Comparison of biosorption of Congo red on the templated cross-linked chitosan nanoparticles

Dilyana Zvezdova, Stoyanka Stoeva, Zilya Mustafa, Rumyana Milina, Angel Zvezdov

Abstract: *The nanoparticles of templated crosslinked chitosan-epichlorohydrin and chitosan-epichlorohydrin–Congo Red, were prepared through the imprinting process using Congo Red dye as template and epichlorohydrin as a crosslinker. The nanoparticles exhibited significantly higher adsorption capacities of the dye than other nanoparticles formed without a dye template and with crosslinker epichlorohydrin. FTIR spectroscopy studies showed that the possible pathways for Congo Red adsorption onto crosslinked chitosan particles may include ion-ion interactions and hydrogen bond formation.*

Key Words: *biosorption, Congo Red, templated crosslinked-chitosan, FTIR-spectroscopy.*

INTRODUCTION

Synthetic dyestuffs widely exist in the effluents of industries such as textiles, printing, paper, plastics and leather. Colored industrial effluent contains many varieties of synthetic dyes (including azo dyes) which are mostly toxic and mutagenic, and even carcinogenic in nature) [10]. Congo red (CR) [disodium 3,3'-((1,1'-biphenyl)-4,4'-diylbis(azo))bis(4-amino-1-naphthalenesulfonate)] is a benzidine-based anionic diazo dye (Fig.1). This dye has been known to cause an allergic reaction and to be metabolized to benzidine, a human carcinogen.

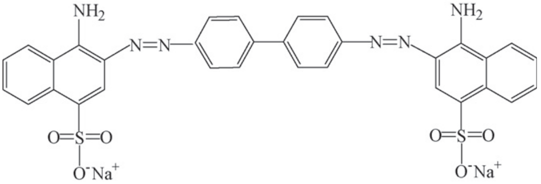

Fig. 1. Structure of Congo Red (molecular formula: $C_{32}H_{22}N_6O_6S_2Na_2$)

Synthetic dyes such as CR are difficult to biodegrade due to their complex aromatic structures, which provide them physico-chemical, thermal and optical stability. The conventional methods for the removal of dye molecules from colored effluents are costly and sometimes not readily adapted to effluent treatment. Dye removal by adsorption onto different adsorbents has been the subject of intense interest because of its simplicity and high efficiency. Commercial activated carbon, which is usually derived from natural materials such as coal, wood, or coconut shell, is a material with a remarkably high adsorption capacity [18], but the high cost and difficulty in regeneration of this adsorbent limit its commercial application [4]. Many alternative low cost and locally available adsorbent materials, such as agricultural solid wastes [3] and industrial by-products [20], have been used to remove dye molecules from colored effluents. In some recent publications, different low-cost adsorbents such as montmorillonite [2], fly ash [15], rice husk [13], and fungi [10]) had been used for the removal of CR from aqueous solutions. However, these adsorbents do not have good adsorption capacities when used with anionic dyes because most have hydrophobic or anionic surfaces.

The use of chitosan-based adsorbents over commercially available adsorbents for the removal of dye molecules is becoming popular due to its low cost, abundant availability, non-toxicity and potential for ion exchange. It has been recently reported in a review paper that chitosan-based adsorbents have high adsorption capacities towards many classes of dyes [8]. Chitosan (CS) shows high adsorption capacity towards dyes [3,11], and metal ions [19], because of chitosan's multiple functional groups. To improve the adsorption capacity of the chitosan beads, several chemical modification methods such as cross-linking [6,7,19], the addition of ionic molecules [5], and the insertion of new functional groups [21] have been used. Hence, the crosslinking reactions of chitosan with various crosslinkers have been studied to improve its chemical stability in any acidic media for the extraction of dyes from industrial wastewater. Chiou *et al.* studied the adsorption of different dyes onto chitosan beads crosslinked with epichlorohydrin (ECH) [9]. Hu *et al*. [14] and Du *et al*. [12] worked on the biosorption of Acid Green 27 and ecosin Y dyes, respectively, on chitosan nanoparticles prepared by ionic gelation with sodium triphosphate (TP). Rosa *et al*. utilized quaternary chitosan salt crosslinked with glutaraldehyde (GLA) for the adsorption of Reactive Orange 16 dye [17]. Although the crosslinking method may enhance the resistance of chitosan against acids, the process may reduce its adsorption capacity for dyes. This may be attributed to the decreased amount of amino and hydroxyl groups. Chen *et al*. [8] were studied the competitive biosorption of some azo dyes (Remazol Black 5 and Remazol Brilliant Orange 3R) on the templated crosslinked chitosan nanoparticles to improve the adsorption capacity.

The aim of this study was to investigate the adsorption capacity of Congo Red dye on the templated chitosan nanoparticles using epichlorohydrin as cross-linker agent. In addition, the structure of crosslinked chitosan with and without CR dye was characterize by FTIR spectroscopy.

EXPERIMENTAL

1. Materials and methods

1.1. Chemicals

Chitosan was purchased from Sigma–Aldrich Co., USA. The degree of deacetylation (DD=79.1%) was determined by ^{1}H NMR spectroscopy. Congo Red with 97% purity (Mw = 696.66 g/mol; λ_{max} = 500 nm) and ECH with 98% purity were purchased from Fluka. Pentasodium triphosphate (TP) with 98% purity was purchased from Sigma–Aldrich Co., USA.

1.2. Preparation

The nanoparticles of the templated crosslinked CS-ECH-TP and CS-ECH-TP-CR dye were prepared according to the procedure described by Chen et al.[8].

A solution with 50 mg of chitosan dissolved into a 50 mL aqueous solution of acetic acid (0.5%, v/v) was prepared. A 5.8 mL aqueous solution of CR dye (8.7 mg) was added, and the mixture was stirred for 30 min. A 5.0 mL aqueous solution of ECH was added dropwise, and the mixture was stirred for 2 h at 50 °C. Using a syringe, 30 mL of 1.45% TP solution was slowly dropped into the chitosan solution by mechanical stirring (1000 rpm) to obtain a milky emulsion. The resulting emulsion was frozen at −4 °C and then thawed in the atmosphere to produce nanoparticle precipitates, which were collected using a centrifuge. Finally, the nanoparticle precipitates were stirred with a pH 14.0 NaOH solution to remove the dye. This stage was monitored by a UV/visible spectrophotometer (BOECO S-20, Germany). The process was followed by collecting the precipitates with a centrifuge and by intensive washing of the nanoparticle precipitates with distilled water to remove any unreacted ECH.

1.3. Adsorption of azo dyes

The nanoparticles prepared with or without the CR dye as template and with crosslinker ECH, were studied to determine the adsorption capacity of the CR dye. This process was conducted by adding 10 mL of each kind of the nanoparticles (9 mg/mL) into a 10 mL of 6.0 mg/mL dye solution, then adjusting to pH 3.0 using HCl or NaOH solutions while stirring at 30 °C for 120 h. The mixture solution was centrifuged to remove adsorbents. The filtrate was adjusted to a pH level of 6.0 using HCl or NaOH solutions, and then diluted to 50 mL. The dye concentration was measured using a UV/visible spectrophotometer at 500 nm for the CR dye.The adsorption capacity (Q) was calculated using Eq. (1):

$$Q = \frac{(C_i - C_f)V}{W} \quad (1)$$

where C_i is the initial concentration of dye (mg/mL); C_f is the final concentration of dye (mg/mL); *V* is the volume of dye solution (mL); and *W* is the weight of the nanoparticles (g) used.

1.4. FTIR spectroscopy

FTIR spectra were obtained using a PerkinElmer Tensor 27 Fourier transform infrared spectrometer (Germany). The spectral region between 4000 and 400 cm $^{-1}$ was scanned. Specimens prepared as KBr pellets were used. Dried, powdery chitosan nanoparticle (2 mg) was mixed thoroughly with KBr (300 mg) and then pressed in vacuo to homogeneous disc with a thickness of about 0.9 mm.

RESULTS AND DISCUSSION

The CS nanoparticles were prepared using the imprinting process through the following steps: chelation of the CR dye as template into chitosan through ion–dipole and ion–ion interactions, crosslinking reaction of chitosan with ECH crosslinker, formation of chitosan nanoparticles through ionic crosslinking with TP, and removal of the dye template molecules with NaOH solution [8].

The changes taking place as a result of consequently performed experiments in the presence of CS, ECH, TP and CR dye are shown in Fig. 2.

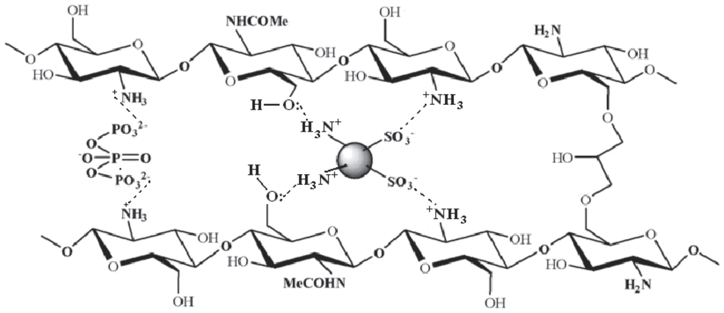

Fig. 2. Schematic representation of the templated crosslinked-chitosan nanoparticles with ECH, pentasodium TP and CR dye

The interaction of ECH with hydroxymethyl groups of properly oriented glucopyranose rings can take place leading to the crosslinking of chitosan chains together with the formation of covalent ether bonds. The addition of pentasodium TP causes ionic gelation of CS due to the corresponding ionic crosslinking reaction between phosphate anions and ammonium cations. As a result, the absorbance of CR dye on the chitosan nanoparticles in acidic medium should be facilitated significantly. The CR dye itself is retained onto the chitosan nanoparticles by specific physical interactions.

This changes can be characterized qualitatively using FTIR spectroscopy. The FTIR spectra of both CS samples containing ECH and TP as well as ECH, TP and CR dye are shown in Fig. 3a and 3b. The stretching vibrations of associated hydroxyl and amine groups in crosslinked CS samples were registered in the range 3500-3000 cm^{-1} as a broad and intensive peak.

The absorption bands at 2925 and 2854 cm^{-1} are associated with the asymmetric and symmetric vibrations of CH_2 and CH groups. The shift of the second band to the lower wavenumbers (i.e. from 2880 cm^{-1} for the initial chitosan to 2854 cm^{-1} for the crosslinked samples) is probably influenced by the covalent and ionic interactions between the pyranose functional groups and low-molecular components.

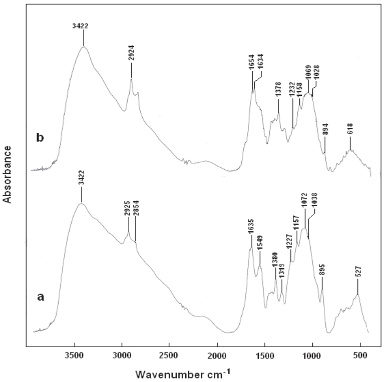

Fig. 3. FTIR spectra of the templated crosslinked-chitosan nanoparticles prepared through crosslinker ECH (a) and crosslinker ECH with a CR dye as template

In the cross-linked chitosans only Amide I absorption band was registered at 1654-1634 cm^{-1}. It is obvious that the position of this band and its shape depends both on the type of cross-linking agent (ECH) and the CR dye used, which should determine the nature of intermolecular interactions.

The well pronounced peak observed at 1549 cm^{-1} in the crosslinked samples with ECH and TP was associated with bending vibrations of protonated primary amino groups, i.e. ammonium ions formed in acidic medium (Fig. 3a). This band is ussualy registered at 1600-1575 cm^{-1} in the spectra of low-molecular compounds [16,22]. The shift of the band to the lower wavenumbers is obviously influenced by the ionic interactions between the phosphate anions of TP and the ammonium cations of chitosan chains. In CS samples containing CR dye, together with ECH and TP, it appeas as a multiple shoulder near 1549 cm^{-1} (Fig. 3b). The low intensity of this band in the presence of CR may be due to the inclusion of ammonium cations in the formation of additional non-covalent ionic interactions (salt bonds) with sulfonate anions of the CR dye.

The absorption peak at 1422 cm^{-1} in unmodified chitosan is associated with the bending vibrations of CH_2 moiety in primary CH_2OH groups [16]. This band showed variable intensity due to the different arrangement of the primary OH groups [1]. So, in the FTIR spectra of crosslinked chitosan without and with CR dye, only broad and low intensive multiplet with maximum around 1419 cm^{-1} is registered (Fig. 3a,b). The difference between the spectra of unmodified and crosslinked chitosans is obviously related to both the participation of primary OH groups in crosslinking reaction with ECH and also with their involvement in hydrogen bonds with the ammonium groups of CR dye (Fig. 2). Unlike them, the stretching vibrations of secondary OH groups are well defined with maxima at 1072 and 1069 cm^{-1}, respectively.

The adsorption capacity of an azo dye CR on the CS nanoparticles prepared from crosslinker ECH with or without the CR dye as template was conducted at 6.0 mg/mL initial dye concentration at pH 3.0 and a temperature of 30 °C for 120 h. During adsorption protonation of amine groups of chitosan is necessary to occur for the interaction with negatively charged CR sulfonate groups. The results showed that the adsorption capacities of the CR dye on the templated nanoparticles were significantly higher (*Q* = 843.7 mg/g) than those of the crosslinked nanoparticles formed without a dye template (*Q* = 685.6 mg/g). Therefore, the technique for the preparation of templated particles at pH 3.0 yielded a higher adsorption capacity and a more efficient adsorption of dye molecules in an aqueous solution.

CONCLUSION

The chitosan nanoparticles were prepared using imprinting process together with a crosslinker epichlorohydrin and pentasodium triphosphate. The adsorption capacity of Congo Red dye onto the templated and non-templated chitosan nanoparticles was studied. Crosslinked chitosan nanoparticles containing CR dye as template exhibited higher adsorption capacity compared to that without dye template. Different types of electrostatic and covalent interactions between the chitosan macromolecules and the additives were suggested and discussed based on the results of FTIR spectroscopy.

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About the authors:

Assist. Prof. Dr Dilyana Zvezdova, Department of Organic Chemistry, Assen Zlatarov University - Burgas 8010, Bulgaria, Phone: +35956858254, e-mail: dzvezdova@yahoo.com.

Assoc. Prof. Dr Stoyanka Stoeva, Department of Organic Chemistry, Assen Zlatarov University – Burgas 8010, Bulgaria, Phone: +35956858371, e-mail: sstoeva@btu.bg.

Chemist Zilya Mustafa, Central Research Laboratory, Assen Zlatarov University – Burgas 8010, Bulgaria, Phone: +35956858332, e-mail: btu_cnil@abv.bg.

Assoc. Prof. Dr Rumyana Milina, Central Research Laboratory, Assen Zlatarov University – Burgas 8010, Bulgaria, Phone: +35956858332, e-mail: rumjana_milina@abv.bg.

Assoc. Prof. Dr Angel Zvezdov, Department of Water Treatment Technology, Assen Zlatarov University - Burgas 8010, Bulgaria, Phone: +35956858254, e-mail: azvezdov@btu.bg.

The paper is reviewed.