



# Ethyl acrylate grafted chitosan for heavy metal removal from wastewater: Equilibrium, kinetic and thermodynamic studies



Afshin Maleki<sup>a</sup>, Elmira Pajootan<sup>b</sup>, Bagher Hayati<sup>a,\*</sup>

<sup>a</sup> Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran

<sup>b</sup> Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran

## ARTICLE INFO

### Article history:

Received 28 September 2014

Revised 29 December 2014

Accepted 6 January 2015

Available online 28 January 2015

### Keywords:

Chitosan–ethyl acrylate (CEA) biopolymer

Adsorbent

Heavy metal removal

FTIR

NMR

Desorption

## ABSTRACT

In this study, the preparation, characterization and heavy metal removal ability of chitosan–ethyl acrylate (CEA) biopolymer were investigated. Ethyl acrylate was successfully grafted to chitosan, which was characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). Three heavy metal cations ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ ) were removed from the simulated wastewater in batch mode, and the effect of initial metal ions concentration, adsorbent dosage, solution temperature, contact time and initial pH on the adsorption efficiency was illustrated. The maximum  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  removal efficiency of 92%, 86% and 98% were achieved, respectively. The biosorption isotherm, kinetic, and thermodynamic parameters were also studied. The isotherm and kinetic data followed the Langmuir and pseudo-second-order models, respectively. The thermodynamic data showed that the biosorption process was a spontaneous, endothermic, and physisorption reaction. Efficient desorption of metal ions from the loaded CEA was found to be 98%, using HCl (0.6 M) at contact time of 80 min. The results indicated that CEA could be employed as a promising biopolymer for the removal of heavy metal from effluents.

© 2015 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

The presence of heavy metal ions in water streams has readily increased in the last 50 years due to the industrialization and urbanization. Heavy metals are considered to be non-biodegradable; and they have great impacts on environment, public health and economics. In the removal of heavy metals, adsorption process seems to be the most versatile and effective method if it is combined with the appropriate regeneration steps [1].

Heavy metal removal from aqueous solutions has been investigated using different types of adsorbents such as: mesoporous materials with wide range of surface area and pore size such as 2D-hexagonal mesoporous organosilica and phosphonate-rich organosilica layered hybrid, etc., various synthetic polymers containing carboxylic, sulfonic, amide, amine and imino groups, and semi-natural polymers [2–6]. The functional groups existing in the structure of polymer can provide binding sites to remove the metal ions from aqueous solutions.

The biopolymers such as chitin and chitosan are the emerging adsorbents for the removal of dyes and heavy metal ions, even at

low concentrations [1]. Chitosan is a natural polyaminosaccharide, synthesized from the deacetylation of chitin which predominantly consists of unbranched chains of  $\beta$ -(1→4)-2-acetoamido-2-deoxy-D-glucose. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans [1]. Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. Chitosan can also be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups in its structure, which can serve as the adsorption active sites. Amino groups of chitosan can be protonated, after which they can strongly adsorb anionic compounds like dyes by electrostatic attraction in the acidic media [3]. However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values. The cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycol diglycidyl ether and isocyanates have been used to improve the chitosan's performance as an adsorbent [7]. Cross-linking agents not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance its mechanical properties [2].

Different chitosan derivatives such as chitosan containing nitrogen, phosphorus and sulfur as heteroatoms, and other derivatives such as chitosan crown ethers and chitosan ethylene diamine tetra acetic acid (EDTA)/diethylene triamine penta acetic acid (DTPA)

\* Corresponding author. Tel.: +98 871 6626969.

E-mail addresses: [malaki@oa.muk.ac.ir](mailto:malaki@oa.muk.ac.ir) (A. Maleki), [pajootan@aut.ac.ir](mailto:pajootan@aut.ac.ir) (E. Pajootan), [bagherhayati90@gmail.com](mailto:bagherhayati90@gmail.com) (B. Hayati).

complexes have been extensively investigated as adsorbents [8,9]. Recently, chitosan composites have also been developed to adsorb heavy metals and dyes from wastewater. Different kinds of substances have been used to form composite with chitosan such as montmorillonite, polyurethane, activated clay, bentonite, poly vinyl alcohol, poly vinyl chloride, kaolinite, oil palm ash and perlite. Chitosan composites have been proven to have better adsorption capacity and resistance to acidic environment [1].

The modification and evaluation of chitosan molecules as a biopolymer adsorbent for heavy metal removal from contaminated wastewaters are the main goals of the present study. In this regard, chitosan was modified by introducing ethyl acrylate anionic entities. Literature reviews indicated that the adsorption performance of the similar chitosan derivative has not yet been studied for the removal of hazardous heavy metals from effluents, although heterogeneous chitosan cross-linking has been thoroughly investigated in the literature [10]. The effect of important parameters including initial metal ions concentration, adsorbent dosage, contact time and initial pH of the solution was investigated on the removal efficiency. The adsorption isotherm, kinetic and thermodynamic parameters were also demonstrated to understand the mechanism of the adsorption process and adsorbent behavior.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Chitosan (extracted from snow crab shell, deacetylation degree: 98.5%; average molecular weight: 200 kDa) was supplied by Sigma Aldrich Co. and it was used as received. Ethyl acrylate (Ea) and hydrochloric acid (HCl) were provided from Merck. All solvents were of analytical grade. Lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), cadmium nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), NaOH and  $\text{H}_2\text{SO}_4$  were procured from Kanto Chemical Co. Inc., Japan. Stock solutions of Pb(II), Cd(II) and Zn(II) metal ions were prepared

by dissolving the exact amount of ( $\text{Pb}(\text{NO}_3)_2$ ),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  separately in double-distilled water. The metal salt stock solutions were diluted to give the metal ions concentration in the range of 50–200 mg/L to be used in the adsorption experiments.

### 2.2. Chemical modification of chitosan

The grafting of Ea onto chitosan was performed at optimum reaction parameters [11,12]. Chitosan (5 g) was dissolved in aqueous media containing AcOH (1.5 mL) and water/methanol 40/40 (80 mL). Ethyl acrylate (10 equiv/ $\text{NH}_2$  in chitosan, 0.5 mL) was added to the solution and it was stirred at 50 °C for 10 days. The aliquot of the reaction mixture (40 mL) was quenched by precipitation with salt (80 mL of  $\text{NaHCO}_3$  in acetone). The precipitate was collected by filtration and dispersed in  $\text{H}_2\text{O}$  (20 mL) containing salt,  $\text{NaHCO}_3$  (5 mL), and the mixture was dialyzed against  $\text{H}_2\text{O}$  (4 L) for 2 days and lyophilized to give *N*-carboxyethyl chitosan ethyl ester (Fig. 1). To obtain *N*-carboxyethyl chitosan 3, 0.1% NaOH (50 mL) was added to *N*-carboxyethyl chitosan ethyl ester, and the mixture was stirred for 2 h, dialyzed, and lyophilized as above. The precipitated powders were obtained in quantitative yield (95%) and the degree of substitution (DS) was 0.27. The prepared product (CEA) was milled to fine powders in the range of 0.2–0.4 mm.

### 2.3. Characterization techniques

FTIR spectra were recorded on a Perkin–Elmer instrument using KBr pellets containing the prepared materials. The spectra presented are baseline corrected and converted to absorbance mode. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker DRE AVANCE-500 MHz.

### 2.4. Adsorption procedure

The heavy metals adsorption processes were accomplished by mixing various amounts of CEA (0.05–0.2 g) for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  in

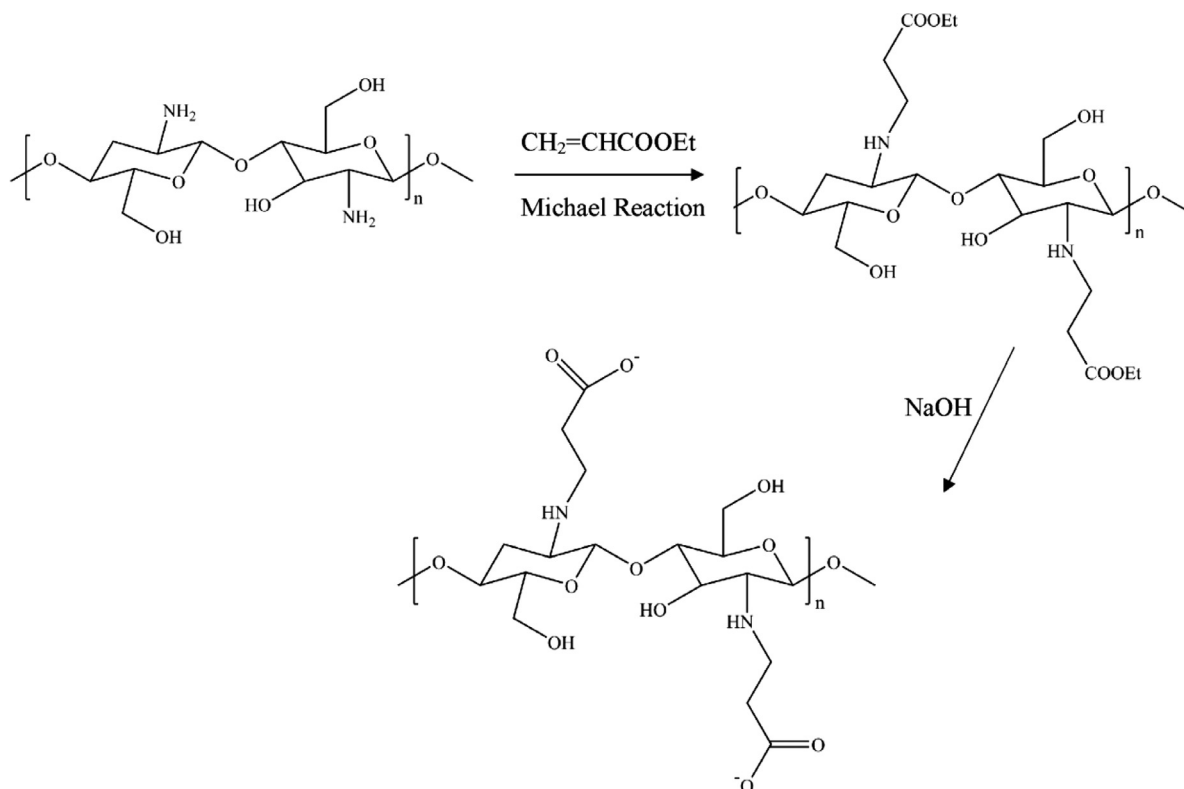


Fig. 1. The approach to the substitution of ethyl acrylate onto chitosan.

Download English Version:

<https://daneshyari.com/en/article/690779>

Download Persian Version:

<https://daneshyari.com/article/690779>

[Daneshyari.com](https://daneshyari.com)