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Adsorption of remazol brilliant blue R by carboxylated multi-walled carbon nanotubes

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ABSTRACT

The unique structure and extraordinary properties of carbon nanotubes make them a promising adsorbent for the removal of contaminants from aqueous solutions. In this study, the adsorption of remazol brilliant blue R (RBBR) from aqueous solutions onto carboxylated multi-walled carbon nanotubes (CCNTs) was investigated in a batch system. The influences of the initial pH value and the adsorbent concentration on the capacity of the CCNTs to adsorb the dye were studied. The adsorption isotherms were evaluated using the Langmuir and Freundlich adsorption isotherms, and the adsorption kinetics were investigated with pseudo-first-order and pseudo-second-order models. The optimal pH value for RBBR adsorption by CCNTs was 4.0 when the pH ranged from 4 to 9. The experimental data fitted the Langmuir isotherm model ($R^2 > 0.990$), and the maximum adsorption capacity of CCNTs for RBBR was 95.24, 103.63, and 109.41 mg/g at 25°C, 35°C, and 45°C, respectively. The RBBR uptake by the CCNTs was found to be rapid and almost reached equilibrium in 90 min. The kinetic data of the CCNTs followed a pseudo-second-order model ($R^2 > 0.999$). Thermodynamic studies were also performed to evaluate different parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$). The adsorption process was found to be endothermic. The values of $\Delta H°$ and $\Delta S°$ were 44.91 and 0.192 kJ/mol, respectively, indicating that the adsorption process was chemisorption. The results demonstrate that CCNTs are very promising adsorbents for the effective removal of RBBR from aqueous solutions.

Keywords: Remazol brilliant blue R; Carboxylated multi-walled carbon nanotubes; Adsorption; Adsorption isotherm; Kinetics; Thermodynamic

1. Introduction

Synthetic dyes are usually aromatic molecules with complex structures and are extensively used in the textile, leather, paper, rubber, plastic, cosmetic, pharmaceutical, and food industries. Their discharge as colored wastewater often causes pollution and environmental issues, such as the coloration of large water bodies, inhibition of sunlight penetration, reduction of photosynthetic action, resistance to photochemical and biological attacks, and increasing the chemical and biological oxygen demands in aquatic environments. Moreover, some dyes and their secondary products are toxic, mutagenic, or carcinogenic [1,2].

Numerous methods such as coagulation and flocculation [3], oxidation and ozonation [4], membrane separation [5], and adsorption [6] have been developed and used for the removal of dyes from wastewaters. However, the complex aromatic structures of the synthetic dyes make them stable to heat and oxidizing agents [7,8]. Among the existing techniques, adsorption is best suited for dye scavenging, because this technique can treat large flow rates and remove different types of pollutants without formation of harmful substances [9,10]. Therefore, a large number of materials have

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been developed as sorbents for the removal of dyes and other hazardous substances from aqueous solutions. Bhatti et al. [11] reported that agricultural wastes (corncobs, sugarcane bagasse, cotton sticks, sunflower, and peanut husk) were good options as adsorbent materials for the removal of color and chemical oxygen demand (COD) from textile industry effluents. Sadaf and Bhatti [12] found that corncobs biomass is a potential and cost-effective biomaterial for the treatment of textile industry effluents. Modified *Hibiscus cannabinus* fibers were also found to be useful for the removal of dyes from aqueous systems [13]. Hen feather waste material has also been successfully used as adsorbent for the removal of toxic azo dyes from wastewaters [14]. Adsorption has also been used for heavy metal removal from aqueous solutions. For instance, Naushad et al. [15] investigated ion-exchange kinetic studies for four heavy metals over a composite cation exchanger and found that the kinetic studies are very important. Nanoparticles have been demonstrated to be highly efficient materials for the removal of heavy metals by adsorption due to their excellent properties. Recently, L-cystein-modified montmorillonite (MMT)-immobilized sodium alginate biopolymer-based nanocomposite and iron oxide-impregnated dextrin (Dex-Fe_3O_4) nanocomposite were demonstrated to be very promising for the removal of heavy metals from aqueous solutions [16,17]. Although various materials have been explored as sorbents for the removal of hazardous substances, there is still a growing need for finding more efficient sorbents.

Carbon nanotubes (CNTs), which were re-discovered by Iijima, have potential applications in various fields such as medicine, hydrogen storage, sensors, and environment [18] due to their unique one-dimensional hollow structure and extraordinary mechanical, electrical, thermal, and optical characteristics [19]. These unique properties allow them to interact with other molecules or atoms through π–π electronic and hydrophobic interactions. Therefore, CNTs are a promising adsorbent for the removal of contaminants such as heavy metals [20] and dyes [21] from aqueous solutions.

Functional groups such as –OH, –C=O, and –COOH can be introduced on the CNT surface in order to tune the adsorption behavior. The surfaces of CNTs can be modified by the reaction with nitric acid, hydrogen peroxide, ammonium persulfate, and ethylene diamine among others. These modified CNTs having more hydrophilic functional groups exhibit a higher cation adsorption capacity than the pristine CNTs [22,23]. Although numerous reports demonstrated that CNTs have excellent adsorption capacities for dyes, there is limited information on the adsorption of reactive dyes by modified CNTs.

The dye remazol brilliant blue R (RBBR) is frequently used as a starting material in the production of polymeric dyes and represents an important class of toxic and recalcitrant organopollutants [24]. Novotný et al. [25] reported that EC_{50} values of RBBR for bacteria *Vibrio fischeri* and microalgae *Selenastrum capricornutum* were 813 ± 15 and 81.1 ± 3.5 mg/L, respectively. The authors found RBBR exhibited a potential mutagenic effect based on the results of Ames test.

In the present study, we investigated the adsorption capacity, adsorption isotherms, and kinetics of RBBR adsorption by carboxylated multi-walled carbon nanotubes (CCNTs). Thermodynamic studies were also performed to determine the feasibility of the adsorption process.

2. Materials and methods

2.1. Chemicals and characterization

RBBR (CAS 2580-78-1; pure grade) was purchased from Acros Organics (M/s Morris Plains, NJ, USA). The CCNTs were purchased from the Nanjing XFNANO Materials Tech. Co., Ltd. (M/s Nanjing, China) and produced by chemical vaporization deposition (CVD). They presented the following characteristics: purity >95 wt%, outer diameter 10–20 nm, and inner diameter 5–10 nm. The CCNT surface was characterized by Fourier transform infrared (FTIR) spectroscopy, and the spectra were recorded between 4,000 and 400 cm^{-1} (FTIR, AVATAR-360, M/s Nicolet, USA). The morphology of the adsorbent was visualized by transmission electron microscopy (TEM; JEM-1400, M/s JEOL, Japan). The specific surface area (SSA) was determined using the multi-point Brunauer–Emmett–Teller (BET) method. The –COOH content (wt%) was assessed by titration with 0.05 M sodium hydroxide (NaOH) and 0.05 M hydrochloric acid (HCl) [26].

2.2. Batch biosorption experiments

All batch kinetic and equilibrium studies were carried out in a thermostatic rotary shaker (CHA-SA, M/S Jiangsu, China; 150 rpm, 25°C) using 50 mL flasks, which contained 40 mL of RBBR solutions. The effect of the initial pH value on the capacity of the CCNTs to remove the dye was studied by adjusting the initial pH values between 4 and 9 with nitric acid (HNO_3, 0.1 M) or NaOH (0.1 M). The effect of the sorbent dose on the adsorption process was also examined by varying the concentrations of the sorbents (0.01–1.6 g/L) at 25°C and pH 4, while the initial dye concentration was fixed at 50 mg/L. The effect of the initial dye concentration on the adsorption capacity of the CCNTs was evaluated for different concentrations of the dye (5–250 mg/L) until equilibrium was reached. The equilibrium adsorption isotherms for RBBR were analyzed using the Langmuir and Freundlich models. The kinetic experiments were carried out at 25°C using the optimized pH value, initial dye concentration, and a biosorbent concentration of 0.8 g/L. To determine the influence of temperature on the adsorption process, batch sorption experiments were carried out at three different temperatures (25°C, 35°C, and 45°C) using a range of initial dye concentrations from 5 to 250 mg/L.

For all batch experiments, different doses of sorbent were separately added to each flask followed by the sealing of the flasks to prevent evaporation and maintain a constant volume of the solution. After shaking for predetermined time intervals, the samples were centrifuged (5,000 *g*, 15 min, 25°C, M/s Cence, Hunan, China), and the dye concentration in the supernatant was estimated by measuring the absorbance at 592 nm (spectrophotometer, VIS-7220, M/s Shanghai, China). The amount of dye adsorbed by CCNTs was calculated based on the initial and equilibrium liquid-phase concentrations of the dye, the initial volume of the dye solution, and the weight of CCNTs.

The experiments were conducted in triplicate, and the mean values were calculated. The negative controls (experiments with no sorbent) were simultaneously carried out to ensure that the dye was adsorbed by the CCNTs and not by the container.

3. Results and discussion

3.1. Characteristics of the CCNTs

Observations by TEM showed that the CCNTs ranged in length from 0.5 to 2 μm. The SSA was 212.5 m^2/g, and the –COOH content was 2.00 wt%. The FTIR spectra of the CCNTs revealed a strong stretching vibration adsorption band of the –OH group at 3,425.3 cm^{-1} and of the carboxyl group at 1,552.6 cm^{-1}.

3.2. Effect of pH on the capacity of CCNTs to remove the dye

The pH of the solution is an important parameter affecting the adsorption process. To study the influence of pH on the adsorption capacity of CCNTs, mixtures having initial dye concentration of 100 and 800 mg/L of CCNTs were incubated for 6 h. The pH value ranged from 4 to 9. The maximum adsorption capacity (approximately 96%) of CCNTs for RBBR was observed at pH 4 according to the results illustrated in Fig. 1. The capacity of the CCNTs to remove the dye decreased when the value of the pH increased in acidic conditions. The capacity remained constant when the pH value was beyond 7. Therefore, the pH value of 4 was selected for the following experiments.

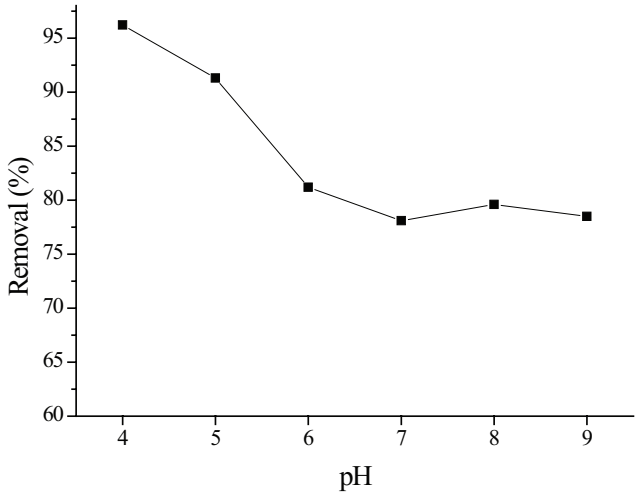

Fig. 1. Effect of the initial pH value on the adsorption of remazol brilliant blue R (RBBR) by carboxylated carbon nanotubes (CCNTs) at 25°C. The RBBR concentration was 50 mg/L, and the CCNT concentration was 800 mg/L.

3.3. Effect of the sorbent dose on the dye removal

Adsorbent dosage is another important parameter for the determination of the adsorption capacity. Therefore, the concentration of the CCNTs was varied between 10 and 1,600 mg/L while the initial concentration of RBBR was fixed at 50 mg/L in a total dye solution of 40 mL. The percentages of the removal of RBBR as a function of the concentration of CCNTs are shown in Fig. 2. The removal capacity increased from 7.5% to 92.9% when the adsorbent dose increased from 0.4 to 32 mg. This result can be attributed to an increase of the adsorbent SSA revealing more available adsorption sites. Nevertheless, when the capacity is expressed in mg of adsorbed dye per gram of adsorbent, the value decreases when the amount of sorbent increases [27]. In the present study, when the adsorbent dose increased from 0.4 to 64 mg, the adsorption capacity decreased from 375.0 to 29.6 mg/g. A similar trend was observed by Wu [8] who employed multi-walled CNTs (MWCNTs) to adsorb the reactive dye Procion red MX-5B.

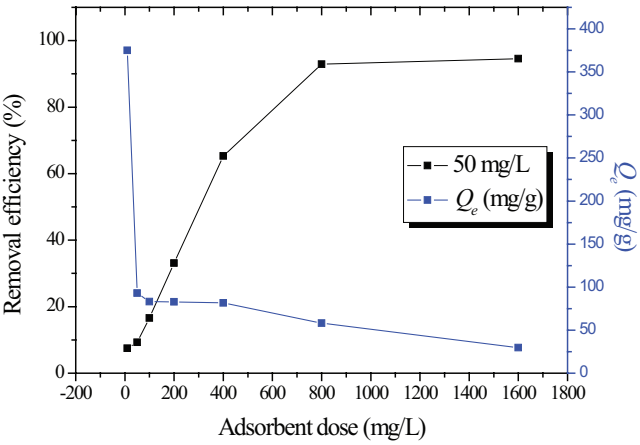

Fig. 2. Effect of the sorbent dose on the adsorption of RBBR by CCNTs at 25°C. The RBBR concentration was 50 mg/L, and the pH value was 4.

3.4. Adsorption isotherms

The capacity of the CCNTs to absorb RBBR was studied at different dye concentrations (5–250 mg/L). The experimental data were fitted by the Langmuir and Freundlich models. The adsorption isotherms describe the distribution of the adsorbed molecules between the liquid and the solid phases when an adsorption process reaches an equilibrium state. The commonly used Langmuir isotherm assumes that a single adsorbate binds to a single site of the adsorbent, and that the adsorption follows a monolayer process. The saturation monolayer can be represented by the following expression [28]:

$$\frac{C_e}{Q_e} = \frac{1}{K_a Q_m} + \frac{C_e}{Q_m} \quad (1)$$

where Q_e is the amount of dye adsorbed by the CCNTs (mg/g); C_e is the equilibrium concentration of the dye in a solution (mg/L); K_a is the Langmuir constant (L/mg); and Q_m is the theoretical saturation capacity of the monolayer (mg/g). The values of Q_m and K_a were extracted from Eq. (2) by plotting C_e/Q_e vs. C_e.

The Freundlich isotherm is an empirical equation applied in the case of heterogeneous adsorbent surfaces due to various functional groups on the surface and different adsorbent-adsorbate interactions. The linear form of the Freundlich equation is as follows [8]:

$$\lg Q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (2)$$

where Q_e is the amount of dye adsorbed by the CCNTs (mg/g); C_e is the equilibrium concentration of the dye in a solution (mg/L); and K_f and n are the Freundlich constants, which correspond to the adsorption capacity and the adsorption intensity of the adsorbent, respectively. The values of K_f and $1/n$ can be calculated from the intercept and slope values of the logarithmic plot of Q_e vs. C_e. A high affinity of the adsorbate is described by a high value of K_f and values of the empirical parameter $1/n$ ranging from 0.1 to 1.

In the present study, linearized Langmuir and Freundlich isotherms for the RBBR adsorption by the CCNTs at 25°C are shown in Fig. 3, and the relative parameters at 25°C, 35°C, and 45°C are displayed in Table 1. The fitting of the experimental data showed a good fit with correlation coefficients (R^2) of 0.9915 and 0.8275, for the Langmuir and Freundlich isotherms, respectively. The Langmuir isotherm gave maximum adsorption capacity values of 95.24, 103.63, and 109.41 mg/g at 25°C, 35°C, and 45°C, respectively.

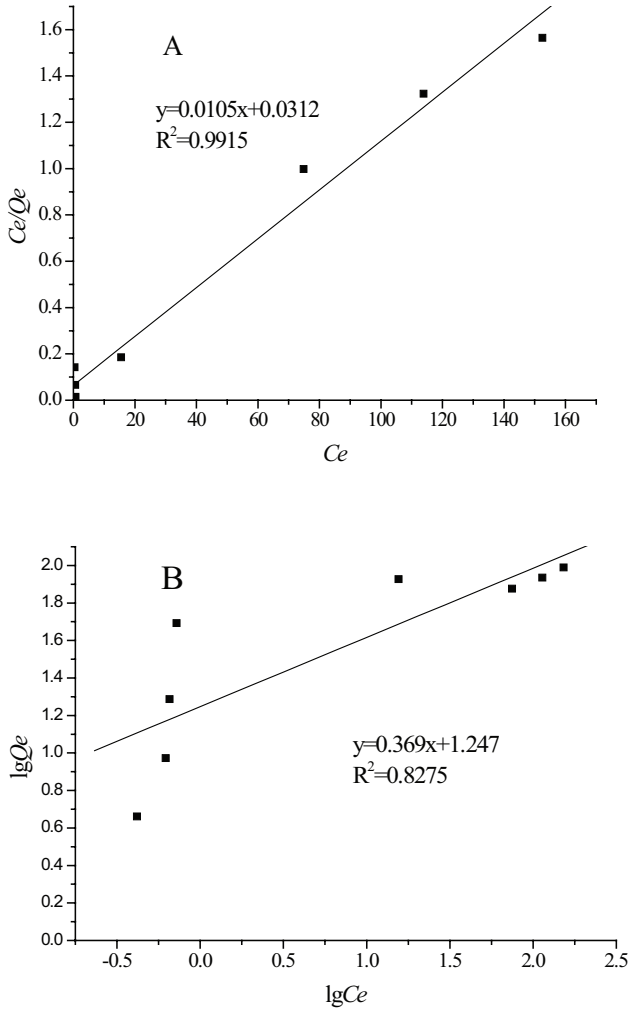

Fig. 3. Linearized Langmuir isotherms (A) and Freundlich isotherms (B) for the adsorption of RBBR by CCNTs.

Numerous studies investigated the adsorption of RBBR dissolved in aqueous solutions by various adsorbents. In particular, Ahmad et al. [29] reported the adsorption of RBBR on Pinang frond-based activated carbon (PF-AC) and found that PF-AC adsorption of RBBR followed a multi-layer adsorption process. On the other hand, our results fit the Langmuir isotherm model indicating a monomolecular adsorption. This difference may be attributed to the heterogeneous surface of the zinc oxide particles with average sizes of 37 and 46 μm used by the authors [30]. Other adsorbents such as *Jatropha curcas* [31] and activated carbon prepared from peanut hull [32] also showed adsorption of RBBR. Both materials showed good adsorption capacities following the Langmuir isotherm model. The adsorption of reactive blue 4 (RB4) dye on an MWCNT was investigated by Wang et al. [33], and they reported an adsorption capacity of 69 mg/g at 25°C.

The maximum adsorption capacities of various CNTs and CNT-based composites toward different dyes are compared in Table 2. The Q_m values of most materials were lower than 90 mg/g. Carboxylate-functionalized MWCNTs have been used for the removal of malachite green dye in aqueous solution and displayed Q_m value of 49.45 mg/g. The CCNTs in the present study with Q_m value of 95.24 mg/g clearly have excellent potential as adsorbents for the removal of RBBR.

3.5. Adsorption kinetics

The CCNTs showed a rapid adsorption rate and a considerable capacity to remove RBBR (Fig. 4). The adsorption equilibrium was almost reached within 60 min. After 90 min of adsorption, the removal capacity reached 97.4%, which was close to that at 6 h (98.5%). The adsorption kinetics curve is smooth and continuous leading to saturation, suggesting the possibility of a monolayer coverage of the RBBR molecules on the surface of the CCNTs [51].

The kinetics of the RBBR adsorption on the CCNTs was investigated using two common models used to describe the dye sorption on solid adsorbents: the pseudo-first-order kinetic model and the pseudo-second-order kinetic model. The best-fit model was chosen on the basis of the best linear regression correlation coefficient value (R^2). The linear form of the pseudo-first-order model can be expressed as follows [52]:

Table 1
Parameters of the linear isotherms for adsorption of remazol brilliant blue R (RBBR) onto the carboxylated carbon nanotubes (CCNTs)

T (K)	Langmuir			Freundlich		
	Q_m (mg/g)	K_a (L/mg)	R^2	n	K_f	R^2
298	95.24	0.0231	0.9915	2.71	17.66	0.8275
308	103.63	0.0498	0.9935	2.54	17.98	0.9307
318	109.41	0.0720	0.9977	2.78	24.04	0.9534

Table 2
Maximum dye adsorption capacities of CNTs and CNT-based composites

CNTs	Dye adsorbed	Q_m (mg/g)	Reference
MWCNTs	Procion red MX-5B	44.68	[8]
MWCNTs	Sufranine O	43.48	[34]
MWCNTs/Fe_2O_3	Methylene blue	42.3	[35]
	Natural red	77.5	
Carboxylate-functionalized MWCNTs	Malachite green	49.45	[36]
MWCNTs	Methyl orange	52.86	[37]
Oxidized MWCNTs	Bromothymol blue	55	[38]
MWCNTs	Direct Yellow 86	56.2	[39]
	Direct Red 224	61.3	
CNTs	Methylene blue	64.7	[40]
Magnetic graphene-CNT composite	Methylene blue	65.79	[41]
MWCNTs	Orange II	66.12	[42]
	Methylene blue	54.54	
MWCNTs	Methyl violet	71.76	[43]
Carboxylated MWCNTs	Remazol brilliant blue R	95.24	This study
MWCNTs	Methylene blue	132.6	[44]
Functionalized MWCNTs	Congo red	148	[45]
	Reactive green HE4BD	152	
	Golden yellow MR	141	
MWCNTs	Alizarin red S	161.29	[46]
MWCNTs	Acid red 18	166.67	[47]
MWCNTs/Fe_3C	Direct Red 23	172	[48]
Magnetic CNT–cyclodextrin composite	Methylene blue	196.5	[49]
MWCNTs	Reactive red M-2BE	335.7	[50]

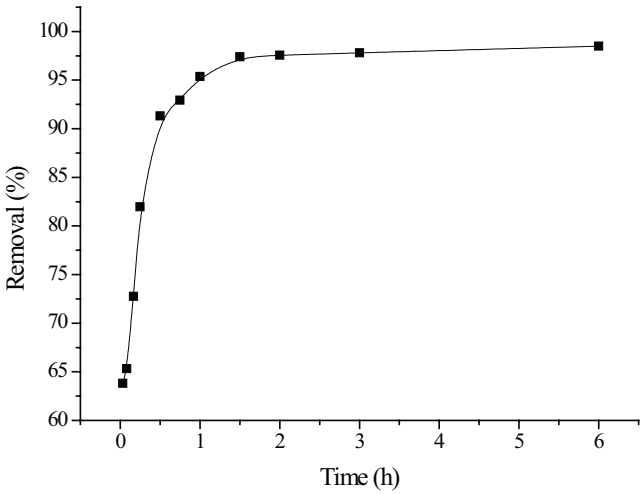

Fig. 4. Adsorption kinetics of RBBR by CCNTs at 25°C. The RBBR concentration was 50 mg/L; the initial pH value was 4, and the CCNTs concentration was 800 mg/L.

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \quad (3)$$

where Q_e and Q_t are the amounts of RBBR adsorbed (mg/g) at equilibrium and time t (min), respectively, and k_1 is the rate constant of the pseudo-first-order kinetic model (1/min). The parameters k_1 and Q_e could be extracted from the slope and the intercept of the plot of $\log(Q_e - Q_t)$ vs. t of Eq. (3).

The linear form of the pseudo-second-order rate equation is as follows [53]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}t \quad (4)$$

where k_2 (g/mg·min) is the rate constant of the pseudo-second-order reaction. The values of Q_e and k_2 can be obtained from the slope and the intercept of the plot of t/Q_t vs. t. The linearized forms of the pseudo-first-order and pseudo-second-order models at an initial RBBR concentration of 50 mg/L are shown in Figs. 5(A) and (B), respectively. The correlation factor obtained for pseudo-second-order model (0.9997) is higher than that for the pseudo-first-order (0.9899), indicating that the experimental data for adsorption of RBBR onto CCNTs was best fitted with pseudo-second-order model. In addition, the Q_e value (49.75 mg/g) calculated from the pseudo-second-order model was closer to the experimental value (49.26 mg/g) than that from the pseudo-first-order model. The results also suggested that the adsorption kinetics of RBBR on CCNTs can be best described by the pseudo-second-order rate equation.

3.6. Thermodynamic parameters

The Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) are important

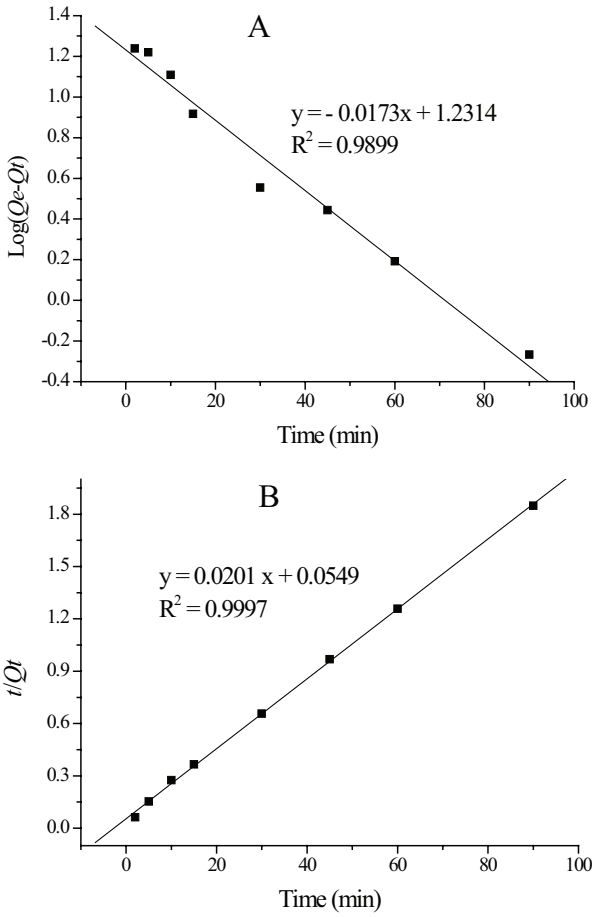

Fig. 5. Pseudo-first-order (A) and pseudo-second-order (B) kinetic curves for the adsorption of RBBR by CCNTs.

Table 3
Values of thermodynamic parameters for the adsorption of remazol brilliant blue R (RBBR) onto the CCNTs

T (K)	K_a (L/mol)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol)
298	1,4473.07	–23.74	44.91	0.192
308	31,201.69	–26.50		
318	45,110.88	–28.33		

thermodynamic parameters to define the feasibility, spontaneity, and heat change for the biosorption process, respectively. $\Delta G°$ can be related with the sorption equilibrium constant K_a by the following equation:

$$\Delta G° = -RT\ln K_a \quad (5)$$

where R is the universal gas constant, 8.314 J/K mol, and T is the absolute temperature (K). The changes of $\Delta H°$ and $\Delta S°$ can be estimated by the following equation:

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H°}{RT} \quad (6)$$

A plot of $\ln K_a$ vs. $1/T$ was linear. The $\Delta H°$ and $\Delta S°$ values were determined from the slope and intercept of this plot, respectively. Q_m, K_a (L/mol), and the values of thermodynamic parameters obtained from Eqs. (5) and (6) are shown in Table 3.

The negative values of $\Delta G°$ indicated the feasibility and the spontaneous nature of the adsorption process. The value of $\Delta H°$ was positive (44.91 kJ/mol), indicating that the adsorption reaction was endothermic. The adsorption process was chemical as the $\Delta H°$ value was greater than 40 kJ/mol [54]. The positive value of $\Delta S°$ (0.192 kJ/mol) reflected the affinity of CCNTs for RBBR and also showed the increase of randomness at the solid/liquid interface during the sorption of dye on the sorbent [55]. Our results agreed with most of the previous studies, which demonstrated that the adsorption processes of dyes by various CNTs or CNT-based composites were endothermic and the adsorption data fitted Langmuir isotherm model and pseudo-second-order model well [21].

4. Conclusions

The adsorption of RBBR in an aqueous solution using CCNTs as adsorbent has been investigated in a batch mode. The batch experiments were performed for the optimization of important process parameters. The experimental data were best described by the Langmuir isotherm model, with maximum adsorption capacities of 95.24, 103.63, and 109.41 mg/g at 25°C, 35°C, and 45°C, respectively. The adsorption kinetics closely followed the pseudo-second-order kinetic model. The positive $\Delta H°$ value demonstrated the endothermic nature of the adsorption interaction. The negative value of $\Delta G°$ indicated the feasibility and the spontaneous nature of the adsorption process. Overall, the results of this work demonstrate that CCNTs have excellent potential for the removal of RBBR from aqueous solutions.

Acknowledgments

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