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RESEARCH ARTICLE

Preparation of Poly (Hydroxamic Acid) from Poly (Styrene-co-Methyl Metha Acrylate) and the Study of the use of Water Purification of Heavy Metal Elements

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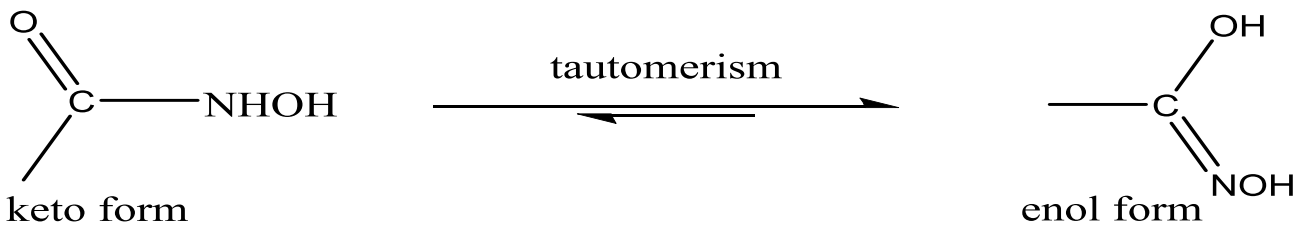
Abstract

In this study, the poly (styrene-co-Methyl metha acrylo hydroxamic acid) was prepared from the poly(styrene-co-methyl metha acrylate) which prepared by free radical polymerization using the benzoyl peroxide initiator to co- polymerization between (methyl metha acrylate) and (styrene) at atemperrature 70 ^{0}C a mixing ratio (1:1) a conversion rate 20% and then conversion the polymer output to poly (hydroxamic acid) by reacting with hydroxyl amine hydrochloride in a strong base medium using potassium hydroxide with thermal escalation for 48 hours. The resulting poly (hydroxamic acid) and poly (styrene-co-Methyl metha acrylate) were identified by the FT-IR spectra. An adsorption study of heavy metal ions such as Fe^{3+}, Cu^{2+}, $Co^{2+}$and pb^{2+} by poly (hydroxamic acid) was done. The effects of time, temperature and an acid function on adsorption ions were also studied. Calculation of desorption temperature of the metallic ions at two thermal degrees 10, 20 ^{0}C shows that adsorption is chemical type.

Keywords: *Hydroxamic acid, Poly Hydroxamic acid, heavy metals, Adsorption.*

Introduction

Chelating resins have received considerable attention in the removal of dangerous trace metal ions because of their highly selective adsorption capacity for heavy metal ions [1, 4]. The hydroxamic acid derivatives and their polymers are synthesized for a variety of purposes and are widely used in the industrial, medical, pharmaceutical, textile fields and agricultural [5]. The hydroxamic acid group is well-known for its ability to form a stable chelate with various heavy metal ions. The hydroxamic acids are regarded as derivatives of the nitrogen bound hydrogen in the hydroxylamine molecules, and have a general formula R-CO-NHOH (R = alkyl or aryl) having a tautomerism of keto and enol forms [6].



R may be saturated or unsaturated alkyl group or group Ariel imitative or polymer. Effective group retain their properties and are not affected by installing the rest of the molecule, and the effective totals owned acid (OH) and (NH) and a carbonyl [7, 8].

Experimental

Materials

Styrene (98% SIGMA), methyl methacrylate (99% HIMEDIA), hydroxyl amine hydrochloride (97%), potassium hydroxide

GPR, initiator used benzoyl peroxide (B.P), (solvent gasoline 99%), (ethanol 99.8%) Sodium sulfate anhydrous and nitrogen gas [9].

Instruments

For completion of the research the following hardware is used, a delicate balance and water bath equipped with a cooling and heat pump for liquid recycling, centrifuge, and infrared, ultraviolet and visible radiation device type device GBC, Atomic Absorption Spectroscopy Absorption Atomic device (AAS) Model Berkin, pH meter pH meter and thermometer.

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

The Poly (St- co- MMA) was synthesized by using free radicals polymerization. As follow 20 mL (18.6 g) of Methyl methacrylate, 20 mL (18.1 g) of styrene and 0.03 g of Benzyl peroxide were mixed. The mixture was heated with stirring at (70-80 °C) under nitrogen atmosphere for one hour. The resulting polymer was precipitated by ethanol with hydrochloric acid-charged and collected by filtration. The Poly (St- co- MMA) was washed by ethanol and distilled water and dried. Then poly (St- co- MMA) was identified by sing a (FT.IR) [10, 11].

Preparation of Poly (styrene-co-methylmathacrylate) hydroxamic Acid

The Poly (St-co-MMAHA) was prepared by reaction of Poly (St-co-MMAHA) with Hydroxylamine which was prepared by dissolving (20 g) hydroxyl amines hydrochloric ($NH_2OH.HCl$) in (100 mL) solution (ethanol: water) (1:10) cooled to 0°C. Then HCL was removed from (HAHA) by treated the ($NH_2OH.HCl$) 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 (20 g) of the poly (St- co- MMA) in round bottom flask. Then the solution of the potassium hydroxide 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 48 hours. The Poly (St- co- MMAHA) was collected by filtration and washed several times with ethanol/ hydrochloric acid then dry at 65°C. The polymer was identified by using (FT.IR) [11, 13].

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

Study of Adsorption Capacity of Ferric ions by Poly (St- co –MMAHA)

One gram of poly (St- co –MMAHA) was mixed with (50 mL) of 100 ppm of ferric ion solution. The solution was shaken for 5 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 adsorption capacity of poly (St- co –MMAHA**)** for Ferric ion was determined from the following equation [13, 14]

$$Q_e = \frac{V(Co - Ce)}{M}$$

Where Q_e ($mg.g^{-1}$) is the amount of sorbed metal ion; (C_o, 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-M.M.A). In the same way the adsorption capacity of Copper ion, Cobalt ion and Lead ion was determined by poly (St-co-MMAHA).

Study of adsorption Isotherm of Poly (St- co –MMAHA)

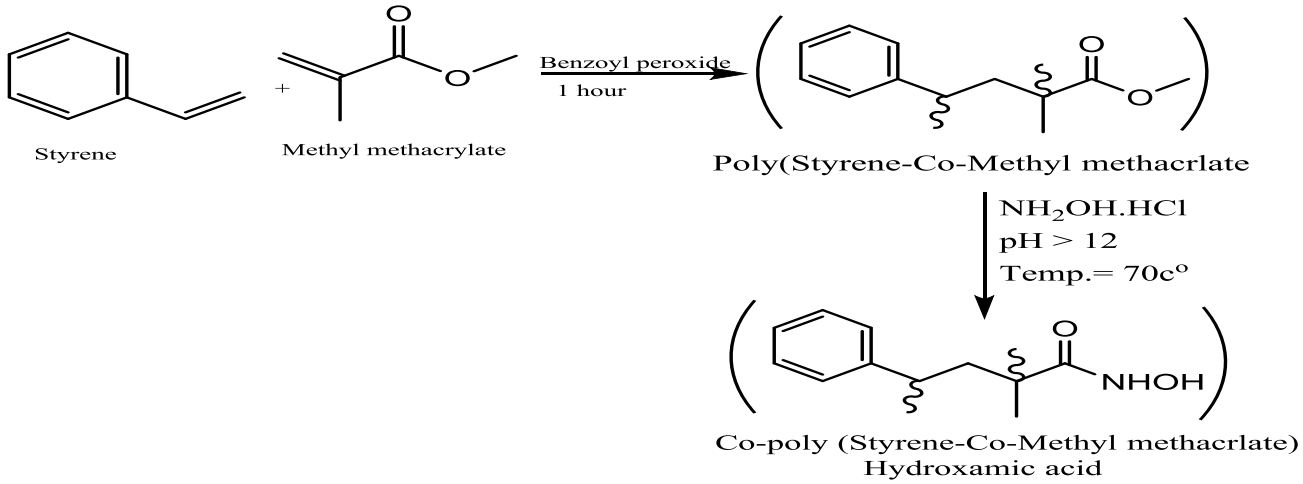
Study of the Effect of Temperature on Adsorption Capacity of Ferric ions Poly (St- co-MAHA)

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 ferric ions. Where each solution was placed in a thermocouple within temperature range of (10, 20, 40, 60 and 80 °C).The adsorption capacity was determined at each temperature. In the same way the adsorption capacity of ions (Cu^{2+}, Co^{2+} and Pb^{2+}) was determined. And the effect of pH of solution and time on the adsorption capacity of poly (St- co-MMAHA) for ions (Fe^{3+}, Cu^{2+}, $Co^{2+}$and Pb^{2+}) was also studied [15, 16].

Results and Discussion

Characterization of Poly (hydroxamic acid)

The poly(styrene–co-Methyl metha acrylate) which gained by a free radical initiating process for Co-polymerization between styrene and methyl metha acrylare with a mixing ratio(1:1), using benzoyl peroxide as an initiator at (70°c) under N_2 atmosphere by ratio of conversion (20%). The poly (St-co-M.M.A) was specified by (FT.IR) spectroscopy. (FT.IR) spectra Fig(1) appendix(2) of poly (St-co- M.M.A) graphed shows a new absorption bonds at (1726cm^{-1}) of C=O (2945 cm^{-1}) of (C-H),and (1375 cm^{-1}) of (C-O). Poly (hydroxamic acid) prepared via a conversion of the ester group of the poly (St-co- M.M.A) into hydroxamic acid was carried out by treatment of poly (St-co- M.M.A) with hydroxyl amine hydrochloride in alkaline medium at (pH=12-13) using potassium hydroxide. Poly (hydroxamic acid) was synthesized by the general ways previously employed [14, 17].



The poly (hydroxamic acid) was identified by (FT.IR) spectroscopy. The infrared spectrum Fig(2) appendix(2) of (P St-Co-M.M.A HA) resin showed the characteristic absorption bands of hydroxamic (O-H), carbonyl (C=O), amide (N-H) and (N-O) groups at (3444, 1670 and 930 cm^{-1}).

The Study of Sorption Capacity of the Poly Hydroxamic Acid (PHA) to Heavy Metal Elements:

The hydroxamic acid compounds are considered as binary bi-age ligands with a single negative charge. When the acid loses an acid hydroxyl proton, each ligand connects with the metallic ion (M) by the oxygen of the hydroxyl and carbonyl groups, which is of the hydroxamic acid. Through this bonding, we get a pentagonal loop with high stability, where the metal ion is within the pentagonal loop. The poly hydroxamic acid (PHA) adsorption capacity of the heavy metal ions is identified through specifying the remaining concentration (C_e) of the metallic ion in a separation filter after the treatment with poly hydroxamic acid, which represents the concentration of equilibrium. Where the remaining concentration of the metallic ion is being identified with an atomic absorption device and the UV and visible spectroscopy (UV-Vis), where it is found that the concentration of equilibrium (C_e) and the adsorption capacity (Q) of the metallic ions Fe^{3+}, Cu^{2+}, Co^{2+}, Pb^{2+} [5, 18].

The Effect of the Time on the Sorption Capacity of the Poly Hydroxamic Acid (PHA)

Table (1) appendix 1 shows the effect of time on the total sorption capacity of ferric ion **Fe^{3+}**, copper **Cu^{2+}**, cobalt **Co^{2+}**, and lead **Pb^{2+}** by poly hydroxamic acid (PHA) and through the values of (Q) which increases by time. It is noticeable that the value (Q) is higher after five hours.

The Effect of Temperature on the Sorption Capacity of the Poly Hydroxamic Acid (PHA)

Table (2) appendix 1 shows the effect of temperature on the total sorption capacity of ferric ion **Fe^{3+}**, copper **Cu^{2+}**, cobalt **Co^{2+}**, and lead **Pb^{2+}** by poly hydroxamic acid (PHA) and through the values of (Q) which decreases when the temperature is higher.

Also, the sorption capacity increases when there is a decrease in the temperature, where it is noticeable that the value (Q) is at the highest when it is 10° c. However, a decrease in the values of the adsorption capacity takes place when the temperature goes higher because the high temperature causes a separation in the metallic ions at the surface of the adsorptive material [19]

The Effect of Acid Function on the Sorption Capacity of the Poly Hydroxamic Acid (PHA)

Table (3) appendix 1 shows the effect of (PH) values on the adsorption capacity of ferric ion **Fe^{3+}**, copper **Cu^{2+}**, cobalt **Co^{2+}**, and lead **Pb^{2+}** by poly hydroxamic acid (PHA) and through the initial concentration values (C_o), the concentration of equilibrium (C_e), and the adsorption capacity. We can find that the values of (Q) are higher at (pH=6, pH=8), while the values of (Q) decreases during the increase and the decrease of (pH) value when it is below (pH=6, pH=8). This happens because the metallic ion, within a basal medium, creates a gelatinous compound, which deposits in the form of hydroxides. However, when the (pH) is low in an acidic medium, there will be a rivalry between (H^+) ions and the ones existed on the binding sites in the hydroxamic acid groups, which are bonded to the polymer, and lead to a decrease in the adsorption capacity (Q) [15, 20].

Measuring the adsorption temperature of the Poly Hydroxamic Acid of Metallic Ions (St-co-M.M.A)

The temperature of adsorption (He) is set by applying Clausius-Clapeyron equation on the chemical adsorption. As an equilibrium process, it is possible to measure the adsorption temperature by knowing the adsorption capacity of the metallic ions at different temperatures, for instance, (T_1 and T_2) we get (Ce_1, Ce_2) to achieve the same breakage of the covered surface by using the following equation: [21]

$$ln\frac{C_{e2}}{c_{e1}} = \frac{H_e}{R}\left(\frac{T_2 - T_1}{T_2 * T_1}\right)$$

Where (He) represents the adsorption temperature.

While Ce_1, Ce_2 are equilibrium concentration.

R represents the general constant for the gases which equal 2.cal .mol^{-1}

Applying the above equation shows the adsorption temperature of the chemical reaction. As shown in Table (4) appendix 1.

Conclusion

It is possible to prepare poly hydroxamic acid from the copolymer (styrene, methyl methacrylate MMA). The copolymers have poly hydroxamic acid groups because it is binary bi-age ligands with the transition metals such as ferric, copper, cobalt, lead … Etc. The sorption capacity of the studied metallic ions increases through time, where it is at the highest after five hours. Also, the adsorption capacity increases whenever there is a low temperature, while the adsorption decreases when there is a high temperature in the metallic ions because the high temperature causes a separation in the metallic ions at the surface of the adsorptive material. However, for the acid function, the sorption capacity of the metallic ions increases, within the range (6-8). Therefore, from the sorption temperature values, it can conclude that it is chemical adsorption

Table 1: shows the effect of time on adsorption capacity of metal ions by poly (St-co-M.M.A) hydroxamic acid

Metal Ions	(Total Sorption Capacities) Q_e(mg/g)*10^2				
	1hr	2hr	3hr	4hr	5hr
Fe^{3+}	8.8	9.9	10.3	10.7	10.9
Cu^{2+}	7. 1	8.9	9.4	9.8	10.1
Co^{2+}	4.3	5.1	5.6	5.9	6.2
Pb^{2+}	2.1	3.2	4.1	4.3	4.6

Table 2: shows the effect of temperature on adsorption capacity of metal ions by poly (St-co-M.M.A) hydroxamic acid

Metal Ions	(Total Sorption Capacities) Q_e(mg/g)*10^2						
	10 °c	20 °c	30 °c	40 °c	50 °c	60 °c	80 °c
Fe^{3+}	10.0	9.4	9.0	8.3	7.6	6.4	5.3
Cu^{2+}	8.0	7.6	7.2	6.7	5.8	5.2	4.6
Co^{2+}	5.1	4. 8	4.3	3.5	3.1	2. 5	1.9
Pb^{2+}	3.6	3.3	3.0	2.7	2.3	1.9	1.3

Table 3: shows the effect of acid function on adsorption capacity of metal ions by poly (St-co-M.M.A) hydroxamic acid

Metal Ions	(Total Sorption Capacities) Q_e(mg/g)*10^2				
	PH =2	PH=4	PH=6	PH=8	PH=10
Fe^{3+}	8.9	9.8	10.6	10. 4	9.5
Cu^{2+}	8.5	9.2	9.6	9.4	9.0
Co^{2+}	3.2	5.6	7.0	6.5	4.9
Pb^{2+}	1.2	2.6	2.9	2.6	2.0

Table 4: shows the effect of heat adsorption (He)

Metal Ion	Temperature of Adsorption
Fe^{3+}	132.75.cal.mol^{-1}
Cu^{2+}	81.33.cal.mol^{-1}
Co^{2+}	63.5.cal.mol^{-1}
Pb^{2+}	74.16.cal.mol^{-1}

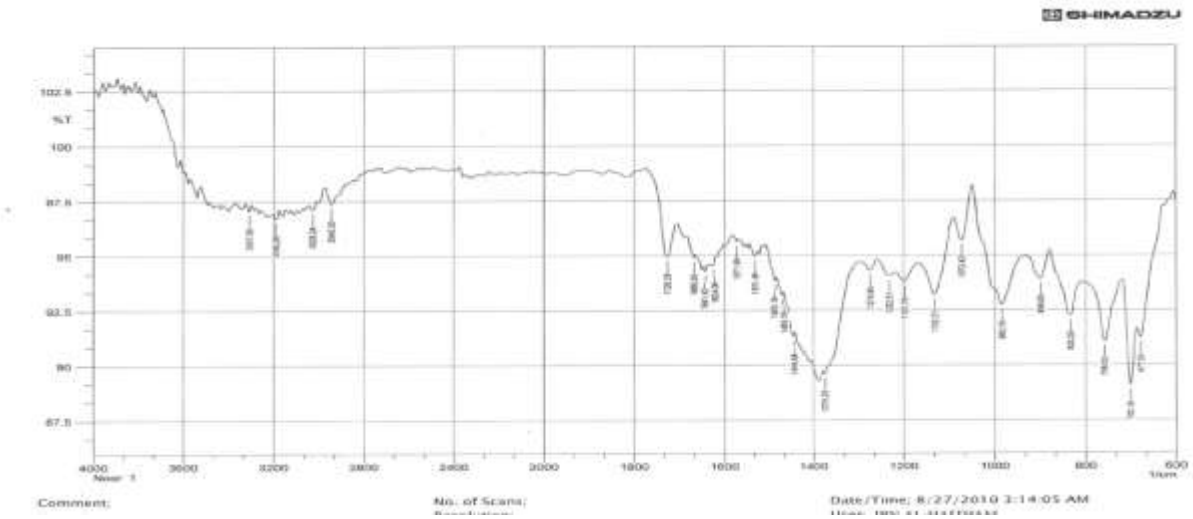


Fig 1: FT-IR spectra of Pol (St –co-M.M.A)

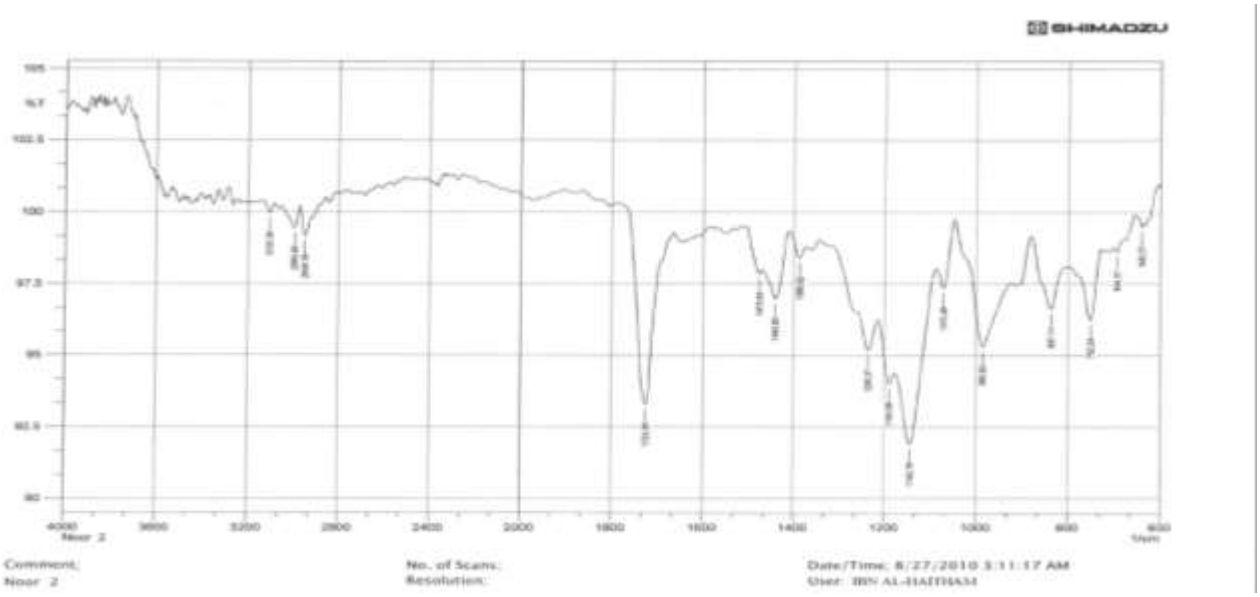


Fig 2: FT-IR spectra of Pol (St –co-M.M.A) Hydroxamic acid

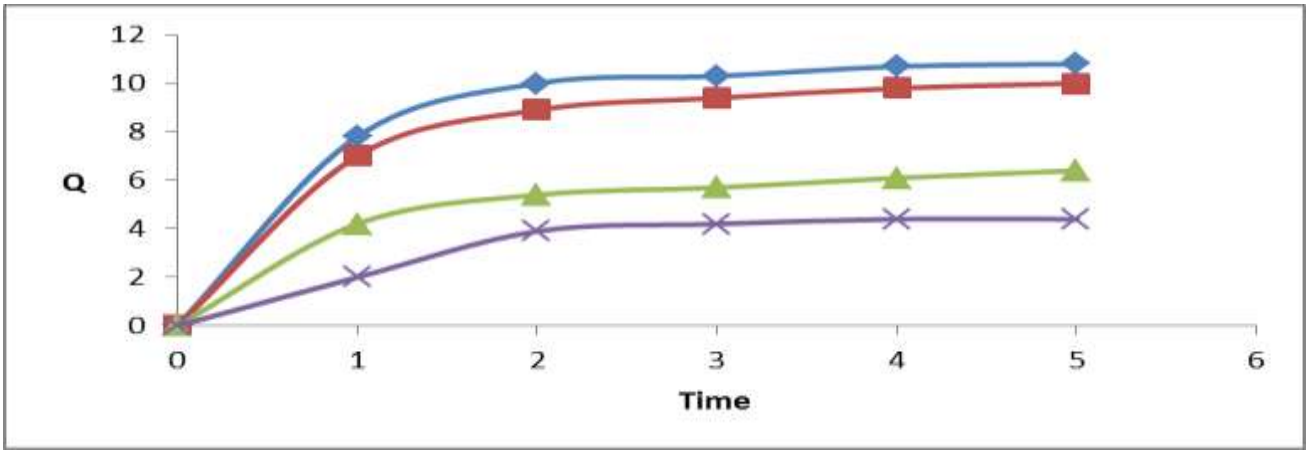


Fig 3: The effect of initial time on the Sorption of metal ions by (PHA)

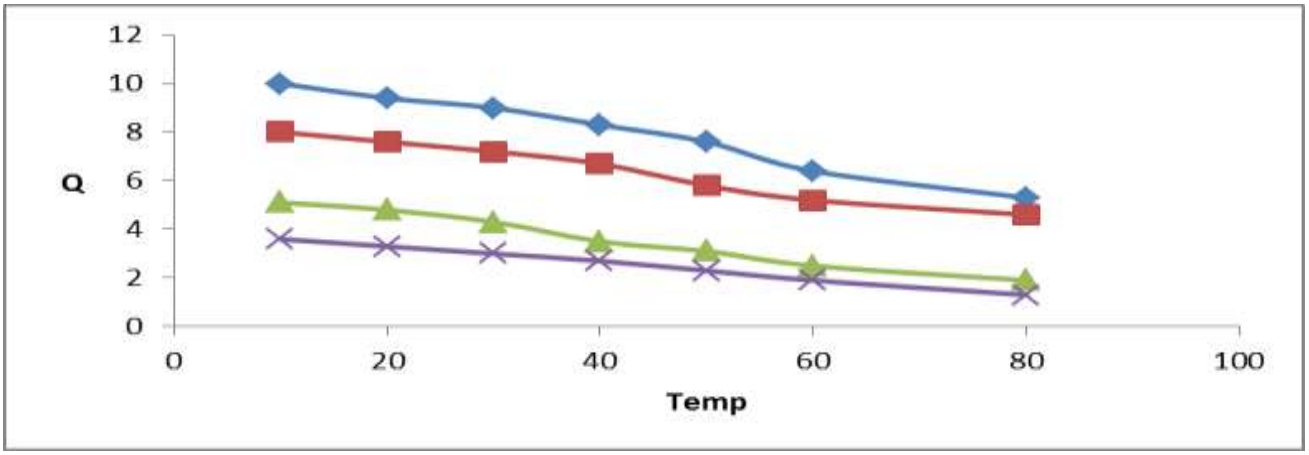


Fig 4: The effect of initial temperature on the sorption of metal ions by (PHA)

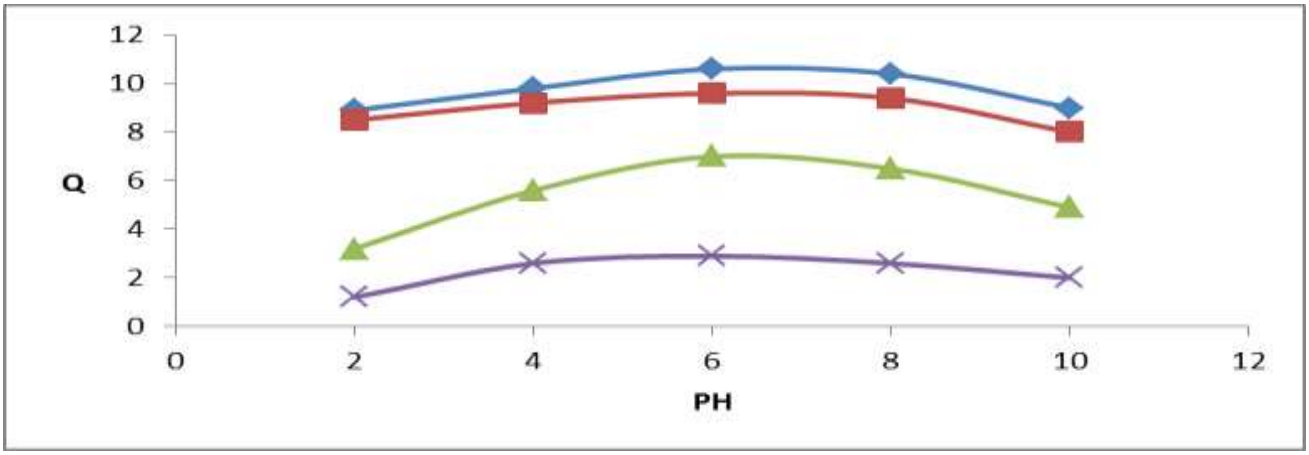


Fig 5: The effect of initial pH on the sorption of metal ions by (PHA)

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