the gel bead was low and needed long time, this may be due to the strong interaction between Fe (III) ion and internal bead structure due to the high value of the ratio (charge/radius) of the Fe (III) ion which lead to strong interaction.

4. Conclusions:

In this study, a hydrogel bead of polyacrylic acid (PAA) was used for adsorbed Fe(III) from aqueous solution . The results have indicated that the adsorption of Fe(III) was increased with increasing of time. The maximum capacity was reached at 24 hr with 155. 4 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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