



## Investigation of equilibrium, kinetics and thermodynamics of extracted chitin from shrimp shell in reactive blue 29 (RB-29) removal from aqueous solutions

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### ABSTRACT

The presence of reactive dyes in aqueous medium cause many problems; therefore, it is necessary to reduce its content in industrial effluents before their discharge into environment. The aim of this study was to investigate the removal of reactive blue 29 (RB-29) dye from aqueous solutions using extracted chitin from shrimp shells as an adsorbent. This study was conducted in a batch experimental system. After extraction of chitin from shrimp shells, the effects of different variables such as pH, RB-29 concentration, contact time and adsorbent dose were investigated. Furthermore, adsorption isotherms, thermodynamics and kinetics of the process were also studied. The results of this study showed that the maximum adsorption capacity ( $q_{\max}$ ) of chitin was 116.07 mg/g at a RB-29 concentration of 50 mg/L and contact time of 90 min. In addition, the maximum adsorption was observed at pH = 3 and adsorbent dosage of 0.2 g/L. The experimental data showed that the results were consistent with the Langmuir isotherm model. According to the results of thermodynamic study, standard entropy change  $\Delta S$  is equal to 25.40 J/mol K, standard enthalpy change  $\Delta H$  is equal to 7,054.39 J/mol and standard Gibbs free energy values ( $\Delta G$ ) were negative, that represents a spontaneous and endothermic process of RB-29 adsorption by the extracted chitin. Moreover, adsorption kinetics followed the pseudo-second-order kinetic model. Based on the results of this study it can be concluded that chitin can efficiently remove RB-29 dye from aqueous solutions.

*Keywords:* Reactive blue 29; Chitin; Adsorption; Isotherms; Thermodynamics; Kinetics

### 1. Introduction

Natural water conservation is vital to protect the land and save the next generations [1]. Textile industry is one of the largest water consumer industrial sectors [2]. Today, dye plays an important role in the manufacturing of paints, pigments and textile products. Nowadays, at least 100,000 different dyes are commercially available. To meet industrial demand, it is estimated that annually 1.6 million tons of colorants are

produced and 10%–15% of this amount is released to wastewater effluents [3]. Synthetic dyes are widely used in many industries such as textile, leather, cosmetics, pulp and paper, inkjet printing, plastics, food and pharmaceutical industries [4]. The dyes are generally classified based on structural or functional groups as well as by the ionic charge when dissolving in an aqueous solution [3].

Dyes are also categorized as non-ionic (e.g., vat and disperse dyes) and ionic (e.g., cationic (basic) and anionic (reactive, acid, direct) dyes) [5]. Generally, azo dyes are widely used in textile industry [6]. In other hand, various types of dyes such as acid, direct and reactive dyes are azo

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type [7]. Azo dyes have one or more ( $-N=N-$ ) bond and widely used for fibers dyeing and are considered as one of the largest synthetic dyes due to low cost, simple use and less toxicity [8]. In comparison, anionic dyes, especially reactive type, seem to be more problematic and more costly to remove than cationic and disperse dyes [9].

Nowadays, reactive dyes are the most common dyes used because of several advantages such as sleek dyeing, fast and easy to use and high tonality [10]. Many of reactive dyes are toxic to certain organisms and may cause damage to aquatic life. In addition, this type of dyes is very soluble in water and cannot easily be eliminated from wastewater through common biological or physico-chemical treatment methods [11]. Adsorption of reactive dyes by biomass is very weak and do not degrade under aerobic conditions [12]. Furthermore, azo dyes and related intermediates are toxic, carcinogenic and mutagenic for aquatic life [13]. In addition, most of these colorants cause allergies, dermatitis and skin rashes and accelerate cancer progression and mutagenicity effects in humans [14]. Colored wastewater also may cause operational problems in treatment plants such as foaming and stable color formation, increase in pH, temperature and heavy metals [15]. Various methods such as, coagulation, flocculation, membrane filtration, enzymatic process and adsorption are used for dyes removal from aqueous solutions [16–22]. Conventional anaerobic wastewater treatment methods cannot remove dyes efficiently [23]. The conventional treatment methods like electrodialysis, ion exchange, reverse osmosis, micro- and ultra-filtration, oxidation and solvent extraction are expensive compared with adsorption [24].

Coagulation process produces large volume of sludge and need higher sludge disposal costs, ion-exchange process has not been adapted for a wide range of colors and it is expensive. Although membrane process is effective in dyes separation, the related investment is relatively high and the problem of membrane fouling is still a challenge [25]. Adsorption is the most acceptable technique to reduce the concentration of dissolved dyes from aqueous solutions [26]. Adsorption is a better option in terms of cost, simplicity of design and operation, availability, effectiveness and lack of sensitivity to toxic substances compared with other methods [25]. This technique is also able to separate wide range of chemical compounds [27].

Recently, efforts have been made to obtain more cost-effective material as adsorbent in tertiary wastewater treatment [28]. Chitin is the second most abundant polysaccharide found after cellulose [29]. Chitin can be found in the shells of crustaceans such as crabs, shrimps, cuticle of insects and fungal cell walls [30]. Chitin in the solid state has three different forms: alpha ( $\alpha$ ), beta ( $\beta$ ) and gamma ( $\gamma$ ) [31]. Alpha chitin is derived from fungal cell membrane and shell of crustaceans such as crabs and shrimps. Beta chitin obtained from diatoms and squid arms. However, there is a small percentage of natural gamma chitin as the combination of alpha and beta. The distribution of alpha chitin in nature is less than the two others [32]. Chitin has been considered for a long time due to its insoluble nature [33]. Chitin has been used in agriculture, food industry and other industrial fields. Recently, it has been considered as biopolymer in the field of biomedical, pharmaceutical and biotechnology due to the properties such as biocompatibility, biodegradability and biological activities [34]. In addition, chitin is widely used as an adsorbent in the adsorption studies.

The advantages of chitin study as a selected adsorbent for this study are: (1) possibility of marine product wastes reuse, especially in coastal areas, (2) low cost and easy preparation and (3) high adsorption capacity of this material has been reported for other pollutants [8]. Unavailability of shrimp shell and marine wastes in all regions of the world is the main drawback of this adsorbent. But there is still little knowledge on dye adsorption process using this material [10].

Since there are a few studies conducted on dye removal using chitin as a capable adsorbent and the elimination of reactive dyes, as the most common color groups used in textile industry, has not been evaluated by chitin. Thus, in this study, we focused on the investigation of the application of a naturally abundant and less expensive adsorbent (chitin) for the removal of reactive blue 29 (RB-29) dye.

## 2. Materials and methods

This experimental study was conducted in a batch mode, in which the chitin was used as an adsorbent for RB-29 removal from aqueous solutions. Commercial reactive RB-29 with known characteristics (Fig. 1) was obtained from Sigma-Aldrich Company (St. Louis, MO, USA) and used without further purification. Other required chemicals in this study such as NaOH and HCl were prepared from Merck (Darmstadt, Germany) company.

### 2.1. Extraction and preparation of adsorbent

Shrimp peel was prepared from shrimp fishery wastes (Persian Gulf area). Chitin extraction was conducted in two main steps as follows [35,36]:

- Demineralization: removal of minerals by use of dilute inorganic acids.
- Deproteinization: removal of organic materials.

Mineralization was completely carried out within 15 min at room temperature in the presence of HCl 0.25 M (40/1 (w/v)). Deproteinization was easily conducted using NaOH (1 M) over 24 h at 70°C [37]. The obtained chitin was completely dried at room temperature and then powdered.

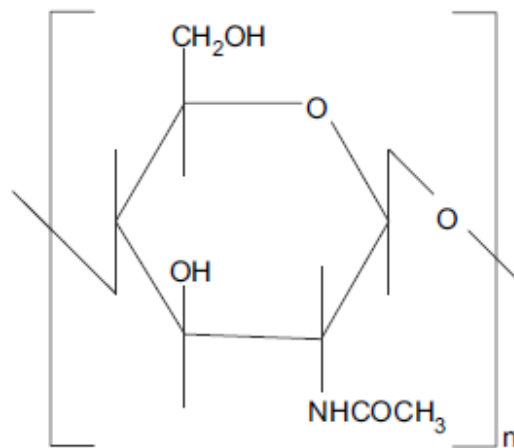


Fig. 1. Structure of chitin [10].

## 2.2. Adsorption experiments

At the beginning, a stock solution of 200 mg/L RB-29 was prepared by adding a known amount of dye to deionized water. Then, by diluting the stock, the initial concentrations of 10, 30, 20 and 50 mg/L were provided. In all experiments, a known volume of 100 mL of colored solution was applied for adsorption tests. The effects of various experimental parameters such as pH, initial dye concentration, adsorbent dosage and contact time were evaluated on the adsorption efficiency of RB-29. Also, the adsorption isotherms, kinetics and thermodynamics were also investigated. Accordingly, initial RB-29 concentrations of 10, 20, 30 and 50 mg/L; pH of 3, 4, 5, 7 and 9; chitin doses of 0.2, 0.3, 0.4, 0.5 and 0.75 g/L and different time intervals of 2, 5, 10, 15, 30, 45, 60, 75 and 90 min were evaluated. The influence of each parameter on all stages of the experiments was carried out by changing one variable at the time. All the experiments were carried out in duplicate and the averages were reported. Spectrophotometric (UV/Vis Spectrometer T80) readings of the dye were obtained at 589 nm wavelength. The adsorption capacity of RB-29 by chitin was calculated using the following equation:

$$q_e = \left( \frac{C_0 - C_e}{m} \right) \times V \quad (1)$$

where  $C_0$  is the initial concentration of RB-29 dye (mg/L);  $C_e$  is the final concentration RB-29 (mg/L);  $m$  is the adsorbent mass (g) and  $V$  is the volume of the solution (L).

## 2.3. Adsorption isotherms

To study the adsorption isotherms, the experimental data were analyzed using Freundlich and Langmuir isotherm models. The linear forms of Langmuir (Eq. (2)) and Freundlich (Eq. (3)) can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (2)$$

$$\ln q_e = \left( \frac{1}{n} \right) \ln C_e + \ln K_f \quad (3)$$

where  $q_e$  is the equilibrium concentration of RB-12 dye in the solid phase (mg/g);  $q_{\max}$  is the maximum adsorption capacity (mg/g);  $K_L$  is the Langmuir adsorption equilibrium constant (L/mg);  $K_f$  is the Freundlich constant that represents the adsorption capacity ( $\text{mg}^{1-1/n} \text{L}^{1/n} / \text{g}$ ); and  $n$  is the constant that represents the intensity of adsorption.

## 2.4. Adsorption thermodynamics

To investigate the influence of temperature and thermodynamics of RB-29 adsorption by chitin, RB-29 initial concentration of 50 mg/L was applied, that the pH of the solutions was adjusted at the pretested optimal pH value. Then, 0.2 g/L of chitin was added to each set of the dye solutions at 15°C, 30°C, 40°C and 50°C in an incubator shaker for 90 min.

Finally, the flasks were removed from the incubator shakers and the samples were filtered through a 40  $\mu\text{m}$  filter and dye concentration was detected by use of a spectrophotometer. The following equations were applied:

$$\Delta G = -RT \ln k_d \quad (4)$$

where  $\Delta G$  is the Gibbs free energy changes;  $R$  is the universal gas constant, equal to 8.314 J/mol/K;  $T$  is the temperature in K; and  $k_d$  is the thermodynamic equilibrium constant.

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

where  $\Delta S$  is the standard entropy (J/mol K);  $\Delta H$  is the changes in enthalpy (kJ/mol);  $R$  is the universal gas constant (J/mol K) after calculating the thermodynamic equilibrium constant for different temperatures and calculating the related free energy,  $\ln k_d$  was plotted vs.  $1/T$ . The slope and intercept of the plotted line was used to determine  $\Delta H$  and  $\Delta S$ .

## 2.5. Adsorption kinetics

To study the adsorption kinetics, two common models including pseudo-first-order and pseudo-second-order models were used to analyze the equilibrium data. The correlation coefficient ( $R^2$ ) was considered as a measure of agreement between experimental data and the model. Pseudo-first-order kinetic model is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where  $q_t$  and  $q_e$  are adsorbate value on the adsorbent at time  $t$  and equilibrium time, respectively (mg/g);  $k_1$  is the pseudo-first-order constant ( $\text{min}^{-1}$ ) and  $\log(q_e - q_t)$  vs. time was applied to determine  $R^2$  coefficient and  $k$  constant value.

Furthermore, the employed pseudo-second-order model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (7)$$

where  $k_2$  represents the constant of pseudo-second-order adsorption (g/mg min). To get the process rate and the compliance of the kinetic model with the experimental data,  $t/q_t$  was plotted against time. Accordingly,  $q_e$  and  $k_2$  values are calculated from the slope and intercept of the plotted line.

## 3. Results and discussion

### 3.1. Characterizations of extracted chitin

Fig. 2 illustrates the scanning electron microscope (SEM) micrograph of prepared chitin isolated from shrimp shell. From the figure, the chitin structure appears dense and non-porous. Furthermore, heterogeneous surface of the particles is clear. A wide range of particles ranging from about

700 nm to 5  $\mu\text{m}$  exist. The surface morphology of chitin considerably depends on the origin of raw chitin source and preparation method [38].

Fig. 3 exhibits the X-ray diffraction (XRD) pattern of the chitin. The observed patterns of the crystalline peaks were revealed at  $9.33^\circ$ ,  $10.6^\circ$  and  $19.3^\circ$  for the lower angle for chitin. From the figure, chitin gives two obvious peaks at  $2\theta = 10.6^\circ$  and  $2\theta = 19.3^\circ$ . The intensity of the broad signal centered at  $2\theta = 10.6^\circ$  due to *N*-acetyl-D-glucosamine. Similarly, the peak at about  $2\theta = 19.3^\circ$  is assigned to the *N*-glucosamine sequences. Although the similar pattern can be seen from previous works but origin of chitin and isolation procedure is important in chitin crystalline structure [38].

### 3.2. Influence of pH on RB-29 adsorption by chitin

The effect of solution pH in the range of 3–9 on the removal of RB-29 by chitin was evaluated. Reactive blue 29 solutions with the prepared concentration of 10 mg/L, adsorbent dosage of 0.2 g/L and contact time 60 min were used for all solutions. The results of the pH effect on RB-29 removal are shown in Fig. 4.

The results showed that the highest amount of RB-29 removal happened at pH = 3. As Fig. 4 illustrates, adsorption

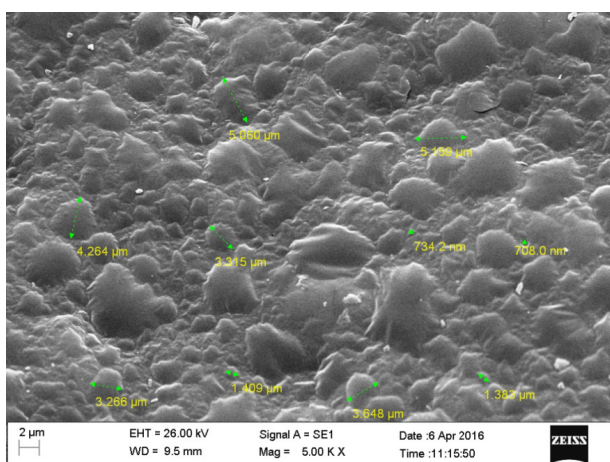


Fig. 2. SEM micrograph of the prepared chitin.

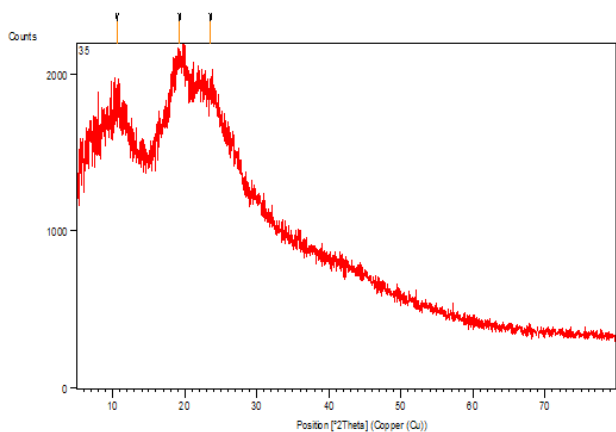


Fig. 3. XRD pattern of the prepared chitin.

of RB-29 at concentration of 10 mg/L and pH of 3 is 48.31 mg/g. From this figure, the maximum removal occurred at pH of 3. However, by increasing the pH value, dye removal efficiency declines. Sakayawong et al. [39] reported that the efficiency of reactive red 141 adsorption was higher at acidic conditions. The results of Özacar and Şengil [11] for reactive blue 114 adsorption also showed that better removal happened at acidic condition, which is consistent with the results of the present study. Reactive dyes containing  $-\text{SO}_3$  group in their structure that makes the dyes fairly acidic. In chitin structure amino group exists (Fig. 1) [40]. Depending on the water pH, polymers may contain neutral amino group ( $-\text{NH}_2$ ) or cationic amino ( $-\text{NH}_3^+$ ). At low pH values, these groups lose protons and get neutral in the aquatic environment, and negatively charged ions are adsorbed. Thus, affinity to adsorb more anionic dyes at low pH values (3–4) is higher. The results show a higher affinity for attraction of more anionic dyes in pH range of 3–4 [41].

### 3.3. Effect of initial concentration of RB-29 on its adsorption by chitin

The results of initial concentrations of RB-29 on the removal efficiency by the chitin at different contact times are depicted in Fig. 5.

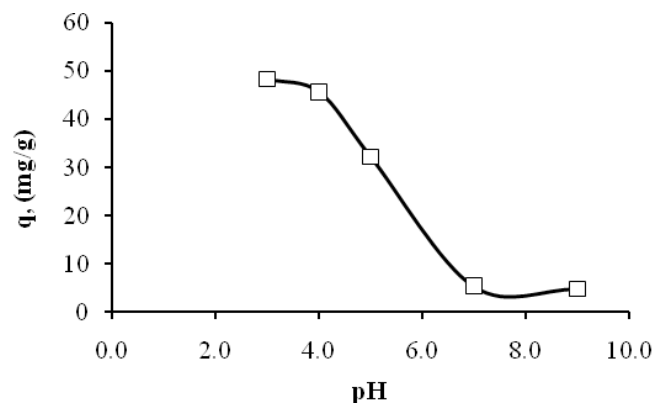


Fig. 4. The effect of initial pH on the adsorption of RB-29 by chitin (adsorbent dosage = 0.5 g/L, equilibrium time = 90 min, volume of solution = 0.1 L).

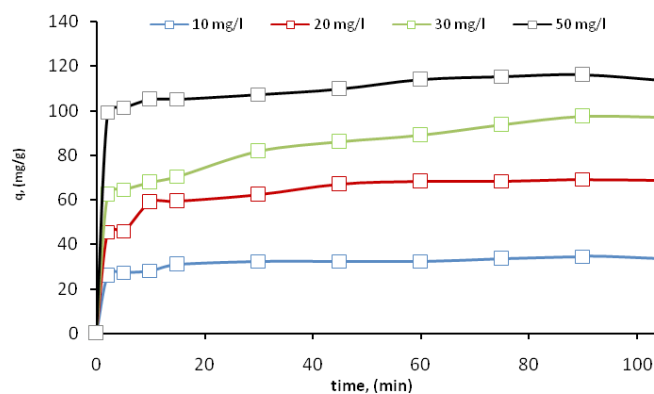


Fig. 5. The effect of initial concentration of RB-29 dye on adsorption by chitin at different contact times (pH = 3, adsorbent dosage = 0.2 g/L, volume of solution = 0.1 L).

From Fig. 5, at concentrations of 10 and 20 mg/L after the first 60 min and at concentrations of 30 and 50 mg/L after 90 min, equilibrium condition reached. However, at equilibrium time the adsorbate to adsorbent value for concentration of 10, 20, 30 and 50 mg/L are 32.46, 68.08, 97.3 and 116.07 mg/g, respectively. This can happen because, with increasing the concentration of dyestuff molecules, the contact between the dyestuff and adsorbent molecules increases which in general increase the adsorption of dye by the adsorbent and this finally increases the adsorption capacity [8]. Radaei et al. [42] reported that the maximum adsorption occurred at the first few minutes of the process after that the adsorption rate declined due to likely filling the adsorbent pores. In the first few minutes, due to strong van der Waals force adsorption process occurred rapidly. Dehghani et al. [2] also reported the high adsorption of the same dye occurred at first 15 min which can be attributed to the reduction of available adsorption sites [2].

3.4. The effect of adsorbent dosage on the adsorption of RB-29 by chitin

The dye solution with a concentration of 50 mg/L was prepared and the pH was adjusted to 3 for the solutions. Adsorbent dosage of 0.2, 0.3, 0.4, 0.5 and 0.75 g/L at 15 min were studied for dye adsorption. The values of the adsorbate at different adsorbent dosages are shown in Fig. 6.

With regard to the effect of adsorbent dosage on the RB-29 removal by chitin, it was revealed that with increasing the adsorbent dosage, adsorption amount decreased. The maximum adsorption was obtained at a dose of 0.2 g/L. So, this adsorbent dose was used as the optimal dosage for further process analysis.

From Fig. 6, the adsorption of RB-29 by chitin at dosages of 0.2, 0.3, 0.4, 0.5 and 0.75 g/L were 49.10, 35.95, 31.39, 29.08 and 21.82 mg/g, respectively. As shown, the adsorption efficiency decreased with increase in adsorbent dose. Li and

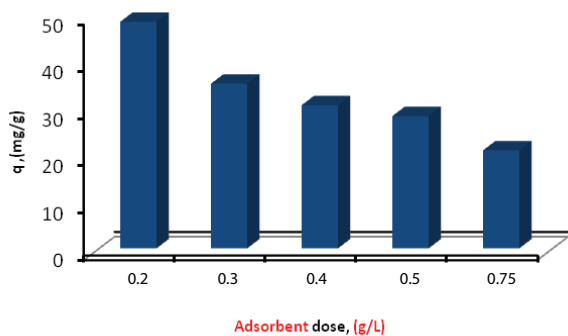


Fig. 6. Effect of adsorbent dosage on the removal of RB-29 by chitin (pH = 3, equilibrium time = 90 min, volume of solution = 0.1 L).

Table 1 Isotherms coefficients for RB-29 removal using chitin

Langmuir isotherm				Freundlich isotherm			
q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	coefficient of Langmuir equation	R <sub>L</sub>	R <sup>2</sup>	K <sub>f</sub> (mg/g)	n	R <sup>2</sup>
128	0.029		0.5	0.97	5.81	1.48	0.94

Ding [43] concluded that reduction in adsorption capacity revealed when the dose of chitosan was 0.1 g/L. The reduction of adsorption capacity with increase in adsorbent dosage at constant dye concentration and solution volume is primarily due to unsaturation of adsorption sites through the adsorption process, and secondly particulate interactions as a result of high adsorbent dose [43].

3.5. Adsorption isotherm models

In this part, the results of the two mostly used isotherms including Freundlich and Langmuir are presented in Figs. 7 and 8 and the summary of the isotherms parameters are presented in Table 1.

As Figs. 7 and 8 illustrate, the adsorption isotherms for RB-29 by chitin is better fitted to Langmuir model (R<sup>2</sup> = 0.97). However, the same model has been reported for adsorption of other reactive dyes by chitosan [37], calcined alunite [11] and activated carbon [40]. Based on Langmuir model, a maximum adsorption capacity (q<sub>max</sub>) of 128 mg/g was obtained for

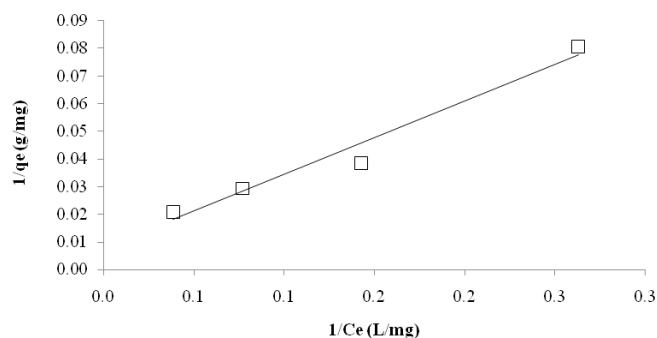


Fig. 7. Langmuir isotherm analysis for RB-29 adsorption using chitin (pH = 3, adsorbent dosage = 0.2 g/L, equilibrium time = 90 min, volume of solution = 0.1 L).

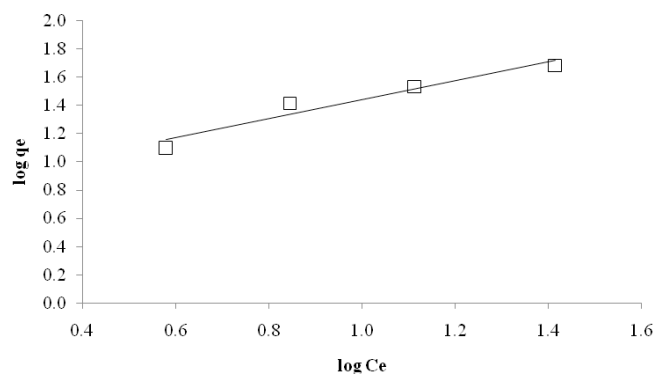


Fig. 8. Freundlich isotherm analysis for RB-29 adsorption using chitin (pH = 3, adsorbent dosage = 0.2 g/L, equilibrium time = 90 min, volume of solution = 0.1 L).

the removal of RB-29 by chitin. Also, we studied the tendency of RB-29 adsorption by dimensionless parameter ( $R_L$ ), which is derived from Langmuir model. If  $R_L = 0$ , the adsorption is irreversible; if  $0 < R_L < 1$ , the adsorption is desirable; if  $R_L = 1$ , the adsorption is linear; and if  $R_L > 1$ , then the adsorption is undesirable [44]. According to the results of the Langmuir isotherm for adsorption of RB-29, the amounts of  $R_L$  for chitin adsorbent were between 0 and 1, so RB-29 adsorption by chitin is desirable.

### 3.6. The effect of temperature and thermodynamic analysis on adsorption of RB-29 by chitin

The results of solution temperature effect on the performance of RB-29 dye removal process are shown in Fig. 9. As seen, with increasing the temperature, the adsorption of dye increased, reflecting an endothermic reaction. The parameters of thermodynamic equations are summarized in Table 2.

Fig. 9 shows the effect of temperature on the process and thermodynamics analysis of RB-29 adsorption by chitin. After calculating the thermodynamic equilibrium constant for different temperatures and calculating the free energy, it was revealed that increasing temperature from 15°C to 50°C resulted in an increase of dye removal. Negative sign of Gibbs free energy ( $\Delta G$ ) represents the spontaneous nature of the adsorption process [45]. Positive value of  $\Delta H$  indicates that the adsorption process is normally endothermic and the adsorption capacity increases with temperature increase [8]. Positive  $\Delta S$  value also indicates an affinity of adsorbent to adsorbate in the solution and some structural changes in the adsorbent and adsorbate materials [46]. Positive values of standard entropy changes ( $\Delta S$ ) indicate that the degree of

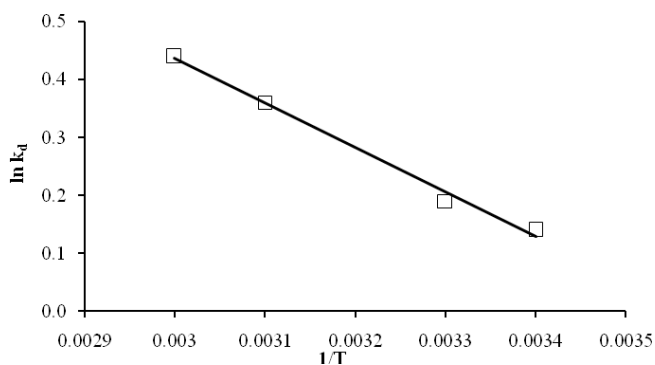


Fig. 9. Linear plot of  $\ln k_d$  vs.  $1/T$  for RB-29 adsorption using chitin (pH = 3, adsorbent dosage = 0.2 g/L, equilibrium time = 90 min, volume of solution = 0.1 L).

Table 3  
Coefficients of kinetic models for RB-29 adsorption by chitin

$C_0$ (mg/L)	Pseudo-first-order			Pseudo-second-order			$q_{e,exp}$ (mg/g)
	$k_1$ (min <sup>-1</sup> )	$q_{e,cal}$ (mg/g)	$R^2$	$k_2$ (g/mg min)	$q_{e,cal}$ (mg/g)	$R^2$	
10	0.03	3.92	0.41	0.04	32.91	1.00	33.47
20	0.03	10.88	0.32	0.01	68.96	1.00	69.09
30	0.03	14.94	0.27	0.01	90.02	1.00	89.89
50	0.02	8.62	0.18	0.01	113.00	1.00	114.95

freedom in the intermediate of solid–liquid phase is increased [47]. According to Crini and Badot [48], increase in temperature leads to an increase in the adsorption rate. However, these effects are low and temperature variations of a typical wastewater have no considerable impact on the overall performance of decolorization process [48]. Other works have also reported the positive values of  $\Delta H$  and  $\Delta S$  [49,50].

### 3.7. Kinetics of RB-29 dye adsorption by chitin

The kinetic parameters of RB-29 adsorption on chitin are given in Table 3. As seen, by comparing  $R^2$  coefficient of the kinetic models, pseudo-second-order model is better fitted for this adsorption process. The linear plot of  $\log(q_e - q_t)$  vs. time (Fig. 10) and  $t/q_t$  vs. time (Fig. 11) represent the pseudo-first-order and pseudo-second-order kinetic models, respectively.

According to Figs. 10 and 11 and also Table 3, comparing  $R^2$  coefficient indicated that the data revealed a good compliance with pseudo-second-order kinetic model that is consistent with the results of other works [40].

On the other hand, with studying the pseudo-second-order equations, it can be seen that there is little difference between capacity of adsorption under empirical equilibrium conditions ( $q_{cal}$ ) and the capacity of adsorption under calculation based conditions ( $q_{exp}$ ). So, pseudo-second-order kinetic model can be used properly for explaining the kinetics of these dyes with chitin.

### 3.8. Comparison between adsorbent of the present study with other adsorbent in reactive blue dye removal from aqueous solution

Table 4 shows the comparative evaluation of various adsorbents for removal of fluoride from aqueous solutions. As can be seen in the table, adsorption capacities of modified

Table 2  
Thermodynamic parameters obtained for RB-29 adsorption by chitin

$T$	Thermodynamic equilibrium constant ( $k_d$ )	$\Delta G$ (kJ/mol)	$\Delta S$ (J/mol k)	$\Delta H$ (J/mol)
288	0.14	-0.33	25.40	7054.39
303	0.19	-0.44		
313	0.36	-0.95		
323	0.44	-1.18		

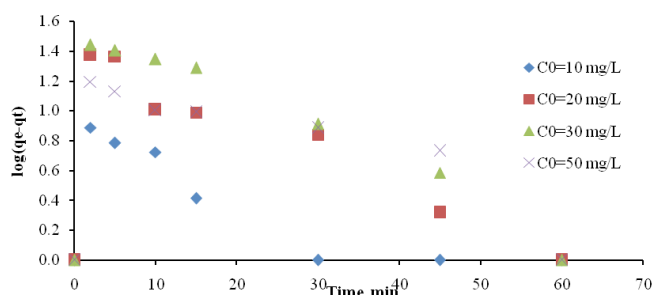


Fig. 10. Pseudo-first-order kinetic model for the experimental data (pH = 3, adsorbent dosage = 0.2 g/L, equilibrium time = 90 min, volume of solution = 0.1 L).

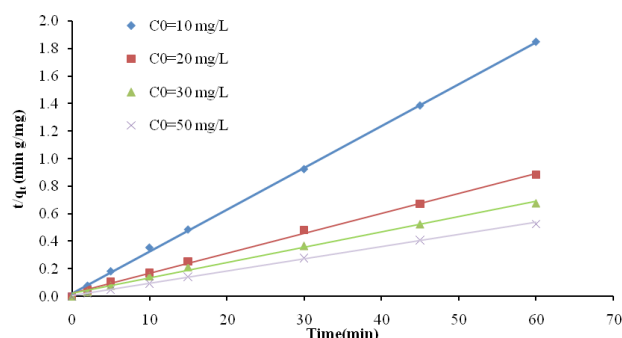


Fig. 11. Pseudo-second-order kinetic model for the experimental data (pH = 3, adsorbent dosage = 0.2 g/L, equilibrium time = 90 min, volume of solution = 0.1 L).

Table 4  
Comparative evaluation of various adsorbents for reactive blue dye removal

Adsorbent	Adsorbate	pH range	Type of isotherms	$q_{\max}$ (mg/g)	References
Chitin	RB-29	3	Langmuir	72.47	This study
Multi-wall carbon nanotubes	RB-29	2	Freundlich	49	[35]
Modified chitosan	RB-29	2	Langmuir	10	[8]
Modification bentonite	RB-19	1.5	Langmuir	206.6	[51]
Modified bentonite	RB-19	1.5	Langmuir	52.12	[52]
Cross-linked chitosan/oil palm ash composite beads	RB-19	8	Redlich–Peterson	175.44	[53]
MgO nanoparticles	RB-19	8	Langmuir	166.7	[54]
Cross-linked chitosan beads	RB-2	3–4	Langmuir	249.8	[55]
Activated carbon	RB-2	7	Langmuir	22.7	[56]
Multi-wall carbon nanotubes	RB-4	2	Langmuir	502	[57]
Single-wall carbon nanotubes	RB-4	2	Langmuir	567	[57]

chitosan, activated carbon and modified bentonite are lower than the adsorbents used in the present study. Other adsorbents have higher adsorption capacities.

#### 4. Conclusion

In recent years, several studies aimed at the development and use of natural and low-cost adsorbents instead of commercial activated carbon for the removal of pollutants from aqueous environment. Chitin and chitosan as natural aminopolysaccharides, because of their unique outstanding properties, high performance, multi-dimensional characteristics, have attracted much attention in various industries. In this study for RB-29 dye removal, chitin extracted from shrimp shells was used. The maximum adsorption capacity was 116.07 mg/g at RB-29 concentration of 50 mg/L and contact time of 90 min, compared with other adsorbents in other research indicates the high efficiency and good adsorbents for the dye removal. The effect of the main parameters in the adsorption process at optimal condition was initially at pH of 3, adsorbent dose of 0.2 g/L, dye concentration of 50 mg/L and at 15 min of contact time. Kinetics and adsorption isotherms indicated that the adsorption process is consistent with the

Langmuir isotherm and pseudo-second-order kinetic equation, respectively. Based on the results of this work, it can be concluded that chitin is a suitable option for reactive blue dye removal from aqueous solutions.

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