

Synthesis and Characterization of Hydroxyethyl Cellulose Grafted Copolymers and its Application for Removal of Nickel Ions from Aqueous Solutions

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Abstract – Hydroxyethyl cellulose (HEC) was grafted by acrylic acid (AA), and a mixture of acrylic acid (AA) and Acrylamide (Am) with two different AA/Am composition ratios (70/30 & 30/70) to produce HEC-g-AA (copolymer I), and of HEC-g-AA-Am copolymers (copolymer II & copolymer III) respectively, using potassium persulphate/sodium bisulphate as redox initiation system at 65°C for 1hr. The obtained grafted copolymers were characterized using Fourier Transform Infrared (FTIR), Thermo Gravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and X-ray diffraction (XRD). The optimal conditions for removal of Ni from aqueous solutions using the prepared copolymers were studied through variation of pH, agitation time, and metal ion concentrations. The obtained data clarified that the optimum heavy metal removals were significantly dependent on the sorbent type. For the studied sorbent type it was found that the removal efficiency of Ni from aqueous solution follows the sequence: HEC-g-AA (I) > HEC-g-AA-Am (II) > HEC-g-AA-Am (III). At optimum conditions of metal removal it was found that 94.6%, 91.2% and 86.1% of Ni ion was removed using I, II & III copolymers respectively.

Keywords – Hydroxy Ethyl Cellulose, Acrylic Acid, Acrylamide, Ion Exchange, Heavy Metals, Characterization.

I. INTRODUCTION

Cellulose is the most naturally abundant and renewable polymer in the world. In addition, it is one of the most promising raw materials due to its abundance, easy availability, and low cost. Due to absence of side chains or branching, cellulose chains can exist in an ordered structure. Therefore, cellulose is a semi crystalline polymer having crystallinity 60% [1].

Although the properties of cellulose cannot be modified by conventional copolymerization methods, they can be changed by physical or chemical techniques [2].

Graft copolymerization is a commonly used method for the modification of either physical or chemical properties of polymers [3]. In order to obtain a cellulose graft copolymer with high water or moisture absorbency, hydrophilic monomers such as acrylic acid (AA), acrylamide (AAM) and 2-acrylamidomethylpropane sulfonic acid (AASO₃H) should be grafted onto cellulose. In order to improve the compatibility and adhesion of hydrophilic cellulose fibers to the components of hydrophobic composites, hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile, butadiene, isobutyl vinyl ether, and vinyl acetate should be grafted onto the surface of cellulose [4]. During grafting, the side

chains are covalently bonded to the main polymer backbone or substrate to form a copolymer with branched structure. Grafting methods can be classified mainly according to grafting medium and the type of initiation mechanisms; grafting can be performed in a homogeneous or in a heterogeneous medium.

In case of grafting in a heterogeneous medium, cellulose exists in dispersed form in an aqueous medium, the reaction proceeds only in the amorphous regions of cellulose. For that reason, unpurified graft product is not homogeneous, and it consists of cellulose graft copolymer, ungrafted cellulose, and homopolymer. In addition, chain degradation of cellulose backbone takes place during the creation of free radicals in heterogeneous grafting. Another drawback of the heterogeneous grafting is non-uniformity of graft chain lengths, namely, formation of short and very long graft chains or high molecular weight distribution of graft chains. In heterogeneous grafting reactions, grafting percentage decreases with the increase in crystallinity and intermolecular hydrogen bondings in cellulose [5].

The grafting reactions in homogeneous medium can be performed by using a soluble cellulose derivative (mostly water-soluble cellulose derivative) such as hydroxyethyl cellulose (HEC), carboxymethyl cellulose sodium salt (CMCNa), carboxymethyl cellulose (CMC), ...etc. The grafting is performed mostly by creation of free-radical sites on the cellulose backbone either by chemical means or by irradiation [6].

Adsorption is a well known technique widely employed for separation and purification to eliminate heavy metal ions from drinking or waste water. In removing heavy metal ions from aqueous solutions, adsorbents can bind and capture heavy metal ions from the aqueous solutions. The key part of an adsorption process is the adsorbents. Thus, good adsorbents should be abundant and easy to process, and have high selectivity, large surface area and long service time [7, 8]. So far, many natural materials and synthetic compounds have been used as adsorbents, including bark, lignin, dead biomass, zeolite, peat, xanthate, clay, modified wool and cotton, fly ash, chitosan [9], as well as homopolymer, copolymer and composites of water soluble monomers (e.g., acrylic acid and acrylamide). In this research work, the synthesis and applications of synthetic adsorbent for the removal of heavy metal ions will be discussed.

II. EXPERIMENTAL MATERIALS

Both hydroxy ethyl cellulose (HEC) and acrylamide were purchased from Fluka AG, Buch Sc. Company. Acrylic acid and potassium persulphate were obtained from Merck cooperation and used without any further purification. Other chemicals were of analytical grade used through the experiments.

Graft copolymerization:

Synthesis of HEC-g-poly-AA and HEC-g-poly-AA-Am copolymers:

The graft copolymerization of AA and/or Am/AA, admixtures with two different composition ratios (70/30 & 30/70) onto HEC was carried out by adding 5 g of HEC to 250 ml of distilled water in three-necked flask fitted on an electrical stirrer. 10 g of AA was dissolved in 50 ml distilled water and neutralized using sodium carbonate solution, the neutralization was performed with 20% of the AA content in an ice water bath to avoid possible polymerization of AA due to the increasing temperature resulting from the neutralization process. Moreover, 7gm AA/3g Am and 3g AA/7g Am in 50 ml distilled water were independently neutralized using 20% of the AA content with sodium carbonate solution. Each of the neutralized liquors (10g AA, 7g AA/3g Am and 3g AA/7g Am) was independently added to HEC solution, followed by adding 0.45g/0.41g of potassium persulphate/sodium bisulphate dissolved in 20ml. Each mixture was heated up to 65 °C for 1 hr. The obtained three copolymers HEC-g-AA (copolymer I), HEC-g-AA/Am (70/30)(copolymer II) and HEC-g-AA/Am (30/70) (copolymer III) were independently precipitated over ethyl alcohol, washed with alcohol/water (70/30) to get rid of poly-AA, poly-Am and poly-AA-Am homopolymers, filtered and finally dried at ambient conditions. The graft yield percent (GY%) of the obtained copolymers were calculated according to the following equation:

$$GY\% = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Where: W2 is weight of HEC substrate after graft copolymerization and W1 is the weight of initial HEC before grafting.

Testing and analysis

FTIR

The FTIR spectra of HEC and the graft copolymers were recorded in solid state using KBr pellets by means of Nicolet 380 Spectrometer using a zinc selenid crystal, in the wavelength range 400- 4000 cm⁻¹. The FTIR absorbance frequencies for the tested samples were recorded with an average of 128 scans using a resolution of 4 cm⁻¹.

XRD

X-ray diffraction patterns of HEC samples and the graft copolymers were recorded at ambient conditions on an X-ray diffractometer, Philips Analytical X-ray B.V, using Co K α radiation. The scattering angle (2 θ) was varied from 5° to 70°. The degree of crystallinity (CrI) of cellulose, namely, the fraction of crystalline content in the cellulose

sample, is calculated from XRD patterns by using the peak intensities at 2 θ = 18°

$$Cr.I. = [(I_{200} - I_{am})/I_{200}] \times 100 \quad (2)$$

Where: I_{am} is the intensity due to amorphous portion 2 θ = 22.5° and I₂₀₀ is the intensity attributed to both amorphous and crystalline phases [10, 11].

Thermal analysis

Thermal analysis of HEC and grafted HEC copolymers was carried out using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was performed on a TGA-50 Shimadzu instrument at a flow rate of 30 ml/min. under nitrogen atmosphere with temperature range from room temperature to 650 °C, where the thermal behavior of all the samples was investigated. A Shimadzu DSC-50 Japan Analyzer was used for differential scanning calorimetric. DSC experiments were carried out on all samples with heating rate 10 °C /min., using dry nitrogen (N₂) as a carrier gas and at a flow rate of 30 ml/min. Samples were repeated three times to ensure repeatability . Scans were started at temperature 30 °C to a final temperature of 750 °C.

Ion exchange procedure

Preparation of aqueous solution of metal ions

Nickel acetate aqueous solution was prepared by dissolving 0.423 g of the salt in bi-distilled water then completed to one liter.

Adsorption experiments

2 g/l from each of the grafted copolymers I, II and III were added separately, each to 100 ppm of the metal ion solution and shacked at constant temperature for several time intervals (15, 30, 60, 120 and 180 minutes). Each of the resulted solutions was filtered and then Ni ion concentrations in the filtrates were determined using Atomic absorption M6 thermoscientific (Flash EA 1112). The percent removal of the metal ions was calculated using the following equation [12]:

$$(E\%) = \frac{c_i - c_f}{c_i} \times 100 \quad (3)$$

Where: C_i and C_f are the initial and remaining concentrations (mg/l) of the metal ions in water, respectively.

III. RESULTS AND DISCUSSION

Performance of the prepared HEC grafted copolymers

Graft yield percent (GY%) of the prepared copolymers was calculated according to equation (1) alongside with the carboxyl contents (meq/100g copolymer) and water absorbency (g/g). The obtained data is listed in table 1. It is clear that, the GY%, carboxyl content and water absorbency are considerably increased by increasing the AA contents in the prepared copolymers. Increasing AA contents leads to more reaction medium polarization which in turn enhance the monomer (AA) substrate (HEC) interactions, thereby increasing GY% and carboxyl content.

Table 1: The characteristic performance of the prepared HEC grafted copolymers

Synthesized copolymer	[HEC] (g)	[AA] (g)	Am (g)	GY (%)	-COOH meq/100g	Water Absorbency (g/g)
HEC-g-AA (Copolymer I)	5	10	-	186	733.6	10.3
HEC-g-AA/Am (70/30) (copolymer II)	5	7	3	171	487.6	8.6
HEC-g-AA/Am (30/70) (copolymer III)	5	3	7	153	211	5.4

It is also obvious that, increasing of the acrylic acid (sodium acrylate) co-monomer content in the copolymers, leads to increasing the water absorbency. This may be due to the fact that, increasing the number of carboxyl groups in the copolymer is expected to increase the mononuclear and binuclear interaction formed. Thus, the water uptake gradually increases with the increment of the acrylic acid (sodium acrylate) in the copolymer.

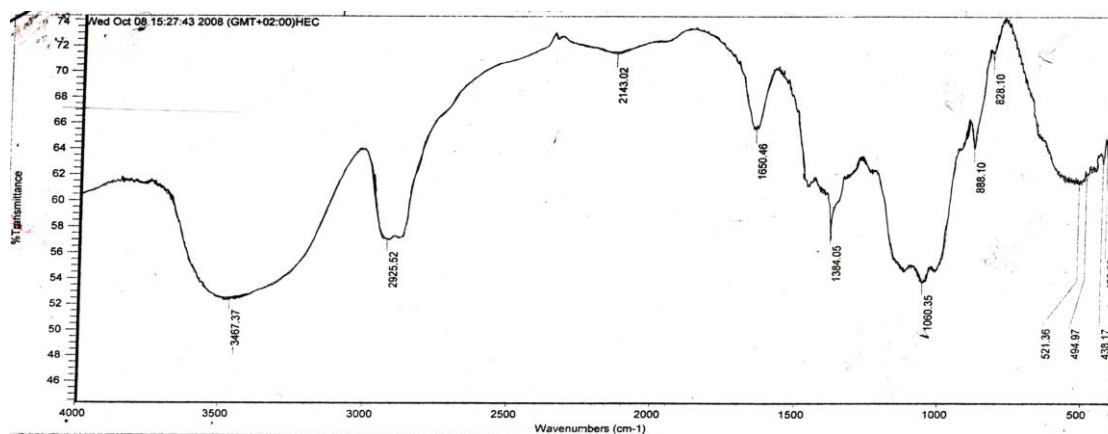
Copolymers Characterization

FTIR

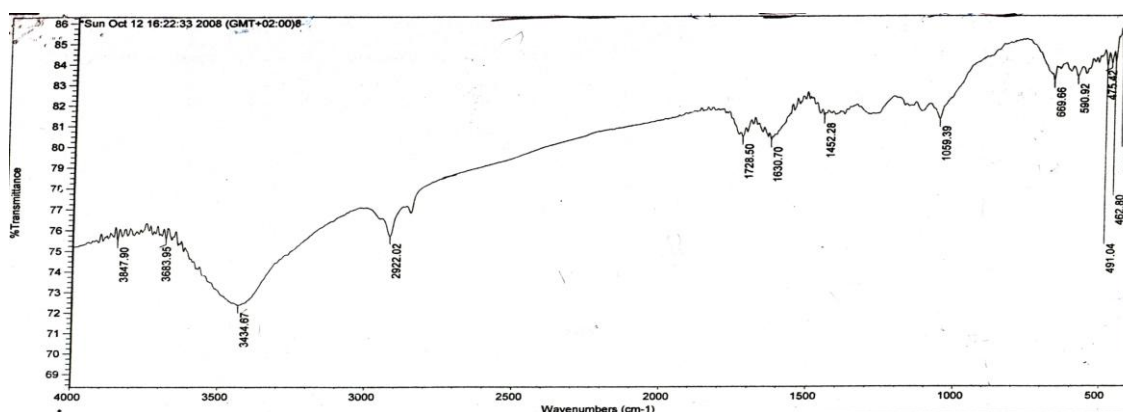
Figure 1 (a-d) reveals the spectral analysis of HEC, copolymer I, copolymer II and copolymer III respectively. The results showed that, the characteristic functional bands assigned to HEC are 18: OH-stretching at around 3467 cm⁻¹, CH-stretching \approx 2925 cm⁻¹, CH-stretching first overtone \approx 1650 cm⁻¹, and OH-primary alcohol \approx 970 cm⁻¹. On the other hand, grafting of HEC was marked by

the presence of additional bands appeared in the spectrum of grafted derivatives at: \approx 1750-1780 cm⁻¹ attributed to the Carbonyl (C=O) of copolymer I-III samples confirming grafting of AA onto such samples [13].

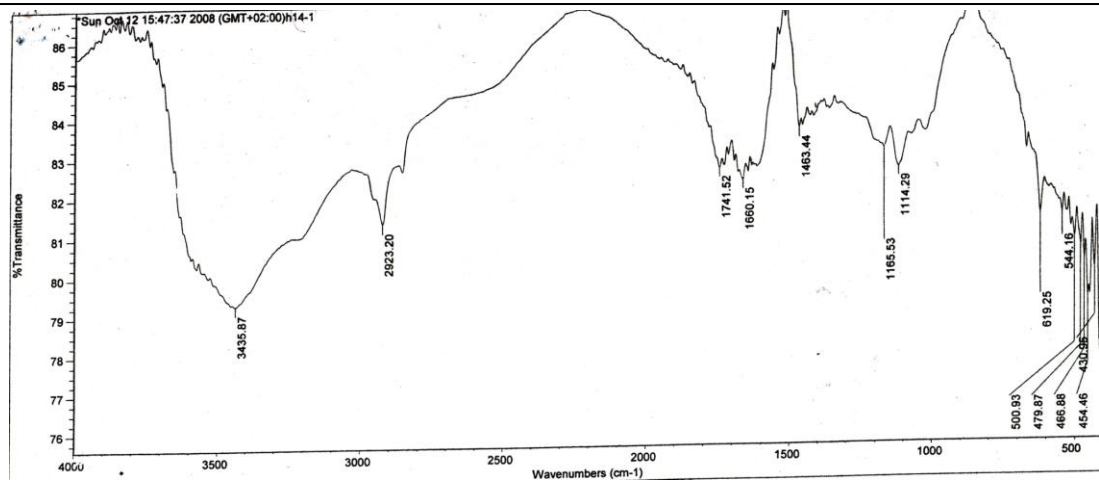
Moreover, bands found at 1640 (amide I, ν C=O) and 1450 cm⁻¹(amide II, ν C-N + δ N-H) for copolymers II & III (Figure 1c&d) also confirm grafting of Am. On comparing the peak intensities of different functional groups of each modified form it was noticed that, the peak intensities for each function group increases by increasing the concentration of its corresponding monomer. The remaining important peaks in this spectrum were assigned as: 2948 cm⁻¹(asymmetric stretching of aliphatic CH groups); 2865 cm⁻¹ (symmetric stretching of aliphatic CH groups); 1160 cm⁻¹ and 1114 cm⁻¹ (stretching vibrations of ester linkages) and 1452 cm⁻¹(bending of aliphatic CH groups) [14].



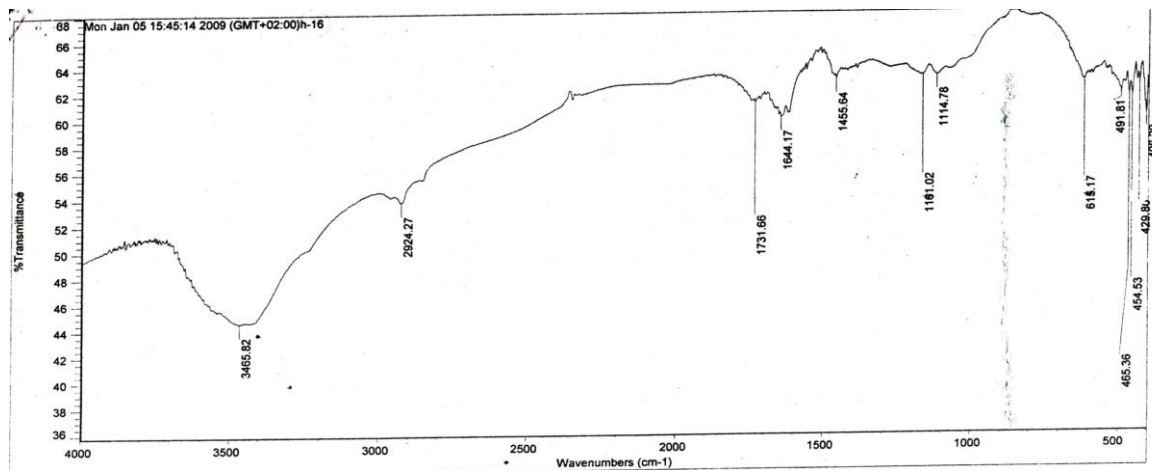
(a) HEC Blank



(b) Copolymer I:



(c) Copolymer II:



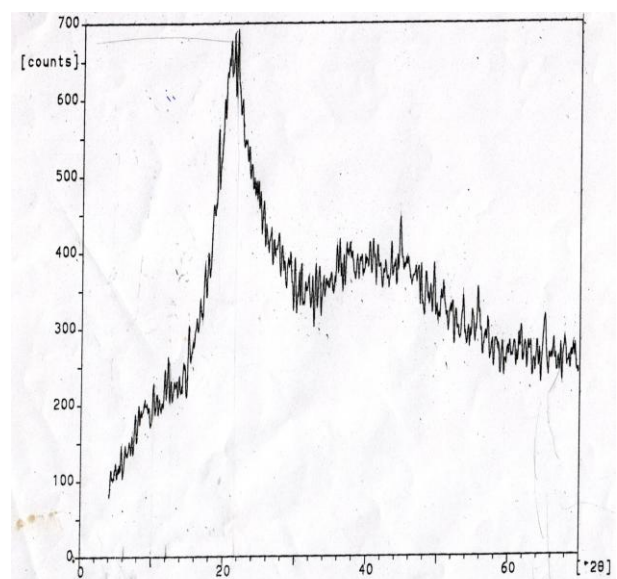
(d) copolymer III:

Fig.1. The FTIR spectra of the examined samples, where a): native HEC, b): copolymer I, c): copolymer II and d): copolymer III

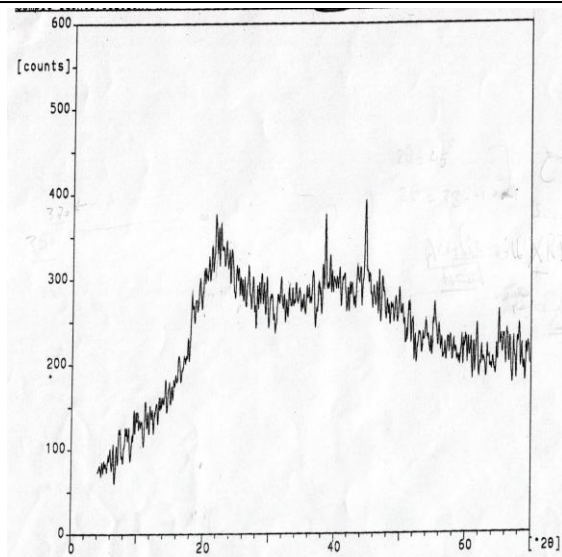
X-Ray Diffraction

Figure 2 (a-d) show x-ray diffraction patterns of the studied samples. It is clear that, there are three distinguished bands centered at $[2\theta \sim (15^\circ, 19^\circ, 29^\circ)]$ that characterize native HEC (figure 2a). On the other hand, figure 1(b – d) representing the spectra of the all grafted HEC samples (copolymers I, II, III), show another two sharp peaks appeared at $2\theta = 38^\circ, 45^\circ$ [Ao] which were not found in native HEC indicating the performance of grafting process. The data clarified in figure 2 (a-d) represents many interesting points: (a)

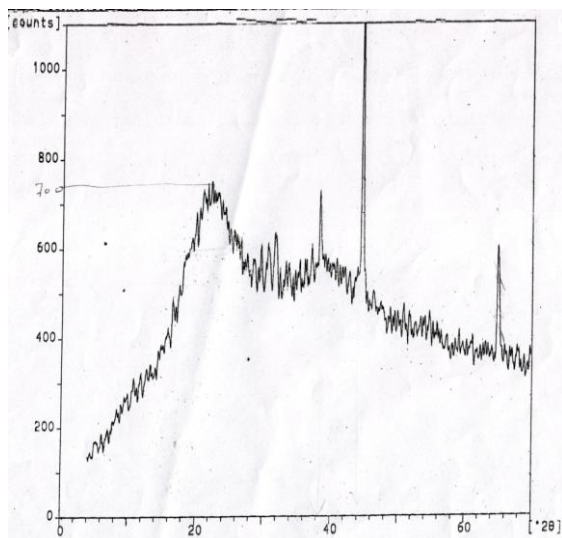
The fundamental peak at $2\theta = 19^\circ$ became more broader on all the grafted samples than that of the native HEC which indicate and verify less crystallinity and more amorphousness of these samples, (b) for copolymer II sample (figure 2c), the band centered at $2\theta = 45^\circ$ [Ao] is the sharpest comparing to that found in the other modified ones, indicating highest crystallinity to amorphousness ratio; and (c) for copolymer III sample (figure 2d), the two bands that verified the grafting process centered at $2\theta = 38^\circ, 45^\circ$ [Ao] were of lower intensity than other modified forms.



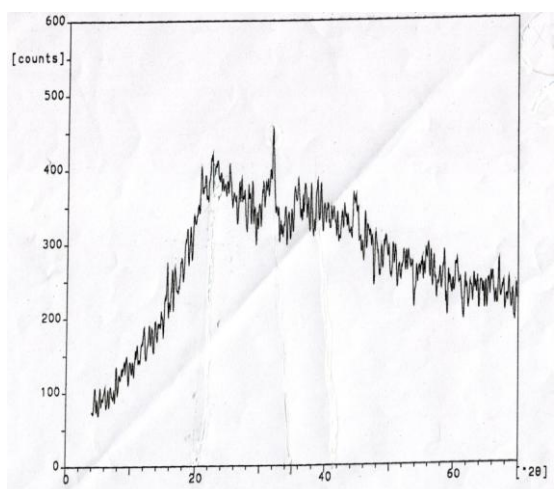
(a) HEC Blank



(b) Copolymer I



(c) Copolymer II



(d) Copolymer III

Fig.2. The XRD diffractograms of the tested samples, where: a) native HEC, b) HEC-g-AA, c) HEC-g-AA/Am (70/30) and d) HEC-g-AA/Am (30/70).

Thermal analysis

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure (3) shows that, HEC has two distinct zones of weight loss. The initial weight loss starts at temperature of (T_i) 40 °C and ends at (T_f) 75 °C with decomposition temperature (T_d) of 63 °C, due to loss of water with 9.3% wt loss. The second step has T_i , T_f and T_d values of 267 °C, 299 °C and 284 °C, respectively, with 39% wt loss due to loss of CO₂ from polysaccharide, as there are COO⁻ groups which are decarboxylated at this temperature.

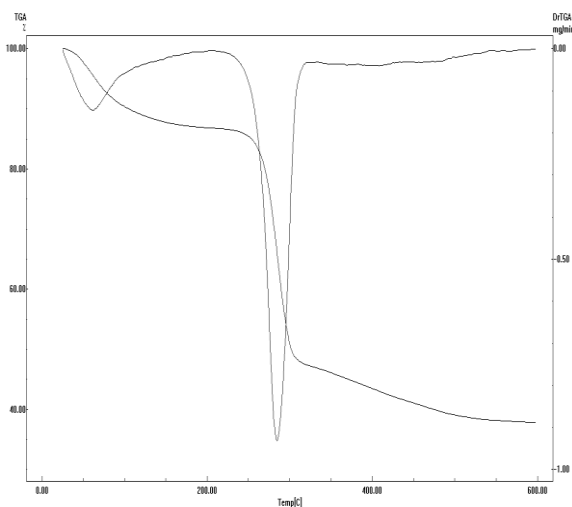


Fig.3. Thermo gravimetric analysis (TGA%) of native HEC.

Figure (4) shows the TGA of HEC-g-PAA (copolymer I), the thermal degradation of grafted copolymer has four distinct steps. The first step has T_i , T_f and T_d values of 37 °C, 62 °C and 53°C respectively with 2.4 wt% loss, due to loss of water. The second step has T_i , T_f and T_d values of 281, 253 °C and 235 °C respectively with 18% wt loss due

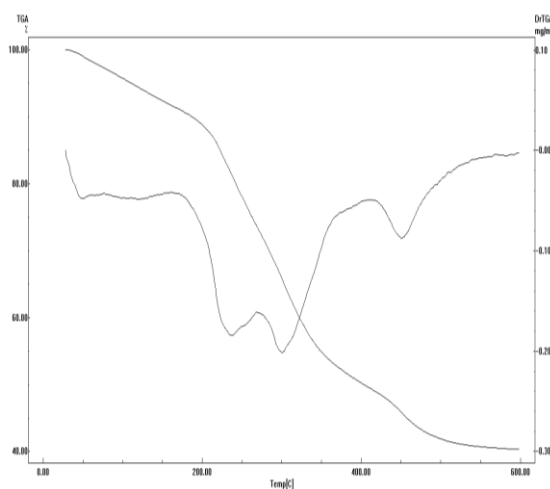


Fig.4. Thermo gravimetric analysis (TGA%) of HEC-g-PAA (copolymer I).

to decomposition of polysaccharide. The third step has T_i , T_f and T_d values of 288 °C, 339 °C and 318 °C respectively with 22 wt% loss, due to degradation of PAA, and loss of water with the formation of unhydride via cyclization. The fourth step T_i , T_f and T_d values of 420 °C, 485 °C and 457 °C with 8.64 wt% loss, due to the decomposition of cyclized product [15].

Figure (5) shows the TGA of HEC-g-(PAM-co-PAA) (70/30) (copolymer II), the thermal degradation of grafted copolymer has four distinct steps. The first step has T_i , T_f and T_d values of 39 °C, 81 °C and 70 °C respectively with 7 wt% loss, due to polymer dehydration. The second step has T_i , T_f and T_d values of 190 °C, 207 °C and 227°C respectively with 20% wt loss due to decomposition of polysaccharide. The third step has T_i , T_f and T_d values of 278 °C, 353 °C and 329 °C respectively with 34 wt% loss, due to degradation of PAM and PAA, and loss of ammonia and water with the formation of cyclized products. The fourth step has T_i , T_f and T_d values of 434 °C, 540 °C and 501°C respectively with 18 wt% loss, due to the decomposition of cyclized product.

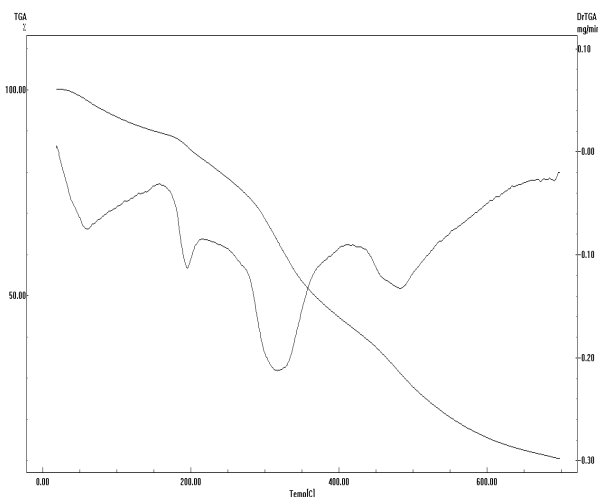


Fig.5. Thermo gravimetric analysis (TGA%) of HEC-g-(PAM-co-PAA) (70/30) (copolymer II).

Based on the above discussion, the thermal stability of the examined samples, according to the remaining residue at 550 °C of the examined samples verified that HEC grafted with acrylamide showed the highest stability, while native cellulose had the lowest one and the rest of samples lied in between.

Differential scanning calorimetry (DSC)

The DSC curves of HEC and grafted copolymers are shown in Figure (6), HEC shows endothermic peak at 76 °C, due to loss of moisture in sample. The exothermic peaks at 276 °C and 306 °C, due to degradation of polysaccharide, which proceeds due to the cleavage of glycosidic linkage, the exothermic peak at 390 °C, is due to the combustion of the degraded products [16].

HEC -g-PAA shows endothermic peak at 255 °C due to loss of water. The exothermic peak at 311°C is due to degradation of polysaccharide. The peak at 411°C is due to the decomposition of cyclized anhydride groups. HEC-

g-(PAM-co-PAA), have the same peaks mentioned above for grafted copolymers, but at 258 °C, 330 °C and 421°C respectively.

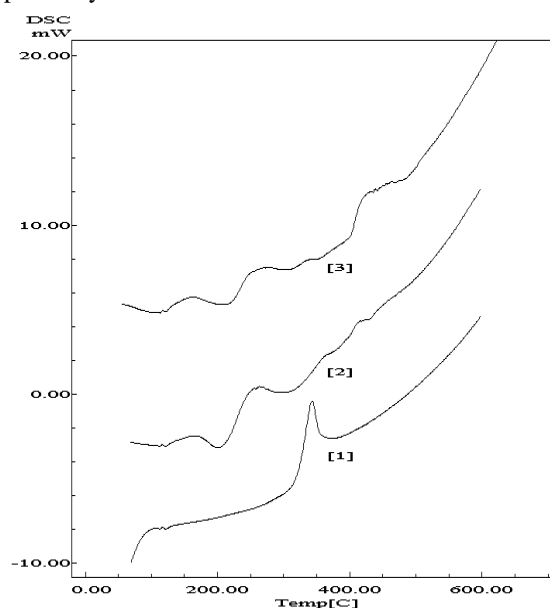


Fig.6. DSC curves of: 1) native HEC, 2) HEC-g-PAA (copolymer I) and 3) HEC-g-PAM-co-PAA (copolymer II).

Evaluation of the prepared HEC copolymers for Ni (II) removal from aqueous solution

Effect of pH:

The most important factor governing sorption of metal ion on hydrous solid of sorbent substrate is the pH of metal containing solution. This could be related to the competition between the hydrogen ions and sorbates as well as the solution pH influences the chemical speciation of metal ions [17]. The effect of the initial pH of the solution on nickel sorption onto copolymer (I); copolymer (II) and copolymer (III) was studied at room temperature through varying the pH from 3.0 up to 7.0 (Figure 7). It was noticed that, at pH range 3-5 the Ni ion uptake is approximately 50–70%, 57-81%, and 61-85% for copolymers (I),(II) and (III), respectively. While, at pH=6 the influence of H^+ on the uptake of Ni (II) by the grafted copolymers sorbents is minimized and maximal Ni (II) uptake occurs. At this pH value, Ni (II) uptake values of 84, 89, and 93% were obtained which correlates closely with maximum uptake, as outlined in Figure 7. Moreover, at pH higher than 6, precipitation of Ni (II) as $Ni(OH)_2$ is occurred causing significant interference with the estimated uptake onto the grafted copolymers [18].

On the other hand, it is clear that, irrespective of pH, the highest absorption occurs using copolymer-III followed by copolymer-II and the lowest absorption is obtained when using copolymer-I. This could be explained due to the assumption that nickel ions have stronger interactions with the carboxyl groups in macromolecular chains than the amide groups. When nickel ions are associated with macromolecular ligands, both mononuclear and binuclear nickel ion chelate complexes will be formed.

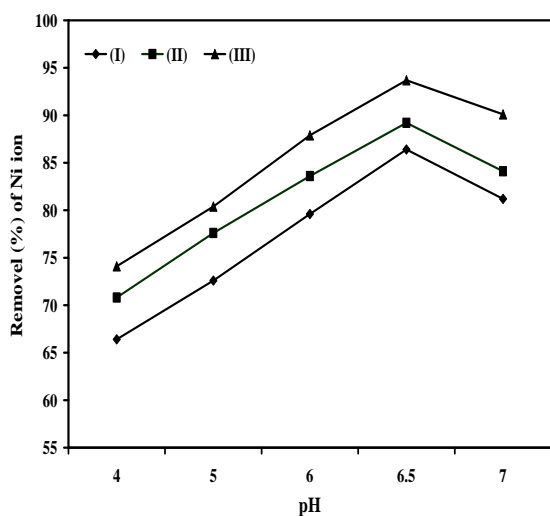


Fig.7. Effect of pH on percent removal of Ni (II) on the prepared adsorbents. [Ni (II)],50 ppm; agitation time, 1 h; agitation speed, 200 rpm; amount of each adsorbent, 2.0 g/L; temp, 25 °C.

Effect of agitation time

The effect of time on the percent removal of Ni (II) ions from their aqueous solutions on the prepared sorbents was examined at their optimum sorption pH. The data obtained in Figure (8) shows that the percent removal of Ni metal ions increases gradually by increasing the contact time up to 60 min after which equilibrium was attained [19]. Moreover, the sorption of Ni (II) ion on the prepared copolymers sorbent follows the descending order: grafted copolymer III> grafted copolymer II> grafted copolymer I. At beginning, the removal rate of metal ions was faster due to the larger surface area of the sorbent. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [20].

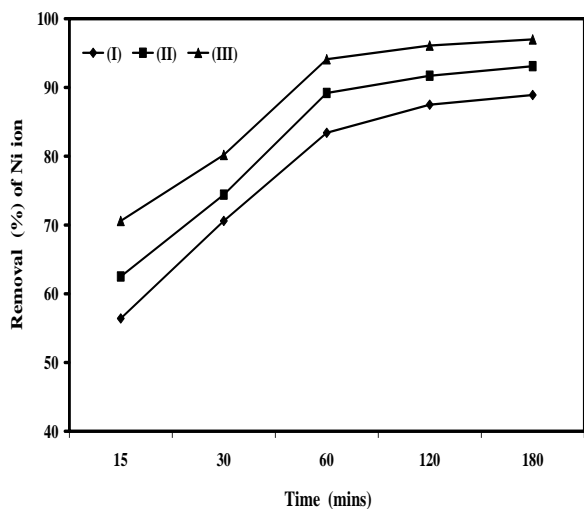


Fig.8. Effect of agitation time on percent removal of Ni (II) on the prepared adsorbents. [Ni (II)],50 ppm; agitation speed, 200 rpm; amount of adsorbent, 2.0 g/L; pH of solution: 6.5; temp, 25 °C.

Effect of adsorbent amount

The accumulation of metal ion onto adsorbent surface was also investigated as a function of adsorbent dosage. Figure (9) shows the effect of the prepared adsorbents concentration on the percent removal of Ni (II) metal ions from their aqueous solutions after 60 min and at pH= 6. It is clear that the percent removal increased by increasing the amount of these adsorbents and follows the ranking order:

grafted copolymer III> grafted copolymer II> grafted copolymer I.

Increasing the concentration of each of the grafted copolymers (I, II& III) from 0.5 to 2 g/l are accompanied by increasing the removal of Ni (II) ions from 40.6 to 83.4%, from 44.5 to 89.2% and from 51.7 to 93.2%, respectively. This is expected because of increasing the adsorbents surfaces and consequently more active sites subjected to bind more ions [21].

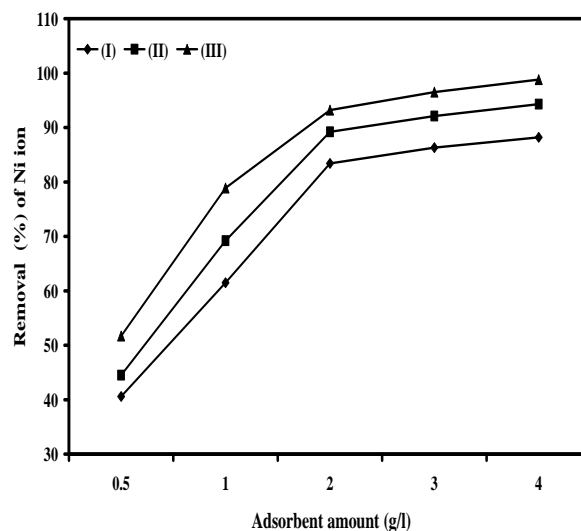


Fig.9. Effect of adsorbent amount on percent removal of Ni(II) on the adsorbents. [Ni (II)], 50 ppm; agitation time: 1 h; agitation speed 200 rpm pH of solution: 6.5; temp, 25 °C.

Effect of metal ion concentration

The concentration of trace element is also a factor of paramount importance, which controls its adsorption. Figure 10 shows the effect of Ni ion concentration on the percent removal from their aqueous solutions after 60 min, at pH=6 and by 2 g/l of the prepared adsorbents.

It is clear that increasing the concentration of the Ni (II) ion concentration results in a gradual decrease in the percent removal. This can be attributed to the gradual shortage in the active sites of the adsorbents till saturation at which there will be remaining un-adsorbed metal ions in the solutions.

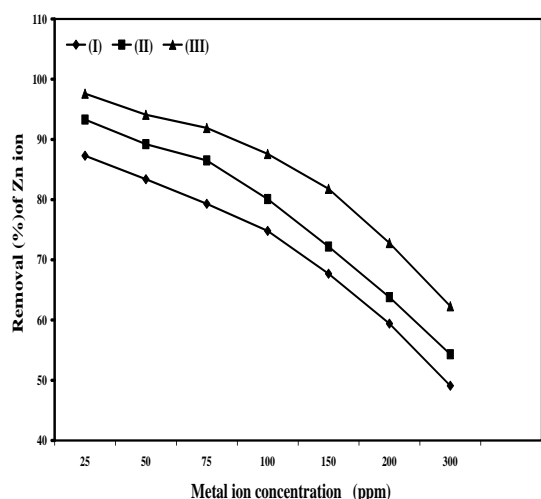


Fig.10. Effect of metal ion concentration on percent removal of Ni(II) on the prepared adsorbents. Adsorbent amount, 2.0 g/L; agitation time, 1 h; agitation speed, 200 rpm; pH, 6.5; temp, 25°C

IV. CONCLUSION

In this study graft copolymers were prepared via graft polymerization of acrylic acid (AA) and admixture of AA/AM (70/30 & 30/70) onto HEC initiated by potassium persulphate in homogenous aqueous medium at 60°C for 180 min and LR 1/20.

FTIR spectra of grafted copolymers, showed the characteristic bands of AM and/or AA, conforming the grafting copolymerization of monomers onto HEC backbone.

XRD patterns of HEC and grafted copolymers clarified that the grafted polymers chains were formed after copolymerization, it was also seen that the graft process decreases the crystallinity of HEC.

Thermogravimetric analysis (TGA) of HEC and grafted copolymers showed that the thermal stability according to the remaining residue at 550 °C, followed the order: HEC-g-PAA > HEC-g-(PAM-co-PAA) > HEC, whereas the thermal stability, according to the initial decomposition temperature (IDT), followed the order: HEC-g-PAA > HEC > HEC-g-(PAM-co-PAA).

The removal of nickel metal [Ni (II)] ion from aqueous solution using the prepared HEC-g-AA and HEC-g-AA/Am (70/30 & 30/70) confirmed that best optimum conditions were at pH 6.5, agitation time 1 hr., sorbent concentration of 2g/l. Briefly, 2.0 g/l of HEC-g-AA, HEC-g-AA/Am (70/30) and HEC-g-AA/Am (30/70) removed 83%, 89% and 94% respectively, of Ni (II) ions at optimum conditions from aqueous solutions of concentration 50 ppm of the Ni (II) ions.

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