Enhanced Adsorption of Malachite Green onto Carbon Nanotube/Polyaniline Composites

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ABSTRACT: To enhance adsorption of organic dyes like malachite green (MG) onto polymeric absorbents, we prepared carbon nanotube (CNT) filled polyaniline (PANI) composites with large surface areas by simply using entangled CNTs as porous frameworks during PANI polymerization. Adsorption behavior of the CNT/PANI composites in MG solutions was experimentally investigated and theoretically analyzed. The CNT/PANI composites exhibit much higher equilibrium adsorption capacity of 13.95 mg g^{-1} at an initial MG concentration of 16 mg L^{-1}, increasing by 15% than the neat PANI, which is mainly attributed to large surface areas and strong CNT-PANI interactions of the composites. In addition, theoretical analyses indicate that the adsorption kinetics and the isothermal process of the composites can be well explained by using the Ho pseudosecond-order model and the Langmuir model, respectively. In light of their high MG adsorption and easy operation, the CNT/PANI composites have great potential as high-efficiency adsorbents for removal of dyes from wastewater. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Malachite green (MG) is an important water-soluble cationic dye which has been widely used in textiles, printing, and plastics industries. However, it is hazardous to human beings and is prone to developing a liver tumor.[1,2] Hence, high-efficiency removal of MG dye from aqueous solution has been a crucial issue for health of human beings and protection of ecological environments. There are generally many ways to dispose of MG dye in wastewater treatment industries, such as chemical degradation,[3] bio-sorption,[4] and physical adsorption.[5] Among these methods, the physical adsorption is a promising technique due to the easy operation and convenient recycling of absorbents,[6] and some high-efficiency MG adsorbents have been developed on the basis of inorganic minerals,[7–10] plants and its derivatives,[11–14] activated carbon based on various precursors,[5,15–21] polymers,[22–24] and so on. Recently, conductive polymers like polyaniline (PANI) as polymeric adsorbents for dye removal from aqueous solution have attracted great interest due to their environmental stability, controllable quality, and good processability.[25,26]

Dye-adsorption behavior of PANI has been investigated to remove various cationic/anionic dyes from aqueous solution.[27–29]

Research shows that PANI in different forms can exhibit selective adsorption of dyes, that is, protonated PANI emeraldine salts (ES) and deprotonated PANI emeraldine base (EB) exhibit preferential adsorption of anionic and cationic dyes, respectively.[29] The chemical structures of PANI in different forms and its conversion mechanism during simple chemical treatments were shown in Scheme 1. It is worth mentioning that the deprotonated PANI-EB is more prone to selectively adsorb cationic dyes like MG than the PANI-ES due to the electrostatic interactions between the cationic dye groups and the amine and imine nitrogen in PANI-EB structure.[6,29] On the other hand, enlarging surface areas of PANI has been proved to be an effective route for high adsorption capacity.[6,23] Ayad and Ai et al.[6,23,30] have recently synthesized PANI microspheres and nanotubes and consequently obtained high dye-adsorption capacity due to much larger surface areas of these PANI than conventional PANI powders; however, there exist complicated synthesis procedures of these PANI microspheres and nanotubes. Therefore, fabrication of large-surface-area PANI-EB in a simple way will be beneficial to enhance the MG adsorption onto adsorbents and improve the removal of hazardous dyes from aqueous solution.
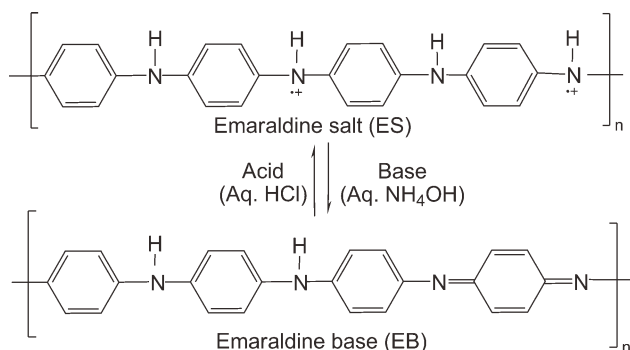
Scheme 1. Conversion mechanism between the PANI-ES and the PANI-EB

Carbon nanotubes (CNTs) have a unique quasi-one-dimensional hollow structure with high elastic modulus, high specific surface areas, and good chemical and thermal stability, and their applications in water treatments have attracted much attention.[31,32] It is notable that commercial CNTs are generally prone to twist and entangle each other and consequently form entangled CNT networks due to their small size and high aspect ratio (the ratio of length to diameter) over 100. Such entangled CNT networks may play a role of rigid porous frameworks for supporting PANI during polymerization to enlarge surface areas of the PANI and consequently result in a high adsorption of MG dye. The PANI-coating CNT (CNT/PANI) composites have been widely investigated including microstructure, morphology, porosity, surface area, interactions, and electrochemical properties, etc.[33–37] To the best of our knowledge, enhanced adsorption of MG dye onto the CNT/PANI composites by simply using entangled CNTs as frameworks for enlarging surface areas of PANI has not been reported so far.

The objective of this work is to design and fabricate the CNT/PANI composites with a high MG-adsorption capacity by simply using entangled CNTs as frameworks. The CNT/PANI composites were prepared by synthesizing PANI-EB onto the surfaces of entangled CNTs, and their adsorption behavior in aqueous MG solutions was measured experimentally and analyzed theoretically. Result shows that the CNT/PANI composites exhibit much higher MG-adsorption capacity than the neat PANI, which is mainly attributed to porous structure, large surface areas, and strong CNT-PANI interactions of the CNT/PANI composites, showing that fabrication of large-surface-area adsorbents by simply using CNTs as frameworks is feasible for significantly improving dye removal from wastewater in a short-cut way.

EXPERIMENTAL

Materials

Entangled multiwalled CNTs, produced by catalytic decomposition of hydrocarbons using an improved floating catalyst method, were supplied from Institute of Metal Research, Chinese Academy of Sciences, China, and their average diameter and length were 50–100 nm and 5–10 μm, respectively; specific surface area of the CNTs, measured by using a surface-area and porosimetry analyzer (Micrometritics, ASAP2010M), was 36.97 m^2 g^{-1}. Aniline monomer (analytical grade, AG) was produced

by Shenyang Xinxi Reagent Factory, China. Chemical reagents such as ammonium peroxidisulphate (APS, AG), hydrochloric acid (35% HCl), carbon tertrachloride (CCl_4, AG), ammonium hydroxide ($NH_3 \cdot H_2O$), and malachite green (MG, $C_{23}H_{25}ClN_2$,) were received from Sinopharm Chemical Reagent (Shenyang) Co.

Preparation of the CNT/PANI Composites

The CNT/PANI composites were synthesized by using a static interfacial polymerization technique. Firstly, APS of 5.71 g was dissolved in 50 mL aqueous HCl solution of a concentration of 0.5 M, and the entangled CNTs of 0.23 g were added into the solution and ultrasonicated for 2 h at room temperature to obtain uniform dispersion of the CNTs. Secondly, aniline monomer of 2.28 mL was dissolved in 50 mL CCl_4 solution and then poured into a 300 mL beaker. Thirdly, the prepared CNT-containing aqueous solution was slowly transferred into this beaker, showing a distinct interface between these two immiscible solutions, and static interfacial polymerization of aniline began to occur without any stirring. Green protonated PANI-ES gradually formed in the interface region and migrated into the upper CNT-containing aqueous solution, and subsequently deposited onto the surfaces of the entangled CNTs. After 24 h, the upper aqueous solution was filled with black-green CNT/PANI-ES composites, and then these composites were filtered and fully washed with deionized water and alcohol in turn to remove unreacted components. To obtain preferential adsorption of cationic dyes, the CNT/PANI-ES composites were further chemically treated with $NH_3 \cdot H_2O$ solution of pH 14 for 24 h, and the green PANI-ES coating on CNT surfaces was converted into blue PANI-EB with a preferential MG-adsorption as a result of deprotonation reaction.[38,39] The prepared CNT/PANI-EB composites were fully washed with deionized water and thoroughly dried at 60°C for 24 h, and consequently the blue-black CNT/PANI composites were obtained. Neat PANI was prepared following the same procedures without CNT additions.

Microstructure of the CNT/PANI Composites

Microstructure and morphology of the neat PANI and the CNT/PANI composites were observed by using a scanning electron microscopy (SEM, Nova NanoSEM 430, FEI). Phase identifications of the neat PANI, pristine CNTs, and CNT/PANI composites were characterized on the basis of X-ray powder diffraction (XRD) patterns recorded on a diffractometer (D/Max-2500PC, Japan) with Cu-K_α radiation at a scanning rate of 1° min^{-1}.

Adsorption Behavior of the CNT/PANI Composites

Adsorption behavior of the neat PANI and CNT/PANI composites in aqueous MG solution was investigated. Firstly, aqueous MG solutions of different initial concentrations (8, 12, and 16 mg L^{-1}) with a pH value of 7 were prepared in advance. Secondly, the weighted neat PANI or CNT/PANI composite of 0.1 g were added into the prepared MG solutions of 100 mL and mixed well at 20°C in a thermostatic water bath. At intervals of 10 min, a small amount of samples were collected from the absorbent-containing MG solutions and separated by using a high-speed centrifuge. Concentrations of the upper MG solutions were measured by using an UV-vis spectroscopy (U-2800,
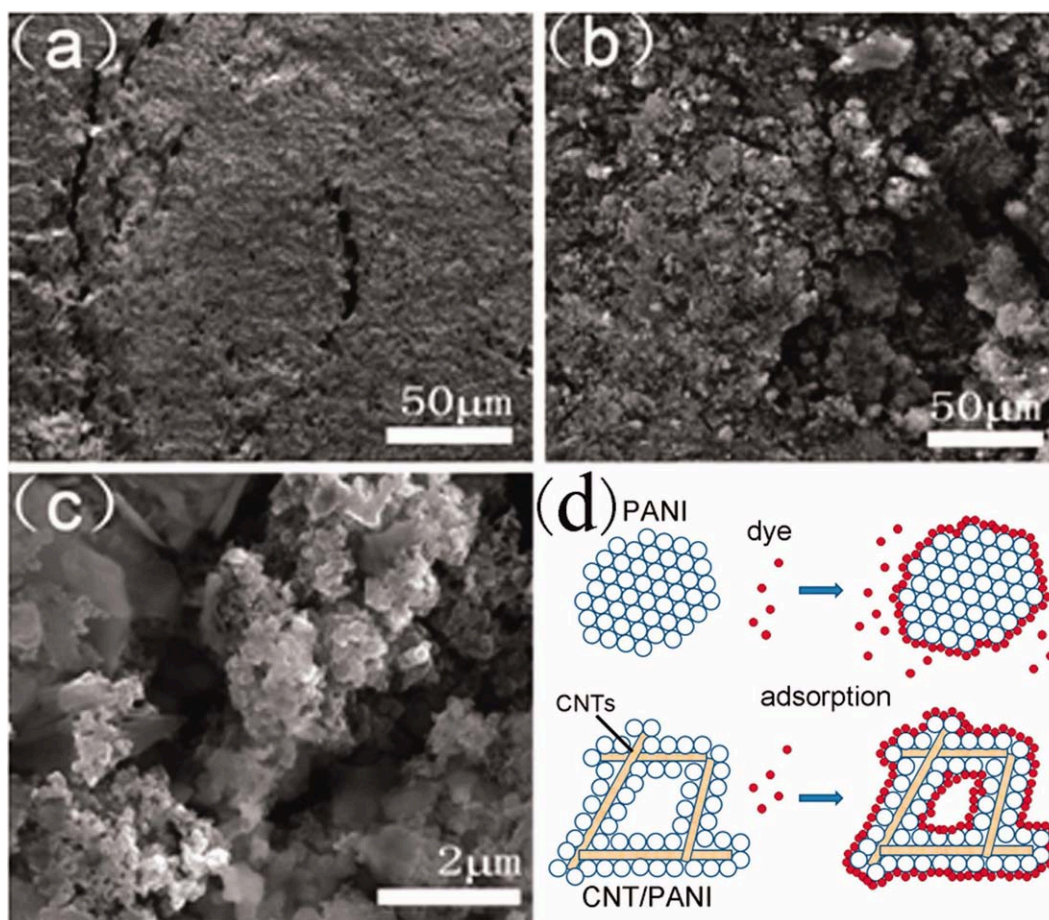
Figure 1. SEM images of (a) the neat PANI and (b and c) CNT/PANI composites at different magnifications, and (d) the schematic of dye-adsorption onto adsorbents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hitachi) and calibrated with the Beer-Lambert law at λ_{max} value of 620 nm for the MG dye, and the MG-adsorption capability of the used adsorbents was evaluated in terms of dye-adsorption amount (Q) and dye-removal ratio (R) as functions of adsorption time (t). At t time, Q_t and R_t were calculated according to the following equations:

$$Q_t = V(C_0 - C_t)/m \quad (1)$$

$$R_t = (C_0 - C_t)/C_0 \times 100\% \quad (2)$$

where C_0 and C_t are concentrations of the MG solutions at initial and t time, respectively; V is volume of the MG solutions, and m is mass of the adsorbents used. Meanwhile, electrical conductivity of the upper MG solutions was also measured at intervals by using a digital conductivity meter (DDS-11A, Shanghai Youke Instrument Co.) and was converted into molar conductivity to indicate the change of MG concentrations as a function of adsorption time in the whole adsorption process.

RESULTS AND DISCUSSION

Structure and Morphology Characterization

Microstructure and dye-adsorption schematic of the neat PANI and CNT/PANI composites were shown in Figure 1. Comparing with the closely-grained structure of the neat PANI shown in Figure 1(a), the CNT/PANI composites clearly exhibit multiscale porous structure in Figure 1(b,c), implying high porosity and large surface areas. Such a high porosity of the CNT/PANI composites is mainly attributed to multiscale porous structure of the entangled CNTs as rigid frameworks for PANI coating. Because the PANI-coated CNTs generally exhibit higher porosity and larger surface areas than the neat PANI,[36,37,40,41] the CNT/PANI composites probably process higher dye-adsorption capacity than the neat PANI, as illustrated in Figure 1(d). On the other hand, there are less CNTs observed in the SEM images of the CNT/PANI composites, indicating a high-efficiency PANI coating on CNT surfaces by means of the static interface polymerization, which is due to strong interactions between PANI and CNTs.[33,34] It is worth mentioning that such strong $\pi - \pi^\star$ interactions in the CNT/PANI composites are also beneficial to improve charge transfer between PANI and CNTs for enhancing adsorption of ionic dyes.

We further measured the XRD patterns of the CNTs, neat PANI, and CNT/PANI composites. It can be seen in Figure 2 that both the neat PANI and the CNT/PANI composites show strong peaks at 2θ angles of 18.2 and 25.1°, indicating typical crystalline regions of PANI as a result of periodic arrangements of macromolecular chains;[42] whereas the CNTs show a
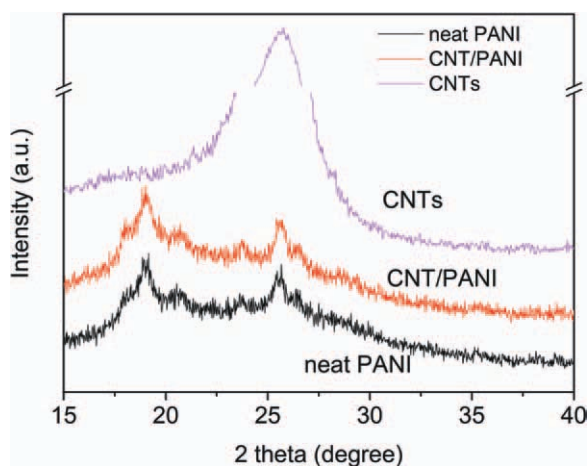
Figure 2. XRD patterns of the CNTs, neat PANI, and CNT/PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

diffraction peak at 25.8°, corresponding to graphite-like structures.[43] We cannot find apparent differences in XRD patterns between the neat PANI and the CNT/PANI composites, implying that the presence of CNTs does not strongly influence the crystallinity of PANI, which is mainly attributed to the full PANI-coating onto CNT surfaces due to the strong PANI-CNT interactions.[43,44] Therefore, the high-efficiency PANI coating and the porous structure of the CNT/PANI composites are beneficial to enlarge surface areas of PANI, increase adsorption sites of PANI, and consequently greatly enhance dye-adsorption of the composites.

Adsorption Behavior of the CNT/PANI Composites
Figure 3 shows adsorption behavior of the neat PANI and CNT/PANI composites in MG solutions of different initial concentrations. We can see that the CNT/PANI composites exhibit larger MG-adsorption amounts (Q) and higher removal ratio of MG dye (R) than the neat PANI, which is mainly attributed to the large surface area of the porous CNT/PANI composites. All the adsorbents show a rapid increase in MG-adsorption amounts at
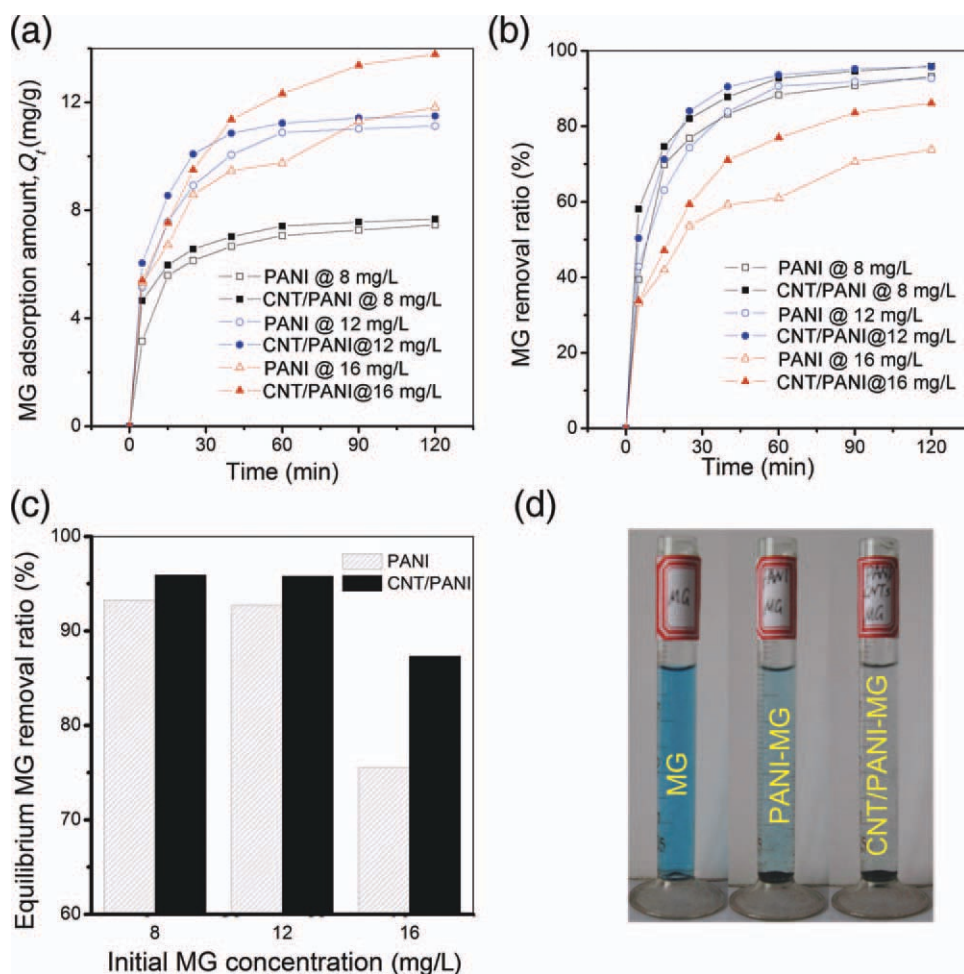

Figure 3. Adsorption behavior of the neat PANI and CNT/PANI composites in MG solutions of different concentrations. (a) Adsorption amount and (b) removal ratio of MG dye as functions of adsorption time, (c) equilibrium MG-removal ratio at different MG concentrations, and (d) optical photographs of the MG solutions containing the PANI and CNT/PANI composites before and after adsorption. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
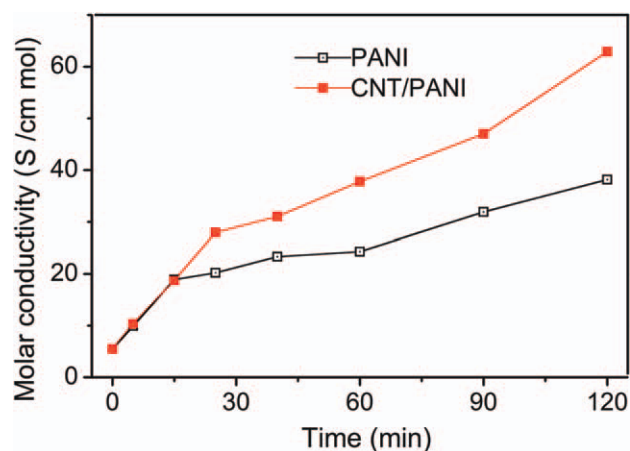
Figure 4. Change in molar conductivity of the MG solutions containing the neat PANI and CNT/PANI composites in the adsorption process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

initial stages, and their MG adsorption gradually levels off at the end of the adsorption process. Such a change in adsorption amounts (Q) as a function of adsorption time (t) implies a typical physical-adsorption mechanism: the MG dye was adsorbed firstly onto the PANI surfaces due to the preferential adsorption of cationic dyes onto the prepared PANI-EB,[6] resulting in a sharp increase in the MG-adsorption amounts; when the adsorption sites on the PANI surfaces are gradually saturated by the MG dye, the adsorption process of the adsorbents slows down due to gradual enhancement of charge repulsive forces between the absorbed and unabsorbed dyes.[29]

We can see in Figure 3(a,b) that the adsorption behavior of all the adsorbents strongly depends on the initial MG concentrations. At the MG concentrations lower than 12 mg L^{-1}, both the neat PANI and the CNT/PANI composites exhibit small equilibrium adsorption amounts less than 11 mg g^{-1} and high removal ratios over 90%; the reason is that both two adsorbents have enough surface areas for full adsorption of the small amounts of MG dye at low concentrations. On the contrary, both two adsorbents show slow adsorption processes, large adsorption amounts, and low removal ratio at a high MG concentration of 16 mg L^{-1}, which is because that the MG amount in that case is too high to be thoroughly absorbed by the adsorbents. It is worth mentioning that equilibrium adsorption amount of adsorbents in aqueous solution, especially in the solution of high dye concentrations, is a crucial criterion for evaluating adsorption efficiency of adsorbents in wastewater treatments.

It is notable that the CNT/PANI composites at the high MG concentration of 16 mg L^{-1} exhibit much higher adsorption capacity than the neat PANI, as shown in Figure 3(a–c). The equilibrium MG-adsorption amount and the removal ratio of the CNT/PANI composites are 13.95 mg g^{-1} and 88%, respectively, increasing by 21.7 and 15% in comparison with those of the neat PANI. Such a high-efficiency adsorption of the CNT/PANI composites can also be clearly observed from the optical

photographs shown in Figure 3(d). It is worth mentioning that the MG-adsorption capacity of the CNT/PANI composites in our work is lower than that of other adsorbents such as modified rice straw and inorganic minerals,[45,46] but higher than some bio-sorbents,[47] which is mainly attributed to different adsorption mechanisms in various systems. In our work, the higher adsorption capacity of the CNT/PANI composites than the neat PANI mainly results from the following two aspects: (1) the CNT/PANI composites have much larger surface areas and more adsorption sites for MG adsorption than the neat PANI, resulting in the rapid MG adsorption and high MG removal from aqueous solutions; (2) the strong $\pi-\pi^\star$ interactions existing in the CNT/PANI composites are helpful for effective charge transfer between the two components,[34] and thus enhance the adsorption of the cationic MG dye onto PANI surfaces. Therefore, the high adsorption capacity of the CNT/PANI composites is closely associated with the large surface area of the composites and the strong CNT-PANI interactions.

We further measured the changes in molar conductivity of the MG solutions in the whole adsorption process to evaluate the MG-adsorption capacity of the neat PANI and the CNT/PANI composites. Based on the law of independent migration of ions, the molar conductivity of solutions is strongly concentration dependent for weak electrolytes; the more dilute a solution, the greater its molar conductivity.[48] It can be seen in Figure 4 that the molar conductivity of both two adsorbent-containing solutions gradually increases with adsorption time, implying a gradual decrease in the MG concentration due to the effective MG removal from aqueous solutions.[29] On the other hand, the solution containing CNT/PANI composites exhibits much higher molar conductivity and more rapid increase in conductivity than that containing neat PANI, implying higher MG-adsorption capacity of the CNT/PANI composites than the neat PANI due to the porous structure, large surface area, and strong CNT-PANI interactions of the CNT/PANI composites, which is consistent with the adsorption behavior shown in Figure 3.

Theoretical Analyses on the Adsorption Behavior

We used the Ho pseudosecond-order model and the intraparticle diffusion model to theoretically analyze the adsorption kinetics of the neat PANI and CNT/PANI composites. The Ho pseudosecond-order equation and the intraparticle diffusion equation are expressed by Eqs. (3) and (4), respectively[6,49]:

$$t/Q_t = 1/(k_{ps}Q_e^2) + t/Q_e \qquad (3)$$

$$Q_t = k_{id}t^{1/2} + C \qquad (4)$$

where Q_e and Q_t are the dye-adsorption amounts at equilibrium and t time, respectively, and k_{ps} is the rate constant; C and k_{id} are constants of the intraparticle diffusion equation. Figure 5 shows the linear fitting of our experimental data to the calculated data from these two models, and related kinetic parameters were listed in Table I. It can be seen clearly that there is a good linear relationship between t/Q_t and t in Figure 5(a), and its corresponding correlation coefficients (r^2) in Table I are more than 0.99, but there is not such a relationship between Q_t
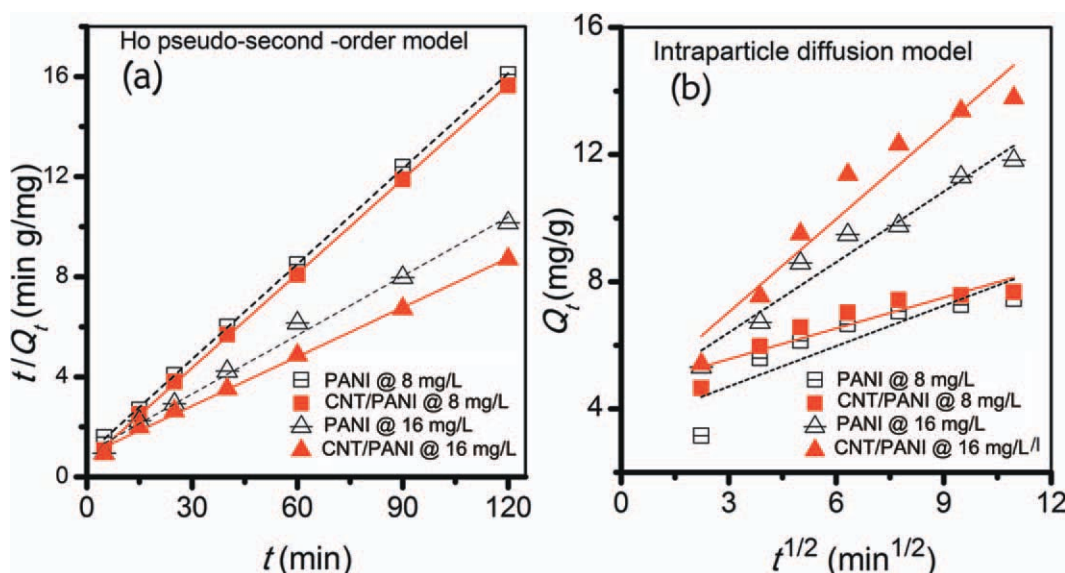
Figure 5. Linear fitting of adsorption behavior of the neat PANI and CNT/PANI composites based on (a) the Ho pseudosecond-order model and (b) the intraparticle diffusion model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and $t^{1/2}$ as shown in Figure 5(b), implying that the adsorption behavior of both the neat PANI and the CNT/PANI composites can be well explained by the Ho pseudosecond-order model rather than the intraparticle diffusion model. It means that the adsorption behavior of the adsorbents in our work is mainly dominated by the MG adsorption onto the PANI surfaces, not by the intraparticle diffusion.[50] On the other hand, it can be seen in Table I that the CNT/PANI composites exhibit an equilibrium dye-adsorption amount (Q_e) of 15.23 mg g^{-1}, more than 12.72 mg g^{-1} for the neat PANI, which is mainly attributed to the large surface area of the porous CNT/PANI composites.

We further investigated the adsorption isothermal process of the neat PANI and CNT/PANI composites by using the Langmuir model to evaluate dye distribution on the surfaces of adsorbents. The Langmuir equations are represented as follows[27]:

$$C_e/Q_e = 1/(Q_m k_L) + C_e/Q_m \qquad (5)$$

$$Q_e = Q_m k_L C_e/(1 + k_L C_e) \qquad (6)$$

Table I. Kinetic Parameters for MG-Adsorption onto the PANI and CNT/PANI Composites

	Ho pseudosecond-order model				Intraparticle diffusion model	
	r^2	Q_e	k_{ps}	$k_{ps}Q_e^2$	r^2	k_{id}
PANI	0.991	12.72	6.5×10^{-3}	1.05	0.945	0.739
CNT/PANI	0.997	15.23	5.0×10^{-3}	1.16	0.923	0.977

Initial MG solution concentration of 16 mg L^{-1}; correlation coefficient, r^2; dye-adsorption amount at equilibrium, Q_e (mg g^{-1}); k_{ps} (g mg^{-1} min^{-1}) and K_{id} (mg g^{-1} min$^{-0.5}$) are rate constants for corresponding models.

where C_e and Q_m are the equilibrium dye concentration and the Langmuir monomolecular adsorption capacity, respectively, and k_L is the Langmuir constant. The values of Q_e as a function of C_e were plotted in Figure 6, and the related parameters were listed in Table II. We can see in Figure 6 that the relationship between the equilibrium adsorption amount (Q_e) and the equilibrium dye concentration (C_e) is well fitted to the Langmuir model, and their corresponding correlation coefficient (r^2) in Table II are more than 0.99, revealing that the dye adsorption mainly occurs at specific adsorption sites existing on the PANI surfaces and strongly depends on the dye-PANI interactions.[33,34]
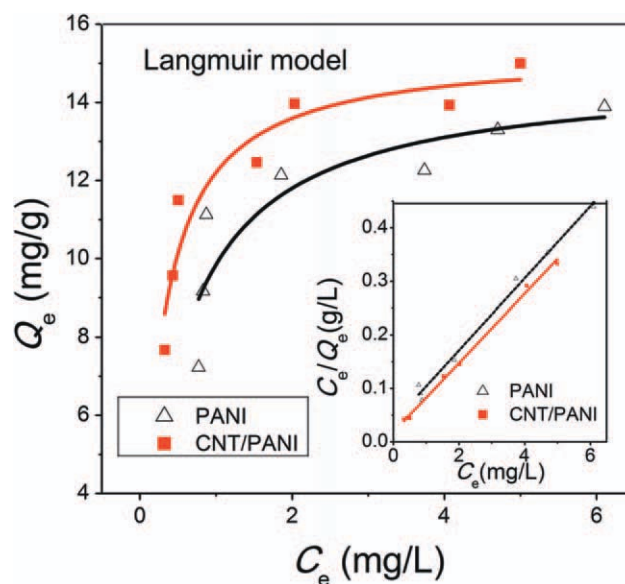

Figure 6. Change in the equilibrium MG-adsorption amount (Q_e) as a function of the equilibrium concentration (C_e), the inset showing a linear relationship between the C_e/Q_e and C_e. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Parameters for MG-Adsorption onto Adsorbents Based on the Langmuir Model

	r^2	Q_m	K_L
PANI	0.990	14.88	1.824
CNT/PANI	0.996	15.45	3.591

Langmuir monomolecular adsorption capacity, Q_m (mg g^{-1}); Langmuir constant, K_L (L mg^{-1}).

In our work, there exist strong electrostatic and $\pi-\pi^\star$ interactions between the components of the CNT/PANI-MG system, which is beneficial to enhance the MG-dye adsorption and thus results in higher value of Q_m than the neat PANI. Therefore, the high MG adsorption of the CNT/PANI composites is mainly attributed to the large surface area and the strong interactions between components.

It is worth mentioning that the dye-adsorption behavior of the CNT/PANI composites was strongly influenced by many factors, such as pH value of solution, temperature, surface area, porosity, mass or volume fraction of CNTs, protonation/deprotonation degree of PANI, interactions between components in dye-CNT/PANI systems, and so on. Some detailed research on the CNT/PANI composites should be further carried out in the future to obtain optimal MG-removal from wastewater for exploring practical application of the CNT/PANI composites as high-efficiency adsorbents.

CONCLUSIONS

The CNT/PANI composites were prepared by simply using the entangled CNTs as porous frameworks for enlarging the surface area of PANI to enhance the MG adsorption in aqueous solution. The microstructure of the CNT/PANI composites were characterized by using SEM and XRD, and the adsorption behavior of the composites in MG solutions of different concentrations was experimentally investigated and theoretically analyzed. The CNT/PANI composites exhibit much higher MG-adsorption capacity than the neat PANI, their equilibrium MG-adsorption amount and MG removal ratio are 13.95 mg g^{-1} and 88%, respectively, increasing by 21.7 and 15% than those of the neat PANI. Such a high MG adsorption of the CNT/PANI composites is mainly attributed to the large surface area and strong interactions of the CNT/PANI composites. In addition, theoretical analyses show that the MG-adsorption behavior of the CNT/PANI composites can be well explained by the Ho pseudosecond-order model and the Langmuir model. In light of their high MG-adsorption capacity and easy operation, the CNT/PANI composites have great potential as high-efficiency MG adsorbents in the fields of wastewater treatments.

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