Adsorption characteristics of reactive black 5 onto chitosan-intercalated montmorillonite

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ABSTRACT

The adsorption behavior of reactive black 5 (RB5) on a biocomposite (chitosan-intercalated montmorillonite: CTS/MMT) was studied in batch operation. The precursor and the CTS/MMT were characterized by X-ray diffraction and scanning electron microscopy. The effects of contact time, initial solution pH, initial dye concentration, and temperature on adsorption capacity were investigated. The optimum conditions were found as the following: contact time 1 h, initial solution pH 2.0, initial dye concentration 200 mg L^{-1}, and temperature 60°C. The kinetic data followed the pseudo-second-order model. The Langmuir and Freundlich models were applied to describe the isotherm data, of which Langmuir and Freundlich models proved good correlation. Various thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, and $\Delta S°$, were also evaluated, which indicated a spontaneous and endothermic process. Finally, desorption experiments revealed that the adsorbent can be reutilized by regeneration with dilute NaOH solution.

Keywords: Chitosan intercalated montmorillonite; Reactive black 5; Kinetics; Isotherms; Thermodynamics

1. Introduction

Nowadays, much attention has been given to the environmental contamination of dyes due to their toxicity and low biodegradability. Reactive dyes are widely used in many industries due to their bright color, excellent color fastness and ease of application [1]. Reactive dyes are typically azo-based chromophores combined with different reactive groups. More than 80,000 tonnes of reactive dyes are produced cause by their possibility uses [2]. Reactive dyes differ from all other dye classes in that they bind to the textile fiber, such as cotton, through covalent bonds and thus are highly recalcitrant to conventional wastewater treatment processes [3,4]. Reactive black 5 (RB5) is a reactive dye that is the most toxic and mutagenic, and even carcinogenic, in nature [5,6]. As the RB5 is designed to resist breakdown with time and exposure to sunlight, water, soap, and oxidizing agent, they cannot be easily removed by conventional wastewater treatment process due to their complex structure and synthetic origins [7].

The application field of adsorption process is growing to dye removal from colored effluents [8]. Recently, there have been many attempts to develop

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biosorbents derived from natural biomasses, for replacing the activated carbon which is high cost and low reutilization. Biosorbents are not only low-cost materials but also plenty, natural origin, and high dye sorption capacity; for instance, animal feature, agricultural waste residues, mineral clays, saw dust, fruit peel, and biopolymers [9–23]. Among them, the use of chitosan (CTS) as a biosorbent for dye removal has been intensively studied. CTS is the deacetylated product of chitin, which is the second most abundant polymer in nature after cellulose and can be extracted from crustacean shell such as prawns and crabs [24]. CTS has been used to remove transition metal ions and dyes from wastewater because they contain high content of amino ($-NH_2$) and hydroxyl ($-OH$) groups that serve as the active sites of interaction [25,26]. CTS is very sensitive to pH solution which dissolves in an acidic media because the amino groups are fully protonated at pH 3.0, and the biopolymer chains with positive charges fall apart in the solution resulting in dissolution in an acid medium and its capacity to adsorb dye cannot be evaluated. Furthermore, CTS is unfavorable mechanical property (high swollen in water) and low specific gravity, which causes inconvenient for the use as adsorbents either batch or column modes. Several chemical modifications can be made to CTS to improve its chemical stability under acidic medium, mechanical strength, and adsorption capacity. The most common chemical modifications are cross-linking, grafting of a new functional group, and acetylation. Although the CTS modified by chemical routes may enhance the resistance against acids, during the modifying process, the amino and hydroxyl groups are reduced, which may reduce its adsorption capacity to dyes [27].

To prevent the reduction of the active sites of CTS, the synthesis of CTS composites has been stepping in. The CTS composite materials had a higher specific strength, lower specific gravity, and higher resistances to corrosion and oxidation. Various types of materials have been used to form composites with CTS such as mineral clays, polyurethane, polyvinyl alcohol, and polyvinyl chloride [28]. Clay minerals have been investigated due to their high disponibility and their promising chemical and physical properties. Among the mineral clays, montmorillonite (MMT) has been highlighted for the preparation of CTS composites [29] because of its high cationic exchange capacity and the possibility of lamellar expansion, which provides greater versatility in the interaction and interaction of bulky molecules such as natural polymers. It has been reported that the CTS can be adsorbed on MMT up to 180% of the cation exchange capacity (CEC) [30].

Although there have been numerous studies relating to CTS composites, those studies focusing on the synthesis and characterization of the CTS/MMT have been documented. Only few studies about the application of CTS/MMT for anionic dyes removal have been reported in the literatures [31–34]. The use of CTS/MMT and CTS/MMT derivatives for removal of reactive dyes such as Congo Red and Reactive Red exhibited much higher sorption capacity on CTS/MMT than that of the only MMT [35–37]. A study focusing on the effect of pH on the adsorption of tannic acid on CTS/MMT has been reported by An and Dultz [38]. It has also been emphasized that anion exchange at low pH and van der Waal force besides ionic forces at alkaline medium governs the sorption mechanism of dyes onto CTS/MMT. Due to the anion exchange capability of the free amine group, CTS/MMT might also be an interesting adsorbent for other anionic organic pollutants [39]. However, the studies above have not reported the performance of CTS/MMT at the pH, which is the condition that CTS completely dissolves (pH < 4.0). Furthermore, effect of temperature, thermodynamic, and desorption studies have not been almost included. The composite of CTS directly coated on MMT for RB5 removal is seldom studied.

As a result, the present work deals with the adsorption of RB5 on CTS/MMT in high acidic and alkaline media and also study the effects of contact time, dye concentration, and temperature. The adsorption behavior of RB5 on CTS/MMT was evaluated in terms of isotherm and kinetic. Then, thermodynamic studies and desorption experiment were also investigated.

2. Materials and methods

2.1. Materials

RB5 obtained from Aldrich (Ireland) was used as the adsorbate. The chemical structure of the RB5 was depicted in Fig. 1. The chitosan was of high-molecular weight (10,104 g mol^{-1}) with a 82.5% degree of deacetylation and was purchased from Sigma-Aldrich. The commercial MMT was supplied by Thai Nippon Chemical Industries Co. Ltd., and used without further purification. A CEC of the MMT providing by a supplier was at 0.8 meq g^{-1}.

2.2. Preparation of CTS/MMT

The amount of 1.0 g MMT was dispersed in 100 mL of distilled water. Hundred milliliter of 2 g L^{-1}
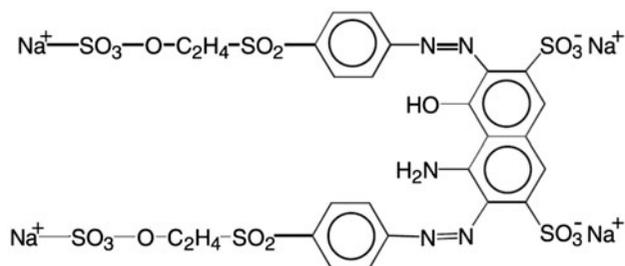
Fig. 1. Chemical structure of RB5 [4].

chitosan solution was slowly added into the MMT suspension. The mixture was stirred at a constant rate for 1 h at 298.2 K. The pH of suspension was adjusted to 7.0–7.5 using 1 N NaOH or 1 N HCl and left for 30 min for gel formation [40]. The CTS/MMT was removed from the suspension by filtration with a GF/C filter (77 mm pore diameter) and then washed with distilled water until the pH of the washed water became natural. It was then dried at 313.2 K for 12 h. The CTS/MMT was grounded and sieved to 200 mesh size. The CTS/MMT powder was kept in desiccator for further use.

2.3. Characterization

X-ray diffraction (XRD) analyses of the powdered samples were performed using an X-ray powder diffractometer. The surface morphologies of MMT and CTS/MMT were studied using SEM images.

2.4. Batch adsorption experiments

Adsorption studies were performed using a thermostat shaker. A series of 250 mL Erlenmeyer flasks were used and filled with 100 mL of dye solution. An amount of 0.1 g adsorbent was added. The flasks were shaken at 200 rpm. The pH values of the initial solution were then adjusted by the addition of 0.1 N NaOH or 0.1 N HNO_3 solutions. The following adsorption experiments were then carried out. The effect of contact time investigated first. A 200 mg L^{-1} RB5 solution was shaken at 298.2 K with contact times ranging from 5 min to 12 h. Secondly, the effect of the initial pH was among 2.0 to 10.0 with 200 mg L^{-1} RB5 solutions, shaken for 24 h at 298.2 K, then investigated and analyzed. Thirdly, the effect of the initial RB5 concentration was performed. The initial dye concentration was varied between 50 and 300 mg L^{-1} prepared (pH 7.0 ± 0.5) and treated as the same procedure of the second experiment. Finally, the final experiment effect of temperature was conducted following the same procedures as the first and second

experiments, but the studies were performed at 308.2–328.2 K. The loaded adsorbents were harvested from the suspended solution by centrifuge at 6,000 rpm for 30 min. The RB5 concentration in supernatant was measured using a UV–vis-spectrophotometer at wavelength corresponding to the maximum absorbance for the RB5 of 614 nm.

2.5. Desorption experiments

Desorption experiments were studied to investigate the possibility for repeated use of adsorbent. Sample of CTS/MMT saturated with 200 mg L^{-1} of RB5 solution was harvested from the adsorption isotherm experiment in Section 2.4 by filtration and then washed three times with deionized water and then finally air dried for one day. The saturated CTS/MMT was treated with 0.1 M NaOH solutions (200 mL) at shaking speed of 200 rpm for 24 h. After treatment the RB5 has been released into the bulk alkaline solution, the adsorbent was removed from the suspension by filtration. The concentration of RB5 in the filtrate was determined.

3. Results and discussion

3.1. Powder XRD

The intercalation caused expansion of the basal spacing (d_{001}), interlayer inside the MMT. The d_{001} reflection for the basal spacing determined by XRD was found to shift from 1.27 nm (precursor) to 1.52 nm (CTS/MMT). This confirmed that the CTS molecules were successfully placed in the interspaces of MMT [41].

3.2. Scanning electron microscopy

The scanning electron micrographs of MMT and CTS/MMT are shown in Fig. 2. From Fig. 2(a), it is clear that the SEM pictures of MMT sample show a considerable numbers of pores where there is a high possibility for RB5 dye to be trapped and physically adsorbed into. Fig. 2(b) shows the CTS layer coated on the MMT surface, especially in the circle, formed a disordered film, which confirms existence of the CTS on the CTS/MMT.

3.3. Effect of contact time

Fig. 3 shows the increase of sorption capacity of RB5 onto CTS/MMT as function of contact time. It was found that sorption rate was rapid during the first 5 min, and then, the rate was slower during the 5–60 min range, and a plateau was reached after 60 min.
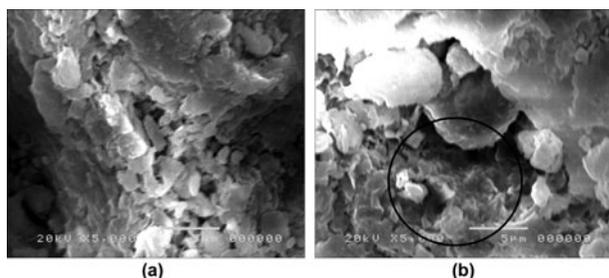
Fig. 2. SEM micrograph of sample: (a) MMT; (b) CTS/MMT.

It can be stated that the rapid rate in the initial stage was due to more available adsorption sites on the outer and inner surfaces of the adsorbent, and the slower rate in the later stage was due to less availability of outer surfaces and slower diffusion of adsorbate into the interior of the adsorbent. The final stage indicates that the adsorbent began saturation with the RB5 at 60 min, which was the sorption equilibrium time.

3.4. Effect of initial solution pH

Fig. 4 shows that the amount of RB5 adsorbed on the CTS/MMT was strongly dependent on the initial pH of the solution. The sorption capacity decreased greatly when the pH increased from 2.0 to 6.0 and gradually decreased further when the pH increased from 6.0 to 10.0. At low pH levels, there were small amounts of hydroxide ions in the solution, and the negative RB5 molecules adsorbed freely into the positive surface, protonated amino groups, of the CTS/MMT without competition with hydroxide ions. This resulted in high sorption capacity under this condi-

tion. As higher pH levels, there were more hydroxide ions in the solution, and there were sorption competition between hydroxide ions and RB5 molecules on the positive surface of adsorbent, which caused a low sorption capacity of RB5 under this condition. However, the adsorption of anionic RB5 dye on the CTS/MMT was still observed in the alkaline medium. This was attributed to a chemical interaction that occurred between RB5 molecules and positive charges on the CTS/MMT [35].

3.5. Adsorption isotherms

The adsorption isotherm was constructed by plotting equilibrium quantities of RB5 adsorbed on CTS/MMT: q_e (mg g^{-1}) vs. equilibrium RB5 concentrations: C_e (mg L^{-1}) as shown in Fig. 5. The equilibrium data obtained were then fitted to the Langmuir and Freundlich models to analyze adsorption behavior and determine model parameters for the RB5 as shown in Table 1.

The Langmuir isotherm is valid for monolayer adsorption of adsorbate onto a surface of adsorbent with a finite number of identical sites [42]. The Langmuir model in its linear form is written as follows:

$$C_e/q_e = \frac{1}{K_L \cdot q_m} + C_e/q_m \qquad (1)$$

where q_m (mg g^{-1}) is the maximum adsorption capacity and K_L (L g^{-1}) is the Langmuir constant.

The essential characteristics of the Langmuir isotherm can be expressed by means of "R_L" which is a

Fig. 3. Effect of temperature on the adsorption of RB5 onto CTS/MMT for a solution initially containing 200 mg L^{-1} of CTS/MMT as a function of time.
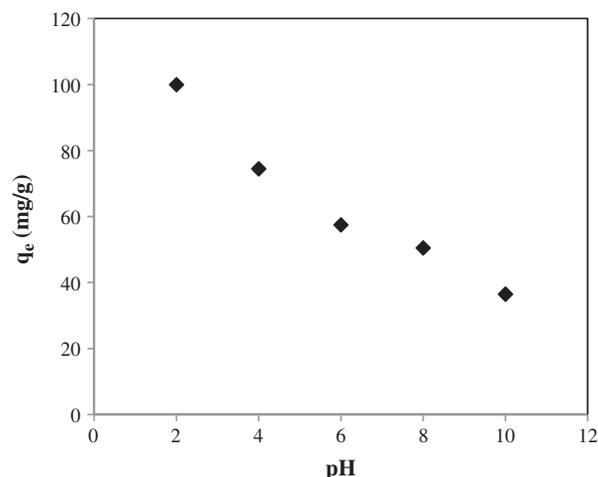
Fig. 4. Effect of initial pH solution on the adsorption of RB5 onto CTS/MMT for a solution initially containing 200 mg L^{-1} of CTS/MMT.
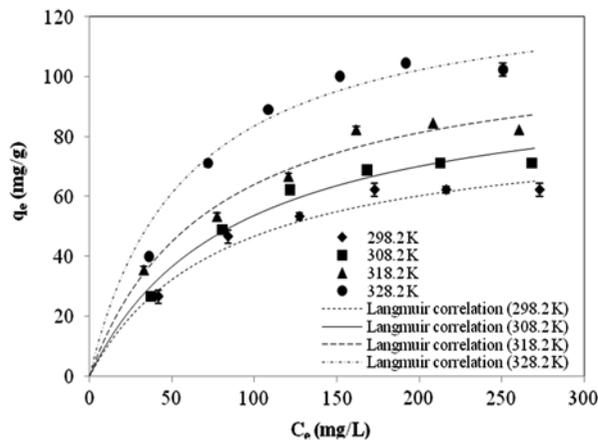
Fig. 5. Effect of temperature on the adsorption of RB5 onto CTS/MMT for solution initially containing 200 mg L^{-1} of CTS/MMT as a function of equilibrium concentration.

dimensionless constant referred to as a separation factor or equilibrium parameter. The R_L is defined by

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (2)$$

This parameter suggests the type of isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). As can be seen from Table 1, at all temperatures, the R_L values are between 0 and 1.0, indicating that the adsorption of RB5 onto CTS/MMT is favorable.

The Freundlich model is usually adopted for heterogeneous adsorption [43]. The linear form of the Freundlich equation can be written as follows:

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

Table 1
Isotherm constants and correlation coefficients for the adsorption of RB5 on CTS/MMT at different temperatures

Model	T(K)			
	298.2	308.2	318.2	328.2
Langmuir isotherm q_{max} (mg g^{-1})	82.64	94.34	111.11	138.89
K_L (L g^{-1})	1.14	1.25	1.51	2.00
R_L	0.745	0.728	0.689	0.625
r^2	0.9616	0.9531	0.9775	0.9870
Freundlich isotherm K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	4.59	4.55	6.65	8.27
n	2.03	1.93	2.10	2.07
r^2	0.8565	0.8761	0.9425	0.9408

where K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) and n are the physical constants of the Freundlich isotherm. The K_f and n are the indicators of adsorption capacity and adsorption intensity, respectively [44].

The results showed the best fit to the Langmuir isotherm for RB5 indicating that the monolayer of dye molecules covers along CTS/MMT surface. It was observed in Table 1 that the monolayer capacity of absorbed RB5 onto CTS/MMT increased from 82.64 to 138.89 mg/g when the temperature increased from 298.2 to 328.2 K.

3.6. Thermodynamics studies

To further understand the effect of temperature on the sorption capacity and determine whether the adsorption processes occurred spontaneously, the thermodynamic parameters including change in the enthalpy ($\Delta H°$), entropy ($\Delta S°$), and Gibbs free energy ($\Delta G°$) were investigated. The values of $\Delta H°$ and $\Delta S°$ were estimated using the van't Hoff plot, the plot of $\ln K_L$ vs. $1/T$ according to Eq. (4). The value of $\Delta G°$ can be determined by Eq. (5).

$$\ln K_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (4)$$

$$\Delta G° = -RT \ln K_L \quad (5)$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}) and T(K) is the absolute solution temperature.

As seen in Table 2, all $\Delta G°$ values were negative for all the experimental temperatures indicating the adsorption of RB5 on CTS/MMT was spontaneous. The magnitude of $\Delta G°$ shifted to a high negative value when the temperature increased suggesting the adsorption occurred more spontaneously at higher temperatures.

The positive value of the $\Delta H°$ indicated that the sorption was an endothermic process. This also suggested that a large amount of heat was consumed to transfer the RB5 from aqueous solution into a solid phase.

The positive value of entropy change ($\Delta S°$) corresponded to an increase in the degree of freedom of the adsorbed species. However, a little change of entropy can be observed showing that CTS/MMT did not change significantly as a result of adsorption.

3.7. Adsorption kinetics

The kinetic data were fitted to pseudo-first-order, pseudo-second-order, and intra-particle diffusion

Table 2
Thermodynamic parameters for the adsorption of RB5 onto the CTS/MMT

T (K)	K_L (L mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})
298.2	1,133.7	−17.44	+15.53	+0.0527
308.2	1,234.8	−18.24		
318.2	1,494.7	−19.34		
328.2	1,982.7	−20.72		

models in order to gain a better understanding of the adsorption dynamic behavior. The q_t (mg g^{-1}) is the amount of dye adsorbed at time t.

The pseudo-first-order kinetic model is applicable over the initial 30 min of adsorption process. If the diffusion rate of adsorbate across the boundary layer is at a rate of limiting step, the kinetic data are well fitted to the pseudo-first-order model [45]. It is generally expressed as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where k_1 (min^{-1}) is the rate constant of first-order adsorption.

The pseudo-second-order kinetic model was proposed by Ho in 1995 [45]. If the chemical sorption is the rate-limiting step, the experimental data follow the pseudo-second-order expression according to Eq. (7). It is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 (min^{-1}) is the rate constant of second-order adsorption.

If the diffusion of RB5 molecules into internal surfaces within pores and capillaries of the adsorbent is the rate-limiting step, the adsorption data can be presented by the following equation [40]:

$$q_t = k_p \cdot t^{1/2} + C \tag{8}$$

where k_p represents intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and C is a constant (mg g^{-1}) which gives information on the thickness of the boundary layer.

The linear plot of t/q_t against t according to Eq. (7) was observed. The constant k_2 and the corresponding linear regression correlation coefficient values, r^2, are given in Table 3. The values of r^2 were limited to unity (0.9986–0.9995) for all temperatures indicated that the adsorption data fitted well to the pseudo-

second-order model. This indicated that the rate of limiting step was the formation of chemical bonding between the RB5 anions and the protonated amino groups on the surface of the CTS/MMT.

According to Eqs. (6) and (8), a straight line was obtained from both plots of ln ($q_e - q_t$) vs. t and that of q_t vs. $t^{1/2}$ with poor correlation coefficient values as shown in Table 3. Therefore, the experimental data did not conform to either of these models [46].

3.8. Activation parameter

The activation parameter can be obtained by the Arrhenius equation. The slope of the plot of log k_2 vs. T^{-1} can then be used to evaluate the activation energy, E_a, according to Eq. (9). The Arrhenius equation is expressed as:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{9}$$

where E_a is the activation energy (J mol^{-1}) and A is the Arrhenius factor (g mol^{-1} s^{-1}).

The experimental results obtained gave $E_a = −27.63$ kJ mol^{-1} for the adsorption of RB5 onto CTS/MMT. The negative value of the E_a indicates that energy barriers in the reaction process are absent and that the reaction is exothermic. On increasing the temperature, there is a decrease in probability of the colliding molecules capturing one another resulting in negative E_a [47]. Low E_a values (<42 kJ/mol) indicate diffusion control processes, and the higher E_a values (>42 kJ/mol) indicate chemically controlled process. In this study, low value of the E_a indicates that the

Table 3
Pseudo-first order, pseudo-second and intra-particle diffusion kinetic parameters for RB5 adsorption on CTS/MMT

Model	T(K)			
	298.2	308.2	318.2	328.2
Pseudo-first order q_e (exp) (mg g^{-1})	62.14	73.78	85.44	102.91
$k_1 \times 10^2$ (min^{-1})	2.06	3.13	2.90	2.70
q_e (cal) (mg g^{-1})	2.15	12.73	2.08	2.84
r^2	0.5386	0.8061	0.6641	0.6636
Pseudo-second order $k_2 \times 10^3$ (g mg^{-1} min^{-1})	2.39	1.67	1.23	0.85
q_e (cal) (mg g^{-1})	62.89	75.19	87.72	105.26
r^2	0.9995	0.9989	0.9987	0.9986
Intra-particle diffusion k_p (L mg^{-1})	1.40	1.93	2.25	2.73
C (L g^{-1})	34.61	35.05	40.76	48.57
r^2	0.4885	0.5559	0.5492	0.5431

adsorption process of RB5 adsorption on CTS/MMT might be by a physical adsorption [48].

3.9. Desorption of RB5

Percentages desorption of RB5 from the CTS composite after three desorption cycles was 84.71, 77.01, and 57.07%, respectively. An incomplete desorption of RB5 anions from the CTS/MMT was observed because the RB5 molecules might have been trapped in the interior of the adsorbent and was then difficult to release [49]. The RB5 molecules adsorbed were easily desorbed by the dilute NaOH solution, which indicated that the CTS/MMT can be reused for the adsorption of RB5.

4. Conclusion

The results of the study revealed that CTS/MMT exhibited good adsorption capacity for RB5 removal from aqueous solutions. The intercalation of CTS on MMT caused an expansion of the basal spacing (d_{001}) of the MMT from 1.27 to 1.52 nm (CTS/MMT), and the presence of CTS on surface of the CTS/MMT was observed in the SEM images. The adsorption was dependent on contact time, initial solution pH, initial dye concentration, and temperature. The adsorption reached equilibrium within 60 min. A pH of 2.0 was favorable for adsorption. Studies of adsorption isotherms suggested that Langmuir isotherm fitted better than Freundlich isotherm. The adsorption capacity increased with temperatures indicating an endothermic process. The calculated values of $\Delta H°$, $\Delta S°$, and $\Delta G°$ suggested that the adsorption was endothermic and spontaneous. Regarding kinetic studies, the dynamic behavior followed the pseudo-second-order model indicating the chemical reaction on the adsorbent surface was at a rate of limiting step. The activation energy of -27.63 kJ mol^{-1} was determined. The desorption experiment indicated that the adsorbed RB5 can be reused with dilute NaOH solution. Results of this study suggested that the CTS/MMT is a reliable and dependable adsorbent with promising potential for the removal of RB5 normally found in effluents of the textile industry.

Acknowledgements

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