

Preparation, characterization and adsorption properties of chitosan nanoparticles for congo red as a model anionic direct dye

Dilyana Zvezdova

Preparation, characterization and adsorption properties of chitosan nanoparticles for congo red as a model anionic direct dye: *The present study dealt with the adsorption of congo red (CR), as a model anionic dye, from aqueous solution using chitosan nanoparticles. The particles of templated crosslinked chitosan-epichlorohydrine-CR, was prepared through the imprinting process using CR dye as a template and ECH as a crosslinker. The nanoparticles were characterized by FTIR spectroscopy. A batch system was applied to study the adsorption of CR from aqueous solution by chitosan nanoparticles. The results show that the adsorption of CR on imprinting chitosan nanoparticles was affected by contact time, CR concentration, pH and temperature. The results are in accordance with the second-order adsorption model.*

Key Words: *Adsorption, Congo Red, Crosslinked-chitosan epichlorohydrine, FTIR-spectroscopy.*

INTRODUCTION

Azo dyes are the largest class of dyes with the greatest variety of colours. Approximately 10–15 % of the dyes are released into the environment during dyeing of different substrates, such as synthetic and natural textile fibres, plastics, leather, paper, mineral oils, waxes, and even foodstuffs and cosmetics [9]. They exhibit great structural variety, thus they are not uniformly susceptible to microbial attack. Azo dyes are not typically degraded under aerobic conditions; however, under anaerobic conditions, the azo linkage can be reduced to form aromatic amines which are colourless but can be toxic and carcinogenic [3]. These toxic amines have been defined as the so-called Maximal Arbeitsplatz Konzentration (MAK) III A1 amines [8].

Currently, all the European Union legal and customs regulations which are being prepared follow this trend and prohibited the manufacture and sale of benzidine based azo dyes from September 2003 [4].

Congo red is the first synthetic azo dye produced that is capable of dyeing cotton directly. Congo red containing effluents are generated from a number of industrial activities: textiles, printing and dyeing, paper, rubber, plastics industries etc. [10].

The present paper highlights the physicochemical, spectral, equilibrium, kinetic aspects of congo red adsorption on the nanoparticles of templated crosslinked chitosan, depicting the effect of a number of factors on the mechanism of the process and the probable sorbate/sorbent interactions. The nanoparticles were used for the removal of CR as a model anionic dye, to obtain information for treating effluents from the dye industry.

EXPERIMENTAL

Materials and methods

Chemicals

Chitosan (CS) was purchased from Sigma–Aldrich Co., USA. CR ($M_w = 696.66$ g/mol; $\lambda_{max} = 575$ nm (pH=3); $\lambda_{max} = 498$ nm (pH=4); $\lambda_{max} = 497$ nm (pH=6)), epichlorohydrine (ECH) with 98% purities, respectively, were purchased from Fluka. Sodium triphosphate pentabasic (TP) was purchased from Sigma–Aldrich Co., USA.

Preparation

A solution with 50 mg of chitosan dissolved into a 50ml 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 (1200 rpm) to obtain a milky emulsion. The resulting emulsion was frozen at –4 °C and then thawed in the atmosphere to produce particle precipitates, which were collected using a centrifuge. Finally, the nanoparticle precipitates were stirred with a pH 10.0 NaOH solution to remove

the dye. This stage was monitored by a UV/visible spectrophotometer. The process was followed by collecting the precipitates with a centrifuge and by intensive washing of the particle precipitates with distilled water to remove any unreacted ECH. The particle precipitates were re-suspended in distilled water for characterization and were directly used in the adsorption study [1].

FTIR spectra were obtained using a Perkin Elmer 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 chitin was mixed thoroughly with KBr and then pressed in vacuo to homogeneous disc with a thickness of 0.5 mm.

Adsorption of azo dyes

The particles prepared from a 0.5 molar ratio of crosslinker/CS, with CR dye as templates and with crosslinker ECH, were studied to determine the adsorption capacity of the CR dye. This process was conducted by adding 50 ml of each kind of the particles (9 mg/ml) into a 50 ml ml (2.0 mg/ml) dye solution, then adjusting to pH 3.0 using HCl or NaOH solutions while stirring at 30 °C for 72 h. The mixture solution was centrifuged to remove adsorbents. The pH value was adjusted by adding a few drops of dilute HCl or NaOH if necessary, and then diluted to 10 ml. The dye concentration was measured using a UV/visible spectrophotometer at $\lambda_{\text{max}} = 575 \text{ nm}$ (pH=3); $\lambda_{\text{max}} = 498 \text{ nm}$ (pH=4); $\lambda_{\text{max}} = 497 \text{ nm}$ (pH=6) 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.

Batch kinetics

The study of adsorption kinetics of the CR dye on the particles was carried out in a batch process. The variable parameters were studied, including the initial pH values, initial concentrations of dye, and temperatures. In each test, 10ml of the nanoparticles (9 mg/ml) was added into 10ml of aqueous solution of the dye with a known concentration. Whenever necessary, the pH value was adjusted with diluted NaOH or HCl solutions. Then 0.1ml aliquots of the solution were added to 10ml distilled water at different time intervals. The mixture solution was centrifuged to remove adsorbents. The filtrate was adjusted to correct pH for λ_{max} . The dye concentrations were measured using a UV/visible spectrophotometer. The amount of adsorption was calculated using Eq.(1).

To measure the rate-controlling and mass transfer mechanism, kinetic data were correlated to linear forms of the first-order equation (2):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t, \quad (2)$$

and the second-order equation (3):

$$\frac{1}{Q_t} = \frac{1}{(k_2 Q_e^2)} + \frac{t}{Q_e} \quad (3)$$

where Q_e and Q_t are the adsorption capacities of dye (mg/g) at equilibrium and at a given time t , respectively; and k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mg min})$) are the first-order and the second-order rate constants, respectively. According to Eq. (2), the plot of $\ln(Q_e - Q_t)$ versus t yields a straight line with a slope of $-k_1$ and an intercept of $\ln Q_e$. In Equation (3), the plot of t/Q_t versus t gives a straight line with a slope of $1/Q_e$ and an intercept of $1/(k_2 Q_e^2)$ [5,6].

RESULTS AND DISCUSSION

Characterization and azo dye adsorption

The chitosan nanoparticles were prepared using the imprinting process through the following steps: (1) chelation of the CR dye as template into chitosan through ion-dipole

and ion–ion interactions, (2) crosslinking reaction of CS with ECH as a crosslinker, (3) particles were prepared with a narrow size distribution based on ionic gelation between positively charged CS and negatively charged TP (Fig. 1) and (4) removal of the dye template molecules with NaOH solution. Nanoparticles prepared through crosslinker, namely, ECH, with a dye template, had mean diameters ranging from 205 to 277 nm.

Fig. 2 show the FTIR spectra of the templated nanoparticles prepared through ECH with the CR dye as templates before and after CR adsorption process. The spectrum CS-ECH- CR beads before adsorption displays a number of adsorption peaks, an indication of different types of functional groups present in the crosslinked beads. The broad and strong band ranging from 3350 to 3550 cm^{-1} indicates the presence of $-\text{OH}$ and $-\text{NH}_2$ groups, which is consistent with the peak 1072 and 1158 cm^{-1} assigned to alcoholic C-O and C-N stretching vibration. The peaks at 2924 and 2855 cm^{-1} can be assigned to asymmetric and symmetric $-\text{CH}_2$ groups. The peak located at 1634 cm^{-1} is characteristic of amine deformation. The peak at 1240 cm^{-1} can be attributed to the C-O-C stretching [7,11].

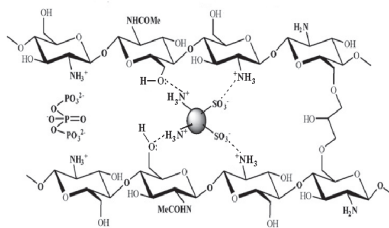


Fig.1. Schematic representation for preparation of the templated crosslinked-chitosan particles with epichlorohydrin and imprinting dye (CR).

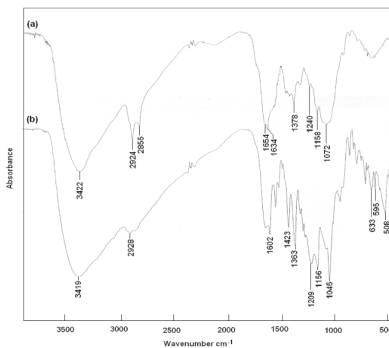


Fig. 2. FTIR spectra of the templated crosslinked-chitosan particles before (a) and after (b) CR adsorption process.

The estimation of adsorption capacities of CS nanoparticles prepared from crosslinker ECH with CR dye as templates during the CR adsorption experiments, was conducted at 2.0 mg/ml initial dye concentration with an initial pH of 3.0 and a temperature of 30 °C for 72 h. The adsorption processes may involve ion–dipole and ion–ion interactions between sulfonate anions of the dye molecules and the hydroxyl and protonated amino groups of chitosan molecules as well as a physical adsorption phenomenon in the porous structure of bioorganic matrix. The results show that the adsorption capacities of the templated nanoparticles for CR dye were significantly higher than those of the chitosan nanoparticles and the crosslinked nanoparticles formed without a dye template.

Adsorption kinetics

The adsorption of CR onto CS nanoparticles was carried out in a batch process by using aqueous solution of CR. The variable parameters were tested including contact time, initial dye concentration, pH of the medium and temperature. The effect of pH for adsorption capacities of CR dye on the nanoparticles is given in Fig. 3. The contact time curves show slow adsorption of CR in the first 1000 min. This curves may be ascribed to the fact that at a lower pH solution, more protons are available to protonate the amino groups of chitosan to form $-\text{NH}_3^+$ groups. This increases the electrostatic attraction between the anionic group ($-\text{SO}_3^-$) of the dye and the protonated amino group ($-\text{NH}_3^+$) of

chitosan, causing an increase in dye adsorption [2]. The effect of different initial concentration for adsorption capacities of CR dye on the nanoparticles is given in Fig. 4.

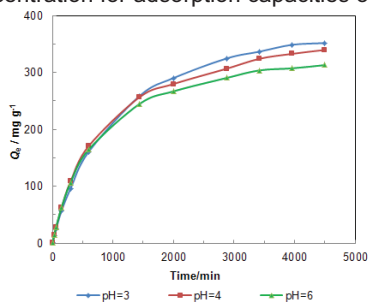


Fig. 3. The effect of pH for adsorption capacities of CR dye on the nanoparticles.

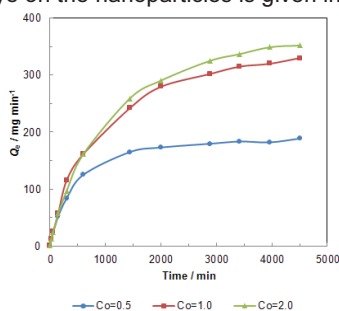


Fig. 4. The effect of different initial concentration for adsorption capacities of CR dye on the nanoparticles.

Adsorption kinetics is an important parameter for designing adsorption systems and is required for selecting optimum operating conditions for batch adsorption study. To investigate the adsorption kinetics of CR onto CS-ECH-CR particles, two different kinetics models, pseudo first-order and pseudo second-order rate models, were used in this study. Table 1 present the rate constants for CR dye on the CS-ECH-CR particles with a different initial pH, initial dye concentrations, and temperatures that were calculated by the first-order and second-order kinetic models. The correlation coefficients (R^2) of the second-order adsorption model exhibited higher values than those of the first-order kinetics. In addition, the calculated equilibrium adsorption capacities ($Q_{e,cal}$) fitted the experimental Q_e values well. This suggests that the second-order adsorption mechanism was predominant and that the overall rate of the dye adsorption process appeared to be controlled by the chemical process but not by the physical adsorption phenomenon.

Table 1. The first-order and second-order adsorption rate constants, calculated $Q_{e,cal}$ and experimental Q_e values for different initial dye concentrations, pH, and temperatures for the CS-ECH-CR particles.

Parameter	Q_e mg/g (S.D.)	First Order kinetic model			Second Order kinetic model		
		$k_1(\times 10^{-4})$ min^{-1} (S.D.)	$Q_{e,cal}$ mg/g (S.D.)	R^2	$k_2(\times 10^{-6})$ mg/g min	$Q_{e,cal}$ mg/g (S.D.)	R^2
Initial pH: 2 mg/ml initial CR concentration, 30°C							
3	429.5 (15.1)	3.60 (0.62)	387.1 (35.5)	0.9708	2.41 (0.19)	434.8 (32.2)	0.9992
4	392.1	5.24	346.0	0.9647	3.09	400.8	0.9962
6	358.3	5.01	387.1	0.9612	3.80	363.6	0.9821
Initial concentration (mg/ml): Initial pH, 30°C							
0.5	222.5	6.08	158.6	0.9439	1.08	207.4	0.9902
1	415.3	5.23	359.8	0.9687	2.66	408.3	0.9988
2	429.5 (15.1)	3.60 (0.62)	387.1 (35.5)	0.9708	2.41 (0.19)	434.8 (32.2)	0.9992
Temperature °C: 2 mg/ml initial CR concentration, Initial pH, 30°C							
20	502.1	3.65	476.3	0.9799	1.65	512.8	0.9995
30	429.5 (15.1)	3.60 (0.62)	387.1 (35.5)	0.9708	2.41 (0.19)	434.8 (32.2)	0.9992
40	428.1	5.21	317.1	0.9709	3.37	375.9	0.9989

CONCLUSION

The nanoparticles of the templated crosslinked chitosan, CS-ECH-CR was prepared through the imprinting process with the CR dye as templates, and with ECH as a crosslinker. Their chemical structure was studied and characterized by the frequencies of the absorption bands in the FTIR spectra of the compounds involved to these adsorption nanoparticles. The results obtained showed that the particles possess an excellent capacity for adsorption of direct anionic dye CR. It was estimated that the adsorption kinetics followed the second order mechanism, which was the model that provided the best correlation with the experimental data. The results obtained showed that this new adsorbent material could be tested on textile effluents treatment processes independent of the pH of the aqueous medium.

Kinetic results are an important parameter for designing adsorption systems and it is required for selecting optimum operating conditions. The research data obtained in this study should be useful for laboratory and technological batch adsorption applications.

REFERENCES

- [1] Chen Chia-Yun, Jen-Chao Chang, Arh-Hwang Chen, Competitive biosorption of azo dyes from aqueous solution on the template crosslinked-chitosan nanoparticles, *Journal of Hazardous Materials*, 2011, 185, 430–441.
- [2] Chen A.H., Chen S.M., Biosorption of azo dyes from aqueous solution by glutaraldehyde-crosslinked chitosans, *J. Hazard. Mater.*, 2009, 172, 1111–1121.
- [3] Cripps C., Bumpus J.A., Aust S.D., Biodegradation of azo and heterocyclic dyes by *Phanerochaete chrysosporium*, *Appl. Environ. Microbiol.* 1990, 56, 4, 1114- 1118.
- [4] Dritte Verordnung zur Änderung der Bedarfsgegenständenverordnung, *Bundesgesetzblatt, Jahrgang 12 (1994)*, Azo Dyestuffs and ECOTEX testing for Europe STR, in <http://www.erols.com/strlab/azodyes.htm>.
- [5] Georgiev D., B. Bogdanov, Y. Hristov, I. Markovska, Second-order kinetic model for the sorption of Cu(II) ions in aqueous solutions of Zeolite NaA, *Advanced Materials Research Vols.*, 2012, 560-561, 1174-1177.
- [6] Georgiev D., B. Bogdanov, Y. Hristov, I. Markovska, The Removal of Cu(II) Ions from Aqueous Solutions on Synthetic Zeolite NaA, *World Academy of Science Engineering and Technology*, 2012, 64 751-755
- [7] Spasov, S.; Arnaudov, M. *Application of Spectroscopy in Organic Chemistry*; Nauka and Izkustvo: Sofia, 1978.
- [8] Snyderwine E. G., Sinha R., Felton J. S., Ferguson L. R., Highlights of the eight international conference on carcinogenic/mutagenic N-substituted aryl compounds, *Mut. Res.* 2002, 506, 1–8.
- [9] Sponza D. T., M. Isik, Toxicity and intermediates of C.I. Direct Red 28 dye through sequential anaerobic/aerobic treatment, *Process Biochem.*, 2005, 40, 2735–2744.
- [10] V. Vimonsees, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, *Chem. Eng. J.*, 2009, 148, 354–364.
- [11] Wan Ngah W. S., M. A.K.M. Hanafiah, S. S. Yong, Adsorption of humic acid from aqueous solutions on crosslinked chitosan-epichlorohydrin beads: Kinetics and isotherm studies, *Colloids and Surfaces B: Biointerfaces*, 2008, 65, 18-24.

About the authors:

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

This paper has been reviewed