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Adsorptive Removal of Reactive Black 5 from Aqueous Solution using Chitin Prepared from Shrimp Shells

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Abstract

The utilization of chitin as adsorbent for the removal of Reactive Black 5 (RB5) from aqueous solution was investigated. Chitin was prepared from shrimp shells using conventional method. Prepared chitin was characterized by FT-IR spectral and thermogravimetric analysis. Batch adsorption experiments were carried out as a function of contact time, initial concentration of RB5 solution, temperature and pH of the solution. The amount of adsorption of RB5 from aqueous solution on chitin increased with the increase of initial concentration of RB5 solution and temperature of the solution. The equilibrium adsorption data were fitted to the Langmuir and Freunlich isotherms. The best result was achieved with Langmuir isotherm model. The thermodynamics of reactive dye by chitin indicated its spontaneous and endothermic nature. The kinetic of the sorption was analysed using the pseudo first-order and second-order kinetic models. The data showed that the pseudo second-order equation was the more appropriate. The experimental data showed that the adsorption capacity was gradually decreased with the increment of pH.

Keywords: Shrimp shells, chitin, Reactive Black 5, adsorptive removal.

Introduction

The textile, leather, paper, carpet and printing industries usually use dyes to colour their products. Due to their good solubility in water, synthetic dyes are frequently found in industrial wastewater as common water pollutants. The disposal of coloured wastes into receiving waters damages the environment, as they are carcinogenic and toxic to human and aquatic life. Now a days, concern has increased about the long-term toxic effect of water containing these dissolved pollutants. Therefore, wastewater decolourisation process has been the subject of research in recent years. Dye removal is a complex and expensive process. The techniques such as chemical and electrochemical oxidation, membrane processes, coagulation-flocculation, adsorption and ion exchange have been recommended (Robinson *et al.*, 2001). Among the numerous techniques, adsorption is rapidly gaining prominence as a method of removal of different types of colouring materials.

Now a days, numerous low cost, commercially available adsorbents have been used for the removal of dyes from coloured wastewater (Gupta, 2009). However, the adsorption capacities of all the above adsorbents are not satisfactory. So, the new effective adsorbents which are of low-cost and biodegradable are highly demanded. Chitin is a natural polysaccharide, poly-[β-(1→4)-2-acetamido-2-deoxy-glucose] (Figure 1), found particularly in the shells of crustaceans such as crab and shrimp, the cuticles of insects, and the cell walls of fungi (Rinaudo, 2006). In Bangladesh, shrimps are cultivated extremely around the coastal region of Satkhira, Khulna, Bagerhat and Cox's Bazar district. A significant amount of shrimp head part is being discarded from the shrimp processing industries every day. Chitin and its derivatives have been considered as attractive adsorbents that demonstrate a high efficiency of dye removal due to a high number of functional groups: N-acetyl amine, amine and hydroxyl (Rinaudo, 2006; McKay *et al.*, 1984; Longhinotti *et al.*, 1998; Annadurai *et al.*, 1999; Akkaya *et al.*, 2007; Filipkowska, 2007; Saha *et al.*, 2011). In addition, chitin is attractive for its abundance in nature, non-toxicity, hydrophilicity and biodegradability.

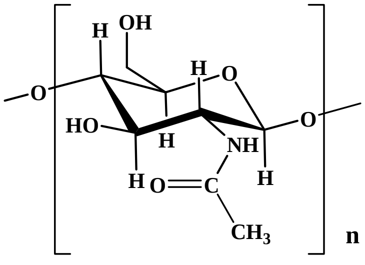

Figure 1. Structure of chitin

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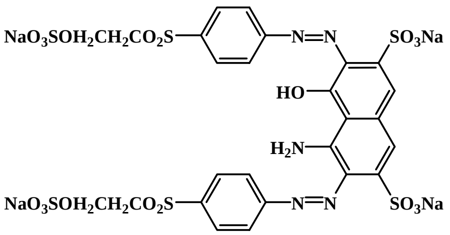

Figure 2. Structure of Reactive Black 5 (RB5)

In the present investigation, chitin was prepared from shrimp shells, an industrial waste material. The aim of this work was to utilize the potential of the prepared chitin as a biosorbent in the removal of a reactive dye, Reactive Black 5 (RB5), from aqueous solution. RB5, an anionic dye, was selected as a model pollutant (Figure 2) to characterize the adsorptive properties of prepared chitin. The effect of contact time, initial concentration of dye solution, pH and temperature on adsorptive removal of RB5 from aqueous solution by chitin was studied in a batch system. Models to fit adsorption equilibrium and kinetic data were also formulated. Thermodynamic parameters for the present system were evaluated based on isotherm data.

Materials and Methods

The anionic dye used in this study, Reactive Black 5 (RB5) was purchased from AG Merck, Germany and used without further purification. The dye stock solution was prepared by dissolving accurately weighed dye in deionized double distilled water (DDW). The experimental solutions were obtained by diluting the stock solution (5000 ppm) in accurate proportions to the needed initial concentrations (30 to 120 ppm). The other reagents used in this study were of pure analytical grade.

Preparation of chitin from shrimp shells: The shells of shrimp head part were collected from a shrimp processing industry of Satkhira, Bangladesh. Shrimp shells were scraped free of loose tissue, washed with water and dried in sun for 3 days. Chitin was prepared from shrimp shells according to the methodology described earlier (Hossain *et al.*, 2005; Rødde *et al.*, 2008). The process mainly involved the following steps-

(i) Demineralisation of shrimp shells: In this step, the shells were suspended in 1.0 M HCl at room temperature. After 24 hours, the shells were quite squashy that were rinsed with water to remove acid and calcium chloride.

(ii) Deproteinisation of shrimp shells: The demineralised shrimp shells were then boiled with 1.0 M NaOH at 90°C for 2.0-2.5 hours. The residue was then collected and washed to neutrality in running water. Then it was dried in oven at 60°C and the final product was obtained as chitin.

(iii) Decolourisation of prepared chitin: The prepared chitin contained some pigments which were removed by extraction with acetone following by bleaching with 0.5 % NaOCl.

The prepared chitin was grounded and sieved through a set of metallic sieves ranging from 0.212 mm to 0.300 mm. The sieved chitin sample was used as adsorbent for the removal of RB5 from aqueous solution.

Characterisation of prepared chitin: FTIR spectrophotometry (FT-IR 8400S, Shimadzu, Japan) within the range of 400-4000 cm^{-1} was used to characterise the prepared chitin as KBr disc. FT-IR spectrum of chitin is shown in Figure 3. Thermogravemitric analyzer (TGA-50 Shimadzu, Japan) was used to observe the decomposition steps of chitin. The experiment was done in nitrogen atmosphere and temperature rate 10°C/min upto 800°C. TGA curve of chitin is presented in Figure 4.

Determination of zero point charge (pH_{ZPC}) of prepared chitin: The pH_{ZPC} (pH at zero point charge) of chitin was determined by pH-metric titration (Islam *et al.*, 1997). For this 0.5 g of chitin was added to four identical portions of 60 mL 0.1 M NaCl solution at pH 7. The mixtures were shaken for 24 hours with a thermostatic shaker. Two bottles of suspension were titrated directly with 0.05 M HCl and 0.05 M NaOH separately using micro burette. The constant pH values were noted after each aliquot of titrant (acid or alkali) addition. From other two bottles, the supernatants after filtration were titrated with acid and alkali as described above. The net titration curve was obtained by finding the difference between the titration curves of the supernatants and that of the sample with adsorbent (Figure 5). The net titration curves meet at a point, which is defined as the pH_{ZPC}.

Estimation of equilibrium time for adsorption of Reactive Black 5 on chitin: The equilibrium time of the adsorption of RB5 on prepared chitin was estimated at pH 3.2. The prepared chitin (0.05 g) and 40 mL of 30, 40 and

70 mg/L of RB5 solution were used in each of the 12 bottles. The bottles were shaken in a thermostatic mechanical shaker at 30°C. For blank 0.05 g of prepared chitin and 40 ml of deionised double distilled water (DDW) solution added in a bottle and was shaken for 5 hours at 30°C. After a definite interval of time each bottle was withdrawn from the shaker. The supernatant of the bottle was transferred and centrifuge repeatedly until a clear liquid was obtained. The absorbance of the clear solution was measured spectrophotometrically at λ_{max} 598.0 nm. The amount of RB5 adsorbed at time t (mg/g), q_t, onto chitin was calculated by a mass balance relationship,

$$q_t = (C_0 - C_t)\ V / m \quad ....(1)$$

At equilibrium time, the amount of RB5 adsorbed q_e (mg/g), was calculated by the following relationship,

$$q_e = (C_0 - C_e)\ V / m \quad ....(2)$$

where C_0 is the initial dye concentration in the solution (mg/l), C_t is the residual dye concentration in the solution at any time t (mg/l), C_e is the residual dye concentration in the solution at equilibrium time (mg/ L), V is the solution volume (L) and m is the mass of chitin (g).

The plot of amount adsorbed, q_t (mg/g) versus the time (min) of adsorption has been presented in Figure 6.

Effect of pH on adsorption: In order to study the effect of pH on dye adsorption process, the pH of the solutions was varied from 2.0 to 9.0 by adding a small amount of NaOH or HCl solution without affecting the volume. After adjustment of pH, the initial absorbance of the solutions was measured at λ_{max} 598.0 nm. 0. 05 g of chitin was taken in each of the eight bottles and 40.0 mL of RB5 solution (30 mg/l) of different pHs (ranging from 2.0 to 9.0) was added in each bottles. The bottles were placed in the thermostatic shaker for shaking continuously at 30°C. The reagent bottles were successively withdrawn after four hours and the solution was centrifuged. After centrifugation, the pHs of the solutions were readjusted to the initial pH of the RB5 solutions and the absorbance of the solutions were measured using the λ_{max} as before. The plot of amount adsorbed (mg/g) versus initial pH of solution is shown in Figure 7.

Adsorption isotherm of RB5 on chitin at different temperatures and pHs: Adsorption experiments were carried out on chitin using different initial concentrations of RB5 from 10 to 70 mg/l at pH 3.2. Chitin sample (0.05 g) and 60 mL of RB5 solution where taken in each of the eight bottles. The bottles were shaken in thermostatic mechanical shaker at 30°C for four hours. The bottles were withdrawn at the stipulated time from the shaker and the supernatant was transferred to the centrifuge tube for centrifugation. The absorbance of the clear solution was measured spectrophotomtrically. Similar experiments were performed at 38, 46 and 54°C to obtain the adsorption isotherms at different temperatures. Plots of amount adsorbed at equilibrium, q_e (mg/g) versus equilibrium concentration, C_e (mg/l) at different temperatures are shown in Figure 8.

Results and Discussion

Characterization of prepared chitin by FT-IR Spectroscopy: The FT-IR spectrum of chitin prepared from shrimp shells is presented in Fig. 3 (Cardenas *et al*., 2004). The FT-IR spectrum showed a broad absorption band at around 3475 cm^{-1} corresponding to the vibrational stretching of hydrogen bonded O-H and N-H. The spectrum also shared characteristic peaks of amide I at 1648 cm^{-1} (C=O stretching), amide II at 1562 cm^{-1} (N-H in plane deformation coupled with C-N stretching), amide III (C-N stretching coupled with O-H in plane deformation) and CH_2 wagging coupled with O-H in plane deformation at 1317 cm^{-1}. The peaks observed at around 2932 and 2891 cm^{-1} were assigned to sp^3 C-H stretching (symmetric and asymmetric). The band at 1380 cm^{-1} corresponded to C-H bending and symmetric CH_3 deformation, while the band at 1421 cm^{-1} was due to CH_2 bending and CH_3 deformation. The band observed at 1158 cm^{-1} was indicated a bridged oxygen stretching (C-O-C linkage of ring). The C-O stretching vibration bands were

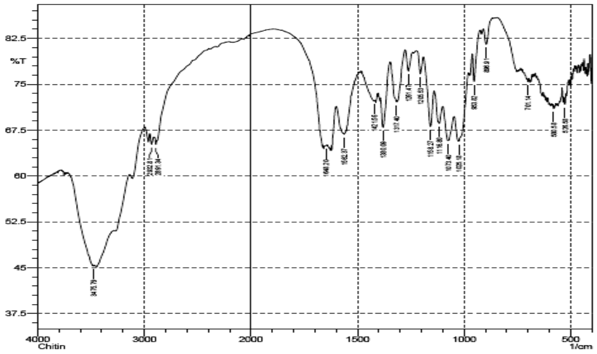

Figure 3. FT-IR spectrum of prepared chitin

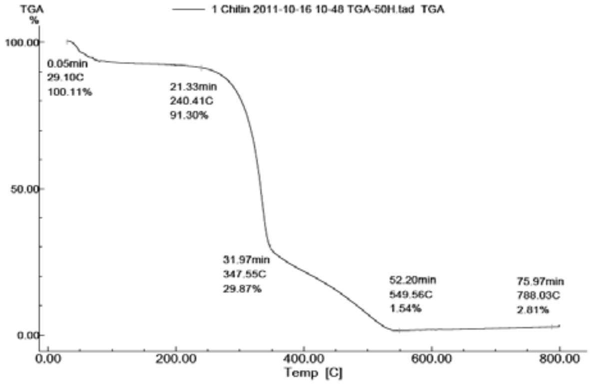

Figure 4. Thermogravimetric curve of prepared chitin

observed at 1116, 1073, and 1025 cm^{-1}. The characteristic peak for CH deformation of the β-glycosidic bond was observed at 896 cm^{-1}.

Characterization of prepared chitin by TGA: In the thermogravimetric curve of prepared chitin (Fig. 4), three decomposition steps could be observed, the first occurred in the range of 40-90°C, attributed to water evaporation (Pawlak, 2003). The second occurred in the range of 240.41-347.55°C, and could be ascribed to the degradation of the saccharide structure of chitin, including the dehydration of saccharide rings and the polymerization. The third decomposition in the range of 347.57-549.56°C, could be explained due to the decomposition of the acetylated and deacetylated units of chitin. The percentage of residual mass after heating at 800°C was 2.81%, and this suggested the presence of some minerals that were not extracted in the acidic stage.

Determination of zero point charge (pH_{ZPC}) of adsorbent: Determination of zero point charge of biosorbent is important in elucidating biosorption mechanism. Biosorption of cations is favoured at pH > pH_{ZPC}, while anion biosorption is facilitated at pH < pH_{ZPC}. The specific biosorption of cations shifted pH_{ZPC} towards lower values whereas the specific biosorption of anions shifted pH_{ZPC} towards higher values. The surface zero point charge (pH_{ZPC}) of chitin was found to be 6.29 (Figure 5).

Effect of initial dye concentration: For the estimation of equilibrium time, the adsorption experiment was carried out at pH 3.2 and concentration of solution was 30, 40 and 70 mg/L at 30°C. From Figure 6, it was observed that as the initial dye concentration was increased, the time required to reach equilibrium was also increased. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration (Chiou, 2002). Under the experimental condition, the equilibrium time for the adsorption of RB5 on chitin was estimated and found to be 3 hours for low initial dye concentration (30 and 40 mg/L). It was observed that amount of RB5 adsorbed from 30, 40, and 70 mg/L solution were found to be about 24.95, 32.86, and 41.82 mg/g, respectively.

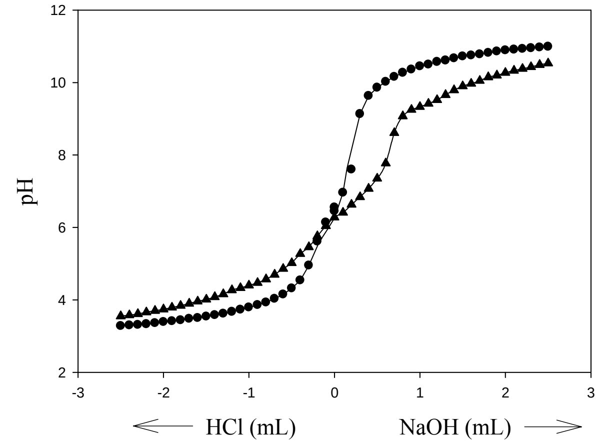

Figure 5. pH titration curve of chitin in 0.1 M NaCl solution (▲Suspension ● Filtrate)

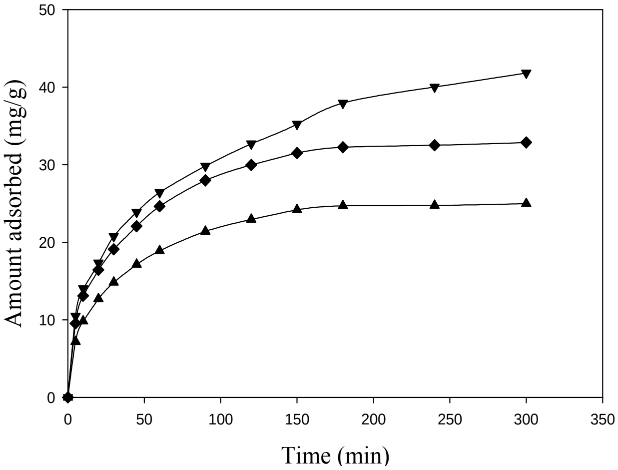

Figure 6. A plot of amount adsorbed vs time for different concentration of RB5 at 30°C (▲=30 mg/l, ●= 40 mg/l, ■ = 70 mg/l)

Effect of pH on adsorption: The pH of the solution is an important parameter for controlling the adsorption process. It influences the biosorption process by affecting the surface charge of adsorbent, the degree of ionization of the adsorbate. Further, it is also directly related with competition ability of hydrogen ions with adsorbate ions to active sites on the adsorbent surface. The effect of pH of the RB5 solution on adsorption process of RB5 onto chitin at 30°C is shown in Figure 7, where initial dye concentration was 30 mg/l. At lower pHs, from pH 2.2 to 5.9, higher values of the adsorption capacity were observed. Above pH 5.9, the adsorption capacity decreased significantly with increase in solution pH. In chitin, the presence of hydroxyl, N-acetylamine and amine groups could make it a potential adsorbent for dye effluents. Recently, a report has been published on the probable mechanism of dye adsorption (Annadurai *et al.*, 1999). According to this report, in the adsorption process at lower pH, more protons were available to protonate N-acetyl amino groups (R-$NHCOCH_3$) and amino group (R-NH_2) of chitin molecules into (R-NH_2COCH_3)$^+$ and (R-NH_3)$^+$ forms. Sulfonate (R-SO_3^-) group of reactive dye might be attracted by these protonated groups. Therefore, with the increase of the electrostatic attraction between negatively charged dye anions and positively charged adsorption sites, an increase in dye adsorption was evident. This explanation agrees well with our result on pH effect.

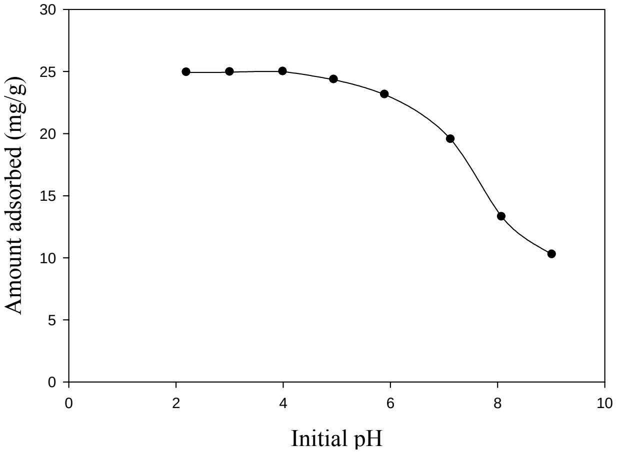

Figure 7. A plot of amount adsorbed vs. initial pH of RB5 solution (30 mg/L) at 30°C.

Adsorption isotherms: Adsorption isotherms were determined at four different temperature using RB5 solutions at pH 3.2 and 30°C shown in Figure 8. The adsorption isotherms for RB5 on chitin exhibited H-type curves, indicating a very strong interaction between the adsorbate and adsorbent (Giles et al., 1974).

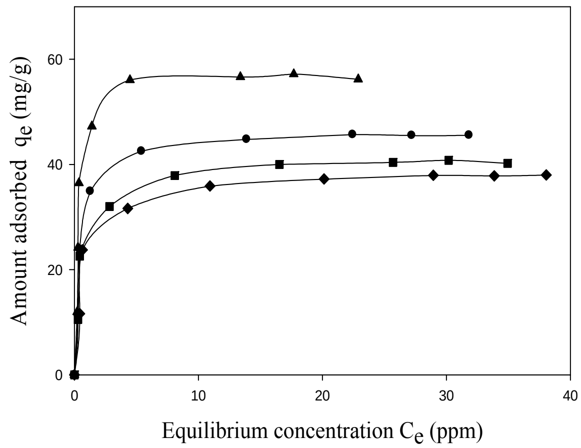

Figure 8. A plot of amount adsorbed vs. equilibrium concentration at different temperatures (◆ =30°C, ■ = 38°C, ● = 46°C, ▲= 54°C)

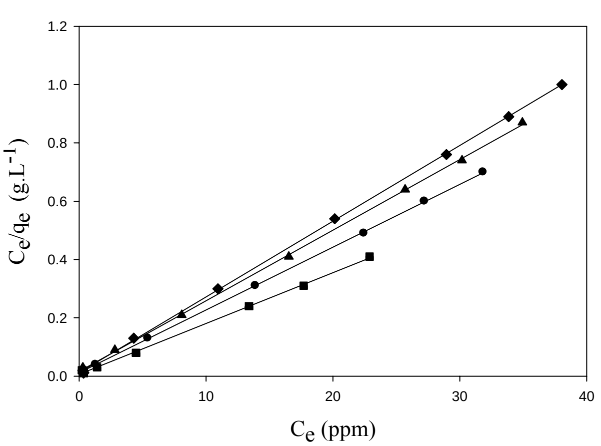

Figure 9. Langmuir isotherm for adsorption of RB5 on chitin (◆ =30°C, ▲ =38°C, ● =46°C, ■ = 54°C)

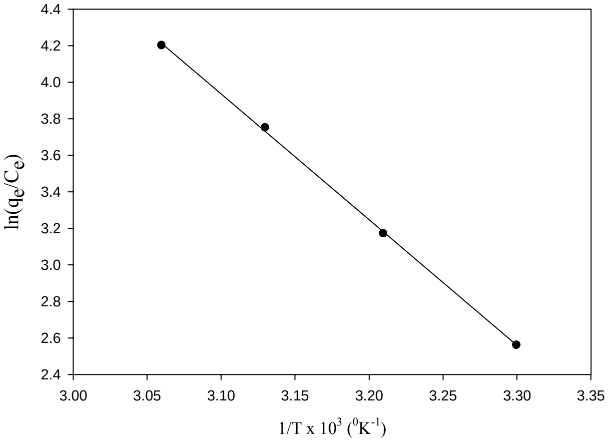

Figure 10. A plot of ln(q_e/C_e) vs. 1/T to determine the heat of adsorption

The experimental data were analyzed using Langmuir and Freundlich isotherm models (Langmuir, 1916; Freundlich, 1906). The linear correlation coefficients were determined for each isotherms and the Langmuir provided the best fit. The value of V_m varies from 38.49 to 57.36 mg/g with increasing the temperature (Figure 9 and Table 1).

Table 1. Langmuir and Freundlich parameters of adsorption of RB5 on chitin at different temperatures

Temperature (°K)	Freundlich	Langmuir		
	r^2	r^2	V_m (mg/g)	B
303	0.7775	0.9998	38.49	2.20
311	0.7968	0.9997	41.30	1.50
319	0.7559	0.9999	46.44	1.81
327	0.6869	0.9990	57.36	2.72

Effect of temperature: A plot of adsorption capacity as a function of temperature showed that the amount of Reactive Black 5 adsorbed on chitin increased with increasing temperature from 30°C to 54°C at pH 3.2, indicated that the adsorption capacity depends on temperature (Figure 8). The increase in sorption with temperature suggested that the chemical interaction occurred with increasing temperature, as a result the increase of adsorption intensity with temperature was observed. A similar phenomenon was found in the adsorption of RB5 on chitin (Akkaya *et al.*, 2007). They suggested that chemical interaction occurring between negative groups in the RB5 structure and protonated amine group in the structure of chitin at lower pH.

The values of ΔH and ΔS were estimated from the slope and intercept of the linear plot of $\ln(q_e/C_e)$ vs 1/T (Figure 10). The value of differential heat of adsorption (ΔH) for amount adsorbed 28.0 mg/g was estimated and found to be 57.20 kJ mol^{-1}. The positive differential heat of adsorption indicated that the adsorption process was endothermic and it favoured the activated chemical interaction between adsorbent and adsorbate. The values of ΔG were calculated from the values of ΔH and ΔS (Table 2). The values of Gibbs free energy (ΔG) are negative and increase with the increase of temperature from −6.43 to −11.47 kJ mol^{-1}.

Table 2. Thermodynamic parameters of adsorption of RB5 on chitin

Temperature (K)	ΔH (kJ/mole)	ΔS (kJ/K.mol)	ΔG ($kJ.mol^{-1}$)
303	57.20	0.21	−6.43
311			−8.11
319			−9.79
327			−11.47

Kinetic study: Effect of contact time on removal of RB5 from three solutions of different initial concentrations on chitin is shown in Figure 6. In order to investigate the mechanism of adsorption kinetics, Lagergren's pseudo-first order equation (Lagergren, 1898) and Ho's pseudo-second order equation (Ho, 1999) were used to study the biosorption kinetic onto chitin as shown below:

Pseudo-first order: $\log(q_e\text{-}q_t) = \log q_e - (k_1/2.303)t$ -----(3)

Pseudo-second order: $t/q_t = 1/(2k_2q_e^2) + (1/q_e)t$ ----------(4)

where, q_e and q_t are amount of adsorbate adsorbed (mg/g) at equilibrium time and at any time t, k_1 and k_2 are the rate constants of pseudo first-order adsorption (min^{-1}) and pseudo second-order adsorption ($mg.g^{-1}.min^{-1}$).

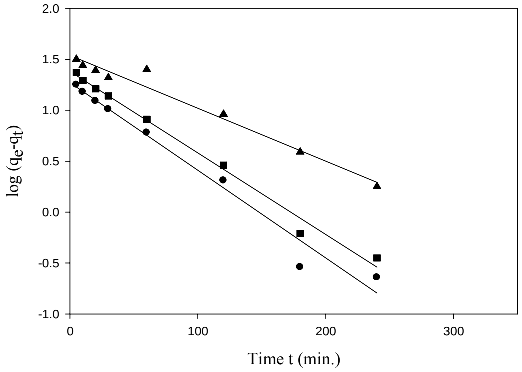

Figure 11. Pseudo-first order kinetic plot for adsorption of RB5 on chitin (● =30 mg/l, ■ = 40 mg/l, ▲= 70 mg/l)

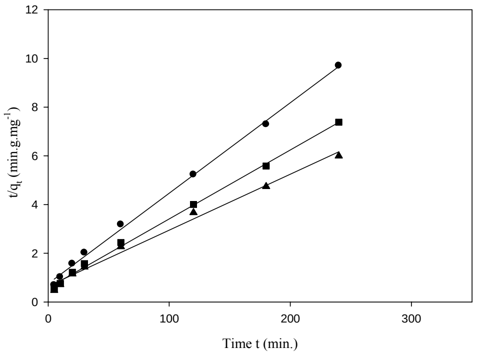

Figure 12. Pseudo-second order kinetic plot for adsorption of RB5 on chitin (● =30 mg/l, ■ = 40 mg/l, ▲= 70 mg/l)

Table 3. Kinetic parameters for biosorption of RB5 onto chitin

Conc. (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first-order kinetic model				Pseudo second-order kinetic model			
		Rate const. k_1 (min^{-1})	Regression coefficient r^2	$q_{e,cal}$ (mg/g)	Deviation (%)	Rate const. k_2 (mg/g/min) $\times 10^4$	Regression coefficient r^2	$q_{e,cal}$ (mg/g)	Deviation (%)
30	24.98	19.80	0.9759	18.62	25.46	9.12	0.9978	27.03	8.21
40	32.86	18.42	0.9905	23.99	26.99	6.76	0.9974	35.71	8.67
50	41.82	11.95	0.9719	34.67	17.10	4.07	0.9904	43.45	3.90

The pseudo first-order and pseudo second-order kinetic plots using equation (3) and (4) are shown in Fig. 11 and 12. The parameters of pseudo first-order and pseudo second-order kinetic models are summarized in Table 3. In the pseudo first-order kinetic plots for all initial concentrations, the regression coefficient r^2 are generally more than 0.97. However, the deviations between the calculated and experimental q_e values were very large. Therefore, pseudo first-order kinetic model does not fit well. In the pseudo second-order kinetic plots for all initial concentrations, the regression coefficient r^2 are generally more than 0.99. The variation between the calculated q_e and experimental q_e were very minimal for this model. The high regression coefficient and high agreement that exist between the calculated and experimental q_e values of pseudo second-order kinetic model over pseudo first-order kinetic model confirms that the adsorption kinetics of RB5 onto chitin are well represented by pseudo second-order kinetic model.

Conclusion

This present study investigates the potential use of chitin, prepared from shrimp shells for the removal of RB5, an anionic dye from simulated waste water. The adsorption increased with the increment of initial concentration of RB5 solution. The amount of adsorption of RB5 increased with the increase in temperature. The experimental data were analyzed using Langmuir and Freundlich isotherm models and the Langmuir provided the best fit. The experimental data shows that the uptake of RB5 gradually decreases with the increment of pH. The kinetic data fitted very well to the pseudo second-order kinetic model. Therefore it may be concluded from the experimental data that chitin is a potential biosorbent for the removal of dyes from aqueous solution.

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