

Synthesis and characterization of hydroxamated polyacrylamide

Nehal FA Mohammed^{1*}, El mugdad AA², Ahmad EEM³

¹⁻³ Department of Chemistry, College of Science, Sudan University of Science & Technology, Khartoum, Sudan

Abstract

Hydroxamated poly acrylamide (HPAAM) was prepared by coupling reaction of polyacrylamide (PAAm) and free hydroxylamine in alkaline solution (pH>12) at 70°C. The synthesized HPAAM was characterized by CHN elemental analysis, Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (¹HNMR) and thermogravimetric analysis (TGA). CHN elemental results have demonstrated that HPAAM composes of 29.71% carbon, 4.08% hydrogen and 12.66% nitrogen. Characteristics absorption bands of HPAAM functional groups at 3300-3600cm⁻¹ (OH), 1666 cm⁻¹ (C=O) and (N-H) 3211 cm⁻¹ were noticed from FTIR spectrum. Furthermore, ¹HNMR has shown the disappearance of the olefinic protons and the presence of the characteristics signals of methylene and methyne of the main chain of the PAAm at 2.3-2.8 ppm and 3.2-3.7 ppm respectively. TGA thermogram of HPAAM has shown three characteristics mass loss and it was less thermally stable than PAAm.

Keywords: chelating resin, poly (acrylamide); hydroxamated polyacrylamide

1. Introduction

Chelating resins having wide applicability for the selective removal of metal ions and polymeric substances with the ability to complex with metal ions are very common. These materials, which have polyelectrolyte characteristics, have a very large number of sorption sites per macromolecule and have been used to remove toxic and polluting metal ions from wastewater and mine water [1-7]. The number of chelating polymers, containing hydroxamic acid group, have been prepared from various starting materials using different methods. Hydroxamic acids have been known for their chelation ability with heavy metals and they form very stable complexes with a large number of them [8].

Polyhydroxamic acids (HPAAM) have been synthesized from acrylamide and ethyl acrylate and various crosslinking agents and were used to extract and separate metal ions [9-16]. Several other resins containing hydroxamic acid groups were prepared from Amberlite IRC-50 by conversion of the carboxylic acid to acid chloride [17] or to an ester [18] and nitrile [19] followed by treatment with hydroxylamine.

Synthesis of HPAAM resins from acrylonitrile-divinyl benzene copolymers and crosslinked poly (acrylamide) (PAAm) hydrogels containing different types of crosslinker and their chelating abilities for various metal ions have been reported in the literature [15,20,21,22].

The present study deals with the synthesis, modification and characterization of hydroxamated polyacrylamide (HPAAM).

2. Materials and methods

2.1 Chemicals

Acrylamide for synthesis as a monomer, N, N-methylene bisacrylamide (NMBA) as a crosslinker, ammonium persulfate (APS) as an initiator, N, N, N', N'-tetramethylethylenediamine (TEMED) as a catalyst and hydroxylamine hydrochloride were all obtained from S d fine chem Limited (SDFCL), India.

Hydrochloric acid, sodium hydroxide pellets and methanol were obtained from LOBA Chemie, India.

All chemicals used were AR grade or of a high purity and were used directly without further purification.

2.2 Methods

2.2.1 Preparation of poly (acrylamide) (PAAm)

PAAm was prepared by polymerizing a solution of acrylamide (monomer) and NMBA according to the method described in the literature [9,21,22]. In a typical experiment, 28.5g of acrylamide were weighed into a 300 cm³ beaker, dissolved in 100 cm³ of distilled water and 1.5g of N,N'-methylenebisacrylamide were added. The molar ratio between AM and NMBA was kept at (95:5). 2 cm³ of ammonium persulfate (2% w/v in water) and 0.2 cm³ of N, N, N', N'-tetramethylethylenediamine (1% w/v in water) were all added to the content of the beaker and temperature was kept at 35°C. A gel was formed after 30 min of reaction which was left for 24 h then was crumpled, washed with 2 L of distilled water and dried.

2.2.2 Preparation of hydroxylamine (NH₂OH) solution

Exactly 22.93 g of hydroxylamine hydrochloride (NH₂OH.HCl) was dissolved in a 300 cm³ methanolic solution (methanol: water (2:1)). The hydrochloric acid (HCl) was neutralized by the sodium hydroxide (NaOH) solution (40%, w/v) in a cold condition and the precipitated NaCl was removed by filtration. The pH of the reaction solution was adjusted to pH 12 by the addition of the NaOH solution. The reaction medium was maintained at a methanol-to-water ratio of 2:1.

2.2.3. Preparation of hydroxamated polyacrylamide resin

A 20 g of a dry-cross linked PAAm were suspended in a 300 cm³ of free hydroxylamine solution and the resulting mixture was stirred for 30 min at room temperature. The reaction was continued for 6 h at 70°C. Ammonia was liberated during the reaction. After completion of the reaction, the content was left for 24 h at room temperature.

The resulting white polymer was washed with distilled water first which followed by 3M hydrochloric acid and again with distilled water until it is chloride-free. Finally, methanol was added to the precipitated polymer for complete isolation^[9].

2.2.4. Qualitative Test of Hydroxamic Acid Functional Groups

About 0.2 g of the wet resin was shaken with the Copper (Cu^{2+}) ion, Iron (Fe^{3+}) ion and Vanadium (V^{5+}) in a solution and the developed color was noticed and reported^[9, 23,24].

2.2.5 CHN Elemental analysis

Carbon, hydrogen, and nitrogen contents were determined on CHNS/O analyzer.

2.2.6 FTIR analysis

FTIR spectra of PAAm and HPAAM were obtained using a Thermo Nicolet IR300 Spectrophotometer in the range (400-4000) cm^{-1} . Few milligrams of each of the samples were mixed thoroughly with few milligrams of a spectroscopic grade KBr powder, pressed into a transparent disk and the FTIR spectrum was recorded with 8 scans and a resolution of 4cm^{-1} .

2.2.7 ^1H NMR analysis

Proton (^1H) nuclear magnetic resonance (NMR) measurements were carried out using 700MHz NMR Spectrometer Bruker Avance III HD. ^1H NMR data were processed with Top Spin 3.5 pl 6 software, Chemical shifts (δ) are reported in ppm.

2.2.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Simultaneous Thermal Analyzer Netzsch STA449 F3 Jupiter. The analysis was carried out under nitrogen gas flow from 20°C to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$.

3. Results and Discussion

3.1 Color test and CHN Elemental analysis

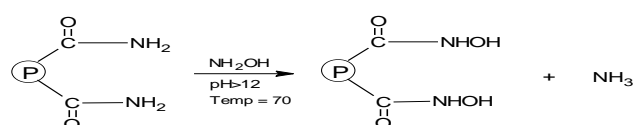
Color tests of HPAAM with copper (II), iron (III) and vanadium (V) were conducted to confirm the availability

and the ability of hydroxamic acid functional groups to bind to the above metals. The results have shown the presence of characteristics dark green, reddish brown and dark purple colors of these metals/HPAAM complexes respectively. The reaction scheme for the conversion of PAAm to HPAAM is shown in Figures 3.1 and 3.2.

The yield and the CHN elemental analysis of HPAAM are shown in Table 3.1. As can be seen from the Table, the percentage of nitrogen is 12.66% and despite the percentage of oxygen was not determined but the data indicate reasonable conversion to hydroxamic acid groups.

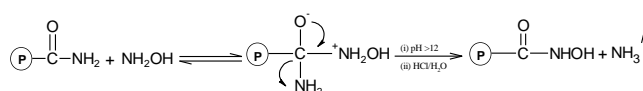
Table 1: The yield and the elemental analysis of hydroxamated polyacrylamide.

Sample	Color	Yield (%)	C (wt %)	H (wt %)	N (wt %)
HPAAM	white	54.65	29.71	4.08	12.66



Scheme 1: Conversion of PAAm to HPAAM.

Where **P** = polymer backbone



Scheme 2: Mechanism of synthesis of HPAAM

3.2 FTIR analysis

The FT-IR spectra of crosslinked polyacrylamide (PAAm) and crosslinked hydroxamated polyacrylamide (HPAAM) are given in Figures 3.3 and 3.4. As can be noticed from Figure 3.3 of the crosslinked PAAm the characteristic absorption bands of N-H stretching, -CH and CH_2 stretching as well as carbonyl group stretching and -CH bending were appeared at 3429, (2928, 2850), 1653 and 1451 cm^{-1} , respectively. In addition, the stretching vibration of the C-N bond has appeared at 1400 cm^{-1} .

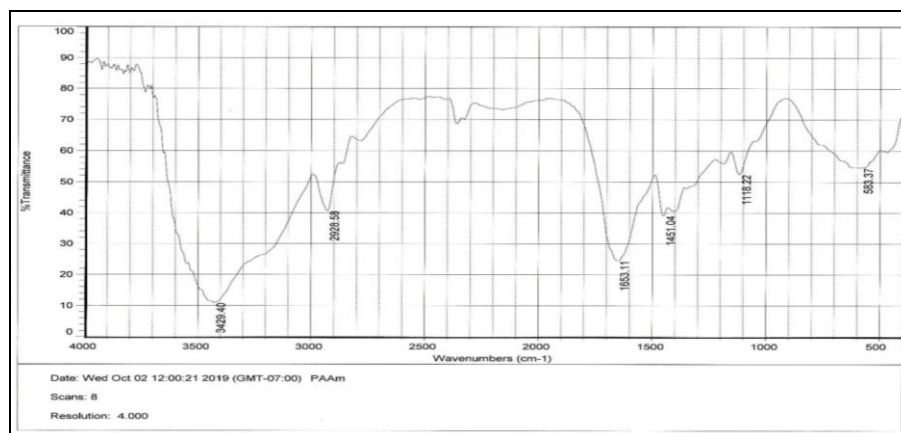


Fig 1: FT-IR spectrum of crosslinked PAAm

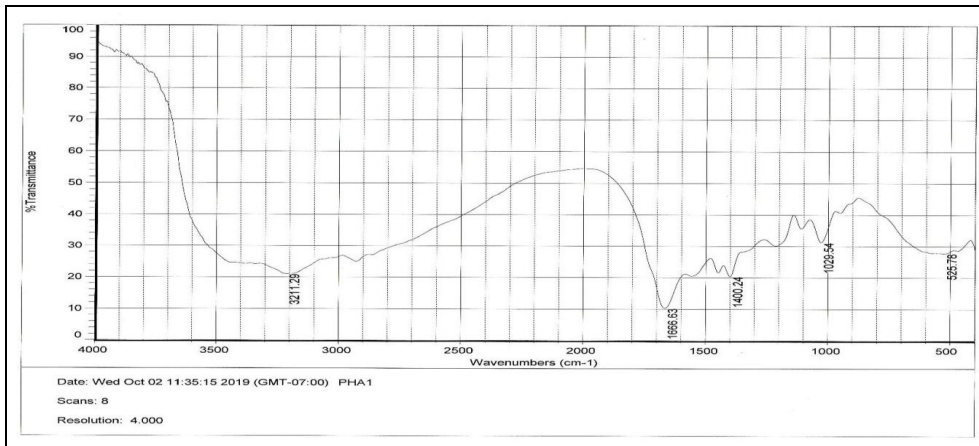


Fig 2: FT-IR spectrum of HPAAM

Similar to crosslinked PAAm, the infrared spectrum of the crosslinked HPAAM resin showed the presence of the characteristics absorption bands of symmetric and asymmetric -CH_2 stretching and C-N stretching at (2928, 2850) and 1400cm^{-1} . However, the absorption band of hydroxamic carbonyl group has shifted to 1666 cm^{-1} and the N-H stretching as well as the -OH group stretching vibration were both appeared as a broad band in the range between $3100 - 3500\text{ cm}^{-1}$.

3.3 ^1H NMR spectrum of HPAAM

The ^1H NMR spectrum of the HPAAM is shown in Figure 3.3. As can be seen from the Figure, two distinct signals were appeared at 2.3 - 2.8 ppm and 3.2 - 3.7 ppm. These delta values are attributed to methylene and methyne of the backbone of the HPAAM. Moreover, the olefinic-protons signals which usually appear in the range 5.5 - 6.5 ppm was not detected in the spectrum. This further confirms the conversion of acrylamide to a polymeric material. The proton of -NH group of PAAm which appears in the range 4.5-5.5 ppm was not detected also in the ^1H NMR spectrum of HPAAM.

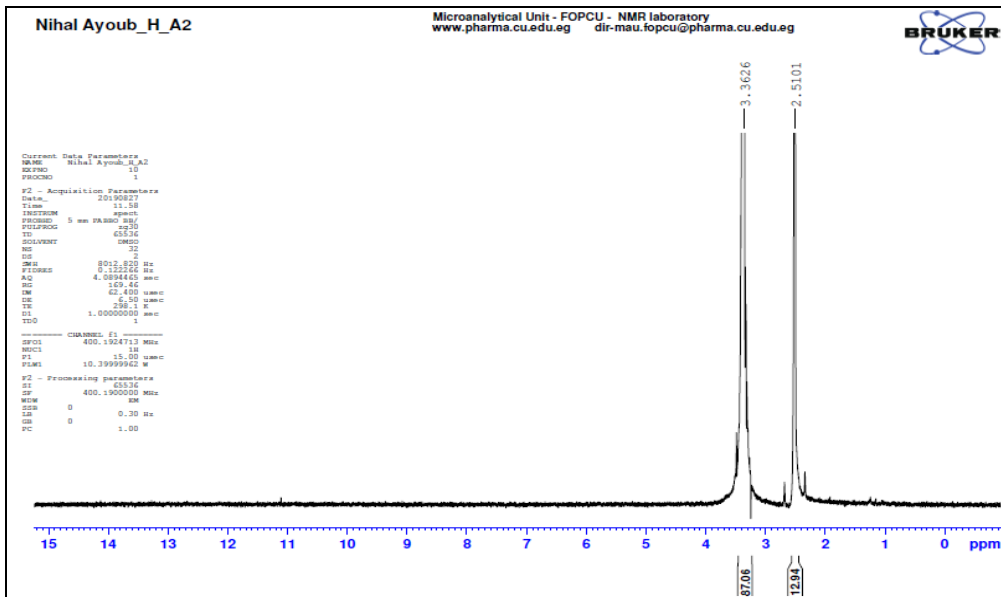


Fig 3: ^1H NMR of the HPAAM

3.4 Thermal stability analysis

The thermal stability of the PAAm and HPAAM were investigated using thermogravimetric analysis (TGA). The TGA thermograms of PAAm and HPAAM were shown in Figures 3.4 and 3.5. The crosslinked PAAm showed two distinct degradation stages or mass loss. However, there is a relatively small mass change (4%) that starts at about $100\text{ }^\circ\text{C}$ and continues up to $200\text{ }^\circ\text{C}$ which could be attributed to loss of moisture. The maximum degradation temperature of the first degradation step was at $240\text{ }^\circ\text{C}$ with accompanying mass loss of 7% while for the second stage it was at $406\text{ }^\circ\text{C}$ and the mass loss was 15%.

The first degradation step could be due to the release of ammonia due to the imidization reaction between the amide groups of the monomer units while the second weight loss region is attributed to the breakdown of the crosslinked polymer backbone and the imides formed in the first decomposition stage. Heating PAAm up to $700\text{ }^\circ\text{C}$ was produced a mass loss of 77.44% which could possibly be attributed to carbonization of the crosslinked PAAm sample. Alternatively, HPAAM displayed three characteristics degradation steps that differ from PAAm in both the maximum degradation temperature as well as the mass loss. The maximum degradation temperatures of the three steps

of HPAAM were 220, 350 and 600 °C and their accompanying mass losses were 5, 13 and 50 % respectively. Similar to PAAm the possible degradation

steps could be ascribed to the release of ammonia, breakdown of the crosslinked backbone and carbonization process respectively.

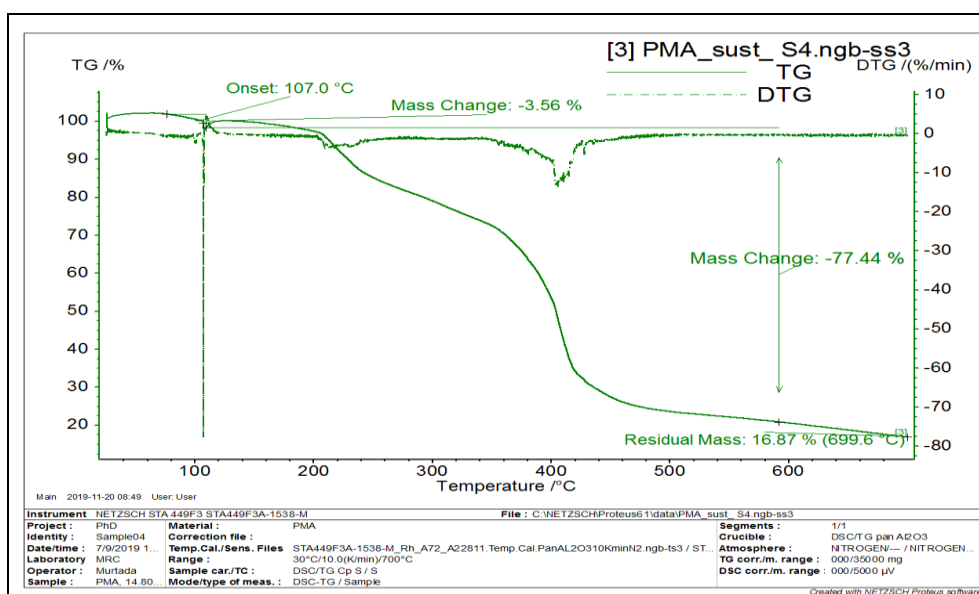


Fig 4: TGA curve of polyacrylamide (PAAm)

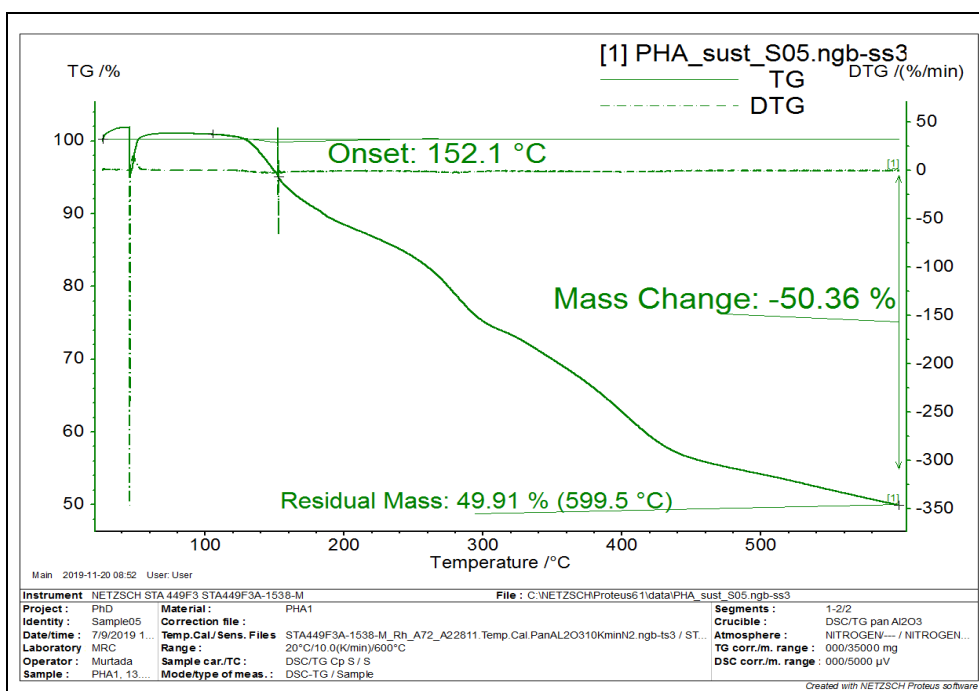


Fig 5: TGA curve of polyhydroxamic acid (HPAAM)

4. Conclusion

Crosslinked hydroxamated polyacrylamide (HPAAM) was synthesized via polymerization of acrylamide in the presence of N, N'-methylenebisacrylamide and the resulting polymer was functionalized with hydroxylamine. FTIR and ¹HNMR were both confirmed the successful conversion of PAAm to HPAAM. The synthesized HPAAM has shown noticeable ability to bind to iron (III), vanadium (V) and copper (II) (color test).

5. References

1. O'connell, David W., Colin Birkinshaw, and Thomas F. o'dwyer. (2006). Removal of lead (II) ions from

aqueous solutions using a modified cellulose adsorbent. *Adsorption science & technology*, 24.4: 337-347.

- Farkas, E., Enyedy, É. A., Zékány, L., & Deák, G. (2001). Interaction between iron (II) and hydroxamic acids: oxidation of iron (II) to iron (III) by desferrioxamine B under anaerobic conditions. *Journal of inorganic biochemistry*, 83(2-3),107-114.
- Gurgel, L. V. A., & Gil, L. F. (2009). Adsorption of Cu (II), Cd (II), and Pb (II) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine. *Carbohydrate Polymers*, 77(1), 142-149.
- Lutfor, M. R., Silang, S., lin, W. Md., Rahman, M. Z. Ab., Ahmad, M. & Haron, J. (2000). Preparation and

- characterization of poly(amidoxime) chelating resin from poly(acrylonitrile) grafted sago starch. *European Polymer Journal*, 36: 2105- 2113.
5. Andrzej, W.T., Bozena, N.K. and Dorota, J.B. (2001). Metal ion uptake by ion-exchange/chelating resins modified with cyclohexene oxide and cyclohexene sulphide, *European Polymer Journal*, 37: 559-564.
 6. Chang, Q., Hao, X., & Duan, L. (2008). Synthesis of crosslinked starch-graft-polyacrylamide-co-sodium xanthate and its performances in wastewater treatment. *Journal of Hazardous Materials*, 159(2-3), 548–553.
 7. Lacour, S., Bollinger, J.C., Serpaudm B., Chantron, P., Richard, R. (2001). Removal of heavy metals in industrial wastewaters by ion-exchange grafted textiles, *Analytica Chimica Acta*, 428: 121–132.
 8. Jemal, A., Siegel, R., Ward, E., Hao, Y., Xu, J., & Thun, M. J. (2009). Cancer Statistics, 2009. *CA: A Cancer Journal for Clinicians*, 59(4) :225–249.
 9. Domb, A. J. G. Cravalho, and R. Langer. (1988). Synthesis of hydroxamated polyacrylamide from poly(acrylamide), *Journal of Polymer Science, Part A*, 26, no. 10, pp. 2623–2630.
 10. Lee, T. S., D. W. Jeon, J. K. Kim, and S. I. Hong, (2001). Formation of metal complex in a hydroxamated polyacrylamide resin bead, *Fibers, and Polymers*,(2) 1: 13–17
 11. Lee, T.S., S.I. Hong, (1994). Synthesis of porous hydroxamated polyacrylamide from poly(ethylacrylate-co-divinylbenzene), *Polym. Bull*, 32: 273–279.
 12. Lee, T.S., S.I. Hong, (1995). Porous chelating resins from poly(acrylonitrile-co-ethyl acrylate-co-divinylbenzene), *J. Macromol. Sci. Part A* 32: 379–392.
 13. Lee, T.S., S.I. Hong, (1995). Synthesis and metal-binding behaviour of hydroxamic acid resins from poly(ethyl acrylate) crosslinked with divinylbenzene and hydrophilic cross-linking agents, *J. Polym. Sci., Part A* 33: 203–210.
 14. Lee, T.S., S.I. Hong, (1995). Synthesis and metal-binding properties of hydroxamated polyacrylamide resins from poly(ethylacrylate-co-divinylbenzene) beads, *Appl. Polym. Sci*, 57: 311–317.
 15. Vernon, F., Wan Md.Zin (1981). Chelating ion-exchangers containing n-substituted hydroxylamine functional groups: Part 6. Sorption and separation of gold and silver by a polyhydroxamic acid, *Analytica Chimica Acta*, 123, 1, Pages 309-313.
 16. Shah, A. and DevI, S. (1987). Hydroxamated polyacrylamide chelating resins. Part II.* separation of zinc from cadmium and of cobalt from copper and nickel. *Analyst*, 112: 325- 328.
 17. Crumbliss, A.L., J.M. Garrison, C.R. Bock, A. Schaaf, C.J. Bonaventura, J. Bonaventura, (1987). Synthesis and characterization of iron(III) chelating analogues of siderophores on organic solid supports, *Inorg. Chem. Acta* 133: 281–287.
 18. Petrie, G., D. Locke, C.E. Meloan, (1965). Hydroxamic acid chelate ion exchange resin, *Anal. Chem.* 37: 919–920.
 19. Schouteden, F., (1958). On the conversion of amidoxime groups into hydroxamic acid groups in polyacrylamidoximes, *Macromol. Chem. Phys*, 27: 246–255.
 20. Vernon, F., H. Eccles, (1975). Chelating ion exchangers containing N-substituted hydroxylamine functional groups: Part I. N-arylophenylhydroxylamines, *Anal. Chim. Acta*, 77: 145–152.
 21. Isikver, Yasemin, Dursun Saraydin, Nurettin Sahiner,(2001). Hydroxamated polyacrylamide hydrogels from poly(acrylamide): preparation and characterization, *Polymer Bulletin* 47:71–79.
 22. Kumar. Sanjukta A, Shailaja P., Pandey, Niyoti S. Shenoy, Sangita D. Kumar (2011). Matrix separation and preconcentration of rare earth elements from seawater by poly hydroxamic acid cartridge followed by determination using ICP-MS, *Desalination*. 281: 49–54.
 23. Lutfor, M.R., S. Sidik, W.M.Z. Wan Yunus, M.Z.A. Rahman, A. Mansor, M.J. Haron, (2001). Synthesis and characterization of hydroxamated polyacrylamide chelating resin from poly(methyl acrylate)-grafted sago starch, *J. Appl. Polym. Sci*, 79 1256–1264.
 24. Rahman, M. L. Ab., M. J. Haron et al., (2001). Preliminary study on application of sago starch-based hydroxamated polyacrylamide resin for extraction of lanthanide group elements from aqueous media, *Malaysian Journal of Analytical Sciences*,(7) 2:453–456.