# Studying the effect of adding nano-carbon to poly (hydroxamic acid) prepared from poly (methyl methacrylate) on the adsorption capacity of chromium (III) and cadmium (II) ions.

Nibras Basim Mohammed[1], Sadaa Abed Abedullah[2]
[1]Chemistry Department: College of Education for Pure Sciences, University of Anbar, Ramadi, Iraq
[2]Chemistry Department: College of Education for Women, University of Anbar, Ramadi, Iraq.
edw.nibras.basim@uoanbar.edu.iq
edw.saddaa.abd62@uoanbar.edu.iq

## Abstract

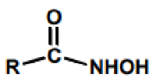
Using the polymerization of free radicals by the initiator bnzoyl perduoxide at a temperature (70oC) and a conversion rate of 10%, and then converting the resulting polymer to polyhydroxamic acid by treating the polymer with hydroxylamine hydrochloride in an alkaline medium (pH = 13) with the use of 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 nanocarbons. Polyhydroxamic acid was used to assess the retention capacity of chromium (Cr+3) and cadmium (Cd+2) ions before and after adding the nanocarbon. The influence of time, temperature, and pH on the retention capacity (Qe) of chromium and cadmium heavy metal ions was also investigated. The heat of adsorption was determined, and through the values of the heat of adsorption for chromium and cadmium ions, it was found that the adsorption is physical. The adsorption capacity was higher in the presence of nanocarbons , 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.

Keywords: Nano carbon, Poly hydroxamic acid, Adsorption

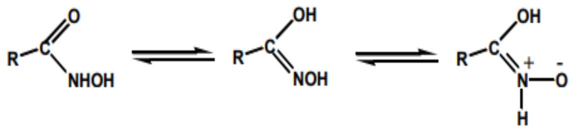
## 1. Introduction

With regard to being able to tackle a number of environmental concerns by regulating the size and structure of materials at the nanoscale, nanotechnology is regarded one of the advanced technologies of the 21 century [1]. Carbon nanomaterials are distinct in that they have a large surface area and are biodegradable. The simplest and most beneficial treatment for the environment [2].

The family of the hydroxamic acid is well-known due to its propensity to form stable chelates with a variety of the ions of the heavy metals [3, 4], it can form colorful complexes with iron(III) and copper(II), and it can be utilized in chromatography to detect the metal ion and hydroxamic acid [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]. The aim of the research preparation of polyhydroxyamic acid from the

doi.org/10.31838/hiv22.02.194 Received: 03.05.22, Revised: 02.05.22, Accepted: 06.08.22

polymer methyl methacrylate, and study of the effect of adding nano carbon to the prepared polyhydroxyamic acid on the adsorption capacity of chromium and cadmium ions and study of some factors affecting the adsorption capacity

## 2. Experimental 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 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 Abdorption SpecTrophotometer (AAS)

### Preparation of Poly (Methyl metha acrylate)

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 metha acrylate 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 Contere Filter, dried in a drying oven, and then weighed several times until the weight was stable. Person using the FTIR [16, 17].

### Hydroxamic Acid Preparation of Poly (Methyl matha acrylate)

(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, polymethyl 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).

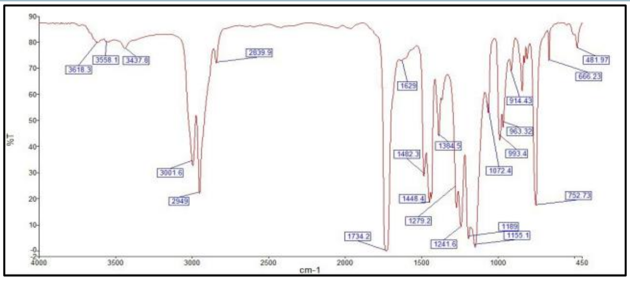


*Figure 1. FTIR spectra pol (MMA) hydroxamic acid*

### Addition of nanocarbons to poly (Methyl metha acrylate) 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 nanocarbon was added to the contents of the previous beaker, mixed well and left to dry.

### Studying of Applications of poly (MMA) HA

#### Determining chromium (III) ion's Sorption Capacity by the Poly (MMA)HA

The chromium (III) ions adsorption capacity was studied by mixing (50 ml) of a chromium ion solution at a concentration of (400 ppm) with (0.5 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 cadmium (II) ions. As for the adsorption capacity, it can be calculated from the following equation:

**Sorption capacity:**

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

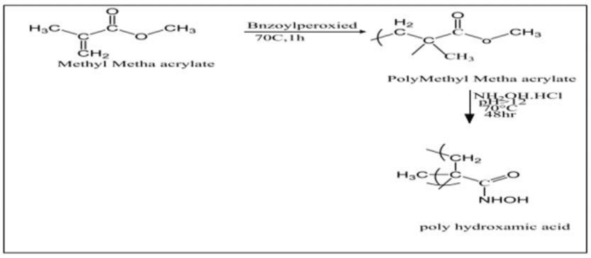
In which $Q_e$(mg/g) represent the metal ion amount that had been sorbed; $C_0$ and $C_e$ represent the initial and equilibrium concentration regarding metal ion in solution (mg/L); V(L) represent the volume of the solution and M (g) represent PMMAHA weight.

The impact of temperature has been investigated by making a series of the solutions with similar proportions through combining 1 g of the poly (MMAHA) with 50mL of the chromium (III) ions at a concentration of (400 ppm). Each one of the solutions was placed in a thermocouple at temperatures of 10, 30, 50, and 70 degrees Celsius. At each temperature, the adsorption capacity was calculated. The adsorption capacity of ions ($Cd^{+2}$) was specified in the same way. The influence of solution pH and time on poly (MMAHA) adsorption capacity for ions ($Cr^{+3}$, $Cd^{+2}$) was also studied.

## 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 (70oC).




*The (PMMAHA) was identified via FT -IR spectroscopy. FT-IR spectrum Fig1 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).*

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

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 ($C_e$) in separation filter after the treatment with the PHA , which reflects the equilibrium concentration [21].

Impact of Time on PHA's Sorption Capacity before and when adding nanocarbon:

Table1,2, depicts impact of time on total capacity of sorption regarding cadmium ion $Cd^{+2}$ and chromium ion $Cr^{+3}$ via PHA prior to and following adding nano carbon, as measured by the values of (Q), which rise with time. After five hours, the value (Q) is noticeably greater. The inclusion of nano carbon increases the adsorption ability of PHA.

**Table 1. Impact of the time upon the capacity of adsorption that is related to metal ions via poly (M.M.A) hydroxamic acid**

| Metal Ions | Qe (mg/g) | | | | |
|---|---|---|---|---|---|
| | 1 hr | 2 hr | 3 hr | 4 hr | 5 hr |
| Cr+3 | 15.77 | 19.44 | 22.25 | 25.93 | 30.28 |
| Cd+2 | 13.11 | 15.01 | 18.50 | 22.23 | 25.41 |

**Table 2. the impact of the time upon the capacity of the adsorption that is related to the metal ions via poly (M.M.A) hydroxamic acid with nano carbon**

| Metal Ions | $Q_e$ (mg/g) | | | | |
|---|---|---|---|---|---|
| | 1 hr | 2 hr | 3 hr | 4 hr | 5 hr |
| Cr+3 | 21.43 | 25.63 | 28.71 | 31.17 | 34.22 |
| Cd+2 | 19.44 | 21.27 | 23.88 | 26.42 | 30.04 |

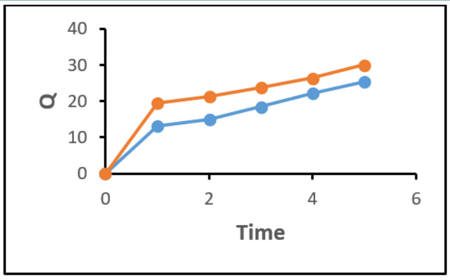



*Figure 2. The initial time's impact on the sorption related to Cr+3 ions by (PHA) before and when adding nano carbon*

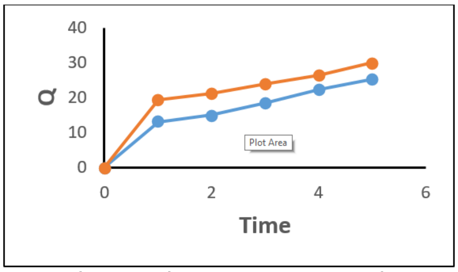



*Figure 3. The initial time's impact on the sorption related to Cd+2 ions by (PHA) before and when adding nano carbon*

### Temperature Effects on PHA's Sorption Capacity before and when adding nanocarbon

The impact of the degree of the temperature on total sorption capacity related to chromium ion Cr+3 and cadmium ion Cd+2 via PHA prior to and following adding nano carbon is shown in Table (3, 4) via values of (Q) that is decreased as the degree of the temperature rises. The existence of nano carbons increases the adsorption ability of PHA.

**Table 3. the impact of the temperature on the capacity of the adsorption that is related to metal ions via poly (M.M.A) hydroxamic acid**

| Metal Ions | 0 | | | |
|---|---|---|---|---|
| | 10° C | 30 °C | 50 °C | 70 °C |
| $Cr^{+3}$ | 30.28 | 25.56 | 19.41 | 15.90 |
| $Cd^{+2}$ | 25.41 | 21.55 | 16.39 | 10.67 |

**Table 4. the impact of the degree of the temperature upon the capacity of the adsorption that is related to metal ions via poly (M.M.A) hydroxamic acid with nano carbon**

| Metal Ions | $Q_t$ (mg/g) | | | |
|---|---|---|---|---|
| | 10° C | 30 °C | 50 °C | 70 °C |
| $Cr^{+3}$ | 35.16 | 30.64 | 24.01 | 18.85 |
| $Cd^{+2}$ | 29.28 | 25.94 | 20.15 | 14.62 |

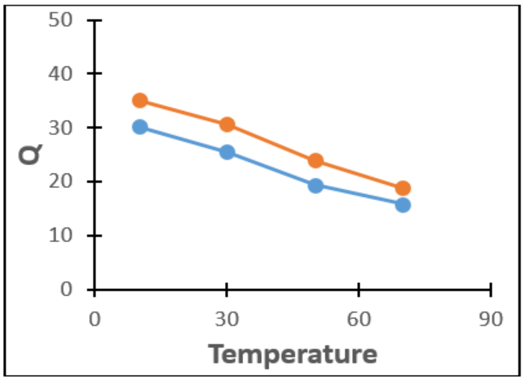



*Figure 4. The initial temperature's impact on the sorption related to Cr+3 ions by (PHA) before and when adding nano carbon*

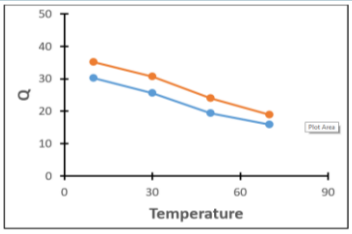



*Figure 5. The initial temperature's impact on the sorption related to Cd+2 ions by (PHA) before and when adding nano carbon*

## Acid Function Effects on PHA's Sorption Capacity before and when adding nanocarbon:

Table (5, 6) exhibits impact of the values of PH on adsorption ion Cr+3 and Cd+2 via PHA prior to and following adding nano carbon, as measured via concentration of equilibrium (Ce), initial concentration values (C°), and capacity of adsorption. We might see that the values of (Q) are higher at (pH=6, pH=8), and that (Q) values fall when (pH) value increases and decreases below (pH=6, pH=8). Which occurs since metallic ion generates gelatinous compound in the basal medium, which then deposits as hydroxides. In an acidic medium, on the other hand, there will be a competition between (H+) ions and those on binding sites in hydroxamic acid groups, linked to polymer, resulting in the reduction in the capacity of the adsorption (Q). The inclusion of nano carbon increases adsorption ability of the PHA.

**Table 5. the impact of the function of the acid upon the adsorption capacity that is related to the metal ions via poly (M.M.A) hydroxamic acid**

| Metal Ions | Qe (mg/g) | | | | |
|---|---|---|---|---|---|
| | (pH)= 2 | (PH)= 4 | (pH)= 6 | (pH)= 8 | (pH)= 10 |
| $Cr^{+3}$ | 11.79 | 17.12 | 31.09 | 25.80 | 21.59 |
| $Cd^{+2}$ | 8.52 | 14.78 | 25.99 | 20.11 | 17.45 |

**Table 6. the impact of function of the acid on capacity of adsorption that is related to metal ions via poly (M.M.A) hydroxamic acid with nano carbon**

| Metal Ions | $Q_e$ (mg/g) | | | | |
|---|---|---|---|---|---|
| | pH= 2 | pH= 4 | pH= 6 | pH= 8 | pH= 10 |
| $Cr^{+3}$ | 15.73 | 20.42 | 34.02 | 29.82 | 25.19 |
| $Cd^{+2}$ | 13.45 | 17.33 | 29.48 | 24.17 | 20.78 |

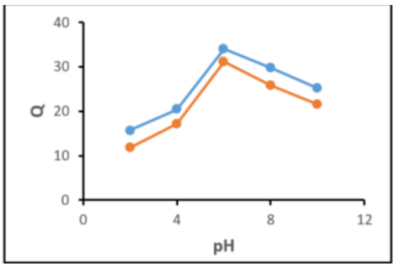



*Figure 6. The initial pH's impact on the sorption related to Cr+3 ions by (PHA) before and when adding nano carbon*

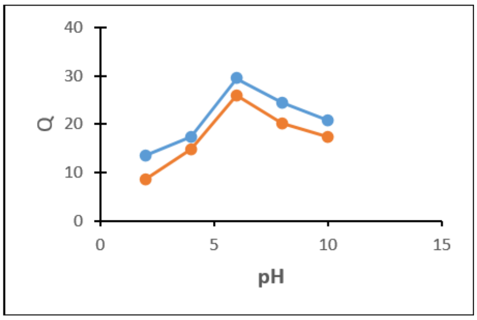



*Figure 7. The initial pH's impact on the sorption related to Cd+2 ions by (PHA) before and when adding nano carbon*

## Measuring temperature of adsorption of Metal Ions' PHA

By using the Clausius-Clapeyron equation on the chemical adsorption, the temperature of adsorption (He) is determined. It is feasible to measure the adsorption temperature as an equilibrium process through obtaining the value of the capacity of adsorption regarding metallic ions at various temperature degrees, for example, (T 1 and T2), to obtain the (C e1, C e2) for achieving same breakage that is related to covered surface through applying equation below [22]:

$$ln\frac{C_{e2}}{C_{e1}} = \frac{He}{R}\left(\frac{T_2 - T_1}{T_2 \cdot T_1}\right)$$

The adsorption temperature is represented by (He). Ce1, Ce2 are the equilibrium concentrations. General constant for the gases is R, and it equals 2cal/mol. The adsorption temperature regarding chemical reaction can be calculated using the above equation, as can be seen in (Table 7)

**Table 7. the impact of the adsorption of heat (He)**

| Metal Ions | Adsorption Temperature Cal/mol |
|---|---|
| $Cr^{+3}$ | 6106.79cal/mol |
| $Cd^{+2}$ | 3613.89cal/mol |

# 4. Conclusion

The polymer (methyl methacrylate MMA) can be converted into poly hydroxamic acid. Due to the fact that the polymers include binary bi-age ligands including transition metals like the Cadmium and Chromium, they have poly hydroxamic acid groups. The adsorption capacity is increased by the presence of nano carbon. The examined metallic ions' sorption capability increases over time, peaking after 5 hrs. Furthermore, in the case when the metallic ions' temperature is low, then there will be an increase in the adsorption capacity; but, in the case when there is high temperature, then there will be a decrease in the adsorption capacity since high temperatures cause separation in metallic ions at adsorptive material's surface. The function of the acid boosts the metallic ions' capacity for sorption, yet just within a limited range (i.e. 6-8). As a result of the sorption temperature data, it may be concluded that physical adsorption is taking place.

# References

1. Adetunji CO, Panpatte DG, Bello OM, Adekoya MA. Application of nanoengineered metabolites from beneficial and eco-friendly microorganisms as a biological control agents for plant pests and pathogens. In: Nanotechnology for Agriculture: Crop Production & Protection. Springer, 2019. p. 273-302. https://doi.org/10.1007/978-981-32-9374-8_13
2. Baby R, Saifullah B, Hussein MZ. Carbon nanomaterials for the treatment of heavy metal-contaminated water and environmental remediation. Nanoscale research letters. 2019;14(1):1-17. https://doi.org/10.1186/s11671-019-3167-8
3. Bíró L, Buglyó P, Farkas E. Diversity in the Interaction of Amino Acid-and Peptide-Based Hydroxamic Acids with Some Platinum Group Metals in Solution. Molecules. 2022;27(3):669. https://doi.org/10.3390/molecules27030669
4. Jamal SAA, Alywee AK. Study of the Sorption Kinetics of Fe (III) by Polyhydroxamic acid Chelating Exchanger Prepared from Polystyrene-Co-Methyl methacrylate. Journal of Applicable Chemistry. 2012;1(3):433-41. Available from: https://www.researchgate.net/publication/319260366
5. Tulaib SF, Abd Khthem M, Hussien MO. Preparation of new complexes for hydroxamic acids with Iron; Copper and Cobalt and studying their spectrum properties and biological activity. 2010. Available from: https://iraqjournals.com/article_130476_512a127be5f1316cb2da99387de96d67.pdf
6. Ibrahim FK, Abedullah SA. 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. 2021;15(2):45-52. Available from: https://iraqjournals.com/article_172452_af13a1bd84c6a14e46abad7bddbe6d5c.pdf
7. Mzinyane NN, Ofomaja AE, Naidoo EB. 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. 2021;35(1):137-52. https://hdl.handle.net/10520/ejc-chemeng-v35-n1-a17
8. Pal D, Saha S. Hydroxamic acid–A novel molecule for anticancer therapy. Journal of advanced pharmaceutical technology & research. 2012;3(2):92. https://doi.org/10.4103%2F2231-4040.97281
9. Ruiz-Torres V, Encinar JA, Herranz-López M, Pérez-Sánchez A, Galiano V, Barrajón-Catalán E, Micol V. An updated review on marine anticancer compounds: The use of virtual screening for the discovery of small-molecule cancer drugs. Molecules. 2017;22(7):1037. https://doi.org/10.3390/molecules22071037
10. Giddings L-A, Newman DJ. Extremophilic fungi from marine environments: underexplored sources of antitumor, anti-infective and other biologically active agents. Marine Drugs. 2022;20(1):62. https://doi.org/10.3390/md20010062
11. Nikolaou A, Ninou I, Kokotou MG, Kaffe E, Afantitis A, Aidinis V, Kokotos G. Hydroxamic acids constitute a novel class of autotaxin inhibitors that exhibit in vivo efficacy in a pulmonary fibrosis model. Journal of Medicinal Chemistry. 2018;61(8):3697-711. https://doi.org/10.1021/acs.jmedchem.8b00232
12. Alakhras FA, Dari KA, Mubarak MS. Synthesis and chelating properties of some poly (amidoxime-hydroxamic acid) resins toward some trivalent lanthanide metal ions. Journal of applied polymer science. 2005;97(2):691-6. https://doi.org/10.1002/app.21825
13. Rahman ML, Sarjadi MS, Guerin S, Sarkar SM. Poly (amidoxime) Resins for Efficient and Eco-friendly Metal Extraction. ACS Applied Polymer Materials. 2022;4(4):2216-32. https://doi.org/10.1021/acsapm.1c01716
14. Abedullah Jamal SA, Hmadi WF, Al-Obaidi O. Preparation Some of Hydroxamic Acid Derivatives from Honey Wax Compounds and Study the Biological Activity on Cancerous Tumors. Systematic Reviews in Pharmacy. 2020;11(2).
15. Zhang Q. Synthesis of hydroxamic acid resin and its adsorption characteristics for acid mine drainage. Cent South Univ. 2010:26-7.
16. Ferruti P, Bettelli A, Fere A. High polymers of acrylic and methacrylic esters of N-hydroxysuccinimide as polyacrylamide and polymethacrylamide precursors. Polymer. 1972;13(10):462-4. https://doi.org/10.1016/0032-3861(72)90084-5
17. Gamal SAA. 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. 2013;26(5):314-24. http://dx.doi.org/10.33899/edusj.2013.163109
18. Rikiishi H, Shinohara F, Sato T, Sato Y, Suzuki M, Echigo S. Chemosensitization of oral squamous cell carcinoma cells to cisplatin by histone deacetylase inhibitor, suberoylanilide hydroxamic acid. International journal of oncology. 2007;30(5):1181-8. https://www.spandidos-publications.com/ijo/30/5/1181
19. Jamal SAA. 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. 2012;47. Available from: https://www.iasj.net/iasj/download/378143722674bfbe
20. Ali L, Ahmad M, Aamir MN, Minhas MU, Rasul A, Yousuf M, Hussain H, Khan JA, Sohail M. Venlafaxine-loaded sustained-release poly (hydroxyethyl methacrylate-co-itaconic acid) hydrogel composites: their synthesis and in vitro/in vivo attributes. Iranian Polymer Journal. 2019;28(3):251-8. https://doi.org/10.1007/s13726-019-00697-4
21. Cao X, Wang Q, Wang S, Man R. Preparation of a novel polystyrene-poly (hydroxamic acid) copolymer and its adsorption properties for rare earth metal ions. Polymers. 2020;12(9):1905. https://doi.org/10.3390/polym12091905
22. Yayayürük E. The use of acrylic based polymers in environmental remediation studies. in Acrylic Polymers in Healthcare, IntechOpen. 2017.