

# New hydrogels based on modified chitosan as metal biosorbent agents



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## ABSTRACT

In this study, two new green biodegradable hydrogels (**A<sub>1</sub>**, **A<sub>2</sub>**) based on modified chitosan by dialdehydes were prepared via reaction of chitosan with [4,4'-diformyl- $\alpha$ - $\omega$ -diphenoxy-ethane or 4,4'-diformyl-2,2'-dimethoxy- $\alpha$ - $\omega$ -diphenoxy-ethane] under different reaction conditions. Characterization techniques were applied to the prepared hydrogels as FTIR, TGA, SEM, and X-ray. The efficiency of adsorption of Cu (II), Co (II), Zn (II), Hg (II) and Pb (II) ions from aqueous solution under different pH values were investigated. The results revealed that these hydrogels showed pH sensitive behavior in metal removal. Hydrogel (**A<sub>2</sub>**) showed the highest adsorption of Hg (II) ion at pH 5.

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## 1. Introduction

Metal ions are one of the important categories of water pollutants that are toxic to humans through the food-chain pyramid. Various toxic heavy metal ions discharged into the environment through different industrial activities constitute one of the major causes of environmental pollution. Biosorbents gain wide attention as these are available in large quantities worldwide and are eco-friendly. The use of adsorbents containing natural polymers has received increased recognition, in particular polysaccharides such as chitin and its derivate chitosan. Chitosan has drawn particular attention as an effective biosorbent due to its low cost compared to activated carbon and its high content of amino and hydroxyl groups that are readily functionalized. Modified chitosans have shown high adsorption potential for various aquatic pollutants [1–5]. This biopolymer represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behavior, and high selectivity toward pollutants [1–5]. Natural chitosan has been modified by several methods (either physically or chemically) in order to enhance the adsorption capacity for various types of pollutants.

Different forms of chitosan, e.g. membranes, microspheres, gel beads and films have been prepared and examined for the removal of various pollutants from wastewaters. Description of the various forms of chitin and chitosan, their physical and chemical properties has been extensively reviewed [1–7].

Inefficient ways of managing heavy metal ions in wastewater will cause long-term risk to the ecosystem and humans. Harmful toxic heavy metals that are discharged by chemical industries include cadmium, mercury, lead, copper, nickel, chromium, and zinc.

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters which originate for example from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries [8,9]. Unlike organic wastes, heavy metals are non-biodegradable and they accumulate in living tissues, causing various diseases and disorders. Therefore they must be removed before discharge.

In continuation of our previous work for synthesis of new hydrogels for metal ions removal from aqueous solution [10–14], in this paper, new green biodegradable hydrogels for metal ion removal were designed and synthesized. The structural, thermal stability and the morphology of the new hydrogels were studied. Moreover evaluation of the performance of the removal of different metal ions from aqueous solutions at different pH values was investigated.

## 2. Experimental

### 2.1. Materials

Chitosan with 67% degree of deacetylation, M.W > 6305, anhydrous sodium carbonate (Merck), 4-hydroxybenzaldehyde (Aldrich), 4-hydroxy-3-methoxy-benzaldehyde (Aldrich)

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1,2-dichloroethane (Alpha), acetic acid (glacial) (Fluka), ethanol (Aldrich), dimethylformamide (Adwic, Egypt), dimethylsulfoxide (Fluka), copper sulfate, cobalt acetate, zinc sulfate, mercury acetate and lead acetate of analytical grade were purchased from (Sigma) and used for preparation of the aqueous solutions. All other chemicals and reagents were analytical grade.

## 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 the 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 Shimadzu TGA-50H thermal analyzer. The morphology of the different hydrogels was investigated using JXA 850 prop micro analyzer scanning electron microscope (SEM) at 50  $\mu\text{m} \times 1000 \mu\text{m}$  and at 20  $\mu\text{m} \times 2000 \mu\text{m}$ .

## 2.3. Methods

### 2.3.1. Synthesis of starting materials

**2.3.1.1. General procedure.** A mixture of solid anhydrous sodium carbonate (26.5 g, 0.25 mol) and 1,2-dichloroethane (9.91 g, 0.1 mol) dissolved in dimethylformamide (DMF) (25 ml) were added to a solution of the appropriate aldehyde (0.2 mol) in DMF (25 ml) with stirring and then heated at 120 °C for 4 h. The reaction mixture was cooled to 50 °C, then poured into cold water (400 ml) and allowed to stand overnight in a refrigerator. The precipitate was filtered off, washed with water, dried under vacuum and crystallized from the appropriate solvent.

**2.3.1.2. Synthesis of 4,4'-diformyl- $\alpha$ - $\omega$ -diphenoxy-ethane.** Obtained from condensation of 4-hydroxybenzaldehyde (24.4 g, 0.2 mol) with 1,2-dichloroethane (9.91 g, 0.1 mol) for 4 h as colorless needles from ethanol, yield: 65%, m.p.: 114 °C [15,16].

**2.3.1.3. Synthesis of 4,4'-diformyl-2,2'-dimethoxy- $\alpha$ - $\omega$ -diphenoxy-ethane.** Obtained from condensation of 4-hydroxy-3-methoxybenzaldehyde (30.43 g, 0.2 mol) with 1,2-dichloroethane (9.91 g, 0.1 mol) for 4 h as colorless needles from ethanol, yield: 75%, m.p.: 176 °C [15,16].

### 2.3.2. Synthesis of the hydrogels

**2.3.2.1. Modification of chitosan with dialdehydes.** A mixture of dialdehyde [4,4'-diformyl- $\alpha$ - $\omega$ -diphenoxy-ethane or 4,4'-diformyl-2,2'-dimethoxy- $\alpha$ - $\omega$ -diphenoxy-ethane] (0.5 mmol) in 10 ml dimethylformamide, and (0.56 g) of chitosan in 60 ml acetic acid solution (0.03% in distilled water) were stirred for 2 h. The crosslinked hydrogels that formed were washed with dimethylformamide and dried under vacuum to give the corresponding modified chitosan hydrogels [**A<sub>1</sub>**, **A<sub>2</sub>**] respectively.

## 2.4. Determination of metal ions capacity of the prepared hydrogels

Accurately weighed 50 mg of dry hydrogels samples were placed in 100 ml beakers containing 50 ml of aqueous copper sulfate, cobalt acetate, zinc sulfate, mercuric acetate and lead acetate solutions. At regular intervals, an aliquot of supernatant solution was withdrawn.

Thereafter its  $\text{M}^{2+}$  concentration was determined using UV–vis spectrometry. The adsorbed  $\text{M}^{2+}$  was calculated from the difference between the initial  $\text{M}^{2+}$  concentration and that measured at each

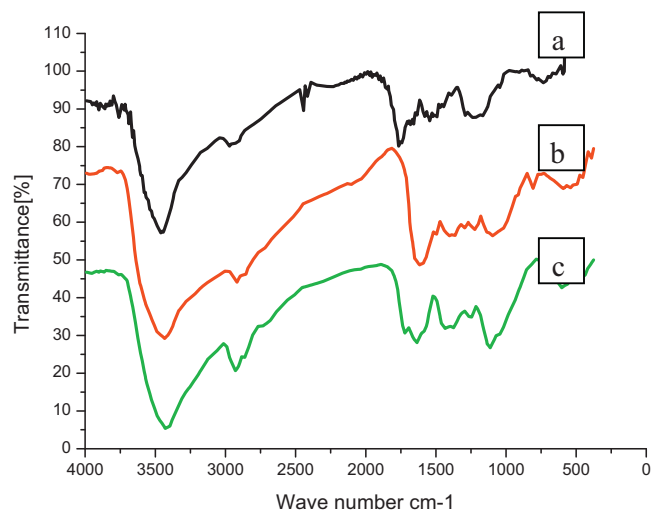


Fig. 1. FTIR spectra of (a) chitosan, (b) hydrogel **A<sub>1</sub>** and (c) hydrogels **A<sub>2</sub>**.

interval. Data points are the mean of three independent determinations. The efficiency of metal ion uptake of the hydrogels was calculated using the following equation:

$$F = \left( \frac{1 - C}{C_0} \right) \times 100$$

where  $F$  = efficiency (%);  $C$  = concentration of  $\text{M}^{2+}$  in the solution after a certain time period;  $C_0$  = initial concentration of  $\text{M}^{2+}$  solution.

## 2.5. Desorption studies

Batch processing was also used for the desorption studies. The desired amount of each crosslinked hydrogel with adsorbed  $\text{M}^{2+}$  was taken in a conical flask then treated for the fixed time of 8 h with 50 ml of each 0.1 M HCl, 0.1 M  $\text{HNO}_3$ , 0.1 M NaCl, and 0.01 M EDTA solution. The amount of  $\text{M}^{2+}$  desorbed was then determined by back EDTA titration [17].

## 3. Results and discussion

### 3.1. Synthesis of the new hydrogels [**A<sub>1</sub>**, **A<sub>2</sub>**]

The new hydrogels **A<sub>1</sub>** and **A<sub>2</sub>** were synthesized in a simple and controllable manner by the reaction of chitosan with [4,4'-diformyl- $\alpha$ - $\omega$ -diphenoxy-ethane or 4,4'-diformyl-2,2'-dimethoxy- $\alpha$ - $\omega$ -diphenoxy-ethane] respectively to give the corresponding hydrogels [**A<sub>1</sub>** and **A<sub>2</sub>**] via nucleophilic attack of the amino group of the chitosan on the carbonyl carbon of the aldehyde groups as presented in Scheme 1. The modified chitosan hydrogels were characterized by FT-IR spectrum, thermal stability, morphology and X-ray diffraction.

### 3.2. Characterization of the hydrogels

#### 3.2.1. FTIR spectra

The FTIR spectra for unmodified chitosan and the modified chitosans [**A<sub>1</sub>** and **A<sub>2</sub>**] are shown in Fig. 1. The FTIR spectrum for chitosan shows peaks at 2930  $\text{cm}^{-1}$  due to  $-\text{CH}$  stretching, 1100  $\text{cm}^{-1}$  due to  $\text{C}-\text{OH}$  stretching, 1725  $\text{cm}^{-1}$  is characteristic of the carbonyl  $\text{C}=\text{O}$  group due to the acetyl groups in chitosan, and peaks at 3450  $\text{cm}^{-1}$  are due to  $\text{OH}$  and  $\text{N}-\text{H}$  stretching, whereas the FTIR spectra for modified chitosan (**A<sub>1</sub>**, **A<sub>2</sub>**) can be attributed as follows: 1374–1385  $\text{cm}^{-1}$  CH the symmetric bending vibration in  $-\text{CHOH}$ ;

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