

Chitosan and chemically modified chitosan beads for acid dyes sorption

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Abstract

The capabilities of chitosan and chitosan-EGDE (ethylene glycol diglycidyl ether) beads for removing Acid Red 37 (AR 37) and Acid Blue 25 (AB 25) from aqueous solution were examined. Chitosan beads were cross-linked with EGDE to enhance its chemical resistance and mechanical strength. Experiments were performed as a function of pH, agitation period and concentration of AR 37 and AB 25. It was shown that the adsorption capacities of chitosan for both acid dyes were comparatively higher than those of chitosan-EGDE. This is mainly because cross-linking using EGDE reduces the major adsorption sites $-NH_3^+$ on chitosan. Langmuir isotherm model showed the best conformity compared to Freundlich and BET. The kinetic experimental data agreed very well to the pseudo second-order kinetic model. The desorption study revealed that after three cycles of adsorption and desorption by NaOH and HCl, both adsorbents retained their promising adsorption abilities. FT-IR analysis proved that the adsorption of acid dyes onto chitosan-based adsorbents was a physical adsorption. Results also showed that chitosan and chitosan-EGDE beads were favourable adsorbents and could be employed as low-cost alternatives for the removal of acid dyes in wastewater treatment.

Key words: cross-linking; acid dyes; adsorption capacities; adsorption rates; adsorption isotherm; desorption

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Introduction

Nowadays, environmental research has paid strenuous attention to dye compounds because of the extensive environmental contamination arising from dyeing operations including textiles, cosmetics, printing, paper, plastics, as well as in the food industry. Although most dyes are non-toxic at the concentration detected in wastewaters, the color is undesirable to the water user (Gibbs *et al.*, 2003). Dyes are difficult to be removed, since they are recalcitrant organic molecules, resistant to aerobic digestion and is stable to light, heat and oxidising agents (Sun and Yang, 2003).

Amongst numerous techniques, adsorption process is the most commonly used for the decontamination of the dye-containing effluents. Most commercial systems currently use activated carbon as sorbent because of its excellent adsorption ability (Crini, 2006), but it is expensive and difficult to regenerate (Sakkayawong *et al.*, 2005). In recent years, most studies have been focused on the development of cheap and effective new adsorbents (Babel and Kurniawan, 2003; Crini, 2005). Numerous low-cost alternatives have been studied for dyes removal, including chitosan (Cheung *et al.*, 2007), cotton (Chairat *et al.*, 2008), guava leaf powder (Ponnusami *et al.*, 2008), fly ash (Lin *et al.*, 2008), sugarcane bagasse pith (Amin, 2008),

rice husk (Han *et al.*, 2008), yellow passion fruit waste (Pavan *et al.*, 2008), and coconut coir pith (Sureshkumar and Namasivayam, 2008). Biopolymers have received a great deal of attention due to the fact that they represent renewable resources and more environmental friendly than commercial materials (Guibal *et al.*, 2002).

Chitin, a naturally abundant mucopolysaccharide and the supporting material of crustaceans, insects, etc., is well known to consist of 2-acetamido-2-deoxy- β -D-glucose through a β (1 \rightarrow 4) linkage. An alkaline treatment at boiling temperature allows the acetylated groups to be removed and the deacetylation degree to be increased. This chemical treatment leads to the formation of chitosan, a partially deacetylated form of chitin. Chitosan is non-toxic, hydrophilic, biocompatible, biodegradable and anti-bacterial, which has led to a diverse range of applications in the biomedical field and in cosmetic, food and textile industries (Ravi Kumar *et al.*, 2004). Chitosan appears to be more useful as compared to chitin, since it has a large number amine and hydroxyl groups that can serve as chelating sites and can be chemically modified (Sun and Wang, 2006). Several methods have been used to modify raw chitosan flake either physically (Onsøyen and Skaugrud, 1990; Wan Ngah *et al.*, 2002) or chemically (Zubieta *et al.*, 2008; Wang and Wang, 2008). Physical modification allows: the polymer network to be expanded, the increase in the polymer network opening enhances

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the diffusion of large size molecule and the crystalline state of the polymer to be reduced (Erosa *et al.*, 2001). Chemical modifications were proposed to improve mechanical strength and chemical stability of the chitosan in acidic media. They may also increase its resistance to biochemical and microbiological degradation (Wan Ngah *et al.*, 2004). A cross-linking step is required to reinforce the chemical stability of the biosorbents in acidic solutions. Some common cross-linking agents such as glutaraldehyde (Morais *et al.*, 2007; Cestari *et al.*, 2008), epichlorohydrin (Chiou and Chuang, 2006; Hasan *et al.*, 2008) and ethylene glycol diglycidyl ether (Li and Bai, 2005; Wan Ngah *et al.*, 2005) have widely been used in cross-linking of chitosan beads.

The objective of this research is to ascertain the feasibility of using chitosan and chitosan-EGDE beads as adsorbents for the removal of Acid Red 37 (AR 37) and Acid Blue 25 (AB 25). The influences of pH, agitation period and concentration of AR 37 and AB 25 were studied. The Langmuir, Freundlich and BET equations were used to fit the equilibrium isotherm. The adsorption rates were determined quantitatively by the pseudo first-, second-order and the intraparticle diffusion model. Desorption study was also carried out using NaOH and HCl as desorption agents. This information will be useful for further applications of system design in the treatment of practical waste effluents.

1 Materials and methods

1.1 Materials

Samples of chitosan flakes with average molecular weights 10^5 – 10^6 g/mol and with a deacetylation percentage of approximately 87.94% (defined by an IR method), prepared from shells of prawns were purchased from Chito-Chem (M) Sdn. Bhd., Malaysia. Ethylene glycol diglycidyl ether (EGDE) obtained from Fluka was analytical-reagent grade. The commercial dye AR 37 (CI 17045; relative molecular weight 514.53) and AB 25 (CI 62055; relative molecular weight 416.38) were purchased from Sigma Chemical Company (USA). These anionic dyes were used without further purification. Doubly distilled water used to prepare all solutions.

1.2 Preparation of chitosan beads

Chitosan solution was prepared by dissolving 2.00 g of chitosan flakes into 60 mL of 5% (V/V) acetic acid solution. The chitosan solution was sprayed into a precipitation bath containing 500 mL of 0.50 mol/L NaOH, which neutralised the acetic acid within the chitosan gel and thereby coagulated the chitosan gel to spherical uniform chitosan gel beads. A magnetic stirrer was used to stir the aqueous NaOH solution. The wet chitosan gel beads were extensively rinsed with distilled water to remove any NaOH, filtered and finally air-dried to remove the water from the pore structure (hereafter called chitosan beads). The beads were then ground using a laboratory jar mill and sieved to a constant size ($< 250 \mu\text{m}$) before use.

1.3 Preparation of chitosan-EGDE beads

Chitosan-EGDE beads were prepared according to the method of Wan Ngah *et al.* (2005). Recently prepared wet chitosan beads were suspended in 0.025 mol/L EGDE to obtain a cross-link ratio of 1:1 (EGDE:NH₂, mol:mol) with chitosan. The solution was heated to a temperature range 50–60°C for 3 h and stirred continuously. Then, the newly cross-linked chitosan beads were intensively washed and air-dried. The chitosan-EGDE beads were ground and sieved to a constant size ($< 250 \mu\text{m}$) and were confirmed by a Perkin-Elmer FT-IR System 2000 Model spectrometer (USA).

1.4 Characterisation of chitosan and chitosan-EGDE beads

The physical properties of chitosan and chitosan-EGDE beads were measured using a Micromeritics ASAP 2010 gas adsorption surface analyser (USA) according to the BET equation. The surface morphology of the adsorbents was observed with a Leica Cambridge S360 scanning electron microscopy (SEM) (USA) with energy dispersive spectroscopy.

1.5 Batch adsorption experiments

Stock solutions of AR 37 and AB 25 were prepared without pH adjustment. The wavelength of maximum absorbance (λ_{max}) for AR 37 and AB 25 were 603 and 525 nm, respectively. About 0.05 g of chitosan or chitosan-EGDE beads and 50 mL of the standard solutions were placed in 250 mL beakers and stirred for a certain period. After filtration, the concentration of AR 37 and AB 25 in supernatant was analysed by an ultraviolet-visible spectrophotometer (U-2000 Hitachi, Japan) with 2 nm resolution using calibration curve at λ_{max} . The adsorption of AR 37 and AB 25 was studied in pH range 2–12, through adjusting pH using either HCl or NaOH. Chitosan and chitosan-EGDE beads were equilibrated at a particular pH value for about 30 min at 400 r/min. The effect of agitation period was determined to study the optimum condition for adsorption of AR 37 and AB 25.

Adsorption equilibrium tests were conducted at optimum conditions. Isotherm studies were conducted with a constant chitosan and chitosan-EGDE beads weight (0.05 g) and varying initial concentrations of AR 37 and AB 25 in the range of 50–500 mg/L. The adsorption capacity (q_e) were calculated according to Eq. (1):

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

where, C_0 (mg/L) and C_e (mg/L) are the initial and the final or equilibrium AR 37 and AB 25 concentration, respectively. V (mL) is the volume of the AR 37 and AB 25 solution, and W (g) is the weight of the chitosan and chitosan-EGDE beads.

For desorption studies, 0.1 g of chitosan and chitosan-EGDE beads were loaded with 50 mL of AB 25 and 200 mg/L of AR 37 at optimum pH. The agitation period was 100 min for chitosan beads and 140 min for chitosan-EGDE at 400 r/min. The loaded chitosan and

chitosan-EGDE beads were collected and gently washed with distilled water to remove any unadsorbed AR 37 and AB 25. The amount of adsorbed AR 37 and AB 25 per gram of chitosan and chitosan-EGDE beads were determined according to the supernatant concentration. The chitosan and chitosan-EGDE beads were agitated with 50 mL of NaOH and HCl (10^{-1} – 10^{-3} mol/L) and the percentage of desorption (D) of AR 37 and AB 25 was calculated from Eq. (2):

$$D = \frac{m_r}{m_0} \times 100\% \quad (2)$$

where, m_r (mg) and m_0 (mg) is the amounts of desorbed and adsorbed AR 37 or AB 25, respectively.

2 Results and discussion

2.1 Characteristics of chitosan and chitosan-EGDE beads

According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the pores can be divided into macropores ($d > 50$ nm), mesopores ($2 < d < 50$ nm) and micropores ($d < 2$ nm). In this study, chitosan and chitosan-EGDE beads correspond to mesopores with average pore diameter 4.759 and 6.438 nm. Moreover, the chitosan beads have higher BET surface area (average $0.96 \text{ m}^2/\text{g}$) that facilitates the adsorption of AR 37 and AB 25 with its loose pore structure as compared to chitosan-EGDE ($0.62 \text{ m}^2/\text{g}$).

The SEM images of chitosan and chitosan-EGDE beads after ground and sieved are depicted in Fig. 1. It can be seen that there is a significant difference in surface morphology of the two forms of chitosan beads. A striking feature of this image is the appearance of porous internal structure for chitosan-EGDE beads. The chitosan beads (Fig. 1a) displayed a smooth and nonporous surface, while the chitosan-EGDE beads (Fig. 1b) displayed a rough and microporous structure, which may offer more adsorption sites for adsorbate. This result also indicated that chitosan has been chemically modified.

2.2 Effect of pH

The adsorption capacity of chitosan and chitosan-EGDE beads decrease significantly with increasing pH (Fig. 2). At low pH, most of the amine groups ($-\text{NH}_2$) will be protonated which is necessary for the attraction of anionic sulfonic groups. The similar trend was also mentioned by Yoshida *et al.* (1993) and Chiou and Li (2003). The adsorptions were drastically decreased after pH reached 6.0 and 4.0 for AR 37 and AB 25, respectively. This could be explained by the fact that at high pH, more OH^- will be available to compete with the anionic sulfonic groups of AR 37 and AB 25 for the adsorption sites. This phenomenon will then decrease the number of adsorption sites for anionic AR 37 and AB 25. In this study, pH_{PZC} for chitosan and chitosan-EGDE beads are 7.1 and 7.3, respectively. Thus, the adsorption of anionic AR 37 and AB 25 dyes onto chitosan and chitosan-EGDE beads took place at pH 6.0 and 4.0 (lower than pH_{PZC} values).

2.3 Effect of agitation period

The adsorption by chitosan and chitosan-EGDE beads under studied condition occurred rapidly (Fig. 3). The adsorption of both dyes increased with agitation period and attained equilibrium at 100 min for chitosan and 140 min for chitosan-EGDE beads. Therefore, the optimum agitation period for the adsorption of AR 37 and AB 25

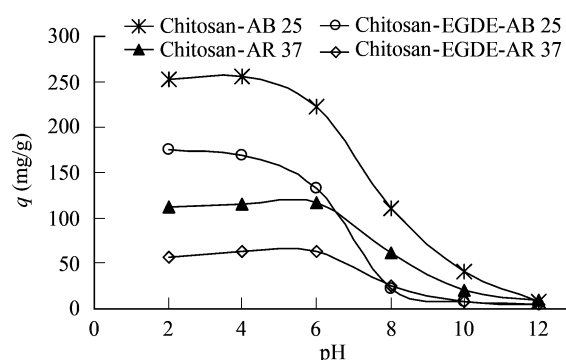


Fig. 2 pH effect on Acid Red 37 (AR 37) and Acid Blue 25 (AB 25) adsorption onto chitosan and chitosan-EGDE beads.

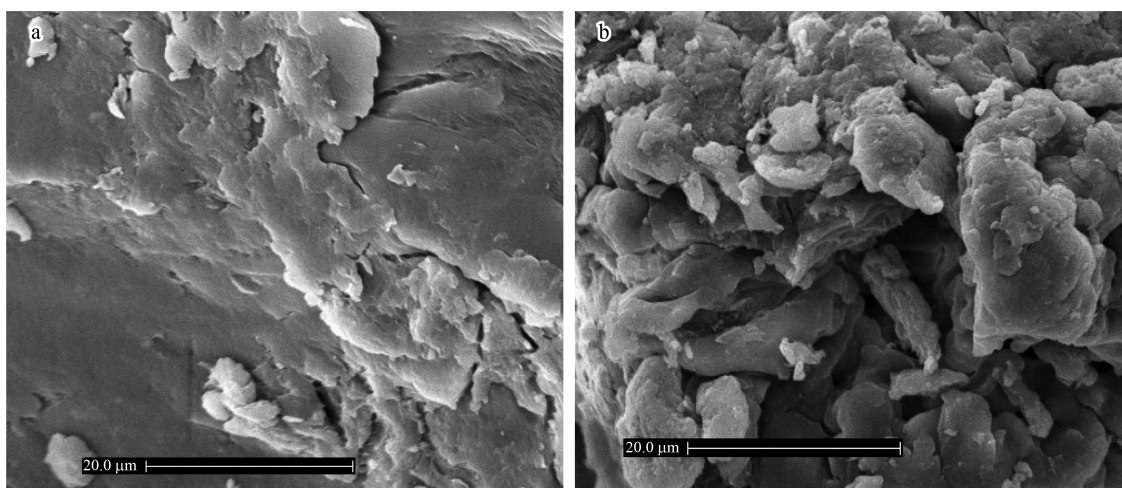


Fig. 1 SEM images of chitosan (a) and chitosan-EGDE (b) beads at 1500 \times .

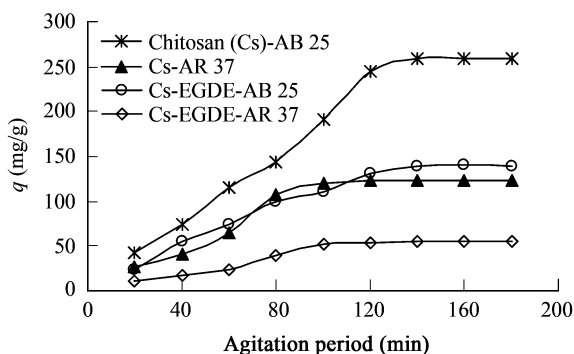


Fig. 3 Effect of agitation period on the adsorption of AR 37 and AB 25 onto chitosan and chitosan-EGDE beads.

onto chitosan and chitosan-EGDE beads are 100 and 140 min, respectively.

2.4 Adsorption equilibrium isotherm

As shown in Fig. 4, there were gradual increases of adsorption for AR 37 and AB 25 until equilibrium at 28 mg/L for both chitosan and chitosan-EGDE beads. The Langmuir, Freundlich and BET models are expressed by Eqs. (3), (4), and (5), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \quad (3)$$

where, Q (mg/g) is the maximum adsorption at monolayer, C_e (mg/L) is the equilibrium concentration of AR 37 or AB 25, q_e (mg/g) is the amount of AR 37 or AB 25 adsorbed per unit weight of chitosan and chitosan-EGDE beads at equilibrium concentration, b (mL/mg) is the Langmuir constant related to the affinity of binding sites and is a measure of the energy of adsorption.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

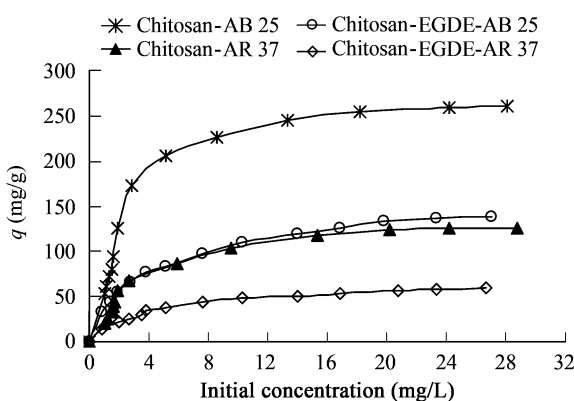


Fig. 4 Adsorption isotherms of AR 37 and AB 25 on chitosan and chitosan-EGDE beads.

where, K_F (mg/g) and n are Freundlich constants indicating sorption capacity and intensity, respectively.

$$\frac{C_e}{(C_i - C_e)(q_e)} = \frac{1}{BQ} + \frac{B-1}{BQ} \times \frac{C_e}{C_i} \quad (5)$$

where, C_i (mg/L) is the saturation concentration of the solute, B is the BET constant expressive of the energy of interaction with surface.

The calculated results of the Langmuir, Freundlich and BET isotherm constants are given in Table 1. It is found that the adsorption of AR 37 or AB 25 on the chitosan and chitosan-EGDE beads were correlated well ($R > 0.99$) with the Langmuir equation.

It has been reported that the effect of isotherm shape with a view to predict if an adsorption system is “favourable” or “unfavourable”. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is expressed by the Eq. (6):

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

Table 2 lists the calculated results. Based on the effect of separation factor on isotherm shape, the R_L values are in the range of 0–1, which indicates that the adsorption of AR 37 or AB 25 on chitosan and chitosan-EGDE beads are favourable.

2.5 Kinetics of adsorption

The pseudo first-order (Eq. (7)), the pseudo second-order (Eq. (8)) adsorption and the intraparticle diffusion model were used to test the experimental data.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where, q_t (mg/g) is the amount of AR 37 or AB 25 adsorbed onto adsorbent at time t . k_1 (min^{-1}) is the rate constant of pseudo first-order adsorption.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Table 2 Separation factor or equilibrium parameter (R_L) based on the Langmuir equation

Dye	Initial concentration (mg/L)	R_L	
		Chitosan	Chitosan-EGDE
AR 37	50	0.1843	0.2914
	100	0.0476	0.6401
	150	0.0508	0.1448
AB 25	50	0.4023	0.1317
	100	0.1957	0.0705
	150	0.1723	0.1869

Table 1 Langmuir, Freundlich and BET isotherm constants and correlation coefficients

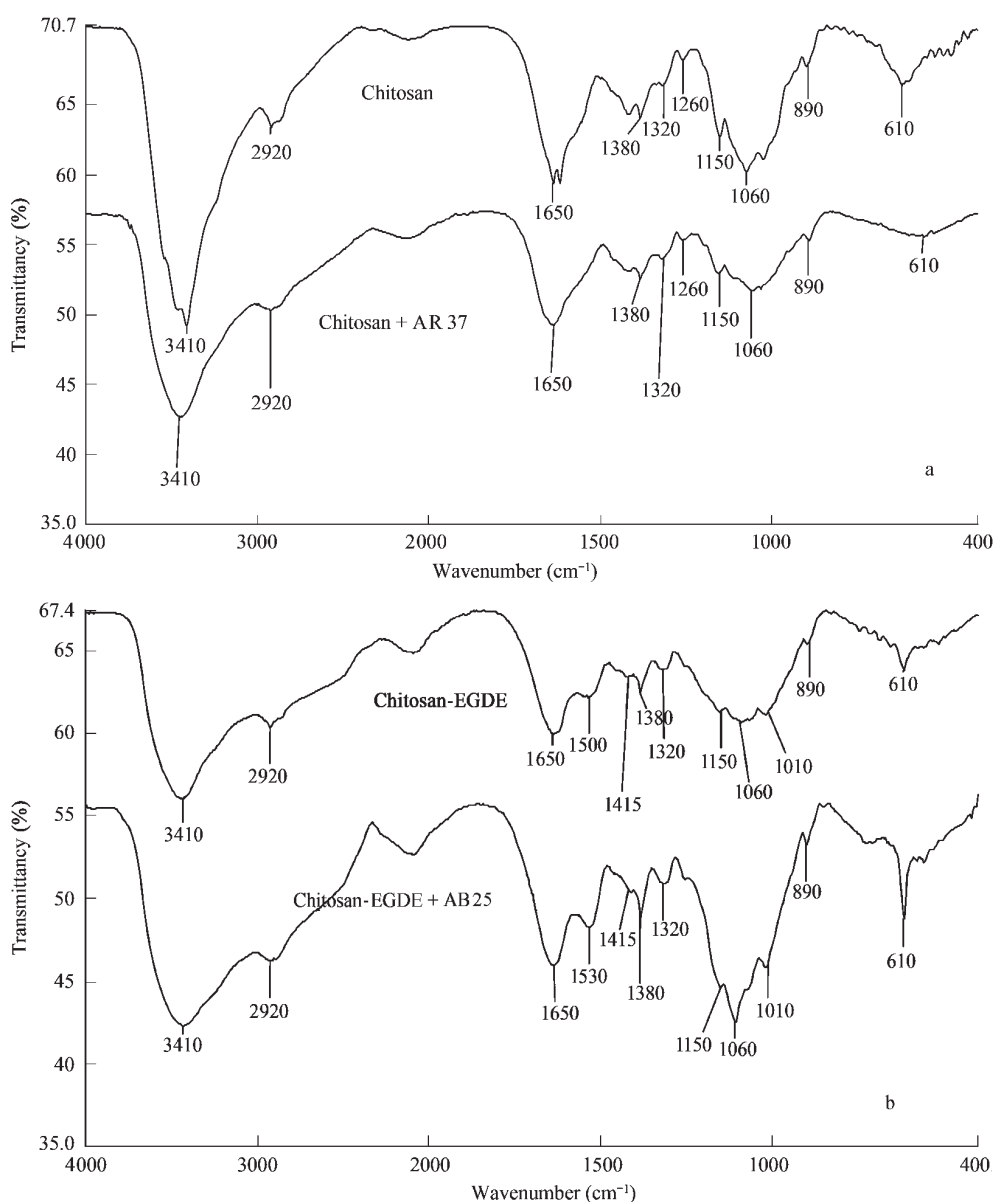
Dye	Beads	Langmuir			Freundlich			BET		
		Q (mg/g)	b (mL/mg)	R	K_F (mg/g)	n	R	Q (mg/g)	B	R
AR 37	Chitosan	128.21	1218	0.9989	97.42	6.18	0.8155	74.57	61.25	0.8843
	Chitosan-EGDE	59.52	2533	0.9995	36.19	7.94	0.9248	21.16	94.83	0.8738
AB 25	Chitosan	263.15	785	0.9984	248.36	3.94	0.8924	203.65	12.32	0.8911
	Chitosan-EGDE	142.86	1496	0.9992	115.98	4.25	0.9582	88.53	47.71	0.9562

Table 3 Kinetic parameters for AR 37 and AB 25 adsorption onto chitosan and chitosan-EGDE beads

Dye	Beads	Pseudo first-order		Pseudo second-order		Intraparticle diffusion	
		$k_1 \times 10^{-2} \text{ (min}^{-1}\text{)}$	R	$k_2 \times 10^{-3} \text{ (g/(mg}\cdot\text{min))}$	R	$k_i \text{ (mg/(g}\cdot\text{min}^{0.5}\text{))}$	R
AR 37	Chitosan	2.69	0.9891	2.33	0.9997	3.14	0.9814
	Chitosan-EGDE	3.42	0.9713	4.74	0.9998	2.28	0.9751
AB 25	Chitosan	1.37	0.9987	1.07	0.9998	5.40	0.9603
	Chitosan-EGDE	1.99	0.9952	1.82	0.9996	4.77	0.9843

Table 4 Desorption of AB 25 from chitosan and chitosan-EGDE beads

Beads	Extractant concentration (mol/L)	Desorption (%)					
		First cycle		Second cycle		Third cycle	
		NaOH	HCl	NaOH	HCl	NaOH	HCl
Chitosan	1.0×10^{-1}	89.3	84.2	84.9	78.4	80.7	71.9
	1.0×10^{-2}	85.6	80.8	81.5	74.0	75.2	68.1
	1.0×10^{-3}	80.7	75.5	76.2	68.5	68.6	57.4
Chitosan-EGDE	1.0×10^{-1}	92.6	86.1	89.6	81.3	83.6	75.2
	1.0×10^{-2}	89.8	85.4	86.4	77.4	81.1	70.0
	1.0×10^{-3}	82.2	77.3	78.4	72.7	74.3	64.5

**Fig. 5** FT-IR spectra of chitosan beads before and after the adsorption of AR 37 (a) and of chitosan-EGDE beads before and after the adsorption of AB 25 (b).

where, k_2 (g/(mg·min)) is the rate constant of pseudo second-order adsorption. The straight-line plots of t/q_t against t have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data. The intraparticle diffusion rate can be described as Eq. (9)

$$q_t = k_i t^{0.5} \quad (9)$$

where, k_i (mg/(g·min^{0.5})) is intraparticle diffusion rate.

Based on the correlation coefficients, the adsorption of AR 37 and AB 25 is best described by the pseudo second-order equation (Table 3). The pseudo first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the pseudo second-order kinetic model assumes that the rate-limiting step may be the adsorption mechanism but not the mass transport. In many cases, the pseudo second-order equation correlates well to dyes sorption studies (Lin *et al.*, 2008; Ponnusami *et al.*, 2008).

2.6 Desorption study

The recovery of adsorbed material, as well as regeneration of adsorbents, is become important (Kalyani *et al.*, 2007; Suksabye *et al.*, 2007). However, only a limited number of dye desorption studies on chitosan and chitosan derivatives have been carried out. In this study, three cycles of adsorption/desorption were performed by using NaOH and HCl solution as the desorption agents. Percentage of desorption of AB 25 from chitosan and chitosan-EGDE beads are listed in Table 4. It can be observed that the percentage of desorption was quite high in all cases. This indicates that the electrostatic attraction probably involves in this study. This result is in accordance with the desorption data reported by Pavan *et al.* (2008), who confirmed that the adsorption of methylene blue onto yellow passion fruit waste was via electrostatic attraction. Chitosan-EGDE beads showed better desorption results than chitosan beads at high concentration of NaOH, due to its mechanical strength and chemical resistance in basic media. According to Chiou and Li (2003), in basic solutions, the positively charged amino group is deprotonated such that the electrostatic interaction between chitosan and dye becomes weaker and then the adsorbed dye leaves the adsorption site.

2.7 FT-IR analysis

Figure 5 represents the FT-IR spectra (400–4000 cm⁻¹) of chitosan and chitosan-EGDE beads before and after adsorption of AR 37 and AB 25. There was no significant change in the adsorption intensity at wavenumbers 3410 cm⁻¹ (–OH stretching vibration), 1650 cm⁻¹ (–NH stretching vibration), 1380 cm⁻¹ (–CH₃ deformation), 1150 cm⁻¹ (C=O stretching), 1060 cm⁻¹ (C–N bend) and 617 cm⁻¹ (–OH bending) after dyes adsorption. This implies that the adsorption processes are physical adsorption and may not involve a chemical interaction. The similar observations had been also reported by Xue *et al.* (2001), Wan Ngah *et al.* (2006), Wan Ngah and Fatinathan (2006) and Dolphen *et al.* (2007).

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