



Environment friendly modified chitosan hydrogels as a matrix for adsorption of metal ions, synthesis and characterization

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ABSTRACT

Environment friendly modified chitosan hydrogels for metal ions absorption from aqueous systems were designed using simple technology. Chitosan was modified with [*N,N'*-bi- α -azidosuccinimide and *N*-phthalimido- α -azide succinimide] under different reaction conditions to prepare new hydrogels with high metal ion absorption efficiency. The hydrogels were characterized by FTIR, thermal stability, crystallography, solubility and swelling capacity. Promising results were obtained from this preliminary study to evaluate the efficiency of the new hydrogels to uptake copper and cobalt ions from aqueous systems.

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1. Introduction

Environmental pollution has become more and more serious, especially regarding heavy metal ions. Heavy metals, mainly from industrial activities such as plating, metallurgy, and dyeing industries are a serious threat to human beings and the environment, due to their toxicity and persistence after being released into the natural environment. The amount of heavy metals produced from metal industries, agricultural activities, and waste disposal has increased dramatically. Many conventional adsorbents are used for removal of toxic metals, such as activated carbon (Kalpakli & Koyuncu, 2007), cellulose (Gnanasambandam & Proctor, 1997; Hacker, Roller, & Schmauder, 2000) and zeolite (Liu, Liu, Wang, Wang, & Shang, 2000).

Additionally, mining and mineral processing operations generate huge volumes of toxic liquid waste (Modak & Natarajan, 1996).

Much research on the biosorption for heavy metal ions has been carried out. Many new kinds of bioadsorbents (Kanazawa, Urano, Kokado, & Urushigawa 2001; Volesky, 2001) have been developed such as mycelium adsorbents (Su, Wang, & Tan, 2003a, 2003b), surface molecular imprinting adsorbent (Li, Xu, Shi, & He, 2001; Su, Wang, & Tan, 2005; Su, Zhao, Li, Qiang, & Tan, 2006; Su et al., 2003a, 2003b), surface coated (Li et al., 2001), and imprinted chitosan adsorbents (Fu et al., 2004; Guo, Xia, Hao, & Zhang, 2004). A number of methods exist for the removal of heavy metal pollutants from liquid wastes when they are present in high concentrations. These include methods such as precipitation, evaporation, electro-

plating, ion-exchange and membrane processes (Matheickal & Yu, 1999). These processes are expensive, and also have other shortcomings, such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, very high or low working levels of metals, and production of toxic sludge or other waste products that also need disposal (Bunke, Gotz, & Buchholz, 1999; Eccles, 1999). Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushroom, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product, such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well (Nuhoglu, Malkoc, Gurses, & Canpolat, 2002).

Chitosan is an amino polysaccharide obtained by deacetylating of chitin. The main characteristics of chitosan are hydrophilicity, harmlessness for living things and biodegradability, ease of chemical derivatization, and its capability to adsorb a number of metal ions. Therefore chitosan presents as a very promising starting material for chelating resins.

Chitosan has many $-NH_2$ and $-OH$ groups that can chelate heavy metal ions, providing high adsorption capacity and selectivity (Findon, McKay, & Blair, 1993).

The alkalinescence of chitosan, which has a close relation to its adsorption capacity, will be reduced after reaction with crosslinking agents. The alkalinescence can be improved through chemical modification of chitosan to increase the adsorption capacity for heavy metal ions. Many studies have been carried out on the preparation of anionic chitosan derivatives, such as carboxymethylated

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derivations, but few exist that have studied cationic chitosan derivatives (Wang & Liu, 2005).

In continuation of our previous work on metal uptake from aqueous solutions (Kandile, Mohamed, Zaky, Nasr, & Mohamed, 2009), we modified chitosan using [*N,N'*-bi- α -azidosuccinimide and *N*-phthalimido- α -azide succinimide] under different reaction conditions to design new hydrogels with high metal absorption efficiency.

Both chemical and physical characteristics of the new hydrogels (solubility, swelling, thermal stability, and crystallography) were investigated. The effects of reaction conditions on the extent crosslinking were also studied. A preliminary study was then carried out to evaluate the ability of this new hydrogels to uptake copper and cobalt ions from aqueous systems.

2. Experimental

2.1. Materials

Chitosan (67% degree of deacetylation MW > 6305), glutaraldehyde (25%) (Aldrich), acetic acid (glacial), dimethylsulfoxide, sodium azide (GPR), maleic anhydride (Merck), acetic anhydride, methanol, (Alpha), hydrazine hydrate (99%) (Fluka), benzene, sodium carbonate (Bio. Chem. for Laboratory Fine Chemicals) dimethylformamide (ADWIC), 1,2-bis(3-carboxyacrylyl) hydrazine (Feuer & Rubinstein, 1958), *N,N'*-biisomaleimide (B) (Feuer & Rubinstein, 1958), *N*-phthalimidomaleimide (M) (Awad, Kandile, & Ismail, 1979), copper sulfate and cobalt acetate of analytical grade were purchased from Sigma and used for preparation of the aqueous copper and cobalt solutions, respectively. All reagents used were of analytical grade and used as received.

2.2. Measurements

Melting points were determined on a Boetius hot-stage apparatus and are uncorrected.

The infrared spectra were measured on Perkin-Elmer-1430 Infrared Spectrophotometer using the potassium bromide Wafer technique. X-ray diffractograms of polymers were obtained with a Phillips X-ray unit (Generator PW-1390) and a Ni-filtered Cu. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere using a Shimadzo TGA-50H thermal analyzer. The solubility of the hydrogels was examined using 0.02 g of polymer in 10 ml solvents at room temperature 25 °C.

2.3. Methods

2.3.1. Synthesis of starting materials

2.3.1.1. Synthesis of 1,2-bis(3-carboxyacrylyl) hydrazine. A cold solution of hydrazine hydrate in acetic acid was prepared by slowly adding (5 g, 0.1 mol) of 99% hydrazine hydrate to (25 ml) of cold glacial acetic acid. This was added to a solution of (19.6 g, 0.2 mol) of maleic anhydride in (100 ml) of glacial acetic acid. The temperature was maintained below 25 °C throughout the addition and then the reaction mixture was let stand at 25 °C for 3 h. The crude hydrazide was filtered off, washed thoroughly with ethanol and dried in a vacuum for 3 h to yield 19.9 g (85%) of product, mp 185 °C (Feuer & Rubinstein, 1958; mp 183–184 °C).

2.3.1.2. Synthesis of *N,N'*-biisomaleimide. A mixture of 1,2-bis(3-carboxyacrylyl)hydrazine 3 g in benzene 25 and 10 ml of acetic anhydride was refluxed for 5 h. The solid product was filtered off and crystallization from dimethylformamide gave yellow crystals of *N,N'*-biisomaleimide, yield: 36%, mp 260–262 °C (Feuer & Rubinstein, 1958; mp 260 °C).

2.3.1.3. Synthesis of *N,N'*-bi- α -azidosuccinimide. An aqueous solution of sodium azide (2 g) was added to the solution of the biisomaleimide (1 g) in acetic acid 20 ml and the reaction mixture was left at room temperature 25 °C for 2 h. The solid obtained was filtered off, washed with water and crystallized from benzene to give *N,N'*-bi- α -azidosuccinimide as colorless crystals, yield: 71%, mp 169 °C (Awad, Ismail, & Kandile, 1976; mp 170 °C).

2.3.1.4. Synthesis of *N*-phthalimidomaleimide. A mixture of *N*-aminophthalimide (1.62 g, 0.1 mol), maleic anhydride (1.46 g, 0.1 mol) in glacial acetic acid (10 ml) was heated under reflux for 10 min. The clear solution obtained was concentrated and left to cool. The colorless solid obtained was filtered and washed with sodium carbonate solution. The solid product was crystallized from benzene as colorless crystals, yield: 83%, mp 198 °C (Awad et al., 1979; mp 199 °C).

2.3.1.5. Synthesis of *N*-phthalimido- α -azide succinimide. An aqueous solution of sodium azide (1 g) was added to the solution of the *N*-phthalimidomaleimide (0.38 g) in acetic acid (10 ml) and the reaction mixture was left at room temperature 25 °C for 2 h. The solid obtained was filtered off, washed with water and crystallized from benzene to give *N*-phthalimido- α -azide succinimide as colorless crystals, yield: 63%, mp 179 °C (Awad et al. 1979; mp 178 °C).

2.3.2. Synthesis of the hydrogels

2.3.2.1. Modification of chitosan with *N,N'*-bi- α -azidosuccinimide and *N*-phthalimido- α -azide succinimide. A solution of (0.56 g) chitosan in 60 ml acetic acid (0.03% in distilled water) and *N,N'*-bi- α -azidosuccinimide or *N*-phthalimido- α -azide succinimide in 4 ml glacial acetic acid were stirred for 2 h. The hydrogels formed were washed with dimethylformamide and then dried under vacuum to give the new hydrogels:

[(Chitosan-A) (*I*_{1–3})] produced from modification of chitosan with *N,N'*-bi- α -azidosuccinimide and [(Chitosan-B) (*III*_{1–3})] from modification of chitosan with *N*-phthalimido- α -azide succinimide at different concentrations (0.5, 1.0, and 1.5 mmol).

2.3.2.2. Modification of chitosan with *N,N'*-bi- α -azidosuccinimide and *N*-phthalimido- α -azide succinimide compounds using glutaraldehyde. A mixture of (0.56 g) of chitosan in (60 ml) acetic acid solution (0.03% in distilled water) and [*N,N'*-bi- α -azidosuccinimide or *N*-phthalimido- α -azide succinimide] (0.5 mmol) in 4 ml glacial acetic acid and glutaraldehyde (25%, 5 ml) was stirred for 2 h. The crosslinked hydrogels were formed after washing with dimethylformamide and drying under vacuum to give the new hydrogels [(Chitosan-AG) (*II*₁)], and [(Chitosan-BG) (*IV*₁)], respectively.

3. Evaluation of swelling capacity

3.1. The soluble fraction of the hydrogels [(Chitosan-A) (*I*_{1–3})], [(Chitosan-B) (*III*_{1–3})], [(Chitosan-AG) (*II*₁)] and [(Chitosan-BG) (*IV*₁)] was determined using the following procedures

A sample of the hydrogel (0.5 g) was placed in a 100 ml beaker containing 20 ml of different solvents as (DMF, MeOH, DMSO and acetic acid) and then boiled for 1 h. The swollen hydrogel samples were taken and dried in oven at 70 °C to remove water. The drying was continued to a constant weight (*W*₁). The soluble fraction was calculated according to the following equation:

$$\text{Soluble Fraction (SF\%)} = \frac{W_0 - W_1}{W_0} \times 100$$

where *W*₀ is the initial weight of the hydrogel and *W*₁ is the weight of dried hydrogel after removal of the solvent.

A certain weight (*W*₁) of hydrogel was placed in 4 × 50 ml beakers. A single solvent (20 ml of either DMF, MeOH, DMSO or acetic acid)

was added to each beaker and the sample soaked for 24 h at room temperature. The sample was removed from the beaker and blotted with a filter paper to remove the droplets of solvent on the surface.

The solvents uptake was calculated using the following equation:

$$\text{Solvent Uptake (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the weight of dry hydrogel and W_2 is the weight of swollen hydrogel.

3.2. Determination of metal ions absorption of the prepared hydrogels

The affinity of the hydrogels for different metal ions (copper and cobalt ions) was studied by immersing a known weight of hydrogel in a known volume and concentration of a solution of metal ions at a known concentration for different immersion times.

To investigate metal ion absorption from copper sulfate or cobalt acetate solutions (0.05 g in 25 ml water), the different hydrogels were first pre-swollen in water until constant weights were obtained (i.e. they become saturated with water). The pre-swollen hydrogels were then immersed in the solution of the metal salt for up to 10 h. The absorbance of the M^{2+} ions was measured at different time periods using a UV spectrophotometer.

The efficiency of metal ion uptake of the hydrogels was calculated using the following equation:

$$F = (1 - C/C_0) \times 100$$

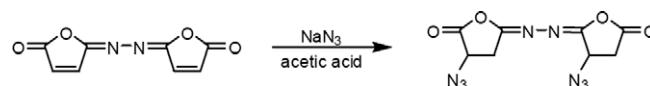
where F is the efficiency (%), C is the concentration of M^{2+} in the solution after a certain time period, and C_0 is the initial concentration of M^{2+} solution.

4. Results and discussion

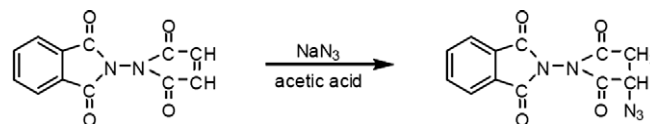
In the present study, chitosan was modified using [*N,N'*-bi- α -azidosuccinimide and *N*-aminophthalimido- α -azide succinimide] under different reaction conditions to design new hydrogels of high metal ions absorption efficiency.

The modified crosslinked hydrogels [(Chitosan-A) (I_{1-3})] and [(Chitosan-B) (III_{1-3}) (IV_1)] were prepared from the reaction of chitosan with different concentrations of [*N,N'*-bi- α -azidosuccinimide and *N*-phthalimido- α -azide succinimide] at room temperature.

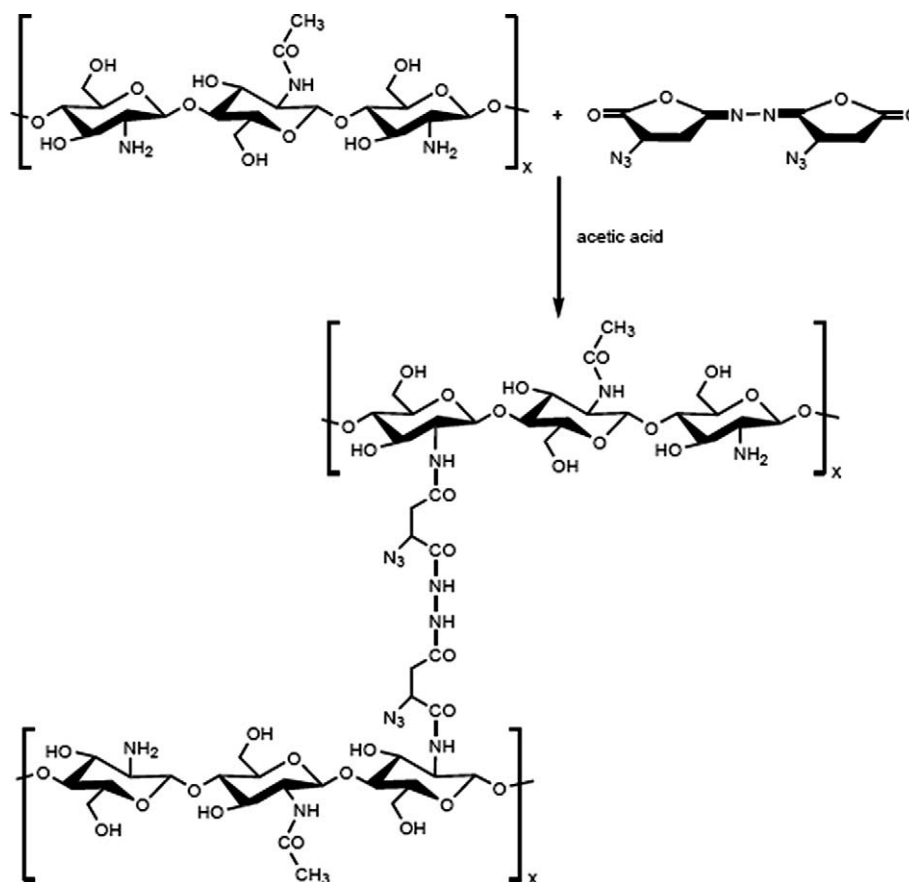
The *N,N'*-bi- α -azidosuccinimide and *N*-phthalimido- α -azide succinimide chitosan hydrogels were further modified repeated using glutaraldehyde as a crosslinker agent to give the corresponding crosslinked hydrogels [(Chitosan-AG) (II_1)], and [(Chitosan-BG) (IV_1)], respectively, Schemes 1–4. The reaction mechanism would be expected to undergo ring opening of azidosuccinimide at the



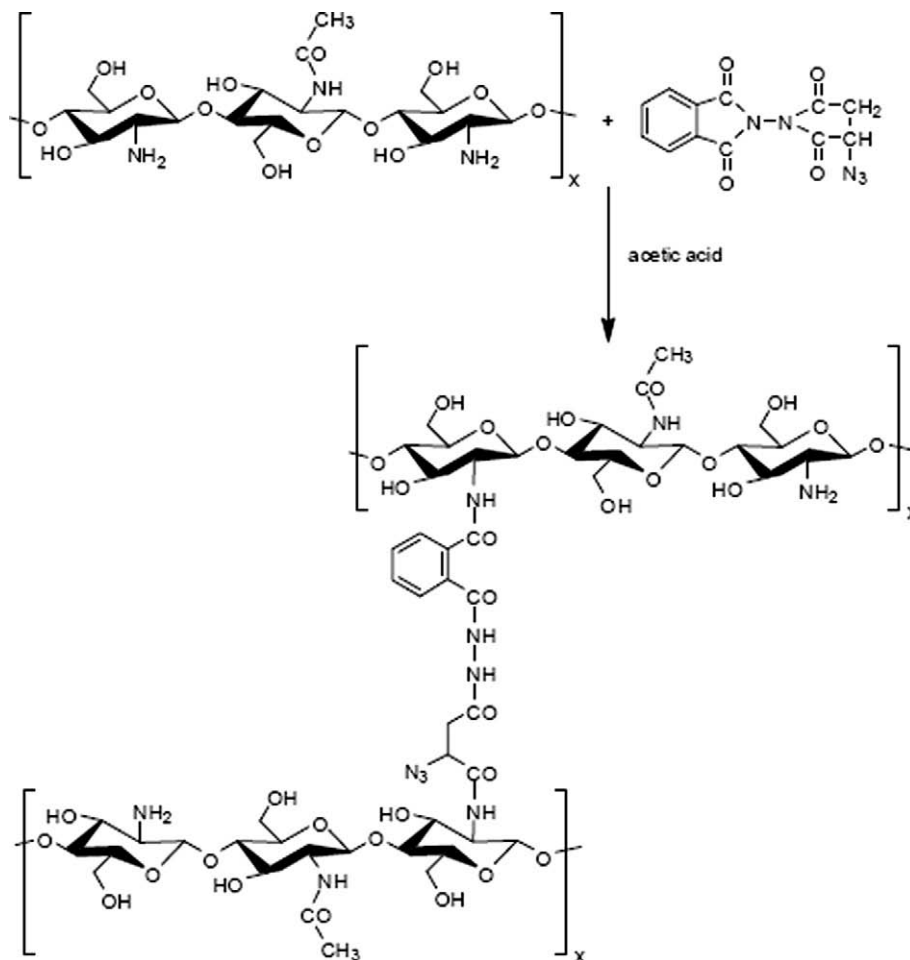
Scheme 1. Synthesis of *N,N'*-bi- α -azidosuccinimide.



Scheme 2. Synthesis of *N*-phthalimido- α -azide succinimide.



Scheme 3. Synthesis of [(Chitosan-A) (I_{1-3})].



Scheme 4. Synthesis of [(Chitosan-B) (III₁₋₃)].

carbonyl groups with nucleophiles of the amino group of chitosan similar to the behavior of the reaction of amine with maleimide (Feuer & Rubinstein, 1958).

4.1. Characterization of the hydrogels

The new hydrogels were characterized by FTIR, thermal stability, crystallography, solubility, swelling capacity and metal ion adsorption.

4.1.1. FTIR spectra

The FTIR spectra show bands at 1520–1560 cm^{-1} assigned to the C=C skeletal in-plane vibrations of the phenyl ring, at 1705–1720 cm^{-1} to the carbonyl group of amide and absorption bands, 2110–2114 cm^{-1} for azido group and at 3423–3444 cm^{-1} for (OH) to the N–H stretching as shown in Figs. 1 and 2.

4.1.2. Thermal stability (thermogravimetric analysis) (TGA)

The thermograph of the hydrogels was evaluated by TGA in air at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The thermograph of the hydrogels shows that the weight loss of the crosslinked hydrogels in the low temperature range may be attributed to the ease of degradation of amide groups present in the biimides, however the weight loss in the high temperature range is attributed to the degradation of the main chain as shown in Figs. 3 and 4, and in Tables 1 and 2, respectively.

When the modification reaction between chitosan and [N,N'-bi- α -azidosuccinimide and N-phthalimido- α -azide succinimide]

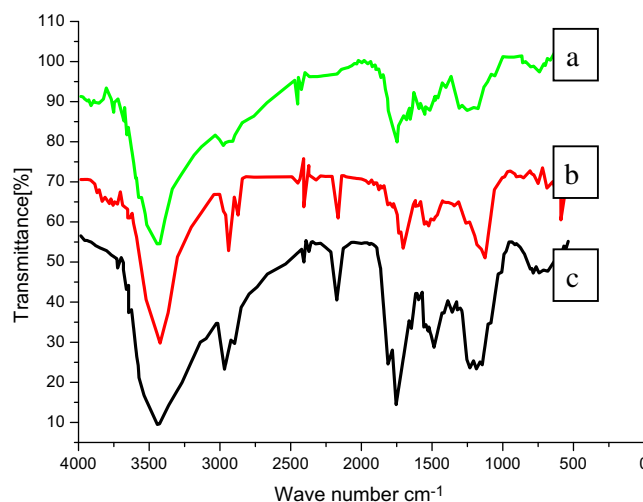


Fig. 1. Infrared spectra of (a) chitosan, (b) Chitosan-A (I₁), and (c) Chitosan-AG (II₁).

occurred in presence of glutaraldehyde, the thermal stability of the produced hydrogels [(Chitosan-AG) (II₁)], and [(Chitosan-BG) (IV₁)] was improved.

When the modification reaction of chitosan with the biimides was carried in presence of high concentrations of glutaraldehyde, hydrogels of increased levels of crosslinking were achieved and the thermal stability of these hydrogels was improved.

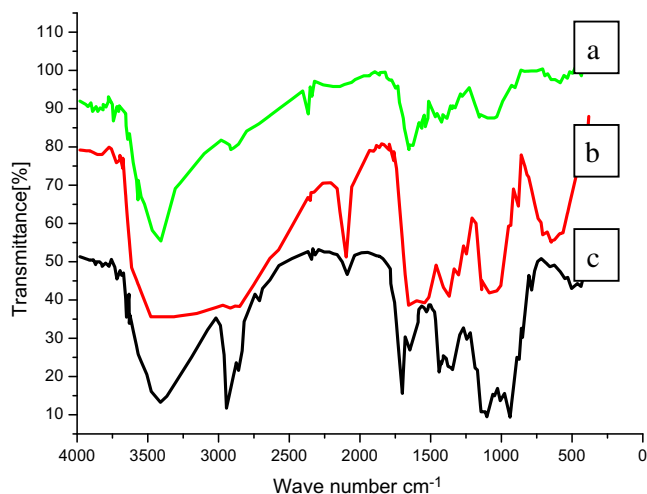


Fig. 2. Infrared spectra of (a) chitosan, (b) Chitosan-B (III₁), and (c) Chitosan-BG (IV₁).

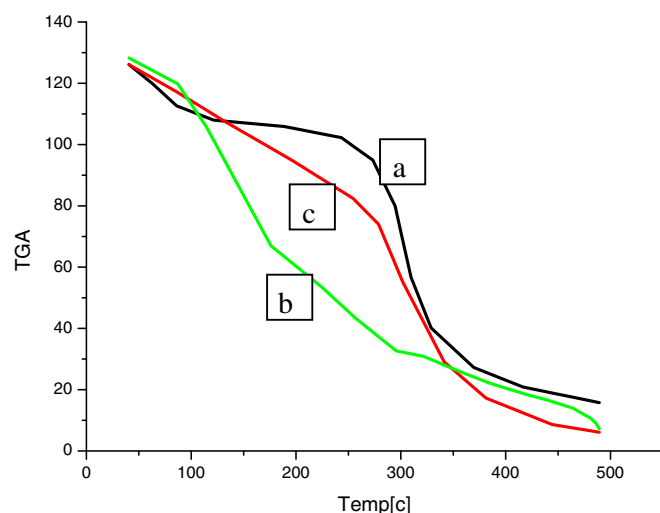


Fig. 4. TGA for (a) chitosan, (b) Chitosan-B (III₁), and (c) Chitosan-BG (IV₁).

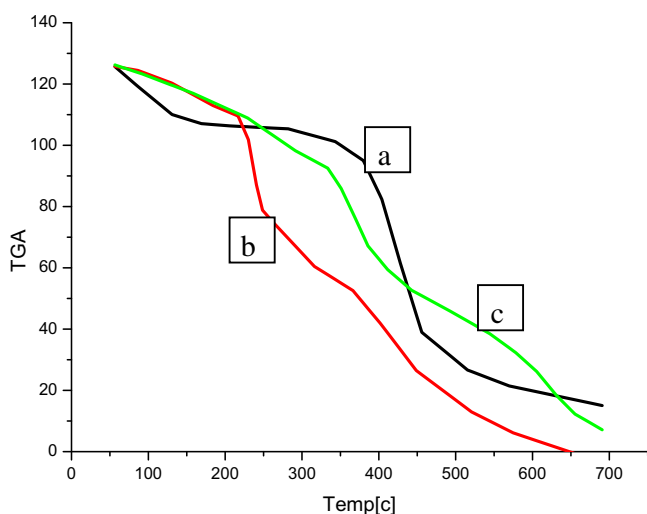


Fig. 3. TGA for (a) chitosan, (b) Chitosan-A (I₁), and (c) Chitosan-AG (II₁).

4.1.3. X-ray diffraction

The X-ray diffraction of the hydrogels shows that the crystallinity of the new hydrogels decreases with increasing the concentration of *N,N'*-bi- α -azidosuccinimide or *N*-aminophthalimido- α -azide succinimide. This is due to increasing the degree of crosslinking in the hydrogels as shown in Figs. 5 and 6. The interfering peaks at 2θ in

the range $4-90^\circ$ indicate the intermediate properties of hydrogel between crystalline and amorphous leading to amorphous properties. The X-ray diffraction of patterns of the hydrogels [(Chitosan-B) (III₁₋₃)], [(Chitosan-AG) (II₁)] and [(Chitosan-BG) (IV₁)] formed in presence of glutaraldehyde show less crystallinity than those of the uncrosslinked hydrogels as would be expected.

4.1.4. Solubility

The solubility test for the new hydrogels [(Chitosan-A) (I₁₋₃)], [(Chitosan-AG) (II₁)], [(Chitosan-B) (III₁₋₃)] and [(Chitosan-BG) (IV₁)] were studied in different solvents at room temperature. The hydrogels were found to be insoluble in DMF, DMSO, THF, NMP, chloroform, acetone, and methanol; however in concentrated H₂SO₄ they produced a dark color.

4.1.5. Swelling measurements

The solvent uptake values from swelling the hydrogels [(Chitosan-A) (I₁₋₃)], [(Chitosan-B) (III₁₋₃)], [(Chitosan-AG) (II₁)] and [(Chitosan-BG) (IV₁)] at 25 °C are shown in Tables 3 and 4.

The presence of hydrophilic amino and amide groups is known to increase the hydrophilicity of the system and consequently they increase the equilibrium swelling values of the samples in aqueous medium.

From Tables 3 and 4, the swelling values of the hydrogels decrease as the concentration of *N,N'*-bi- α -azidosuccinimide or *N*-aminophthalimido- α -azide succinimide swelling increases due to the increase in the hydrophobicity and crosslinking of the hydrogels.

Table 1

Thermal properties of the hydrogels [(Chitosan-A) (I₁), and (Chitosan-AG) (II₁)].

Hydrogel code	Temp.	Wt. loss%	Temp.	Wt. loss%	Temp.	Wt. loss%	Temp.	Wt. loss%
Chitosan	100	8.6	350	45.4	600	25.7	–	–
Chitosan-A 1	75	3.6	180	25.9	219	5.9	400	29.3
Chitosan-AG 1	140	12	255	25	440	25	–	–

Table 2

Thermal properties of the hydrogels [(Chitosan-B) (III₁), and (Chitosan-BG) (IV₁)].

Hydrogel code	Temp.	Wt. loss%	Temp.	Wt. loss%	Temp.	Wt. loss%
Chitosan-B 1	150	56.5	280	15.2	450	12.7
Chitosan-BG 1	100	11.9	400	46.8	–	–

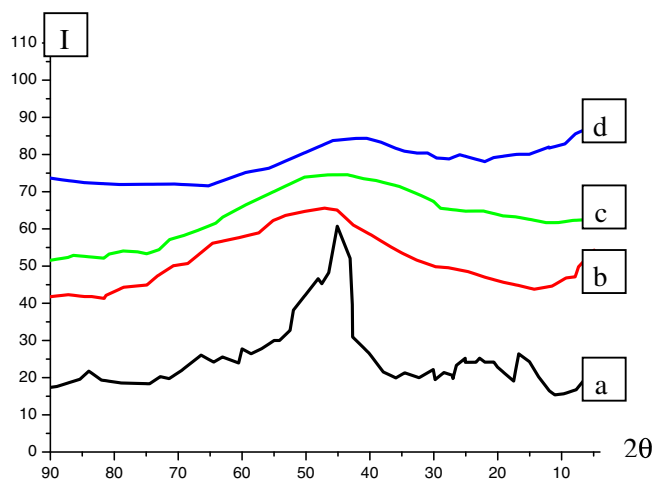


Fig. 5. X-ray diffraction pattern of (a) chitosan, (b) Chitosan-A (I_1), (c) Chitosan-A (I_2), and (d) Chitosan-A (I_3).

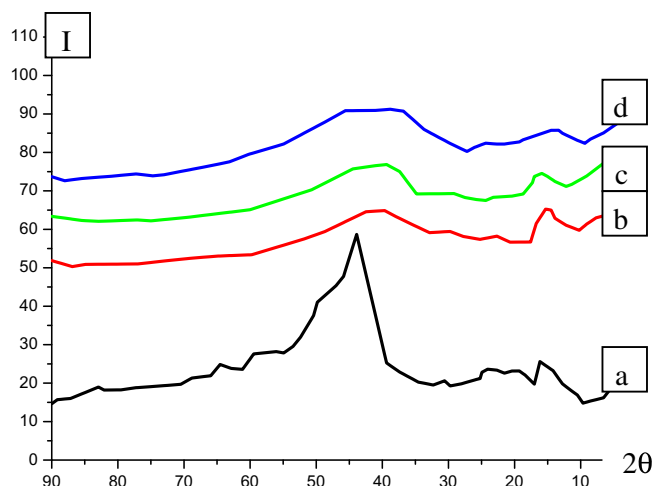


Fig. 6. X-ray diffraction pattern of (a) chitosan, (b) Chitosan-B (III_1), (c) Chitosan-B (III_2), and (d) Chitosan-B (III_3).

Table 3
Solvent uptake for the hydrogels (Chitosan-A) and (Chitosan-AG).

Hydrogel code	Chitosan-A			Chitosan-AG
Solvent uptake %	I_1	I_2	I_3	II_1
DMF uptake %	98	70	63	15
MeOH uptake %	126	114	107	28
DMSO uptake %	129	118	105	60
Acetic acid soln. uptake %	145	130	115	62

Table 4
Solvent uptake for the hydrogels (Chitosan-B) and (Chitosan-BG).

Hydrogel code	Chitosan-B			Chitosan-BG
Solvent uptake %	III_1	III_2	III_3	IV_1
DMF uptake %	364	346	324	176
MeOH uptake %	582	554	531	245
DMSO uptake %	440	421	394	198
Acetic acid soln. uptake %	530	495	456	275

The highest degree of swelling capacity for the hydrogels is observed with acetic acid as opposed to the aprotic solvents.

Table 5
Effect of immersion time of different hydrogels and their efficiency.

Hydrogel code	Immersion time (h)	Cu^{2+} (g/l)	Efficiency (%)
Chitosan-A	0	2.0	–
	5	1.66	17
	10	1.05	47.5
Chitosan-B	0	2.0	–
	5	1.63	18
	10	1.6	20
Chitosan-AG	0	2.0	–
	5	1.88	5.5
	10	1.77	11.5
Chitosan-BG	0	2.0	–
	5	1.68	16
	10	1.61	19.5

Table 6
Effect of immersion time of different hydrogels and their efficiency.

Hydrogel code	Immersion time (h)	Co^{2+} (g/l)	Efficiency (%)
Chitosan-A	0	2.0	–
	5	1.69	15.5
	10	1.65	17.5
Chitosan-B	0	2.0	–
	5	1.73	13.5
	10	1.34	33
Chitosan-AG	0	2.0	–
	5	1.89	5.5
	10	1.36	32
Chitosan-BG	0	2.0	–
	5	1.69	15.5
	10	0.80	60

It is readily noted that the hydrogels [(Chitosan-A) (I_{1-3})] and [(Chitosan-B) (III_{1-3})] possess higher degree of swelling capacity than those produced in the presence glutaraldehyde [(Chitosan-AG) (II_1)] and [(Chitosan-BG) (IV_1)], respectively, due to the increase of the degree of crosslinking.

4.1.6. Metal ion uptake capacity

A preliminary study was carried out to evaluate the efficiency of the new hydrogels to uptake copper and cobalt ions from aqueous systems. The recovery of M^{2+} ions increases with increasing time of immersion of the hydrogels as shown in Tables 5 and 6. This may be attributed to the increase of the number of chelating side chains of the hydrogels.

Tables 5 and 6 indicate that the highest efficiency of the hydrogels for Cu^{2+} ions uptake was obtained from the hydrogels resulting from reacting chitosan with *N,N'*-bi- α -azidosuccinimide [(Chitosan-A)] (47.5%), and the highest for Co^{2+} ions was obtained from the hydrogels resulting from reacting chitosan with *N*-phthalimido- α -azide succinimide [(Chitosan-BG)] (60%).

The above data points to the possibility of designing these hydrogels for preferential metal uptake beyond just Cu^{2+} and Co^{2+} . Thus results showed that these hydrogels may be used as effective materials for metal ion removal from aqueous systems.

5. Conclusions

Using simple technology, novel modified chitosan hydrogels were prepared through modification of chitosan with *N,N'*-bi- α -azidosuccinimide or *N*-phthalimido- α -azide succinimide under different reaction conditions. The *N*-phthalimido- α -azide succinimide hydrogel showed the highest swelling values in different solvents.

All the new environment friendly hydrogels may be tailored to uptake metal ions, at the very least Cu^{2+} and Co^{2+} ions, preferentially from aqueous systems at different levels of efficiency. Thus they may be used for targeted treatment of industrial waste water and other waters polluted with heavy metals.

Chitosan-*N,N'*-bi- α -azidosuccinimide hydrogel [(Chitosan-A)] can recover Cu^{2+} ions with efficiencies reaching 47.5%, and for Co^{2+} ions with efficiencies up to 17.5%.

However for chitosan-*N*-phthalimido- α -azide succinimide hydrogel [(Chitosan-BG)] can recover Cu^{2+} ions with efficiencies reaching 19.5% and Co^{2+} ions with efficiencies up to 60% from aqueous systems.

The thermal stability of the new hydrogel chitosan-*N,N'*-bi- α -azidosuccinimide [(Chitosan-A)] is higher than the chitosan *N*-phthalimido- α -azide succinimide hydrogel [(Chitosan-B)]. It was also clear that modification of chitosan in absence or presence of glutaraldehyde improved the thermal stability of these hydrogels.

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