Adsorption of reactive dye onto carbon nanotubes: Equilibrium, kinetics and thermodynamics

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Abstract

The adsorption efficiency of carbon nanotubes for Procion Red MX-5B at various pHs and temperatures was examined. The amount adsorbed increased with the CNTs dosage; however, the adsorption capacity initially increased with the CNTs dosage (<0.25 g/l) and then declined as the CNTs dosage increased further (>0.25 g/l). The linear correlation coefficients and standard deviations of Langmuir and Freundlich isotherms were determined and the results revealed that Langmuir isotherm fitted the experimental results well. Kinetic analyses were conducted using pseudo first- and second-order models and the intraparticle diffusion model. The regression results showed that the adsorption kinetics were more accurately represented by a pseudo second-order model. Changes in the free energy of adsorption (\(\Delta G^\circ\)), enthalpy (\(\Delta H^\circ\)) and entropy (\(\Delta S^\circ\)), as well as the activation energy (\(E_a\)) were determined. \(\Delta H^\circ\) and \(\Delta S^\circ\) were 31.55 kJ/mol and 216.99 J/mol K, respectively, at pH 6.5 and 41.47 kJ/mol and 244.64 J/mol K at pH 10. The activation energy was 33.35 kJ/mol at pH 6.5. \(\Delta G^\circ\), \(\Delta H^\circ\) and \(E_a\) all suggested that the adsorption of Procion Red MX-5B onto CNTs was by physisorption.

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1. Introduction

Dyes are used extensively in the textile, leather, paper, plastic and other industries. Reactive dye production is characterized by the great losses that are caused by the high solubility of the dyes, which also creates an economical and environmental problem. Removing reactive dyes by coagulation is difficult because the dyes are highly soluble in water. Hence, the removal of dye from colored reactive dye wastewater is an important environmental issue. Adsorption has been found to be superior to other techniques for treating wastewater: it is low-cost, highly efficient, simple, easy to perform and insensitive to toxic substances. Moreover, liquid-phase adsorption has been demonstrated to be highly efficient in removing dyes from waste effluent. Hence, adsorption was selected herein as the approach used to treat reactive dye wastewater.

Carbon nanotubes (CNTs) are attracting increasing research interest as a new adsorbent. They are an attractive alternative for the removal of organic and inorganic contaminants from water, because they have a large specific surface area, small size, and hollow and layered structures. Recently, CNTs have been found to be efficient adsorbents with a capacity that exceeds that of activated carbon [1,2]. Much attention has been paid to the adsorption by CNTs such as ZnP2+ [2], CdP2+ [3], PbP2+ [4–7], CuP2+ [7], CrP6+ [8], fluoride [9], arsenate [10], trihalomethanes [11], 1,2-dichlorobenzene [12] and dioxin [1]. Experimental results demonstrate that compared with activated carbon (AC), CNTs comparatively improve adsorption of Procion Red MX-5B onto TiO2; the saturation adsorption capacity of TiO2, TiO2/AC and TiO2/CNTs is 6.3, 13.3 and 14.2 mg/g, respectively [13]. Furthermore, Yu et al. [14] indicated that TiO2/CNTs composites have higher photocatalytic activity than TiO2 and the TiO2/AC composite. Earlier investigations have suggested that CNTs may be a promising adsorbents for treating wastewater. However, few studies have been conducted on the adsorption of organic pollutants by CNTs, except for dioxin [1]; trihalomethanes [11] and 1,2-dichlorobenzene [12]. The reactive dye, Procion Red MX-5B, was employed as the organic pollutant to be treated by CNTs in this work.
An understanding of adsorption equilibrium, kinetics and thermodynamics is critical in supplying the basic information required for the design and operation of adsorption equipment. Earlier studies have obtained only equilibrium and kinetic adsorption data and few works have measured the thermodynamic parameters of adsorption on CNTs: Peng et al. [12] measured those of the adsorption of 1,2-dichlorobenzene and Li et al. [5] examined the thermodynamics of the adsorption of PbP₂⁺ on CNTs. Few investigations focused on the adsorption of organic pollutants on CNTs and simultaneously determined the equilibrium, kinetics and thermodynamic parameters. Hence, this study elucidates the equilibrium, kinetics and thermodynamics of the adsorption of Procion Red MX-5B onto CNTs. The Langmuir and Freundlich isotherms were used to fit the equilibrium data. The effects of temperature on the dynamic behaviors of adsorption were determined. The adsorption rates were determined quantitatively and those obtained using the pseudo first- and second-order models and the intraparticle diffusion model was also compared. The objectives of this study were: (i) to determine the appropriate CNTs dosage to adsorb Procion Red MX-5B; (ii) to measure the coefficients of Langmuir and Freundlich isotherms; (iii) to evaluate the adsorption rate using various kinetic models; (iv) to derive the thermodynamic parameters—activation energy ($E_a$), and the changes in free energy ($\Delta G^o$), enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) during adsorption at various pH values.

2. Materials and methods

2.1. Materials

The CNTs adopted herein were multi-wall nanotubes (CBT, MWNTs-2040, which were used without further purification). CNTs were produced by the pyrolysis of methane gas on particles of Ni in a chemical vapor deposition. The length of CNTs was 5–15 μm and the mass proportion of amorphous carbon in CNTs was less than 2%. The parent compound, Procion Red MX-5B, was purchased from Aldrich Chemical Company. The formula, molecular weight and maximum wavelength of light absorbed by Procion Red MX-5B (CI Reactive Red 2) were C₁₀H₁₀Cl₂N₆Na₂O₂S₂, 615 g/mol, and 538 nm, respectively. The structure of Procion Red MX-5B is shown in Fig. 1. All solutions were prepared using deionized water (Milli-Q) and reagent-grade chemicals.

2.2. Characterization of CNTs

CNTs were subjected to energy dispersive spectrometer for surface distribution of elemental composition and scanning electron microscopy (SEM) with a JEOL JSM-6500F. Size and morphology of CNTs were recorded by transmission electron microscopy (TEM) with a Philips/FEI Tecnai 20 G2 S-Twin. The specific surface area of CNTs was measured by the BET method using a Quantachrome-Autosorb1. The zeta potential of the CNTs was measured at pH values of 2–9 using a Zeta-Meter 3.0. Ten measurements were made of each sample at each pH and the average was determined as the zeta potential.

2.3. Adsorption experiments

All experiments were conducted in a closed 250 ml glass pyramid bottle and HClO₄ or NaOH was used to adjust the pH. The 250 ml glass pyramid bottle, containing 0.05 g of CNTs and 200 ml of Procion Red MX-5B solution, was placed in a water bath and shaken at 160 rpm. In experiments to determine CNTs dosage, Procion Red MX-5B (20 mg/l) was equilibrated with a suspension of CNTs (0.025, 0.05, 0.25, 0.5 and 0.75 g/l) at pH 6.5 for 24 h. In the experiments on the effect of temperature (Procion Red MX-5B = 20 mg/l and CNTs = 0.25 g/l), the temperature was held at 281, 291, 301 and 321 K and the pH was fixed at 6.5 and 10. At the end of the equilibrium period, the suspensions were centrifuged at 4000 rpm for 10 min, and the supernatant was then filtered through 0.2 μm filter paper (Gelman Sciences) for later analysis of the dye concentration. The adsorption of Procion Red MX-5B was detected using a spectrophotometer (Hitachi-U2001) at 538 nm. Each experiment was performed twice and experimental results are average values. The adsorbed amounts $q_i$ were calculated from:

$$q_i = \frac{C_i - C_o}{m} \quad (1)$$

where $C_i$ and $C_o$ are the initial and equilibrium concentrations, respectively, in mg/l, and $m$ is the amount of CNTs in g/l.

3. Results and discussion

3.1. Effects of CNTs dosage

Fig. 2 displays the surface morphology of CNTs. The SEM and TEM figures show that the CNTs were cylindrical and that the range of main external and internal diameters was 20–80 and 5–10 nm, respectively. Additionally, the distance between the wall and wall of CNTs was approximately 0.5–1 nm and the TEM analysis confirmed the hollow structure of CNTs. The specific surface area of the CNTs used in this study was 106.9 m²/g. The pH of the zero point of charge (pH_zpc) for CNTs was determined to be 4.9, which was the same as that measured by Lu and Chiu [2] for multi-wall nanotubes. This result indicated that the surface of CNTs was positively charged at a solution pH of <4.9. The element characteristics of CNTs showed the content of C, O and Ni was 90.6, 8.1 and 1.3%, respectively. Since the CNTs were generated by the pyrolysis of methane gas on particles of...
Ni by chemical vapor deposition, the major element was carbon, with only a few Ni atoms present.

Fig. 3 presents the effect of CNTs dosage on the adsorption of Procion Red MX-5B. The amount adsorbed increased with the dose of CNTs; however, the adsorption capacity initially increased and then dropped as the CNTs dosage increased. In dilute CNTs suspensions (<0.25 g/l), CNTs are suggested to be separated and dispersed. In this case, the adsorption capacity at the external surface predominated, and for this reason, the adsorption capacity of Procion Red MX-5B would be high. Increasing the CNTs dose (>0.25 g/l) increases the probability of the CNTs entanglement in the solution, causing adsorption in the interlayer space and a decrease in the aggregation of dye at the external surface.

Accordingly, the adsorption capacity declined as the CNTs dosage increased above 0.25 g/l. Moreover, the high CNTs dosage may influence the physical characteristics of the solid–liquid suspensions, such as by increasing the viscosity and inhibiting the diffusion of dye molecules to the surface of the CNTs. Since the concentration of Procion Red MX-5B was fixed, the adsorption capacity decreased as the CNTs dosage increased (>0.25 g/l). The increase with CNTs dosage of the amount of dye adsorbed was caused by the availability of more surface area of the CNTs. Direct evidence of CNTs entanglement was unclear and unobtainable. However, similar observations can be found in literature. Bhattacharyya and Sharma [15], who utilized Neem leaf powder to adsorb dyes, suggested that the amount adsorbed (mg/g) decreased as the amount of the adsorbent increased; similar results were also obtained for algae cell walls by Marungrueng and Pavasant [16] and for cross-linked chitosan beads by Chiou et al. [17]. Gemeay [18] employed Na+-montmorillonite to adsorb rhodamine-6G and obtained similar results to those in this study: adsorption increased as Na+-montmorillonite increased (<0.2 g/l) and decreased with further increases of Na+-montmorillonite (>0.2 g/l). Since the adsorption capacity was greatest when 0.25 g/l CNTs was added, this dosage (0.25 g/l) was used in the following experiments.

3.2. Adsorption isotherms

The correlation of equilibrium adsorption data by either theoretical or empirical equations is important in the design and operation of adsorption systems. This study employed the Langmuir and Freundlich models to describe the equilibrium adsorption. The expression of the Langmuir model is:

\[
q = \frac{q_m K_L C}{1 + K_L C}
\]

where \(q\) is the amount of dye adsorbed per gram of CNTs (mg/g); \(C\) denotes the equilibrium concentration of dye in solution (mg/l); \(K_L\) represents the Langmuir constant (l/mg) that relates to the affinity of binding sites and \(q_m\) is the theoretical saturation capacity of the monolayer (mg/g). The values of \(q_m\) and \(K_L\) are calculated from the intercept and slope of the linear plot of \(1/q\) versus \(1/C\). Furthermore, the effect of the isotherm shape is considered with a view to predict whether an adsorption system is favorable or unfavorable. Another important parameter, \(R_L\), called the separation factor or equilibrium parameter, also evaluated in this study, is determined from the relation:

\[
R_L = \frac{1}{1 + K_L C_0}
\]
4. Conclusion

This investigation examined the equilibrium and the dynamic adsorption of Procion Red MX-5B onto CNTs at various pHs and temperatures. The adsorption capacity was highest when 0.25 g/l CNTs was added. $K_1$ increased with temperature and declined as the pH increased. The results suggested that the adsorption of Procion Red MX-5B on CNTs decreased as the pH rose but increased with temperature. $R_t$ lied between zero and unity, revealing that the adsorption of Procion Red MX-5B on CNTs was favorable. The values of $k_2$, $h$, $q_{exp}$ and $q_{cal}$ all increased with the temperature, suggesting that increasing the temperature increased the adsorption capacity and the adsorption rate. The regression results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate-controlling step. Positive $\Delta H^\circ$ and $\Delta S^\circ$ values indicated that the adsorption of Procion Red MX-5B onto CNTs was endothermic, which result was supported by the increasing adsorption of Procion Red MX-5B with temperature. The values of $\Delta H^\circ$, $\Delta G^\circ$ and $E_a$ all suggested that the adsorption of Procion Red MX-5B onto CNTs was a physisorption process and was spontaneous.

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