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Influence of impregnation of chitosan beads with cetyl trimethyl ammonium bromide on their structure and adsorption of congo red from aqueous solutions

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ABSTRACT

The effect of impregnation of chitosan (CS) beads with cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, on the structural organization of the beads was investigated using various techniques such as infrared spectroscopy, zeta potential, X-ray diffraction, transmission electron microscopy and scanning electron microscopy equipped with energy dispersive X-ray. Impregnation of chitosan beads with this surfactant (CTAB) significantly increased adsorption capacity from 178.32 (0 wt% CTAB) to 373.29 mg/g (0.05 wt% CTAB) for adsorption of congo red (CR) from an initial concentration of 1000 mg/l. The results of zeta potential analysis of CS beads impregnated with various CTAB concentrations indicated that zeta potential was not significantly increased by CTAB impregnation up to 0.1%. Based on different characterization results, enhanced adsorption of CR onto CTAB-impregnated CS beads not only involves electrostatic interactions between CR molecules, and multiple functional groups of CS and positively charged head group of CTAB molecules, but also involves significant hydrophobic interactions between the hydrophobic tail of CTAB and hydrophobic moieties of CR molecules.

1. Introduction

Colored effluent that is discharged from different industrial facilities (such as textile, paper and cosmetics plants) is one of the most important indicators of water pollution, and the presence of dyeing effluent in a watercourse is also aesthetically undesirable [1]. The removal of color from such effluent is extremely important from an environmental point of view because the discharge of colored effluent into receiving water bodies can damage aquatic life [2]. Colored industrial effluent contains many varieties of synthetic dyes (including azo dyes, which are mostly toxic and mutagenic, and even carcinogenic in nature) [3]. Congo red (CR) [1-naphthalene sulfonic acid, 3,3′-(4,4′-biphenylenebis (azo))bis(4-amino-)disodium salt] is a benzidine-based anionic diazo dye. This dye is known to metabolize to benzidine, a known human carcinogen. Treatment of effluent containing azo dyes is difficult to biodegrade because they are not much susceptible to biological degradation [4].

The conventional methods for the removal of dye molecules from colored effluents are costly and sometimes not readily adapted to effluent treatment [1,2]. Dye removal by adsorption onto different adsorbents has been the subject of intense interest because of its simplicity and high efficiency [5–7]. 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 [8], but the high cost and difficulty in regeneration of this adsorbent limit its commercial application [9,10]. Many alternative low cost and locally available adsorbent materials, such as agricultural solid wastes [11–13] and industrial by-products [6,14,15], have been used to remove dye molecules from colored effluents. In some recent publications, different low-cost adsorbents (such as coir pith [16], leaf [17], red mud [18], montmorillonite [19], fly ash [20], rice hull ash [21], rice husk [22], and fungi [23,24]) 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, and it has been recently reported in a review paper that chitosan-based adsorbents have high adsorption capacities towards many classes of dyes [2]. Chitosan (CS), a naturally occurring linear polymer of glucosamine, can be obtained from crustacean chitin on an industrial scale because a large amount of crustacean's exoskeleton is available as a by-product of food processing industries. Chitosan shows high adsorption capacity towards dyes [25], metal ions [26], and other ionic molecules [27,28] because of chitosan's multiple functional groups [29]. To improve the adsorption capacity of the chitosan beads, several chemical

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modification methods (such as cross-linking [26], the addition of ionic molecules [28], and the insertion of new functional groups [30]) have been used. In our earlier publication, the impregnation of CS beads with cationic surfactant was first introduced, and it was found that CR adsorption by these CS beads was dramatically increased [31].

The aim of this study was to explore the facts behind the enhanced CR adsorption of CS beads which resulted from their impregnation with cetyl trimethyl ammonium bromide (CTAB). We investigated the adsorption performance of CTAB-impregnated CS (CS/CTAB) beads along with normal CS beads towards CR in order to gain a better understanding of the effect of CTAB impregnation on adsorption. To determine the mode of interaction of the CR molecules and CTAB-impregnated CS beads during adsorption, X-ray diffraction (XRD) and transmission electron microscopy (TEM) of the CS/CTAB beads and CS beads, infrared (IR) spectroscopy, a scanning electron microscope (SEM) study, and an energy dispersive X-ray (EDX) analysis of the samples before and after adsorption were carried out. In order to reveal the exact mechanism of the adsorption process, zeta potential experiments were performed on the CS beads that were impregnated with different concentrations of CTAB. A desorption study, which involved varying the pH and organic solvents, was also performed to give some insight on the effects of CTAB impregnation.

2. Materials and methods

2.1. Materials

Chitosan (CS, >85% deacetylation), cetyl trimethyl ammonium bromide (CTAB) and congo red (CR) were purchased from Sigma Chemical Co., USA. All of the other analytical grade chemicals were purchased from Sigma Chemical Co., USA.

2.2. Preparation of CTAB-impregnated CS beads (CS/CTAB beads)

CTAB-impregnated CS beads (CS/CTAB bead) were prepared by adding the desired amount of CTAB solution from a stock solution (2 wt%) to a CS-acetic acid solution, followed by the dropwise addition of a CS/CTAB solution to an alkaline coagulating solution (H_2O:MeOH:NaOH 4:5:1, w/w). The CTAB concentration was varied from 0.01 to 0.1 wt% (with respect to CS (1 wt%)) in a CS/CTAB solution. The CS beads were prepared from a CS-acetic acid solution (1 wt% of CS in 2 vol% of acetic acid) using an alkaline gelation method. The as-prepared beads were extensively washed with deionized water to remove the presence of alkali residue.

2.3. Characterization of the adsorbent

Infrared (IR) spectra of the CS/CTAB and CS beads before and after adsorption were characterized using a FTIR Spectrophotometer (Nicolet 6700, Thermal) with KBr pellet. X-ray diffraction (XRD) patterns of the samples were studied using D/MAX2500H (Rigaku). Transmission electron microscopy (TEM) of thin sections of freeze-dried CS/CTAB beads and CS beads was performed with JEOL, which is a JEM-1011 instrument operated under an acceleration voltage of 100 kV. The surface morphology of the freeze-dried samples before and after adsorption was recorded using HR FE-SEM (JSM-7401F, JEOL) equipped with energy dispersive X-ray (EDX) analysis capabilities. The zeta potential analysis of the CS/CTAB beads that were impregnated with various concentrations of CTAB (0–0.1%) was done at pH 5 with a Malvern Zetasizer (Nano ZS, Malvern, UK) and no background electrolyte was added to the sample.

2.4. Batch adsorption

Adsorption experiments were conducted in a batch mode using 10 ml of an aqueous CR solution and CS/CTAB beads and CS beads as adsorbents. Three different concentrations of CR solutions (10, 100 and 1000 mg/l) were selected for the adsorption experiments, and 0.2 g of wet beads were added to the CR solution. Equilibrium adsorption data were obtained with an adsorption period of 24 h at 30 °C and a pH of 5. The adsorption performance of the CTAB-impregnated CS beads was studied by fixing the CTAB concentration at 0.05 wt% in beads. The effect of the adsorbent dosage on CR adsorption was studied at a pH of 5 with an initial CR concentration of 500 mg/l. All of the adsorption experiments were conducted in triplicate, and the concentration of CR in the experimental solution was determined from the calibration curve. The calibration curve was prepared by measuring the absorbance of different predetermined concentrations of CR solutions at λ_{max} 497 nm using a DR5000 spectrophotometer (HACH, USA). The amount of CR adsorbed (mg/g) was calculated based on a mass balance equation given below:

$$q = \frac{(C_0 - C_{eq}) \times V}{W}, \tag{1}$$

where q is the adsorbent capacity in mg/g; C_0 is the initial concentration of CR in mg/l; C_{eq} is the final or equilibrium concentration of CR in mg/l; V is the volume of dye solution in contact with the adsorbent in l; and W is the dry weight of CS and CTAB-impregnated beads in g.

2.5. Desorption

CS and CS/CTAB beads (0.2 g of wet beads) were collected via filtration after 24 h of adsorption in a CR solution with an initial concentration of 100 mg/l. It was followed by the addition of CR-loaded beads to 10 ml of deionized water at different pH levels (pH 10, 11 and 12) in order to facilitate the desorption of CR from the beads. Different organic solvents such as acetone, methanol and acetonitrile were also used to bring about desorption of CR from the beads. Desorption experiments were carried out at 100 rpm and 30 °C, and the concentration of the eluted CR was measured at λ_{max} 497 nm after 24 h desorption. The desorption of CR from the beads was evaluated by the following equation:

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of desorbed CR}}{\text{Amount of adsorbed CR}} \times 100 \tag{2}$$

3. Results and discussion

3.1. Characterization of CS/CTAB beads

It has been already reported in our recent publication that CS beads impregnated with 0.05% CTAB have higher CR adsorption capacity than normal CS beads [31]. In order to explore the reason behind the enhancement of CR adsorption by CS beads after CTAB impregnation, the results of the characterization of the CS/CTAB beads using infrared (IR) spectra, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were included along with those of normal CS beads.

As shown in Fig. 1a, characteristic peaks obtained for normal CS hydrogel beads are: 3442.72 (stretching vibrations of the –OH and –NH groups), 2878.63 (C–H stretching), 1651.03 (amide II band, N–H bending and C=O stretching of acetyl groups), 1381.88 (C–N stretching or O–H bending) and 1071.09 cm^{-1} (alcoholic C–O and C–N stretching).

The peaks obtained for CS/CTAB hydrogel beads (Fig. 1b) are: 3419.83 (wide peak of O–H stretching overlapped with N–H stretch-

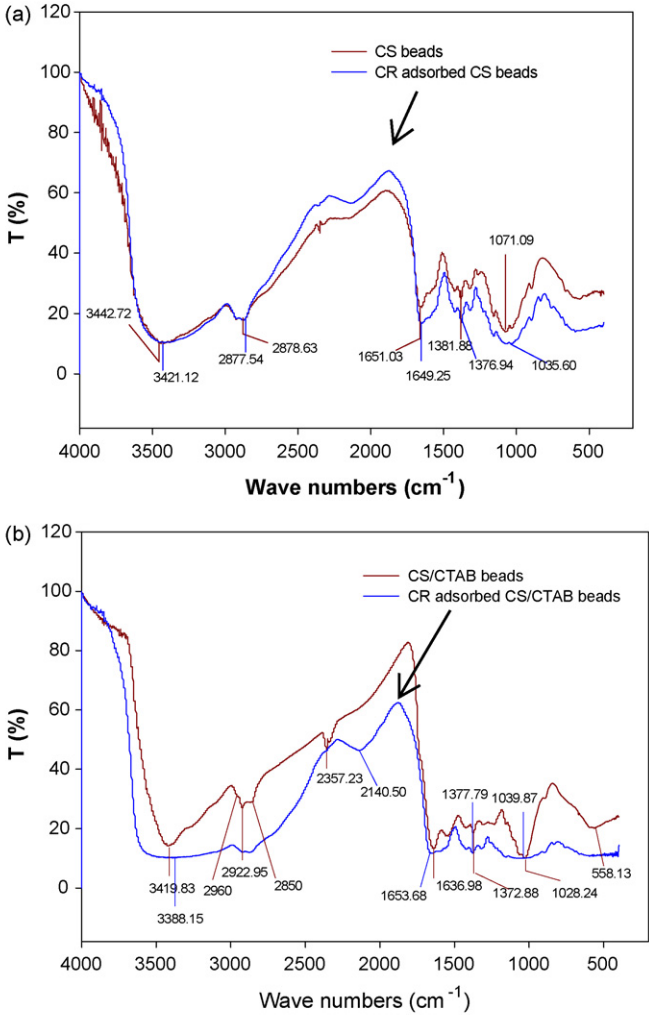

Fig. 1. FTIR spectra of (a) CS beads and (b) CS/CTAB beads before and after CR adsorption.

ing of CS molecules), 2922.95 (C–H stretching of CS molecules and asymmetric C–H stretching from methylene [CH_2] chain in CTAB molecules), 2850 (symmetric C–H stretching of methylene [CH_2] chain in CTAB molecules), 2960 (asymmetric C–H stretch of methyl [CH_3] group of CTAB molecules), 1651.03 (amide II band, N–H bending and C═O stretching of acetyl groups), 1381.88 (C–N stretching or O–H bending) and 1071.09 cm^{-1} (alcoholic C–O and C–N stretching). The peak at 2960 cm^{-1} is unique to CTAB and is related to both trimethyl head group and the terminal methyl of this surfactant [32]. The bands at 2922 and 2850 cm^{-1} for asymmetric and symmetric C–H stretching, respectively, of methylene, and another band at 2960 cm^{-1} for asymmetric C–H stretching of methyl group of CTAB molecules [32] confirm that CTAB molecules are successfully impregnated in CS beads. The peak at 3442.72 cm^{-1} has shifted to lower wave number (3419.83 cm^{-1}) after CTAB impregnation. Other significant changes are noted at 1651.03–1636.98, 1381.88–1372.88 and 1071.09–1028.24 cm^{-1} after CTAB impregnation. These spectral changes indicate that CTAB molecules have interacted with both amino and hydroxyl groups of CS molecules during impregnation.

The FTIR spectra of CR-adsorbed CS beads (Fig. 1a) indicate the involvement of functional groups (–OH and –NH groups) of the CS molecules in the adsorption process. As shown in Fig. 1b, the peaks for CTAB molecules in the beads at 2960 and 2850 cm^{-1} disappear after CR adsorption and it clearly suggests that CTAB molecules can bind CR molecules. The wide adsorption band at 3419.83 cm^{-1} shifts to lower wave number (3388.15 cm^{-1}) with a significant decrease in the peak intensity, and the peak at 2922.95 cm^{-1} disappears after CR adsorption onto CS/CTAB beads. The peak at 2357.23 cm^{-1} assigned to N–H stretching disappears, a new peak appears at 2140.50 cm^{-1}, and some changes at the wave numbers 1636.98–1653.68, 1372.88–1377.79 and 1028.24–1039.87 cm^{-1} are noted after adsorption. Therefore, the adsorption of CR onto CS/CTAB beads occurs through involvement of both CS and CTAB molecules.

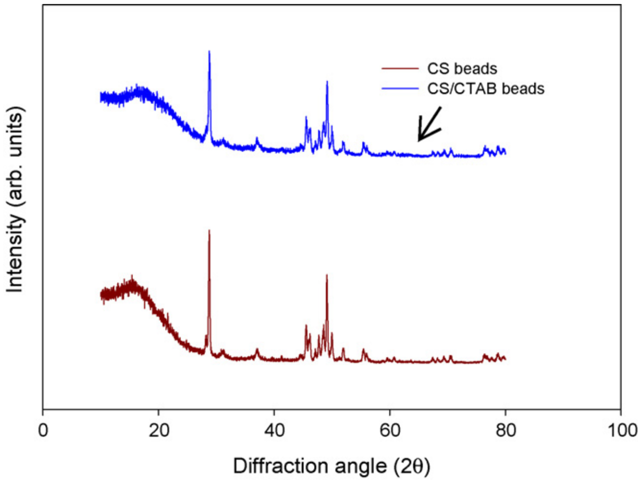

Fig. 2. X-ray diffraction patterns of CS beads and CS/CTAB beads.

The XRD pattern of CS/CTAB beads is similar to the characteristic peaks of CS beads (as illustrated in Fig. 2). As our results indicate, CTAB impregnation does not affect the crystalline structure of CS. Both diffractograms show characteristic peaks around $2\theta = 28^\circ$, indicating the existence of an amorphous structure.

Fig. 3 shows TEM micrographs of freeze-dried samples of CS beads (Fig. 3a) and CS/CTAB beads (Fig. 3b); the CTAB molecules are easily visualized in the CS matrix of CTAB-impregnated beads via contrast differences between CTAB and CS. The CTAB distribution might not be homogeneous but, in some places, it is present in a self-aggregated form due to hydrophobic interactions.

Scanning electron microscopy (SEM) images of the CS beads (Fig. 4a) and CS/CTAB beads (Fig. 4b) at 4000× magnifications show heterogeneous and porous surface structures of adsorbents, which favor the adsorption of CR onto different parts of the beads. Both varieties of beads have well-developed networks and shallow membranes between the networks. The impregnation of CS beads with CTAB makes the surface of the CTAB-impregnated CS beads denser than that of CS beads.

The results of an EDX (energy dispersive X-ray) analysis (Table 1) indicate that CS beads and CTAB-impregnated CS beads consist mainly of carbon (C) and oxygen (O). CR adsorption onto CS and CS/CTAB beads produces a sulfur (S) peak in the EDX spectra, indicating the binding of CR on the adsorbent. The weight percentage of S (%) in CS/CTAB beads (1.99%) was higher than that of CS beads (1.83%) after adsorption, indicating that CS/CTAB beads have a higher CR binding capacity than the CS beads.

Table 1
Elemental analyses of CS beads and CS/CTAB beads by EDX spectra.

Element	CS beads		CS/CTAB beads (0.05% CTAB)	
	Before adsorption	After adsorption	Before adsorption	After adsorption
C (wt.%)	56.60%	60.07%	55.28%	58.79%
O (wt.%)	43.40%	38.10%	44.72%	39.22%
S (wt.%)	0%	1.83%	0%	1.99%

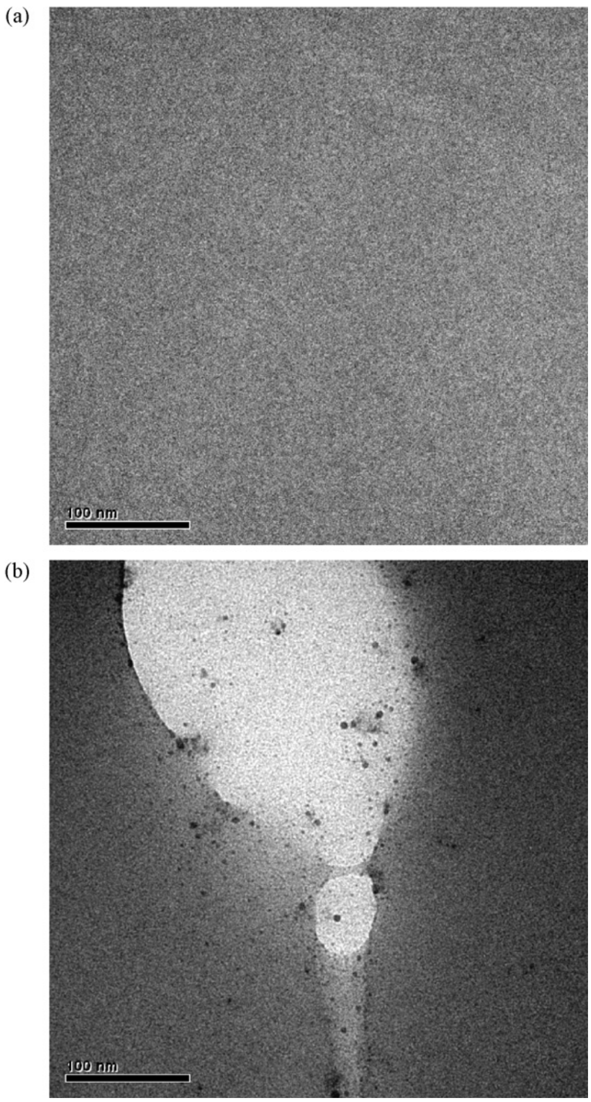

Fig. 3. TEM images of (a) CS beads and (b) CS/CTAB beads.

As can be seen in Fig. 5, the zeta potential values of CTAB-impregnated CS beads were not significantly increased when the impregnated CTAB concentration in the beads was increased. The zeta potential value of the CS/CTAB beads was not consistent with an increase in the CTAB concentration, and even the zeta potential value of the CS/CTAB beads was found to decrease slightly from 29.4 (0% CTAB) to 26.6 mV after impregnating the beads with 0.1% CTAB (Fig. 5). This is because the molar ratio of the charge is quite low (0.052 mol NH_2/mol CTAB), even in the case of 0.1% CS/CTAB beads. Thus, CTAB impregnation in this concentration range could not significantly alter the surface potential of CS/CTAB beads.

3.2. Adsorption characteristics and mechanism of CR adsorption by CS/CTAB beads

The adsorption characteristics of CS/CTAB beads and CS beads were investigated so that we could understand the mechanism of CR adsorption. As shown in Table 2, the equilibrium adsorption capacity of the CS/CTAB beads impregnated with 0.05% CTAB was higher than that of CS beads for all of the initial concentrations of CR (10, 100 and 1000 mg/l) tested here. Also, the volumetric adsorption capacity of CS/CTAB beads increased due to CTAB impregnation because the dry weight (g)/ml volume of the CS/CTAB beads increased from 0.023 g/ml volume of CS beads to 0.035 g/ml of CS/CTAB beads, as shown in Table 2. As shown in Fig. 6, an increase in dosage of CS/CTAB beads into a 500 mg/l CR solution resulted in higher CR removal (%) than that of CS beads. The removal of CR increased from 17.62% to 74.89% with an increase in the dosage of CS/CTAB beads (0.2–2 g dry weight of beads/l of CR solution), whereas a similar increase in the adsorbent dosage of CS beads increased the CR removal from 8.30% to 36.46%. The results obtained from these adsorption experiments clearly indicated that the equi-

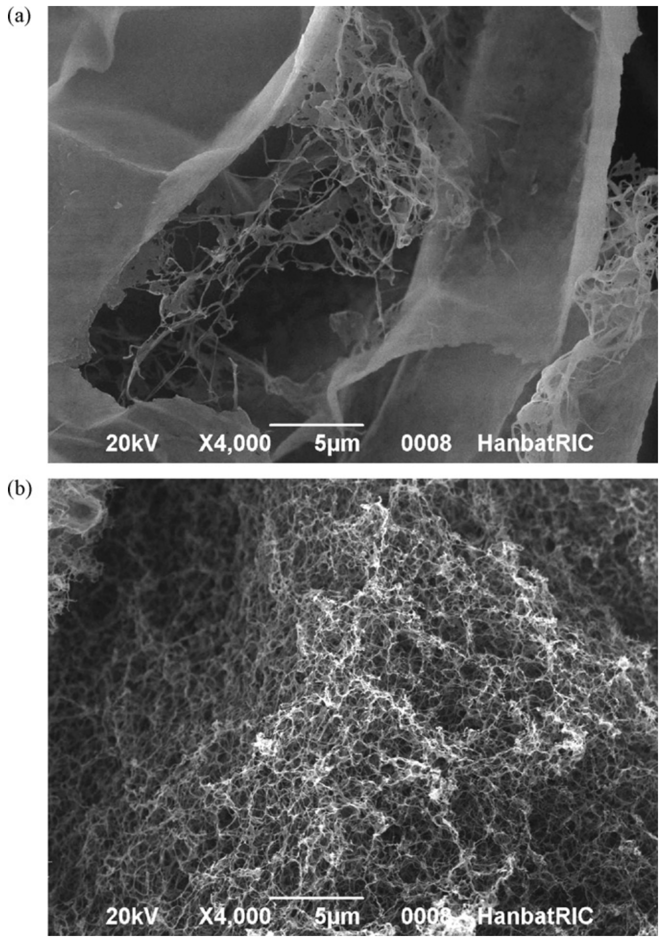

Fig. 4. SEM images (4000×) of CS beads (a) and CS/CTAB beads (b).

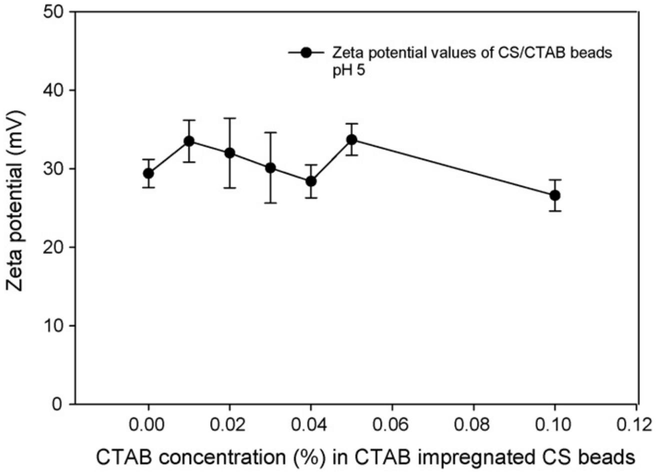

Fig. 5. Zeta potentials of CS beads impregnated with various CTAB concentrations.

Table 2
Adsorption performance of CS beads and CS/CTAB beads.

Adsorbent	dw (g)/ml beads	C_0 (10 mg/l)		C_0 (100 mg/l)		C_0 (1000 mg/l)	
		q_e (mg CR/g dw)	q_e (mg CR/ml beads)	q_e (mg CR/g dw)	q_e (mg CR/ml beads)	q_e (mg CR/g dw)	q_e (mg CR/ml beads)
CS beads	0.023	12.61 (±0.11)	0.29 (±0.003)	86.30 (±1.11)	1.99 (±0.03)	178.32 (±1.32)	4.1 (± 0.03)
CS/CTAB beads	0.035	13.48 (±0.12)	0.47 (±0.003)	114.29 (±1.20)	4.00 (±0.04)	373.29 (±2.51)	13.10 (±0.09)

librium adsorption capacity of CS/CTAB beads was higher than that of CS beads, and that adsorption of CR onto CS/CTAB beads might involve mainly electrostatic interactions between CR molecules and multiple functional groups of CS [29] as well as the positively charged head group of CTAB molecules. However, inconsistent zeta potential values of the CS/CTAB beads were observed after impregnating the beads with different concentrations of CTAB, indicating that the surface potential of the CS/CTAB beads could not be significantly altered by CTAB impregnation. Therefore, the electrostatic interactions between CR and CTAB molecules as well as some of the hydrophobic interactions between a hydrophobic tail of CTAB and hydrophobic moieties of CR enhanced the adsorption capacity of the CS/CTAB beads.

The comparison of adsorption capacity of CS/CTAB beads (373.29 mg/g) with some previously reported adsorbents, such as activated carbon obtained from coir pith (6.70 mg/g) [16], neem leaf powder (41.20 mg/g) [17], acid activated red mud (7.08 mg/g) [18], bagasse fly ash (11.89 mg/g) [20], *Aspergillus niger* biomass (8.19 mg/g) [23], etc., towards CR indicates that adsorption capacity of these novel CS hydrogel beads was very high. Therefore this impregnation method using CTAB could be applied to enhance the adsorption performance of CS hydrogel beads.

3.3. Desorption study

The desorption of CR from the adsorbent is necessary for its reuse as well as to help us understand the mechanism of adsorption. As can be seen in Table 3, desorption increased with an increase in the pH of the eluent for both beads, indicating that an ionic interaction was clearly involved during CR adsorption and that desorption was increased via deprotonation of $-NH_3^+$ groups of CS molecules to NH_2 groups at high pH values. However, low values of the desorption ratio for CS beads as well as the CS/CTAB beads were found in the range of 23.56–38.53% by pH treatment, indicating the involvement of interactions other than pure electrostatic interactions between adsorbent and adsorbate during adsorption. The amount of desorption of CR from the CS/CTAB beads was lower than that of the CS beads at all pHs values tested, indicating that adsorption of CR onto CS/CTAB beads involves some hydrophobic interactions between CR and CTAB molecules. Some organic solvents such as acetone, methanol, and acetonitrile were found to be more effective (up to 45.43% more desorption) than pH treatment in terms of enabling desorption, which demonstrates that hydrophobic interactions are also involved in an important way.

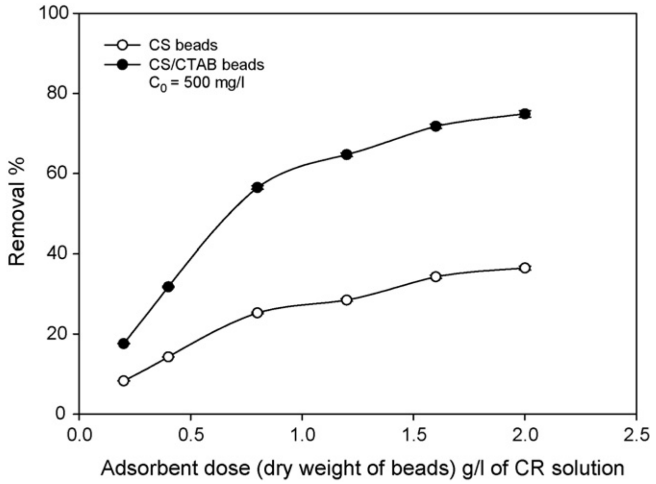

Fig. 6. Effect of the CS and CS/CTAB beads adsorbent dosage on CR adsorption; initial CR concentration, 500 mg/l, pH 5.

Table 3
Desorption ratio (%) of CR from loaded CS beads to CS/CTAB beads.

pH	CS beads	CS/CTAB beads
10	25.62	23.56
11	33.87	28.97
12	38.53	31.45
Organic solvent	**CS beads**	**CS/CTAB beads**
Acetone	43.25	36.43
Methanol	45.43	39.45
Acetonitrile	38.64	32.83

4. Conclusions

The adsorptive behavior of cetyl trimethyl ammonium bromide-(CTAB) impregnated CS beads (CS/CTAB beads) was investigated via the removal of CR from aqueous solutions in this study. CS/CTAB beads were prepared by alkaline gelation of a CS (1 wt%) solution containing 0.05 wt% of CTAB. The characterization of CTAB-impregnated CS beads by infrared (IR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) analysis capabilities gave us information about the structural changes of the beads due to CTAB impregnation. The higher CR adsorption capacity of CS/CTAB beads compared to that of CS beads was clearly supported by EDX analysis. The zeta potential values of CS beads impregnated with different CTAB concentrations indicated that the surface potential of the CS beads was not significantly altered by CTAB impregnation. Therefore, the enhanced capacity of CS/CTAB beads to adsorb CR is partly due to electrostatic interaction between impregnated CTAB molecules and CR, and partly due to some hydrophobic interactions between the hydrophobic tail of CTAB and hydrophobic moieties of CR.

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