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Synthesis and properties of chitosan hydrogels modified with heterocycles

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ABSTRACT

Preparation and properties of chitosan modified with heterocycles in absence or presence of gluteraldehyde as a cross linker is described. New modified chitosan–heterocyclic hydrogels were prepared from chitosan and heterocyclic compounds such as *N*,*N*′-biisomaleimide, *N*,*N*′-biisophthalimide, and *N*,*N*′-phthalimidomaleimide via a crosslinking reaction. The new hydrogels chemical structure was characterized by spectral analysis (IR), X-ray diffraction, thermal gravimetric analysis (TGA), solubility, and swellability in water and different organic solvents. Evaluation of the efficiency of the new hydrogels to uptake copper and cobalt ions from aqueous systems was carried out and promising results were obtained.

1. Introduction

Heavy metals are considered to be amongst the most dangerous polluting agents in water. Their danger comes from their bioaccumulation and non-biodegradability. Chitosan is a biocompatible, non-toxic, biodegradable and a strong adhesive polymer, with a gel forming ability at low pH (Ravi Kumar, 2000; Ravi Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004).

Also the chitosan biopolymer has a large capacity for the fixation of molecules such as pesticides, protein, and dyes. The free amino function of chitosan gives it a better ability to chelate ions of transition metals than other natural compounds such as cellulose derivatives. These chelating properties are turned to account for water treatment and particularly to recover metals.

Chitosan is also one of the most abundant natural polysaccharides, and is well known for its biocompatible and biodegradable properties (Mi, Tan, Liang, & Sung, 2002).

It was reported that chitosan, because of its high amino content, has been found to posses good sorptive capacities for many heavy metal ions (Onsoyen & Skaugrud, 1990; Guibal, Milot, & Tobin, 1998; Bailey, Olin, Bricka, & Adrian, 1999; Bassi, Prasher, & Simpson, 2000), through complexation of heavy metal ions with the amino groups in chitosan (Ogawa, Oka, Miyanishi, & Hirano, 1984; Piron & Domard, 1998).

Chitosan hydrogel beads were studied for the adsorption of lead ions and humic acid from aqueous solutions to examine the adsorption behaviors and mechanisms. Three types of batch adsorption experiments, including single species adsorption, sequential adsorption of one species after another and co-adsorption of both species, were investigated (Yan & Bai, 2005).

To increase the uptake capacity of mercury ions, several chemical modifications of chitosan beads crosslinked with glutaraldehyde were performed. Among them, aminated chitosan bead prepared through chemical reaction with ethylenediamine had a high uptake capacity (Jeon & Holl, 2003).

In the present work, modifications of chitosan was made to the basic matrix using heterocyclic compounds such as: *N*,*N*′-biisomaleimide, *N*,*N*′-biisophthalimide, and *N*,*N*′-phthalimidomaleimide to form new hydrogels for uptake of metal ions and wastewater treatment .

2. Experimental

2.1. Materials

Chitosan: 67% degree of deacetylation MW > 6305 (ALDRICH), Glutaraldehyde (25%) (G) (ALDRICH), Maleic anhydride (MERCK), Phthalic anhydride (ALDRICH), Acetic anhydride (Alpha), Acetic acid (glacial) (GPR), Hydrazine hydrate (99%) (Fluka), *N*,*N*′-biisomaleimide (B) (Feuer & Rubinstein, 1958), *N*,*N*′-phthalimidomaleimide (M) (Awad, Kandile, & Ismail, 1979), *N*,*N*′-biisophthalimide (P) (Drew & Hatt, 1937).

2.2. Measurements

Melting Points were determined on a Boetius hot-stage apparatus and are uncorrected. The infrared spectra were measured on

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Perkin-Elmer-1430 Infrared Spectrophotometer using potassium bromide Wafer technique (Micro Analytical Center) (Cairo University). X-ray diffractograms of polymers were obtained with a Phillips X-ray unit (Generator PW-1390) and a Ni-filtered Cu (Faculty of Women) (Ain Shams University). Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere using a Shimadzo TGA-50H thermal analyzer (Micro Analytical Center) (Cairo University).

The solubility of the polymers was examined using 0.02 g of polymer in 3–5 ml of each solvent at room temperature.

2.3. Reaction of chitosan with different heterocyclic compounds in absence of glutaraldehyde

A mixture of (0.56 g) of chitosan in 60 ml acetic acid solution (0.03% in distilled water) with each heterocyclic compound at different concentrations (0.25, 0.5, 1.0, and 1.5 mmol), (*N*,*N*′-Biisomaleimide, *N*,*N*′-biisophthalimide, and *N*,*N*′-phthalimidomaleimide) in 4 ml glacial acetic acid was stirred for 2 h at room temperature. The crosslinked hydrogels formed were washed with dimethylformamide and dried under vacuum to give the corresponding new hydrogels, (Chitosan-B) (I_{1-4}), (Chitosan-P) (III_{1-3}), and (Chitosan-M) (V_{1-3}), respectively.

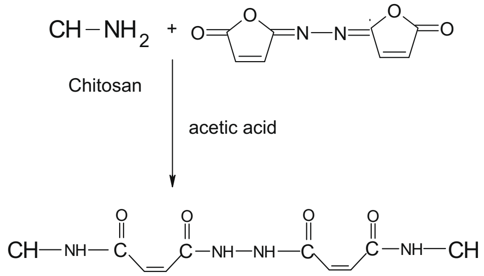
2.4. Reaction of chitosan with different heterocyclic compounds in presence of glutaraldehyde

A mixture of (0.56 g) of chitosan in 60 ml acetic acid solution (0.03% in distilled water) with each heterocyclic compound at different concentrations (0.25, 0.5, 1.0, and 1.5 mmol), (*N*,*N*′-Biisomaleimide, *N*,*N*′-biisophthalimide, and *N*,*N*′-phthalimidomaleimide) in 4 ml glacial acetic acid was stirred in presence of 5 ml glutaraldehyde (25%) for 2 h at room temperature. The crosslinked hydrogels formed were washed with dimethylformamide and dried under vacuum to give the corresponding new hydrogels (Chitosan-BG) (II_1), (Chitosan-PG) (IV_1), and (Chitosan-MG) (VI_1), respectively.

2.5. Determination of the soluble fraction in solvents

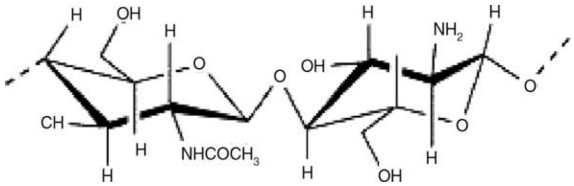
Weighed samples of each hydrogel were boiled for 1 h in 20 ml of the following solvents DMF, MeOH, DMSO, or acetic acid. The swollen samples were then dried in oven at 70 °C to remove the solvent. The drying was continued to constant weight (W_1). The soluble fraction was calculated according to the following equation:

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

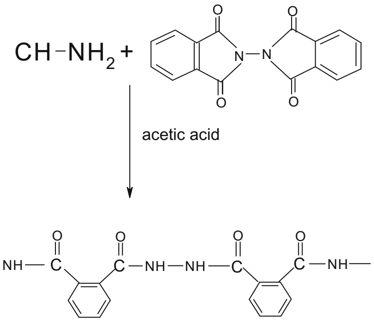


[(Chitosan-B) (I_{1-4})]

Scheme 1.

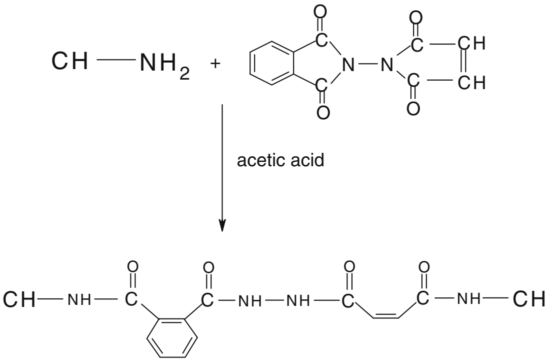


Where: **CH-NH₂ is**



[(Chitosan-P) (III_{1-3})]

Scheme 2.



[(Chitosan-M)(V_{1-3})]

Scheme 3.

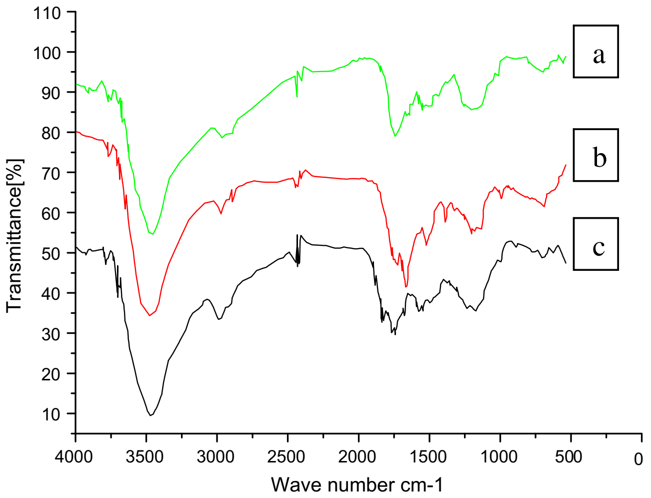


Fig. 1. Infrared spectra of: (a) Chitosan, (b) Chitosan-B (I-1), and (c) Chitosan-BG (II-1).

where W_0, is the initial weight of the hydrogel and W_1, is the weight of the oven dried hydrogel.

2.6. Determination of solvent uptake

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 just to remove the droplets of solvent on the surface.

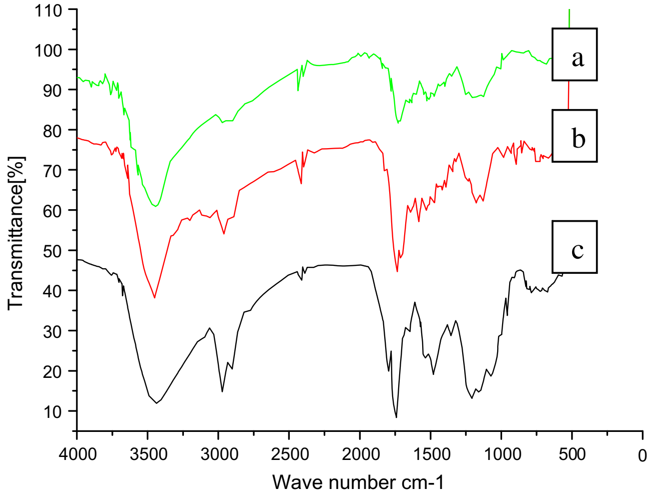


Fig. 2. Infrared spectra of: (a) Chitosan, (b) Chitosan-P (III-1), and (c) Chitosan-PG (IV-1).

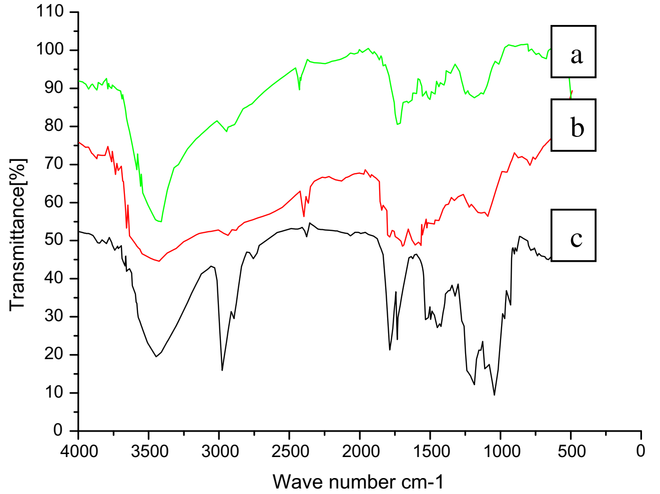


Fig. 3. Infrared spectra of: (a) Chitosan (b) Chitosan-M (V-1), and (c) Chitosan-MG (VI-1).

Table 1
Solvent uptake for the hydrogels (Chitosan-B) and (Chitosan-BG)

Hydrogel code	Chitosan-B (%)				Chitosan-BG (%)
Solvent uptake	I_1	I_2	I_3	I_4	II_1
DMF uptake	48	14	12	10	44
MeOH uptake	15	13	12	10	13
DMSO uptake	16	7	5	4	14
Acetic acid solution uptake	840	766	659	530	89

The solvents uptake was calculated using the following equation:

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

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

3. Results and discussion

3.1. Modification of chitosan with heterocyclic compounds

In the present study, different heterocyclic compounds were selected to modify chitosan to make use of the functional groups present in the structure of the heterocyclic compounds. For example, employing the amide groups as centers for bonding bioactive materials for drug delivery systems. In addition to these functional groups, groups such as carbonyl and NH-groups can act as chelating groups for different metal ions. The hydrogels produced can be used as effective materials for metal ion removal from water.

3.1.1. Modification of chitosan with different heterocyclic compounds

Chitosan was reacted with different concentrations of *N,N′*-biisomaleimide via ring opening of both the maleimide moieties with

Table 2
Solvent uptake for the hydrogels (Chitosan-P) and (Chitosan-PG)

Hydrogel code	Chitosan-P (%)			Chitosan-PG (%)
Solvent uptake	III_1	III_2	III_3	IV_1
DMF uptake	38	34	30	12
MeOH uptake	102	91	84	35
DMSO uptake	86	72	63	72
Acetic acid solution uptake	162	137	115	79

Table 3
Solvent uptake for the hydrogels (Chitosan-M) and (Chitosan-MG)

Hydrogel code	Chitosan-M (%)			Chitosan-MG (%)
Solvent uptake	V_1	V_2	V_3	VI_1
DMF uptake	536	487	423	327
MeOH uptake	80	76	68	73
DMSO uptake	872	793	724	862
Acetic acid solution Uptake	304	276	245	247

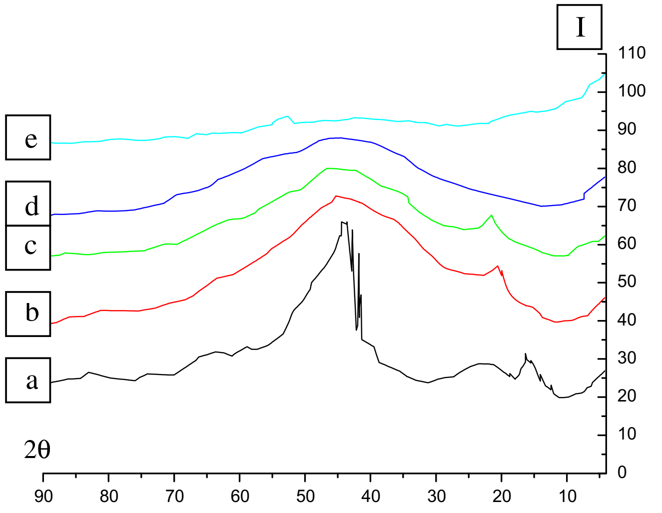


Fig. 4. X-ray Diffraction pattern of: (a) Chitosan, (b) Chitosan-B (I-1), (c) Chitosan-B (I-2), (d) Chitosan-B (I-3), and (e) Chitosan-B (I-4).

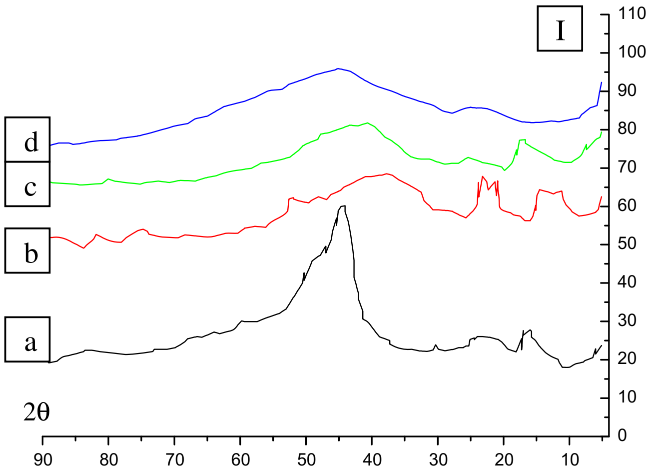


Fig. 5. X-ray Diffraction pattern of: (a) Chitosan, (b) Chitosan-P (III-1), Chitosan-P (III-2), and (c) Chitosan-P (III-3).

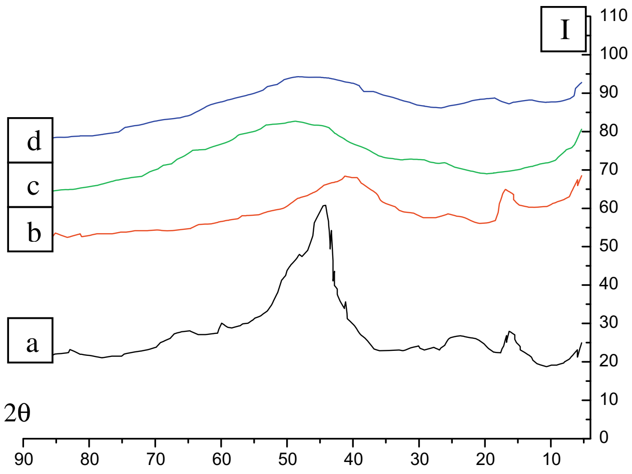


Fig. 6. X-ray Diffraction pattern of: (a) Chitosan, (b) Chitosan-M (V-1), (c) Chitosan-M (V-2), and (d) Chitosan-M (V-3).

the amino group of chitosan, *N,N′*-biisophthalimide and *N,N′*-phthalimidomaleimide to give the corresponding crosslinked hydrogels (Chitosan-B) (I_{1-4}), (Chitosan-P) (III_{1-3}), and (Chitosan-M) (V_{1-3}), respectively, as shown in Scheme 1–3.

Chitosan was also reacted with this heterocyclic compounds in the presence of glutaraldehyde as crosslinker to improve the characteristics of the produced hydrogels to give (Chitosan-BG) (II_1), (Chitosan-PG) (IV_1), and (Chitosan-MG) (VI_1), respectively.

The IR spectra for the hydrogels produced show characteristic absorption bands at 1558–1559 cm^{-1} assigned to the C=C skeletal in-plane vibrations of the phenyl ring, at 1700–1740 cm^{-1} to the carbonyl group of amide and absorption bands, and at 3422–3446 cm^{-1} for (OH) implies to the N–H stretching as shown in Figs. 1–3.

3.1.2. Hydrogel characterization

The new hydrogels were characterized by the following methods: solubility, X-ray diffraction, thermal analysis, solvent uptake, and metal uptake.

3.2. Solubility

It is well known that the high hydrophilicity of chitosan is due to the primary amine group that makes chitosan readily soluble in dilute acetic solution to yield a hydrogel dissolved in an aqueous medium (Heisen & Rorrer, 1995). Hence the solubility of the new hydrogels was studied in different solvents at room temperature. The results show that the hydrogels are insoluble in acetic acid solution, DMF, DMSO, THF, NMP, chloroform, acetone, and methanol. This indicates successful formation of crosslinked networks in this hydrogels.

3.3. The swelling behaviour

The swelling of the different hydrogels decreased as the concentration of the heterocyclic compounds increased due to the increase in the hydrophobicity and crosslinking of the hydrogels. The solvent uptake values are shown in Tables 1–3.

The highest degree of swelling for the hydrogels (Chitosan-B) and (Chitosan-BG) and, (Chitosan-P) and (Chitosan-PG) is observed with acetic acid as opposed to the aprotic solvents. The highest

Table 4
Thermal properties of the hydrogels (Chitosan-B) (I_{3-4}) and (Chitosan-BG) (II_1)

Hydrogel code		Temperature	Weight loss (%)	Temperature	Weight loss (%)	Temperature	Weight loss (%)
Chitosan		100	8.6	350	45.4	600	25.7
Chitosan-B	3	150	34	325	30.9	600	19.9
	4	170	12	252	26.8	550	21.5
Chitosan-BG	1	100	7	256	28.8	446	25

Table 5
Thermal properties of the hydrogels (Chitosan-P) (III_1) and (Chitosan-PG) (IV_1)

Hydrogel code		Temperature	Weight loss (%)	Temperature	Weight loss (%)	Temperature	Weight loss (%)	Temperature	Weight loss (%)
Chitosan-P	1	110	11.3	350	54	–	–	–	–
Chitosan-PG	1	100	25.9	280	32.7	446	20.2		

Table 6
Thermal properties of the hydrogels (Chitosan-M) (V_1) and (Chitosan-MG) (VI_1)

Hydrogel code		Temperature	Weight loss (%)	Temperature	Weight loss (%)	Temperature	Weight loss (%)
Chitosan-M	1	120	11	400	47.6	–	–
Chitosan-MG	1	180	66.2	350	11	450	8.6

swelling degree for the aprotic solvents is observed in DMSO for the hydrogels (Chitosan-M) and (Chitosan-MG).

It is readily noted that the hydrogels produced from the reaction of chitosan with different heterocyclic compounds possess higher degree of swelling than those produced in with glutaraldehyde crosslinking.

3.4. X-ray diffraction

The X-ray diffraction patterns of the hydrogels shows that the crystallinity of hydrogels decreases with increasing concentration of the heterocyclic compounds. This is due to increased degree of crosslinking as shown in Figs. 4–6. The interfering peaks at 2θ in the range 4–90° indicate intermediate properties of the hydrogels between crystalline and amorphous leading to amorphous properties. The X-ray diffraction patterns of the glutaraldehyde crosslinked hydrogels are show less crystallinity than those of the uncrosslinked hydrogels as would be expected.

3.5. Thermal characterization: thermogravimetric analysis (TGA)

The thermograph of the hydrogels are evaluated by TGA in air at a heating rate of 10 °C/min. The thermograph of the hydrogels shows that the weight loss of the crosslinked hydrogel in the low temperature range may be attributed to the ease of degradation of amide groups present in the heterocyclic compounds. The

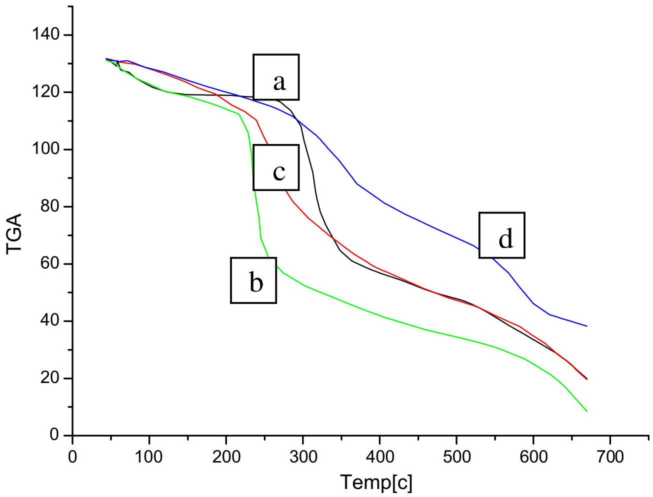


Fig. 7. TGA for: (a) Chitosan, (b) Chitosan-B (I-3), (c) Chitosan-B (I-4), and (d) Chitosan-BG (II-1).

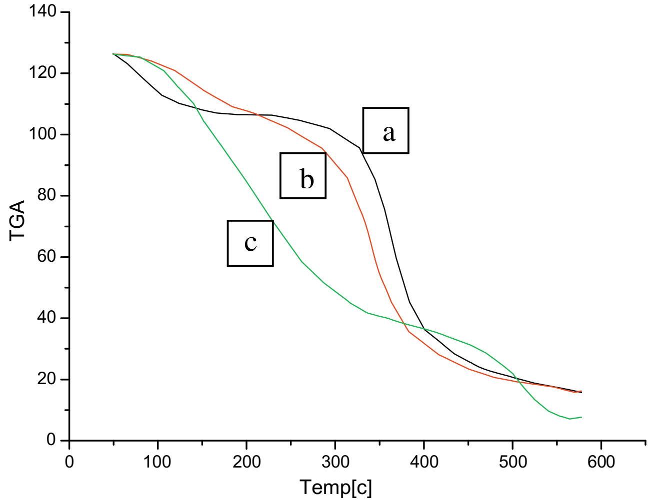


Fig. 8. TGA for: (a) Chitosan, (b) Chitosan-P (III-1), and (c) Chitosan-PG (IV-1).

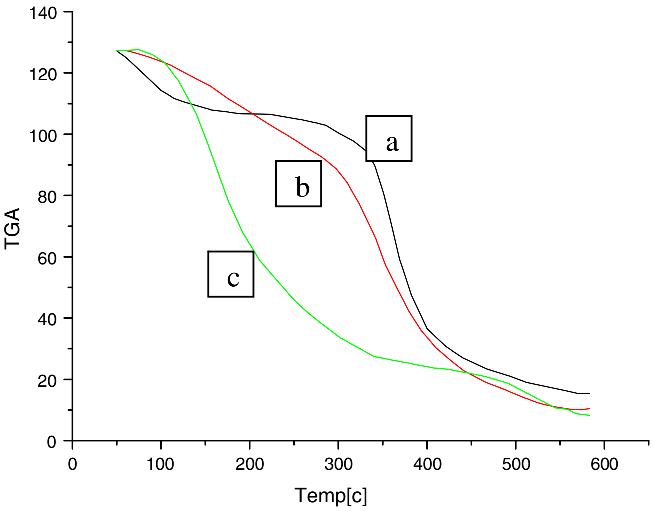


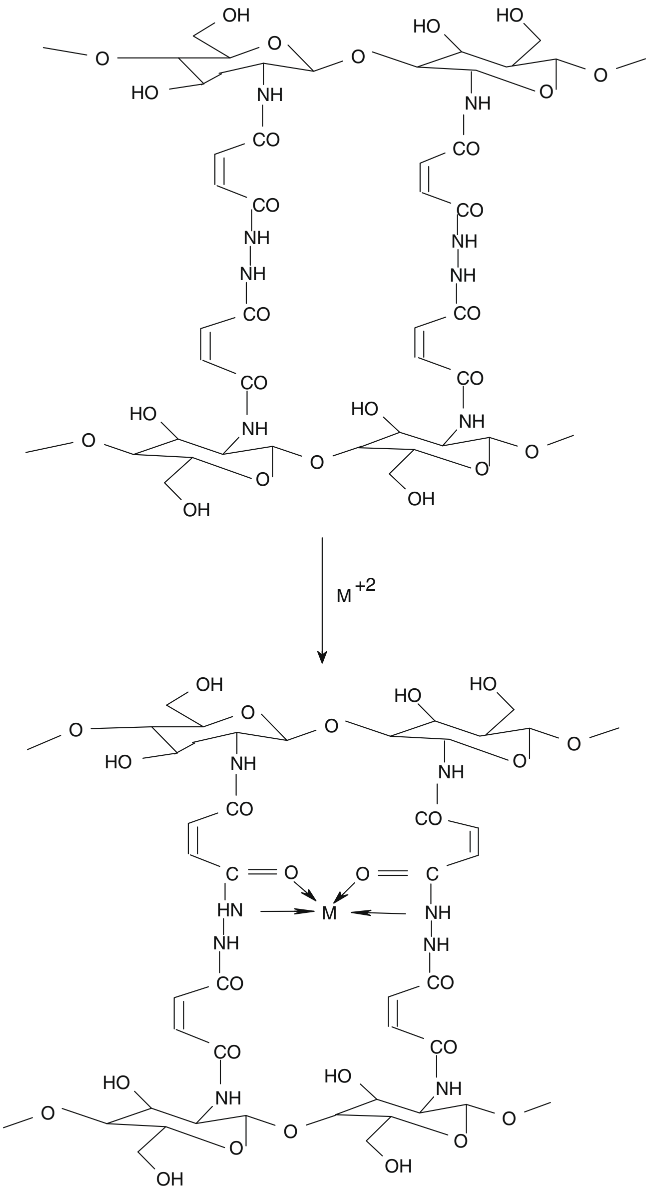
Fig. 9. TGA for: (a) Chitosan, (b) Chitosan-M (V-1), and (c) Chitosan-MG (VI-1).

Table 7
Effect of immersion time of different hydrogels and their efficiency

Hydrogel code	Immersion time (h)	Cu^{+2} (g/l)	Efficiency (%)
Chitosan-B	0	2.0	–
	5	1.88	6
	10	1.79	10.5
Chitosan-P	0	2.0	–
	5	1.22	39
	10	1.15	42.5
Chitosan-M	0	2.0	–
	5	1.885	5.7
	10	1.88	6
Chitosan-BG	0	2.0	–
	5	1.8	9.5
	10	1.79	10.5
Chitosan-PG	0	2.0	–
	5	1.95	2.5
	10	1.88	6
Chitosan-MG	0	2.0	–
	5	1.79	10.5
	10	1.63	18.5

Table 8
Effect of immersion time of different hydrogels and their efficiency

Hydrogel code	Immersion time (h)	Co^{+2} (g/l)	Efficiency (%)
Chitosan-B	0	2.0	–
	5	1.75	13
	10	1.75	13
Chitosan-P	0	2.0	–
	5	1.23	38.5
	10	0.97	51.5
Chitosan-M	0	2.0	–
	5	1.84	8
	10	1.72	14
Chitosan-BG	0	2.0	–
	5	1.65	17.5
	10	1.41	29.5
Chitosan-PG	0	2.0	–
	5	1.73	13.5
	10	1.34	33
Chitosan-MG	0	2.0	–
	5	1.65	17
	10	0.94	53



M= Co(II), Cu(II)

Scheme 4.

weight loss in the high temperature range is due to the degradation of the main chain as shown in Tables 4–6 and Figs. 7–9.

When additional crosslinking was achieved with higher concentrations of the glutaraldehyde crosslinker, the thermal stability of the modified chitosan was improved.

3.6. Metal ions recovery

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 of a solution of metal ions at a known concentration for different immersion times.

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

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

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

where, F, efficiency (%); C, concentration of M (II) in the solution after a certain time period; C_o, initial concentration of M (II) solution.

The removal of heavy metal ions was achieved via complexation between metal ion and the NH-groups. The recovery of M^{+2} ions decreases with increasing time of immersion of the hydrogels as shown in Tables 7 and 8. Tables 7 and 8 indicate that the highest efficiency of the hydrogels for Cu^{+2} ions and Co^{+2} ions was obtained from the hydrogels resulting from reacting Chitosan with *N*,*N*′-biisophthalimide 42.5%, and 51.5%, respectively.

It can be concluded from the above data that the affinity order of the metal ions is Co (II) > Cu (II) and these hydrogels can be used as effective materials for metal ion removal from water. The expected structure of the complexes is shown in Scheme 4.

4. Conclusions

The reaction products of chitosan with heterocyclic compounds allow preparation of new hydrogels with various affinities for metal ions in different solvents. The swelling in different solvents decreases in the following order:

N,*N*′-biisomaleimide > *N*,*N*′-phthalimido maleimide > *N*,*N*′-biisophthalimide. The hydrogels obtained from modified chitosan are able to recover heavy metals such as Cu and Co from aqueous solutions.

Chitosan–*N*,*N*′-biisophthalimide hydrogel can recover Cu ions with efficiencies reaching 42.5% and Co ions with efficiencies up to 51.5%. The thermal stability of the reaction products of heterocyclic compounds with chitosan can be arranged in the following order:

N,*N*′-biisophthalimide > *N*,*N*′-phthalimidomaleimide > *N*,*N*′-biisomaleimide.

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