

Cross-linked quaternary chitosan as an adsorbent for the removal of the reactive dye from aqueous solutions

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Abstract

Adsorption of reactive orange 16 by quaternary chitosan salt (QCS) was used as a model to demonstrate the removal of reactive dyes from textile effluents. The polymer was characterized by infrared (IR), energy dispersive X-ray spectrometry (EDXS) analyses and amount of quaternary ammonium groups. The adsorption experiments were conducted at different pH values and initial dye concentrations. Adsorption was shown to be independent of solution pH. Three kinetic adsorption models were tested: pseudo-first-order, pseudo-second-order and intraparticle diffusion. The experimental data best fitted the pseudo-second-order model, which provided a constant velocity, k_2 , of $9.18 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ for a 500 mg L^{-1} solution and a value of k_2 , of $2.70 \times 10^{-5} \text{ g mg}^{-1} \text{ min}^{-1}$ for a 1000 mg L^{-1} solution. The adsorption rate was dependent on dye concentration at the surface of the adsorbent for each time period and on the amount of dye adsorbed. The Langmuir isotherm model provided the best fit to the equilibrium data in the concentration range investigated and from the isotherm linear equation, the maximum adsorption capacity determined was 1060 mg of reactive dye per gram of adsorbent, corresponding to 75% occupation of the adsorption sites. The results obtained demonstrate that the adsorbent material could be utilized to remove dyes from textile effluents independent of the pH of the aqueous medium.

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1. Introduction

The textile industry consumes a significant volume of water in the process of dyeing fibers and fabrics. This water is highly colored due to the presence of dyes and can affect the photosynthesis process due to the occurrence of reduced water transparency, which makes the penetration of sun rays more difficult [1]. Although many organic molecules are degradable, many others are stable and, due to their complex chemical structures and synthetic organic origin, are not totally degradable [2]. Due to their xenobiotic nature, azo reactive dyes can cause toxicity to aquatic organisms [3].

The classes of dyes mostly used by the textile industry are azo dyes containing reactive groups. Reactive dyes are compounds that contain one or more reactive groups, which form covalent links with oxygen, nitrogen or sulfur atoms from cellulose fibers

(hydroxyl group), protein fibers (amino, hydroxyl and mercaptan groups) and polyamides (amino group), providing greater stability to the fabric color [4].

The conventional treatment process of textile effluents involves numerous stages due to the characteristics of the production process. The effluents can exit the processes at high temperature, between 60 and 90 °C, or at ambient temperature. The effluents are collected and receive an injection of carbon dioxide gas to neutralize the pH. In the neutralization tank, new pH measurements are necessary, since the stations are projected to treat effluents with pH varying between 8 and 10 [5].

Conventional treatment involves a process of coagulation/flocculation. This is a versatile process, which can be used alone or combined with biological treatments, as a way of removing suspended solids and organic material, as well as promoting the extensive removal of dyes from textile industry effluents [6,7]. However, this approach presents the disadvantage of generating a large volume of sludge. This sludge is rich in dyes, as well as other substances used in the textile process. This is

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a problem, as the waste must be discarded properly to avoid environmental contamination [5].

Other techniques that have been employed for toxic substance content reduction in industrial wastewater include advanced oxidation; membrane filtration; and reverse osmosis [6–10]. However, these methods are limited due to their high operational costs [2,7].

The adsorption method has been used for dye removal from the aquatic environment [8,11–15]. The major advantage of this technique over others is its low generation of residues and the possibility of adsorbent recycling and reuse [16]. Several literature reports concern the development of more effective, selective and cheaper adsorbent materials [2,8,9,11–13,17,18]. It is important to mention that an increase in adsorption capacity may help compensate for the cost of additional processing.

Biopolymers constitute a promising class of biosorbents used for the removal of pollutant from aquatic environments and among these, chitosan should be highlighted. This polymer is derived from chitin, which is one of the most abundant biopolymer in nature, obtained from crustacean shells of shrimps, crabs and lobsters, which are themselves waste products of the seafood processing industry [19,20].

Chitosan has excellent properties for the adsorption of anionic dyes, principally due to the presence of protonated amino groups ($-\text{NH}_3^+$) in the polymer matrix, which interact with dyes in solution by ion exchange, at an appropriate pH [21–23]. The high content of amino groups also facilitates various chemical modifications in the polymer, for the purpose of improving its adsorbent properties and adsorption capacity.

The purpose of this work was to study the kinetics and adsorption equilibrium of reactive dye orange 16, which is used in the dyeing process in the textile industry, in aqueous solution with modified chitosan biopolymer.

2. Experimental

2.1. Materials

Chitosan, used for the preparation of the adsorbent, was obtained from Purifarma (Brazil) and reported to have 90.0% degree of deacetylation, 8.0% water content, 1.0% maximum ash content and pH between 7.0 and 9.0. Glycidyl trimethyl ammonium chloride was purchased from Fluka Biochemica (Switzerland). The dye, reactive orange 16 (RO16, 50%) in sodium form, was acquired from Aldrich (USA). A stock solution of 2000 mg L^{-1} of the reactive dye was prepared by massing an appropriate amount of the dye and diluting to final volume with distilled water. Fig. 1 shows the structure of RO16.

2.2. Instrumentation

Infrared spectra were obtained using a PerkinElmer PC FTIR 16 spectrophotometer. The initial microprobe analysis using energy dispersive X-ray spectrometry (EDXS) of the new adsorbent was realized using Philips equipment, model XL 30, by placing a sample in stabs and covering it in gold. The number of quaternary functional groups was determined by conducto-

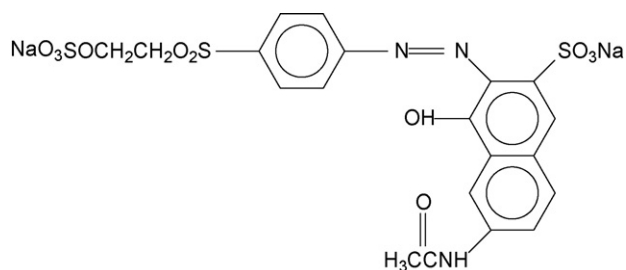


Fig. 1. Structure of RO16.

metric titration using a Mettler MC 226 conductivimeter from Micronal, model B 330, and a Schott Geräte automatic titrator, model T 80/20. UV–vis absorption measurements using a Micronal B572 spectrophotometer were employed to determine the reactive dye concentration in solution.

2.3. Preparation of quaternary chitosan with glycidyl trimethyl ammonium chloride

Quaternary chitosan salt (QCS) was prepared according to the method proposed by Lang et al. [24]. Cross-linking of quaternary chitosan salt was achieved by taking a chitosan suspension in ethanol and adding glutaraldehyde 25% (w/v) to the suspension [25]. The mixture was continuously stirred for 24 h at room temperature. The product was filtered and dried at 50°C and sieved size using 80–270 mesh. Fig. 2 shows the structure of cross-linked QCS.

2.4. Adsorption experiments

The removal of reactive dyes by the adsorption process in aqueous medium depends on various factors, such as the amount of adsorbent, pH, contact time and temperature. The effect of these parameters with the affinity of the quaternary chitosan to adsorb a model textile azo dye, RO16, from aqueous solution was examined.

A known amount of adsorbent and a measured volume of reactive dye solution were placed in 250 mL closed Erlenmeyer flasks. The system remained under agitation in a thermostated bath (Shaker Lab-line). The material was separated from the solution by decantation and the non-adsorbed dye concentration was determined by UV–vis spectrophotometry using calibration curve in λ_{max} of 508 nm.

The pH effect on adsorption was conducted using 50 mg of QCS, 50 mL of 170 mg L^{-1} dye solution, shaking rate at 250 rpm and buffered with $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ (pH 3–6); $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$; (pH 7 and 8); $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ (pH 9 and 10).

The adsorption kinetics were carried out in closed flasks each containing 100 mg of QCS and 100 mL of dye solutions 500 and 1000 mg L^{-1} buffered at pH 4.0. At predetermined times, the shaker was turned-off and immediately thereafter the adsorbent material was decanted for 15 min, and 200 μL aliquots of the 1000 mg L^{-1} solution was removed, diluted with 3 mL of distilled water in a cuvette, and the absorbance was determined. The

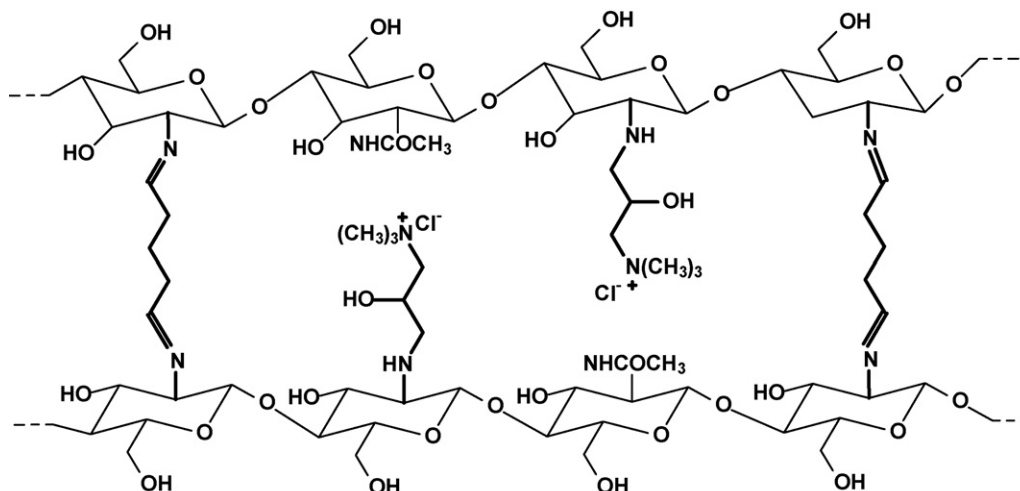


Fig. 2. Structure of cross-linked QCS.

absorbance of the 500 mg L^{-1} solution was determined without dilution.

For adsorption equilibrium experiments, 100 mg of QCS and 100 mL of buffered solutions, containing different concentrations of dye ($100\text{--}1000 \text{ mg L}^{-1}$), were maintained under shaking at 250 rpm until adsorption equilibration was attained. Aliquots were then removed, diluted in volumetric flasks, and the dye concentration determined from absorption measurements.

3. Results and discussion

3.1. Adsorbent characterization

The new adsorbent material was characterized by means of infrared (IR) and EDXS analyses and its quaternary groups quantified by conductometric titration.

The bands obtained in the infrared of chitosan and the new adsorbent material were very similar, however, there are minor differences which allowed for the identification of the quaternary group inserted into the chitosan. Relative to chitosan the infrared spectra QCS, exhibited a new band at 1482 cm^{-1} , which was attributed to the asymmetric angular deformation of the methyl groups of the quaternary nitrogen [25]. In addition, the presence of counter-ion chloride of the quaternary group was identified by EDXS, as illustrated in Fig. 3.

After characterization, the material was cross-linked with glutaraldehyde, which rendered it insoluble in water. The amount of the quaternary groups was determined by conductometric titration of chloride ions using a standard AgNO_3 solution and to end to be 2.29 mmol g^{-1} [25].

3.2. Effect of pH on adsorption

Fig. 4 illustrates the effect of pH on reactive dye adsorption by QCS. The pH-dependence profile indicates that adsorption is independent over the entire pH range examined. Both the adsorbent and the dye are completely dissociated, which is attributed to the fact that the adsorbent is a strong basic anionic

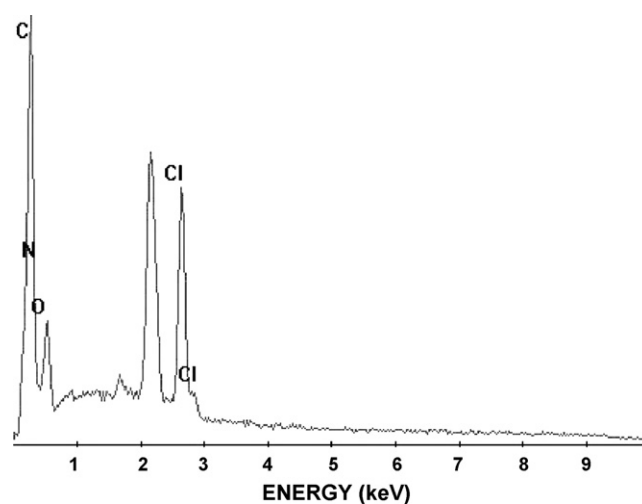


Fig. 3. EDXS spectrum of the QCS.

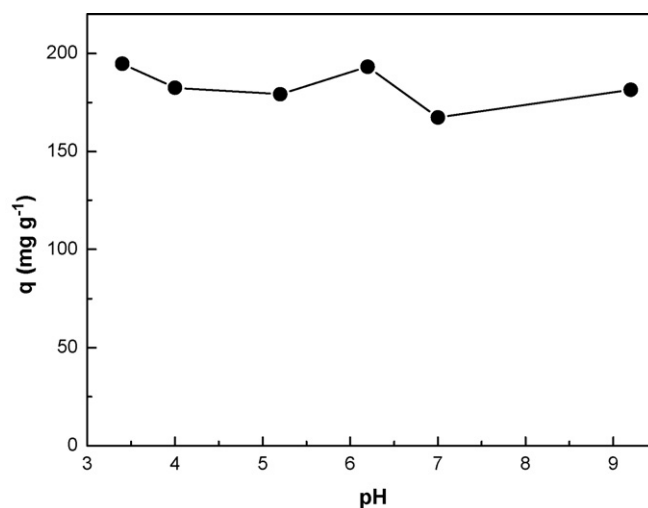


Fig. 4. Quantity of RO16 adsorbed by QCS at different pH values. Adsorbent mass = 50 mg; [Dye] = 170 mg L^{-1} ; temperature = $25 \text{ }^\circ\text{C}$; contact time = 3 h, shaking rate = 250 rpm.

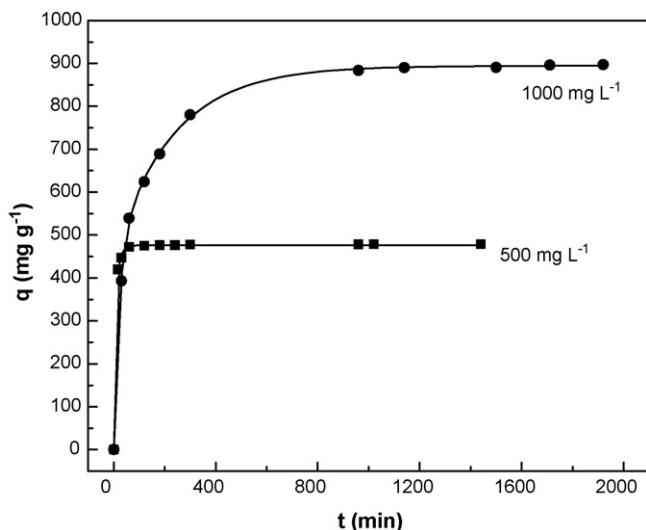


Fig. 5. Amount of dye adsorbed by QCS as a function of time. Adsorbent mass = 100 mg; [Dye] = 500 and 1000 mg L⁻¹; pH = 4.0, temperature = 25 °C; shaking rate = 250 rpm.

exchanger and the dye sulfonate is derived from a strong acid. Previous work with microspheres of cross-linked chitosan and RO16 dye indicated that adsorption is dependent on pH [26]. At pH < 3, chitosan is completely protonated and adsorption is principally attributed to ionic interaction between its cationic sites, the protonated polymer groups and the dye sulfonate groups. In an alkaline medium, adsorption decreased because the polymeric chain was not positively charged and does not interact with the negative charges of the dye.

3.3. Adsorption kinetics

Fig. 5 shows the amount of dye adsorbed by QCS as a function of time. The adsorption kinetics curve was studied at dye concentrations of 500 and 1000 mg L⁻¹ and showed a faster kinetic adsorption at a concentration of 500 mg L⁻¹, reaching equilibrium in 2 h, while at a concentration of 1000 mg L⁻¹, equilibrium was reached in 19 h. Thus, the slower equilibrium for the higher concentrated dye solution could be attributed to the adsorption driving force being stronger than that for lower initial concentrations [22,27].

In order to evaluate the kinetic mechanism which controls the process, the pseudo-first-order [28], pseudo-second-order [29] and intraparticle diffusion [30] models were tested, and the validity of the models were verified by the linear equation analysis $\log(q_e - q_t)$ vs. t , (t/q_t) vs. t and q_t vs. $t^{1/2}$, respectively. Good correlation with the kinetic data explains the dye adsorption mechanism in the solid phase [21–23,29].

Eq. (1) represents the pseudo-first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where k_1 (min⁻¹) is the pseudo-first-order adsorption kinetic parameter; q_t is the amount adsorbed at time t (min); and q_e denotes the amount adsorbed at equilibrium, both in mg g⁻¹.

The plot of the $\log(q_e - q_t)$ as a function of t provides the k_1 and q_e values. The correlation coefficient obtained for the two concentrations were $R^2 = 0.810$ (500 mg L⁻¹) and $R^2 = 0.973$ (1000 mg L⁻¹), however, they did not present good linearity and a discrepancy was observed, the experimental $\log q_e$ value is not equal to the intercept of the $\log(q_e - q_t)$ vs. t graph. When these values were compared with the experimental values, deviations of 68 and 43%, respectively, were observed.

The pseudo-second-order equation based on the adsorption capacity at equilibrium may be expressed by the following equation:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order adsorption kinetic parameter. From the intercept and slope of the graph (t/q_t) as a function of t , k_2 and q_e can be obtained.

The plots according to Eq. (2) provided excellent linearity $R^2 = 1.000$ with (500 mg L⁻¹) and $R^2 = 0.998$ (1000 mg L⁻¹) with rate constants (k_2) of 9.18×10^{-4} and 2.7×10^{-5} g mg⁻¹ min⁻¹, respectively. Comparison of the experimental values of q_e ($q_e = 476$ and 890 mg g⁻¹) and those obtained from the slope ($q_e = 485$ and 917 mg g⁻¹) showed good agreement with deviations of 2.1 and 3.1%.

Adsorption passes through several stages involving the transport of the adsorbate from the aqueous phase to the adsorbent surface and diffusion of the adsorbate into the interior of the adsorbent pores, which is a slow process. The kinetic model of intraparticle diffusion, proposed by Weber and Morris, consists of a simple model in which the intraparticle diffusion rate can be obtained from the following equation:

$$q_t = k t^{1/2} \quad (3)$$

When intraparticle diffusion controls the adsorption kinetics process, the plot of q_t vs. $t^{1/2}$ gives a straight line passing through the origin and the slope gives a rate constant k .

The plot of q_t vs. $t^{1/2}$ gave a poor correlation coefficient $R^2 = 0.676$ (500 mg L⁻¹) and $R^2 = 0.765$ (1000 mg L⁻¹) and the straight lines did not pass through the origin, indicating that intraparticle diffusion is not a determinant factor in the kinetic process. Table 1 shows the kinetics parameters obtained by fitting the kinetic models.

The analysis of the kinetic models showed that adsorption process was best described by pseudo-second-order kinetics, and the adsorption rate was dependent on the dye concentration at the adsorbent surface and on the amount of dye adsorbed at equilibrium.

The initial adsorption rate were 216.4 mg (g min)⁻¹ for the 500 mg L⁻¹ solution and 22.72 mg (g min)⁻¹ for the 1000 mg L⁻¹ solution. The comparative data of adsorption kinetics showed that the initial adsorption rate of the reactive dye for the 500 mg L⁻¹ solution was 9.53-fold faster than for the 1000 mg L⁻¹ solution; an important parameter that must be taken into consideration regarding the removal of reactive dyes from textile effluents.

Table 1
Parameters kinetic model obtained by fitting kinetic models

C_0 (mg L ⁻¹)	q_e , experimental (mg g ⁻¹)	Pseudo-first-order				Pseudo-second-order				Intraparticle diffusion		
		k_1 (1 min ⁻¹)	q_e , calculated (mg g ⁻¹)	R^2	d (%)	k_2 (1 min ⁻¹)	q_e , calculated (mg g ⁻¹)	R^2	d (%)	K (min ^{1/2})	R^2	d (%)
500	475.6	0.0372	151.78	0.8098	68.08	9.2E-4	485.4	0.9999	-2.06	40.83	0.6759	0.67
1000	890.0	0.0037	504.18	0.9726	43.35	2.7E-5	917.4	0.9982	-3.08	21.40	0.7647	39.5

Previous dye adsorption kinetic studies indicated that the pseudo-second-order kinetic model also provided the best fit for the experimental data observed; these are presented in Table 2 [21–23,31–37].

3.4. Adsorption isotherm

The equilibrium studies were carried out at pH 4.2 with the contact time required to reach adsorption equilibrium. For adsorption data interpretation, the Langmuir isotherm model [38,39] was used due to the homogeneous surface of the adsorbent, since the Freundlich isotherm [40] is applied in the case heterogeneous surfaces. The Langmuir isotherm considers the adsorbent surface as homogeneous, with identical

sites in terms of energy. Eq. (4) represents the Langmuir isotherm:

$$q = \frac{q_m K_{ads} C_{eq}}{1 + K_{ads} C_{eq}} \quad (4)$$

where q is the amount adsorbed (mg g⁻¹); q_m is the maximum quantity of adsorption (mg g⁻¹); K_{ads} is the adsorption equilibrium constant; and C_{eq} is the equilibrium concentration (mg L⁻¹).

In the dye adsorption by QCS represented Fig. 6a, the relationship between the amount of metal ions adsorbed at the adsorbent surface and the concentration remaining in the aqueous phase at equilibrium can be verified. This relationship showed that the adsorption capacity increased with the

Table 2
Comparison of the kinetic mechanisms of the present work and other studies from the literature, involving several reactive dyes

Reference	Adsorbent	Dye	Model
This work	Quaternary chitosan salt cross-linked (powder)	RO16	Pseudo-second-order
[31]	Chitosan (powder)	RR222	Intraparticle diffusion
	Chitosan (beads)	RR222	Intraparticle diffusion
[21]	Chitosan	RR222	Intraparticle diffusion
	Chitosan	RY145	Intraparticle diffusion
	Chitosan	RB222	Intraparticle diffusion
[32]	Chitosan cross-linked	RR222	Pseudo-second-order
	Chitosan cross-linked	RY145	Pseudo-second-order
	Chitosan cross-linked	RB222	Pseudo-second-order
	Chitosan (powder)	RR222	Pseudo-second-order
	Chitosan (powder)	RY145	Pseudo-second-order
	Chitosan (powder)	RB222	Pseudo-second-order
[33]	Chitin	RY2	Intraparticle diffusion
	Chitin	RBK5	Intraparticle diffusion
[23]	Chitosan	RY2	Intraparticle diffusion
	Chitosan	RBK5	Intraparticle diffusion
[34]	Chitosan (beads)	RR222	Pseudo-first-order
	Chitosan + clay (beads)	RR222	Pseudo-first-order
[35]	Chitosan dried (bead)	RR222	Pseudo-first-order
	Chitosan wet (wet)	RR222	Pseudo-first-order
[22]	Chitosan cross-linked (beads)	RR189	Pseudo-second-order
	Chitosan cross-linked (beads)	RR189	Pseudo-first-order
[36]	Chitosan cross-linked (beads)	RR189	Pseudo-second-order
[37]	Chitosan cross-linked beads	RB2	Pseudo-second-order
	Chitosan cross-linked beads	RR2	Pseudo-second-order
	Chitosan cross-linked beads	RY2	Pseudo-second order
	Chitosan cross-linked beads	RY86	Pseudo-second-order

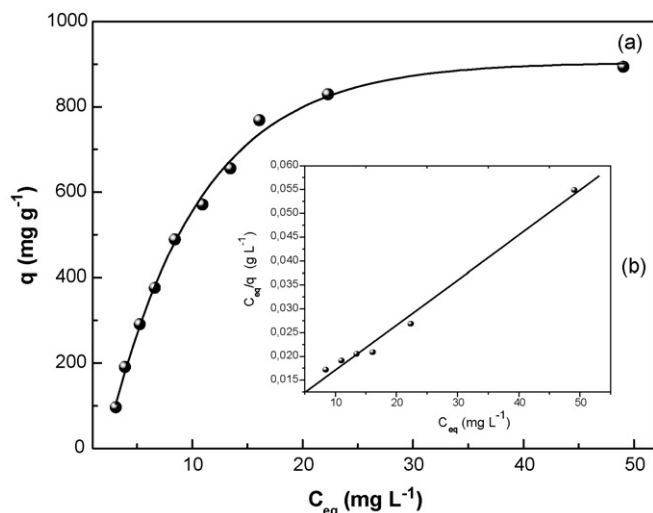


Fig. 6. Amount dye absorbed by QCS at different concentrations. Adsorbent mass = 100 mg; [Dye] = 100–1000 mg L⁻¹; pH = 4.0; temperature = 25 °C; shaking rate = 250 rpm.

equilibrium concentration of dye in solution, progressively reaching adsorbent saturation.

The adsorption parameters can be determined by transforming the Langmuir equation into linear form. The following equation represents the best linear regression of the

isotherm [41]:

$$\frac{C_{eq}}{q} = \frac{1}{K_{ads}q_m} + \frac{1}{q_m}C_{eq} \quad (5)$$

The plot of C_{eq}/q as a function of C_{eq} allows for calculation of the q_m and K_{ads} values. From the adsorption parameters, the maximum adsorption capacity of the adsorbate by the adsorbent and the Langmuir constant can be evaluated. Fig. 6b represents the linearization of the adsorption isotherm according to the Langmuir model.

The linear regression equation obtained, $Y = 7.69 \times 10^{-3} + 9.436 \times 10^{-4}X$, gave a correlation coefficient of 0.988. The value determined for maximum saturation capacity of the adsorbent monolayer was 1060 mg of dye per gram of adsorbent and the Langmuir constant was 0.123 L mg⁻¹.

Several adsorption studies have been carried out using different adsorbents and reactive dyes. Table 3 illustrates the capacity of reactive dye adsorption using different chitosan as adsorbent [22,26,27,31,32,34–37,42].

3.5. Surface fraction occupied by the reactive dye

If the adsorption mechanism is an ionic exchange, then it can be represented by the following chemical equation:



Table 3
Comparison of maximum adsorption capacity of the present work and various studies from the literature involving different reactive dyes

Reference	Adsorbent	Dye	pH	q _m (mg g ⁻¹)	Model
This work	Quaternary chitosan salt cross-linked (powder)	RO16	4.0	1060	Langmuir
[31]	Chitosan (powder)	RR222	–	494, 293, 398	Langmuir
	Chitosan (beads)	RR222	–	1026, 1106, 1037	Langmuir
[32]	Chitosan cross-linked-(beads)	RR222	–	1653	Langmuir
	Chitosan cross-linked-(beads)	RY145	–	885	Langmuir
	Chitosan cross-linked-(beads)	RB222	–	1009	Langmuir
	Chitosan (flakes)	RR222	–	339	Langmuir
	Chitosan (flakes)	RY145	–	188	Langmuir
	Chitosan (flakes)	RB222	–	199	Langmuir
[26]	Chitosan cross-linked (beads)	RO16	2	30	Langmuir
	Chitosan cross-linked (beads)	RO16	10	5.6	Langmuir
[34]	Chitosan (beads)	RR222	–	1965	Freundlich
	Chitosan (beads) + clay	RR222	–	1912	Freundlich
[35]	Chitosan (beads) dried	RR222	–	1215	Freundlich
	Chitosan (beads) wet	RR222	–	1498	Freundlich
[22]	Chitosan cross-linked-beads	RR189	3	1936, 1686, 1642	Langmuir
	Chitosan	RR189	3	1189	Langmuir
[36]	Chitosan cross-linked beads	RR189	3	1840	Langmuir
	Chitosan	RR189	3	950	Langmuir
[37]	Chitosan cross-linked beads	RB2	3	2498	Langmuir
	Chitosan cross-linked beads	RR2	3	2422	Langmuir
	Chitosan cross-linked beads	RY2	3	2171	Langmuir
	Chitosan cross-linked beads	RY86	3	1911	Langmuir
[27]	Chitosan cross-linked (beads)	RB15	4	722	Langmuir
[42]	Chitosan	RR141	2–5	156	Langmuir

where, “s” represents the solid phase and “sol” represents the solution.

The surface fraction occupied by the Dye⁻ ion upon dislocation from the chloride ion to the solution is given by the following equation:

$$\theta_{\text{Dye}^-} = \frac{N}{N_0} \quad (7)$$

where θ_{Dye^-} represents the surface fraction occupied by dye in the solid phase, N_0 is the amount of exchangeable Cl⁻ ion per gram of adsorbent (2.29 mmol/g) determined by conductometric titration and N is the amount of dye adsorbed; calculated from the maximum adsorption capacity of the reactive dye by the adsorbent (1.72 mmol/g). The value calculated, 0.75 or 75%, represents the occupation of the adsorption sites on the adsorbent by the reactive dye.

4. Conclusions

The IR and EDXS techniques used for characterization proved that the quaternary ammonium group was immobilized on the chitosan surface, thus forming a new adsorbent. The results indicated that the adsorption process is not dependent on solution pH, since the most probable mechanism for adsorption is the interaction of the polymer quaternary ammonium groups with the dye sulfonate groups. Adsorption kinetics followed the pseudo-second-order mechanism, which was the model that provided the best correlation with the experimental data. In the adsorption equilibrium studies, the Langmuir equation was used to fit the experimental data obtained, providing a maximum adsorption capacity of 1060 mg g⁻¹ corresponding to 75% occupation of the adsorption sites. The results obtained showed that the new adsorbent material could be tested on textile effluents independent of the pH of the aqueous medium.

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