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Removal of reactive dyes by a solid waste product from food processing: crayfish carapace

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ABSTRACT

Crayfish carapace micropowder (CM), an economical and environmentally benign material, was used as adsorbents to remove reactive black 5(RB-5) and reactive yellow K-4G (RY-K4G) textile dye from aqueous effluents. The batch adsorption system was evaluated in relation to pH, ionic strength, contact time, initial dye concentration and temperature. Combined alkaline and acidic condition, the absorption capacity was enhanced. Ninety percent of the dyes could be removed by CM when the adsorption experiment was carried out under pH 10 for 2 h and then pH 2 for 30 min. The exothermic adsorption of both dyes onto CM was better fit by the pseudo-second-order kinetic. The adsorption isotherms of RB5 followed the Langmuir model, while that of RY-K4G fitted the Freundlich model, with their maximal adsorption capacity of 285and 1299 mg g^{-1}at pH 2 and 303 K. The possible mechanism was proposed that nucleophilic addition or substitution occurred between CM and reactive dyes under alkaline condition and then electrostatic adsorption appeared between CM and reactive dyes in the acid condition. The adsorption capacity of this low-cost adsorbent is much larger than other adsorbents. Meanwhile, the used adsorbents were successfully applied to adsorb a cationic dye directly at a particular condition in the secondary adsorption. CM can be an economical and promising adsorbent in the wastewater treatment.

Keywords: Crayfish carapace; Reactive dyes; Nucleophilic substitution or addition; Electrostatic adsorption; Secondary adsorption; Chitin

1. Introduction

Nowadays, environmental contamination associated with the dyes present in wastewater arising from the rapid development of modern industries such as dyeing, printing, textile, leather, and coating has drawn much attention. It is estimated that more than 70,000 tons of synthetic dyes are discharged in effluent in the world every year and the dyes used in the textile industry account for 30% [1]. More than 50% of the cotton that occupies the number one position in the textile fibers is dyed with reactive dyes [2]. However, about 10–60% of reactive dyes are lost during the textile dyeing, producing large amounts of colored

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wastewater [1]. The dye-containing wastewater will lead to reduced photosynthetic activity by macrophytes through impeding light penetration, thus adversely affecting the aquatic environment. In addition, synthetic dyes will cause allergy, dermatitis, skin irritation [3], even provoke cancer and mutation [4] in humans. However, reactive dyes are usually difficult to be biodegraded under the natural aquatic environment due to their complex molecular structure [5]. This has resulted in an increased demand for eco-friendly technologies to remove dyes from aqueous effluents [6].

Adsorption is one of the most efficient and economical techniques among adsorption, flocculation, oxidation, and electrolysis [7] employed for the removal of dyes from wastewater [8,9]. Due to the high operational cost, activated carbon, the most effective and commonly used adsorbent, cannot be widely used to eliminate dyes in developing countries. Therefore, developing economical adsorbents to treat dyes wastewater has attracted a great interest in recent years. Recently, many nonconventional, low-cost adsorbents, especially the agricultural residues including pine powder [5], hen feather [10–12], bottom ash [13], de-oiled soya [14], bottom ash and de-oiled soya [15], *Spirulina platensis* [16], coir pith [17], bottom ash and de-oiled soya [18–20], and chemically modified straw [21] have been investigated for the removal of dyestuff.

Crayfish carapace is an abundant waste product from food processing with a great amount being generated annually in China. It is mainly composed of protein, calcium carbonate, and chitin. Its biomass contains a variety of functional groups such as amido, hydroxyl, phosphate, and other charged groups that can mediate pollutant binding. Earlier studies have proved that it was a highly efficient natural material for the removal of heavy metals [22]. In spite of this, there are no studies currently available on the use of crayfish carapace for the removal of textile dyes.

In this work, the crayfish carapace micropowder (CM) was used to eliminate two reactive dyes, reactive black 5(RB5), and reactive yellow K-4G, from aqueous solutions. The fundamental adsorption behaviors of CM for RB5 and RY-K4G, including the pH effect, ionic strength, adsorption isotherms, kinetics, and desorption were investigated to obtain the largest adsorption capacity of CM. It turned out to be an economical adsorbent with high adsorption capacity.

Furthermore, after saturated sorption of reactive dyes, regeneration and reuse of the disused sorbent is also a problem in wastewater treatment. Conventionally, large amounts of solvent are used to wash and recover adsorbents. However, the generated waste eluent usually requires further treatment to avoid secondary pollution. In consideration of these disadvantages, recently, a novel way to make use of the used adsorbents has been raised in the reported literatures [23]. Since the surface structures of adsorbents have been changed after adsorption of some contaminant, the used adsorbents can be applied to adsorb other pollutants in suitable conditions. In this work, the final anionic dyes loaded adsorbents were successfully employed for the removal of a cationic dye, methylene blue (MB).

2. Methods

2.1. Materials

Crayfish carapace (red swamp crayfish) from fresh water aquaculture was collected from a fair trade market (Huazhong Agricultural University in Wuhan, China). The entire crayfish carapace was selected and washed with running water, then dried at 105℃ for 2 h without any further chemical treatment. The dried crayfish carapace was crushed and sieved to desired mesh sizes varying from 10 to 100 μm. The resulting powder was crayfish CM and stored in an airtight container for further use. No other chemical or physical treatments were applied prior to adsorption experiments.

To obtain the decalcified CM (dCM), the CM were immersed in 1 mol L^{-1}HCl for 6 h to remove minerals and then rinsed with distilled water until the wash-solution was neutral [24]. To obtain the chitin sample, the dCM sample was then treated by 11 mol L^{-1}NaOH at 100℃ for 3 h to remove protein [25] and washed with distilled water. Subsequently, the obtained residue was dried for 12 h at 50 ± 1℃ and then sieved to appropriate mesh size.

Reactive black 5 dye (RB-5) and reactive yellow K-4G(RY-K4G) were obtained from Sigma–Aldrich (Switzerland) as a commercially available textile dye, with 80% dye content, and used without further purification.

2.2. Instrument analysis

The surface morphologies of CM and dCM were observed directly with a scanning electron microscope (Type SSX-550; ShimadzuCo; Japan). The range of initial solution pH was 2.0–12. CM was characterized according to the centesimal chemical composition and energy dispersive X-ray spectroscopy (Pioneer). The surface analyses and porosity were carried out with a volumetric adsorption analyzer (Nova 1000, Quantachrome Instruments) at 77 K.

2.3. Adsorption studies

The influence of pH on the adsorption of RB5 and RY-K4G onto CM were conducted. Both the initial concentration of RB5 and RY-K4G solutions were approximately 1,000 mg L^{-1}. About 0.2 g adsorbent was added into 50 mL RB5 dye, and 0.1 g adsorbent was added into 50 mLRY-K4G dye. Since the initial pH of dyes was neutral, after the addition of CM, the pH increased to nearly 10 immediately and the pH was constant because calcium carbonate possesses the buffer capacity. When the dyes were adsorbed for 2 h, the pH of the solution was adjusted to desired pH using HCl or NaOH and was controlled with them during the sorption experiments. So the dyes were adsorbed under the pH 10 for 2 h and then adsorbed under the desired pH for 24 h at 303 K to achieve adsorption equilibrium. The pH range of RB5 and RY-K4G solution was between 2.0 and 12. The initial and final RB5 and RY-K4G concentrations were determined using Vis spectrophotometer (Type 7200; UnicoCorp; China) at fixed wavelengths of 598 and 420 nm, respectively. The amount of adsorption in batch experiments, q (mg g^{-1}), was calculated according to the following equation:

$$\mathrm{Q} = \frac{(C_o - C_e) \times V}{\mathrm{m}} \tag{1}$$

where C_o and C_e (mg L^{-1}) are the initial and final concentration of dyes, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

2.4. Adsorption equilibrium study

The adsorption equilibrium was studied at different temperatures: 303, 323, and 343 K, respectively. The concentration of RB5 aqueous solution ranged from 500 to 1,300 mg L^{-1}, whereas the concentration of RY-K4G aqueous solution ranged from 800 to 1,600 mg L^{-1}. The dyes were adsorbed under the pH 10 (the pH was constant because calcium carbonate possess the buffering capacity) for 2 h and then adsorbed under the pH 2 (the pH was constant during this period) for 30 min to achieve adsorption equilibrium.

Equilibrium biosorption isotherm is the most important design parameter that describes how the adsorbate interacts with the biosorbent. In order to obtain information about the interaction between reactive dyes and CM, Langmuir, Freundlich, Dubinin–Radushkevich and Sips models were used to fit the experimental data.

The Langmuir isotherm model is based on an idealized assumption of identical sorption heat and monolayer sorption [26]. The linear form of Langmuir equation is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_L b_L} + (\frac{1}{q_L})C_e \tag{2}$$

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, q_L (mg g^{-1}) is the theoretical saturate adsorption capacity in the Langmuir model, and b_L (L mg^{-1}) is the Langmuir isotherm constant reflecting the tendency of adsorption.

The Freundlich model is an empirical model for a heterogeneous system. It describes reversible sorption and is not restricted to the formation of the monolayer [27].

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{3}$$

where K_F is the Freundlich isotherm constant and n^{-1} is the heterogeneity factor.

The Sips model was also applied in the current study and could be considered a combination of the Langmuir and Freundlich equation [16]. The Sips isotherm model is represented as

$$q_e = \frac{q_m (bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \tag{4}$$

where q_m (mg g^{-1}) is the amount of dye adsorbed at equilibrium, b (L mg^{-1}) is the median association constant, and n^{-1} is the heterogeneity factor.

The D–R isothermal model is employed to determine the nature of the bio-sorption processes. The linear equation of the D–R model is given as

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{5}$$

where q_m (mg g^{-1}) is the theoretical saturation capacity, K is the constant related to the mean free energy of adsorption, and ε is the Polanyi potential $\left(\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)\right)$. The D–R constant can provide valuable information on the mean energy of adsorption through the following equation [28]:

$$E = (2K)^{-1/2} \tag{6}$$

2.5. Adsorption kinetics study

For the kinetics studies, a set of standard joint-stopper conical flasks were used. The kinetics studies were conducted in the dyes of three different concentrations with initial pH 7. A definite amount W (0.1 g) of CM sample was added into each flask (capacity 150 mL). Then, a definite volume V (50 mL) of dye solution of known concentration C_o was added into each flask. The time of addition was noted by a stopwatch. The flasks were then shaken on a horizontal constant-temperature shaker at 180 rpm, 30 ± 1℃. At different interval of time, each flask was taken away and the biomass and adsorbed dyes were removed of the liquid through a filtration with Whatmann Filter Paper No. 40, which did not present interaction with the dyes and the concentration of dyes was determined. All the experiments were carried out in replicate (three times for each experiment). In order to investigate the adsorption mechanisms further, three popular kinetic models were applied to fit the experimental data.

The pseudo-first-order model developed by Langeren [29] assumed that the sorption rate decreased linearly as the sorption capacity increased. The pseudo-first-order model is given as:

$$\ln(q_e - q_t) = \ln q_e - k_{1t} \tag{7}$$

The pseudo-second-order kinetic model assumed that the rate-limiting step was the interaction between two reagent particles [30]. This model is usually used to describe a chemical sorption. Its linear form is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e^2}} + \frac{t}{q_e} \tag{8}$$

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

The intraparticle diffusion equation is introduced to indicate the behavior of intraparticle diffusion as the rate-limiting step in biosorption [31]. The intraparticle equation could be described as:

$$qt = k_p t^{0.5} + C \tag{9}$$

2. 6. Desorption and secondary adsorption of MB onto RB5 and RY-K4G loaded CM

The effects of initial pH on desorption of RB5 or RY-K4G from RB5 or RY-K4G loaded CM (CM-RB5 and CM-K4G) were studied, respectively. About 0.1 g CM-RB5 and CM-K4G were weighed and added into varied aqueous solution with different initial pH values ranged from 2.0 to 12.0 at 303 K for 24 h. The final dye concentration in solution was analyzed using the same method as mentioned above to estimate the amount of desorption.

Before adsorption of MB, CM-RB5, and CM-K4G were rinsed with distilled water with pH 2 until the eluent became colorless. Adsorption of MB on CM-RB5 and CM-K4G were conducted at initial concentration of 100, 200, and 300 mg L^{-1} under the pH 2, while that of CM was carried out under the pH 10 since the uptake of MB by most adsorbents increased with the increase in initial pH of dye solution [32,33] resulting from negative charge on the surface. About 0.1 g adsorbent was immerged into 50 mL solution for 12 h at 303 K. The final MB concentration was detected at a wavelength of 662 nm by Vis spectrophotometer.

3. Results and discussion

3.1. Characterization of the adsorbents

The major elements on its surface are C, N, O, Ca, P, and Fe and CM consists of 8.4% protein, 71.4% ash, 20.17% carbohydrate (shown in Table 1). CM contains polar functional groups such as hydroxyl, amido, phosphate. These groups will form active sites for sorption on the material surface.

The specific surface area, pore volume, and average pore diameter of the raw crayfish carapace are 7.25 m^2 g^{-1}, 0.05 cm^3 g^{-1}, and 3.449 nm, respectively, which are moderate compared with *Spirulina platensis* microalgae and commercial activated carbon [16]. The surface morphologies of CM and dCM were shown in Fig. 1(a) and (b), respectively. Apparently, the porosity increased and the pore volume became larger for the sample with the acid treatment, which further facilitates adsorption.

Table 1
Centesimal chemical composition and elemental composition of Crayfish carapace

Elemental composition	(%)
C	42.94±0.7
N	5.73±0.3
O	40.69±0.8
Ca	9.14±0.2
P	0.51±0.1
Fe	0.98±0.12
Centesimal composition	(%, dry basis)
Protein	8.41±0.5
Carbohydrate	20.17±0.7
Ash	71.4±0.9

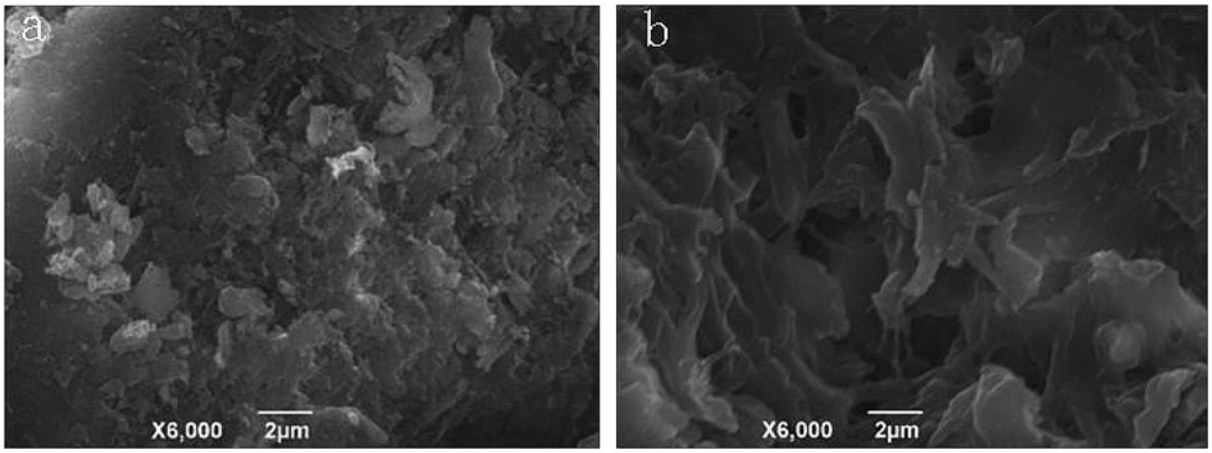

Fig. 1. SEM of CM (a) and dCM (b).

3.2. Comparison of the two adsorption means

It can be observed from Fig. 2, that 90% of the dyes were adsorbed when CM was first shaken in the dyes (initial pH 7) for 2 h, and then the pH of mixture was adjusted to 2 with continuous shaking for 30 min. While only 60% of the dyes were removed when the pH of the mixture was 2 and the shaking lasted for 2.5 h. It should be stated that the RB5 and RY-K4G do not present any color change in the pH range of 2–12, since they are dyes that belong to the reactive dye class [16]. In order to confirm what component caused such difference. The dCM which is composed of protein, chitin and the chitin extracted from CM were used to adsorb dyes under the following condition: (C) the dyes (50 mL, 1,000 mg L^{-1}) were adsorbed under pH 10 (adjusted and controlled with NaOH) for 2 h and then adsorbed under the pH 2 (adjusted with HCl) for 30 min; (D) the dyes were adsorbed under pH 2 for 2.5 h (E) the dyes were adsorbed under the pH 7 for 2 h and then adsorbed under pH 2 for 30 min (adjusted with HCl). It was found from Fig. 2 that both dCM and chitin adsorbed more dyes under the condition of (C), while adsorbed less dyes under the condition of (D) and (E). This indicated the adsorption under the caustic condition caused the difference and further proved the caustic condition caused by the hydrolysis of calcium carbonate in the CM when the initial pH of the dyes was neutral increased the adsorption. The

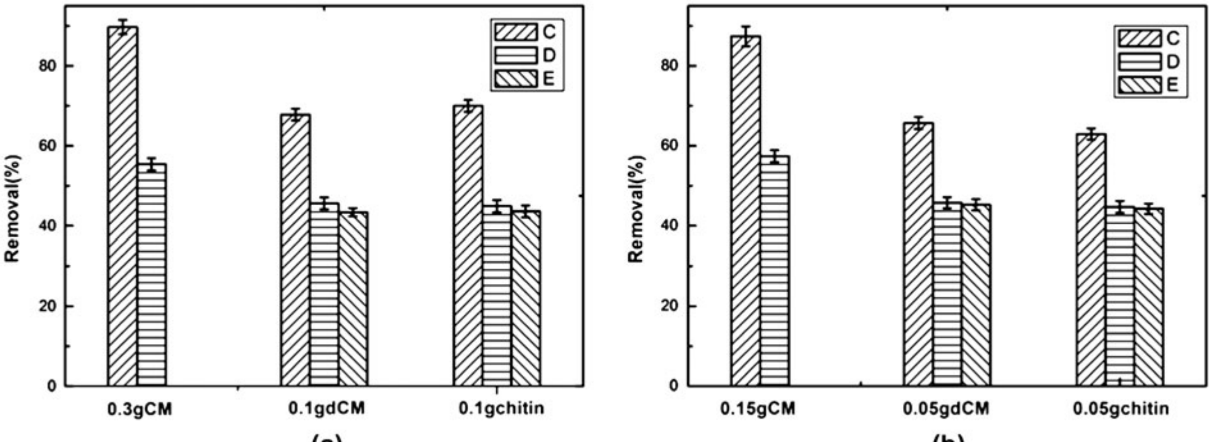

Fig. 2. Removal rate of RB5(A) and RY-K4G(B) with their initial concentrations of 1000 mg L^{-1} adsorbed by different absorbents at 303K under different conditions:
C: adsorbed under the pH 10 for 2 h and then adsorbed under the pH 2 for 30 min;
D: adsorbed under the pH 2 for 2.5 h;
E: adsorbed under the pH 7 for 2 h and then adsorbed under the pH 2 for 30 min.

possible mechanism was shown in Fig. 3, which indicated that nucleophilic addition or substitution occurred between chitin in CM and reactive dyes under the caustic condition and this was consistent with what Sakkayawong [34] have proved, while there was electrostatic adsorption between CM and reactive dyes in the acid condition because CM was positively charged under this condition. Meanwhile, calcium carbonate dissolved when the pH was adjusted to 2, which increased the porosity as mentioned above and further facilitate the adsorption of dyes. So in the subsequent experiments, the absorption condition was set as 2 h absorption under pH 10 and then 30 min under pH 2.

3.3. Effect of pH and ionic strength on adsorption

pH was one of the most important factors that might influence the adsorption capacity. Since the initial pH values of dyes were neutral, after the addition of CM, the pH of the solution increased to 10 immediately. The dyes were adsorbed under pH 10 for 2 h, and then the pH was adjusted from 2 to 12, followed by further absorption for 24 h. It was observed from Fig. 4(a) that the adsorption capacity of both dyes decreased with pH increasing, and was maximum at pH 2, which is consistent with what Akkaya [35] have observed in their research of reactive dyes adsorbed by chitin. This was because there was nucleophilic addition or substitution between chitin in CM and reactive dyes under pH 10, while under the acidic condition, the CM surface was positively charged due to the protonated OH, NH–C=O groups [16]. It is also found that the percentage of positively charged amide of chitin increased from 54 to 91% when the pH decreased from 3.44 to 2.51 [24]. Meanwhile, the RB5, RY-K4G (D–SO_3Na) was converted to anionic ions (D–SO_3^-) under low-pH condition, which could promote their absorption onto the positively charged surface of CM. So the lower pH favors the binding of anionic dyes.

In general, wastewater from many dyeing processes typically contains many kinds of salts and NaCl is the main salt used to enhance the bath dye exhaustion [36]. Thus, it is important to evaluate the influence of salts on the adsorption of reactive dyes. It can be seen from Fig. 4(b) that the effect of the salt concentration on the uptake of both dyes was negligible, which is similar to the result of a previously reported study on reactive orange 16 bio-sorption [37], indicating that Cl^- ions do not compete with the sulfonate groups of the RB5 and RY-K4G molecules for the active sites of the adsorbent. From a practical point of view, these results imply that the waste CM

$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$

$A\text{-}CH_2OH + OH^- \rightleftharpoons A\text{-}CH_2O^- + H_2O$ ($A\text{-}CH_2OH$ represent chitin)

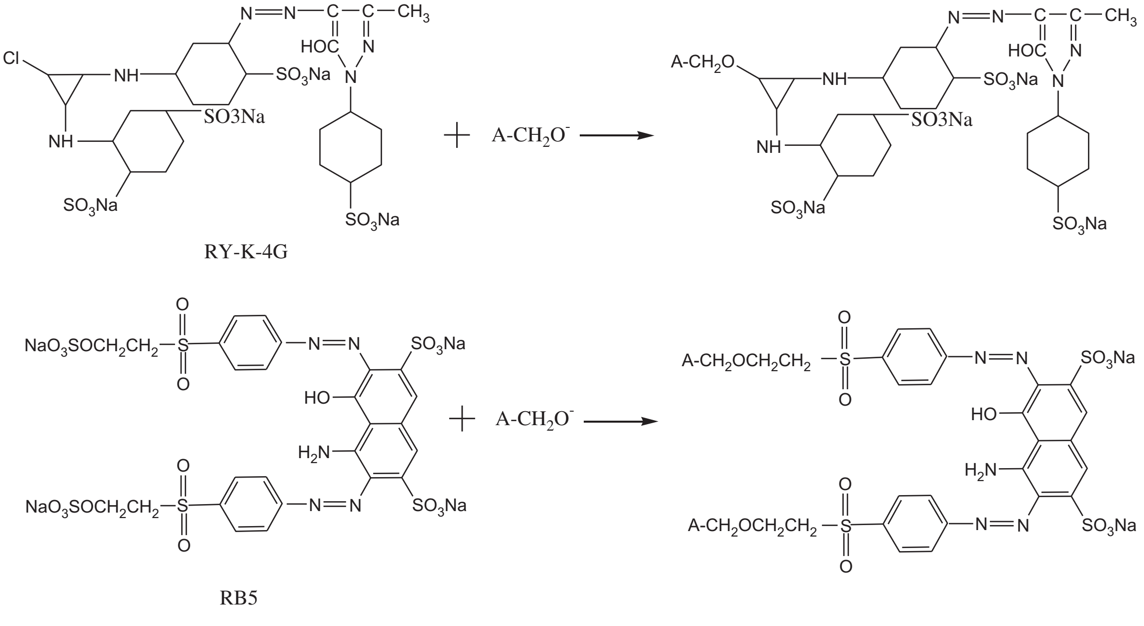

Fig. 3. Mechanism of reactive dyes adsorption under the initial pH 7 by CM.

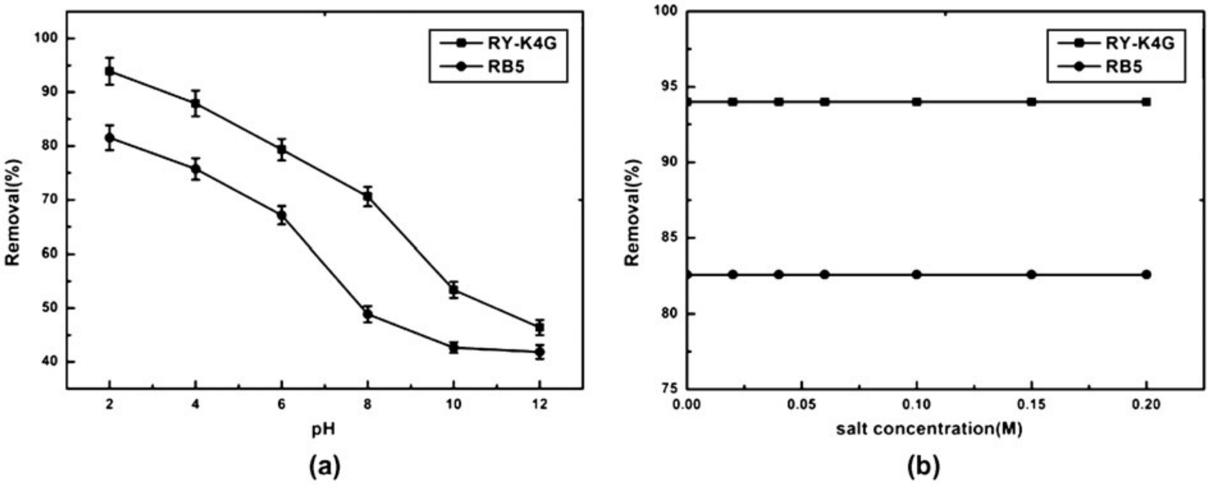

Fig. 4. Effects of pH (a) and ionic strength (b) on the adsorption reactive dyes on CM.

can be used for the removal of reactive dyes from salt-containing wastewater.

3.4. Adsorption kinetics

The experimental results of RB5 and RY-K4G adsorption on CM versus time under three different concentrations were shown in Fig. 5 and the fitted parameters of the three aforementioned popular kinetic models were all listed in Table 2. The adsorption capacity of both dyes on CM increased quickly at the initial stage and then gradually reached equilibrium. Meanwhile, the adsorption capacity increased with an increase in the initial concentration. It can be seen from the R^2 of various kinetics models that the pseudo-second-order model was more suitable to describe the adsorption kinetics than the pseudo-first-order model. This indicated that the rate controlling mechanism for adsorption was chemisorptions, which was in accordance with those drawn from adsorption isotherm analysis. Meanwhile, the values of R^2 fitted by intraparticle diffusion model were not very high, and the lines of q_t against $t^{0.5}$ did not pass through the origin ($I \neq 0$ is not shown here). This indicated that the intra-particle diffusion is involved in the adsorption process but not the only rate controlling step [5]. Meanwhile, as was shown in Table 1, kp values increased with increasing C_o, which indicates that high initial concentrations increased the driving force and promoted intraparticle diffusion of RDS onto CM. The q_e values also increased with increasing C_o, which implied that the boundary layer diffusion effects

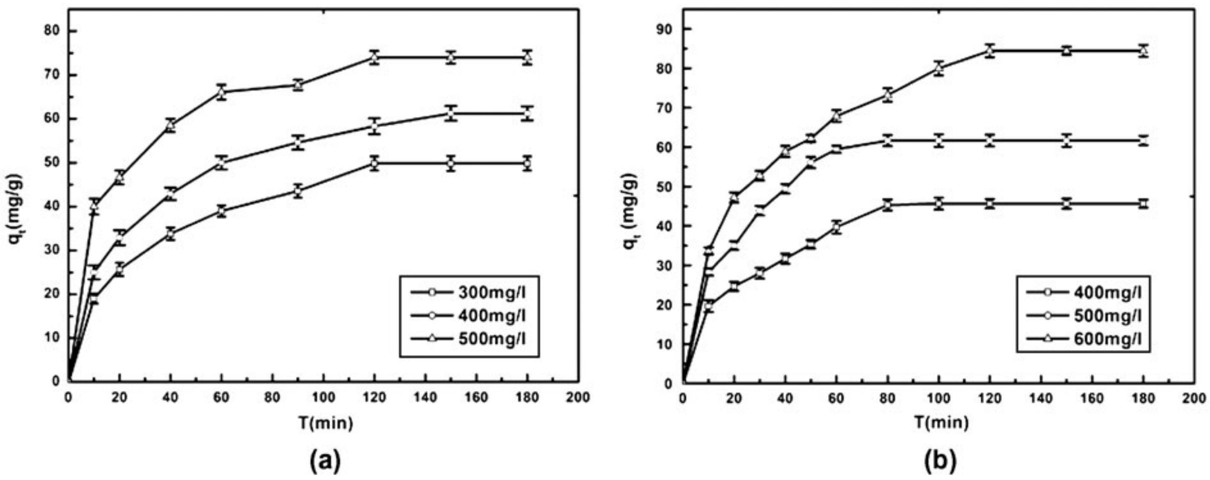

Fig. 5. Kinetics of RB5 (a) and RY-K4G (b) adsorption on CM at 303 K with 0.100 g of CM used in 50 mL of dye solution at different initial concentrations.

Table 2
The kinetics parameters for RB5and RY-K4G adsorption onto CM

Dye	c(mg/L)	q_{exp}(mg/g)^{a}	Pseudo-first order		Pseudo-second order		Intraparticle	
			k_1(min^{-1})	R^2	k_2(10^{-5}min^{-1})	R^2	kp(mg/g min^{-1})	R^2
RB5	300	49.8	0.04	0.814	12.5	0.995	3.301	0.963
	400	61.25	0.025	0.961	6.24	0.997	3.623	0.963
	500	74	0.025	0.886	5.46	0.995	3.985	0.961
RY-K4G	400	45.6	0.048	0.918	7.16	0.984	3.709	0.874
	500	61.6	0.018	0.933	6.31	0.993	4.573	0.956
	600	84.4	0.018	0.971	3.92	0.985	6.199	0.972

increased with the increase in the initial dyes concentration [38]. This was the first stage of the adsorption kinetics. In the second stage (pH 2), adsorption equilibrium achieved within 5 min with the dramatic increase in adsorption capacity, which was not shown here. This was because the porosity increased as mentioned above and electrostatic adsorption at sites was a fast process.

3.5. Adsorption equilibrium study

The equilibrium study was conducted to describe the interactive behaviors between the solutes and adsorbents. The adsorption isotherms for RB5 and RY-K4G onto CM at varied temperatures were presented in Fig. 6 and the simulated parameters by aforementioned models were all listed in Table 3, respectively. The adsorption isotherms showed no significant variations with temperature for both dyes. This phenomenon might indicate the absence of physical adsorption, which was usually notably affected by temperature.

For further interpretation of adsorption behaviors, four common isothermal adsorption equilibrium models were used to fit the results. It was found that the determination coefficients (R^2) of the linear form of Langmuir model were much closer to 1.0 than those of other models for RB5, indicating homogenous adsorption of RB5. While the adsorption of RY-K4G onto CM followed the Freundlich model, indicating the heterogeneous adsorption of RY-K4G is a multilayer adsorption, possibly caused by the coexisting adsorption mechanism(s) such as cation-π bonding between CM and RY-K4G or π–π interactions between dissolved RY-K4G and adsorbed RY-K4G [39].

Furthermore, the values of mean adsorption energy E based on the analysis from D–R model would give information about adsorption mechanisms, physical or chemical process. The adsorption behaviors were ascribed to physical adsorption when E was between 1.0 and 8.0 kJ mol^{-1}, but chemical adsorption while E was higher than 8.0 kJ mol^{-1} [21]. The calculated E for both RB5 and RY-K4G presented

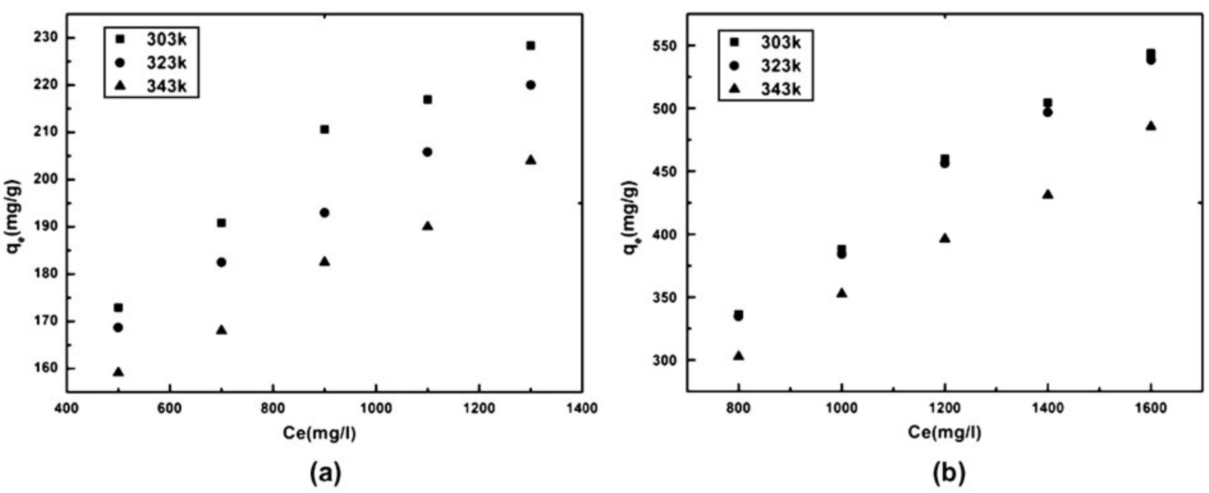

Fig. 6. Isotherms of RB5 (a) and RY-K4G (b) adsorption on CM at 303, 323, and 343 K.

Table 3
The isotherms parameters for RB5 and RY-K4G adsorption onto CM

Dye	Langmuir model				Freundlich model			D–R model		Sips model			
	T(K)	q_m(mg/g)	b_L(Lg^{-1})	R^2	K_F	n	R^2	E(KJ mol^{-1})	R^2	q_m(mg/g)	b*10^3(L mg^{-1})	n	R^2
RB5	303	285	3.53	0.998	28.58	3.44	0.986	9.5	0.93	287	3	0.992	0.988
	323	270	3.2	0.992	28.71	3.64	0.959	11.6	0.95	262	3.23	0.996	0.951
	343	242	3	0.991	30.41	3.75	0.952	12.8	0.92	250	3.3	0.942	0.942
RY-K4G	303	1,331	0.434	0.971	1.761	1.51	0.996	10.6	0.93	1,299	0.431	0.994	0.992
	323	1,260	0.371	0.966	1.213	1.48	0.992	13.4	0.92	1,250	0.371	1	0.993
	343	1,165	0.317	0.99	0.69	1.42	0.998	15.5	0.91	1,140	0.415	0.997	0.996

Table 4
Thermodynamic parameters of RB5 and RY-K4G onto CM at different temperature

Dye	Temperature (T)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
RB5	303	−30.67407	−3.53	0.0895
	323	−32.43519		
	343	−34.25952		
RYK-4G	303	−25.16	−3.35	0.072
	323	26.6		
	343	−28.05		

in Table 3 were higher than 8.0 kJ mol^{-1}, although R^2 were not very high. This further confirmed that the adsorption behaviors were chemical adsorptions. This phenomenon might result in the unobvious variations of the adsorption behavior of CM at different temperatures as mentioned above.

Besides the adsorption equilibrium study at various temperatures could also provide valuable information of adsorption thermodynamics. The thermodynamic parameters for the adsorption process, namely ΔG (kJ mol^{-1}), ΔH (kJ mol^{-1}), and ΔS (kJ mol^{-1} K^{-1}), could be calculated based on the given equations as shown below from the adsorption equilibrium constants [5].

$$\Delta G = -RT\ln(55.5K_D)(10)\ln(55.5K_D) = -\frac{\Delta H}{RT_+}\frac{\Delta S}{R} \quad (10)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), K_D is the thermodynamic equilibrium constant (L mol^{-1}) and 55.5 is the number of moles of water per liter of solution. The K_D values were estimated from the parameters of the best fit isotherm model and the molecular weight of the dyes [16]. As shown in Table 4, the calculated ΔG for RB5 and RY-K4G adsorption were both negative, indicating that the adsorption process was spontaneous. Furthermore, the calculated ΔH were −3.53 and −3.35 kJ mol^{-1} for RB5 and RY-K4G, while the ΔS were 0.0895 and 0.072 KJ mol^{-1} K^{-1} for RB5 and RY-K4G, respectively. This indicated that the dyes adsorption was a spontaneous and exothermal process driven by entropy increase. Besides the adsorption capacity of CM was also compared with some other adsorbents. It was found from Table 5 that the RB5 and RY-K4G uptake of CM were much higher than those of the listed adsorbents that have been reported in the previous literatures. This study indicated that CM is a promising, unconventional, affordable and environmentally friendly adsorbent for the removal of reactive dyes from wastewater.

3.6. Desorption and secondary adsorption of MB onto CM-RB5 and CM-RY-K4G

As known, the reusability was an important factor for developing a novel adsorbent in practical application. Recently, a novel way to make use of these used adsorbents has been reported [23]. Since the surface structure of the adsorbents have been changed when covered by a layer of contaminant, the used adsorbents can be applied to adsorb other pollutants at suitable conditions. In this work, the anionic dyes loaded CM were tried to remove a cationic dye MB. Before this treatment, the stability of CM-RB5 and

Table 5
Adsorption capacities of several adsorbents for RB5 and RY-K4G

Adsorbent	Adsorbate	Q_{max}(mg g^{-1})	Reference
Akai stalks	RB5	52.3	[40]
Octosilicate Na-RUB-18	RB5	54.75	[41]
Afsin-elbistan fly ash	RB5	7.936	[42]
Aspergillus foetidus	RB5	106	[43]
Bone char	RB5	160	[44]
Brown seaweed *Laminaria sp.*	RB5	101.5	[45]
Cationic polymer/bentonite	RYK-4G	99.16	[46]
Crayfish carapace powder	RB5	285	This work
Crayfish carapace powder	RYK-4G	1,299	This work

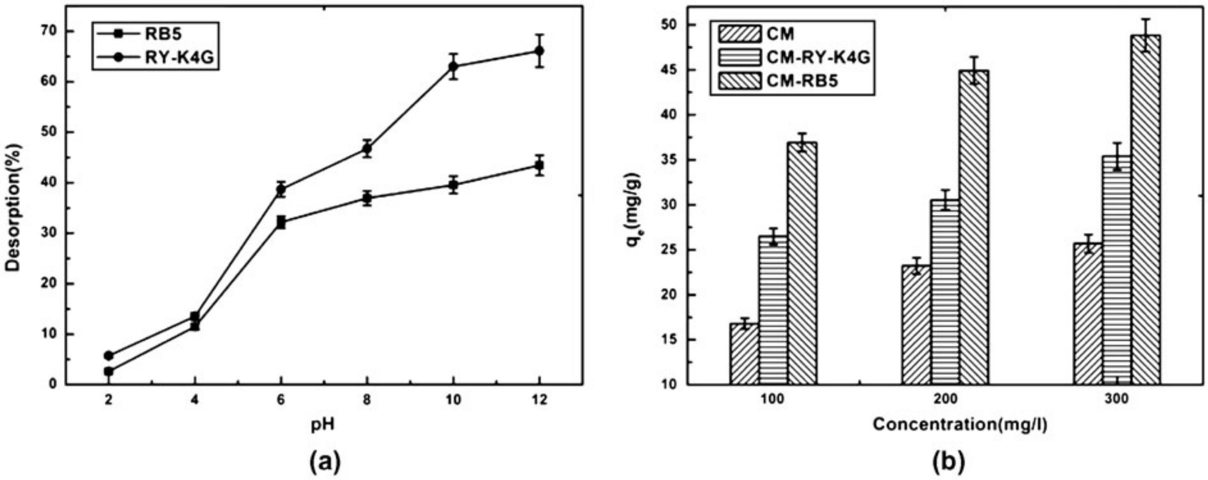

Fig. 7. The effect of pH (a) on reactive dyes desorption from CM-RB5 and CM-RY-K4G at 303 K and MB initial concentration (b) on MB adsorption by CM, CM-RB5 and CM-RY-K4G at 303 K.

CM-RY-K4G at various pH conditions was studied firstly, and the results were shown in Fig. 7(a). It was found that, at pH higher than 2, RB5 and RY-K4G would be partially desorbed from CM owing to the excessive hydroxyl ions competing for the reaction sites on the adsorbent and substituting anionic dyes. Meanwhile, the desorption efficiency increased from 2 to 43% for RB5 and 4 to 65% for RY-K4G with pH increased from 2 to 12 and the trend in the desorption process at different pH values is just converse to that of the adsorption process in the pH effect. This further indicated that the reactive dyes adsorption is mainly due to chemical adsorption. Consequently, the secondary adsorption of MB onto the used adsorbents was carried out at the pH 2. It turned out that the MB uptake of CM, CM-RB5, and CM-RY-K4G increased with increase in initial MB concentration and that were 25, 35, and 48 mg g^{-1} when the initial MB concentration was 300 mg l^{-1}. It can be concluded from Fig. 7(b) that CM-RB5 and CM-RY-K4G was more appropriate for the adsorption of MB than CM. After adsorption of RB5 and RY-K4G, the surface of CM-RB5 and CM-RY-K4G were covered with a layer of anionic dyes, which could adsorb cationic MB through electrostatic interaction.

4. Conclusion

Above all, CM was effective in the removal of both RB5 and RY-K4G from aqueous solution with much larger adsorption capacity compared with other adsorbents. The adsorption of the anionic reactive dyes showed pH-dependent, but no significant variations with temperature. Alkaline condition was first created by the hydrolysis of calcium carbonate in CM, which led to the nucleophilic substitution or addition between chitin and reactive dyes, enhancing the adsorption capacity of CM. The further adsorption mechanism studies indicated that the adsorption of RB5 was a monolayer chemical adsorption, while the adsorption of RY-K4G was a multilayer chemical adsorption, and they are also a spontaneous and exothermal process. In addition, the used adsorbents were employed to adsorb MB from aqueous solution at a particular condition and showed high removal efficiency, indicating that the secondary adsorption was an efficient and economical way for reuse of the used adsorbents. Taking the high extracting cost of chitin and chitosan into account, CM can be an economical and promising adsorbent in the wastewater treatment.

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