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Removal of 1-naphthylamine from aqueous solution by multiwall carbon nanotubes/iron oxides/cyclodextrin composite

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ABSTRACT

The adsorption of 1-naphthylamine on multiwall carbon nanotubes/iron oxides/β-cyclodextrin composite (denoted by MWCNTs/iron oxides/CD) prepared by using plasma-induced grafting technique was investigated by batch technique under ambient conditions. The effect of contact time, pH, adsorbent content, temperature and initial 1-naphthylamine concentration, on 1-naphthylamine adsorption to MWCNTs/iron oxides/CD was examined. The adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD was dependent on pH, adsorbent content, and temperature. The 1-napthylamien was adsorbed rapidly at the first 50 h, and thereafter attained the adsorption saturation at 80 h. The adsorption kinetic data were well described by the pseuso-second-order rate model. The adsorption isotherms were fitted by the Langmuir model better than by the Freundlich model. The maximum adsorption capacity of 1-naphthylamine was 200.0 mg/g. The adsorption thermodynamic parameters of standard enthalpy (ΔH^0), standard entropy changes (ΔS^0), and standard free energy (ΔG^0) were calculated from temperature dependent adsorption isotherms. The values of ΔH^0 and ΔG^0 suggested that the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD was endothermic and spontaneous. The electron-donor–acceptor interaction, Hydrophobic interaction, and Lewis acid–base interaction may play an important role in 1-naphthylamine adsorption. The results show that MWCNTs/iron oxides/CD is a promising magnetic nanomaterial for the preconcentration and separation of organic pollutants from aqueous solutions in environmental pollution cleanup.

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1. Introduction

Water pollution by aromatic compounds is a worldwide problem and has aroused widespread concern of scientists and environmentalists. 1-naphthylamine, a naphthalene derivative with one primary amino group, is one of top priority contaminants and is also the most important substructures of potentially carcinogenic pollutants discharged from dyestuff, photographic, pharmaceutical, and agrochemical industries [1–3]. How to effectively and simply treat the contaminated water is critical important and interesting. Adsorption technology is one of the most effective choices to removal pollutants from aqueous solutions due to its simplicity of design, convenience, low cost, high sorption efficiency and wide adaptability [4]. Carbon nanotubes (CNTs), a novel manufactured nanomaterial, have widespread potential applications such as drug delivery, optical devices, quantum computing, and energy conversion. Due to their large surface area and high reactivity, CNTs have been suggested as superior adsorbents for the removal of toxic chemicals from water and gases [5–9]. However, because of the nanosize, CNTs are difficult to be separated from aqueous solutions and also can enter into cells [10]. Once they are released to the environment, they will cause damage to plants, animals, and humans. Researchers have explored the toxicity of carbon nanomaterials to animal and human cells [10,11]. It was suggested that the toxicity of carbon nanomaterials was not only from their own harmful nature but also from the toxic substances adsorbed by them. Therefore, the recovery of carbon nanomaterials from aqueous solution is crucial for the application of carbon nanomaterials in the removal of pollutants. In recent years, the application of magnetic carbon nanomaterial composites has received considerable attention to remove inorganic and organic pollutions because they can be easily separated from aqueous solutions [12,13]. Magnetic CNTs/iron oxide composites, prepared by chemical coprecipitation method, can be separated from aqueous solution by magnetic separation process.

β-cyclodextrin (β-CD), a whole new family of pharmaceutical excipients, has a doughnut-shaped structure with a hydrophilic outer surface and a lipophilic cavity made up of seven α-1,4-linked D-glucopyranose units with an internal hydrophobic cavity. It is well known that this structure gives rise to a remarkable capacity

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to form inclusion complexes in solution or in the solid state with a variety of organic molecules, especially aromatics, by incorporating them within the hydrophobic cavity [14,15], where poorly water-soluble molecules can shelter their most hydrophobic parts [16]. Therefore, grafting β-CD molecules on the CNTs/iron oxides may lead to a high adsorption of organic pollutants. Generally, β-CD can be grafted on the surface of CNTs/iron oxides by using low temperature plasma-induced grafting technique [17]. For surface modification application, low temperature plasma-induced grafting technique has many particularly appreciated advantages such as free radicals, charged particles and energetic electrons. These particles not only have high enough energy to activate, ionize or bond-break reactant molecules, but also do not decompose or ablate the materials when being disposed. They only modify the surface properties of the materials, but not the bulk properties [18,19]. β-CD has been reported to be efficient in adsorption of organic pollutants from aqueous solutions [15,20]. The introduction of β-CD on CNTs/iron oxides will combine the high adsorption capacity and the separation convenience of magnetic materials. However, the removal of 1-naphthylamine by using CNTs/iorn oxides/CD has never been reported in the literature.

For a better understanding of the molecular interactions of CNTs/iron oxides/CD and 1-naphthylamine under different environmental conditions, the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD as a function of contact time, pH, temperature, adsorbent content, 1-naphthylamine concentration was investigated in this study. The major objectives of this study are: (1) to determine the effects of contact time, pH, adsorbent content, temperature and 1-naphthylamine concentration on the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD; (2) to assess the adsorption kinetics using various kinetic models; (3) to simulate the adsorption data with the Langmuir and Freundlich isotherm models; (4) to determine the thermodynamic parameters according to the temperature dependent isotherms; and (5) to presume the adsorption mechanism of 1-naphthylamine on MWCNTs/iron oxides/CD.

2. Experimental

2.1. Materials

The biochemical reagent β-cyclodextrin (purity 99.0%) was purchased from Tianjin Bodi chemical Co. Ltd. (China). Analytical pure reagent 1-naphthylamine (purity 99.0%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and no significant impurities were detected by HPLC-UV analysis. The concentration of 1-naphthylamine was limited to <50% of its water solubility to ensure complete dissolution. All other chemicals were purchased in analytical purity and used without further purification and all solutions were prepared with Milli-Q water under ambient conditions.

2.2. Synthesis of MWCNTs/iron oxides/CD

MWCNTs were produced by a chemical vapor deposition (CVD) method of acetylene in hydrogen flow at 760 °C using Ni–Fe nanoparticles as catalysts [5]. MWCNTs/iron oxides were prepared by using chemical coprecipitation reaction between ferrous and ferric ions and carboxylic and hydroxylic groups of MWCNTs in the wet process [21]. Plasma-induced grafting of β-CD on MWCNTs/iron oxide composites was composed of the two successive processes, namely, the surface activation of MWCNTs/iron oxides and the grafting of β-CD. First, 1.0 g MWCNTs/iron oxides were activated by using N_2 plasma (power of 70 W, voltage of 650 W, gas pressure of 10 Pa) in a custom-built grafting reactor for 40 min under continuous stirring, and then 20 mL 2 g/L β-CD solution was immediately injected into the grafting reactor and the activated MWCNTs/iron oxides were reacted with β-CD at 80 °C for 1 h under continuous stirring. The obtained sample was repeatedly washed with Milli-Q water until no β-CD was detected by using high performance liquid chromatography–mass spectrometry (HPLC–MS) method in the supernatant. Finally, the magnetic composite of MWCNTs/iron oxides/CD was dried in oven at 95 °C for 12 h [17]. The main physicochemical characteristics of MWCNTs/iron oxides/CD were reported in detail in our earlier work [17]. The characteristics showed that β-CD was successfully grafted on the surfaces of MWCNTs/iron oxides and the grafted β-CD content in MWCNTs/iron oxides was 16.6 mg/g.

2.3. Adsorption experiments

All adsorption experiments were carried out using a batch equilibrium technique in a serial of 8 mL glass vials equipped with aluminum foil-lined teflon screw caps at three different temperatures (T = 293.15, 313.15 and 333.15 K). In our experiments, the background electrolyte solution was prepared, containing 0.01 M $NaClO_4$ to maintain a constant ionic strength and 200 mg/L NaN_3 to minimize biological activity. Adsorbents, background electrolyte solution and 1-naphthylamine were added to glass vial and then the pH was adjusted by using 0.1 M HCl or 0.1 M NaOH. Samples were shaken for 6 days to achieve adsorption equilibrium. After the adsorption, oxidized MWCNTs is separated from solution by centrifugation due to no magnetic properties, MWCNTs/iron oxides, MWCNTs/iron oxides/CD and iron oxides are separated by magnetic separation technique. Then the concentration of 1-naphthylamine in the supernatant was determined using a UV–2550 spectrophotometer at a wavelength of 320 nm. To enhance determination sensitivity, the residual concentration of 1-naphthylamine was basified to pH of 12 with 0.15 mol/L NaOH solution to make sure 1-naphthylamine present in dissociation state.

The removal percent (%) and amounts of 1-naphthylamine adsorbed on solid phase (q_e) were calculated from the concentration difference between the initial concentration (C_0) and the equilibrium one (C_e):

$$\text{Removal } (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), q_e is amounts of 1-naphthylamine adsorbed by MWCNTs/iron oxides/CD or MWCNTs/iron oxides (mg/g) after equilibrium, V is the solution volume (mL), and m is the mass of MWCNTs/iron oxides/CD (g).

2.4. Data analysis

2.4.1. Adsorption kinetics

Kinetic models are applied to examine the rate of the adsorption process and potential rate-controlling step. To investigate the mechanism of adsorption kinetics, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and the intraparticle diffusion model have been tested for the adsorption of 1-naphthylamien onto MWCNTs/iron oxides/CD composite.

The pseudo-first-order kinetic model [22] describes the adsorption of liquid–solid system based on solid capacity. The model can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e and q_t are the amount of 1-naphthylamine (mg/g) adsorbed on MWCNTs/iron oxides/CD at equilibrium and at time t (h), and k_1 is the pseudo-first-order rate constant for the adsorption process (h^{-1}). After integration between boundary conditions ($t = 0$ to t and $q_e = 0$ to q_e), Eq. (3) can be rewritten as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

Thus the values of q_e and k_1 can be determined experimentally by plotting $\log(q_e - q_t)$ versus t and extracting information from the least squares analysis of slope and intercept and substituting into Eq. (4).

The pseudo-second-order adsorption kinetic model consists of all the steps of adsorption including external film diffusion, adsorption, and internal particle diffusion. The equation can be written as [23]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 (g/mg h) is the pseudo-second-order rate constant for the adsorption. Eq. (5) can be rearranged to give the linear expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e}t \quad (6)$$

Thus the values of k_2 and q_e can be calculated from the intercept and the slope of the linear relationship between t/q_t and t (Eq. (6)).

For the intraparticle diffusion model, the process for adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled by any one of several steps, e.g. film or external diffusion, surface diffusion, pore diffusion and adsorption on the pore surface, or a combination of several steps [24]. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model [25], which is expressed as:

$$q_t = k_3 t^{1/2} + C \quad (7)$$

where q_t (mg/g) is the amount of 1-naphthylamine adsorbed at time t (h), k_3 is the initial rate of the intraparticle diffusion (mg/g $h^{1/2}$), and C is the intercept.

2.4.2. Adsorption isotherm models

For isotherm modeling, the Langmuir and Freundlich equations are the two most commonly applied models which are suitable for representing the non-linear adsorption of pollutants to adsorbent. In this study, both the Langmuir and Freundlich models were employed to fit the experimental data.

The Langmuir model [26] is widely used for modeling equilibrium data. The isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. It can be described by the linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (8)$$

where q_{max} is the adsorption capacity at saturation (mg/g) and K_L (L/mg) is the adsorption coefficient related to energy of adsorption.

The Freundlich expression [27] is an empirical equation describing sorption onto heterogeneous surface. The isotherm assumes that the surface sites of the adsorbent have a spectrum of different binding energies. The linear equation is presented as:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (9)$$

where K_F ($mg^{1-1/n} L^{1/n} g^{-1}$) shows the adsorption capacity. The value of n indicates the favorable adsorption ability.

Fig. 1. Photograph of MWCNTs/iron oxides/CD magnetic separation.

2.4.3. Adsorption thermodynamics

The thermodynamic parameters (i.e. the standard enthalpy change (ΔH^0), the entropy change (ΔS^0), and the Gibbs free energy change (ΔG^0)) for the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD were calculated from the following equations:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (10)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

where K_d is the adsorption coefficient, R (8.314 J/mol K) is the ideal gas constant and T is the temperature in Kelvin (K). The values of enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the slope and the intercept of the plot of $\ln K_d$ vs. $1/T$. The Gibbs free energy change (ΔG^0) was determined from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

3. Results and discussion

3.1. Magnetic separation

The separation of MWCNTs/iron oxides/CD by using magnetic separation method is displayed in Fig. 1. It is observed that MWCNTs/iron oxides/CD can be easily separated from the aqueous solution within several minutes by placing a magnet, and then the clear solution can be easily removed by pipet or decanted off. This simple magnetic separation experiment confirms that MWCNTs/iron oxides/CD possesses the property of magnetism. Therefore, it can be used as a magnetic adsorbent to remove pollutants from aqueous solutions. In the following experiments, we measured the concentration of 1-naphthylamine in supernatant after MWCNTs/iron oxides/CD was separated from solution by centrifugation, and we also measured the concentration of 1-naphthylamine in the solution after MWCNTs/iron oxides/CD was separated from solution by magnetic separation. The results indicated that there was no difference in the two different separation techniques. Therefore, MWCNTs/iron oxides/CD were separated by using the magnetic separation technique in our experiment, because this method is simple and convenient.

3.2. Adsorption kinetics

Fig. 2 depicts the content of 1-naphthylamine (mg/g) adsorbed on MWCNTs/iron oxides/CD versus contact time at three different temperatures of 293.15, 313.15 and 333.15 K. It can be found that the content of adsorbed 1-naphthylamine, q_e, increases with

Table 1
Comparison of the pseudo-first-order, pseudo-second-order and intraparticle diffusion adsorption rate constants, and calculated and experimental q_e values obtained at different temperatures.

Tem (K)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model	
		k_1 (h^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg h)	$q_{e,cal}$ (mg/g)	R^2	K_d (mg/g $h^{1/2}$)	R^2
293.15	116.2	0.145	138.9	0.9751	0.0003	118.2	0.9916	10.77	0.9805
313.15	127.5	0.154	144.9	0.9613	0.0004	128.5	0.9963	11.11	0.9758
333.15	139.8	0.151	149.2	0.9922	0.0004	139.2	0.9979	12.30	0.9459

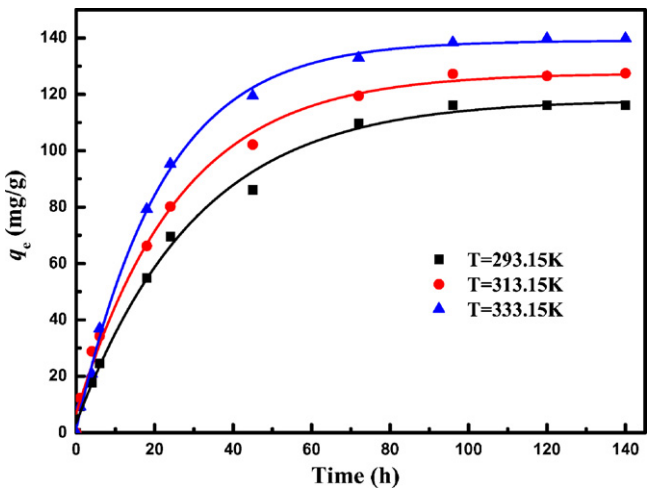

Fig. 2. Adsorption kinetics of 1-naphthylamine on MWCNTs/iron oxides/CD at three different temperatures. m/V = 0.4 g/L, I = 0.01 M $NaClO_4$, pH 6.5, and C_0 = 60 mg/L.

contact time at all different temperatures. The 1-napthylamien is adsorbed rapidly at the first 50 h, and thereafter it proceeds at a slow rate and finally attains saturation at 80 h. The initial rapid adsorption may be due to an increased number of available sites at the initial stage. The increase in concentration gradient tends to increase in 1-naphthylamine adsorption rate at the initial stages. As time proceeds, the concentration gradients become reduced due to the accumulation of 1-naphthylamine adsorbed on the surface sites, leading to the decrease in adsorption rate at the later stages. From the kinetic adsorption, it is clear that the temperature has no effect on equilibrium time. The adsorption kinetic data was analyzed using pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model. From the R^2 values in Table 1, the pseudo-second-order model fitted the adsorption kinetics much better than the other two models. Moreover, the q values ($q_{e,cal}$) calculated from the pseudo-second-order model were more consistent with the experimental q values ($q_{e,exp}$) than those calculated from the pseudo-first-order model. The result suggests the assumption behind the pseudo-second-order model that the 1-naphthylamine adsorption process is due to chemisorption [28]. From Table 1, it was also observed that the equilibrium adsorption capacity increased from 116.2 to 139.8 mg/g with increasing temperature from 293.15 to 333.15 K, which indicated that a higher temperature enhanced the adsorption process. The fact that the adsorption of 1-naphthylamine was favored at high temperature suggested that the 1-naphthylamine molecule should interact more effectively with the functional groups [29].

3.3. Effect of pH

For organic acids and organic bases, the occurrence of their non-dissociated or dissociated species depends on solution pH in relation to their dissociated constants (pK_a). When pH < pK_a, the non-dissociated species and the dissociated species are dominated for organic acids and organic bases, respectively; whereas when pH > pK_a, the dissociated species is dominant for organic acids and the non-dissociated species is dominant for organic bases. The fraction of non-dissociated species for organic acids (f_A^N) and bases (f_B^N) can be respectively estimated by $f_A^N = (1 + 10^{pH-pK_a})^{-1}$ and $f_B^N = (1 + 10^{pK_a-pH})^{-1}$, and the fraction of dissociated species for organic acids (f_A^I) and bases (f_B^I) can be respectively estimated by $f_A^I = (1 + 10^{pK_a-pH})^{-1}$ and $f_B^I = (1 + 10^{pH-pK_a})^{-1}$, respectively [30]. The distribution of non-dissociated and dissociated species as a function of pH values for 1-naphthylamine is shown in Fig. 3A.

The solution pH plays an important role in the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD. Fig. 3B shows the effect of pH on the adsorption of 1-naphthylamine by MWCNTs/iron oxides/CD at two different initial 1-naphthylamine concentrations. The adsorption of 1-naphthylamine to MWCNTs/iron oxides/CD significantly increased when the pH exceeded its pK_a (3.92). Changing the pH over the range of 3.0–11.3 should significantly affect the protonation–deprotonation transition of MWCNTs/iron oxides/CD surface groups such as –OH and –COOH, and it appears that such a transition has significant effect on the adsorptive affinity of 1-naphthylamine. From Fig. 3B, at initial 1-naphthylamine concentration of 60 mg/L, adsorption of 1-naphthylamine increases with increasing pH at the pH range

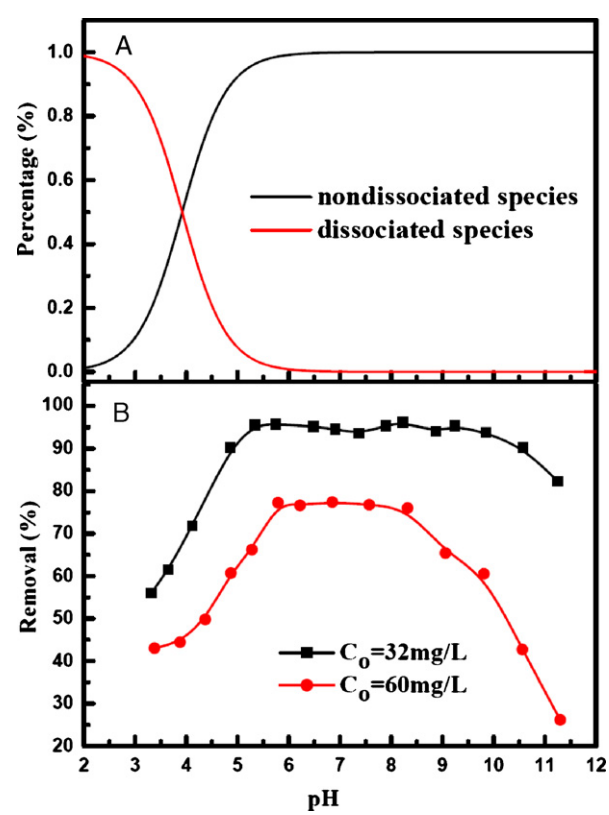

Fig. 3. Adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD as a function of pH values. Species distribution of 1-naphthylamine as a function of pH values (A). m/V = 0.4 g/L, I = 0.01 M $NaClO_4$, contact time = 144 h, and T = 293.15 ± 1 K (B).

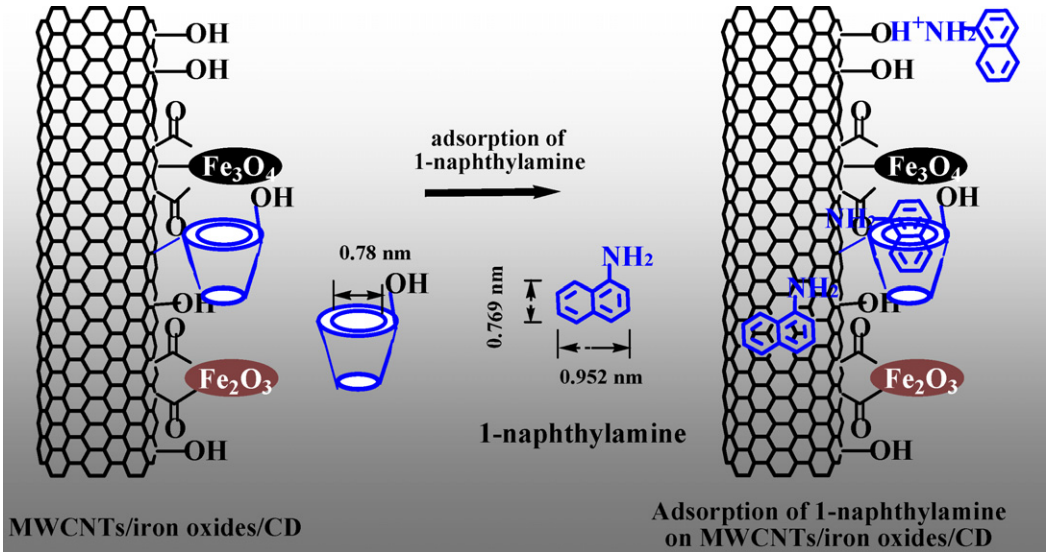

Fig. 4. The proposed mechanisms of 1-naphthylamine adsorption on MWCNTs/iron oxides/CD.

of 3.0–7.0 and then maintains a high level at pH 7.0–9.0, but slightly decreases when the pH further increases at pH > 9.0. Chen et al. [31] also investigated the effect of pH on 1-naphthylamine adsorption to CNTs, and a similar observation was also found. They proposed that the adsorption affinity of 1-naphthylamine on CNTs was due to the electron-donor–acceptor (EDA) interaction and Lewis acid–base interaction. In our investigation, several possible mechanisms should be considered between 1-naphthylamien and MWCNTs/iron oxides/CD: (1) EDA interaction, (2) Hydrophobic interaction, (3) Lewis acid–base interaction, and (4) hydrogen bonding. It has been widely accepted that the strong adsorption of aromatic compounds on CNTs was mainly attributed to the EDA interaction between aromatic molecules and the highly polarizable graphite sheets of CNTs. Amino group ($-NH_2$) of 1-naphthylamine is a strong electron donating group, which makes the benzene rings of 1-naphthylamine π-electron-rich, and thus the electron-rich benzene rings can interact strongly with polarized positively charged regions on MWCNTs/iron oxides/CD, causing extremely strong adsorption of 1-naphthylamine. Nitrogen electron pairs of $-NH_2$ group as *n*-electron donors might directly interact with the electron-depleted sites of MWCTNs/iron oxides/CD (π-electron acceptor) via n-π EDA interactions. On the surface of MWCNTs/iron oxides/CD, the inner hydrophobic cavity diameter of β-CD is 0.78 nm. The size of 1-naphthylamine is presented in Fig. 4, and naphthyl group has a suitable size to the cavity of β-CD [20]. β-CD is capable of forming inclusion complexes with 1-naphthylamine by incorporation them within the hydrophobic cavity [32]. In addition to the EDA interaction and hydrophobic interaction, Lewis acid–base interaction is another possible mechanism for 1-naphthylamine adsorption on MWCNTs/iron oxides/CD, wherein the oxygen functional groups on MWCNTs/iron oxides/CD serves as the Lewis acids and $-NH_2$ serves as Lewis base. Since 1-naphthylamine is a weak acid with pK_a of 3.92, the oxygen functional groups on surface of MWCNTs/iron oxides/CD and most 1-naphthylamine was protonated at pH less than pK_a, the Lewis acid–base interaction impeded 1-naphthylamine adsorbed. At high pH, some of the Lewis acid sites (e.g., –COOH, –OH) of MWCNTs/iron oxides/CD were ionized and, accordingly, the Lewis acid–base interaction was weak. Numerous studies have shown that the oxygen functional groups depressed the adsorption of organic chemicals on carbon materials [31,33] because of the competitive and much stronger interactions of water molecules with the polar sites on carbon materials. It thus appears that the pH-dependence of 1-naphthylamine adsorption on MWCNTs/iron oxides/CD was caused by a combined effect of EDA interaction, Hydrophobic interaction and Lewis acid–base interaction. According to the mechanisms mentioned above, the proposed mechanisms of 1-naphthylamine adsorption on MWCNTs/iron oxides/CD are shown in Fig. 4.

From Fig. 3B, the trend of 1-naphthylamine adsorbed on MWCNTs/iron oxides/CD as a function of pH at initial 1-naphthylamine concentration of 32 mg/L is similar to that at initial 1-naphthylamine concentration of 60 mg/L. However, the removal percentage at 1-naphthylamine concentration of 32 mg/L is higher than that of 60 mg/L. The results can be explained that the amount of polarized positively charged regions on MWCNTs/iron oxides/CD is likely limited. Therefore, low concentrations of 1-naphthylamine have the stronger adsorption than high concentration of 1-naphthylamine with polarized positively charged regions on MWCNTs/iron oxides/CD [31].

3.4. *Effect of adsorbent content on 1-naphthylamine adsorption*

The effects of solid content on the adsorption of 1-naphthylamine are illustrated in Fig. 5. As the adsorbent content increases from 0.1 to 0.6 g/L, the 1-naphthylamine adsorption increases from 32.5% to 90.2%. This can be due to the increased adsorbent surface area and availability of more adsorption sites resulted from the increase content of the adsorbent [34]. Because a fixed content of MWCNTs/iron oxides/CD can only adsorb a certain amount of 1-naphthylamine and therefore the higher the adsorbent content, the larger content of 1-naphthylamine can be adsorbed on solid surfaces. However, the equilibrium adsorption capacity, q_e, decreased from 194.8 to 90.2 mg/g with increasing adsorbent content from 0.1 to 0.6 g/L. The reason is mainly due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent. With increasing adsorbent content, the content of 1-naphthylamine adsorbed onto unit weight of adsorbent decreases, causing a decrease in q_e value [28]. Evidently, the adsorption percentage and equilibrium adsorption capacity are sensitive to the variation of adsorbent content. A 0.4 g/L of adsorbent was selected as adsorbent content for all further experiments in this work because of high adsorption efficiency and acceptable adsorption capacity.

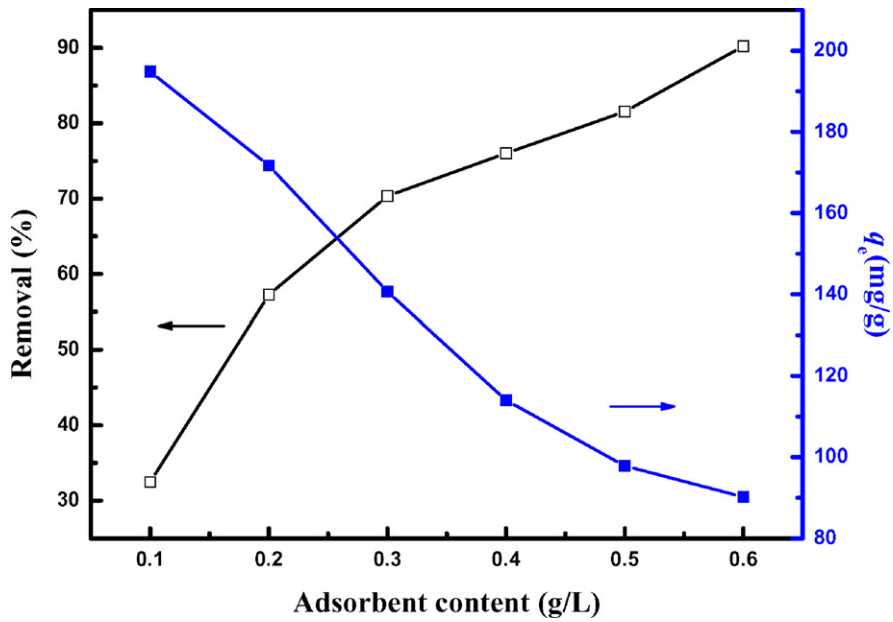

Fig. 5. Adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD as a function of adsorbent content. $I = 0.01$ M $NaClO_4$, contact time = 144 h, $C_0 = 60$ mg/L, pH 6.5, and $T = 293.15 \pm 1$ K.

3.5. Adsorption isotherms

The adsorption isotherms are important to reveal the specific relation between the equilibrium concentration of adsorbate in the bulk and the adsorbed amount at the solid surfaces. Fig. 6 presents the adsorption isotherms of 1-naphthylamine on MWCNTs/iron oxides/CD at three different temperatures, viz. 293.15, 313.15, and 333.15 K, respectively. Fig. 7A and B show the adsorption equilibrium data fitted to Langmuir and Freundlich models, and the relative parameters derived from the Langmuir and Freundlich models are listed in Table 2. It can be seen from Table 2 that the adsorption data of 1-naphthylamine are fitted by the Langmuir model better than by the Freundlich model, as evidenced by higher regression coefficients (R^2). Using the Langmuir model, the maximum adsorption capacity, q_m, increases from 217.4 to 294.1 mg/g with increasing the temperature from 293.15 to 333.15 K, confirming endothermic nature of overall adsorption process. The same effect is also found when the Freundlich model is adopted. The

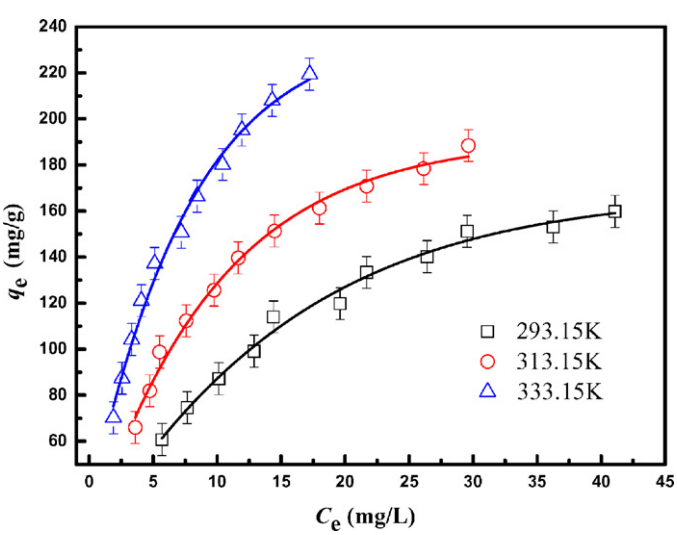

Fig. 6. Adsorption isotherms of 1-naphthylamine on MWCNTs/iron oxides/CD. $m/V = 0.4$ g/L, $I = 0.01$ M $NaClO_4$, pH 6.5, and contact time = 144 h.

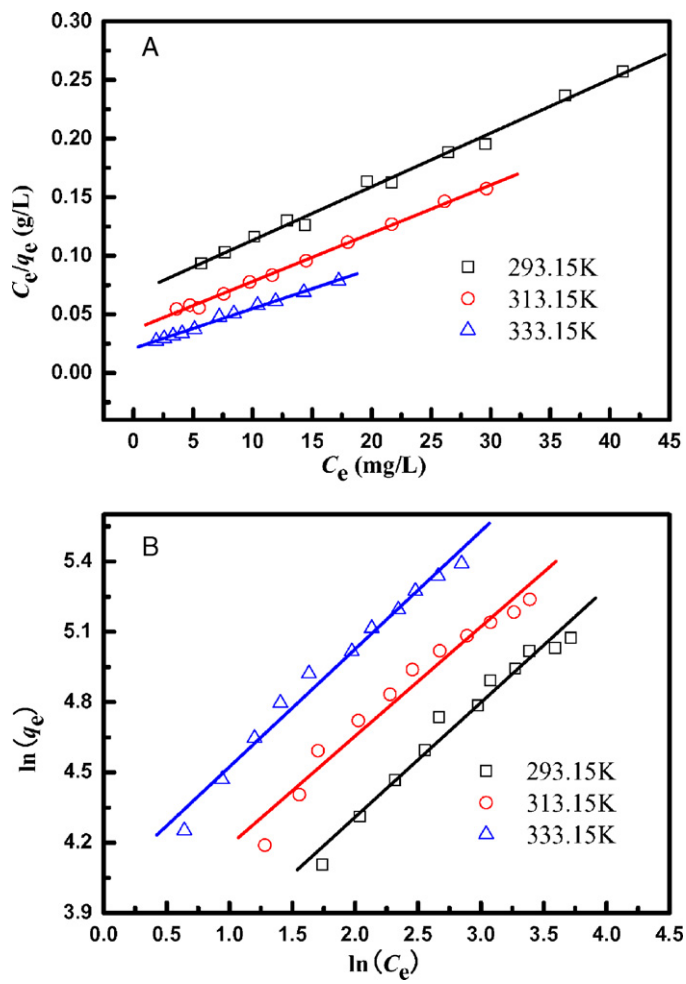

Fig. 7. Langmuir (A) and Freundlich (B) isotherms for the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD at different temperatures. $m/V = 0.4$ g/L, $I = 0.01$ M $NaClO_4$, pH 6.5, and contact time = 144 h.

Table 2
Langmuir and Freundlich isotherm model parameters.

Tem (K)	Adsorbent	Langmuir constants			Freundlich constants		
		q_{max} (mg/g)	K_L (L/mg)	r^2	$1/n$	K_F ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)	r^2
293.15	Iron oxides	78.1	0.014	0.9934	0.607	2.97	0.9898
293.15	Oxidized MWCNTs	217.4	0.185	0.9978	0.489	53.48	0.9678
293.15	MWCNTs/iron oxides	153.8	0.072	0.9938	0.411	25.14	0.9450
293.15	MWCNTs/iron oxides/CD	200.0	0.068	0.9933	0.355	28.00	0.9713
313.15	MWCNTs/iron oxides/CD	243.9	0.111	0.9973	0.467	41.35	0.9605
333.15	MWCNTs/iron oxides/CD	294.1	0.163	0.9956	0.503	55.75	0.9816

adsorption capacity, K_F, increases from 28.0 to 55.8 with increasing the temperature from 293.15 to 333.15 K. The relative parameters in Table 2 show that "$1/n$" is less than unity, indicating that 1-naphthylamine molecules are favorably adsorbed by the adsorbents at the studied temperatures [35]. High temperature generally increases the rate of diffusion of the 1-naphthylamine molecules through the solution to the external surface of the MWCNTs/iron oxides/CD, and may change the equilibrium adsorption capacity of the adsorbent for the particular adsorbate [36].

3.6. Adsorption thermodynamics

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during adsorption. To assess the thermodynamic parameters, the adsorption isotherms of 1-naphthylamine on MWCNTs/iron oxides/CD were measured at 293.15, 313.15, and 333.15 K, respectively (Fig. 6). The distribution coefficients as a function of temperature are shown in Fig. 8, and the thermodynamic parameters are listed in Table 3.

The ΔH^0 values of 1-naphthylamine adsorption on MWCNTs/iron oxides/CD are positive, confirming the endothermic nature of the adsorption process. This is supported by the increase of 1-naphthylamine adsorption on MWCNTs/iron oxides/CD with a rise in temperature (as shown in Fig. 6). The negative ΔG^0 suggests that the adsorption reaction is general spontaneous process and thermodynamically favorable. The values of ΔG^0 decrease with increasing temperature, which indicates that more efficient adsorption at higher temperature. The positive ΔS^0 values indicate that the increased of randomness at the solid–liquid interface during adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD might be expected from acceptor donor complex formation. 1-naphthylamine in solution is surrounded by a tightly bound hydration layer where water molecules are more highly ordered than in the bulk water. When 1-naphthylamine molecule comes into close interaction with the hydration surface of MWCNTs/iron oxides/CD, the ordered water molecules in these two hydration layers are compelled and disturbed, thus increasing the entropy of water molecules. Although the adsorption of 1-naphthylamine molecules on MWCNTs/iron oxides/CD decreases the degree of freedom of 1-naphthylamine molecules, it seems likely that positive entropy associated with the adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD is due to the entropy increase of water molecules overweighing the entropy decrease of 1-naphthylamine molecules [37].

3.7. Comparison of different adsorbents

Fig. 9 illustrates the adsorption isotherms of 1-naphthylamine on MWCNTs/iron oxides/CD, MWCNTs/iron oxides, oxidized MWCNTs and iron oxides, respectively. The adsorption isotherms of 1-naphthylamine on four different adsorbents are simulated by the Langmuir and Freundlich models (Fig. 10), and the relative parameters are listed in Table 2. The maximum adsorption capacities of 1-naphthylamine are 200.0 mg/g for MWCNTs/iron oxides/CD, 153.2 mg/g for MWCNTs/iron oxides, 217.4 mg/g for oxidized MWCNTs, and 78.1 mg/g for iron oxides. It can be seen that the maximum adsorption capacity for the removal of 1-naphthylamine is the highest for oxidized MWCNTs. Similar results are also observed for the 1-naphthol adsorption [17]. This phenomenon may be attributed to the large number of benzene rings of oxidized MWCNTs, which can provide effective adsorption sites for the removal of 1-naphthylamien,

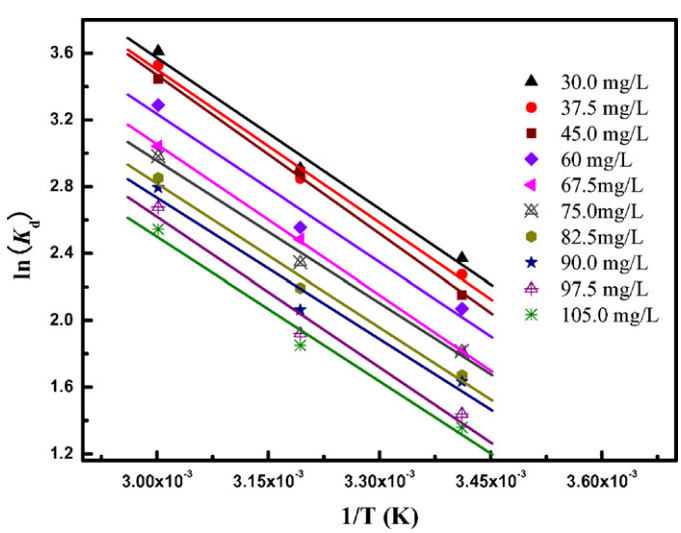

Fig. 8. Linear plots of $\ln K_d$ vs. $1/T$ for 1-naphthylamine adsorption on MWCNTs/iron oxides/CD.

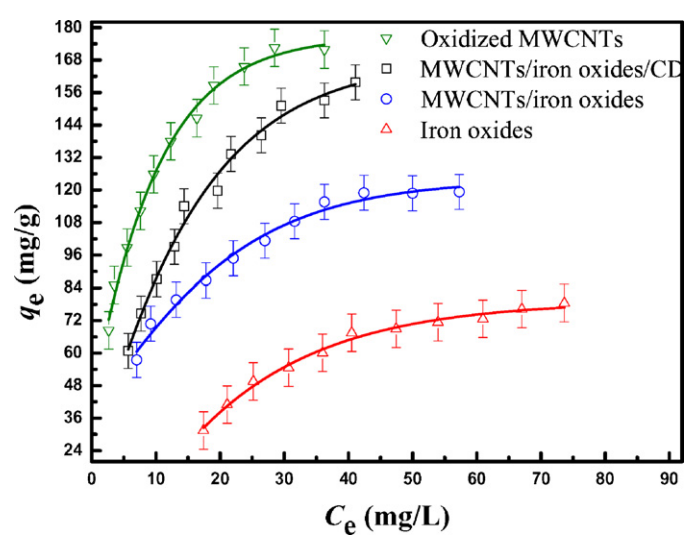

Fig. 9. Adsorption isotherms of 1-naphthylamine on oxidized MWCNTs, MWCNTs/iron oxides/CD, MWCNTs/iron oxides and iron oxides. $m/V = 0.4$ g/L, $I = 0.01$ M $NaClO_4$, contact time = 144 h, pH 6.5, and $T = 293.15 \pm 1$ K.

Table 3
Thermodynamic parameters for 1-naphthylamine adsorption on MWCNTs/iron oxides/CD.

C_0 (1-naphthylamine) (mg/L)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)	ΔG^0 (kJ/mol)		
			T = 293.15 K	T = 313.15 K	T = 333.15 K
30.0	25.09	104.96	−5.68	−7.78	−9.88
37.5	25.40	105.31	−5.47	−7.58	−9.69
45.0	26.33	107.83	−5.28	−7.44	−9.60
60.0	24.60	100.72	−4.92	−6.94	−8.95
67.5	25.03	100.46	−4.42	−6.43	−8.44
75.0	23.61	95.40	−4.36	−6.26	−8.17
82.5	23.88	95.08	−3.99	−5.89	−7.79
90.0	23.43	93.00	−3.84	−5.70	−7.56
97.5	24.96	96.65	−3.38	−5.31	−7.24
105.0	23.96	92.64	−3.20	−5.06	−6.91

thus π–π interaction may be an important adsorption mechanism.

Although the adsorption capacity of 1-naphthylamine on MWCNTs/iron oxides/CD is a little lower than that of oxidized MWCNTs, MWCNTs/iron oxides/CD can be separated from solution easily with a magnet. The adsorption capacity of 1-naphthylamine on MWCNTs/iron oxides/CD is much higher than that of MWCNTs/iron oxides, which may be attributed to the grafted β-CD molecules on the surfaces of MWCNTs/iron oxides/CD. Inner cores of β-CD molecules with hydrophobic cavities can form inclusion complexes with 1-naphthylamine, and thereby enhance the adsorption capacity of MWCNTs/iron oxides/CD.

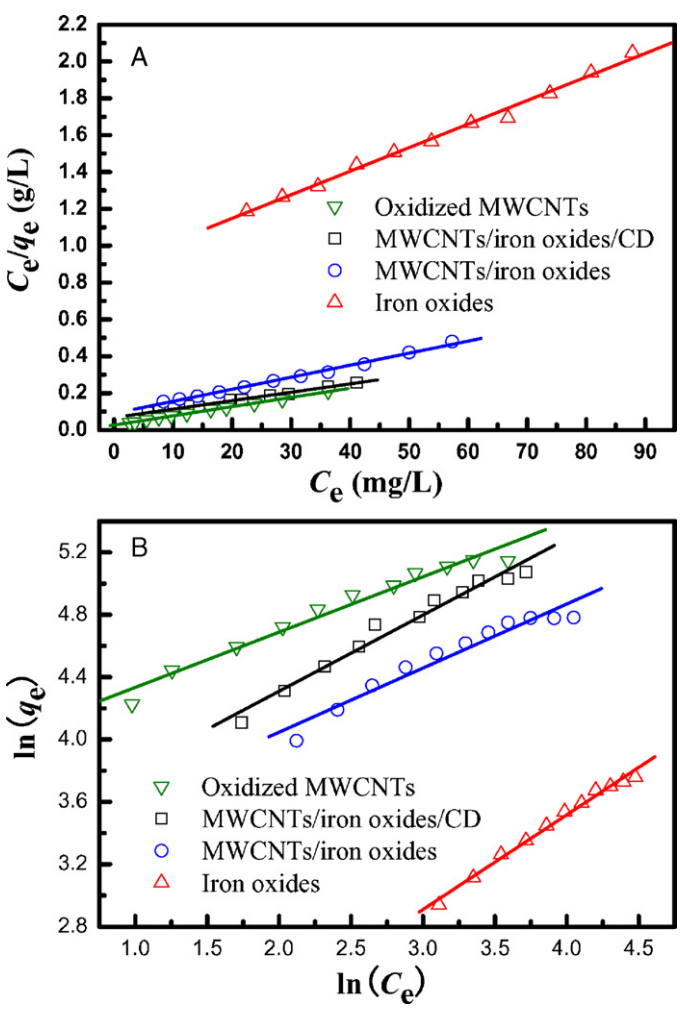

Fig. 10. Langmuir (A) and Freundlich (B) isotherms for the adsorption of 1-naphthylamine on oxidized MWCNTs, MWCNTs/iron oxides/CD, MWCNTs/iron oxides, and iron oxides. m/V = 0.4 g/L, I = 0.01 M $NaClO_4$, contact time = 144 h, pH 6.5, and T = 293.15 ± 1 K.

4. Conclusion

The adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD is strongly dependent on pH values. The adsorption increases over the pH range of 3.0–7.0 and maintains a high level at pH 7.0–9.0, and then decreases when the pH further increases. The removal percent of 1-naphthylamine increases with increasing adsorbent content, however, the equilibrium adsorption capacity, q_e, decreases with increasing adsorbent content. The adsorption data of 1-naphthylamine on MWCNTs/iron oxides/CD are fitted by the Langmuir model better than by the Freundlich model. The adsorption of 1-naphthylamine on MWCNTs/iron oxides/CD is endothermic and spontaneous. The π–π interaction and hydrophobic interaction play important role in 1-naphthylamine adsorption. MWCNTs/iron oxides/CD has very high adsorption capacity in the removal of 1-naphthylamine, and can be separated and recovered from aqueous solution by magnetic separation. The magnetic composite of MWCNTs/iron oxides/CD is very suitable materials for the preconcentration and immobilization of organic pollutants in the natural environmental pollution cleanup. The content in this paper is relevant and important for the application of plasma technique, magnetic separation method and CNTs in the environmental pollution cleanup.

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