

Sustainable Dye Removal Using Synthesized Chitosan For Reactive Black 5 Adsorption

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ABSTRACT

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The exclusion of dyeing in low-cost material is an appropriate method for treating textile wastewater. In this work, low-cost chitosan was synthesized from the oyster as a little-cost friendly adsorbent to eliminate the dye of reactive black five (RB5) from textile wastewater. Three main phases, the creation of chitosan included, demineralization, de proteinization and de acetylation. Fourier transform infrared spectroscopy (FTIR) and 1% acetic acid solubility were used to characterize chitosan. The experiments were managed in the batch system and the operating parameters were included; the pH, primary concentration of dye, quantity of adsorbent, the and the RB5 contact time in the adsorption were examined by synthesized chitosan. The percentage elimination of the dye was increased as the adsorbent dose increases from 0.1 to 0.5 g. Also its increased from 90% to 93% when the pH has been increased from 1 to 7. All the applied experiments proved that the synthesized chitosan can used as ideal adsorbent of RB5 dye.

1. Introduction

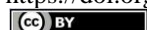
The pollution of water resources by contaminants ranks among the most significant environmental issues [1, 2]. The textile and dyeing industries are primary contributors to wastewater generation, and treating this wastewater is challenging due to the synthetic and intricate composition of the dyes [3-

5]. Because of their chemical composition, the dyes resist biological degradation, heat, and light [6]. Dyes are generally more stable to biodegradation and more rigid due to their complex aromatic molecular structures and synthetic origin [7]. Dyes may be split into three major groups: cationic (alkaline), anionic (direct, acidic and reactive), and nonionic (suspensions). Reactive dyes contribute 30% of the market due to their high color intensity and ease of application [8,9]. They are contaminants numerous times to dye wool, cotton, nylon

and silk [8]. Reactive dyes are commonly used in many textile industries due to their commonly characteristics, for example bright color [10]. However, up to 50% of the reactive dyes are for example by hydrolysis during the dyeing process thus, a large amount of dyes reach the waste water [11]. Usual methods have been used to remove the dye from wastewater, adapting them to biological methods and physical-chemical methods such as filtration, electrocoagulation, buoyancy, coagulation, ion exchange, membrane filtration and oxidation advanced [12-17]. However, there is a high demand for these technologies due to their effectiveness in treating large amounts of wastewater, despite the high cost of these technologies. The adsorption process continues to be the most applied method for the refinement of textile dyeing and effluent industries. Numerous reports have been carried out on the probability that the adsorbents use mineral absorbers, peat, activated carbon, and rice

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husk. Chitosan (CS) is prepared simply from chitin to deacetylate its amidic vinegar units with a strong alkaline solution and is the greatest abundant biopolymer. It has been found that large proportions of NH_2 functions in chitosan add new adsorption resources for some metal ions and an organic dyes [18-23]. The amino (NH_2) groups of acetylates in chitosan may be protonated and it is assumed that the poly cationic properties of the polymer give the interaction charged with a model dye [24,25].

The examination of dye exclusion was conducted using a sequence of separate adsorption experiments. Focus was placed on analyzing the equilibrium processes, kinetics, and mechanisms involved in the absorption of RB5 by chitosan. The effects of pH, contact time, initial dye concentration, and adsorbent dosage on the adsorption process

were examined.

2. Materials and Methods

2.1. Apparatus

All pH data were made with a digital pH meter (Germany). Sensitive digital balance (BP 3015, Sartorius Germany). A double beam UV/Vis spectrophotometer (UV-Visible spectrophotometer, Shimadzu 1650).

2.2. Preparation of Sorbent:

The usual separation of chitin contains of three traditional process, as in (Figure 1): demineralization (DM) in dilute acidic medium to remove minerals, deproteinization (DP) in dilute alkaline medium to remove protein, and deacetylation (DA) in 50% alkaline medium.

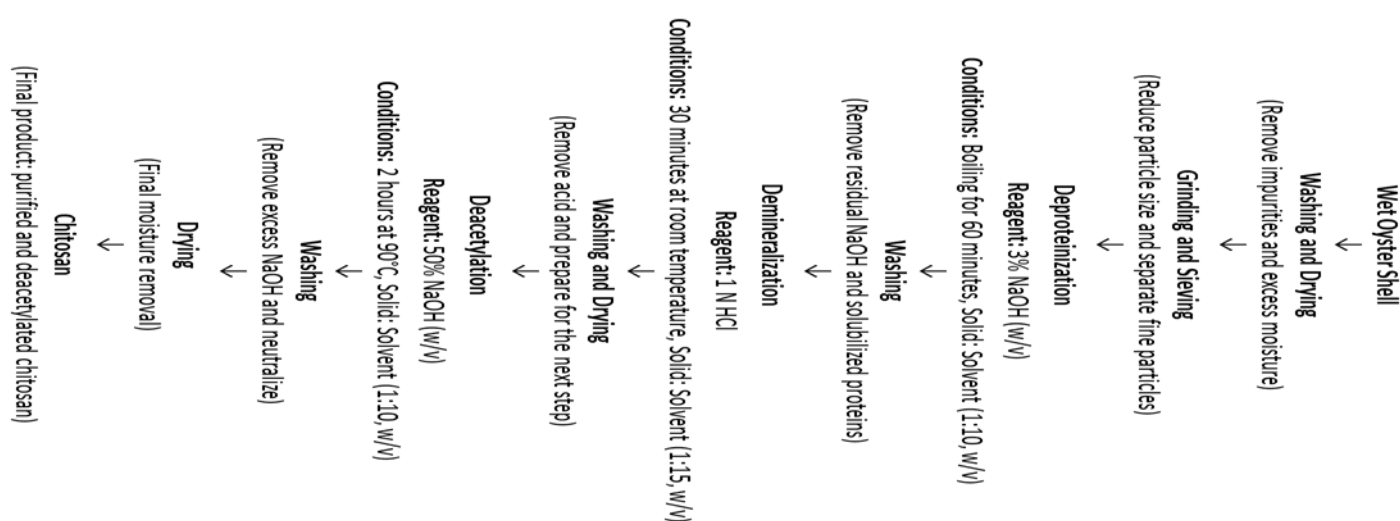


Fig. 1. Traditional Chitosan Creation [26].

2.3. Preparation of (RB5) dye solution

Reactive Black five (RB5) dye, [2, 7-naphthalene disulfonic acid, 4- amino -5-hydroxy-3, 6 -bis ((4((2(sulfooxy) ethyl) sulfonyl) azo)- tetra sodium salt)]. Chemical composition of (RB5) dye used in this work is explained in Figure (2).

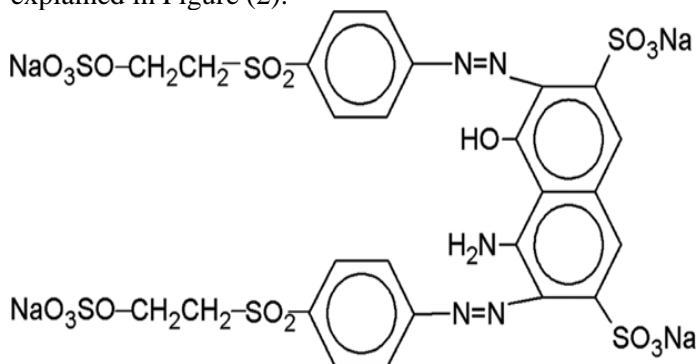


Fig. 2. Reactive Black 5 (RB5) chemical structure.

2.4. Batch adsorption experiments

A stock solution of $1000 \text{ mg}\cdot\text{L}^{-1}$ was prepared with RB5 and in all phases of the study; we want the concentrations to be obtained from the diluted stock solution. The experiments were carried out using equipment of beakers with 200 ml beakers that were lubricated with 100 ml of dye solution. NaOH and 0.1 N HCl were used for pH regulation. The primary concentration effect of the dye, the contact time, solution pH and the absorbing dose were studied. To study the effect of the contact time, 0.1 g of sorbent was added to the solutions with an primary concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ and at pH of 2-1. The sampling was prepared in 15 minutes up to 120 minutes. The effect of pH on the adsorption of the dye was carried out with an initial dyeing concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ in 0.1 g in several solutions of initial pH (1-8) with a contact time of 90 minutes. To study the primary concentration effect of the (RB5) dye and the absorbing dose, solutions were prepared with pH: 2-1 with several initial concentrations of dye ($100\text{-}300 \text{ mg}\cdot\text{L}^{-1}$) and absorbing doses was studied (from 0.025 to 0.25). gm) with a contact time of 90 minutes. All experiments were set at 25°C and the

mixing speed at 100 rpm. The dye concentration was measured using the spectrophotometer (Shimadzu Ultra-Violet 160-A, Japan) at the maximum wavelength of RB5 ($\lambda_{\max} = 597$ nm). The quantity of the ions adsorbed at chitosan (at a programmed time t), the q_t (in mg / g), had been decided applying the equation of mass balance:

$$q\tau = (C_o - C\tau) \times (m \times v^{-1}) \quad (1)$$

The de colorization cost (η) of the ions was edaccount via the equation below:

$$\mu = \frac{(C_o - C\tau)}{C_o} \times 100\% \quad (2)$$

Where C_o is the primary concentration of the ions in mg.L^{-1} , V is the volume of the solution in Liters, C_t is the concentration of the ions at time t in mg.L^{-1} , and m is the mass quantity of chitosan in grams [27].

2.5. A desorption isotherm models[28]

2.5.1. Freundlich and Langmuir pattern

Heat equation data analysis is suitable for design purposes. In the present work, equilibrium fact are discussed by Freundlich equation and Langmuir equation. Langmuir equation may be defined via the equation below [29].

$$q_e = (qm \times K_a \times C_e) \times (1 + K_a \times C_e)^{-1} \quad (3)$$

Where, quantity adsorbed is q_e in line with unit of mass of sorbent at equilibrium (mg.g^{-1}), C_e is the dye concentration at equilibrium (mg.L^{-1}), q_m is the most adsorption potential (mg.g^{-1}), and K_a is adsorption equilibrium regular. The plot of $C_e \times (q_e)^{-1}$ vs C_e as in (equation 4) is a straight which exhibit that the adsorption of RB5 dye on chitosan as low price adsorbent, below Langmuir isotherm form:

$$\frac{C_e}{q_e} = \frac{1}{q_m \times K_a} + \frac{C_e}{q_m} \quad (4)$$

Necessity traits related to Langmuir isotherm may be explicit via a dimensional constant known as equilibrium parameter [30], that is expressed as:

$$R_L = \frac{1}{1 + b \times C_o} \quad (5)$$

Where, C_o is preliminary awareness and b , is Langmuir steady. The cost of R_L shows the shape of isotherm to be either negative (R_L bigger than 1), favorable when ($0 < R_L < 1$), irreversible (R_L equal 0) or linear (R_L equal 1).

The isotherm of Freundlich changed into additionally carried out for adsorption of dye via oyster [31].

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_f \quad (6)$$

Where, C_e is equilibrium dye concentration of solution (mg.L^{-1}), q_e is the quantity adsorbed per unit mass of adsorbent at equilibrium (mg.g^{-1}), n and K_f are Freundlich constants, n gives an illustration of favorability and K_f [$\text{mg.g}^{-1}(\text{L.mg}^{-1})^{1/n}$], The values

of K_f and n may be recieved from plot of $\log q_e$ as opposed to $\log C_e$ and that they equal to the intercept and slop of the plate therefore. The cost of n lies among 2 and 10, that shows top adsorption.

3. Results and Discussion

3.1. Effect of adsorbent dosage

The impact of the adsorbent dose (varies from 0.1 to 0.5 g) on the removal percentage of 100 mg.L^{-1} of ion solution is proven in Figure 3. The percent of removal of the dye from the solution expanded by way of (89, 78% to 89.85%) growing the adsorbent dose from 0.1 to 0.5 g. This end result is expected due to the increase in the surface area of the adsorbent and the availability of several adsorption sites affected by the multiplied dose of the adsorbent [32, 33].

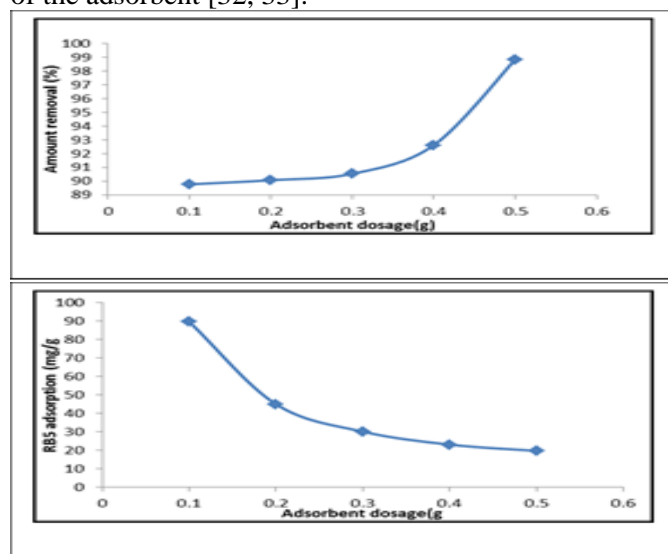


Fig 3. Effect of adsorbent dosage.

100 ml of 100 mg.L^{-1} of black reactive 5 were removed in conical flasks that handled with 0.1 g. Chitosan (adsorbent) many periods (20, 40, 60, 80, 100, 120 and 140 min.). The percentage change in the elimination of the dye over time is confirmed in Figure 4. It turned into found that a fine time to eliminate those metallic ions was 90 minutes. The effects showed that the removal rate occurred 93%, because of the saturation of active sites that don't allow greater absorption [34, 35].

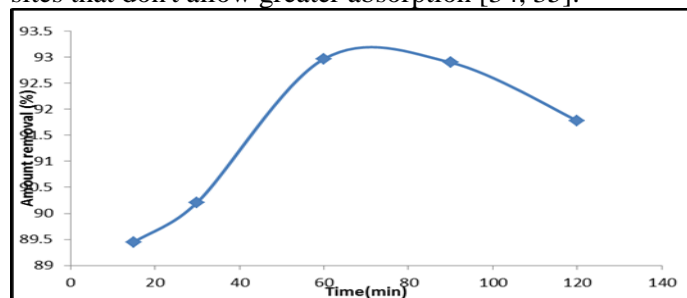


Fig. 4. Effect of contact time on RB5 dye sorption capacity ($C_i = 100 \text{ mg L}^{-1}$, Chitosan quantity of 0.1g, pH 2.3).

3.2. Effect of pH Solution

The acidic function (pH) of the ion solution influences the ionization degree of the materials, the surface rate of the adsorbent, and the uncoupling of the functional groups in the practical corporations sites of the adsorbent [36]. The percentage elimination of the dye at various pH values is displayed in Figure 5. The elimination percentage is increased from 90% to 93% when the pH has been increased from 1 to 7. It can be noticed that the absorption of RB5 depends on large measure of the solution pH. The greatest absorption capacities had been obtained at pH 1. Under these conditions, the elimination of the dye was almost complete. The greater elimination of the dye that has been acquired at acid pH can be interpreted in terms of electrostatic attraction between the dye and chitosan [37].

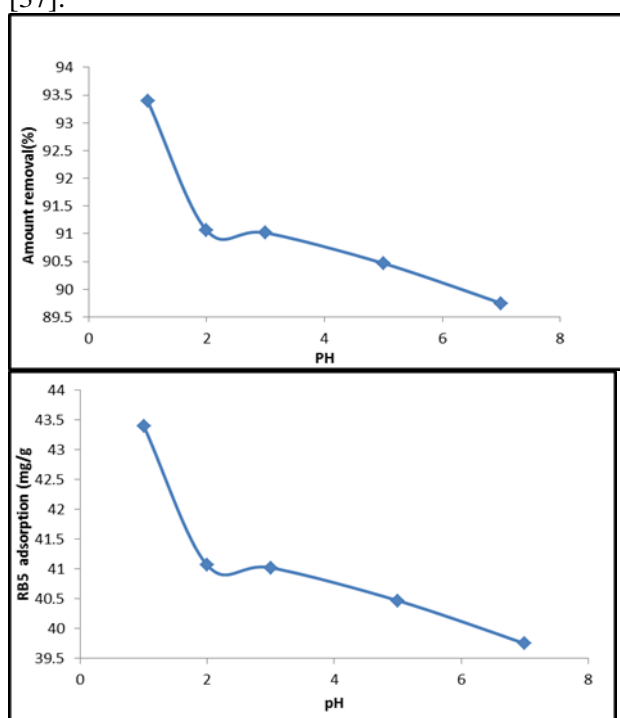


Fig. 5. Effect of pH on adsorption of RB5 dye on chitosan ($C_i = 100$ mg/L, chitosan dosage 0.1 gm, agitation time 90 min.).

3.3. Effect of primary RB5 dye concentration

The impact of dye concentration (RB5) ($100-300$ mg.L⁻¹) turned into additionally examined with a steady dose of adsorbent for 90 mins. The elimination of the dye increased from 86.35% to 93.74%. The effects indicated that the adsorption of the dye depends to a large extent on the concentration of the solution. Figure 6 illustrates the effect of the preliminary awareness of the dye on the adsorption of (RB5) on the adsorbent and we are able to see the increased absorption capacity at (93.74 -259) mg / g when the concentration of (RB5)) increases from 100 to 300 mg / L per chitosan adsorbent. The adsorption sites become less numerous due to adsorption. In addition, the creation of 2nd layer of the dye molecules is enormously impeded at an

preliminary higher dye concentration, due to the repulsive forces between the adsorbed and non-absorbed dye molecules (RB5) at the stable surface and inside the solution, respectively [38].

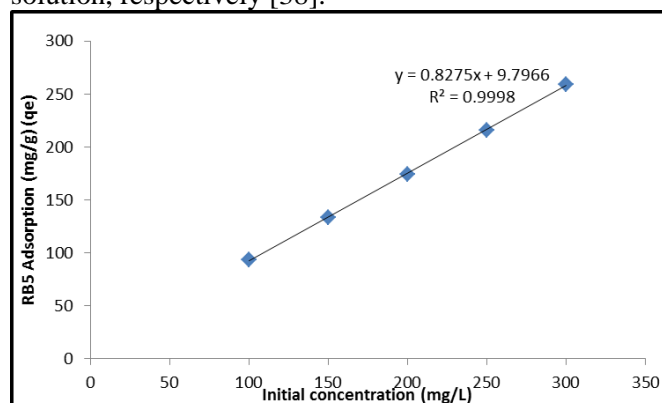


Fig. 6. Effect of primary concentration on adsorption capacity of (RB5) onto (chitosan) ($C_i = 100$ mg/L, chitosan dosage 0.1 gm., agitation time 90 min. and pH=1)

3.4. Isothermal analysis

Equilibrium adsorption facts were suited for the straight from Freundlich and Langmuir's equation (4 and 6). Table 1 indicates adsorption of (RB5) dye the use of chitosan each satisfy of Freundlich and Langmuir's isotherm.

Table 1. Parameters of Adsorption Isotherm of (RB5) dye elimination

Langmuir	Freundlich
$q_m(\text{mg}\cdot\text{g}^{-1})$ 400	$K_F(\text{mg}\cdot\text{g}^{-1})(\text{mg}^{-1})n^{-1}$ 31.9374
$K_a(\text{L}\cdot\text{mg}^{-1})$ 0.0359	n^{-1} 0.5413
R^2 0.8536	R^2 0.9664
R_L (0.2179 – 0.085)	

The liberalization tables of Freundlich and Langmuir are proven in Figure (7a-b). the equilibrium adsorption of Langmuir curves that define the liquid and solid segment concentration of (RB5) and equilibrium absorption of Freundlich curves that describe the liquid and solid phase concentration of (RB5).

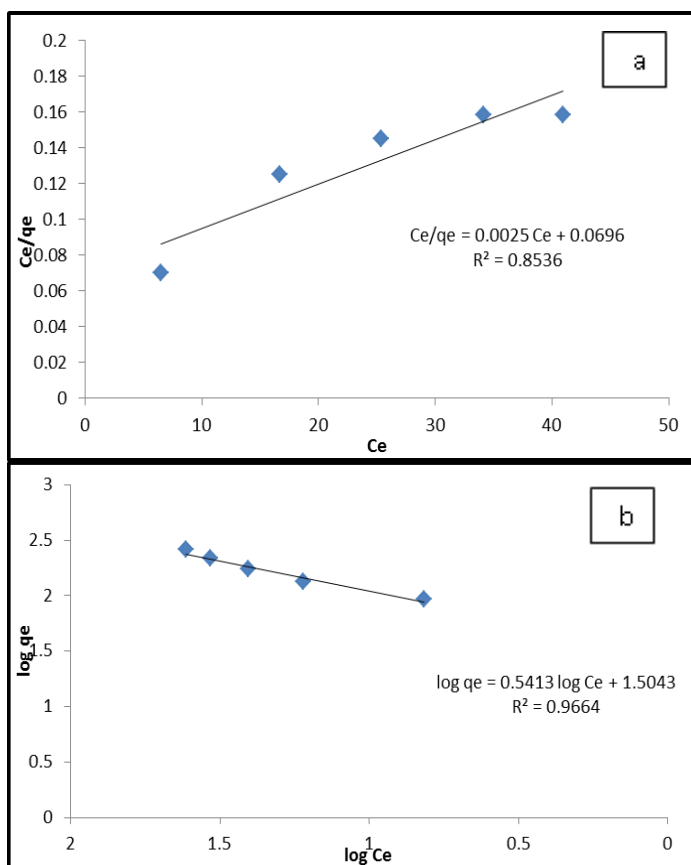


Fig. 7. Model of (RB5) adsorption isotherm on (chitosan)

(a) Langmuir model (b) Freundlich model

The isothermal model of Langmuir carries out the monolayer insurance of the adsorbates on a homogeneous surface of the adsorbent. Good adaptation of the information with the Langmuir isotherm shows a homogeneous spreading of the active sites at adsorbing surface

The alteration of the separation thing (R_L) with the preliminary concentration (RB5) is proven in Figure 8. The values (R_L) of the adsorption of (RB5) vs. (chitosan) are noted in the scale of (0 - 1), which indicates that the adsorption was a favorable process.

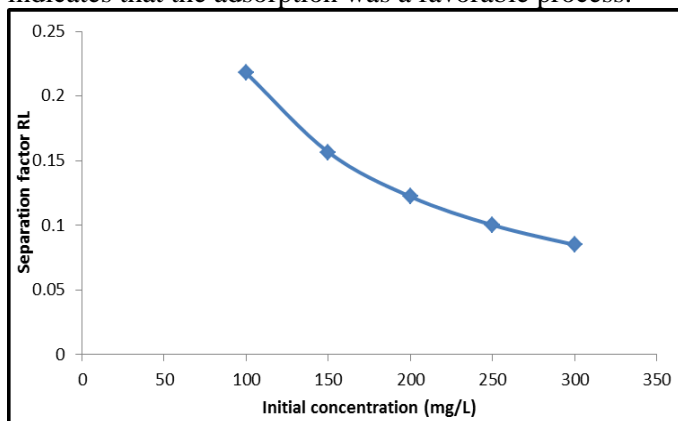


Fig. 8. Separation factor vs. primary (RB5) concentration at (chitosan)

Figure 9 indicates the deviation of those models with respect to the measurement facts. It shows that the adsorption of the dye (RB5) in the activated chitosan may be properly regulated by the binary isotherms. Noticeably, equation of Langmuir furnished a higher suit in phrases of R_L .

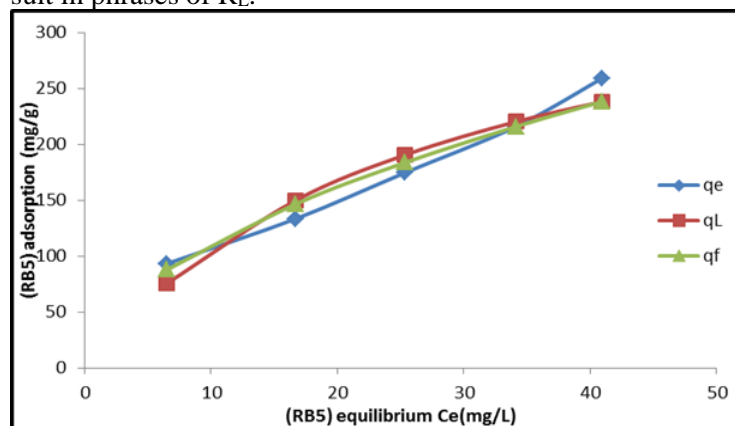


Fig. 9. Comparison of calculated and experimental data by Freundlich and Langmuir equilibrium isotherms of the system (RB5) – chitosan

These outcomes imply the homogeneous nature of the chitosan surface, which means that every chitosan in the molecule (RB5) has the same adsorption activation energy. The product also demonstrates the formation of a monolayer coat of the molecule (RB5) on the outside surface of the chitosan.

4. Conclusion

The results of this work monitor that chitosan, that is readily available, abundant and cheap in our region, be able to be converted into an excellent adsorbent with the aid of simple processes using simple techniques. A suitable quantity (0.1 g/L) of the manufactured adsorbent chitosan can bleach up to 93.47% of the dye in aqueous solution (100 ppm) if stirred for 90 minutes. The results showed that chitosan has sufficient potential as an adsorbent to eliminate the dye (RB5) from aqueous solutions. The outcomes imply the homogeneous nature of the chitosan surface, which means that every chitosan in the molecule (RB5) has the same adsorption activation energy. The product also demonstrates the formation of a monolayer coat of the molecule (RB5) on the outside surface of the chitosan.

Acknowledgements

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