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RESEARCH ARTICLE

Preparation and Characterization of Hydrogel based on Chitosan for Removal of Heavy Metal Ions

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Abstract

The present work describes , graft copolymerization of crotonic acid (CA) and acrylamide (AAm) mixtures onto chitosan (CS) using ceric ammonium nitrate Ce (IV) as initiator in presence of methylene bisacrylamide (MBA) as a crosslinker .The prepared hydrogels were hydrolyzed by alkaline hydrolysis.The structure of the prepared hydrogels were investigated by FTIR before and after hydrolysis. The swelling behaviors of the prepared hydrogel were measured. The results showed that the sample containing high ratio of (CA), showed high swelling before hydrolysis. The ability of the prepared copolymer hydrogels for adsorption metal ions such as Cr (III) and Co (II) was performed. The influence pH on the swelling behavior during metal ions uptake has been observed.

INTRODUCTION

Hydrogel is a three-dimensional network of hydrophilic polymers crosslinked by chemical or physical interactions (Wang et al., 2010) and can be prepared with different functional groups such as carboxylic acid, amine, hydroxyl, and sulfonic acid groups. These groups attached onto the polymeric networks can be tailored easily for a specific application (Wang et al., 2010) . Owing to higher adsorption rate and adsorption capacity, polymer hydrogels can provide many advantages as a novel type, fast-responsive, and high capacity adsorbent materials for the removal of pollutants from aqueous solution(Hiroki et al.,2009 ; Liu et al., 2010) . Lately, stimuli-responsive hydrogels have been studied since they exhibit reversible swelling behavior in response to external stimuli such as pH, temperature or magnetic and electric field. In particular pH-sensitive hydrogels containing pendant acidic (Kost , 2001; Miyata et al.,2002 ; Murdan , 2003) carboxylic and sulfonic acids or basic ammonium salts groups are very interesting to accept or release protons as a responsible to the changes in environmental pH. Many structural factors charge, concentration, pKa of the ionizable group, degree of ionization, crosslink density and hydrophilic character influence the degree of swelling of ionic polymers. (Lee et al.,1999 ; Wu et al.,2001 ; Mahdavinia et al., 2004). The properties of the swelling medium such as pH, ionic strength and the counter ion and its valence effects in the swell characteristics (Gupta et al.,2002 ; Lee and Lin 2001) . Therefore; the responsive or smart hydrogels have become an important area of research and development in the field of environmental pollution. Chitosan as one of the most abundant natural polymers is a cationic poly(amino saccharide), and can be obtained from chitin under acidic treatment condition. Now chitosan and its derivatives had wide application in wastewater treatment. Chitosan has both reactive amino and hydroxyl groups distributed on their chains, allow chitosan to be modified via chemical reaction. Graft copolymerization of monomers onto chitosan and crosslinked superabsorbent polymer was early described (Dutkiewicy, 2002) . Chitosan poor solubility in water and common organic solvents has so far limited its widespred utilization. As a result, there have been many publications about the methods to enhance the solubility of chitosan. The water- soluble chitosan with low molecular weight has some special biological , chemical and physical properties, which are different from that of the ordinary chitosan (_Fouda_et al., 2013) . Chitosan hydrogel, like other hydrogels contain much amounts of water, part of water is tightly bound to the polymer and the other rest is present as free water (Angelis et al., 1998) . Water in crosslinked and uncrosslinked chitosan gives rise to a three-dimension network structure. An efficient approach to modify swelling behavior of chitosan hydrogels in various pHs, is the graft polymerization of vinyl monomers such as acrylic acid (Yazdani et al., 2000) , acrylamid (Neira-Carrilloa et al., 2011) , acrylonitrile (Pourjavadi et al., 2003) , vinyl pyrrolidone (Yazdani- Penzdani and Retuert , 1997) onto chitosan .

In recent years, a number of initiator systems have been developed to initiate grafting copolymerization. Redox systems, such as ceric ammonium nitrate(CAN) have been used to produce free radical sites on many kinds of polymer (Canche et al., 1997 ; Athawale and Lele 1998) . The most popular properties of chitosan is a metal ion adsorption due to the presence of an active amino groups which is very interested for the chelating and complex structure formation with heavy metal ions. There are many chitosan derivatives which have the ability of chelate metal ions(Renbutsu et al., 2007 and El-Hamshary et al., 2014) .

The presence of heavy metal ions in wastewater is considered as severe environmental problem due to the acute toxicity of these metals to living organisms. We aimed in the current work to improve the charged characteristics of chitosan membranes, an anionic monomer as crotonic acid (CA) is grafted onto hydrogel as chitosan containing both cationic and anionic charges. The grafting was carried out by free radical copolymerization for crotonic acid as polyanion and acrylamide monomer onto chitosan to produce hydrogels. The prepared hydrogels were used to remove heavy metal ions such as Co (II) and Cr (III) from the wastewater.

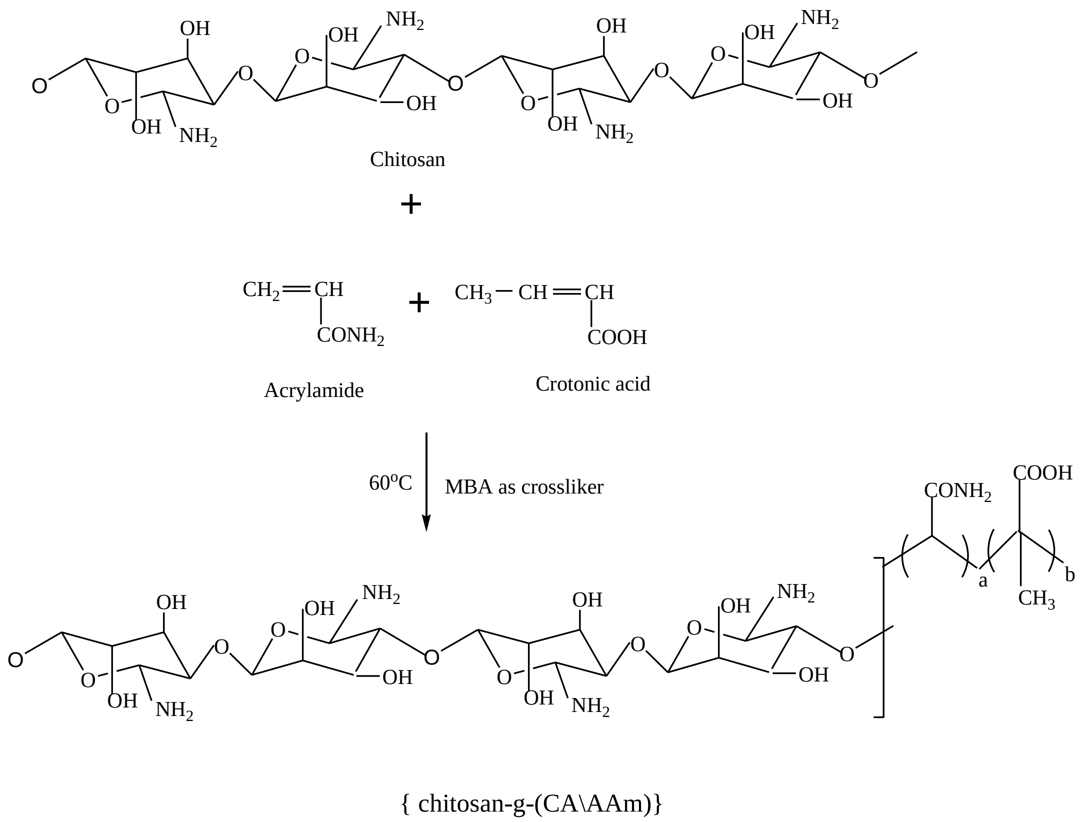
2. Experimental

2.1. Reagents

Chitosan (CS) was purchased from Pronova Biopolymer, Inc. (USA), with degree of deacetylation and molecular weight as 85 % and 50,000, respectively. Crotonic acid (CA) and acrylamide (AAm) of purity 99% were purchased from (Merck, Germany)and were used as received.Methylene bisacrylamide(MBA) as crosslinker , ceric ammonium nitrate Ce(IV) as initiator were purchased from (Aldrich Chemical Co.), other chemicals, such as citrate, phosphate buffer, metals chloride Co(II) , Cr(III) reagents were purchased from El-Nasr Co. for chemical **.** All the solutions were prepared using double distilled water

2.2 Preparation of the hydrogel

0.5 g of CS dissolved in 30 ml of 1 wt.% acetic acid solution was placed in a reactor equipped with mechanical stirrer and gas inlet at 60^{o}C.Then; 1 wt% of ceric ammonium nitrate (CAN) as initiator was added and the stirring was continued for 10 minute at 60^{o}C. 0.2 g of acrylamide was added to the reaction mixture and various amounts of crotonic acid was added in Table 1. Different amounts of , methylene- bis- acrylamide (MBA) as crosslinker solution 5 ml distilled H_2O was added to the reaction mixture after the addition of monomers and the mixture was continuously stirred (400 rpm) for one hour under flow of nitrogen gas. After this time, the reaction product was allowed to cool at room temperature and adjusted its pH to 8 by adding 1N/ NaOH solution. Methanol 100 ml was added to the gelled product for 24 hour after complete dewatering. The hardened gel product were filtered and washed with fresh methanol 20 ml two times and then; dried at 50^{o}C to prepare the samples GP1, GP2, GP3 and GP4 as non hydrolyzed samples, showen in scheme 1. .



Scheme . 1 Schematic illustration of the hydrogel synthesis.

Table (1) : Composition of the feed mixture.

Sample no.	CA (g)	AAm (g)	MBA (g)	Grafting (%)
GP 1	**0.2**	**0.2**	**0.05**	**128.4**
GP 2	**0.6**	**0.2**	**0.08**	**198.7**
GP 3	**1.0**	**0.2**	**0.1**	**270.6**
GP4	**1.5**	**0.2**	**0.15**	**310.2**
GP5*	**0.2**	**0.2**	**0.05**	**160 .4**
GP6*	**0.6**	**0.2**	**0.08**	**266 .7**
GP7*	**1.0**	**0.2**	**0.1**	**350 .1**
GP8*	**1.5**	**0.2**	**0.15**	**411.8**

Reaction condition: 0.5 gm chitosan, CAN, 0.1 gm; Temp. 60 °C; time 1 hr.

A known weight as 0.3 g of chitosan–g-poly(CA/AAm) was hydrolyzed using 12 ml aqueous 1N/ NaOH solution at 100^{o} C for 60 minute . The hydrolysed product was allowed to cool at room temperature and neutralized to pH8 by adding few drops of 10% acetic acid solution. Methanol 100 ml was added to the gelled product with stirring. After complete dewatering 24 hours, then the product was filtered, and washed with fresh methanol 2x20 ml and dried at 50^{o}C to prepare the samples GP5*, GP6*,GP7* and GP8* as hydrolyzed samples. The products were characterized by FTIR in Figure 1.
The degree of grafting was determined by the percentage increase in weight as follows:

Grafting yield (%) = $W_g – W_0 \backslash W_0 \times 100$

WhereW_0 and Wg represent the weight of initial and grafted film (g), respectively.

2.3 Preparation of buffer solutions

Buffer solutions were prepared according to the method described earlier by follows: 0.2 M (citric acid / trisodium citrate) and 0.2M (sodium dihydrogen phosphate/ disodium hydrogen phosphate) were used to prepare buffer solution ranged from 3 to 5 and 6 to 8, respectively. 0.2 M HCl was used to prepare solutions of pH 1and 2.

2.4 Swelling studies

Dynamic swelling studies were performed by placing a known amount of dried disks of the gel in 10 ml of the buffer solutions with pH 1.0, 4.0, 7.4 and 8.5 at room temperature for one day. The swelling of the CS-g-poly (CA/AAm) hydrogels was followed by measuring the weight of swollen polymers. The water uptake (the equilibrium swelling) was calculated from the following equation;

$$\text{Water uptake (\%)} = \frac{W_s - W_d}{W_d} \text{x } 100$$

Where; w_d and w_s represent the weights of dry and swollen hydrogels, respectively.

2.5 Adsorption of heavy metal ions

Adsorption isotherms were determined by the batch method for hydrogels such as {GP4 and GP8*}. Accurately weighed (m in gram) of dry samples were placed in a solution of a definite volume (V) 25 ml and different initial feed concentration (Ci) at 50 , 100, 200 , 300 ,400 and 500 mg/l for heavy metal ions Co (II) and Cr (III) as metal chloride. The system was allowed to stand for a period 5 days at room temperature. The amount of the metal ions adsorbed (mg) per a definite weight of hydrogel (g) was calculated as the following equation;

$$\text{E (mmole/g)} = \frac{C_i - C_f}{\text{W x A x10}}$$

Where:
W : is the weight of the dry hydrogel (g)
A : is the atomic weight of metal ion.
C_i and C_f are the initial and remaining concentrations of metal ions in mg/l (ppm)

The effect of the initial concentration of the metal ions on the hydrogel uptake was investigated. Also, the effect of the pH of the media was studied.

2.6 Instrumentation

Fourier Transform Infra-Red Spectroscopic Analysis (FTIR)

Spectra were recorded on Mattson 1000, Unicam infrared spectrophotometer Cambridge England in the range of 4000 - 400 cm^{-1} using a disc of dried KBr salt mixed well with infinites an amount of dry samples of GP4 and GP8 of hydrogels.

Thermal Gravimetric Analysis (TGA)

Shimadzu TGA system of Type TGA-50 in nitrogen atmosphere 20 ml/min was used in this study. The temperature range was from ambient to 500°C at heating rate of 10°C/min.

Atomic Absorption Analysis

The metal analysis was achieved by using Solar System Unicam 939 Atomic Absorption Spectrometer, England using lamp for Co and Cr. Merck atomic absorption standard solution for these metal ions were used to obtain the calibration curve.

Scanning electron microscopy (SEM)

The surface morphology of the copolymer was examined with a Jeol JSM-5400 scanning electron microscopy (SEM) (JEOL, Tokyo, Japan).

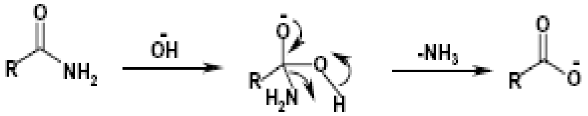
3. Results and Discussion

3.1 Synthesis of Chitosan-g-Poly(CA/AAm) hydrogel

Graft chitosan hydrogel was prepared in a homogenous medium using ceric ammonium nitrate (CAN) as initiator and methylene bisacrylamid (MBA) as crosslinker agent under nitrogen atmosphere. Both the crosslinker concentration and the monomer ratios as shown in table (1).

The synthesis of (CS-g-poly(CA/AAm) hydrogel polymer includes three steps, namely chain initiation , chain propagation , and crosslinking. The ceric(IV) initiator decompose under heating to form free radicals which abstract the hydrogen atom from hydroxyl groups in the polysaccharide chain to form macro radicals (Yoshida et al., 1996) after the processes of chain propagation and crosslinking, the hydrogel polymer is obtained .

The grafted chitosan was not completely pure but containing some impurities from cerium salts. This is due to the precipitation of insoluble cerium salts in the basic medium which has the affinity to be chelated and complexes as free cerium ions with chitosan during grafting processes (Caner et al., 1998) .To obtain the hydrolyzed hydrogels (Gp5* – Gp8*) , the CA , AA grafted chitosan were hydrolyzed with sodium hydroxide solution. During the saponification process, ammonia was evolved and amide groups are converted to carboxylate salt. This reaction can be shown as below :



This result is in a good acquirement with the previously reported results . From the results it was found that the amount of crosslinker and percentage of monomers in the composition of the hydrogel affect largely the swelling capacity in Table (1).

3.2 FTIR analysis of hydrogels

The infrared spectra of (CS-g-poly(CA\AAm) Gp4 and Gp8* hydrogels before and after hydrolysis was shown in Figure (1). The FTIR spectra of hydrogel before hydrolysis showed the presence of the very intense characteristic band at 1560 cm^{-1} due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1434 cm^{-1} which is related to the symmetric stretching mode of the carboxylate anion.The distinctive absorption bands at 1383 cm^{-1}(Amid I), 1663 cm^{-1} (Amid II) .

Combinations of absorption of the carboxylate and alcoholic O—H stretching bands are appeared in the wide range of 2365—3447 $cm^{-1.}$ As shown in the Figure (1), the intensity of carboxylate groups 1560 cm^{-1} is increased after hydrolyzing the hydrogel.and this is attributed to the conversion of amide groups to carboxylate salt. The absorption bands at 1246 cm^{-1}[anti-symmetric stretching of the C-O-C bridge], 1094 cm^{-1} and 1122 cm^{-1} skeletal vibration involving the C—O stretching are characteristics of its saccharide structure (Wu et al., 2000) .

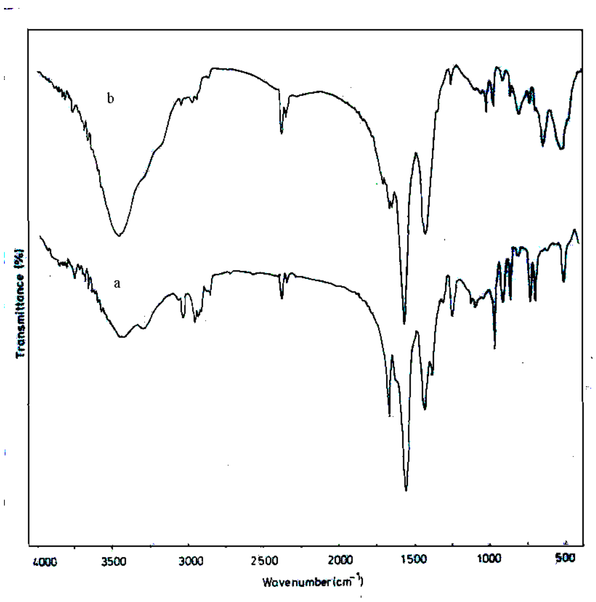


Figure (1) :FTIR spectra of the hydrogels { chitosan-g-(CA\AAm)} (a) befor hydrolysis (GP4) ;(b)after hydrolysis (GP8*).

3.3 Effect of monomers composition on swelling capacity

The influence of equilibrium swelling of the prepared hydrogels with different ratios of monomers was shown in Figure (2). The equilibrium swelling of CS-g-poly(CA\AAm) hydrogels due to the effect of both functional groups of ionic carboxylate (from CA) and non-ionic amide (from AAm). The swelling capabilities for all copolymer compositions are increased by increasing the CA content in the initial comonomer feed solution. The results indicated that, increasing the swelling capacity due to increase the amount of crotonic acid (CA) and hydrogen bond between the carboxylic acid and water molecules.

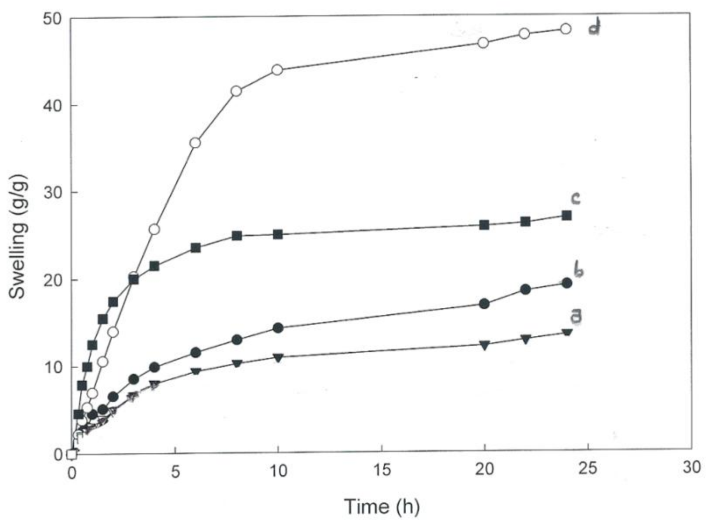


Figure (2): Effect of time (hour) on the equilibrium swelling for different {CS-g-poly(CA\ AAm)} composition (a) Gp1 ; (b) Gp2 ; (c) Gp3 ; (d) Gp4 .

Alkaline hydrolysis of CS-g-poly(CA\-AAm) with NaOH solution to form (Gp5* – Gp8*) resulting higher swelling capacities because the complete conversion of amide groups to more hydrophilic carboxylate groups in the network structure (Silverstein and Webster, 1998) .

In Figure (3), the hydrolyzed hydrogel (Gp8*) increased the swelling capacity almost 10 times higher than the non hydrolysis (Gp4) due to the conversion of amide groups to carboxylate groups, having higher hydrophilic properties.

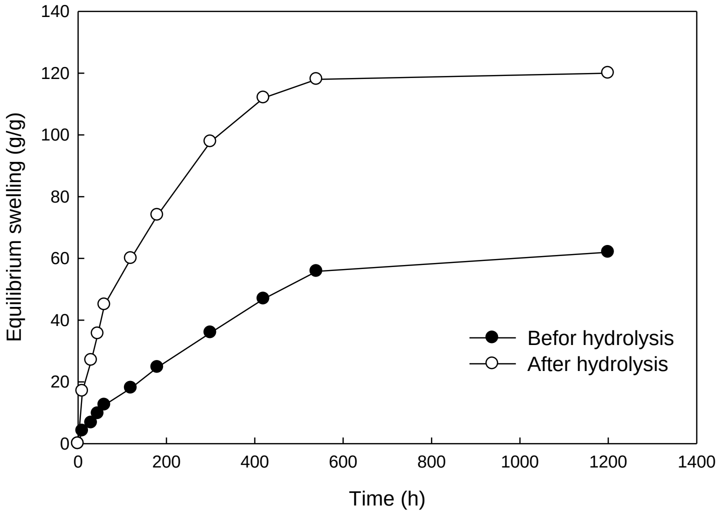


Figure (3): Effect of swelling time on the equilibrium swelling (g/g) for before (Gp4) and after hydrolysis (Gp8*) { CS-g-poly(CA\-AAm)} hydrogels at pH 3.

3.4 Effect of pH on the equilibrium swelling

The swelling of the prepared (CS-g-poly(CA\AAm)) hydrogel (Gp4) at different pH’s was studied Figure (4) due to a combination of attractive or repulsive electrostatic interactions and hydrogen bonding are the main reasons for presence of several phases in various pH's solution .

CS-g-poly(CA\AAm) hydrogel (Gp4) has both amine groups in (chitosan backbone) and carboxylate groups in (poly crotonic acid chains). Chitosan is a weak base with an intrinsic pKa of 6.5. Poly crotonic acid contains carboxylic groups that become ionized at different pH values above its pKa of 4.60. Under acidic conditions, the swelling was controlled by the amino group (NH_2) of the chitosan component, it's protonated and increasing the charge density on the polymer to increase the osmotic pressure inside the gel particles because of the NH^{+}_{3} - NH^{+}_{3} electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the gel (Kost ,1999) .

At pH > 4.7, high swelling capacity due to ionization of the poly crotonic acid above this value. Under pH range, 4-7, the protonation of NH_2 and ionization of COOH groups to create NH^{+}_{3} and COO^{-}species.Therefore, the ionic interaction force between NH^{+}_{3} and COO^{-}species (ionic crosslinking) or hydrogen bonding between amine and carboxylic acid in crotonic acid lead to a kind of crosslinking followed by decreased swelling capacity. At pH ≤ 8, the carboxylic acid groups of the crotonic acid was ionized to (COO^{-}) charged sites, the electrostatic repulsive force between COO^{-} - COO^{-} increases the osmotic pressure between the internal and external solution of the hydrogel lead to enhancement the equilibrium swelling capacity .

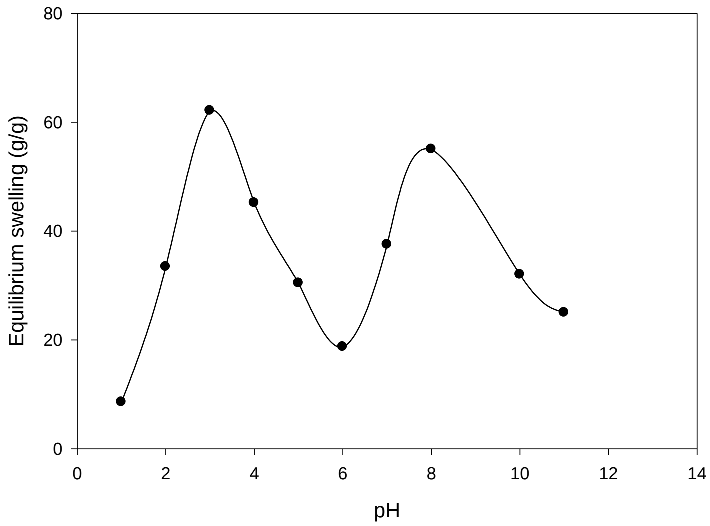


Figure (4): Effect of pH on the equilibrium swelling for { CS-g-poly(CA/AAm)} (GP4) hydrogel at constant temperature 25^{o}C.

3.5.Effect of Temperature on the Swelling

The equilibrium swelling behavior of the hydrogels {CS-g-poly(CA\AAm)} before (Gp4) and after hydrolysis (Gp8*) at constant (pH 7) at different temperature range from 25 to 55 °C was shown in Figure (5). The swelling of the hydrogel samples increased with increasing the temperature due to the association/dissociation of inter/intra molecular hydrogen bond inside the polymeric matrix (Kim et al., 2003) .

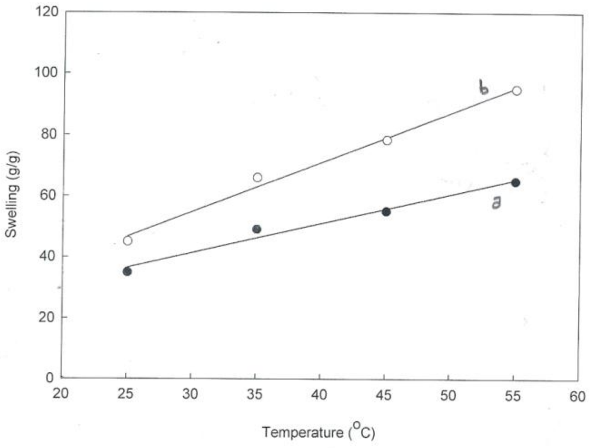
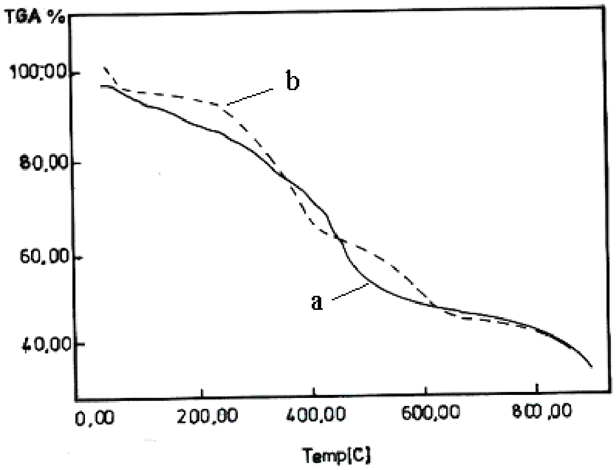


Figure (5): Effect of temperature on the equilibrium swelling for different { CS-g-poly (CA-co-AAm) } compositions at constant pH=7 , (a) befor (GP4) ; (b) after (GP8*) hydrolysis .

3.6. Thermal Gravimetric Analysis (TGA)

Figure (6) shows the weight loss (%) of natural chitosan and the prepared hydrogels{ CS-g-poly (AA\AAm)} hydrogel (Gp4) as a function of temperature. The thermogram of chitosan exhibits two distinct stages. One in the range of 35–120 ^{o}C with maximum decomposition rate at 70^{o}C which is associated with loss water, the other in the range of 220–415 ^{o}C with maximum decomposition rate at 303 ^{o}C which is ascribed to a complex process including dehydration of the saccharine rings (Saraydin et al., 2002) . The thermogravimetric (TGA) curve of the grafted The

{CS-g-poly(CA\AAm)} (Gp4) hydrogel showed three degradation steps. It degrades less slowly than that of chitosan. The CS-g-poly(CA\AAm) hydrogel showed high thermal stability than that of natural chitosan . It indicate the weight loss 12 % of H_2O, NH_3 and dehydration of the hydrophilic structure of CS-g-poly(AA\AAm) hydrogel. After 250^{o}C upto 480^{o}C the weight loss with slow degradation than chitosan with weight loss percent as 80% of copolymer decomposition. This step of degradation in the hydrogel showed the degradation of the crosslinking of crotonic acid with chitosan chains and heating the chains to small units. After 480 ^{o}C complete degradation to carbon residues of other remaining weights as 20% for thermal degradation.



Figure(6):TGA thermal diagram for**(a)** chitosan **(b)** {CS-g-poly(CA-co- AAm)} hydrogel (Gp$_4$) .

4. Factors affecting on the adsorption efficiency of chitosan hydrogel

4.1. Effect of initial metal ions concentration on the uptake

The removal of toxic and pollutants of heavy metal ions such as Co (II) and Cr(III) from the waste water by using hydrogles before (Gp4) and after (Gp8*) hydrolysis . The chitosan based hydrogels are comprised both acidicandbasicgroups,theyexhibitpolyampholyticproperties.

The effect of initial concentration of different heavy metal ions Co $^{+2}$ and Cr^{+3}solution on the adsorption capacities of { CS–g-poly(CA\AAm)} (GP4) and it hydrolyzed sample (GP 8*) hydrogels in batch technique was shown in Figure (7) .

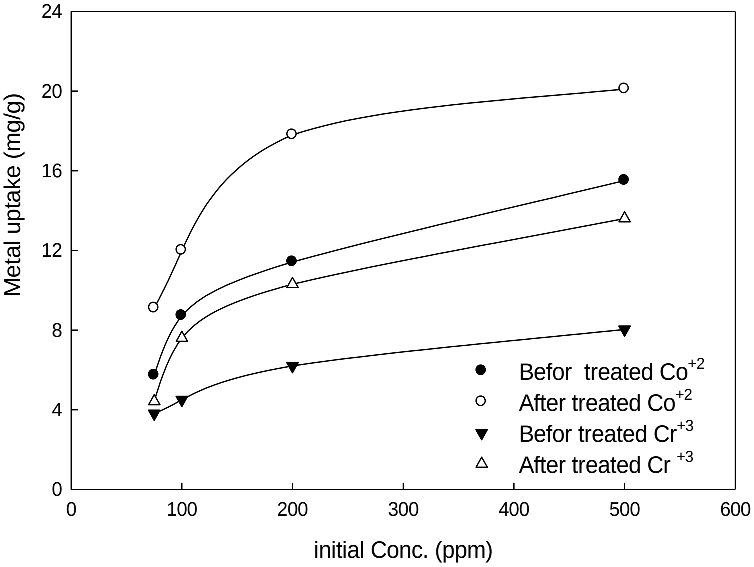


Figure (7): Effect of initial feed concentration metals uptake (mg\g) Co^{+2} and Cr^{+3}onto the { chitosan-g-poly(CA\AAm)} befor (GP4) and after (GP8*) hydrolysis, at constant weight ratio AAm/CA =1.

The results indicated that the adsorption capacity increases with increasing the initial feed concentration C_i for all heavy metal ions concentrations due to the specific interactions between the polymer and the metal ions loaded to form a complex structure [CS-g-(CA/AAm) -metal complex].The adsorption of Co^{+2} more than Cr^{+3}, due to variation of the affinity of such metal ions due to the variation of their ionic radii. The smallest ionic radius is a faster to be diffused through the gel surface and easily interact with the anionic charge $–COO^-$ group of the crotanic acid to form the active chelation complex in the hydrogel (Arh-Hwang et al., 2009 ; Kesenci, et al., 2002) .

The metal ions uptake onto [CS-g-poly(CA\AAm)] (GP4) and its hydrolyzed form (GP8*) decrease with increasing the cationic charge valence of the metal cation as well as $Co^{+2}>Cr^{+3}$ which crosslinked with the anionic sites of the hydrogel (Castel and Audebert , 1990 ; Pourjavadi et al., 2005) . The metal uptake was attributed to charge screening effect of the cations that shields the charge of anion-anion electrostatic repulsion, leading to a decrease of the osmotic pressure difference between the hydrogel network and the external solution (Pourjavadi et al., 2005) . Also, the effective radii of the multivalent cations in aqueous solution, and cationic valence. The smaller hydration radius of the trivalent cation, the more evident the screening affects, and lowered the metal uptake (Pourjavadi et al., 2008) . Therefore, the affinity of metal ion uptake for $Co^{+2}> Cr^{+3}$ onto the grafted chitosan hydrogel.

The ability to form complex structure arising from the coordination the hydrolyzed hydrogel (GP8*) than (GP4) hydrogel. Due to the electronegativity of oxygen atom in carboxylate group show more active and predominant to chelate with metal ions than the less electronegative nitrogen atom in the amide group. Further with more addition of a large density of carboxylate groups generated in polymeric gel caused by a higher degree of hydrolysis that converts $-CONH_2$ to $-COO^-$ which results in higher metal- uptake .

4.2. Effect of pH on the uptake of metal ions

The effect of the metal ions uptake at different pH of metal ion concentration illustrated in Figure (8). Therefore, swelling pKa of the polycrotonic acid (4.60) and pKb of the chitosan (6.50), the ionic groups play the main role in the variation of the degree of swelling. The protonated (NH_3^+) or deprotonated (COO^-) groups increase charge density on the polymer causing the enhancement of the osmotic pressure inside the gel particles due to the NH_3^+—NH_3^+ or COO^- -COO^- electrostatic repulsion. This result was explained the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes an increase in the volume spaces between the chains. Therefore; much volume of water can be uptake carrying much amount of metal ions dissolved in it to penetrate into the hydrogel matrix. Ether protonated (NH^{+3}) or deprotonated ($-COO^-$) groups increase charge density on the polymer causing an enhancement of the osmotic pressure inside the gel particles. The difference in the osmotic pressure between the internal and external solution of the network is balanced by the swelling of the gel and more up-taking of metal.

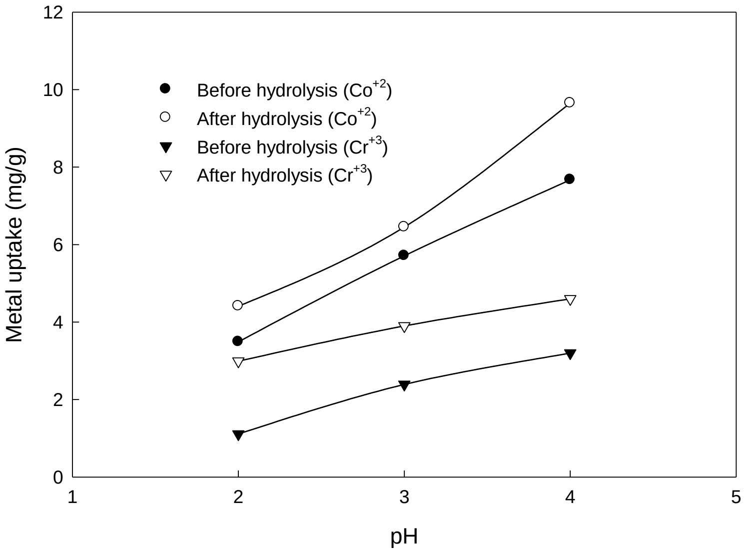
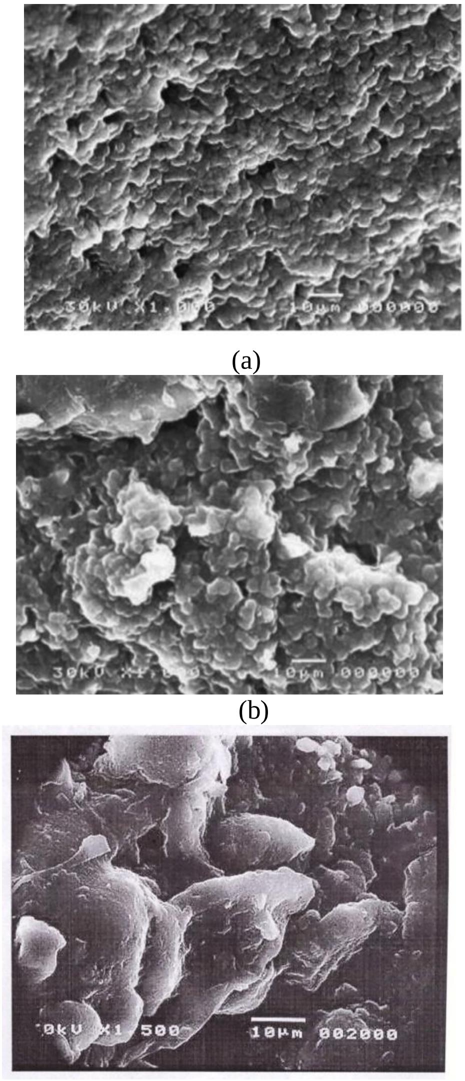


Figure (8): Effect of pH on the metal uptake (mg/g) of {chitosan-g- poly(CA\AAm) } befor (GP4) and after (GP8*) hydrolysis, at constant weight ratio AAm/CA=1 .

4.3. Scanning electron microscopy (SEM

Figure (9) shows the scanning electron micrographs (SEM) image for the surface of chitosan (CA –co- AM) hydrogel before uptake is smooth and its pores are regular arranged on the surface, but the surface of the copolymer after uptake with cobalt and chromium, some aggregation on the surface due to the surface adsorption of the metal-chelated



(a)

(b)

(c)

Figure (9) : SEM graphs for of (a) befor uptake {chitosan (CA \ AM)} hydrogel (GP4), (b) after uptake with Co^{+2} (c) after uptake with Cr^{+3}

Conclusion

CS-g-p (CA-co-AAm) synthesized by free radical polymerization using Ce(IV) as initiator and methylene bisacrylamide (MBA) as a crosslinker . The swelling of the hydrogel exhibited high sensitivity to pH. The hydrogels [chitosan-g-poly(CA\-AAm)] and its hydrolyzed hydrogel used as metal ions uptake .The uptake of the metal ions decreased by increasing the charge of the metal cation {Cr(III) < Co(II) } attributed to charge screening effect of the cations . The effect of the metal ions uptake at different pH has been investigated.

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