Study of the Sorption Kinetics of Fe (III) by Polyhydroxamic acid Chelating Exchanger Prepared from Polystyrene-Co-Methyl methacrylate

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ABSTRACT

The aim of this research is showing the preparation of polystyrene-co-methyl methacrylate which obtained by a free radical initiation process by co-polymerization of methyl methacrylate and styrene using benzoyl peroxide as an initiator at 70°C and 10% ratio of conversion. Conversion of the ester group of the PSCMMA into hydroxamic acid was carried out by treatment of PSCMMA with hydroxyl amine hydrochloride in alkaline medium at (pH=13) using sodium hydroxide. The polyhydroxamic 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). Arrhenius and vant Hoff equation models were used to describe the equilibrium sorption isotherms for using different concentrations of (Fe^{3+}) at pH=4 and at 25 $^\circ$C by polyhydroxamic acid, PHA.

Keywords: Sorption Kinetics of Fe(III), Polyhydroxamic acid, Chelating exchanger.

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INTRODUCTION

The hydroxamic acid group is well-known for its ability to form a stable chelate with various heavy metal ions, particularly iron [1-4].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[5].
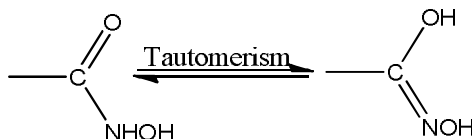
The stability is due in part to the geometry, where three hydroxamic acid units are spaced in such a way that can easily orient themselves about a single iron atom to satisfy the octahedral requirement of (3:1) iron (III) complex[6].A number of poly hydroxamic acid resins have been synthesized by various methods for various purposes [7].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}[8]. Polyhydroxamic acid resins synthesized from Amberlite IRC-50 [9] studied the separation of Fe^{+3} and Al^{+3} from Ca^{+2} and Mg^{+2} using polyhydroxamic acid resins. Katoh et.al., [10] synthesized resin from acrylonitrile and divinyl benzene and studied the structure of resin and the recovery of uranium from sea water. This paper describes two different methods for preparation of hydroxamic acid resins from copolymer acryl amide divinyl benzene and acryl hydroxamic acid with divinyl benzene (by a one –step reaction). The hydroxamic acid capacity of the products are compared .The ion exchange behavior of this resin towards iron (III) ,copper (II), cobalt(II) and lead (II) ions and the effect of the pH of the metal solutions on the cation exchange capacities of the resin [11-13].

MATERIALS AND METHODS

Preparation of polystyrene-co-methyl methacrylate(PSCMMA) : The polystyrene-co-methyl methacrylate was prepared by free radical solution polymerization. For the preparation of 18% styrene – cross linked polymer by mixing 13.27 gm of methyl methacrylate and 7 gm of styrene . 200mg of benzoyl peroxide 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
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Preparation of polyhydroxamic acid (PHA): The preparation of chelating resin was carried out by the reaction between polystyrene-co-methyl methacrylate with hydroxylamine. 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 10gm of polystyrene-co-methyl methacrylate was placed in a two-neck round bottom flask which was equipped with a mechanical stirrer and condenser. Then 150 ml hydroxylamine solution 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 with ethanolic solution and dried at 50°C to constant weight [13-15].

RESULTS AND DISCUSSION

Characterization of polyhydroxamic acid, PHA
Determination of the sorption capacity for Fe^{3+} by PHA : About 1gm of polystyrene-co-methyl methacrylate hydroxamic acid (PSCMMAHA) mixing with 50ml of 100ppm Fe^{3+} solution. The mixture of Fe^{3+} solution and PSCMMAHA was shaken for about 10 hours, after equilibration, the fiber was filtered and analyzed for Fe^{3+} concentration. The initial and the equilibrium metal ion concentrations were determined by using UV/Vis Spectrophotometer Model Biotech 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 $,q= (C_o-C_e) V/ M$ …..(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 $(mg L^{-1})$ respectively; V(L) is the solution volume and M (g) is weight of the PSCMMAHA sorbent. The sorption was obtained by shaking about 1g of PSCMMAHA in 50ml of Fe^{3+} solution of different concentrations (10,20,30,40,5 0,60,70,80,90,100ppm) for 5h at pH 6 and at 25°C .

The initial and the equilibrium concentration of Fe^{+3}were measured and sorption capacity was calculated as above. The effect of pH on the Fe^{3+} sorption was studied by equilibrating 1g of PHA in 50ml of 100ppm Fe^{3+}solution at   pH1,pH2,pH3,pH4,PH5,pH6,pH7,pH8   by using sodium acetate buffer solution[18]. The kinetic study was carried out by shaking about 1g of PSCMMAHA sorbent into 50ml of 100ppm of Fe^{3+} at various time periods 10,20, 30,60,120,180,240 and 300min at 25 °C.

The effect of temperature on the Fe^{3+} sorption was studied by equilibrating 1g of PHA in 50ml of 100ppm Fe^{3} solutions at (10,25, 50,70 °C).

Spectral Studies : The PSCMMA   was identified by FT -IR spectroscopy. FT-IR spectra Fig.1 of PSCMMA graph shows a new absorption bonds at 1714cm^{-1} of C=O, 2954 cm^{-1} of C-H and 1389 cm^{-1} of C-O.
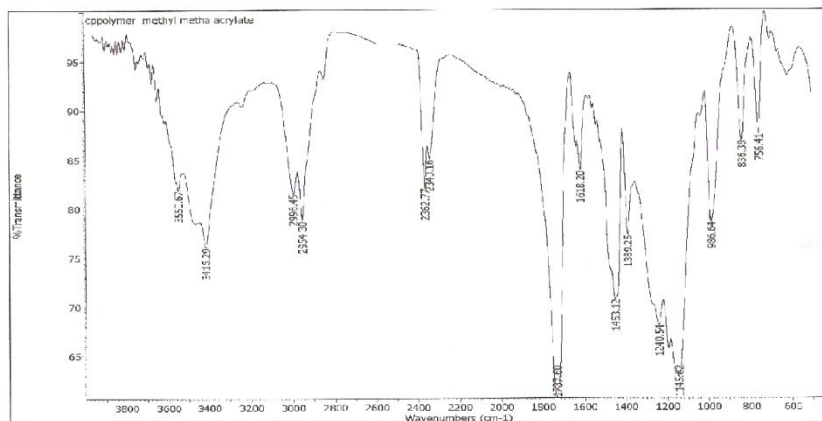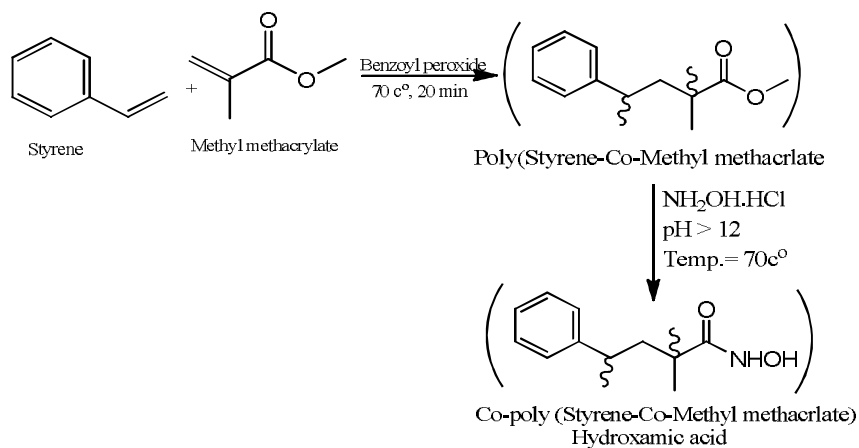

Figure 1. FT-IR spectra of Poly (St –co-MMA) **.**

The PHA 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} respectively.
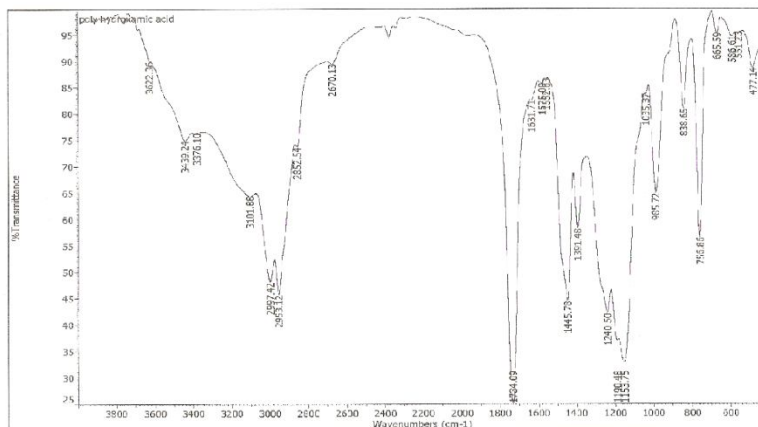
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Figure 2. FT-IR spectra of Poly (St –co-MMA) hydroxamic acid **.**

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 bond 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 non polarizable, highly negative oxygen donor atoms (hard bases)[14,17]. The coordination between metal ions and PHA shown in the below structure[20,21,27].

a Q= 2,3
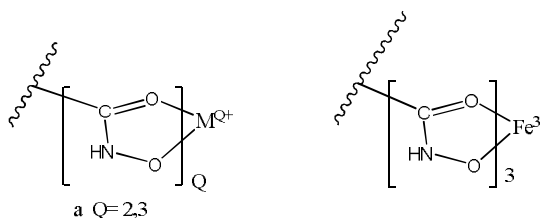
Sorption of Fe^{3+} by polystyrene-co-methyl methacrylate hydroxamic acid: Table .1 shows the initial and the equilibrium metal ion concentrations (C_o, C_e) and sorption capacity(q) of Fe^{3+} after treatment with poly (St-Co-MMEA) hydroxamic acid were determined using standard curve which is shown in Fig.3. The values of C_o, C_e and q were 100 mg L^{-1} ,68 mg L^{-1} and 1600 mg gm^{-1} respectively [22].
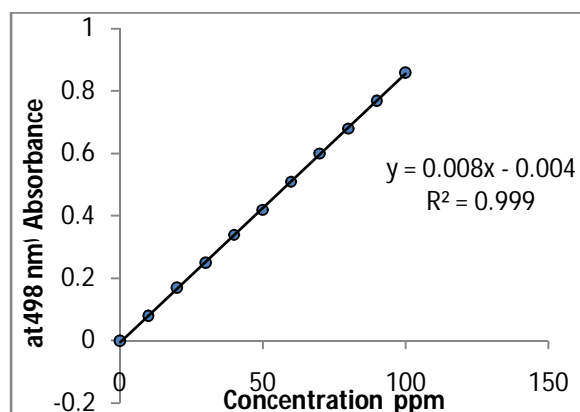

Fig 3. The standard carve for determination equilibrium concentration and sorption capacity for Fe^{32+} by poly (St-Co-MMA) hydroxamic acid

Table 1. The values of C_o, C_e and Sorption Capacity (q) of Fe^{3+} by poly (St-Co-MMA) hydroxamic acid condition: Temperature 25^oC, 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

Effect of Initial Concentration on Fe^{3+} Sorption: Fig .4 shows The effect of initial concentration on the sorption Fe3+ by poly (St-Co-MMA) hydroxamic acid condition 100mg L^{-1}.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 hydroxamic acid , that is , poly hydroxamic acid ,which bound with Fe^{3+} ion by two oxygen atoms of hydroxamic acid group[23].
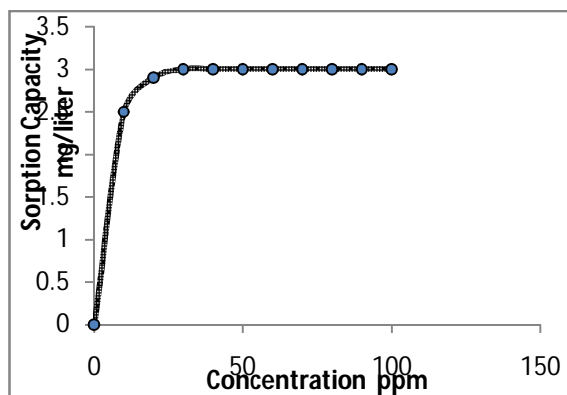
Fig 4. The effect of initial concentration on the sorptionFe^{3+} by poly (St-Co-MMA) hydroxamic acid condition 100mg L^{-1}: contact time 5h; temperature 25°c.

Effect of pH on Fe^{3+} Sorption : Figure .5 shows the effect of pH on sorption capacity of the Fe^{3+} by poly (St-Co-MMA) hydroxamic 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-MMA) hydroxamic acid at pH 1.0 could be due the fact there are more protons at lower pH available to protonate ,the active groups of the poly(St-co-MMA) hydroxamic acid surface and compete with Iron ions in the solution . At higher pH values , a greater number of deprotonated hydroxamic acid functional groups resulted in greater Fe^{3+} ion sorption[24,25]
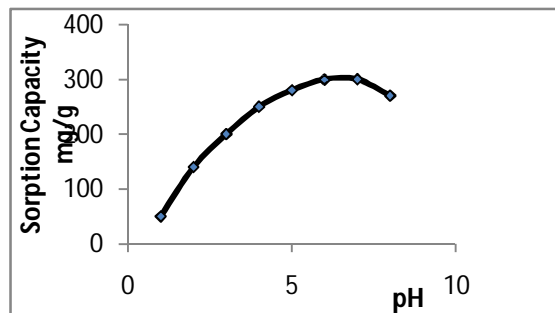
Fig 5. The effect of initial pH on the sorption Fe^{3+} by poly (St-Co-MMA) hydroxamic acid condition 500mg L^{-1}; contact time 15h; temperature 25°C.

Effect of Temperature on Fe^{3+} sorption: Fig.6 shows the effect contact temperature on sorption capacity of Fe^{3+} by poly(St-Co-MMA) 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-MMA) hydroxamic acid increased to a maximum at about temperature 10°C.
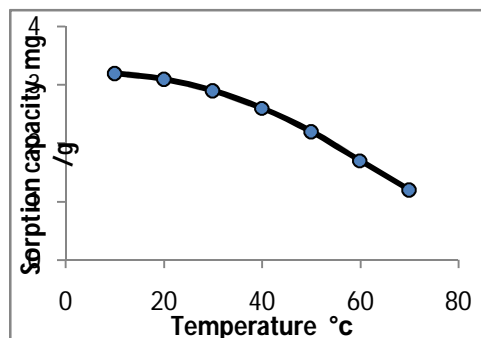

Fig 6. The effect of initial temperature on the sorption capacities of Fe^{3+} by poly (St-Co-MMA) hydroxamic acid condition: Conc. 100mg L^{-1}

Sorption Kinetics : The kinetics of sorption of Fe^{3+} by poly (St-Co-MMA) 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 determined using the following equation can be written as[22,23,26]:

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

where k_2 in $g.mg^{-1}.min^{-1}$ 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 plot 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 .$mg^{-1}.min^{-1}$, $q_e=2469$,1874 , 1316.63 $mg.g^{-1}$, at 25, 50 ,75 °C, respectively Table 2.
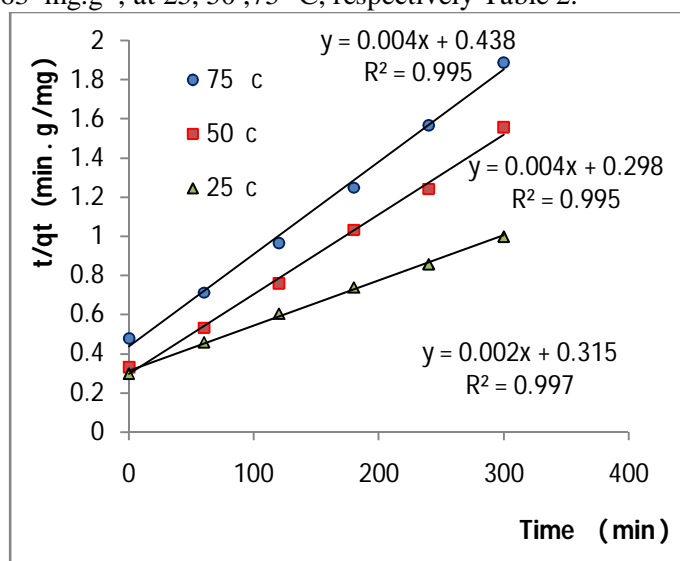

Fig 7. Second order kinetic plots for sorption of Fe^{3+} by poly (St-Co-MMA) hydroxamic acid resin at various temperatures .

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

T($^{\circ}$K)	q_t mg/g *10^2 of Fe^{3+} by PHA at time (min)				
	60	120	180	240	300
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

Thermodynamics of the sorption :

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 in 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. Table. 3 shows the Values of thermodynamic constant for the sorption kinetics of Fe^{3+} by pol-y (St-Co-MMA) hydroxamic acid where is given by Arrhenius equation .The standard enthalpy state ($\Delta H°$) obtained from the following equation:

$$\Delta H° = E_a - RT \quad ……………..(4)$$

The standard Gibbs free energy (ΔG) Was calculated from the equation:

$$\Delta G° = - RT \ln K_2 + RT \ln (KT/h) \quad …………….(5)$$

where :K and h are Boltzmann and Planks constant which is equal to 1.38×10^{-23} J.K^{-1} and $6,62\times 10^{-34}$ J.S^{-1} respectively .The standard entropy ($\Delta S°$) was calculated from the following relation :

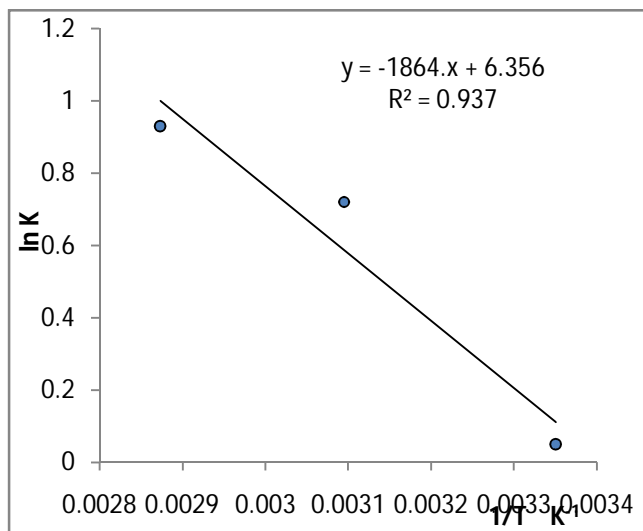$$\Delta S° =(\Delta H° - \Delta G°) / T \quad ……………..(6)$$

Fig 8. Arrhenius plot for second order react constant, k_2 contact time 5h,

Table 3. Values of thermodynamic constant for the sorption kinetics of Fe^{3+} by pol-y (St-Co-MMA) Hydroxamic acid where is given by Arrhenius equation .

T($^{\circ}$K)	K_2 g.mg^{-1}.min^{-}	Ea Kj.mol^{-1}	ΔH Kj.mol^{-1}	ΔS Kj.mol^{-1}K^{-}	ΔG Kj.mol^{-1}
298	0.00001741	9.9768	7.2913	-0.3122	100.132
323	0.000031	9.9768	4.8138	-0.3169	107.166
348	0.0000428	9.9768	4.605	-0.3167	114.821

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Thermodynamic 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]:

$K_d= q_e/C_e$ ……(7)

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-MMA) hydroxamic acid. The values of K_d at initial concentration of 100 mg L^{-1} 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]:

$lnK_d=\Delta S^o/ R + \Delta H^o/ RT$ ….(8)

 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 lnK_d versus 1/T Fig .9 respectively . The standard Gibbs free energy ΔG^o ,value was calculated from the equation[22]:

$\Delta G^o = \Delta H^o - T \Delta S^o$ ….(9)

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 confirmed that the sorption reaction of Fe^{3+} by poly(St-Co-MMA) hydroxamic acid was exothermic. The poly(St-Co- MMA) 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 L^{-1} decreased as temperature increased from (25 to 75 °C)showing that the sorption was spontaneous at all temperatures .
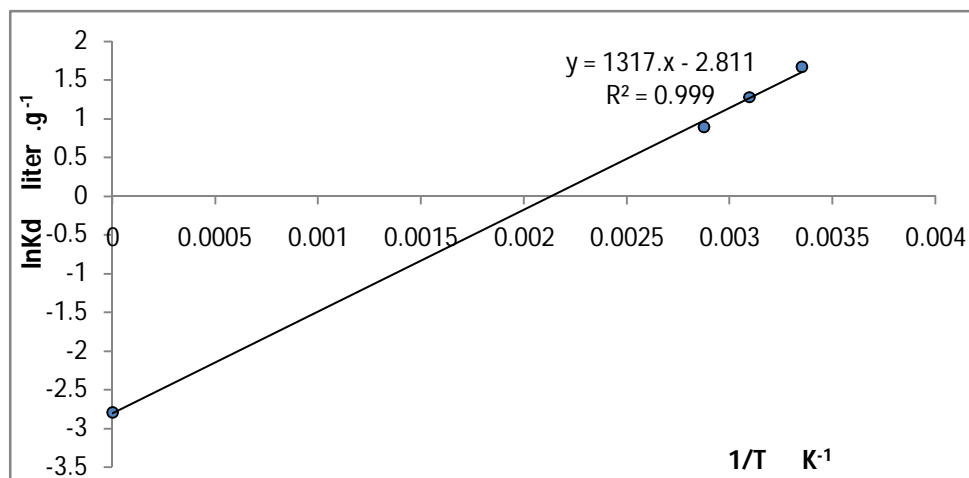

Figure 9 . vant Hoff plot for the sorption of Fe^{3+} by poly (St-Co-MMA) hydroxamic acid resin at various temperatures.

APPLICATION.

This study is applicable for the preparation of polymer polyhydroxamic acid its activity as chelate scavenger and sorption capacity for metal ions especially Fe (III).
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CONCLUSIONS

The polymers of Hydroxamic acid can be prepared from polymers contain Ester such as poly –acrylate. Characterized polymers of hydroxamic acid contain hydroxamic acid groups are the selective chelating compounds with most ions of metallic elements such as iron, copper ,lead …ΔG^o …….

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Increase the capacity of sorption of Fe^{3+} on poly (St-co-MMA) hydroxamic acid   when pH=(6-7) , and less than high temperature

Sorption of Fe^{3+} on poly (St-co-MMA) hydroxamic acid followed the second order kinetics ,and the process of sorption of the exothermic and decline negative enthalpy.

The value of free energy(ΔG^o) for the sorption of Fe^{3+}) on poly (St-co-MMA) hydroxamic acid, showing that the sorption process is spontaneous.

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