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kappa-Carrageenan beads as new adsorbent to remove crystal violet dye from water: adsorption kinetics and isotherm

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ABSTRACT

K^+-Cross-linked *kappa*-Carrageenan beads were prepared and the dried and wet beads of cross-linked carrageenan were evaluated to remove the cationic crystal violet (CV) dye from water. The kinetics and mechanism of CV adsorption onto both wet and dried carrageenan beads were studied. The effect of contacting time and initial concentration of CV on adsorption was investigated. It was revealed that the rate of dye adsorption and removal efficiency is higher for the wet carrageenan beads. The experimental adsorption data were modeled using pseudo-first-order, pseudo-second-order, and Boyd models. The results showed that the pseudo-second-order adsorption kinetics were predominated for the adsorption of CV onto carrageenan beads. The experimental equilibrated adsorption capacity of carrageenan beads was analyzed using Freundlich and Langmuir isotherm models. The results corroborated that the experimental data followed the Freundlich isotherm the best. No significant change in dye adsorption onto beads was observed by varying the pH of initial dye solution.

Keywords: Carrageenan; Bead; Adsorption; Crystal violet; Kinetics

1. Introduction

Plants and algae biomass are renewable materials resources derived from numerous sources, including the by-products from the timber industry, agricultural crops, raw materials from the forest, and seaweeds. The major component of biomass is polysaccharides [1]. Due to the renewability, biodegradability, biocompatibility, and cost-effective properties of polysaccharides from renewable resources have attracted an increasing amount of attention over the last two decades [2]. Polysaccharides from agricultural crops (cellulose, starch, lingo-cellulose, and pectin), marine algae (carrageenan, alginate, and agar), and crustacean (chitin and chitosan) are widely used in a variety of areas such as food industry, pharmaceutical, wastewater treatment, biotechnology, and cosmetic [3–5].

Carrageenan is a collective term for linear-sulfated polysaccharides produced by alkaline extraction from red seaweed. The types of carrageenans differ only in the position and number of ester sulfate groups which determine their physico-chemical properties,

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e.g. viscosity and gelation characteristics. Carrageenans comprise three main forms: *lambda* (non-gelling), *kappa* (strong gelling), and *iota* (weak gelling) [6]. Scheme 1 shows the repeat unites of the *kappa*-Carrageenan. Because of their exceptional properties, carrageenans are broadly used as ingredients in a variety of applications. They have several major characteristics that make them very useful in many food and non-food applications. They are used as cost-effective stabilizers, thermo-reversible gelling agents, binders, thickeners, texture modifiers, and moisture retainers. There are numerous reviews of their chemistry [7] and applications in foods [8] and drug delivery systems [9]. Since carrageenan is a highly negatively charged polysaccharide, it can interact with species carrying a positive charge. Many reports are published in this regard, such as interaction of carrageenan with univalent and divalent cations [10], with gelatin [11], and with chitosan [12]. *kappa*-Carrageenan needs heating to dissolve in water. Carrageenan beads can be produced after cooling it in the presence of positively charged ions (e.g. K^+, Scheme 1, and cationic polyelectrolyte).

Colored water from many industries like dye, textile, paper, and plastic facilities produce considerable polluted waters. The pollutants must be removed from wastewater before discharging it into the environment. Adsorption process, an inexpensive and simple design, can be used to remove the dye contaminations from aqueous environments [13]. The color pollutants are anionic or cationic molecules. While the adsorption of cationic dyes and other pollutants from water was widely evaluated using biopolymers beads such as alginate, chitin, and chitosan [14,15], but carrageenan beads with excellent properties has not extensively examined to remove of pollutants. In this study, we attempted to prepare carrageenan beads using K^+ cations as cross-linker. The beads in both wet and dried state were examined to remove cationic crystal violet (CV) dye from water. The effect of the contact time and initial concentration of CV on the dye adsorption onto carrageenan beads was investigated. Also, the effect of pH of initial dye solution on adsorption, the effect of temperature on the adsorption, and desorption of adsorbed dye was investigated.

2. Experimental

2.1. Materials

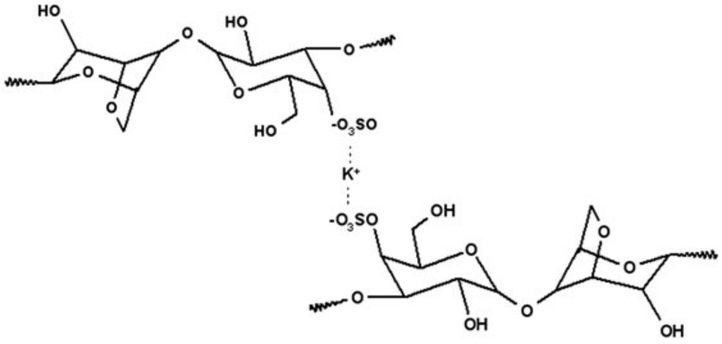
kappa-Carrageenan was obtained from Condinson Co., Denmark and used without any purification. All other ingredients were analytical grades and were used as received.

2.2. Carrageenan beads preparation

One gram of *kappa*-Carrageenan was poured in 40 mL of distilled water and heated at 80°C and stirred until completion of dissolution. Then, the temperature of carrageenan solution was adjusted at 60°C. The beads were formed by dropping the carrageenan solution from a syringe with 2 mm of internal diameter into 1 M of KCl solution at ambient temperature and allowed to stir for 1 h for hardening. The produced beads were collected and washed with distilled water. A part of wet beads were used to remove of CV dye and the remaining beads were dried at ambient temperature to constant weight.

2.3. Dye adsorption

Dye adsorption was carried out by immersing the 0.1 g of dried beads (or 2 g of wet beads) into 50 mL of dye solution with 20 mg/L concentration. All adsorption experiments were examined through a



Scheme 1. Structure of *kappa*-Carrageenan and its cross-linking with K^+ cation.

Fig. 1. Photographs of wet and dried carrageenan beads and carrageenan beads after adsorption of CV.

batch method on a shaker with a constant speed at 120 rpm. To study the adsorption kinetics, at specified time intervals, the amount of adsorbed CV was evaluated using a UV spectrometer at $\lambda_{\max}$ = 590 nm. The content of adsorbed dye was calculated using following Eq. (1):

$$q_t = \frac{(C_0 - C_t)}{m} \times V \tag{1}$$

where C_0 is the initial CV concentration (mg/L), C_t is the remaining dye concentrations in the solution at time t, V is the volume of dye solution used (L), and m is the weight of beads (g). Adsorption isotherm was carried out by immersing of 0.1 g of dried beads (or 2 g of produced wet beads) into 50 mL of dye solutions with 10, 20, 30, 40, 50, 60, 70, and 100 mg/L of CV for 24 h. The equilibrium adsorption capacity of beads, q_e (mg/g), was determined using Eq. (1). At this Eq. the C_t and the q_t will be replaced with equilibrium concentration of dye in the solution (C_e) and equilibrium adsorption capacity (q_e), respectively.

The removal efficiency (RE%) of CV by beads was calculated as bellow:

$$\text{RE\%} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_e is the remaining CV concentration in the solution.

To study the effect of pH on adsorption, the pH of dye solution was adjusted at desired pH using 0.1 M of HCl and NaOH solution. Then, the beads were immersed into 20 mg/L of dye solutions with different initial pHs.

2.4. Desorption–adsorption measurements

For desorption study, the sample containing adsorbed dye was immersed into 50 mL of desorption solution for 5 h at ambient temperature. The desorption solution was prepared from dissolving of KCl in water or ethanol/water mixture (50/50 V/V). The concentration of KCl was 0.5 M. Desorption content was measured using spectrophotometer and according to calibration curves for each desorption solution.

2.5. Characterization

Dried beads was coated with a thin layer of gold and imaged in a SEM instrument (Vega, Tescan). A thermal analyzer (Mettler Toledo) was used for scanning differential calorimetry (DSC) studies. The heating rate was 20℃/min under nitrogen. The FTIR spectra were performed using Bruker Tensor 27 spectrophotometer (KBr pellets).

3. Results and discussion

3.1. Characterization of carrageenan beads

Fig. 1 indicates the photographs of wet and dried carrageenan beads as well as the carrageenan beads after adsorption process. The dark blue color appears after adsorption of CV onto carrageenan beads that confirms the adsorption of cationic CV dye onto carrageenan beads. The FTIR spectra of pristine carrageenan powder and K^+-Cross-linked carrageenan beads are illustrated in Fig. 2. The spectrum of carrageenan powder (Fig. 2(a)) shows characteristic bands at 3,000–3,430 and 1,373 cm^{-1} due to the of O–H and sulfate stretch, respectively. The peaks at 1,026, 928, and 842 cm^{-1} are attributed to the glycoside linkage, 3,6-anhydro-D-galactose, and C–O–S in galactose segments, respectively. Compared with the FTIR of carrageenan powder, the beads showed similar peaks and no significant changes were observed (Fig. 2(b)).

The SEM images of pristine carrageenan powder and dried carrageenan beads are shown in Fig. 3. The microstructure of pristine carrageenan powder (Fig. 3(a)) showed a smooth surface. Compared with

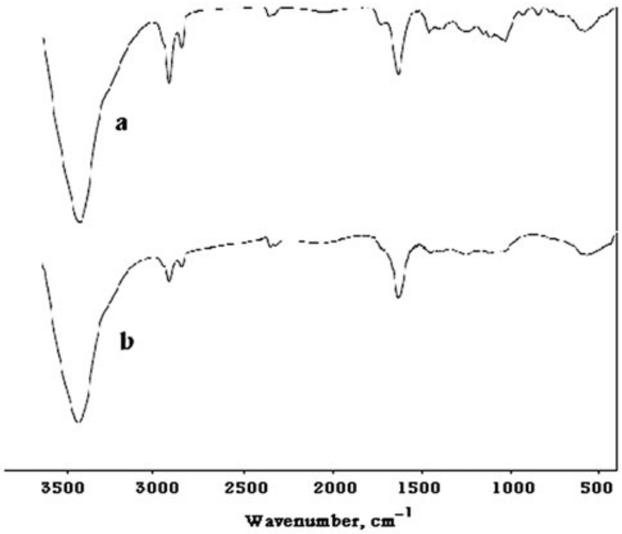


Fig. 2. FTIR of (a) intact carrageenan and (b) K$^+$-Cross-linked carrageenan beads.

the carrageenan powder, the dried K$^+$-Cross-linked beads indicated a slightly undulant, rough, and coarse surface (Fig. 3(b)).

According to FTIR and SEM results, a suitable reason to confirm the cross-linking of carrageenan was not observed. So, we used the DSC technique for studying the thermal behavior of carrageenan powder and K$^+$-Cross-linked carrageenan beads. The DSC thermograms of carrageenan powder and cross-linked carrageenan are shown in Fig. 4. The DSC of intact carrageenan showed a glass transition around 72℃ (Fig. 4(a)). Two additional endothermic peaks were observed for carrageenan powder that may be attributed to the melting and thermal decomposition of *kappa*-Carrageenan. The DSC thermogram of K$^+$-cross-linked carrageenan is shown in Fig. 4(b). No glass transition was obtained for carrageenan beads from 30 to 190℃. A sharp peak around 183℃ was observed that may be attributed to the K$^+$ cations–carrageenan interactions. The difference in DSC thermograms of intact carrageenan and K$^+$-Cross-linked carrageenan beads may confirm the cross-linking of carrageenan with K$^+$ cations. A similar observation has been reported by Mohamadnia et al. [16].

3.2. *Adsorption kinetics*

The effect of contact time on the adsorption of CV dye onto beads was investigated through batch method. The beads were immersed into 20 mg/L of CV dye solution at ambient temperature. The amount of dye adsorption onto beads was increased and then

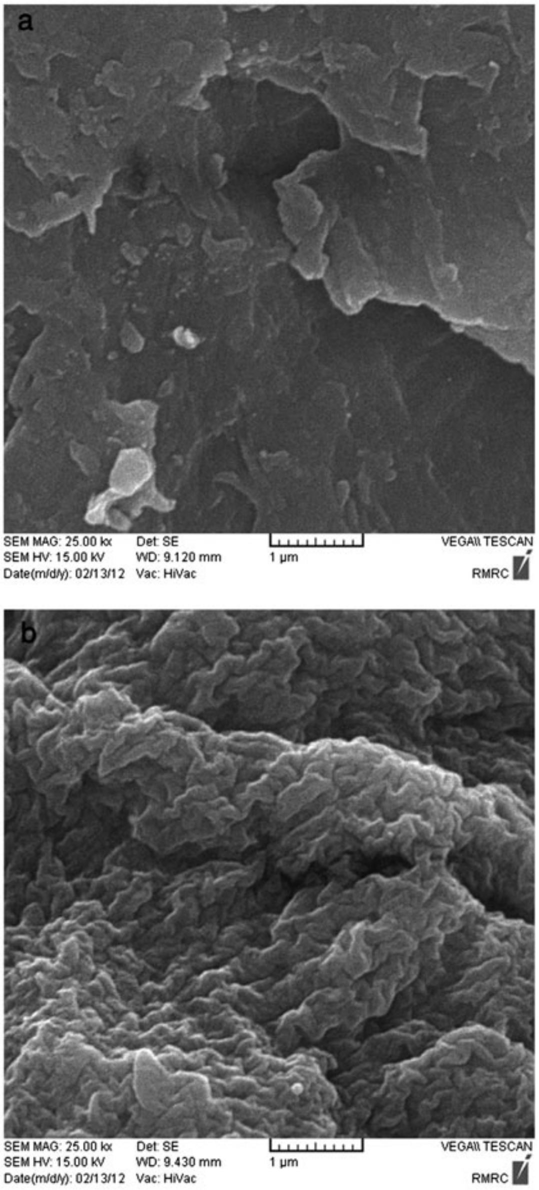


Fig. 3. SEM micrographs of (a) carrageenan powder and (b) K$^+$-Cross-linked carrageenan beads.

begun to level off. A significant difference in dye adsorption content and rate was observed for samples (Fig. 5(a)). In fact, state of the beads can affect the dye adsorption speed and capacity of beads. It was observed that the dye adsorption rate and capacity onto wet beads is higher than that of dried beads. According to degree of swelling of beads in water, the swelling capacity of dried and wet beads was 7.2 and 10 g water/g beads, respectively. The decrease in water absorbency of beads after drying can be attributed to this fact that the drying of wet beads can lead to a rigid and stable matrix [16]. The rigid structure of

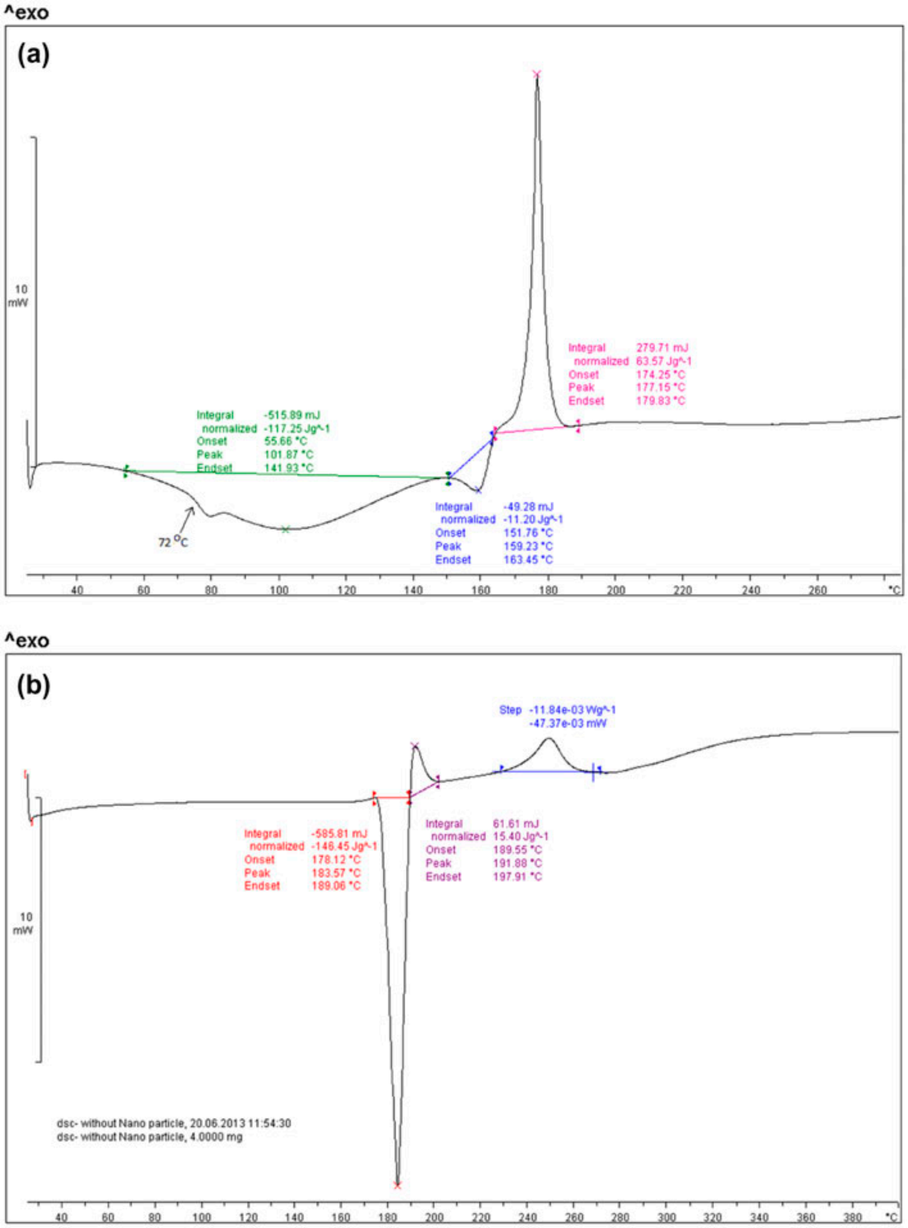


Fig. 4. DSC thermograms of (a) intact carrageenan and (b) K^+-Cross-linked carrageenan beads.

carrageenan beads restricts its expansion to uptake water. So, in compared to wet beads, a decrease in surface area of dried beads is observed that originated from rigid structure. Increase in surface area results in an enhancement in dye adsorption capacity. The lower dye adsorption capacity of dried sample can be attributed to smaller size of dried bead in swollen state. Also, the decrease in dye adsorption speed of dried beads can be due to the fact that the drying of wet beads causes a rigid and stable matrix with small pore size [17]. The removal efficiency of dye by wet and dry beads was obtained 83 and 62%, respectively.

Studying of adsorption kinetics represents the pollutant adsorption rate, which dominates the time of adsorbate adsorption at the solid–liquid surface. In fact, kinetic of adsorption is one of the many factors for finding the efficiency of adsorption. Pseudo-first-order and pseudo-second-order kinetics models were examined to obtain rate constant and equilibrium adsorption capacity for carrageenan beads. So, kinetics data were analyzed by using the pseudo-first-order equation as below [18]:

$$\ln(q_e - q_t) = \ln q_{e1} - k_1 t \tag{3}$$

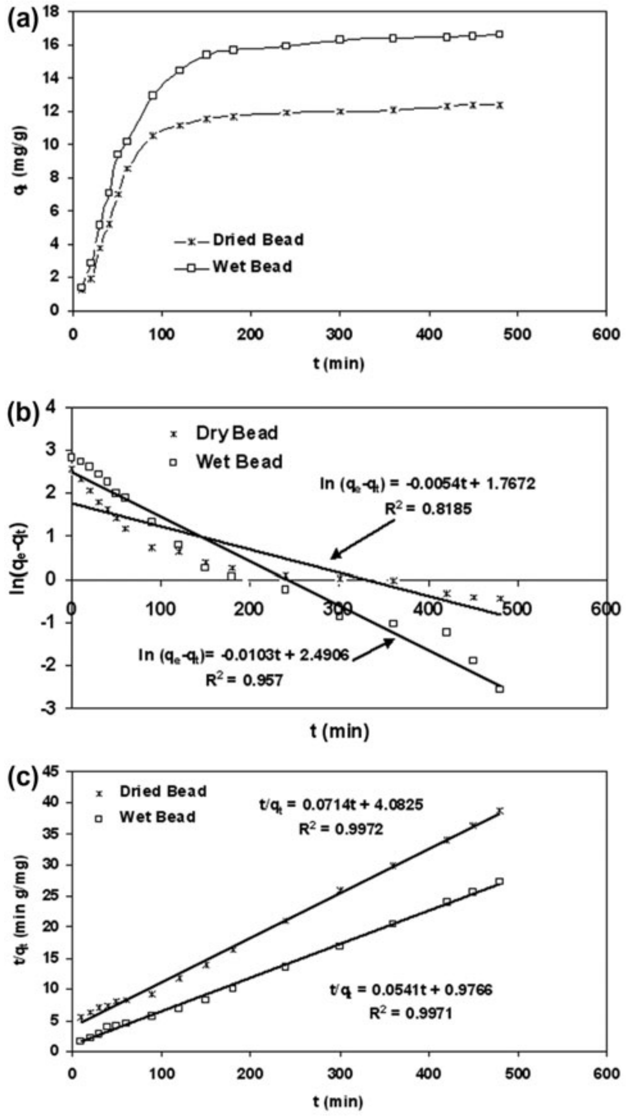


Fig. 5. (a) Effect of contacting time on the removal of CV by wet and dried carrageenan beads. (2 g of wet beads and 0.1 g of dried beads in 50 mL of CV solution with 20 mg/g concentration); adsorption kinetics of the CV onto wet and dried carrageenan beads according to (b) pseudo-first-order model, and (c) pseudo-second-order model.

where, q_e and q_t (mg/g) are the amount of adsorbed dye on the beads at equilibrium and at time t, respectively. k_1 (min^{-1}) and q_{e1} (mg/g) are the pseudo-first-order rate constant and theoretically equilibrium adsorption for the adsorption process, respectively. The k_1 (slope) and q_{e1} (intercept) can be calculated from the linear plot of $\ln(q_e - q_t)$ against t (Fig. 5(b)).

Also, kinetics data were analyzed by using the pseudo-second-order equation as below [18]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_{e2}}^2} + \frac{t}{q_{e2}} \tag{4}$$

where, k_2 (g/mg.min) is rate constant of pseudo-second-order adsorption and q_{e2} is the theoretical equilibrated adsorbed dye (mg/g) that can be calculated from pseudo-second-order. In order to obtain the model calculations k_2 and theoretically equilibrium adsorption (q_{e2}) as well as R^2 (correlation coefficient), we can plot $\frac{t}{q_t}$ against t (Fig. 5(c)). Model calculations for beads were given in Table 1. It was found that the plot of $\frac{t}{q_t}$ against t gives a straight line with a high correlation coefficient ($R^2 > 0.99$) and it can be concluded that adsorption kinetics of dye by both beads has the best fitting to the pseudo-second-order. As can be seen from the data, according to pseudo-second-order kinetics, the theoretical equilibrium adsorption capacities are in agreement with the experimental data.

The adsorption of adsorbate on the surface of the adsorbent can take place through several steps. The steps may be considered as film diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface [19]. In fact, under sufficient speed of stirring, intraparticle diffusion/transport process is the rate-limiting step of adsorption kinetics [20]. The possibility of intraparticle diffusion can be explored according to Eq. (5):

$$q_t = k_{id} t^{0.5} + C \tag{5}$$

where q_t is the amount of dye adsorbed at time t, C is the intercept, and k_{id} is the intraparticle diffusion rate constant (mg $\text{min}^{0.5}$/g).

According to Eq. (5), by plotting q_t vs. $t^{0.5}$, a straight line suggests that the intraparticle diffusion is the rate limiting step. As can be seen from Fig. 6, the diffusion plot of CV onto carrageenan beads is multilinear containing two linear parts. The linear segments did not pass through the origin, indicating that the intraparticle diffusion is not the only rate limiting step. The first linear segment shows that the mass transfer controlling may be due to boundary layer effect [21]. In order to determine exact mechanism of adsorption, experimental data were analyzed according to Boyd's model [22]:

$$F = 1 - \frac{6}{\pi^2} \exp(-\text{Bt}) \tag{6}$$

where F ($F = \frac{q_t}{q_e}$) is the fractional attainment of equilibrium at different times, t, and Bt is a mathematical function of F. The value of Bt can calculate according to Eq. (7):

Table 1
Kinetic parameters for adsorption of CV onto wet and dried carrageenan beads

	Pseudo-first-order			Pseudo-second-order			
	$k_1 \times 10^{-3}$ (min^{-1})	q_{e1}, theo. (mg/g)	r^2	$k_2 \times 10^{-3}$ (g/mg.min)	q_{e2}, theo. (mg/g)	r^2	q_e. Exp. (mg/g)
Wet beads	10.3	11.86	0.957	2.99	18.48	0.9971	16.64
Dry beads	5.4	5.7	0.818	1.24	14	0.9972	12.4

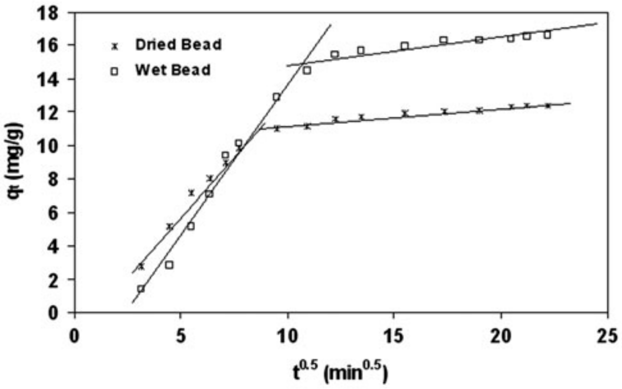


Fig. 6. Intraparticle diffusion kinetics of CV dye onto wet and dried carrageenan beads.

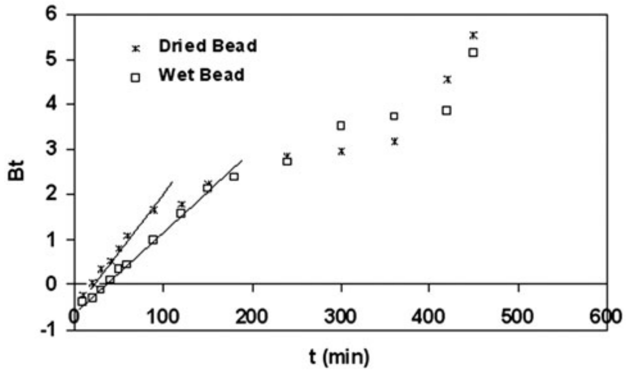


Fig. 7. Boyd plot for adsorption of CV dye onto wet and dried carrageenan beads.

$$\mathrm{Bt} = -0.4977 - \ln(1 - F) \tag{7}$$

The values of Bt can be calculated from F values at each time. The Boyd plot can achieve by plotting of Bt vs. t. A straight line passing through the origin is indicative of sorption process governed by intraparticle diffusion mechanism. Non-linear plot shows that the adsorption dominates by film diffusion [22]. Fig. 7 illustrates the plot of Bt vs. t. According to Fig. 7, the beginning of plot is straight linear and then deviates from origin. In can be concluded that the first time of adsorption obeys layer boundary effect and then the intraparticle diffusion dominates the mechanism of adsorption [22].

3.3. Adsorption isotherm

The adsorption of CV onto beads as a function of initial dye concentration was studied by immersing the beads in dye solutions with concentrations ranging from 10–100 mg L^{-1}. Initially, as the concentration of CV in solution was increased, the amount of adsorbed dye by beads enhanced and, at high concentration of CV, begun to level off. This indicates that the adsorbent gradually became saturated and approached a state of maximum adsorption. In fact, when the beads are reached a saturated state, there are no more vacant adsorption sites and the adsorption capacity remains constant. Fig. 8 shows the effect of initial dye concentration on the equilibrium adsorption values onto wet and dried beads.

The interactions between adsorbate and adsorbent until a state of equilibrium can be studied using adsorption isotherms. The adsorption isotherms describe the optimized adsorption system as well as the effectiveness of adsorbents. In fact, it is important to investigate to obtain an optimum isotherm model indicating the CV adsorption system onto beads. The

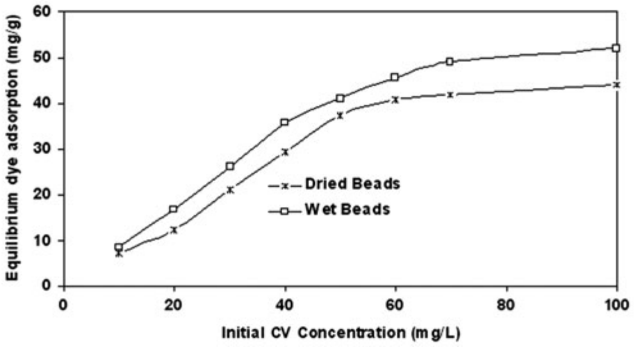


Fig. 8. Effect of initial CV concentration on adsorption capacity of wet and dried carrageenan beads.

practical data were fitted to the Langmuir and Freundlich models. In the Langmuir adsorption model, adsorption of adsorbate takes place at specific homogeneous sites within the adsorbent and valid for monolayer adsorption onto adsorbents. The expression of the applied Langmuir model is given by Eq. (8) [23]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \tag{8}$$

where C_e is the equilibrium dye concentration in the solution (mg L^{-1}), b is the Langmuir adsorption constant (L mg^{-1}), and q_m is the theoretical maximum adsorption capacity (mg g^{-1}). The q_m and b can be calculated from the slope and intercept of a linear plot of $\frac{C_e}{q_e}$ vs. C_e, respectively.

In the Freundlich model, the adsorption of adsorbate occurs on a heterogeneous surface by multilayer sorption and the adsorption capacity can increase with an increase in adsorbate concentration [24]. Freundlich isotherm is represented by the following equation:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{9}$$

where k_f is the equilibrium adsorption coefficient ($mg^{(1-n)} L^n g^{-1}$) and $1/n$ is the empirical constant. The k_f and n values for beads can be achieved from the intercept and the slope of plot of log q_e against log C_e (Fig. 9). All the expressions in Langmuir and Freundlich equations and equilibrated dye adsorption of beads were calculated according to experimental data and summarized in Table 2. In accordance, the high correlation coefficient in Freundlich equation ($R^2 > 0.94$), it depicts that Freundlich isotherm has the best fit on experimental data than the Langmuir model. Considering the results, it is concluded that the adsorption of CV onto carrageenan beads takes place through heterogeneous surface by multilayer sorption. In Freundlich model, when n values being between 1 and 10, the removing process will be beneficial adsorption [25]. The n values for both beads are bigger than one and indicate that Freundlich model is favorable for this system. Also, the k_f values for beads are comparable. While the k_f value of dried beads is 4.86, it is 8.8 for wet beads. This result indicates that the intensity of the adsorbate onto wet bead is preferred. The maximum dye adsorption capacity of carrageenan beads at this study and some other adsorbents is compared in Table 3. The results indicate that the adsorption capacities of both wet and dried carrageenan beads are comparable with other adsorbents.

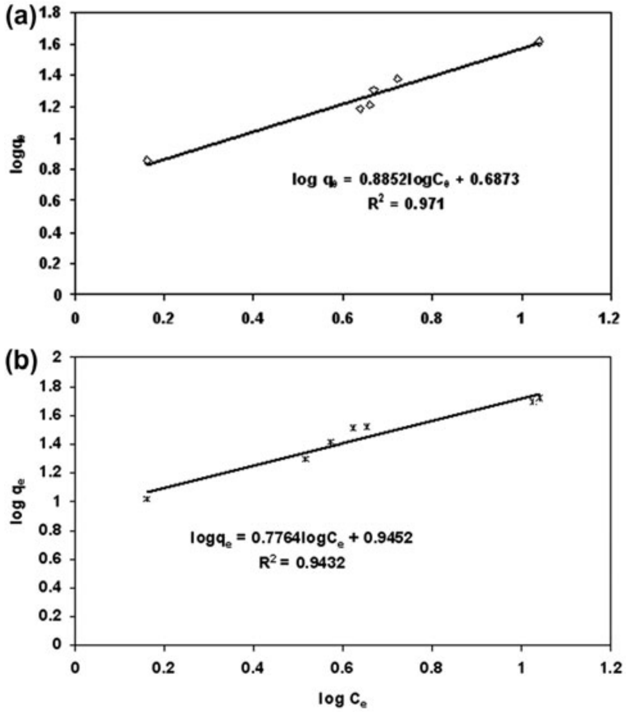


Fig. 9. Freundlich isotherms for CV adsorption onto (a) dried and (b) wet carrageenan beads.

The favorability of the adsorption (R_L) was evaluated from parameters of Langmuir adsorption isotherm model. The R_L can calculate from the following equation [25]:

$$R_L = \frac{1}{1 + bC_o} \tag{10}$$

Table 2
Adsorption isotherm constants of adsorption CV onto carrageenan beads

	Langmuir model			Freundlich model			
	q_m, mg/g	$b \times 10^{-3}$, L/mg	R^2	n	k_f, $mg^{(1-n)} L^n g^{-1}$	R^2	R_L
Dried	277	26	0.105	1.13	4.86	0.971	0.79
Wet	625	7.75	0.007	1.28	8.8	0.943	0.99

Table 3
Maximum adsorption capacity of some adsorbent and carrageenan beads to remove CV dye

Adsorbent	Maximum dye adsorption, mg/g	Reference
Wollastonite	8.8	[26]
Semi-IPN hydrogel	35	[27]
Magnetic nanocomposite	81.7	[28]
Bagasse fly ash	26.2	[29]
Raw kaolin	44.8	[30]
Carrageenan wet beads	52	This study
Carrageenan dried beads	44	This study

where b is the Langmuir constant (L/mg) and C_o is the initial concentration of dye. The R_L can vary: for $R_L > 1$ the adsorption is unfavorable; $R_L = 1$ the adsorption is linear condition; the adsorption is favorable when $0 < R_L < 1$; and $R_L = 0$ is for irreversible conditions [31]. According to Table 2, the R_L values for beads were achieved between zero and one indicating favorable adsorption of CV onto beads.

3.4. Effect of pH on adsorption

Removal of adsorbate from aqueous solution onto adsorbent is influenced by the pH of aqueous solutions. In fact, by the changing the pH of solution, the nature of active center on the adsorbent can change and finally affect the adsorption behavior of adsorbate [32]. *kappa*-Carrageenan is an ionic polysaccharide comprising sulfate groups ($-OSO_3^-$). These pendants are completely dissociated in the overall pH range and the hydrogels from this biopolymer show pH-independent swelling behavior [33]. In fact, in the overall pH range, these anionic groups are in dissociated form. Fig. 10 shows the effect of pH of initial dye solution on the adsorption of CV onto beads. As it is seen from the figure, the change in dye adsorption of both beads was not considerable as the pH of solution was changed. This observation can be attributed to pH-independent behavior of *kappa*-Carrageenan component. A slightly decrease in dye adsorption was observed at acidic pHs and it may be attributed to H^+ screening effect on the sulfate groups [16]. Because of this behavior, the carrageenan beads may be considered as new adsorbent to remove cationic dyes from aqueous solution in the overall range of pHs.

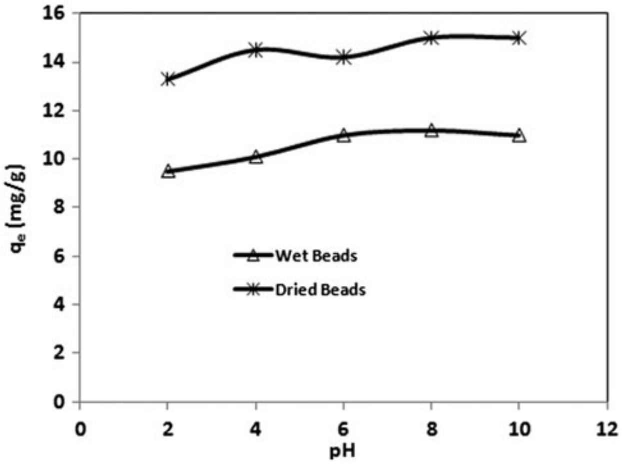


Fig. 10. Effect of pH on the adsorption of CV onto wet and dried beads.

3.5. Thermodynamic studies

The effect of temperature on the dye adsorption capacity of dried beads was studied. The changing in dye adsorption was explained according to thermodynamic parameters. Adsorption enthalpy (ΔH, kJ mol^{-1}), adsorption free energy (ΔG, kJ mol^{-1}), and adsorption entropy (ΔS, J K^{-1} mol^{-1}) can be calculated according to the following equations [34]:

$$K_d = \frac{C_d}{C_e} \tag{11}$$

$$\Delta G = -RT \ln K_d \tag{12}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

where K_d is the equilibrium constant; C_d is the dye adsorbed onto beads (mg L^{-1}), and C_s is the equilibrium concentration (mg L^{-1}); R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). According to Eq. (13), by plotting the $\ln K_d$ vs. $1/T$, we can obtain the ΔH and ΔS from slope and intercept of curve, respectively (Fig. 11). The results are summarized in Table 4. The negative ΔG values for beads indicate the spontaneous adsorption of CV onto beads. The beads indicated an enhancement in dye adsorption as the temperature was increased. These observations at high temperatures depict more favorable adsorption of CV onto carrageenan beads at high temperatures. According to ΔH value, the adsorption process for adsorption of CV onto beads was exothermic. Also, the positive value of ΔS for beads suggests an increase in degree of freedom of the adsorbed species on beads.

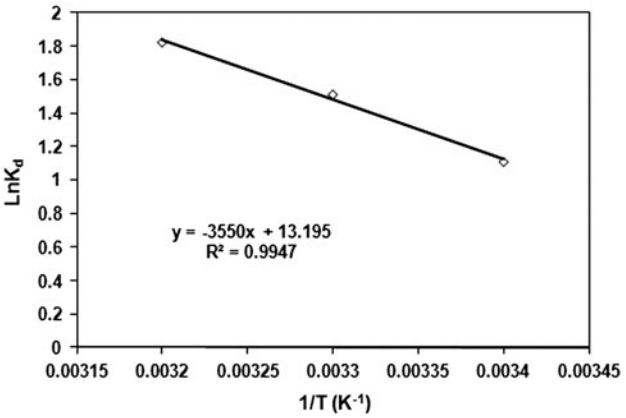


Fig. 11. Plotting of $\ln K_d$ vs. $1/T$ to obtain thermodynamic parameters.

Table 4
Thermodynamic constants of adsorption of CV onto dried beads

T (K)	ΔG kJ mol^{-1}	ΔS J K^{-1} mol^{-1}	ΔH kJ mol^{-1}	R^2
293	−2.68	109	29.5	0.9947
303	−3.8			
313	−4.73			

The ΔH values can suggest the mechanism of adsorption of dye onto adsorbent [27]. The ΔH values lower than 20 kJ mol^{-1} depicts that the physisorption interactions such as van der Waals are dominated. The ΔH values ranging from 20 to 80 kJ mol^{-1} indicates that the physisorption interaction such as electrostatic lead to adsorption of adsorbate onto adsorbent. The chemisorption interaction occurs when the ΔH values are between 80 and 450 kJ mol^{-1}. The enthalpy value for the adsorption of CV onto beads was obtained higher than 20 kJ mol^{-1}. According to the ΔH value for beads, the positive CV dye molecules adsorb electrostatically by sulfate groups on carrageenan beads.

3.6. Desorption study

To evaluate the possibility of reusing of carrageenan beads over multiple cycles, desorption of adsorbed dye was examined using KCl solutions. About 0.5 M of KCl solution in water and water/ethanol (50/50 V/V) was contacted with the beads containing adsorbed CV dye. While desorption efficiency was obtained to be 56% using 0.5 of KCl solution in water, desorption efficiency was achieved to be 91% in 0.5 M KCl solution in water/ethanol. Using 0.5 M of KCl in 50/50 ethanol/water desorption solution, the adsorption–desorption process was examined four times and the results indicated that the removal efficiency has a reduction of about ~16% (Fig. 12).

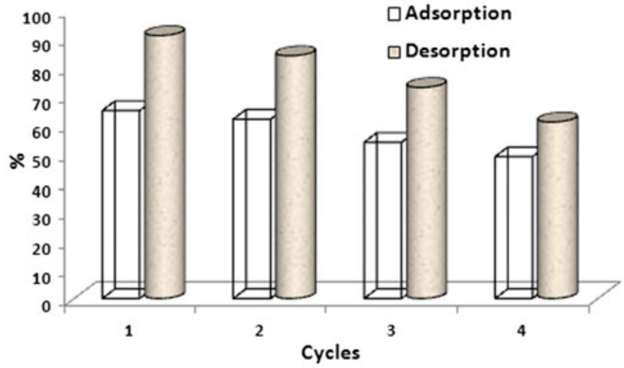


Fig. 12. The adsorption and desorption efficiencies of dried carrageenan beads in consecutive four adsorption–desorption cycles.

4. Conclusions

K^+-Cross-linked carrageenan beads were prepared and both the wet and dried beads were evaluated for adsorption of CV dye onto beads. The beads were efficient for the adsorption of CV dye from aqueous solutions in overall pH range. The adsorption was reached at equilibrium after ~110 min. The kinetics of dye adsorption were analyzed and it was concluded that the pseudo-second-order adsorption kinetics are predominated for the adsorption of CV onto beads. Freundlich model was obtained as the best model for the adsorption of CV onto beads. The effect of pH on the adsorption capacity of beads for CV dye was pH-independent. The thermodynamic parameters revealed the spontaneous adsorption of CV onto beads.

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