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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.

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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.

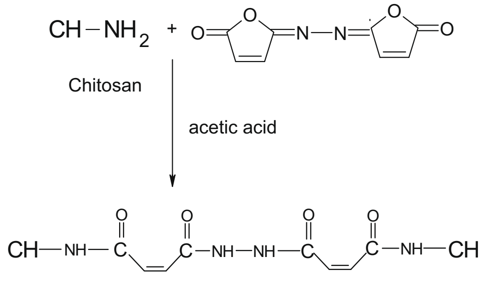
2.4. Reaction of chitosan with different heterocyclic compounds in presence of glutaraldehyde

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

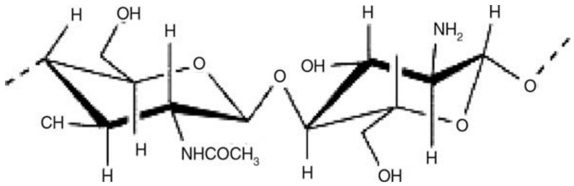
Weighed samples of each hydrogel were boiled for 1 h in 20 ml of the following solvents DMF, MeOH, DMSO, or acetic acid. The swollen samples were then dried in oven at 70 °C to remove the solvent. The drying was continued to constant weight (W_1). The soluble fraction was calculated according to the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

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

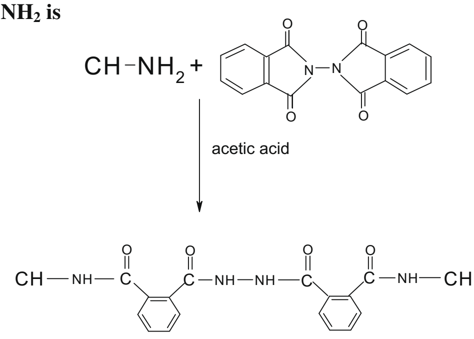


[(Chitosan-B) (I_{1-4})]

Scheme 1.

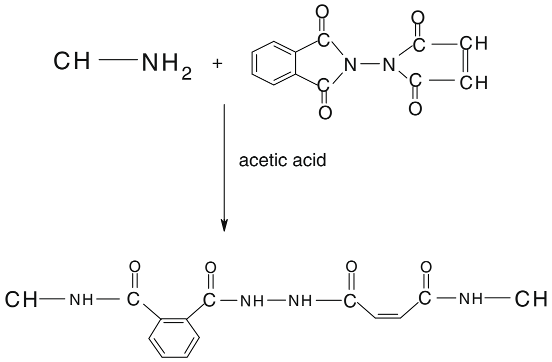


Where: **CH-NH$_2$ is**



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

Scheme 2.



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

Scheme 3.

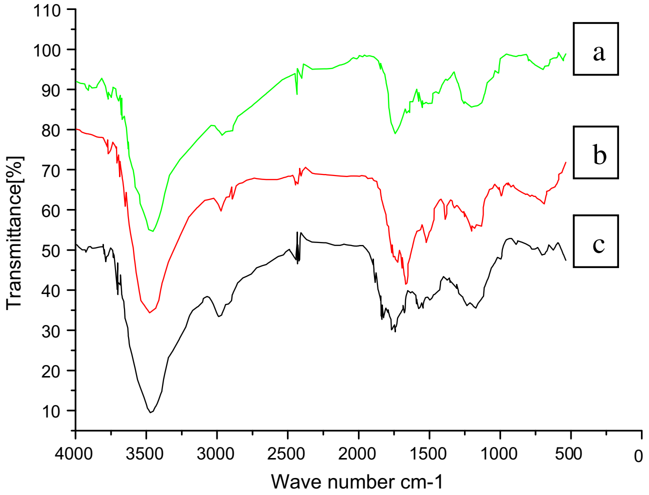


Fig. 1. Infrared spectra of: (a) Chitosan, (b) Chitosan-B (I-1), and (c) Chitosan-BG (II-1).

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