



# Treatment of industrial wastewater containing copper and cobalt ions using modified chitosan



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## ABSTRACT

Chitosan was extracted and characterized using several analyses. The produced chitosan was reacted by glycine and chloroacetic acid. Chemical structures of biosorbents were confirmed. Adsorption efficiencies of the two biosorbents in neutral and alkaline medium at 25 °C were determined using atomic absorption spectroscopic analysis. Adsorption capacity of modified biosorbents toward Cu(II) and Co(II) ions was determined and compared to virgin chitosan. The biosorbents showed lower adsorption efficiency toward copper and cobalt ions compared to virgin biosorbent. Furthermore, adsorption capacity of glycine–chitosan was higher than chloroacetic acid–chitosan biosorbents, which attributed to chelating of amino groups than chloro-substituted polymer. Thermodynamic studies showed the spontaneous behavior of the adsorption process of metal ions under the studied conditions. Entropy changes indicate that the adsorption of the metal ions are endothermic process, and lower values of  $\Delta S^\circ$  indicate the affinity toward metal ions by the biosorbents at different degrees depending on their chemical structures.

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## 1. Introduction

Heavy metal water pollution is the contamination of water in natural resources by heavy metals [1,2]. Traditional treatment methods including: chemical precipitation [2], electrochemical deposition [3], ion exchange, and membrane separation [4] have been applied. Adsorption method using natural biosorbents is alternative to these methods. Numerous studies have demonstrated the effectiveness of chitosan and derived products in the uptake of metal cations such as lead, cadmium, copper, and nickel and the uptake of oxyanions as well as complexed metal ions [5–9,1]. Chitosan is undoubtedly one of the most popular adsorbents for metal ions removal from aqueous solution and is widely used in waste treatment applications [10]. The binding ability of chitosan for metal cations is mainly due to the amine groups ( $-\text{NH}_2$ ) on the chitosan chain which can serve as coordination sites for many metals. The extent of metal adsorption depends on the source of chitosan [11], the degree of deacetylation [12], the nature of the metal ion [13], and solution conditions such as pH [14]. In spite of its

prolific use, the adsorption ability of chitosan has not been realized to a satisfying level. In recent years, attention focused on several adsorbents which have metal-binding capacities and high selectivity to remove heavy metals from contaminated water [15]. In order to improve the sorption selectivity and adsorption ability of chitosan for metal ions, a great number of chitosan derivatives have been prepared by grafting new functional groups such as histidine [16], heparin [17], succinic anhydride [18], N,O-carboxymethyl [19] through a crosslinked chitosan back bone. Further, chemical modifications of chitosan were made to improve the selectivity and the capacities toward heavy metal ions [20]. Substituted chitosan was prepared and regarded as a simple and effective process to facilitate the adsorption ability of chitosan with heavy metals [21,22]. In the present study, two chitosan derivatives were prepared and characterized. Their adsorption efficiency and mechanism of adsorption were determined and discussed.

## 2. Experimental techniques

### 2.1. Materials

$\text{CuSO}_4$ ,  $\text{CoSO}_4$ , and  $\text{NH}_4\text{OH}$  were purchased from Chimia Mirs Company and were used without purification. The transition

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metals solutions were prepared by dissolving known weight of  $\text{CuSO}_4$  and  $\text{CoSO}_4$  salts in deionized water.

## 2.2. Preparation of chitosan

Shrimp shells were collected and washed with warm water to remove soluble organics, adherent proteins and other impurities, and dried at 70 °C for 24 h.

### 2.2.1. Deproteinization

Shrimp shells were treated with 3.5% (w/w) sodium hydroxide solution for 2 h at 65 °C under stirring, considering the ratio between shells to sodium hydroxide at 1:10 (w/v). After 2 h, the reaction was filtered, and the solid mass washed several times with distilled water for 30 min.

### 2.2.2. Demineralization

Demineralization was performed by soaking the deproteinized shells in 1 N HCl for 1 day at room temperature and maintaining shell–HCl ratio at 1:15 (w/v). The reaction medium then filtered under vacuum, the solid obtained washed with distilled water, and oven-dried.

### 2.2.3. Decolouration

Deproteinized and demineralized shells were soaked in acetone to decolorize the shells. The shells were left in acetone for 2 h at 50 °C under stirring, and then filtered and dried in vacuum oven at 30 °C for 2 h.

### 2.2.4. Deacetylation

Treated shrimp shells (500 g) were washed with water and rinsed in 50% solution of sodium hydroxide at 115 °C for 2 h. The obtained deacetylated chitin was washed thoroughly with distilled water till neutralization, filtered, and dried at 60 °C for 24 h. The produced chitosan was about 20% by weight of shrimp shell before treatment [22]. The obtained chitosan was analyzed and characterized using different analytical methods. Fig. 1 represents the methodology of chitosan extraction from shrimp shell.

## 2.3. Preparation of biosorbents

Equivalent molar amounts of chitosan (relative to the amino-glucose units) and glycine/chloroacetic acid were reacted in xylene as solvent at 130 °C for 3 h to eliminate the water of reaction by Dean-stark connection. The reaction was stopped when the equivalent amount of water was obtained. The products were distilled off and dried in vacuum oven at 80 °C, washed with bidistilled water, and dried in vacuum oven at 50 °C. IR spectra were used to confirm the structure of glycine–chitosan, and chloroacetic acid–glycine polymers, Fig. 2.

## 2.4. Adsorption study

Copper (II) and cobalt (II) solutions were prepared by dissolving 0.25  $\text{g L}^{-1}$  of  $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$  in deionized water. For each experiment, 0.5 g of each biosorbent was added in 100 mL of metal solution (250 ppm) in 250 mL Erlenmeyer flask. The flasks were stirred (150 rpm) at 25, 35, 45 °C for different time intervals of: 20, 40, 60, 80, and 100 min. After the treatment, biosorbents were separated by vacuum filtration. Several experiments were conducted to evaluate the effect of pH on biosorption at neutral and alkaline medium (7 and 9) at 250 ppm solution of the different metals. Values of pH were adjusted by adding few drops of  $\text{NH}_4\text{OH}$  or HCl solutions. The residual metal concentrations remained in solutions after treatments were determined by atomic absorption spectroscopy (AAS).

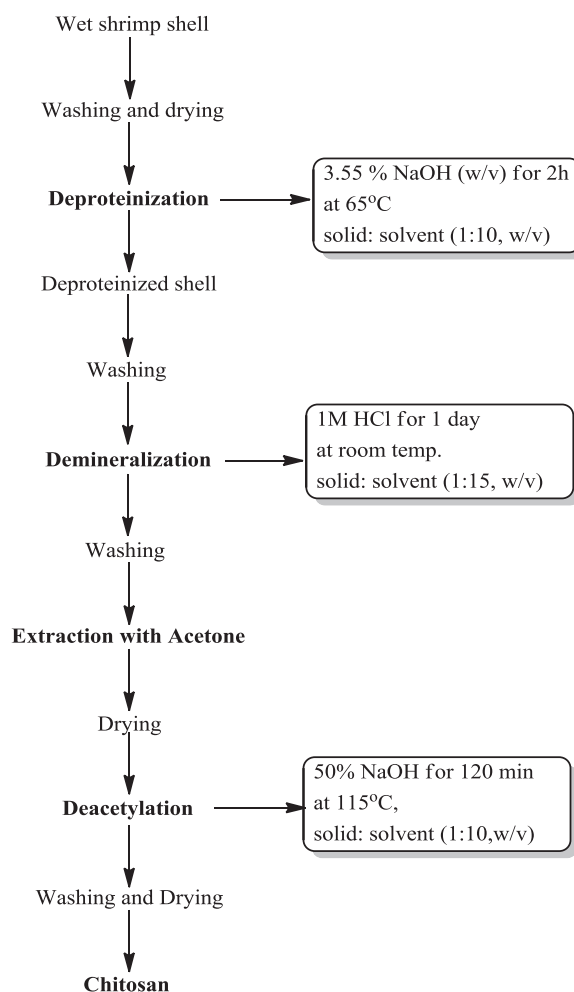


Fig. 1. Chitosan extraction from shrimp shell.

## 2.5. Data processing

The obtained data from adsorption experiments were analyzed using different adsorption isotherms.

The percent removal ( $\eta\%$ ) and the equilibrium adsorption capacity  $q_e$  ( $\text{mg g}^{-1}$ ) of  $\text{M(II)}$  in solutions were calculated using the following equations:

$$\eta\% = \frac{C_0 - C_e}{C_0} \times 100$$

$$q_e = (C_0 - C_e) \frac{V}{M}$$

where  $C_e$ : concentration of adsorbed metal ions at equilibrium ( $\text{mg L}^{-1}$ ),  $C_0$ : initial concentration of metal ions in the solution ( $\text{mg L}^{-1}$ ),  $V$ : volume of solution (L),  $M$ : weight of used biosorbent (g),  $\eta\%$ : efficiency of biosorbent in metal adsorption process, and  $q_e$ : amount of metals adsorbed by 1 g of biosorbent at equilibrium ( $\text{mg g}^{-1}$ ).

## 3. Results and discussion

### 3.1. Structure of biosorbents

Chemical structures of modified biopolymers were confirmed using IR spectroscopy, Fig. 2A and B. IR spectra of the biosorbents

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