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Studying the effect of adding nano-carbon to poly hydroxamic acid prepared from polymer methyl metha acrylate on the adsorption capacity of ferrous and ferric ions

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***Abstract*---**The research includes, the preparation of Polymer methyl methacrylate by free radical polymerization at a temperature of (70-80°C) and using the initiator benzoyl peroxide with a conversion rate of 10% . Then characterize the resulting polymer using infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (HNMR). The ester group in the resulting methyl metha acrylate polymer was converted to poly hydroxamic acid by neutralizing the polymer with hydroxyl amine hydro chloride in a base medium pH = 12-13 using potassium hydroxide with thermal escalation 120-hours , the resulting compound was diagnosed by infrared spectroscopy. A certain amount of nano carbon was added to the same amount of poly hydroxamic acid and mixed well . The adsorption capacity of poly(methyl metha acrylate) hydroxamic acid was determined for the ferric and ferrous ions before and after adding nano carbon to poly hydroxaic acid. The factors that affect the adsorption capacity such as time, acidity function and temperature were studied , Where the adsorption capacity increases with increasing time, and the highest adsorption capacity is at pH = 6 , where the adsorption rate decreases when the acidity increases and decreases from pH equal six , as well as the heat of adsorption was calcution at two different temperatures , Through the values of the adsorption temperature, It turns out that ferrous ions adsorption is chemical and the adsorption of ferric ions is physical.

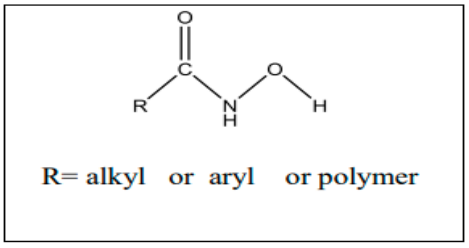
Keywords---nano carbon, poly hydroxamic acid, adsorption.

Introduction

Current research is heading towards understanding or creating advanced materials, devices or systems that take advantage of these new properties that nanomaterials give , Nanotechnology will have a significant impact on many areas of industrial, medical and agricultural life [1] , in the field of aviation, transportation, space research and water technology , and in many vital fields [2]. Methyl matha acrylate is a colorless, transparent liquid monomer that is slightly soluble in water [3]. It is an unsaturated ester with the chemical formula ($C_5H_8O_2$). MMA is used to make resins and plastics, and it is irritating to the skin, eyes and mucous membranes of humans [4]. PMMA polymer can be prepared from methyl methacrylate (MMA) by using a number of polymerization processes such as radical polymerization, ionic polymerization and other polymerization processes. Biomedical and clinical applications, particularly in the field of orthopedics, and is also used in metal plating [5].

The polymers of hydroxamic acid are among the important compounds used to manufacture stable chelating reagents, and they are chelated polymers that have wide applications in analytical chemistry as they have the ability to bind to the metal through more than one donor atom and have a ring structure used to remove ions of toxic heavy elements from aqueous solutions , Such as iron, copper, cadmium , vanadium and other toxic heavy ions the hydroxamic acid units are arranged at appropriate intervals in the polymer chain to allow the acid to coordinate with the metal ion to give an octahedral complex [6,7]. Hydroxamic acid is one of the two-ligands (ligand O,O Di denate) with a single negative charge and hydroxamic acid loses a proton of the hydroxyl group, where each ligand is linked with the metal ion mediated by the oxygen of the carbonyl group that belongs to the hydroxamic acid in the ligand , Thus, three molecules of the acid replace all the molecules attached to the metal ion, forming six coordination sites around the triple positively charged metal ion, which is equivalent to the negative charges belonging to three molecules of the acid, forming three five-membered rings around the metal ion [8] .

Hydroxamic acids are derivatives of hydrogen bonded to nitrogen in hydroxylamine molecules and the general formula for hydroxamic acids is illustrated as below [9,10]:



Where R is a saturated or unsaturated alkyl group or a substituted aryl group or polymer. The active group retains its properties regardless of the composition of the rest of the molecule. Hydroxamic acid polymers are characterized by their high ability to adsorb ions of some toxic metals. Some of them are highly selective polymers made to remove certain ions from aqueous solutions. Hydroxamic acid polymers are also more selective than traditional ion exchangers [11 , 12].

The materials used in this research

Hydroxyl amine hydrochloride (99%) , Sodium hydroxide , Benzoyl peroxide (B.P) , nitrogen gas , Methyl metha acrylate (99%HIMEDIA) , Benzene (99%) , Ethanol (99.9%) , Nano Carbon (>99) , Chloroform (99%) , Iron(III) Chloride , Iron(II) Sulfate.

Equipment and tools used in this research

Sensitive Balance , Magnetic Hote plate stirrer , Electric oven , pH-meter , Centrifuge , Shaker water bath , Infrared ,Ultraviolet and visible , Atomic Absorption Spectroscopy (AAS) , Nuclear magnetic resonance spectroscopy .

Preparation of Poly (Methyl metha Acrylate)

37.4g (40ml) of the purified methyl metha acrylate monomer and (0.03g) of the initiator (Benzyl peroxide) were put into nitrogen gas for 10 minutes and the flask was closed and immersed in a water bath at for 10 minutes ($70^{-}80^{o}C$) for an hour with magnetic stirring , When the viscosity of the mixture increases, we lift the beaker from the water bath, remove the lid from the beaker, add gasoline to dissolve the polymer, and then pour the contents of the beaker into a beaker containing (80ml) of ethanol to precipitate the polymer. Then the polymer is lifted in the form of a white mass and then left to dry and diagnosed by Nuclear magnetic resonance spectroscopy and infrared spectroscopy [13] .

Preparation of Poly (methyl metha acrylate) hydroxamic acid

(10g) of the previously prepared P(M.M.A) is dissolved in (70ml) of chloroform solvent and we add (10g) of Hydroxyl amine hydrochloride in (45ml) of ethanol and (5ml) of deionized water in a ratio of 1:10 and the mixture is cooled To zero degrees Celsius, then we prepare a solution of potassium hydroxide by dissolving (20g) of it in the least amount of deionized water. Then we add the potassium hydroxide solution to the hydroxylamine hydrochloride solution, and the mixture is cooled to $5^{o}C$, then we filter the mixture and neglect the precipitate, which is potassium chloride, and keep the leachate that is (NH_2OH), then we add the filtrate to the polymer solution such as methacrylate and measure the acidity function should be pH(12-13), then put the mixture ingredients in a 250ml circular flask and heat sublimation for 100 hours , Then the resulting compound was diagnosed by infrared spectroscopy [14] .

Addition of nanocarbons to polyhydroxamic acid

(5g) of polyhydroxyamic acid prepared from the homopolymer methacrylate was dissolved in (5ml) of chloroform, then (5g) of nanocarbon was added to the contents of the previous baker, mixed well and left to dry.

Studing of Poly Hydroxamic Acid Sorption Capacity to the Elements of the Heavy Metals

Study of the adsorption capacity of ferric and ferrous ions by polyhydroxamic acid before and after the addition of nano carbon

The adsorption capacity was studied by mixing (50ml) of a solution of ferrous ions at a concentration of (400ppm) with (0.5g) of polyhydroxyacid with continuous shaking for 5 hours , at 25°C and then separate the filtrate from the sediment using a centrifuge Then the residual concentration of the ion in the filtrate was determined by the absorber Atomic and Vis-UV devices from the standard absorbance curve. The equilibrium concentration of the ion was determined, and the adsorption capacity can be calculated from the following equation [15, 16].

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

Study of the factors affecting the adsorption capacity of ferric and ferrous ions by polyhydroxyamic acid before and after the addition of nano carbon :

Effect of time on adsorption capacity

The effect of time was studied by preparing a series of ferrous ion ferric ion and solutions, after which 50ml of (400ppm) was mixed with (0.5g) of polyhydroxyacid in sealed bottles with continuous shaking for different periods of time (1,2,3,4,5 and hr) then we separate the filtrate from the sediment using a centrifuge and estimate the ferrous ion concentration in the filtrate using a UV-Vis device and atomic adsorption device .

The effect of temperature on the adsorption capacity

The effect of temperature was studied by preparing a series of ferrous ion and frric ion solutions, after which (50ml) at a concentration of (400ppm) was mixed with 0.5g of polyhydroxyacid in tight bottles with continuous shaking for five hours at different temperatures (10, 30, 50, 70) degrees Celsius, then separate the filtrate from the sediment by means of a centrifuge and set the concentration of the remaining ferrous ion in the filtrate in the atomic absorption device and the (UV-Vis) device**.**

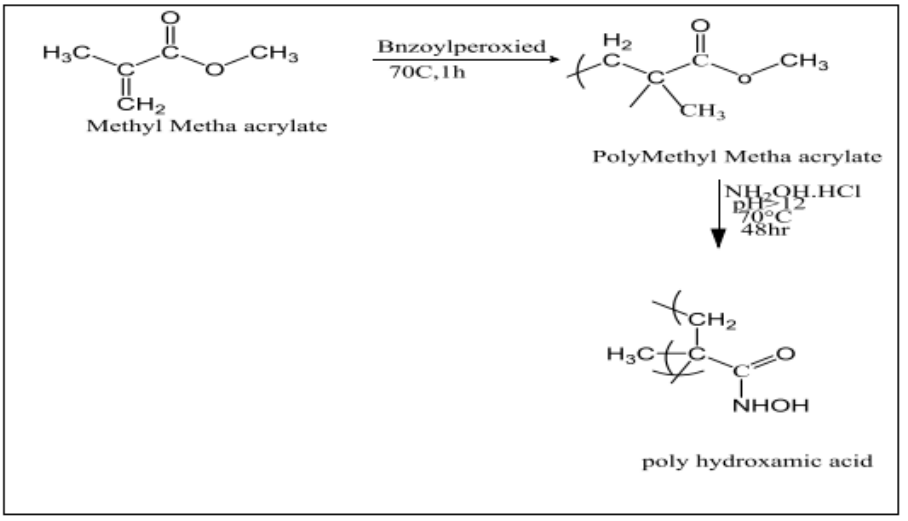
Effect of acidity function on adsorption capacity

The effect of the acidity function on the adsorption capacity was studied by preparing a series of ferrous ion solutions, after which 50 ml of ferrous ion solution was mixed with 0.5 g of polyhydroxyamic acid in tight bottles with continuous shaking for five hours with a range of (2,4,6,8,10) pH Then we separate the filtrate from the sediment by a centrifuge and measure the concentration of ferrous ion remaining in the filtrate by atomic absorption device (UV-Vis) .

Discussion and results

The resulting poly methyl metha acrylate was diagnosed using F.T.I.R spectroscopy, where the infrared spectrum showed an absorption band at (1786 cm^{-1}) due to the vibration of the carbonyl group (C=O), And an absorption band at (2991 cm^{-1}) is due to the absorption of the (C-H) group, and an absorption band at (1440 cm^{-1}) is due to the absorption of the (C-O) group [17] , as shown fig1 . Also, poly methyl metha acrylate was diagnosed using HNMR spectroscopy: Where the Poly(MMA) proton's nuclear magnetic resonance (NMR) spectrum revealed a single signal at chemical displacement = 3.61) that belonged to the methyl group (CH3) ester protons, as well as a medium single signal at (= 2.07) that belonged to the methyl group protons. attached to the carbon atom attached **to the ethylene group , as shown fig2.**

The polymer (methyl metha acrylate) was converted to poly hydroxamic acid. As shown in the following equation:



The resulting compound was diagnosed using infrared spectroscopy (FT-IR), where the spectrum showed an absorption band (3558-3618 cm^{-1}) due to the vibration of the (O-H) group and an absorption band in the region (3437 cm^{-1}) due to the absorption of the amide group (N-H) and a bundle at (1734 cm^{-1}) due to adsorption of the carbonyl group in hydroxamic acid , as shown fig3.

The adsorption capacity of polyhydroxyamic acid (PHA) before and after adding nanocarbons to heavy metal ions the equilibrium concentration was measured by measuring the residual concentration (Ce) of the metal ion in the filtrate following treatment with polyhydroxamic acid. Using an atomic absorption device and UV-Vis spectroscopy, the residual concentration of metal ions was calculated. The metal ions' equilibrium concentration (Ce) and adsorption capacity (Q) (Fe^{+2}, Fe^{+3}). The effect of treatment time on the capacity of multiple adsorption, such as methyl metha acrylate hydroxyamic acid , was studied, in which metal ions were withdrawn from their solutions after fixing other factors. Affecting the adsorption capacity from a specific acidic function and temperature, as the treatment time of ion solutions with polyhydroxyamic acid ranged from (5-1) hours. Polyhydroxamic acid towards the studied ions Fe^{+2} , Fe^{+3} at the longest time of five hours, as shown in table(1,2) – fig(3,4) . Also, the effect of temperature on the adsorption capacity of multiple ions such as methyl metha acrylate hydroxamic acid was studied for the metal ions (Fe^{+2}, Fe^{+3}) through the values of the initial concentrations (C_o) and the equilibrium concentrations (C_e) and the adsorption capacity. The values of (Q) rise with a decrease in temperature, as we find that the highest value of the adsorption capacity at the temperature (10^oC), and the value of the adsorption capacity decreases when the temperature rises, and the decrease in the value of (Q) occurs with the increase in temperature because this leads to the separation of metal ions from Adsorbent surface [18] , as shown in table(3,4) – fig(6,7) . The effect of the acidity function on the adsorption capacity of P(MMA) HA for the studied ions Fe^{+2}, Fe^{+3} was studied through the values of the initial concentrations (C_o) and the equilibrium concentrations (C_e). and the adsorption capacity (Q), where it was found that the adsorption capacity is greater at (pH = 6), while the value of (Q) decreases when the values of (pH) are higher or lower than (6). This is due to the fact that the metal ion in the basic medium forms gelatinous compounds that precipitate In the form of metal hydroxides, but in the acidic medium, metal ions separate from the surface of the adsorbent material, and this leads to a decrease in the value of (Q) and the reason for this decrease is the competition between hydrogen ions, which increases with the increase in acidity and metal ions in the solution, for the binding sites in polyhydroxamic acid present in the polymer and this leads to a decrease in the adsorption capacity with an increase in acidity [19] , as shown table(5,6) - fig(8,9)

Measuring temperature of adsorption of Metal Ions' PHA : as shown table(9,10) the studied ion adsorption heat values before and after adding nano carbon, the temperature of adsorption (H_e) is calculated using the Clausius-Clapeyron equation for chemical adsorption **.** It is possible to measure the adsorption temperature as an equilibrium process by obtaining the value of the adsorption capacity for metallic ions at various temperature degrees, for example, (T_1 and T_2), and obtaining the (C_{e1}, C_{e2}) for achieving the same breakage that is related to the covered surface by using the equation below[20]

$$ln\frac{C_{e2}}{c_{e1}} = \frac{H_e}{R}\left(\frac{T_2 - T_1}{T_{2*}\,T_1}\right)$$

Conclusion

The methyl methacrylate polymer was prepared, and polyhydroxamic acid was prepared from the methyl methacrylate polymer. The adsorption capacity of ferric and ferrous ions was determined before and after the addition of nano carbon, and through the results, the adsorption capacity is higher in the presence of nano carbon. The adsorption capacity also increases with increasing time, with the highest value being five hours, the adsorption capacity also increases with the decrease in temperature and decreases with the increase in temperature of the studied metal ions because this leads to the separation of metal ions from the surface of the adsorbent material, the adsorption capacity is higher at the acidity function(6-8). Through the values of the adsorption heat, it was found that the adsorption was physical, and it was also found that the values of the heat adsorption of the ions studied by polyhydroxyamic acid when adding nano carbon are higher than before the addition .

Table1: Impact of the time upon the capacity of adsorption that is related to metal ions via poly (M.M.A) hydroxamic acid

Metal Ions	Q_e(mg/g)				
	1hrs	2hrs	3hrs	4hrs	5hrs
Fe^{+2}	25.20	29.84	32.12	35.75	37.20
Fe^{+3}	24.11	28.54	31.93	34.29	36.70

Table2 : The values of the adsorption capacity of metal ions by polyhydroxamic acid under the influence of time in the presence of nano carbon

Metal Ions	Q_e(mg/g)				
	1hrs	2hrs	3hrs	4hrs	5hrs
Fe^{+2}	28.92	32.54	36.43	37.99	39.67
Fe^{+3}	27.87	30.77	35.31	37.01	38.85

Table3: The values of the adsorption capacity of metal ions by polyhydroxyamic acid under the influence of temperature

Metal Ions	Q_e(mg/g)			
	10°C	30°C	50°C	70°C
Fe^{+2}	37.20	33.70	29.86	21.75
Fe^{+3}	36.70	33.99	26.95	18.66

Table4: The values of the adsorption capacity of metal ions by polyhydroxyamic acid under the influence of temperature in the presence of nano carbon

Metal Ions	Q_e(mg/g)			
	10°C	30°C	50°C	70°C
Fe^{+2}	39.11	36.42	33.98	25.09
Fe^{+3}	38.76	35.98	29.58	22.10

Table5: Effect of the values of the adsorption capacity of metal ions by polyhydroxyamic acid on the effect of the pH function

Metal Ions	Q_e(mg/g)				
	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
Fe^{+2}	18.69	25.70	38.00	34.70	29.54
Fe^{+3}	16.45	23.73	37.12	32.02	28.26

Table6: Effect of the values of the adsorption capacity of metal ions by polyhydroxyamic acid on the effect of the pH function in the presence of nano carbon

Metal Ions	Qe(mg/g)				
	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
Fe^{+2}	22.50	28.41	39.89	35.91	32.49
Fe^{+3}	20.31	26.79	38.93	35.04	31.62

Table7: Heat adsorption values for ferrous and ferric ions

Metal Ions	Temperature of Adsorption (Kcal.mol^{-1})
Fe^{+2}	12.502
Fe^{+3}	9.260

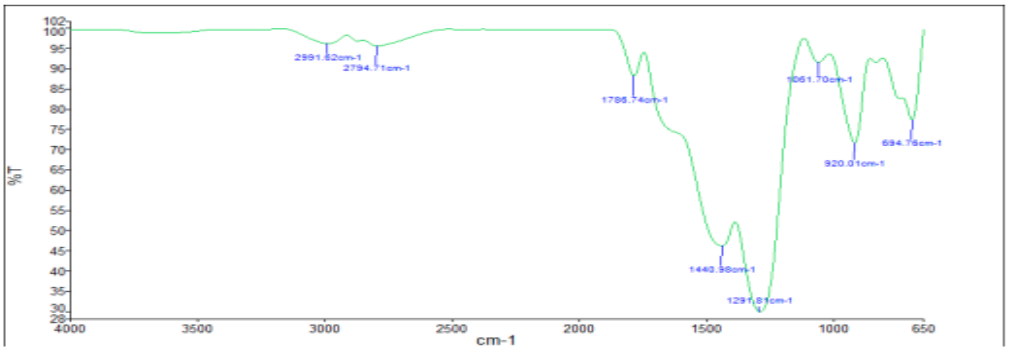


Fig1: Infrared spectrum of methyl methacrylate polymer

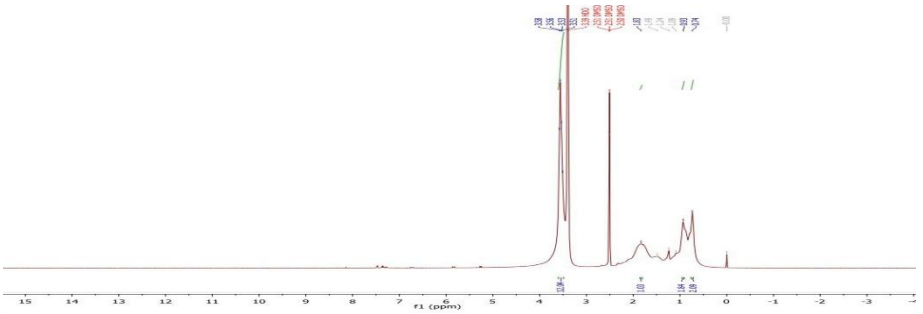


Fig2: Nuclear magnetic resonance spectrum of the methyl methacrylate polymer

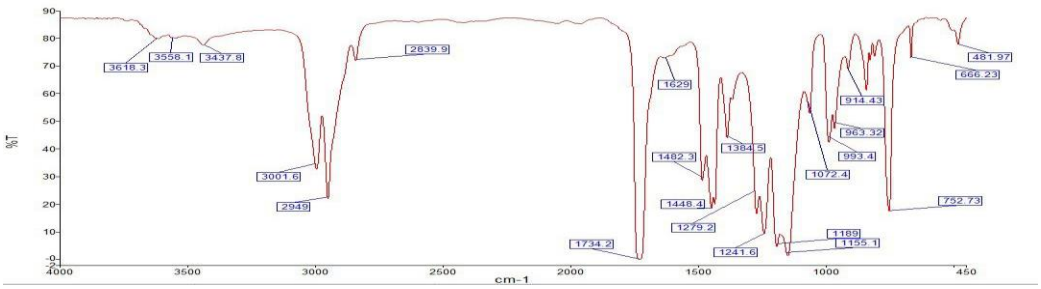


Fig3: Infrared spectrum of polyhydroxy acid

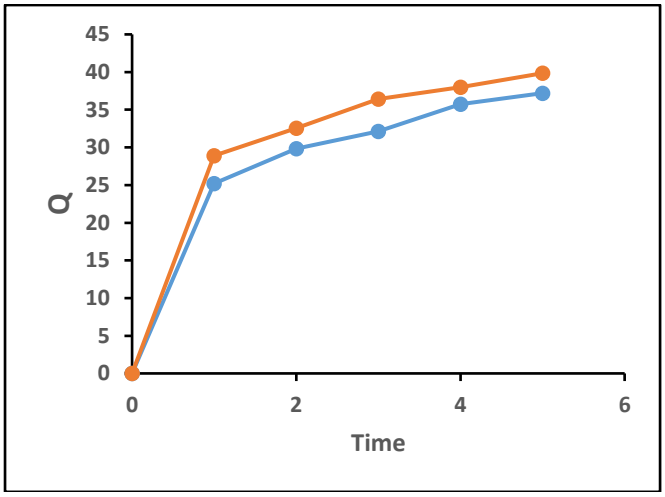


Fig4: The adsorption capacity of ferrous ion by polyhydroxyamic acid before and after the addition of nanocarbons at the effect of time

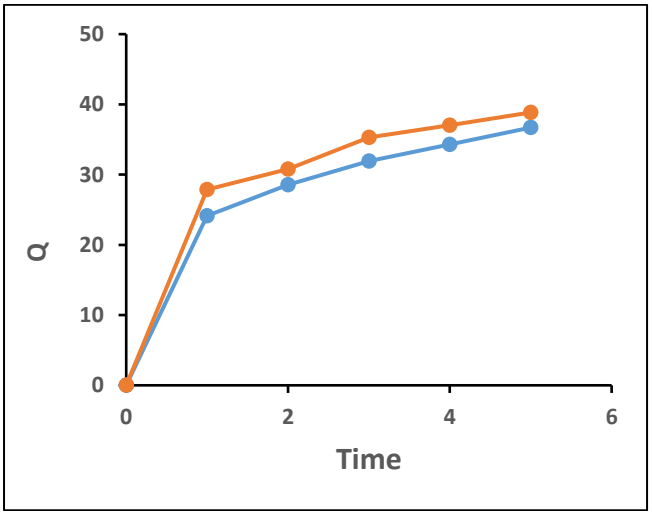


Fig5: Adsorption capacity of ferric ion by polyhydroxyamic acid before and after the addition of nanocarbons at the effect of time

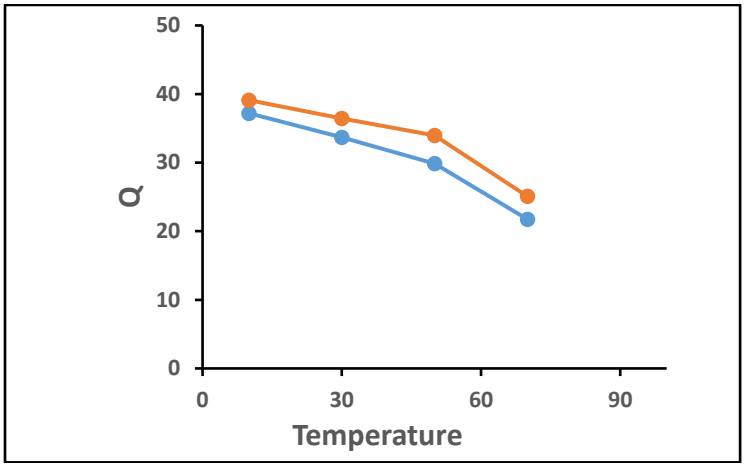


Fig6: The ferrous ion adsorption capacity by polyhydroxyamic acid before and after the addition of nano carbon under the influence of temperature.

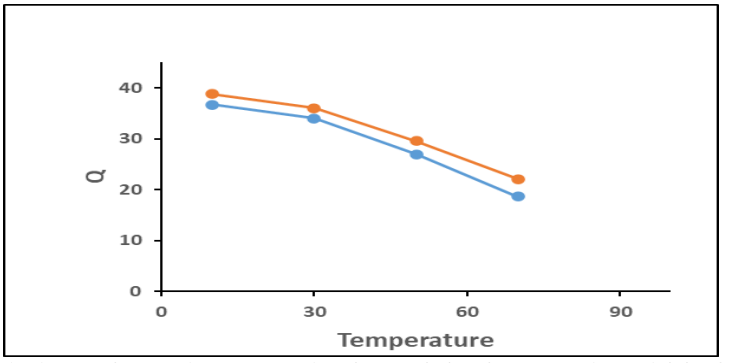


Fig7: The ferric ion adsorption capacity by polyhydroxyamic acid before and after the addition of nano carbon under the influence of temperature.

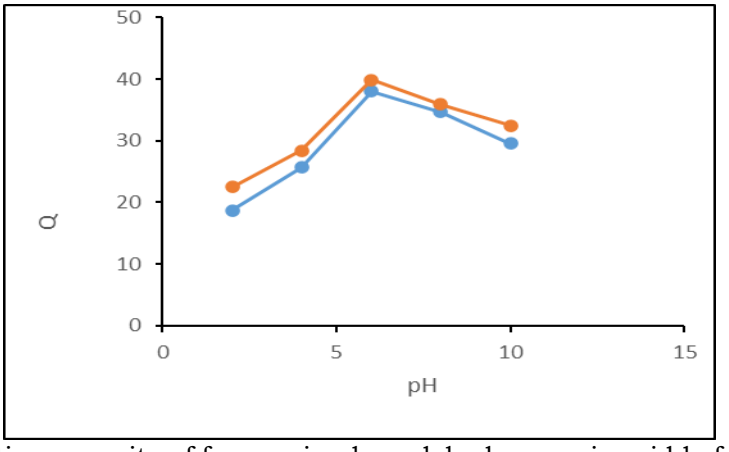


Fig8: Adsorption capacity of ferrous ion by polyhydroxyamic acid before and after the addition of nano carbon when the acidity function is affected

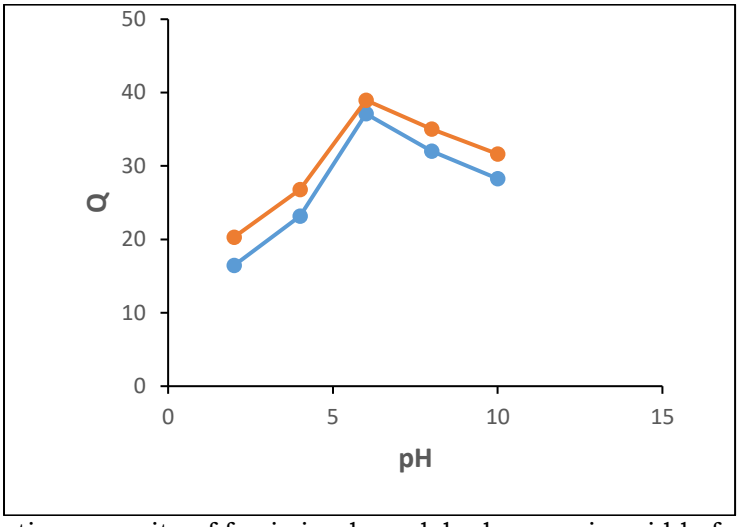


Fig9: Adsorption capacity of ferric ion by polyhydroxyamic acid before and after the addition of nano carbon when the acidity function is affected.

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