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Removal of Congo Red from the aqueous phase by chitin and chitosan from waste shrimp

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ABSTRACT

This work describes the adsorption process at laboratory level of Congo Red on two biopolymers from shrimp exoskeletons. Chitin obtained by demineralization and deproteinization and chitosan by additional deacetylation process of shrimp exoskeletons. Box–Behnken experimental design with three variables at three levels each one was used to evaluate the optimum conditions of the process. The analysis of the results showed that optimal parameters of adsorption process were at pH 7.0, at temperature of 50˚C, and 3 h of contact time. Also, isotherms models were evaluated, showing that adsorption equilibrium for chitin was best described by the Langmuir adsorption model; in contrast the chitosan was better described by the Freundlich adsorption isotherm. The corresponding thermodynamic parameters (ΔG°, ΔH°, and ΔS°) were calculated to evaluate the nature of the adsorption process. The results showed the feasibility of the process and the spontaneous nature of adsorption with both biopolymers. The maximum adsorption capacities of chitin and chitosan obtained from the Langmuir and Freundlich isotherm model were 139 and 320 mg g^{-1}, respectively, indicating that chitosan was the best adsorbent for Congo Red. Finally, the analysis by FT-IR confirmed the adsorption of Congo Red onto chitin and chitosan, since a peak detected at 1,153 cm^{-1} which may attributed to the groups SO_3 of Congo Red.

Keywords: Chitin; Chitosan; Congo Red; Shrimp exoskeleton; Removal

1. Introduction

Wastewaters from textile, cosmetics, printing, dyeing, food coloring, and papermaking industries are polluted by dyes. These colored effluents can be mixed with surface water streams and ground water systems, contaminating sources of potable water. Dyes can cause also allergic dermatitis, skin irritation, cancer, and mutations [1]. Azo dyes represent about 50% of all dye varieties, and these dyes are of great environmental concern due to their huge applications and recalcitrance. The removal of such type of contaminants from effluent before discharging into natural water bodies is extremely important from an environmental point of

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view. Such effluents cause abnormal coloration on the surface of the water and block photosynthetic bacteria and aquatic plants from sunlight [2].

Congo Red [1-naphthalene sulfonic acid, 3,3´-(4,4´-biphenylenebis (azo)) bis(4-amino-) disodium salt] is a benzidine-based anionic diazo dye prepared by coupling tetrazotized benzidine with two molecules of napthionic acid [3]. Effluents containing Congo Red are produced by textile, printing, dyeing, paper, and plastic industries [3,4]. This anionic dye can be metabolized to benzidine, a well-known human carcinogen [5].

Some methods can be used to remove dyes from wastewater, such as membrane filtration, electro-coagulation, electrochemical destruction, ion exchange, irradiation, advanced oxidation, precipitation, and adsorption [6]. However, most of these processes have a high cost and low efficiency. Among all process in practice, adsorption has been found to be a very effective method for most pollutant removal from industrial effluents [7]. Adsorption is a mass transfer process in which the contaminant is concentrated on a surface in order to be subsequently recovered or confined.

The use of natural adsorbents has increased in recent years, which includes agroindustrial waste or biodegradable polymers such as the chitin and chitosan. Chitin is a polymer of N-acetylglucosamine, found in the crustaceans exoskeleton, insects cuticles, and fungi walls cells, is the most abundant aminopolysaccharide, and after cellulose is the second most abundant natural biopolymer found in nature [8]. Chitin is highly hydrophobic and is insoluble in water and most organic solvents; this property has been utilized to the applications development, especially in fiber [9]. Also it has been found that chitin possesses antibacterial properties [10]. Further, have evaluated the recovery of protein during the process of obtaining chitin from shrimp shells [11], and oligomers and monomers are obtained from it [12]. More important than chitin is its derivative, chitosan [13], which is a polysaccharide usually obtained from deacetylation of chitin. Besides being natural and abundant, chitosan possesses interesting characteristics that also make it an effective adsorbent for the removal of dye as it has outstanding adsorption capacities. Three factors have specifically contributed to the growing recognition of chitosan as a suitable biomaterial for dye removal; first is the fact that chitosan is obtained from natural renewable resources and their use as biosorbents is extremely cost-effective; second is the high adsorption capacities reported, and the third factor is the development of new complexing materials, due to chitosan particular properties, allowing it to be manufactured into films, membranes, fibers, gels, sponges, and nanoparticles or supported on inert particles [8]. The use of chemically unmodified chitin/chitosan in wastewater treatment has been described in few recent review articles [8,14–18]. In this work, we report the results of an efficient process of Congo Red adsorption by chemically unmodified chitin and chitosan obtained from shrimp exoskeletons.

2. Materials and methods

2.1. Preparation of chitin and chitosan

Exoskeleton of shrimp obtained from various local restaurants was demineralized and deproteinized to obtain chitin; For this, 35 g of shrimp exoskeleton was mixed with 250 mL of 0.6 N HCl at 30˚C for 3 h with constant stirring, and then, the mixture was filtered, washed with tap water and distilled water to obtain a pH 6.5–7.5. Mix was subsequently placed in an oven at 40˚C for 24 h. The demineralized exoskeleton was mixed with 300 mL of 1% NaOH and continuously stirred for 24 h at 28˚C, and then, the mixture was filtered, washed with tap water and distilled water to a pH 6.5–7.5. Finally, the chitin obtained was dried at 40˚C during 24 h.

Chitosan was obtained by deacetylation process. With this purpose, 20 g of chitin obtained in the previous step was mixed with a 50% NaOH solution in a ratio 1:4 w/v for 2 h at 60˚C, followed by a heating at 100˚C during 2 h with constant stirring. Obtained chitosan was washed with tap water and distilled water to a pH 6.5–7.5. Thereafter, it was placed in a drying oven for 24 h, at a temperature of 40˚C. The degree of deacetylation of chitosan was evaluated by UV spectrophotometry according to method proposed by Liu et al. [19].

2.2. Effect of contact time, pH, and temperature in the adsorption of Congo Red on chitin and chitosan

Experimental Box–Behnken design was used, in which three variables were evaluated at three levels each. The variables considered were contact time (1, 2, and 3 h); pH (5, 7, and 9), and temperature (30, 40, and 50˚C). Fifteen experiments were carried out in 15 mL Falcon tubes containing 10 mL of Congo Red dye at a concentration of 100 mg L^{-1} in the aqueous phase and 0.1 g of chitin or chitosan, under conditions of pH, temperature, and contact time of the design. After each experiment, the supernatant was collected by centrifugation at 12,000 rpm for 10 min. The concentration of dye before and after the adsorption was measured by absorbance at 486 nm in UV–vis spectrophotometer

GENESYS 105. Readings were interpolated at a rate of Congo Red curve of 0–10 mg L^{-1}. The percentage of Congo Red adsorbed was calculated based on a mass balance given by Eq. (1):

$$\text{Removal percentage} = \frac{C_o - C_f}{100} \times 100 \tag{1}$$

where C_o is the initial concentration of Congo Red in mg L^{-1}, and C_f is the final concentration in mg L^{-1} after the contact time as designed. The response surfaces were processed using the STATISTICA 6.0 software.

2.3. Adsorption isotherm

The experiments for analyzing the nature of dye adsorption on the chitin or chitosan were performed at the optimal conditions of pH and temperature selected in the experimental design Box–Benhken. Falcon tubes containing 10 mL of the dye at different initial concentrations (100–3,000 mg L^{-1}), pH was adjusted to 7.0 for chitin and pH 8.0 for chitosan, 0.1 g of the corresponding biopolymer was added and stirred to equilibrium (5 d) at temperatures of 40 and 50°C. At the end of the adsorption period, the solutions were centrifuged at 12,000 rpm for 10 min. All concentrations were measured by absorbance at 486 nm in UV–vis spectrophotometer GENESYS 105; readings were interpolated at a rate of Congo Red curve of 0–10 mg L^{-1}. The amount of adsorbed Congo Red (mg g^{-1}) was calculated based on the mass balance given by Eq. (2):

$$q = (C_o - C_{eq}) \times V/W \tag{2}$$

where q is the capacity of the adsorbent in mg g^{-1}; C_o is the initial concentration of dye in mg L^{-1}; C_{eq} is the equilibrium concentration of the dye in mg L^{-1}; V is the experimental solution volume in L; and W is the dry weight of chitin or chitosan used in grams.

Langmuir and Freundlich isotherms were used to analyze the adsorption process, and these models were statistically analyzed by the non-linear coefficient of determination (R^2). Langmuir equation is expressed as Eq. (3):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_e (mg g^{-1}), and C_e (mg L^{-1}) are the amount of adsorbed dye per adsorbent weight unit and unadsorbed dye concentration in solution at equilibrium, respectively, and q_m (mg g^{-1}) and K_L (L mg^{-1}) are Langmuir constants related to the maximum adsorption capacity of adsorbents and the affinity between the adsorbate and the adsorbents, respectively. Additionally through Langmuir isotherm, the constant called separation factor (R_L) defined by the following Eq. (4) [20,21] was evaluated:

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

where C_o (mg L^{-1}) is the initial concentration of dye and the K_L (L mg^{-1}) is the Langmuir constant related to energy of adsorption. The Freundlich isotherm is expressed by the following Eq. (5):

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F is the Freundlich constant and n (g L^{-1}) is an empirical parameter representing the affinity of the adsorbent and the adsorbate molecules.

2.4. Thermodynamic parameters

The thermodynamic parameters were calculated using the following Eqs. (6)–(8):

$$\Delta G^\circ = -RT \ln K_c \tag{6}$$

$$K_c = \frac{C_s}{C_e} \tag{7}$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \tag{8}$$

where ΔG°, ΔH°, and ΔS° are change in Gibbs energy, change in the standard enthalpy, and change in the standard entropy, respectively; K_c is the equilibrium constant, C_s is the concentration at equilibrium of Congo Red in the adsorbent (mg g^{-1}), C_e is the concentration of Congo Red in the solution at equilibrium (mg L^{-1}), and T is the temperature of adsorption in kelvin.

2.5. Adsorption kinetics

The effect of contact time on adsorption of Congo Red by chitin and chitosan was evaluated by Boxx2013;Benhenken design, and the adsorption kinetics were obtained by the plot equation at 40°C and pH 7. In order to investigate the mechanism of adsorption, pseudo-first-order equation and pseudo-second-order equation of Lagergreen [20,22] and intra-particle diffusion equation [20,23] were used at 40˚C.

The pseudo-first-order equation is given by Eq. (9):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{9}$$

where q_t and q_e are the amounts of Congo Red adsorbed at time t and equilibrium (mg g^{-1}), respectively, and k_1 is the pseudo-first-order rate constant for the adsorption process (h^{-1}). The pseudo-second-order chemisorption kinetic rate equation is expressed as Eq. (10):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

where k_2 is the equilibrium rate constant of pseudo-second-order equation. The intra-particle diffusion equation is presented by the following Eq. (11):

$$q_t = k_i t^{1/2} \tag{11}$$

where k_i is the intra-particle diffusion rate constant (mg g^{-1} h$^{1/2}$) [19].

2.6. Analysis by FT-IR spectrophotometry

After and before the adsorption process, chitin and chitosan from shrimp exoskeleton obtained in the laboratory were analyzed in a Fourier transform infrared (FT-IR) spectrophotometer Cary 630-Agilent Technologies in a range of 650–4,000 cm^{-1}, with 16 scans at a resolution of 4 cm^{-1}. Also, both biopolymers purchased from Sigma-Aldrich were analyzed.

3. Results and discussion

The effect of three variables contact time, pH, and temperature on the removal of Congo Red by chitin is shown in Fig. 1. The increase of temperature from 30 to 50˚C caused removal of Congo Red in the range of 65–93% with pH between 5.0 and 9.0 and with 1 and 3 h of contact time, being range of removal between 55 and 87%. That is, the contact time was the meaningful variable; which was more evident at 30˚C and the removal rate was constant during the three hours of contact time. The pH between 5.0 and 9.0 was not highly significant for removal process, and this could be because Congo Red keeps the anionic form in this range, and maybe only the functional groups of biopolymer as –OH, –NHCOCH$_3$, and –NH$_2$ were changed, that as a function of pH may be mediated, for example, by neutral amino groups (–NH$_2$) or cationic form (–NH$_3^+$). According to Giles and Hassan [24], chitin adsorbs by hydrogen bond formation with the solute in the absence of water, but in the presence of water by van der Waals attraction and by ion exchange. In chitin, the active centers for both hydrogen bond and ion exchange adsorption are the acetamido and amino groups; the hydroxyl groups are believed to be strongly solvated in water and unable to adsorb solutes by hydrogen bonding.

Also, it is known that at pH 9.0, all ion exchange activity of chitin is suppressed, and in the absence of hydrogen-bonding groups in the solute, adsorption by any substrate can take place only by van der Waals interaction [24]. On the other hand, Hu et al. [25] also reported that the effect of pH in Congo Red removal by cattail root was not affected over pH range of 5.5–10.0. As can be seen, this range of pH has no effect on adsorption process using other adsorbents; in spite of being an anionic dye, Congo Red is adsorbed in considerably amounts. According to response surfaces, the optimization of removal of Congo Red by chitin occurred at 50˚C, pH 7, and 3 h of contact time.

Chitosan was also used to remove Congo Red, and the degree of acetylation of chitosan which was prepared from exoskeleton in this work was 0.01; it was identical to commercial chitosan (Sigma-Aldrich), and this result suggests that the deacetylation process was efficient. Fig. 2 shows the effect of contact time, pH, and temperature on the removal of Congo Red by chitosan. The removal was between 95 and 100% using all tested conditions; this higher adsorption capacity may be attributed to the amine groups of chitosan. The degree of deacetylation affects the adsorption capacity of the chitosan; high deacetylation degree generally results from the presence of high amounts of amino groups, and it can increase dye adsorption capacity of the chitosan by protonation [26]. Many researchers have investigated the adsorption process of different forms of chitosan. However, the obtained unmodified chitosan from chitin called chitosan flakes has been used by a few researchers as an adsorbent for dye removal from aqueous solutions [27].

The adsorption process was studied by isotherm analysis, which describes the equilibrium relationships between adsorbent and adsorbate. The correlation of equilibrium data with an equation is essential for the adsorption interpretation and prediction of the extent of adsorption. Fig. 3(a) shows the equilibrium adsorption of Congo Red (q_e vs. C_e) onto chitin. The isotherm was found to be linear over the entire concentration range with a linear correlation coefficient (R^2) of 0.985,

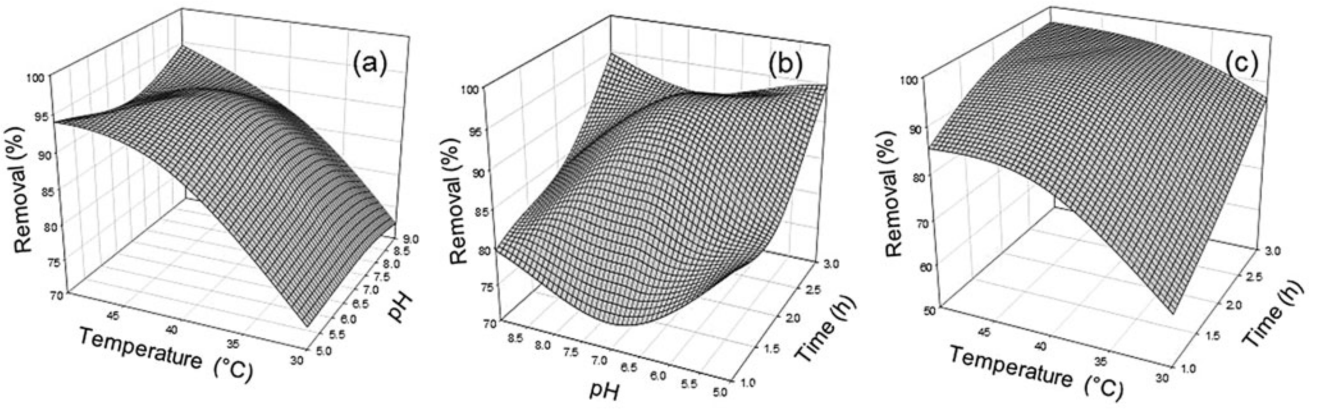


Fig. 1. Removal of Congo Red by chitin on 3D graphics for response surface. (a) vs. temperature and pH, (b) vs. pH and contact time, and (c) vs. temperature and contact time.

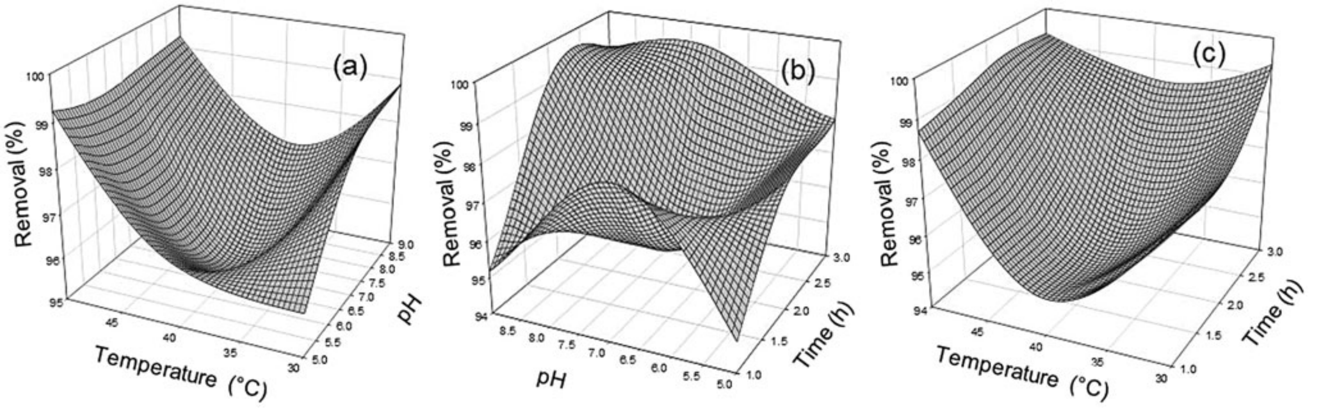


Fig. 2. Removal of Congo Red by chitosan on 3D graphics for response surface. (a) vs. temperature and pH, (b) vs. pH and contact time, and (c) vs. temperature and contact time.

showing that data correctly fit the Langmuir isotherm and was higher than the Freundlich isotherm (Table 1). It suggests homogenous distribution of active sites on the chitin, since the Langmuir equation assumes that the surface is homogeneous. Langmuir isotherm is most widely used for the adsorption of pollutants from liquid solutions [20,28].

The monolayer saturation capacity of chitin was found to be 139 mg g^{-1}. This value was comparable to the adsorption capacities of some others adsorbents materials for Congo Red (Table 2). The Langmuir adsorption isotherm was also used to calculate the dimensionless constant separation factor. The R_L value indicates the type of the isotherm; unfavorable ($R_L \geq 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The obtained values were between 0.001 and 0.00007 and it suggests the favorable uptake of the Congo Red process. The degree of favorability is generally related to the irreversibility of the system.

On the other hand, the adsorption data of chitosan provide slightly higher correlation with Freundlich isotherm model compared with Langmuir model (Table 1). Fig. 3(b) shows the equilibrium isotherm adsorption of Congo Red onto chitosan, and it is possible to see the high correlation between experimental data and both isotherms models. The Freundlich isotherm is used for heterogeneous surface energy systems; it assumes that there is a continuously varying energy of adsorption as the most actively energetic sites are occupied first and the surface is continually occupied until the lowest energy sites are filled at the end of the adsorption process [34].

Adsorption treatment using chitin and chitosan from shrimp exoskeleton was an effective method for the removal Congo Red from aqueous solution; however, chitosan had higher adsorption capacity obtaining 320 mg g^{-1}, and it is similar with the results of Chatterjee et al. [35], who reported a capacity of

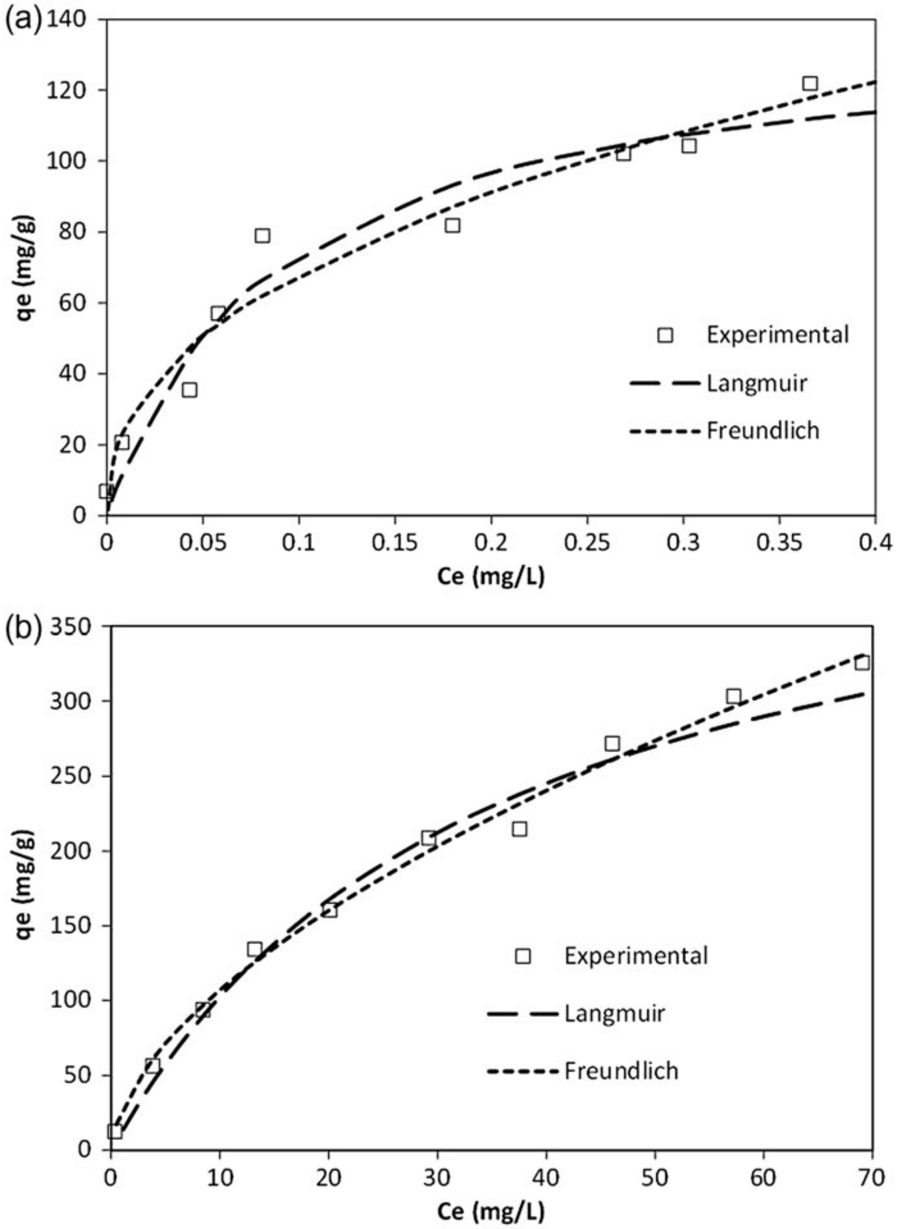


Fig. 3. Equilibrium isotherms of Congo Red on (a) chitin and (b) chitosan. Conditions: 40 and 50°C, respectively, pH 7 and 10 g L^{-1} dose.

Table 1

Langmuir and Freundlich isotherm constant for Congo Red adsorption onto chitin and chitosan

	Langmuir				Freundlich		
	K_L (L g^{-1})	R_L	q_m	r^2	K_F ($mg^{1-1/n}$ $L^{1/n}g^{-1}$)	n (g L^{-1})	r^2
Chitin	11.330	0.00007–0.001	138.90	0.988	180.65	2.35	0.975
Chitosan	0.028	0.00030–0.001	320.83	0.987	27.75	1.70	0.997

Table 2
Reported maximum adsorption capacities for Congo Red obtained on low-cost adsorbents

Adsorbent	Q_o (mg g^{-1})	References
Cattail root	38.79	Hu et al. [25]
Fertilizer plant waste carbon	233.90	Mall et al. [29]
Bamboo dust carbon	101.90	Kannan and Meenakshisundaram [30]
Bentonite	158.70	Bulut et al. [31]
Rice hull ash	171.00	Chou et al. [32]
Banana peel	18.20	Annadurai et al. [33]
Chitin	139.00	This work
Chitosan	320.00	This work

adsorption of Congo Red of 352.5 mg g^{-1} using hydrogel beads impregnated with cetyl trimethyl ammonium bromide.

Thermodynamic parameters such as the Gibb's free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°) for adsorption of Congo Red on chitin and chitosan were determined; Table 3 shows the results. The negative values of ΔG° mean that the process is feasible and adsorption is spontaneous thermodynamically to higher negative values is indicative of a rapid and more spontaneous adsorption [36]. The ΔG° and its trends in this study revealed that the adsorption of Congo Red by chitin and chitosan was spontaneous and more favorable at a low temperature in the studied range. Commonly ΔG° values for physisorption are in the range −20 to 0 kJ mol^{-1}, and those for chemisorption range between −80 and −400 kJ mol^{-1}; therefore, the results of this study suggests that the adsorption is stronger than usual physisorption. The exothermic nature of the process by chitin and chitosan is evident by negative value of ΔH° and compared with the adsorption energy from chemical bond forces ≥60 kJ mol^{-1} [37], the absolute values of ΔH° in the range 65–540 kJ mol^{-1} indicate that bonding could be important to the adsorption process. The positive values of ΔS° suggest randomness at the solid/solution interface [38].

To understand the dynamics of the adsorption process, pseudo-first-order and pseudo-second-order rate models and intra-particle diffusion model were used. The correlation coefficient (R^2) values onto chitin using pseudo-first-order and pseudo-second-order rate models and intra-particle diffusion model were 0.981, 0.993, and 0.867, respectively. The q_e values calculated from the three models give reasonable values; however, q_e values calculated by pseudo-second-order were closer to $q_{e(exp)}$ values that that of pseudo-first-order and intra-particle diffusion model (Fig. 4(a)). That is, the adsorption system obeys the pseudo-second-order kinetic model for the entire adsorption period and thus supports the assumption behind the model that the adsorption is due to chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate [31]. Additionally, although the plot of q vs. $t^{½}$ was linear in the intra-particle diffusion model and possibly Congo Red diffused through the solution to the external surfaces of the adsorbent do not give a good fit to the experimental data for the adsorption of Congo Red, suggesting that other mechanisms such as complexation or ion exchange also play an important role.

The correlation coefficient (R^2) values onto chitosan using pseudo-first-order and pseudo-second-order rate models and intra-particle diffusion model were 0.992, 0.999, and 0.7332, respectively. The first and second order were very similar during the three hours that were studied (Fig. 4(b)), maybe because both models are based on the adsorption capacity: It only predicts

Table 3
Thermodynamic parameters for adsorption of Congo Red onto chitin and chitosan

	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K)	ΔG° (kJ mol^{-1})	
			40°C	50°C
Chitin	−540.99	1.59	−41.35	−25.39
Chitosan	−65.75	0.07	−43.68	−42.95

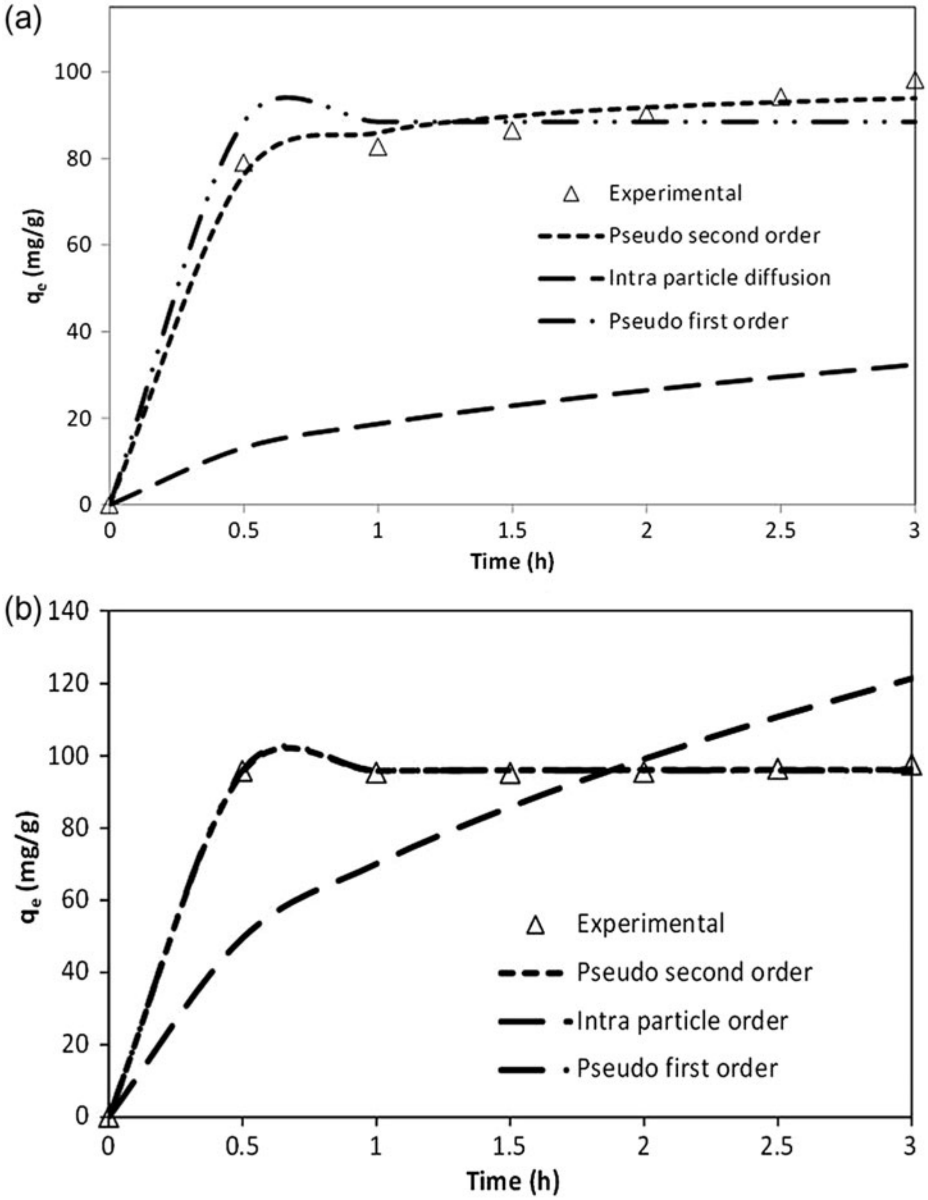
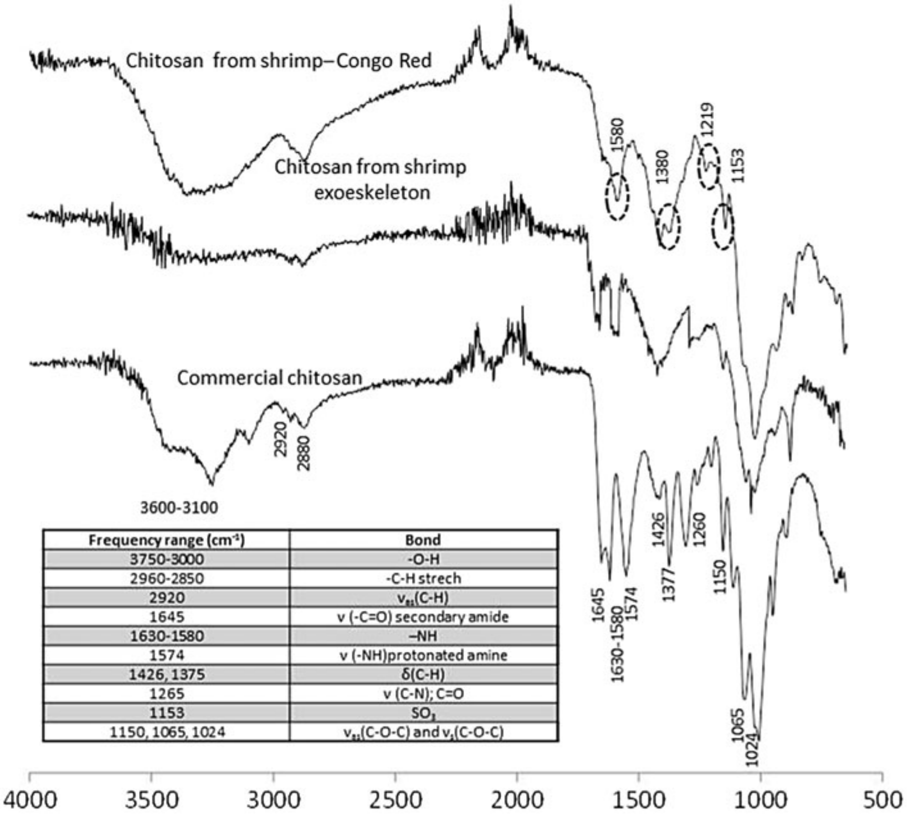


Fig. 4. Plots of q_e vs. t for Congo Red adsorption into (a) chitin and (b) chitosan; initial Congo Red concentration: 100 mg L^{-1}, at pH 7.

the behavior over the "whole" range of studies supporting the validity and is in agreement with chemisorption being the rate control [22,31]. The adsorption process of Congo Red onto chitosan, the pseudo-second-order equation was a better fit than the pseudo-first-order and intra-particle diffusion as well as the adsorption on chitin.

The Fig. 5 displays the FT-IR spectrum of commercial chitosan (Sigma-Aldrich), chitosan from shrimp exoskeleton and the chitosan from shrimp exoskeleton used to adsorb Congo Red. The characteristic absorption of chitosan is located at 3,450 cm^{-1} (–OH), 1,597 cm^{-1} ($-NH_2$), 1,648, and 1,550 cm^{-1} (amide I band and II band) according to Tian et al. [39]; spectrum of commercial chitin in Fig. 5 confirms these bands. Fig. 5 also shows the decrease in peaks intensity at all frequencies in the spectrum of the chitosan from shrimp exoskeleton compared with spectrum of chitosan commercial, only the peaks at 1,375 and 1,426 cm^{-1} corresponding to C–N and C–H, respectively, were not detected, it was possible by the low purity of the chitosan from shrimp exoskeleton; however, it contains the characteristics absorption peaks.



Frequency range (cm^{-1})	Bond
3750-3000	-O-H
2960-2850	-C-H strech
2920	v_{as}(C-H)
1645	v (-C=O) secondary amide
1630-1580	–NH
1574	v (-NH)protonated amine
1426, 1375	δ(C-H)
1265	v (C-N); C=O
1153	SO_3
1150, 1065, 1024	v_{as}(C-O-C) and v_s(C-O-C)

Fig. 5. FT-IR spectra of commercial chitosan, chitosan from shrimp exoskeleton, and chitosan from shrimp Congo Red.

The spectrum of chitosan from shrimp exoskeleton used to adsorb Congo Red (Fig. 5) shows five peaks that were modified: (1) intensity absorbance at 1,580 cm^{-1} was increased, this could be due to the amino groups from adsorbed Congo Red, (2) intensity absorbance at 1,610.5 cm^{-1}, attributed to –N=N– stretching [40,41], (3) at 1,380 cm^{-1}, the absorbance suggests the presence of N–H, which may be formed by hydrogen-bonding interactions between chitosan hydroxyl groups and azoic group of the dye molecules, (4) Also, a peak at 1,219 cm^{-1} was detected that could be due to C–N bond from the amines of the Congo Red, and (5) Finally, at 1,153 cm^{-1}, it was also detected a peak which may be attributed to the groups SO_3 of Congo Red. Overall, the results confirm adsorption process of Congo Red onto chitosan.

The FT-IR spectra of the chitin commercial (Fig. 6) show the presence of two bands characteristic, one at 1,626 cm^{-1} and another at 1,656 cm^{-1}, probably, indicating an amorphous state. These bands are attributed to the vibrations of the amide. Studies indicate that chitin, in the crystalline state, shows only one intense peak at 1,626 cm^{-1} as the chitin from shrimp exoskeleton and this only band at 1,626 cm^{-1} could be attributed to the stretching of C–N vibration [42]. The bands observed between 3,600 and 3,100 cm^{-1} correspond to the vibrational stretching of the hydroxyl groups. The wide peak at 3,500 and 1,650 cm^{-1} indicated that the hydrogen interactions are less accentuated, or the presence of free hydroxyl groups [43]. The band at 1,557 cm^{-1} corresponds to the stretching or N–H deformation of amine, the sharp band at 1,377 cm^{-1} corresponds to a symmetrical deformation of the CH_3 group [44]. When chitin deacetylation occurs, the band observed at 1,655 cm^{-1} decreases, while a growth at 1,590 occurs, indicating the prevalence of NH_2 groups [45].

The Fig. 6 displays also the chitin obtained from shrimp exoskeleton, which shows the same outline spectrum that commercial. Note that for chitin, the band at 1,590 cm^{-1} has a lower intensity than at 1,655 cm^{-1} by effect of not deacetylation. The spectrum of chitin from shrimp exoskeleton used to adsorb Congo Red shows the same five peaks modified than chitosan, it once again confirms adsorption process of Congo Red.

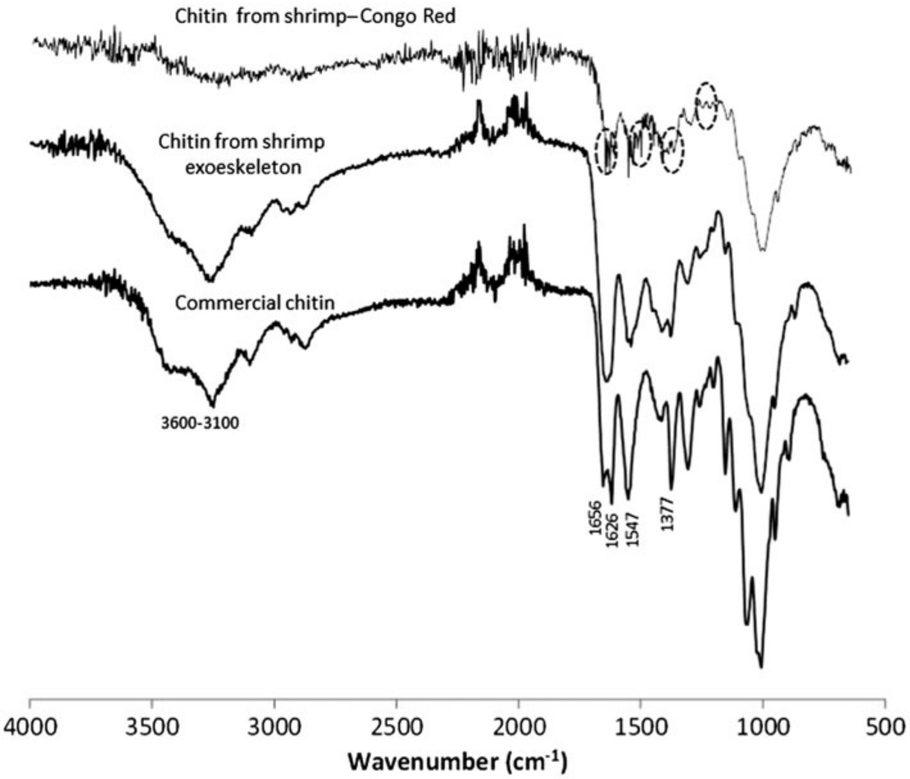


Fig. 6. FTIR spectra of commercial chitin, chitin from shrimp exoskeleton, and chitin from shrimp Congo Red.

4. Conclusion

The use of shrimp exoskeleton waste is a good alternative to produce unmodified chitin and chitosan suitable for Congo Red removal from aqueous solutions. Both biopolymers showed high adsorption capacities being 140 mg g^{-1} for chitin and 320 mg g^{-1} for chitosan; under the optimal conditions determined in this work (pH 7 and 30°C). In addition, the equilibrium adsorption using chitin was best described by the Langmuir adsorption model; meanwhile, the chitosan was described by Freundlich adsorption isotherm. Thermodynamic analysis reveals that the removal of Congo Red in both biopolymers was a spontaneous and exothermic process. These results suggest that chitin and chitosan are potential low-cost adsorbents for the dye removal from industrial wastewater.

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