Study of the sorption kinetic of Fe (III) by poly(Hydroxamic acid) chelating exchanger prepared from poly (Styrene-Co-Ethylacrylate)

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Abstract

The aim of this research is showing the preparation of poly(Styrene-Co-Ethyl acrylate) which obtained by a free radical initiation process for co-polymerization between Ethlyacrylate and styrene with a mixing ratio (1:1) using benzoyl peroxide as an initiator at (70°c) and (10%) ratio of conversion. Conversion of the ester group of the (CPS-EA) in to hydroxamic acid was carried out by treatment of (CPS-EA) with hydroxyl amine hydrochloride in alkaline medium at (pH=13) using sodium hydroxide. The poly hydroxamic acid was identified by (FT-IR) spectroscopy: Sorption capacity (q_e) of the metal ion (Fe^{3+}) was determined This study also shows the effect of initial (pH), temperature and time on the sorption capacity of (Fe^{3+}) by (PHA).The sorption capacity of (Fe^{3+}) on to (PHA) resin which decrease as temperature increases indicates that the sorption was exothermic process . The values of ($\Delta G°$) was negative, showing that the sorption of (Fe^{3+}) on to (PHA) resin is spontaneous .

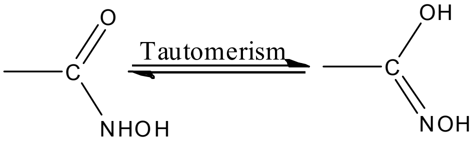
Key words: Poly Hydroxamic acid ,Hydroxamic acid.

الخلاصة

يتضمن البحث تحضير البوليمر المشترك (ستايرين – أثيل أكريلات) وذلك باستخدام ميكانيكية الجذور الحرة للبلمرة المشتركة بين الستايرين و أثيل اكريلات وبنسبة خلط مولية (1:1) وبواسطة بيروكسيد البنزويل كبادئ وبدرجة حرارية (70°c) وبنسبة تحول (10%). ثم تم تحويل البوليمر المشترك الناتج الى بولي حامض الهيدروكساميك وذلك بمفاعلة البوليمر المشترك (ستايرين– أثيل اكريليت) مع هيدروكسيل أمين هيدروكلورايد في وسط قاعدي قوي(pH 13) باستخدام هيدروكسيد الصوديوم مع اجراء تصعيد حراري بدرجة (70°c) ولمدة (18) ساعة . تم تشيخص المركب الناتج باستخدام طيف الأشعة تحت الحمراء (FT-IR). تم تعيين سعة الأحتجاز (sorption Capacity) لأيون الحديديك بوساطة بولي حامض الهدروكساميك . وكذلك تم دراسة تأثير الدالة الحامضية (pH) وتركيز(Fe^{3+}) ودرجة الحرارة على سعة الأحتجاز (q_e) بوساطة بولي حامض الهيدروكساميك .وقد تبين أن سعة الأحتجاز لأيون (Fe^{3+}) بوساطة بولي حامض الهيدروكساميك تقل بارتفاع درجة الحرارة , ويستدل من ذلك أن عملية الأحتجاز هي عملية باعثة للحرارة . ومن قيم ($\Delta G°$) السالبة , تين ان عملية الأحتجازلأيون (Fe^{3+}) بوساطة بولي حامض الهيدروكساميك هي عملية تلقائية .

Introduction

The hydroxamic acid group is well-known for its ability to form a stable chelates with various heavy metal ions, particularly iron (1,2).The hydroxamic acid is regarded as derivatives of the nitrogone- bound hydrogen in the hydroxylamine molecules, and has a general formula R-CO-NHOH (R=alkyl or aryl) having a tautomerism of keto and enol forms(3).



The stability is due in part to the geometry, where three hydroxamic acid units are spaced in such a way that can easily orientation a single iron (III) to satisfy the octahedral requirement of (3:1) iron (III) complex(4).A number of poly (hydroxamic acid) resins have been synthesized by various methods and for various purposes (5).Synthesized the resins from poly methacrylate and studied the sorption of Fe^{+3},Cu^{+2},Ag^{+}, Zn^{+2}, Hg^{+2},Al^{+3},Pb^{+2} and TiO^{+2} Petrie et al.(6). Poly (hydroxamic acid) resins synthesized from Amberlite IRC-50 Wan Yanus(7) studied the separation of $Fe^{+3}$and Al^{+3} from Ca^{+2} and Mg^{+2} using poly (hydroxamic acid) resins. Katoh and Coworkers (8) synthesized resin from acrylonitrile and divinyl benzene and studied the structure of resin and the recovery of UO_2^{2+} from sea water. The newer chelating ionexchange resin,the preparation of this chelating Poly(Hydroxamic acid) resin from Copoly(Acrylamid Divinyl Benzen) and acryl Hydroxamic acid and with divinyl Bezene grafted sag starch is anew starting polymer to obtanin this resine (9). The chelating resins containing Hydroxamic acid group can also play avital role in environmental monitoring of toxic trace metals . There is also apossibility of using poly (Hydroxamic acid)resin to extract rare from sea water (10). The poly (Hydroxamic acid) can be used to measure many elements quantitativdy in chromatography and for separation of various ions such as iron (III) Copper(II) Cobalt(II) and Lead(II) in biological and sensitive solutions (11) .

Experimental

Preparation of poly (styrene-Co-Ethyl acrylate):

The Co-poly (St-EA) was prepared by free radical solution polymerization.For the preparation of 18% styrene – cross linked polymer Ethylacrylate (13.27 gm) and styrene (7g). Benzoyl peroxide (200mg) was added, and the mixture was heated with stirring at (70°c) under N_2 atmosphere for 4hr. The polymer was collected by filtration, washed several times with water, ethanol, benzene and dried at 60°c(12,13) .

Preparation Of Poly (hydroxamic acid):

The preparation of chelating resin was carried out by the reaction between poly (St-Co-EA) with hydroxylamine. Hydroxylamine was prepared by dissolving (21g) of hydroxylaminehydrochloride($NH_2OH.HCl$) in (150 ml) aqueous ethanol solution (ethanol water 5:1). The HCl was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the mixture was adjusted to pH 13 by addition of 1M sodium hydroxide solution about (10g) of poly (S-Co-EA) was placed in a two-neck round bottom flask ,which was equipped with a mechanical stirrer and condenser. Then, 150 ml hydroxylamine solution (prepared earlier) was added into the flask. The reaction was carried out at 75°c for 2hr. The product was separated by filtration and washed several times with ethanolic solution (ethanol: water; 4:1) It was then treated with100ml of methanolic solution of 0.2m HCl for 5minutes. Finally, the fiber product was filtered and washed several times ethanolic solution and dried at 50°c to constant weight (13, 14, 15).

Studying characterization of poly(hydroxamic acid):

Determined of sorption capacity for Fe^{3+} by (PHA).

About (1g) of poly (St-Co-EAHA) mixing with (50ml) of (100ppm) Fe^{3+} solution. The mixture of Fe^{3+} solution and poly (St-Co-EAHA) was shaken for about (10)hours, after equilibration, the mixture was filtered was analyzed for Fe^{3+} concentration. The initial and the equilibrium concentrations of Fe^{3+} mg/g resin (PHA) were determined by using(UV.Vis) Spectrophotometer Model Bioteh Engineering Management Co.LTD.(UK) . Sorption capacity was calculated as mg of metal ion sorbed per gram sorbent by using the following equation: (16,17).

Sorption capacity ,$q= (C_o-_e)V/M$…..(1)

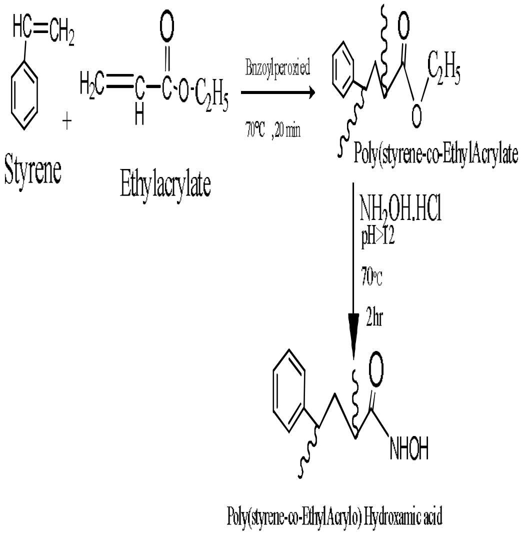
Where $q(mg.g^{-1})$ is the amount of metal ion sorbed; C_o and C_e are initial and equilibrium concentration of the metal ion in solution (mg/L) respectively; V(L) is the solution volume and M (g) is weight of the sorbent poly(St-Co-EAHA).

The sorption was obtained by shaking about 1g of poly(St-Co-EAHA) in 50ml of Fe^{3+} solution of different concentrations (10,20,30,40 ,50,60,70,80,90,100ppm) for 5h at pH 6 and at 25°c . The initial and the equilibrium of Fe^{3+} concentration were measured and sorption capacity was calculated as above. The effect of pH on the Fe^{3+} sorption was studied by equilibrating 1g of poly (hydroxamic acid) in 50ml of 100ppm Fe^{3+}solution at (pH 1-8) by using sodium acetate buffer solution(18). The kinetic study was carried out by shaking about 1g of poly(St-Co-EAHA) sorbent into 50ml of (100ppm) of Fe^{3+} at various time periods ,(10 – 300 min) at 25 °c. The effect of temperature on the Fe^{3+} sorption was studied by equilibrating 1g of poly (hydroxamic acid) in 50ml of 100ppm Fe^{3} solutions at (10,25, 50,70 °c).

Results and Discussion

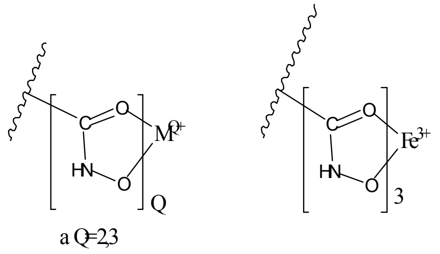
Characterization of poly (hydroxamic acid).

The poly(styrene–Co-Ethylacrylate) which obtained by a free radical initiating process for Co-polymerization between styrene and ethylacrylare with a mixing ratio(1:1), using benzoyl peroxide as an initiator at (70°c) under N_2 atmosphere by ratio of conversion (10%). The poly (St-Co-EA) was identified by (FTIR) spectroscopy. (FTIR) spectra Fig(1) of poly (St-Co-EA) graphed shows a new absorption bonds at ($1714cm^{-1}$) of C=O ($2954\ cm^{-1}$) of (C-H),and ($1389\ cm^{-1}$) of (C-O). Poly (hydroxamic acid) prepared via a conversion of the ester group of the poly (St-Co-EA) into hydroxamic acid was carried out by treatment of poly (St-Co-EA) with hydroxyl amine hydrochloride in alkaline medium at (pH13) using sodium hydroxide. Poly (hydroxamic acid) was synthesized by the general techniques previously employed(16).



The poly (hydroxamic acid) was identified by (FTIR) spectroscopy. The infrared spectrum Fig(2) of (PHA) resin showed the characteristic absorption bands of hydroxamic (O-H), amide (N-H),carbonyl (C=O) and (N-O) groups at (3200,3444, 1670 and 930 cm^{-1}).

This means that the formation of chelating complex weakens the double bonding character of carbonyl group in the hydroxamic acid owing to the Co-ordinate bond between oxygen atom of carbonyl groups and metal ions. The weakening of double bonding is more pronounced in chelating with Fe^{3+} complex in (1:3) because Fe^{3+} is a hard acid which Co-ordinates strongly to ligands made up of small nonpolarizable, Highly negative oxygen donor atoms (hard bases)(14,17). The coordinate between metal ions and poly(hydroxamic acid) now in this structure(20,21,27).



Sorption of Fe^{3+} by poly (St-Co-EA) hydraxmic acid:

Table (1) shows The initial and the equilibrium metalion concentrations (C_o,C_e) and sorption capacity(q) of Fe^{3+} after treatment with poly (St-Co-EA) hydraxmic acid were determined using standard carve wich is shown in fig(3). The values of C_o,C_e and q were 100 mg/liter ,68 mg/ liter and 1600 mg/g respectively (22).

Effect of pH on Fe^{3+} Sorption :

Figure (4) shows the effect of pH on sorption capacity of the Fe^{3+} by poly (St-Co-EA) Hdroxamic acid. The sorption capacity was low at pH(1.0) and increased as the pH increased to a maximum at about pH=(6-7) .But sorption capacity will decreased when pH was increase further. The findings indicates that capacity of sorption decreased in alkaline medium . The low sorption capacity of Fe^{3+} by poly(St-co-EA) Hdroxamic acid at pH 1.0 could be due the fact there are more protons at lower pH availabel to protonate ,the active groups of the poly(St-co-EA) Hdroxamic acid surface and compete with Iron ions in the solution . At higher pH values , a greater number of deprotonated Hydroxamic acid fuctionl groups resulted in greater Fe^{3+} ion sorption(23,24) .

Effect of Initial Concentration on Fe^{3+} Sorption:

Fig (5) shows The effect of initial Cocentration on the sorption Fe3+ by poly (St-Co-EA) hydroxamic acid condition 100mg/ liter.It can be seen that q_e increases initially with an increase of C_e until equilibrium is reached , after q_e remains constant. We can conclude that the sorption capacity does not depend on Fe^{3+} concentration , but on the quantity of Poly

Hdroxamic acid , that is , Poly Hdroxamic acid ,which bound with Fe^{3+} ion by two oxygen atoms of hydroxamic acid group(25).

Effect of Temperature on Fe^{3+} sorption:

Fig(6) shows the effect contact temperature on sorption capacity of Fe^{3+} by poly(St-Co-EA) hydroxamic acid. The sorption capacity was increased at low temperature and decreased when temperature was increased. The sorption capacity of Fe^{3+} with poly(St-Co-EA) hydroxamic acid increased to a maximum at about temperature 10°c.

Sorption Kinetics :

The kinetics of sorption of Fe^{3+} by poly (St-Co-EA) hydroxamic acid resin was studied at various temperatures . Table (3) shows the effect of contact time on sorption of 100mg/liter Fe^{3+} at 25°c ,50◦c and 70◦c. The sorption is rapid during initial stage and decreases when approaching equilibrium . The pseudo second-order kinetic models (Ho and Mckay 1998) rate constant ,K_2 for the sorption was detrmined using the following equation can be be written as(22,23,26):

$$t/q_t = 1/k_2\, qe^2 + t/qe \quad ....(2)$$

where $k_2(g.mg^{-1}.min^{-1})$ is the second-order rate constant, and q_t =$(mg\ g^{-1})$ and q_e=$(mg.g^{-1})$ are the amounts of sorption at time (min) and equilibrium, respectively. A polt of t/q_t versus time (min) gave a straight line in fig(7) and the values of q_e and k_2 were determined from the slope and intercept of the plot, respectively.The values of k_2 and q_e were found to be ($6.75*10^{-6}$, $8.8*10^{-6}$,$1,47*10^{-5}$ (g/mg.min)) , q_e=(2469 ,1874 , 1316.63) mg/g, at (25, 50 ,75) °c, respectively.

Thermodyamics of the sorption process :

Activation energy:

The activation energy is related to be the rate constant by the Arrhenius equation as shown below (18,22).

$$\ln k_2 = \ln A - E_a/RT \quad ....(3)$$

Where A is the Arrhenius factor and E_a the activation energy of sorption $(kJ.mol^{-1})$. From the plot $\ln k_2$ as a function of (1/T) showing in fig (8) the value of activation energy was determined from the slope of straight line and found to be 9.9768 $(kJ.mol^{-1})$. It is known that when activation energy is low the rate is controlled by intra-particle diffusion mechanism and hence it can be concluded the process is governed by interaction of physical nature.

Thermodyamic Parameters:

The amount of Fe^{3+} sorption at equilibrium was measured at 293, 323, and 348 °K. The equilibrium partition constant K_d is calculated as follows(17,26):

$$K_d = q_e/C_e \quad ......(4)$$

The values of K_d where (5.303 ,3.571 and 2.439 ml $.g^{-1}$) at 25,50 and 70 °c) respectively for sorption of Fe^{3+} by poly(St-Co-EA) hydroxamic acid. The values of K_d at initial concentration of 100 mg/liter decreased as temperature increased from (25 to 75 °c),indicating that the sorption is an exothermic process .The relationship between K_d and T is given by the vant- Hoff equation (27, 28):

$$\ln K_d = \Delta S^o/R - \Delta H^o/RT \quad ....(5)$$

Where ΔS^o= standard entropy, ΔH^o = standard enthalpy, T= absolute temperature (K), and R= gas constant. The values of ΔH^o and ΔS^o were calculated from the slopes and intercepts of liner regression of plot of $\ln K_d$ versus 1/T fig (8) respectively . The standard Gibbs free energy ΔG^o ,value was calculated from the equation(22):

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad ....(6)$$

The values of ΔH^o and ΔS^o were(-6.6512 kJ. $mole^{-1}$) and (-32.279 $J.mole.K^{-1}$) respectively. Through the negative value of the ΔH^o confimed that the sorption reaction of Fe^{3+} by poly(St-co-EA) Hydroxamic acid was exothermic. The poly (St-co- EA) Hydroxamic acid was more irregular and less randomized . The values of standard Gibbs free energy ΔG^o where(0.2859 , 0.867917and 1.44984 $kj.mole^{-1}$) at 25,50,75 °c)respectively , The values of ΔG^o at initial concentration of 100 mg/liter decreased as temperature increased from (25 to 75 °c)showing that the sorption was spontaneous at all temperatures .

Conclusions

1-The polymers of Hydroxamic acid can be prepared from polymers containe Ester such as poly –acrylate

2-Characterized polymers of hydroxamic acid containg of Hydroxamic acids groups are the selective chelating compounds with most ions of metallic elements such as Iron,Copper ,Lead …ΔG^o …….

3-Increase the capacity of sorption of Fe^{3+} on poly (St-co-EA) Hydroxamic acid when pH=(6-7) , and less than high temperature.
4- Sorption of Fe^{3+} on poly (St-co-EMA) Hydroxamic acid followed the second order kinetics ,and the process of sorption of the exothermic, and decline negativity of enthalpy.
5-The value of free energy(ΔG^o) for the sorption of Fe^{3+}) on poly (St-co-EA) Hydroxamic acid, showing that the sorption process is spontaneous ,

Table (1): The values of C_o ,C_e and Sorption Capacity (q) of Fe^{3+} by poly (St-Co-EA) Hydroxamic acid condition: Temperature 25c°, concentration of Fe^{3+} 100ppm and time(10 h)

Metal ion	C_o ppm	C_e ppm	C_o mg/liter $*10^2$	C_e mg/liter $*10^2$	Q_e (mg/g) $*10^2$
Fe^{3+}	100	88	1	0.88	3

Table (2): Effect time and Temperature on the sorption kinetics of Fe^{3+} by poly (St-Co-EA) Hydroxamic acid condition: pH=7, concentration 100 mg/50ml.

T(°K)	q_t mg/g $*10^2$ of Fe^{3+} by PHA at time (min)				
	60(min)	120(min)	180(min)	240(min)	300(min)
298	1.65	1.98	2.43	2.79	3
323	1.23	1.56	1.74	1.93	2,25
348	0.84	1.24	1.57	1.86	2.13

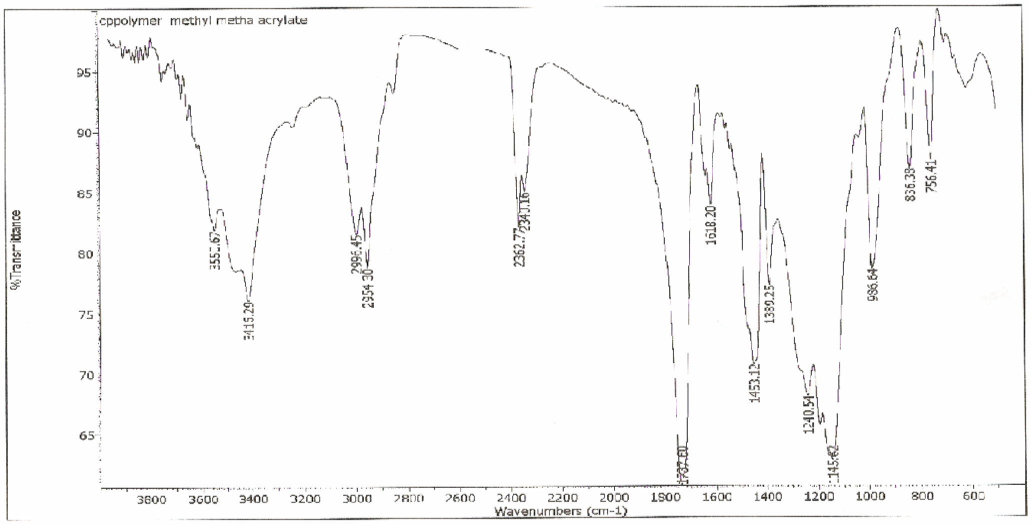


Fig.(1): FT-IR spectra of Pol (St –co-EA) .

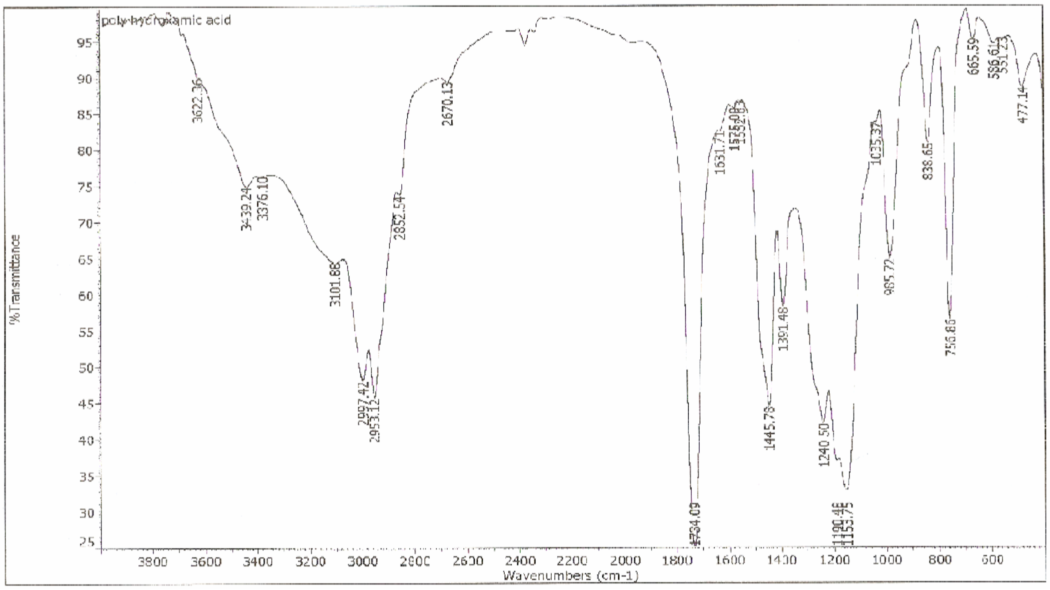


Fig.(2): FT-IR spectra of Pol (St –co-EA) Hydroxamic acid .

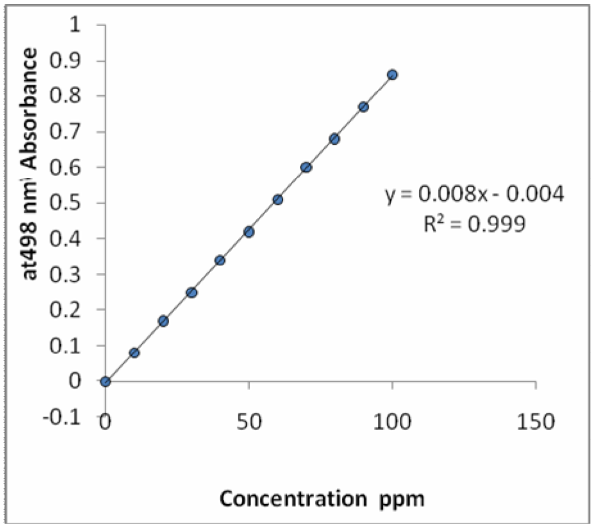


Fig (3):The standard carve for determination equilibriumco Cocentration and capacity sorption for Fe^{32+} by poly (St-Co-EA) hydroxamic acid condition: 0.1M KCN=5 cm^3,Total volume=25cm^3 and Wave Length =498 nm

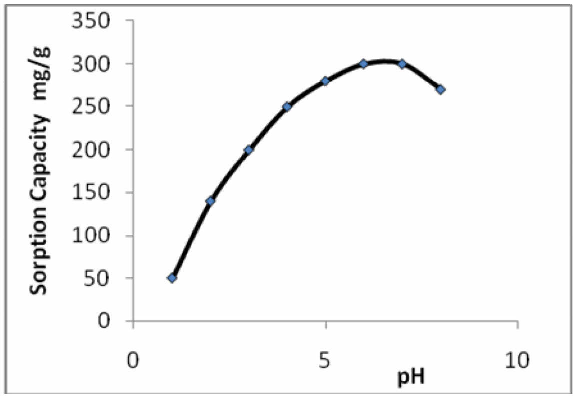


Fig (4): The effect of initial pH on the sorption Fe^{3+} by poly (St-Co-EA) hydroxamic acid condition 500mg/l; contact time 15h; temperature 25°c.

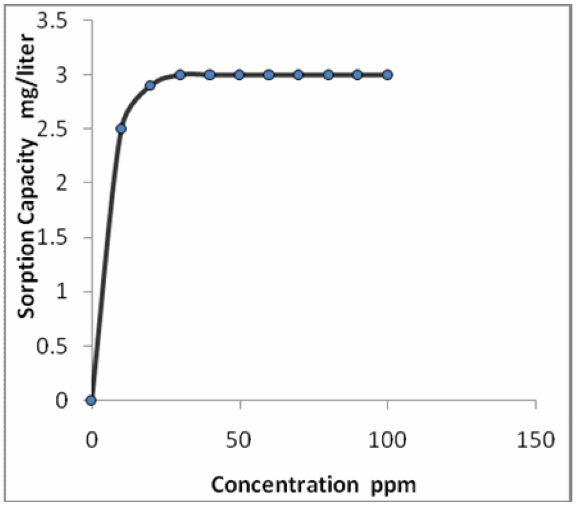


Fig (5): The effect of initial Cocentration on the sorptionFe^{3+} by poly (St-Co-EA) hydroxamic acid condition 100mg/ l: contact time 5h; temperature 25°c.

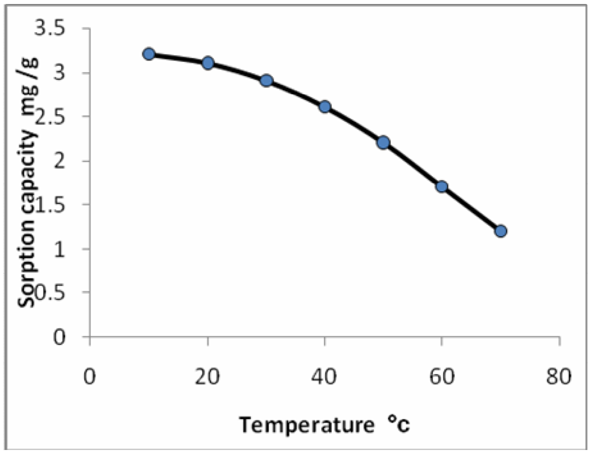
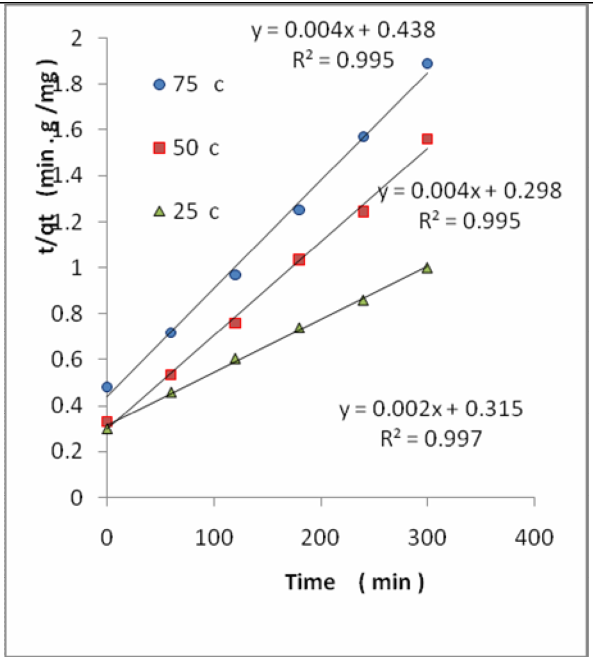


Fig (6): The effect of initial temperature on the sorption capacities of Fe^{3+} by poly (St-Co-EA) hydroxamic acid condition: Conc. 100mg/Liter,



Fig(7): Second order kinetic plots for sorption of Fe^{3+} by poly (St-Co-EA) hydroxamic acid resin at various temperatures .

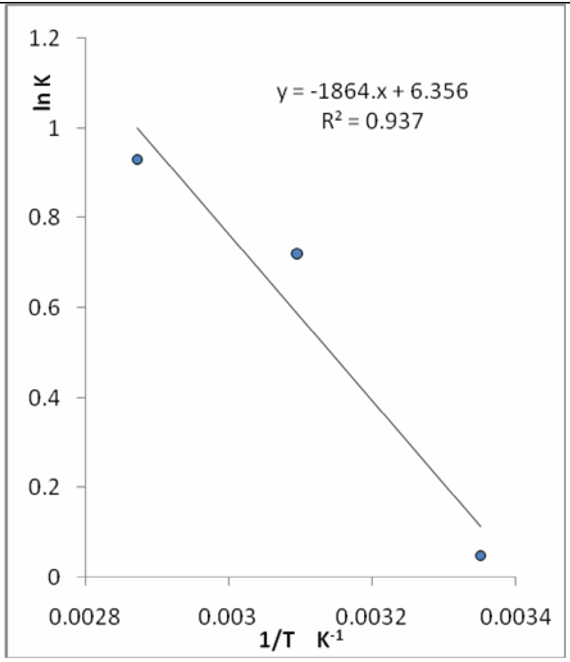


Fig (8): Arrhenius plot for second order react constant, k_2 contact time 5h,

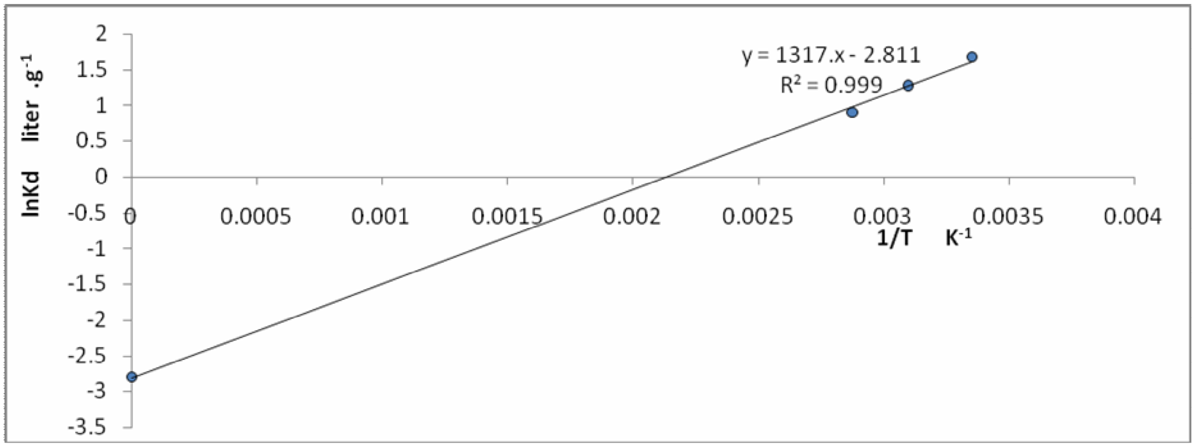


Figure (9): Vant Hoff plot for the sorption of Fe^{3+} by poly (St-Co-EA) hydroxamic acid resin at various temperatures.

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