Preparation and Manufacture of Some Composite Materials and Study of their Use in Water Purification from Organic Compounds and Heavy Metallic Elements

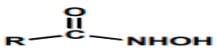
Saddaa Abed Abedullah Jamal
Chemistry Department: College of Education for Women, University of Anbar, Ramadi, Iraq
Email: saddaa.abd62@gmail.com

Abstract

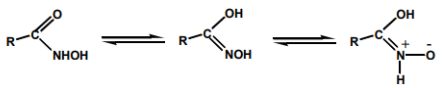
In this research ,the composite materials were prepared and manufactured in several stages ,including the first stage the preparation of poly methyl methacrylate , using the polymerization of free radicals by the initiator Benzoyl Peroxide at a temperature (70oC) and a conversion rate of 10%, and then converting the resulting polymer to Polyhydroxamic acid by treating the polymer with Hydroxylamine Hydrochloride in an alkaline medium (pH = 13) with the use of Potassium Hydroxide with thermal escalation at a temperature of (70oC) for a period of (100) hours. The resulting compound was diagnosed using IR-FT spectroscopy, Polyhydroxyamic acid was mixed with Nano Carbons. The adsorption Capacity of some heavy metal ions from their aqueous solutions, such as (Fe3+, Cu2+,Ni2+,Co2+, Cr2+,V3+,Pb2+ and Cd2+) ions by composite materials before and addition of Nano – Carbon , was determined . Also the Study of the adsorption capacity of Acetic Acid and Oxalic acid Oxalic acid on Polyhydroxyamic Acid before and after treatment with Nano Carbon. study showed the adsorption capacity values were very low or almost non-existent with Polyhydroxamic acid. While there was a significant increase in the values of adsorption capacity of Acetic Acid and Oxalic Acid of Polyhydroxyamic Acid treated with Nano Carbon and camping in the following results.

1. Introduction

Hydroxamic acid and substituted nitrogen derivatives are considered organic compounds, and they use two-tooth clicandites, and they can be used in chromatography, for the determination of the metal ion and Hydroxamic Acid [1,2] .And that the general chemical formula of hydroxamic acids is they use two-tooth clicandites, and they can combine with Fe+3 and Cu+2 to give colored complexes that can be used in [3-5]



Hydroxamic Acid derivatives and polymers are commonly employed in industrial, medicinal, textile, agricultural and pharmaceutical areas, and are produced for a number of reasons[6]. Despite its vital features, poly (Hydroxamic Acid) is one of the few compounds whose properties have been characterized, making it difficult to find the correct chemical composition because it has three similar shapes in chemical compositions, as indicated in the structural formulations below [7].



The essential ideas of Hydroxamic Acid production, reactions, and composition were studied for the first time by researcher (H-Lossen) general (1986), Recent research on Hydroxamic Acid has shown a method for separating the natural chemicals present in algae and fungi that serve as antibiotics and growth factors against cancer cell proliferation [8-10] Hydroxamic Acid also absorbs iron during metabolic processes, and it plays a key role in Iron transport in bacteria, where iron is transferred via a base molecule called Ferrioxamines [11]. Chelating resins with a Hydroxamic Acid group can also be beneficial to the environment Toxic trace metals are being monitored. It's also possible to extract rare elements from seawater using poly (Hydroxamic acid) resin [12,13]. In biological and sensitive solutions, the poly (Hydroxamicacid) can be used to test numerous elements quantified in chromatography and to separate various I ions such as Copper (II), Lead(II), Cobalt(II), and Iron(III)[14]. The poly Hydroxamic acid chelating resins' hydroxyl and oxime groups enable them to chelate for a wide range of metal ions and performance [15].

Experimental

2. Materials

Hydroxyl Amine Hydrochloride (97%), Methyl Methacrylate (99% HIMEDIA), potassium hydroxide GPR, initiator utilized Benzoyl Peroxide (B.P), (solvent gasoline 99%), (ethanol99.8%), sodium sulfate anhydrous and nitrogen gas, Cadmium Sulfate, Chromium (III) Chloride, Nano Carbon powder (>99).

Instruments

A water bath and delicate balance, Shaker water

doi.org/10.31838/hiv23.01.113 Received: 02.09.22, Revised: 03.10.22, Accepted: 08.12.22

bath, infrared, and centrifuge, ultra-violet, as well as visible radiation device type device are utilized to complete the investigation. GBC, thermometer, and pH meter, Atomic Absorption Spectrophotometer (AAS)

Preparation of Poly (Methyl Methacrylate)

The Poly(MMA) has been synthesized with the use of the polymerization of the free radicals, Using the initiator Benzoyl Peroxide (B.P) at a temperature of (70°C), (30) ml of Methyl Methacrylate and (0.03) g of benzoyl peroxide were placed in a dry spherical flask with a tight rubber stopper and prepared for this purpose, a stream of nitrogen gas was passed for a period (10) minutes to expel the dissolved oxygen The flask has been immersed into water bath at degree (70°C) for (15) minutes, then the flask was lifted and suddenly cooled in a beaker containing ice. Then the polymer formed was precipitated using slightly acidified ethanol. Concentrated hydrochloric acid was filtered using a Glass Countered Filter, dried in a drying oven, and then weighed several times until the weight was stable. Person using the FT.IR [16,17]

Hydroxamic Acid Preparation of Poly (Methyl Mathacrylate)

(14) grams of Hydroxylamine Hydrochloride was dissolved in (70) ml in a ratio of (5:1) water: ethanol and (11) grams of Potassium Hydroxide dissolved in a little distilled water by cooling the mixture, taking into account not to allow the temperature to rise more than (10°C) by placing the mixture in an ice bath to precipitate Potassium Chloride, which is removed by filtration. The filtrate, which is Hydroxylamine, was mixed with (20) grams of the polymer prepared in the previous step, Poly Methyl acrylate, potassium hydroxide solution was added until the PH was equal to (13-12). The final product was collected by sedimentation and washed with acidified distilled water [18,20], The poly (MMA) HA has been identified with the use of an (FTIR).

Addition of Nano carbons to poly (Methyl Methacrylate) Hydroxamic Acid

(5g) of poly (MMA) HA acid prepared from the Polymer methyl Methacrylate Hydroxamic Acid was dissolved in (5ml) of Chloroform, then (5g) of Nano Carbon was added to the contents of the previous beaker, mixed well and left to dry [21] .

Studying of Applications of poly (MMA) HA

Determining Ferric ion (Fe^{3+}) Sorption Capacity by the Poly (MMA)HA

The (Fe^{3+}) adsorption capacity was studied by mixing (50 ml) of a Feeric ion solution at a concentration of (200 ppm) with (1 g) of Poly Hydroxyamic Acid with continuous shaking for 5 hours, at 25°C, the precipitate is separated using a centrifuge and then the residual concentration of adsorption in the filtrate was determined by the absorber Atomic and ultraviolet visible, The equilibrium concentration of the ion was determined. Similarly, we study the capacity of the adsorption of Fe^{3+}. As for the adsorption capacity, it can be calculated from the following equation [22]:

Sorption capacity:

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

In which Q_e(mg/g) represent the metal ion amount that had been sorbet; C_0 and C_e represent the initial and equilibrium concentration regarding metal ion in solution (mg/L); V(L) represent the volume of the solution and M (g) represent PMMAHA weight. In the same way, the adsorption capacity (Sorption) was determined for Copper ions (Cu^{2+}), Nickel (Ni^{2+}), Cobalt (Co^{2+}) and Chromium(Cr^{3+}) .

Determining Ferric ion (Fe^{3+}) Sorption Capacity After Addition of Nano carbons to by the Poly (MMA)HA.

The (Fe^{3+})adsorption capacity was studied by mixing (50 ml) of a (Fe^{3+}) solution at a concentration of (200 ppm) with (1 g) of Made of Poly(Hydroxamic acid), treated with Nano-Carbon with continuous shaking for 5 hours, at 25°C, the precipitate is separated using a centrifuge and then the residual concentration of adsorption in the filtrate was determined by the absorber Atomic and ultraviolet visible, The equilibrium concentration of the ion was determined. Similarly, we study the capacity of the adsorption of Fe^{3+}. As for the adsorption capacity, it can be calculated from the following equation:

Sorption capacity:

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

In the same way, the adsorption capacity (Sorption) was determined for Copper ions (Cu^{2+}), Nickel (Ni^{2+}), Cobalt (Co^{2+}) and Chromium(Cr^{3+})

Study of the adsorption capacity of acetic acid on Poly (Hydroxyamic acid before and after treatment with Nano Carbon

One gram of Poly(Hydroxyamic Acid)was added to 50 ml of (0.5N) Acetic Acid, the mixture was placed in a water bath at (25C) and the mixture was shaken for (30) minutes. The filtrate separated using centrifugation. The filtrate was titrated using Sodium Hydroxide and in the presence of Phenolphthalein guide to find out the concentration of acetic acid remaining after adsorption (N_1). Where the concentration of the adsorbent (N_2) on (PMMA-HA) was calculated according to the following equation

$$N_2 = N_2 - N_1$$

The adsorbed quantity was calculated in g/L units using the following relationship:

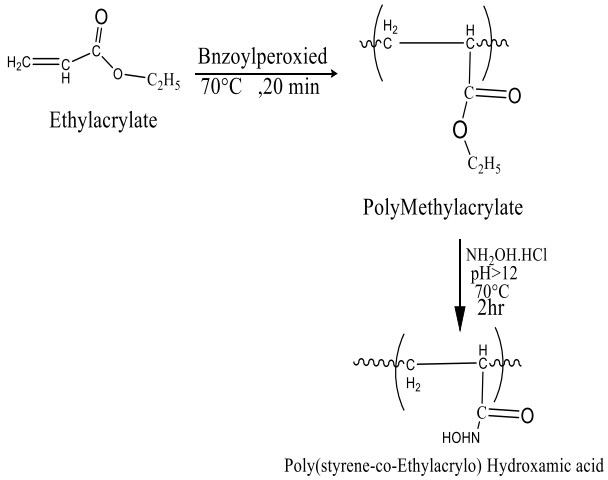
$$C_2 g/L = (N_2 - N_1) \times Ew$$

In the same way, the adsorption capacity of Oxalic acid was determined on (HA-PMMA) before and after the addition of Nano-Carbon.

3. Results and Discussion

Poly (Hydroxamic Acid) Characterization

In this research, (Poly Methyl Methacrylate) Hydroxamic Acid was prepared using free radical polymerization by the initiator Benzoyl Peroxide (B.P) and at a temperature of (70°C).



Poly(styrene-co-Ethylacrylo) Hydroxamic acid

The (PMMAHA) was identified via FT -IR spectroscopy. FT-IR spectrum Fig (1,2) of the (PMMAHA) graph shows a new absorption bond of the hydroxamic (O-H), carbonyl (C=O) and amide (N-H) groups at (3558, 1734, 3437).

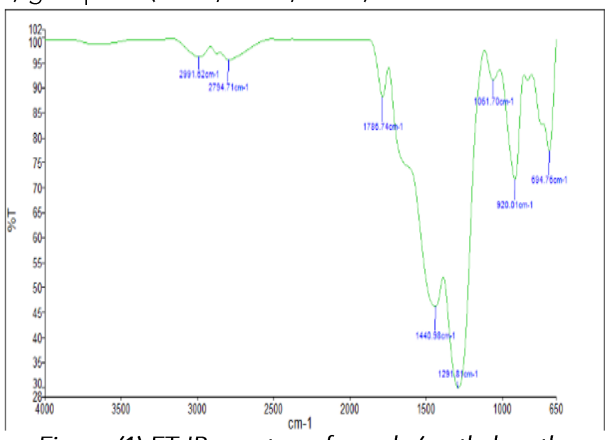


Figure (1) FT-IR spectrum for poly (methyl metha acrylate).

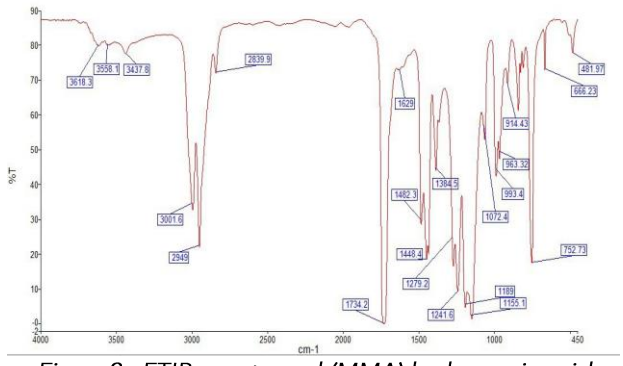
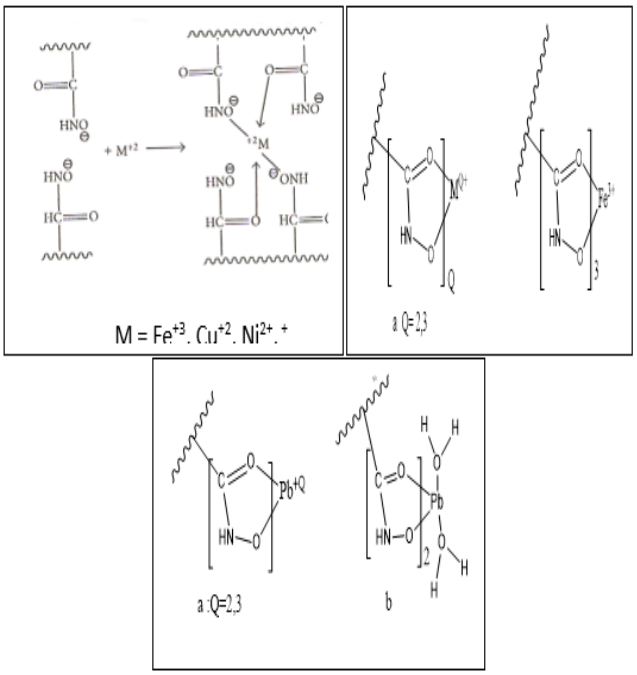


Figure2 : FTIR spectra pol (MMA) hydroxamic acid

Study of the Adsorption Capacity of heavy metal ions on Poly Hydroxyamic Acid (PHA):

Hydroxamic Acid compounds are bi-ligands (O,O, Bivalent Ligand) with a single negative charge and by losing a proton of the Hydroxyl group, where each ligand is bonded with the metal ion (M) through the Oxygen of the Hydroxyl group, as well as through the Oxygen of the Carbonyl group of the Hydroxamic Acid as a result of this Synergy A stable pentagonal ring is formed, in which the metal ion is part of this ring, as shown in this diagram (20,21,22)



With a single negative charge, compounds of the Hydroxamic Acid have been classified as binary Bi-dental chelating ligands. In the case when an acid hydroxyl proton is lost, each one of the ligands is joined to metallic ion (M) by carbonyl and hydroxyl groups' oxygen of Hydroxamic Acid. In addition, the ion of the metal has been contained within a pentagonal loop, which results in a very stable pentagonal loop. The capacity of the PHA adsorption regarding heavy metal ions can be assessed by measuring the metallic ion's remaining concentration (Ce) in separation filter after the treatment with the PHA , which reflects the equilibrium concentration [21]. Tables (1-1) an d (1-2) show the adsorption capacity(Q) of heavy ionic metal elements Ferric ion (Fe3+) Copper ions (Cu2+), Nickel (Ni2+), Cobalt (Co2+) and Chromium(Cr3+) on(PMMA-HA) before and after treatment with Nano-carbon at a temperature (25°C) Celsius and for a period of five hours, where the results showed There is a significant difference in the adsorption capacity(Q) before and after the treatment with nano- carbon, where there was a significant increase in the adsorption capacity(Q) values for heavy metal ions from their aqueous solutions on poly Hydroxyamic acid (PMMA-HA) treated with Nano-Carbon, as shown in the following results [21].

(Table 1): the valuesof the initial concentrations (C°) and equilibrium concentrations (Ce) and (retention capacity (q)) of metal ions mediated by Polyhydroxamic acid at 25°C)) (5 h).

Metal Ion	C_o ppm	C_e ppm	Q_e (mg/g)
Fe3+	200	80	6
Cu2+	200	92	5.4
Ni2+	200	105	4.75
Co2+	200	96	5.2
Cr3+	200	110	4.5

Adsorption Conditions:

1- Total molar volume 50 ml. 2- Adsorption temperature (25°C). 3- Adsorption period (5h)

Table (1-2): the values of the initial concentrations (C°) and equilibrium concentrations (Ce) and (retention capacity (q)) of metal ions mediated by(M.M.A) Hydroxamic Acid with Nano Carbon at 25°C)) (5 h).			
Metal Ion	C_o ppm	C_e ppm	Q_e (mg/g)
Fe^{3+}	200	55	7.25
Cu^{2+}	200	68	6.6
Ni^{2+}	200	65	6.75
Co^{2+}	200	74	6.3
Cr^{3+}	200	83	5.85

Adsorption Conditions

1- Total molar volume 50 ml.
2- Adsorption temperature (25°C).
3- Adsorption period (5h)

Study of Adsorption capacity of some organic acids on Poly (Hydroxyamic Acid) before and after treatment with Nano Carbon.

Tables (1-3) and (1-4) show the values of adsorption capacity (Q) of Acetic Acid and Oxalic acid on Polyhydroxamic Acid (PMMA_HA) before and after treatment with nano carbon at a temperature (25°c) and for a period of shaking for half an hour. where the results were shown A large difference in the values of the adsorption capacity of organic acids such as Acetic aAcid and Oxalic Acid on Polyhydroxyamic acid (PMMA-HA) where the adsorption capacity values were very low or almost non-existent with Polyhydroxamic acid. While there was a significant increase in the values of adsorption capacity of acetic acid and oxalic acid of Polyhydroxyamic acid treated with Nano Carbon and camping in the following results [23].

Table (1- 3): the values of the initial adsorption capacity of Acetic Acid and oxalic acid on Polyhydroxyamic Acid before treatment with Nano Carbon.							
Acid			Initial acid concentration before adsorption (No	Initial acid concentration before adsorption by unit Co(g/L) Co =No× E w	Concentration of the acid adsorbed acid (N2) N2= No-N1	Concentration of the acid adsorbed acid (N2) by unit C2(g/L) C2=N2×Ew	adsorption capacity(Q)mg/gQ= (C –C1) V ml $\boldsymbol{Q} = \frac{C_o - C_1)Vml}{g}$
Acetic acid	0.5	30	0.45	27	0.05	3	0.15
Oxalic acid	0.5	45	0.47	42.3	0.03	7	0.135

Table(1- 4): the values of the initial adsorption capacity of Acetic acid and oxalic acid on Poly(Hydroxyamic Acid) after treatment with Nano Carbon							
Acid	Initial acid concentration before adsorption (No)	Initial acid concentration before adsorption by unit Co(g/L) Co =No× Ew	Initial acid concentration after adsorption (N1)	Initial acid concentration after adsorptionby unit C1(g/L) C1=N1×Ew	Concentration of the acid adsorbed acid (N2) N2= No-N1	Concentration of the acid adsorbed acid (N2) by unit C2(g/L) C2=N2×Ew	adsorption capacity (Q)mg/gQ= (Co –C1) Vml $\boldsymbol{Q} = \frac{C_o - C_1)Vml}{g}$
Acetic acid	0.5	30	0.32	19.2	0.18	9.1	0.54
Oxalic acid	0.5	45	0.34	30.6	0.16	14.4	0.72

4. Conclusions

1- The Poly (Methyl Methacrylate) (MMA) can be converted into Poly (Hydroxamic Acid).
2- Polymers of hydroxamic Acid contain many groups of Aydroxamic Acid, which have double bonds that can bind with heavy metal ions.
3- Hydroxamic Acid polymers are distinguished by their ability to adsorb many heavy metal ions from aqueous solutions.
4- By treating the hyroxamic acid polymers with carbon nanotubes, this led to an increase in their efficiency on the adsorption of many heavy metal ions from aqueous solutions.

Recommendation

1- Study of preparation of other types of Polys (Hydroxamic Acid.
2- Study of adsorption isotherms at different temperature ranges and for specific metallic elements by Poly(Hydroxyambic Acid) after treatment with Nano Carbon.

References

[1] Panpatte, D. G., & Jhala, Y. K. (Eds.). (2019). Nanotechnology for agriculture: crop production & protection. Springer Nature.
[2] Baby, R., Saifullah, B., & Hussein, M. Z. (2019). Carbon nanomaterials for the treatment of heavy metal-contaminated water and environmental remediation. Nanoscale research letters, 14(1), 1-17
[3] Bíró, L., Buglyó, P., & Farkas, E. (2022). Diversity in the Interaction of Amino Acid-and Peptide-Based Hydroxamic Acids with Some Platinum Group Metals in Solution. Molecules, 27(3), 669
[4] Tulaib, S. F., Abd Khthem, M., & Hussien, M. O. (2010). Preparation of new complexes for hydroxamic acids with Iron; Copper and Cobalt and studying their spectrum properties and biological

activity
[5] Jamal, S. A. A., & Alywee, A. K. (2012). Study of the Sorption Kinetics of Fe (III) by Polyhydroxamic acid Chelating Exchanger Prepared from Polystyrene-Co-Methyl methacrylate. Journal of Applicable Chemistry, 1(3), 433-441
[6] Ibrahim, F. K., & Abedullah, S. A. (2021). Preparation of poly hydroxamic acid from poly (styrene–methyl metha acrylate) and study of the kinetics of nickel ion sorption by the prepared acid. structure, 15(2), 45-52
[7] Mzinyane, N. N., Ofomaja, A. E., & Naidoo, E. B. (2021). Synthesis of poly (hydroxamic acid) ligand for removal of Cu (II) and Fe (II) ions in a single component aqueous solution. South African Journal of Chemical Engineering, 35(1), 137-152
[8] Ruiz-Torres, V., Encinar, J. A., Herranz-López, M., Pérez-Sánchez, A., Galiano, V., Barrajón-Catalán, E., & Micol, V. (2017). An updated review on marine anticancer compounds: The use of virtual screening for the discovery of small-molecule cancer drugs. Molecules, 22(7), 1037
[9] Pal, D., & Saha, S. (2012). Hydroxamic acid–A novel molecule for anticancer therapy. Journal of advanced pharmaceutical technology & research, 3(2), 92
[10] Giddings, L. A., & Newman, D. J. (2022). Extremophilic Fungi from Marine Environments: Underexplored Sources of Antitumor, Anti-Infective and Other Biologically Active Agents. Marine Drugs, 20(1), 62
[11] Nikolaou, A., Ninou, I., Kokotou, M. G., Kaffe, E., Afantitis, A., Aidinis, V., & Kokotos, G. (2018). Hydroxamic acids constitute a novel class of autotaxin inhibitors that exhibit in vivo efficacy in a pulmonary fibrosis model. Journal of Medicinal Chemistry, 61(8), 3697-3711
[12] Alakhras, F. A., Dari, K. A., & Mubarak, M. S. (2005). Synthesis and chelating properties of some poly (amidoxime-hydroxamic acid) resins toward some trivalent lanthanide metal ions. Journal of applied polymer science, 97(2), 691-696
[13] Zhang, Q. (2010). Synthesis of hydroxamic acid resin and its adsorption characteristics for acid mine drainage. Cent. South Univ, 26-27
[14] Abedullah Jamal, S. A., Hmadi, W. F., & Al-Obaidi, O. (2020). Preparation Some of Hydroxamic Acid Derivatives from Honey Wax Compounds and Study the Biological Activity on Cancerous Tumors. Systematic Reviews in Pharmacy, 11(2)
[15] Rahman, M. L., Sarjadi, M. S., Guerin, S., & Sarkar, S. M. (2022). Poly (amidoxime) Resins for Efficient and Eco-friendly Metal Extraction. ACS Applied Polymer Materials, 4(4), 2216-2232
[16] Ferruti, P., Bettelli, A., & Fere, A. (1972). High polymers of acrylic and methacrylic esters of N-hydroxysuccinimide as polyacrylamide and polymethacrylamide precursors. Polymer, 13(10), 462-464.
[17] Gamal, S. A. A. (2013). Preparation of poly (acro-yellow hydroxamic acid) from the polymer (methyl acrylate) and study use it in the water purification from heavy metal elements. JOURNAL OF EDUCATION AND SCIENCE, 26(5), 314-324
[18] Rikiishi, H., Shinohara, F., Sato, T., Sato, Y., Suzuki, M., & Echigo, S. (2007). Chemosensitization of oral squamous cell carcinoma cells to cisplatin by histone deacetylase inhibitor, suberoylanilide hydroxamic acid. International journal of oncology, 30(5), 1181-1188
[19] Jamal, S. A. A. (2012). Study of the sorption kinetic of Fe (III) by poly (Hydroxamic acid) chelating exchanger prepared from poly (Styrene-Co-Ethylacrylate). Iraqi National Journal Of Chemistry, 47
[20] Ali, L., Ahmad, M., Aamir, M. N., Minhas, M. U., Rasul, A., Yousuf, M., ... & Sohail, M. (2019). Venlafaxine-loaded sustained-release poly (hydroxyethyl methacrylate-co-itaconic acid) hydrogel composites: their synthesis and in vitro/in vivo attributes. Iranian Polymer Journal, 28(3), 251-258
[21] Mohammed,N,B., & Abedullah Jamal, S. A., (2022). Studying the effect of adding nano-carbon to poly (hydroxamic acid) prepared from poly (methyl methacrylate) on the adsorption capacity of Ferrous andFerric ions.InterNational Journalof Health sciences,6(S4)6611-6622.
[22] Cao, X., Wang, Q., Wang, S., & Man, R. (2020). Preparation of a novel polystyrene-poly (hydroxamic acid) copolymer and its adsorption properties for rare earth metal ions. Polymers, 12(9), 1905.
[23] Yayayürük, A. E. (2017). The Use of Acrylic-Based Polymers in Environmental Remediation Studies. In Acrylic Polymers in Healthcare. IntechOpen.