STUDY OF THE KINETICS OF SEQUESTRATION OF SOME HEAVY METAL BY POLY HYDROXAMIC ACID AS A CHELATING COMPOUND.

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ABSTRACT

The goal of this study is to illustrate how to make poly Styrene - Co- Methyl metha acrylate using a free radical initiation procedure for Co - polymerzation between styrene and methyl metha acrylate with a mixing ratio of (1:1) using benzoyl peroxide as an initiator at (70%) and (10%) diversion ratios. The ester group of a molecule is converted the poly (Styrene- Co- Methyl metha acrylate) in to Hydroxamic acid was carried out by treatment of poly (Styrene- Co- Methyl metha acrylate) together Using sodium hydroxide and hydroxyl amine hydrochloride in an alkaline media with a pH of 13 with a thermal sublimation of (70 $\overset{\circ}{c}$) for a period of (83) hours . FT-IR spectroscopy was used to identify the poly Hydroxamic acid. This study also illustrates the effect of initial pH on the sequestration capacity (Q_e) of the metal ion Mn^{2+}, time and temperature on the sequestration capacity of { Mn^{2+} } by poly Hydroxamic acid . the sequestration capacity of (Mn^{2+}) on to poly Hydroxamic acid resin which decrease as temperature increases , the sequestration capacity increases with increasing time, and decreases with the increase in acid function . Indicates that the process of sequestration was exothermic. The values of (ΔG°) was negative , showing that the sequestration of (Mn^{2+}) on to poly Hydroxamic acid resin is spontanous.

Key words: Hydroxamic acid , Poly hydroxmic acid , Adsorption , Heavy metals, the sequestration capacity **.**

I.   INTRODUCTION

The Hydroxamic acids and the substituted nitrogen derivatives are organic compounds that are used as dichotomies. The following figure shows the general formula for hydroxamic acid .
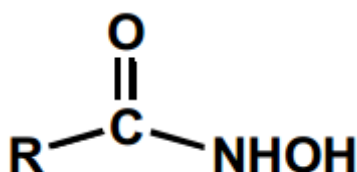

Despite the important properties of poly (hydroxamic acid) , it is considered one of the least compounds whose properties have been described, which make it difficult to determine the correct composition of hydroxamic acid as it has three similar shapes in chemical compositions, as shown in the following structural formulas [1].
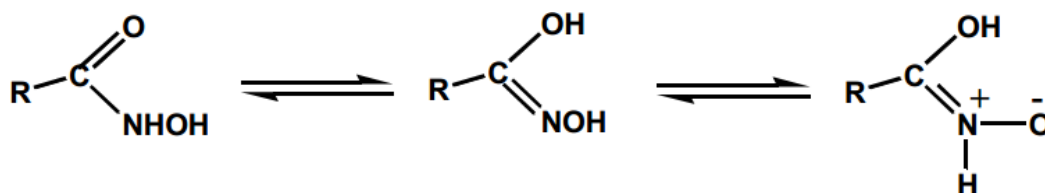
Hydroxamic acids have long been known for their propensity to chelate heavy metals. It has been shown to be effective chelating ligands with the ions such as Fe^{3+}, Mo^{6+}, V^{5+}, Ti^{+4}, Hg^{2+}, UO^{2+} , and Cu^{2+} [2].

They've been used in a variety of analytical applications . For instance , uranium extraction and purification. , cobalt from copper and nickel , copper from lead , separations of iron from copper, extraction and separation of gold and silver , nickel , and cobalt , and uranium from neodymium [3] . The RC(=O)NHOH groups in hydroxamic acid and its derivatives have a strong propensity to bind metal ions. One metal ion can commonly chelate two or three hydroxamate molecules, forming five-membered ring complexes (according to the valence of the metal sample) . Notably, a large proportion of hydroxamic acids has been used as flotation collectors [4] , chelating resins[5, 6], analytical reagents [7,29-33],and drugs [8].

Hydroxamic acid is a derivative of the nitrogen-bound hydrogen in hydroxyl amine molecules, tautomer versions of keto and enol with the generic formula R-CO-NHOH (R=alkyl or aryl) and the generic formula R-CO-NHOH (R=alkyl or aryl) [9] .

Keto form   enol form
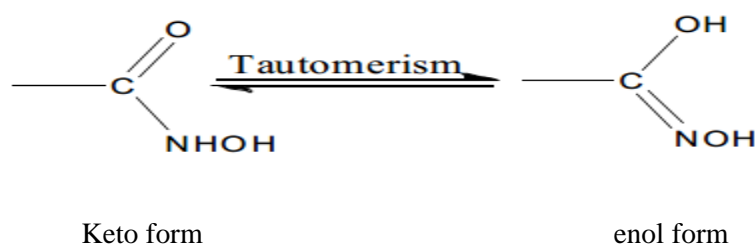
Engineering plays a role in the stability , where three units spacing of hydroxamic acid can easily guide the way iron one (III) to meet the requirements of the eight surfaces (3: 1) complex iron (III) [10,11] . Poly (hydroxamic acid) resins have been produced in a variety of ways and for a variety of applications [12] . The resins were made from poly metha crylate, and the sorption of $Fe^{3+}, Cu^{2+}, Ag^+ , Zn^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}$ and TiO^{2+} Petrie et al [9] . Poly {hydroxamic acid} resins synthesized from Amberlite IRC-50 Wan Yana's [13], studied the separation of Fe^{3+} and Al^{3+} from Ca^{2+} and Mg^{2+} using poly hydroxamic acid resins . Kato and Coworkers [14], acrylontrile and divinyl benzene were used to make resin, which was then examined for its structure and the recovery of $UO2^{2+}$ from sea water . The manufacture of this chelating Poly (Hydroxamic acid) resin from Co-poly (AMDB) and acryl Hydroxamic acid, as well as divinyl Benzene grafted to starch, is a new starting polymer for generating this resin [15] .

Chelating resins with a poly Hydroxamic acid group can also be useful for monitoring harmful trace metals in the environment , over there is also a possibility of using poly(Hydroxamic acid) resin to extract rare from sea water [16]. The poly (Hydroxamic acid) can be used to measure many elements quantitated in chromatography and for separation of various ions such as Copper(II), Cobalt(II), Lead(II) and iron (III), in biological and sensitive solutions [10] .

The hydroxyl and oxime groups of the poly Hydroxamic acid chelating resins enable them to chelate for diverse metal ions and create stable hetrocyclic complexes, resulting in superior adsorption performance [17]. The Hydroxamic acid resins are typically made by grafting a poly acrylate resin. Nonetheless, macromolecule grafting results in a decreased hydroximation rate. In addition , copolymerzation of poly hydroxamic acid cannot form spherical resin [6] .

II.   EXPERIMENTAL:

Materials:

Methyl metha acrylate (99% HIMEDIA) , Styrene (98% SIGMA) , hydroxyl amine hydrochloride (98%) , sodium hydroxide, potassium hydroxide , GPR , initiator used benzoyl peroxide (B.P) , solvent gasoline (99%) , ethanol (99.9%) , Manganese (II) Chloride, and nitrogen gas[18] .

Instruments:

To complete the research , the following devices were used : centrifuge , a delicate balance and water bath equipped with a cooling and heat pump for liquid recycling , pH meter pH meter and thermometer , and infrared, ultraviolet and visible radiation device type device GBC , Atomic Absorption Spectroscopy Absorption Atomic device (AAS) Model Berkin .

Preparation of Poly (styrene -Co- methyl methacrylate):

The Poly (Styrene - Co- methyl metha acrylate) was synthesized by using free radicals polymerzation . By combining methyl metha acrylate (37.2 gm) with styrene, an 18 percent styrene – cross linked polymer can be made (37.2 mg). Benzoyl peroxide (0.03 g) Is added, and the mixture is heated for 15 minutes at (70-80 °c) with stirring under N2 (1hr) . Filtration was used to collect the polymer, which was then washed many times with water, ethanol, and benzene before being dried at 70°C. Then poly (Styrene - Co- methyl metha acrylate) was identified by sing a FTIR [19, 20] .

Preparation of Poly (Styrene-Co-Methyl metha acrylate) hydroxamic Acid :

The Poly (St -Co- MMAHA) was prepared by reaction of Poly (St-co-MMA) with Hydroxylamine which was prepared by dissolving (5g) hydroxyl amines hydrochloric (NH2OH.HCl) in (100 mL) solution (ethanol: water) (1:10) cooled to 0°C. The HCL was removed from (HAHA) by treated the (NH2OH.HCl) with NaOH solution with the preservative to not rise the temperature of solution more than 5°C. The precipitate0f (NaCl) was removed by filtration. After that, (150 mL) of Hydroxylamine was added to (10 g) of the poly (St- Co- MMA) in round bottom flask. Then the solution of the potassium hydroxide (KOH) was added to the mixture to rise the pH of the mixture up to {12 – 13} . Then the mixture was heated at {70-80 °C} with stirring for(83 hr) . The Poly (St- co- MMAHA) is Collected by filtration and washed sevral times with ethanol & hydrochloric acid then dry at 60°C. The polymer was identified by using (FTIR) [19,20, 21].

Studying of Applications of poly (St- co – MMAHA)

Determined of Sorption Capacity of Manganese (II) ion by Poly (St- co –MMAHA):

One gram of poly (St- co –MMAHA) was mixing with (50 mL) of 100 ppm of Manganese (II) ion solution. The solution was shaken for 4 hours and at temperature 25^0C the centrifuge was used to separate the precipitate from the solution. The remaining concentration was determined by using atomic absorption device and (UV.VIS) spectrophotometer. The sorption capacity of poly (St- co –MMAHA) for was Manganese (II) ion determined from the following equation [21, 22] .

$$Q_e = (C_\circ - C_e)\ V/\ M \ldots\ldots\ldots\ldots(1)$$

Where Q_e (mg.g-1) is the quantity of dissolved metal ion, ($C_\circ$, C_e) is the initial and equilibrium metal ion concentration in solution (mg/L), and V (L) is the volume of the solution, and M (g) is the weight of the sorbent poly (St-Co-M.M.A) hydroxamic acid . In the same way the sorption capacity of Iron ion, Zinc ion and Nickel ion was determined by poly (St-Co-MMAHA) [23] .

Study of sorption Isotherm of P(St- Co –MMA) HA:

Study of the Effect of Temperature on sorption Capacity of Manganese (II) ions Poly (St- Co-MAHA):

The effect of temperature was studied by preparing a series of solutions of the same proportions by mixing one gram of poly (St-Co-MMAHA) with 50 mL at a concentration of (100 ppm) of Manganese (II) ions. Where each solution was placed in a thermocouple during temperature range of (20, 40, 60 and 80 °C) . The sorption capacity was determined at each temperature. In the same way the sorption capacity of ions (Fe^{2+}, Ni^{2+} and Zn^{2+}) was determined . In addition, the effect of solution pH and duration on the ion sequestration capability of poly (Styrene-Co-methyl metha acrylate)hydroxmic acid for ions(Mn^{2+}, Fe^{2+}, Ni^{2+} ,and Zn^{2+}) was also studied [21, 24].

III.   RESULTS AND DISCUSSION

Poly hydroxamic acid is characterized :

The p (St- Co- MMA) which obtained by a free radical initiating process for Co- polymerzation between styrene and methyl metha acrylate with a mixing ratio(1:1), using benzoyl peroxide as an initator at (70°c) under N2 atmosphere by ratio of transformation (10 %) . The poly (Styrene- Co- methyl metha acrylate) was particular by (FTIR) spectroscopy. (FTIR) spectra fig (1):
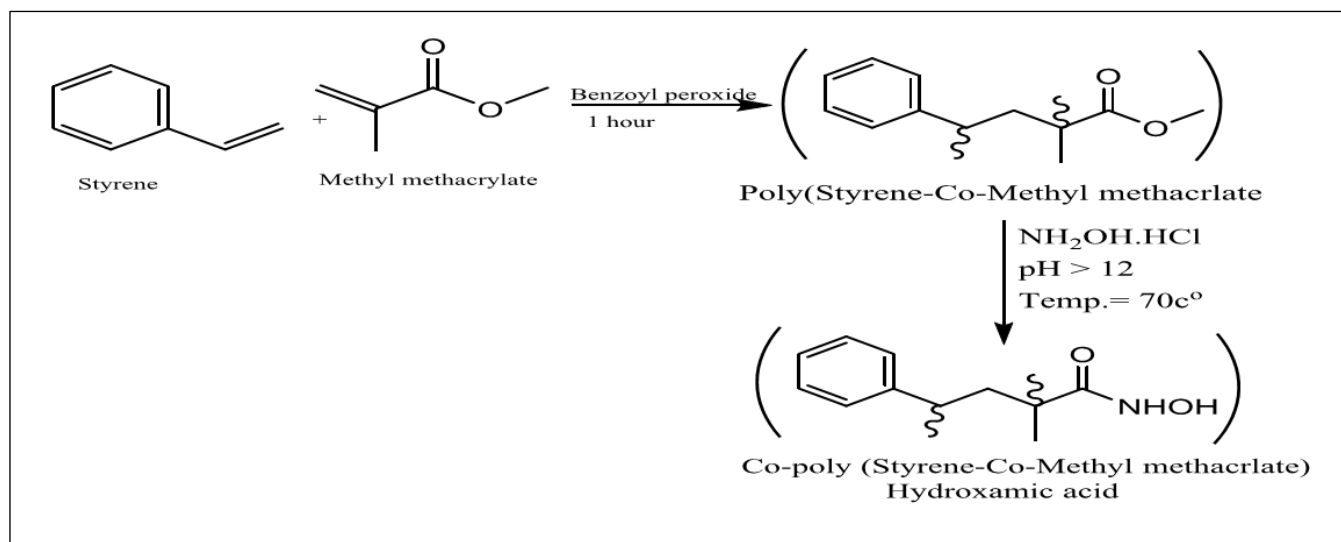
of poly (St-Co- MMA) graphed shows new sorption bonds appear at (1723 cm^{-1}) of { C=O} , (1284 cm^{-1}) of {C-O} , and (2998 cm^{-1}) of {C-H}   Poly hydroxamic acid prepared through a conversion of the ester group of the poly (Styrene- Co- methyl metha acrylate) into hydroxamic acid was It is done by treatment of poly (St-Co-MMA) potassium hydroxide (KOH) or sodium hydroxide (NaOH) in alkaline media at pH =13 for hydroxyl amine hydrochloride . Poly hydroxamic acid was synthesized by the general Technologies previously employed [22, 25].

FTIR spectroscopy was used to identify the poly hydroxamic acid. The (FTIR) spectra Fig (2) of poly (Styrene -Co-methyl metha acrylate) hydroxamic acid resin showed the characteristic absorption bonds of hydroxamic at (3444 cm^{-1}) of (O-H) , (1670 cm^{-1}) of carbonyl (C=O) , (930 cm^{-1}) of (amide (N-H) and (N-O) groups) .

Sorption of Mn^{2+} by poly (St-Co-MMA) Hydroxmic acid

The initial and equilibrium metal ion concentrations are shown in Table 1. (C$_o$, C$_e$) , as well as the adsorption capacity (q) of Mn^{2+} after treatment with poly (Styrene-Co-methyl metha acrylate) HA. The values of (C$_o$,C$_e$) and q were 100 mg/L ,69(mg / liter) and 1610 mg/g respectively [21] .

Effect of pH on Mn^{2+} sequestration capacity

Fig (3) depicts the effect of pH on the capacity of poly (Styrene-Co-methyl metha acrylate) Hydroxamic acid to sequester Mn^{2+}. At pH(1), the capacity for sequestration was modest, but as the pH climbed, it increased to a maximum at (pH= 6) . However, the capacity for absorption declined as the pH increased . The results show that in an alkaline media, the absorption capacity decreases . The reduced capacity of poly (Styrene -Co-methyl metha acrylate) Hydroxamic acid to sequester Mn^{2+} The fact that there are more protons accessible to protonate at pH = 1 could be related to the fact that there are more protons available to protonate at a lower pH , The surface active groups of poly hydroxamic acid (Styrene -Co- methyl metha acrylate) compete with manganese (II) ions in solution . At higher pH values, more deprotonated hydroxamic acid functional groups led in increased Mn2+ ion sequestration [18,24] .

Effect of Initial Concentration on Mn^{2+} sequestration capacity

Figure (4) depicts the influence of initial concentration on Mn^{2+} adsorption by poly (Styrene- Co-methyl metha acrylate) hydroxamic acid at a concentration of 100 mg/L . It should be observed that as Ce rises, qe rises with it until an equilibrium is reached, after which qe remains constant . We can deduce that the amount of Poly Hydroxamic acid determines the absorption capacity, that is, Rather than the concentration of Mn^{2+} , Poly Hydroxamic acid bound with Mn2+ ion before two oxygen atoms of the hydroxamic acid group. [26,27].

Effect of Temperature on Mn^{2+} adsorption capacity

The influence of contact temperature on the adsorption capacity of Mn^{2+} by poly (St- Co- MMA) HA is shown in Fig(5). When the temperature was low, the sorption capacity increased, but when the temperature was raised, it dropped. At about 20°C, the adsorption capacity of Mn^{2+} with poly (St-Co-MMA) HA increased to a maximum. [10]

Adsorption Kinetics

At different temperatures, the kinetics of Mn^{2+} sorption by p (St- Co- MMA) HA resin were examined. At 20 °C, 40 °C, 60 °C, and 80 °C, Table (2) demonstrates the influence of contact duration on the sorption of (100mg/liter) Mn^{2+}. During the early stages of sorption, the rate of sorption is high, but as the system approaches equilibrium, it slows down. The rate of const (Ho and McKay, 1998) is calculated using pseudo second-order kinetic models (Ho and McKay, 1998). [9.18,21]:

$$t/q_t = (1/ k_2 q_e^2) + t/ q_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where q_t = (mg g^{-1}) and q_e=(mg.g^{-1}) are the quantities of sorption at time (min) and equilibrium, respectively, and k_2 (g.mg^{-1}.min^{-1}) is the second-order rate constant . In fig{6 (a-b)}, a plot of (t/q_t) against time (min) yielded a straight line, and the slope and intercept of the plot were used to get the values of qe and k_2 . The values of k_2 were found to be ($1.17*10^{-3}$, $1.27*10^{-3}$, $1.48*10^{-3}$, $1.79*10^{-3}$ (g/mg. min)), q_e= (88, 81 , 72 , 63 (mg/g)) at (20, 40, 60, 80,) °C, respectively.

IV. THRMODYNAMICS OF THE ADSORPTION PROCESS :

Activation energy:

The Arrhenius equation, as illustrated below, considers the activation energy to be the rate constant [9,21]

$$Lnk_2 = lnA - Ea/ RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

The Arrhenius factor is A , while the sorption activation energy is Ea (kJ.mol^{-1}) The slope of a straight line was used to calculate the value of activation energy, which was found to be (8.673) in the plot T lnk_2 as a function of (T K_2) shown in fig (7) . (kJ.mol^{-1}). Because the rate is limited by intra-particle diffusion when the activation energy is low, the process can be concluded to be directed by physical nature interaction.

Thermodynamic Parameters:

At 293, 313,333, and 353 °K, the amount of Mn^{2+} sorption at equilibrium was observed. The equilibrium partition constant K_d can be computed using the formula below [21,22] :

$$K_d = qe/Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

The values of K_d for adsorption of Mn^{2+} by p (St- Co- MMA) H.A were (3.84, 3.42, 3.15, and 2.92 ml.g-1) at 20 °C, 40 °C, 60 °C, and 80 °C, respectively . The values of K_d decreased as the temperature grew from 20 to 80 °C, proving that the sorption process is an exothermic one . The value of the enthalpy (enthalpy) ΔH was calculated using the following equation:

$$ΔH = Ea – RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(5)$$

Where ΔH$^°$ = standard enthalpy, T = absolute temperature (K), R = gas constant, and Ea = activation energy . The values of ΔH$^°$ where (-586.09 , -626.09 , -666.09 , -706.09 kJ. Mol^{-1}) at (20 , 40 , 60 and 80 °C).

The exothermic nature of the adsorption reaction of Mn^{2+} by poly(St- Co- MMA) H.A was confirmed by the negative value of the ΔH.[28]

The thermodynamic functions ΔS, ΔG were also calculated using the following equations:

$$ΔG = -RT Ln K_d \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(6)$$

$$ΔG^° = ΔH - TΔS \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(7)$$

$$ΔS = (ΔH -ΔG) / T \ldots\ldots\ldots\ldots\ldots\ldots..\ldots.(8)$$

Where ΔS$^°$ = standard entropy, ΔG$^°$ = standard Gibbs free energy . The values of ΔG$^°$ where (-785.24 ,-769.98 , -759.24 , and -748.36 kJ.mol^{-1}), ΔS$^°$ where (0.679 , 0.459 , 0.279 , and 0.119 g.mol.K^{-1}) at (20 , 40 , 60 and 80 °C).

At an initial concentration of 100 mg/liter, the values of Go declined as the temperature climbed from 20 to 80 °C, indicating that sorption occurred spontaneous at all temperatures . [21]

Table (1): The values of C_o ,C_e and adsorption Capacity (q) of Mn^{2+} by poly (Styrene-Co-Methyl metha acrylate) H.A condition: at time (4 hr) .

Metal ion	C_o ppm	C_e ppm	C_o mg/L $* 10^2$	C_e mg/L $*10^2$	Q_e (mg/g) $*10^2$
Mn^{2+}	100	78	1	0.78	22

Tab (2): Effect of temperature and time on the adsorption kinetics of Mn^{2+} by poly (St- Co- MMA) H.A condition:

T(K)	Q_t(mg /g) $*10^2$ of Mn^{2+} by P.H.A at time (min)			
	60(min)	120(min)	180(min)	240(min)
293	4.7	5.9	6.8	7.9
313	3.4	4.5	5.7	6.8
333	2.8	3.4	4.5	5.4
353	1.7	2.1	2.8	3.4
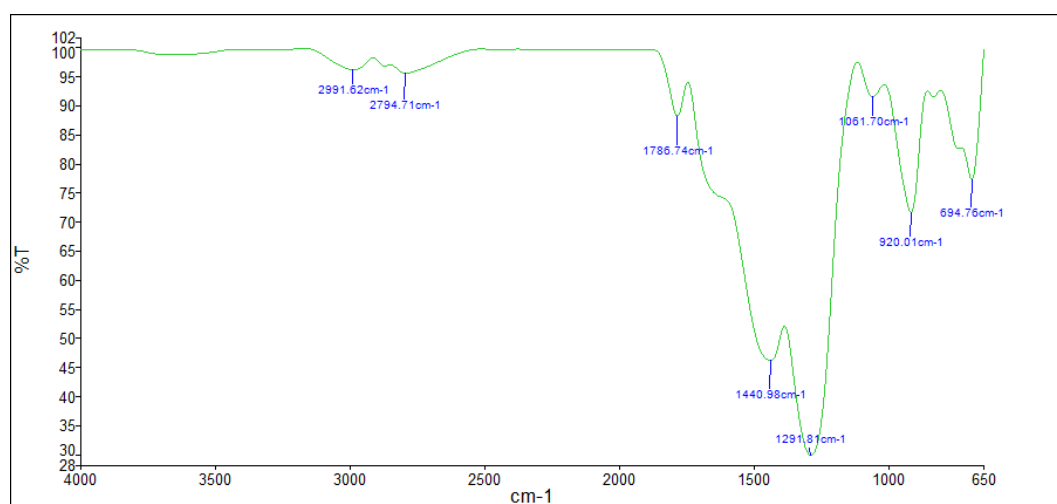
Fig (1) : FT-IR spectra of poly (styrene-co-methyl metha acrylate)
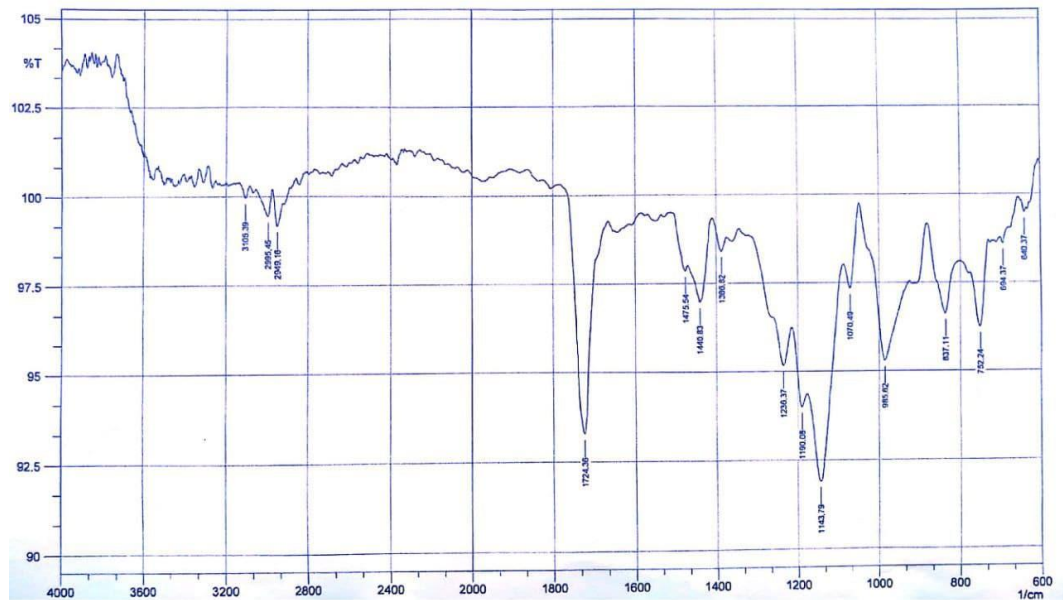
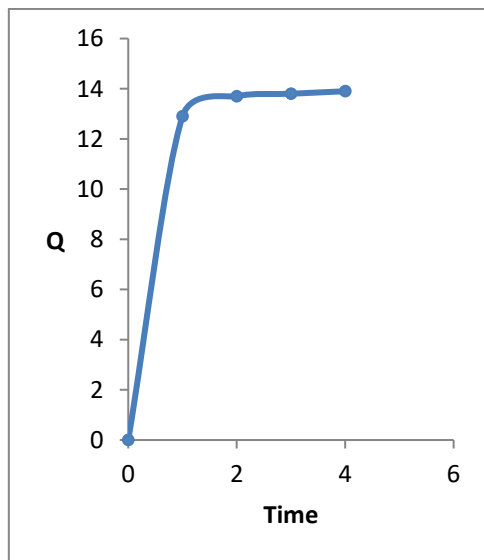Fig (2) : FT-IR spectra of p (styrene-co-methyl metha acrylate) H.A

Fig (3):. The influence of initial pH on Mn^{2+} sorption by p (St-Co-MMA) H.A under the following conditions: 500mg/L; 4h contact period; temperature 25°c
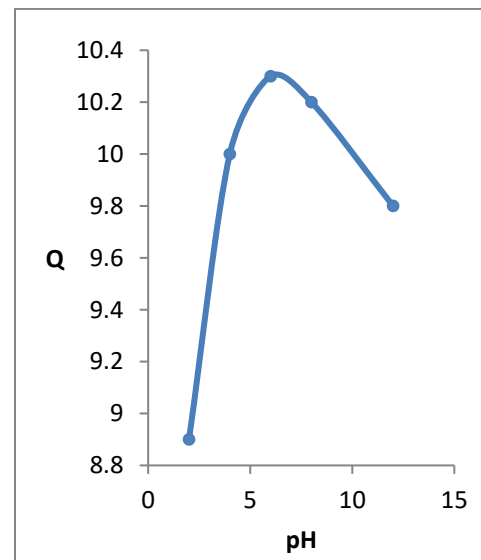
Fig (4). The influence of starting con. on Mn^{2+} adsorption by p (St-Co-MMA)H.A in the presence of 100mg/ L: 4 hours of contact time; temperature of 25°C
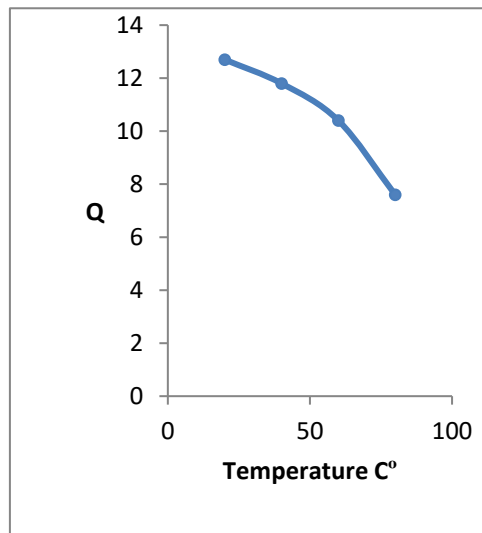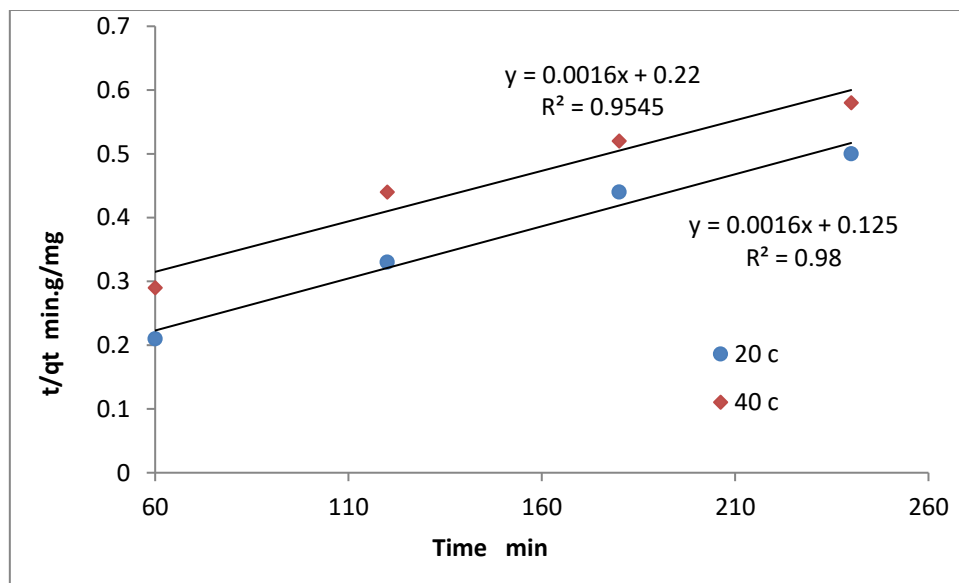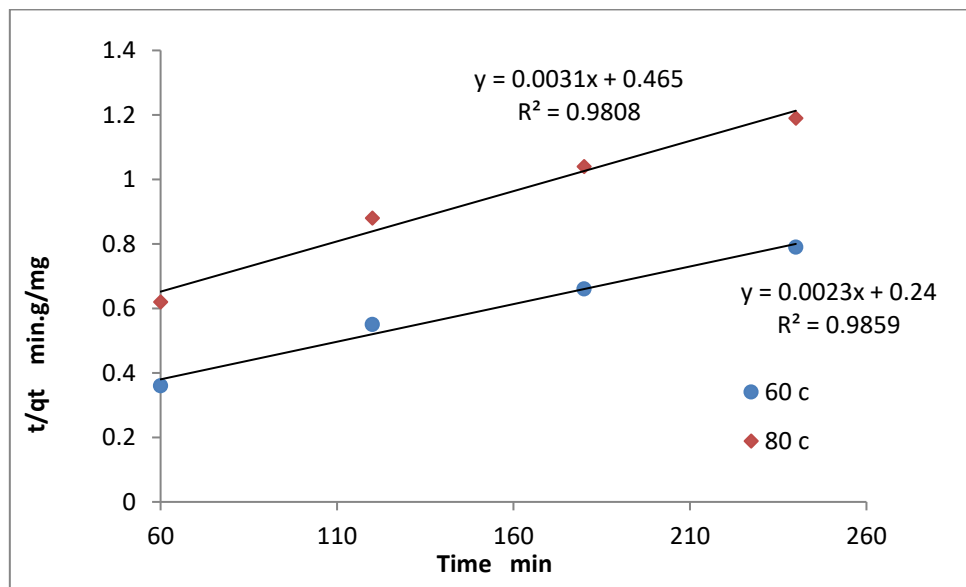
Fig (5): The influence of starting temperature on
Mn^{2+} sorption capabilities by p (St-Co-MMA)
H.A under the following conditions: conc.
100mg/L.

Fig(6-a) At 20°C and 40°C, second order kinetic graphs for Mn2+ sorption by p (St-Co -MMA) H.A resin

Fig(6-b) At 60°C and 80°C, second order kinetic graphs for Mn2+ sorption by p (St-Co-MMA) H.A resin
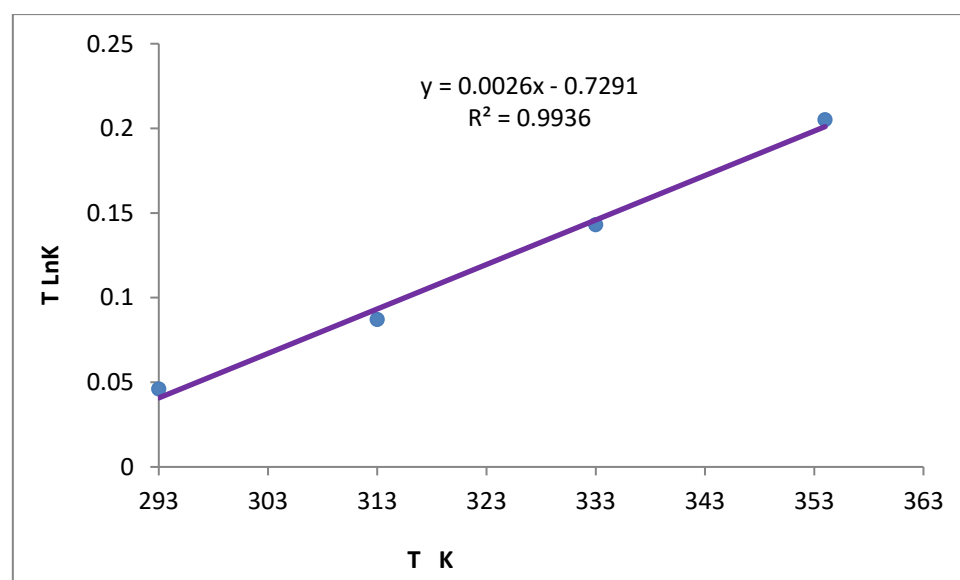

Fig (7) shows the values of the constant for manganese ion retention mediated by poly(such as methacrylate) hydroxamic acid and at different temperatures.

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