Kinetics and thermodynamics of sorption of nitroaromatic compounds to as-grown and oxidized multiwalled carbon nanotubes

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ABSTRACT

The sorption kinetics and thermodynamics of 1,3-dinitrobenzene (DNB), *m*-nitrotoluene (mNT), *p*-nitrophenol (pNP), and nitrobenzene (NB) on as-grown and nitric acid-oxidized multiwalled carbon nanotubes (MWCNTs) were investigated. The sorption kinetics was well described by a pseudo-second-order rate model, while both Langmuir and Freundlich models described the sorption isotherms well and the sorption thermodynamic parameters of equilibrium constant (K_0), standard free energy (ΔG), standard enthalpy (ΔH), and standard entropy changes (ΔS) were measured. The values of ΔH and ΔG suggested that the sorption of nitroaromatics (NACs) onto MWCNTs was exothermic and spontaneous. The structure, number, and position of nitro groups of NACs were the main factors affecting the sorption rate and capacity. Treatment of the MWCNTs with nitric acid increased both the surface area and the pore volume and introduced oxygen-containing functional groups to the MWCNTs, which depressed the sorption of NACs onto MWCNTs.

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1. Introduction

Carbon nanotubes (CNTs) have unique physicochemical and electrical properties and have widespread applications in field emission, in hydrogen storage, and as chemical sensors. Due to their high surface area and large micropore volume, CNTs are also considered to be extremely good adsorbents and since the first report of their successful removal of dioxins [1], CNTs have been utilized for the sorption of a large number of different organic compounds from water [2–8]. The sorption properties of CNTs can be modified by chemical oxidation treatments using sodium hypochlorite (NaOCl), hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), and nitric acid (HNO₃) [2,5]. Such oxidation treatments are able to remove impurities and hemispherical caps, increasing the surface area and introducing oxygen-containing functional groups [6,9], hence altering the sorption properties for organic chemicals [2,3,5]. For example, following treatment with acid, CNTs become more suitable for the sorption of low molecular weight and relatively polar trihalomethane molecules [3]. In another study, oxidation with nitric acid increased the sorption of *p*-xylene, while decreasing the sorption of *o*-xylene on single-walled carbon nanotubes (SWCNTs), suggesting that the sorption

of *o*-xylene and *p*-xylene onto SWCNTs was mainly influenced by the positions of the methyl groups on xylene molecules and the presence of oxygen-containing groups on the surface of SWCNTs [5]. However, a recent study [8] revealed that incorporated surface oxides on CNTs created polar regions that reduced the surface area available for naphthalene sorption, and that as little as a 10% increase in surface oxygen concentration resulted in a 70% decrease in the maximum sorption capacity of naphthalene. This study indicated that oxidative treatments may not always beneficially enhance sorption of organic compounds and pointed to the need to investigate sorption of specific compounds on a case by case basis.

Nitroaromatic compounds (NACs) are widely used as pesticides, explosives, and intermediates in the synthesis of dyes and other high-volume chemicals. NACs are highly polar and often act as strong electron acceptors when interacting with adsorbent-containing structures with high electron polarization or with electron donors such as oxygen-containing groups. It was recently reported [7] that CNTs have a stronger affinity for NACs than for other nonpolar chemicals. This was attributed to the formation of an electron donor–acceptor (EDA) complex between NACs (electron acceptor) and the graphene sheets of the carbon nanotubes (electron donor). Sorption properties of NACs on activated carbon have been studied for many years and involve electrostatic and dispersive interactions between the adsorbate and the activated carbon [10,11]. Electrostatic interactions dominate when the adsorbate is dissociated under the experimental conditions, while three mecha-

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Table 1
Selected properties of NACs used in this study.

NACs	MW ^a (g/mol)	log K_{ow}	pK _a	C _s (25 °C) (mg/L)	V _s (cm ³ /mol)	S _{Vdw} (Å ²)
DNB	168.1	1.49	–	533	106.5	85.26
mNT	137.1	2.42	–	498	103.2	78.21
pNP	139.1	2.04	7.15	16000	94.9	76.61
NB	123.1	1.84	–	1900	89.1	71.92

^a MW, molecular weight; K_{ow} , octanol–water partition coefficient; C_s, water solubility; V_s, molar volume; S_{Vdw}, molecular Van der Waals square.

nisms are proposed for nonelectrostatic interactions, (1) π – π dispersion interaction, (2) hydrogen bonding [12], and (3) electron donor–acceptor complex formation [13]. Of these the π – π dispersion interaction mechanism is the most widely accepted [11, 14]. For the sorption of nitrobenzene onto activated carbon, which is undissociated in solution, the dispersive interactions will be the most important mechanism in the sorption process [15]. Numerous studies have also been conducted on the specific interaction between NACs and phyllosilicate minerals such as clays to which NACs may adsorb strongly and reversibly. Specific sorption to clays was believed to occur via electron donor–acceptor complex formation with oxygen present at the external siloxane surface of the clay minerals [16,17]. Since oxidation of CNTs introduces oxygen-containing functional groups it is possible that this would enhance sorption of organic compounds. However, the exact role of these oxygen-containing functional groups on the specific sorption of NACs on CNTs still needs to be determined.

Understanding the kinetics and thermodynamics of the sorption process is critical for the development of more efficient sorbents suitable for real world applications. While studies of the sorption kinetics and thermodynamics of metals are generally well known, very little information is currently available regarding the sorption of organic compounds, such as trihalomethanes [18] and dyes [19], onto MWCNTs. These limited studies suggested that the sorption of the reactive dye and trihalomethanes was spontaneous and mainly due to physical sorption. In this work, the sorption kinetics and thermodynamics of NACs on CNTs were systematically studied for the first time.

The aim of this work was to understand the interaction between NACs and MWCNTs, and to reveal the effect of oxygen-containing functional groups on the sorption of NACs to MWCNTs.

2. Materials and methods

2.1. Materials

MWCNTs were purchased from Tsinghua University, and were prepared by dissociating methane in a hydrogen flow at 900 K using Ni nanoparticles supported on diatomite as a catalyst. As-grown MWCNTs (2 g) were added to 3 M HNO₃ (400 mL) with ultrasonic stirring for 24 h to dissolve the catalyst support and Ni particles in the MWCNTs. The suspension was then filtered and rinsed with deionized water until the pH of the final suspension reached about 6 before drying at 80 °C. The oxidized MWCNTs were subsequently calcined at 450 °C for 24 h to remove amorphous carbon.

1,3-Dinitrobenzene (DNB), *m*-nitrotoluene (mNT), *p*-nitrophenol (pNP), and nitrobenzene (NB) were purchased from Beijing Chemicals (Beijing, China). No significant impurities were detected by HPLC–UV analysis. Selected properties of DNB, mNT, pNP, and NB are listed in Table 1. The adsorbates were dissolved in 0.01 M NaNO₃ and 100 mg/L NaN₃ solution which was used as support electrolyte throughout this study. The final concentrations were limited to <50% of their water solubility to ensure complete dissolution.

Table 2
Selected properties of MWCNTs.

MWCNTs	BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)	Carbon content (%)	Hydrogen content (%)
As grown	159.7	9.57	0.382	93.0	0.26
Oxidized	274.0	9.52	0.652	90.0	0.19

2.2. Characterization of MWCNTs

The morphology of MWCNTs was characterized by high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010, Tokyo, Japan). The surface area and pore volume were measured by nitrogen gas adsorption and desorption at 77 K with ASAP2000 (Micromeritics Instrument Corporation). The multipoint Brunauer–Emmett–Teller method was used to calculate the surface area. The Barrett–Joyner–Halenda method was used to calculate the mesopore volumes. The functional groups on the surface of MWCNTs were detected by a Fourier transform infrared (FTIR) spectroscopy equipped with deuterated triglycine (DTGS) and mercury–cadmium–telluride (MCT) detectors (NEXUS 670 FTIR, Nicolet, USA). The characteristics of MWCNTs are listed in Table 2.

2.3. Kinetic experiments

Kinetic experiments were performed in 40-mL glass centrifuge tubes sealed with Teflon-lined screw caps at 20.0 ± 0.5 °C. Initially MWCNTs (10 mg) were introduced to the supporting solution of 0.01 mol/L NaNO₃ containing 100 mg/L NaN₃ solution (30 mL) and prior to the introduction of NACs, the tubes were rotated for 1.5 h to hydrate the MWCNTs. The initial concentration was 12 mg/L for each NAC of interest. After the introduction of the NACs, samples were shaken for a certain time intervals, filtered through 0.45-μm cellulose acetate membrane filter, and analyzed for the equilibrium solution concentration of NAC. The quantity of NACs sorbed at time *t* (min), *q_t* (mg/g), was deduced from the mass difference between initial (*t* = 0 min) and final solution concentration taken at time *t* (min).

2.4. Batch sorption experiments

Batch-equilibration sorption experiments were carried out in triplicate by mixing MWCNTs (10 mg) and 0.01 mol/L NaNO₃ and 100 mg/L NaN₃ solution (30 mL) containing various concentrations of adsorbates in 40-mL glass centrifuge tubes sealed with Teflon-lined screw caps. Initial concentrations of NACs were chosen so as to control the amount of NACs adsorbed to be between 20 and 80% of the total initial concentration. The tubes were shaken in the dark on a rotary shaker at 100 rpm for 24 h at 10 ± 1, 20 ± 1, and 35 ± 1 °C. After rotation, all the tubes were placed vertically on a flat surface in the dark for 24 h at the set temperature to ensure separation between solution and MWCNTs. Centrifugation was not used to avoid any temperature change. The concentrations of NACs in the supernatants were analyzed by direct injection of supernatants to HPLC (Agilent Technologies, Wilmington, CT). Blank experiments were performed using the same experimental procedure but without added MWCNTs to check for potential sorption of NACs to the glass centrifuge tubes or the membrane filters, which could potentially result in nonspecific loss and or degradation of the NACs. However, such losses in the blank experiments were less than 5% of the initial concentrations and therefore indicated that since losses were small, the amount of NACs sorbed by MWCNTs could be calculated directly from mass difference between the initial and final equilibrium concentrations.

Control of the pH of the solution suspensions was not considered critical for DNB, mNT, and NB because all the adsorbates were

nondissociable, but for pNP, the pH was controlled to 6.0 ± 0.5 by the dropwise addition of NaOH and HNO₃ as required. The final pH of the supernatant was measured at the end of the equilibration and was shown to be identical to the initial concentration, indicating that the pH remained constant at 6.0 ± 0.5 .

2.5. Data analysis

For kinetic analysis, four kinetic models including (1) pseudo-second-order model, (2) parabolic diffusion model, (3) modified Freundlich model, and (4) Elovich model were tested for goodness of fit of the experimental data using the coefficient of correlation (R^2) as a measure of the agreement between the four proposed models and the experimental data. Each of the models is discussed briefly below.

2.5.1. Pseudo-second-order model

This model includes all the steps of sorption including external film diffusion, adsorption, and internal particle diffusion [20–22]. This model assumes that the differences between the average solid phase concentration at time t (min), q_t (mg/g), and the equilibrium concentration, q_e (mg/g), are the driving force for adsorption and the overall adsorption rate is proportional to the square of the driving force, which can be written as [23]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (1)$$

where k_2 [g/(mg min)] is the rate constant of the pseudo-second-order adsorption, and is a complex function of the initial concentration of solute [24], and q_e and q_t are the adsorbed NACs (mg/g) at equilibrium and at time t (min). Given that the initial sorption rate v_0 [mg/(g min)] is

$$v_0 = k_2 q_e^2, \quad (2)$$

Eq. (1) can be rearranged to give the linearized expression:

$$\frac{t}{q_t} = \frac{1}{v_0} + \frac{1}{q_e} t. \quad (3)$$

Thus the values of v_0 and k_2 can be determined experimentally by plotting t/q_t versus t and extracting information from the least-squares analysis of slope and intercept and substituting into Eq. (2).

2.5.2. Parabolic diffusion model

The parabolic diffusion model can be used to determine whether diffusion-controlled phenomena are a rate-limiting step during sorption [25]. The parabolic diffusion model can be written as

$$\frac{q_t}{q_e} = kt^{-0.5} + a, \quad (4)$$

where q_e and q_t are the adsorbed NACs (mg/g) at equilibrium and at time t (min), a is a constant, and k is the overall diffusion constant for sorption.

2.5.3. Modified Freundlich model

The modified Freundlich model can be written as [25]

$$q_t = kC_0 t^a, \quad (5)$$

where q_t is the adsorbed NACs (mg/g) at time t (min), k is the rate constant for the sorption, a is a constant, and C_0 is the initial concentration of the solute.

2.5.4. Elovich model

The Elovich model can be written as [25]

$$q_t = a \ln(t) + b, \quad (6)$$

where q_t is the adsorbed NACs (mg/g) at time t (min), and a and b are constants whose chemical significance is not clearly defined.

For isotherm modeling, Langmuir and Freundlich equations are the two most commonly applied models suitable for representing the nonlinear adsorption of hydrophobic organic chemicals to activated carbon, charcoal, and carbon nanotubes. In this study, both the Langmuir and the Freundlich models were employed to fit the experimental data. The Langmuir equation is

$$q_e = \frac{Q_m C_e}{K_L + C_e}, \quad (7)$$

where q_e (mg/g) is the equilibrium sorbed concentration, C_e (mg/L) is the equilibrium solution phase concentration, K_L (mg/L) is the affinity parameter, and Q_m (mg/g) is the maximum sorption capacity. The Freundlich model is an empirical equation that assumes heterogeneous adsorption due to the diversity of adsorption sites,

$$q_e = K_F C_e^{1/n}, \quad (8)$$

where q_e (mg/g) is the equilibrium sorbed concentration, C_e (mg/L) is the equilibrium solution phase concentration, K_F is the Freundlich adsorption coefficient [(mg/g)(L/mg)^{1/n}], and $1/n$ is a constant indicating the isotherm curvature.

The isotherms can be expressed either on a mass or on a surface area basis, and in this study, both forms were used. The use of surface area normalized isotherms was necessary to compare the uptake of NACs by nitric acid-oxidized MWCNTs with that of as-grown MWCNTs having different surface areas and pore size distributions.

3. Results and discussion

3.1. Characterization of as-grown and nitric-oxidized MWCNTs

Figs. 1a, 1b, 1c, and 1d are TEM images of the MWCNTs before and after oxidation with nitric acid. Prior to oxidation TEM images of the MWCNTs showed a large amount of impure particles, such as amorphous carbon and metal particles (Figs. 1a and 1b). While after oxidation the MWCNTs bundles had very little visible attachment of particles, indicating that oxidation had successfully removed these impurities (Figs. 1c and 1d). Due to strong van der Waals interactions, MWCNTs adhere to each other and form bundles and the space between the bundles can be considered as pores as shown in Figs. 1a and 1c. Agnihotri et al. [26] identified different adsorption sites on a bundle of CNTs. For an individual carbon nanotube, the intratube and the external graphene surface are the main sorption sites. However, the process of forming bundles or pores creates new adsorption sites, such as the interstitial channel, the external groove, and partial coating of the external surface by nanometer-thick layered carbon. All of these sites contribute to overall adsorption and may also include adsorption due to some carbon-coated catalyst particles. Table 2 lists the physical properties of as-grown and oxidized MWCNTs. The BET surface area (274.0 m²/g) and the pore volume (0.652 cm³/g) of oxidized MWCNTs were greater than those of as-grown MWCNTs (159.7 m²/g and 0.382 cm³/g), but the average pore diameter of the two carbon nanotubes were approximately the same (Table 2). The increase of the BET surface area and pore volume after oxidation was attributed to removal of amorphous carbon and hemispherical caps on the nanotubes

Fig. 1. TEM images of MWCNTs: (a and b) as-grown MWCNTs; (c and d) nitric acid-oxidized MWCNTs.

Fig. 2. FTIR spectra of as-grown and oxidized MWCNTs.

(Fig. 1d). Compared to the as-grown MWCNTs, the FTIR spectrum of the oxidized MWCNTs confirmed the existence of the carboxylic groups ($-\text{COOH}$), carbonyl groups ($-\text{CO}$), and hydroxyl groups ($-\text{OH}$) (Fig. 2). All of the above results showed that after oxidation the carbon nanotubes became more hydrophilic and had more active functional groups on the surface while the physical properties such as specific surface area and pore size distribution were increased.

3.2. Sorption kinetics of NACs

Fig. 3 shows the kinetics of NACs sorption onto the as-grown and nitric acid-oxidized MWCNTs. The plots represented the adsorbed NACs onto the MWCNTs (q_t) versus time at an initial concentration of 12 mg/L. For all the NACs considered, the sorption was very fast on both as-grown and nitric acid-oxidized MWCNTs. Apparent equilibrium was reached within 180 min, for most of the NACs considered within 30 min and for NB, sorption occurred within 10 min. This fast sorption process was similar to that which had been observed for trihalomethanes [18] and reactive dyes [19]. Individual MWCNTs have a dominant adsorption domain which is primarily the outermost graphene surface and defect sites. However, when MWCNTs form bundles in aqueous media, the interstitial channel space between the tubes within the bundles can be regarded as pores. NACs were thought to preferentially occupy the external graphene surface of the carbon nanotube during the initial sorption process, while the overall adsorption of NACs included the contributions from the adsorption on the graphene surface as well as due to pore filling.

The initial steep adsorption curves may therefore be attributed to the rapid sorption onto the surface sites of MWCNTs. After the full occupancy of the surface adsorption sites had been achieved, the NACs molecules then sorbed into the interstitial channel spaces which was considered to be the rate-controlling process since NACs would have to move from the exterior surface to the inner surface of the pores of the MWCNTs to achieve equilibrium. Pore filling for activated carbon generally has a long residence time and adsorption takes, for example, about 6 h for nitrobenzene [15]. In contrast, the equilibrium time for NACs sorption onto CNTs is

Fig. 3. Sorption kinetics of DNB, mNT, pNP, and NB onto MWCNTs at an initial concentration of 12 mg/L. Lines represent the model fitting of pseudo-second-order equation.

Table 3

Kinetic parameters of pseudo-second-order model fitting for the NAC adsorption onto MWCNTs.

MWCNTs	NACs	v_0 [mg/(g min)]	k_2 [g/(mg min)]	R^2
As grown	DNB	44.84	0.0491	0.9996
	mNT	13.12	0.0185	0.9999
	pNP	8.38	0.0203	0.9995
	NB	4.31	0.0793	0.9991
Oxidized	DNB	2.90	0.0038	0.9998
	mNT	5.59	0.0084	0.9999
	pNP	3.98	0.0103	0.9999
	NB	3.13	0.0646	0.9999

comparatively short, suggesting that the contribution to the overall sorption due to a pore filling mechanism is negligible.

While four kinetic models, pseudo-second-order model, parabolic diffusion model, modified Freundlich model, and Elovich model, were fit to the experimental data, only the pseudo-second-order model fit the sorption kinetics well with correlation coefficient consistently >0.999 for all four NACs considered (Table 3). The other three models failed to describe the experimental data well, as indicated by consistently lower $R^2 < 0.9$ (data not shown), implying that the adsorption kinetics of the NACs followed a pseudo-second-order rate law.

As shown in Table 3, the rate constant (k_2) for NB, on both as-grown and oxidized MWCNTs, was the largest among all four NACs considered, indicating that the sorption of NB on MWCNTs was the fastest process. This may be attributed to the smaller molar volume (V_s) and Van der Waals square (S_{Vdw}) (Table 1) for NB compared to the other NACs studied, since it is well known that smaller molecules are adsorbed faster than bigger ones [18].

The initial adsorption rate (v_0) and the adsorption rate constant (k_2) of the oxidized MWCNTs were both smaller than those of the as-grown MWCNTs, suggesting that the sorption of NACs onto as-grown MWCNTs was faster than that onto the oxidized MWCNTs (Table 3). The difference in adsorption kinetics between as-grown and oxidized MWCNTs may be due to the changes in the surface chemistry of MWCNTs after nitric acid oxidation. After oxidation, hydrophilic oxygen-containing groups, including carboxylic,

carbonyl, and hydroxyl groups, were introduced to the outmost surface and defect sites of MWCNTs. The addition of these groups results in a more negatively charged MWCNT surface due to deprotonation of carboxylic groups at the equilibrium sorption pH of 6, since at this pH the adsorption of water is more energetically favorable relative to the sorption of NACs and thus the adsorption of NACs is more difficult.

3.3. Sorption isotherm of NACs

Fig. 4 presents the sorption isotherms of DNB, mNT, pNP, and NB on as-grown and oxidized MWCNTs at different temperatures. Langmuir and Freundlich models fit the sorption isotherms well (Table 4), and the values of $1/n$ were generally lower than 0.5 (Table 4), consistent with the adsorption onto other carbon materials such as activated carbon [27,28] and black carbon [29,30]. Three main mechanisms have been proposed for the sorption of nondissociable aromatic compounds onto carbon materials, (1) π - π dispersion interaction, (2) hydrogen bonding [12], and (3) electron donor-acceptor complex formation [13]. Of the three proposed mechanisms, π - π dispersion interaction is the most widely accepted mechanism for the adsorption of aromatic compounds on activated carbon [11,14]. However, in this study, the π - π donor-acceptor complex mechanism was proposed to better explain the observed results [7]. By comparing the Q_m of NACs adsorbed to as-grown and oxidized MWCNTs at the same temperature, Q_m followed the order DNB $>$ mNT $>$ pNP $>$ NB. In addition to the molecular size of the NACs, the number of nitro groups on the NACs may be another factor affecting or controlling the sorption affinity of NACs to MWCNTs. NACs are highly polar and often act as strong electron acceptors when interacting with adsorbent-containing structures with high electron polarization or electron donors such as oxygen-containing groups. The graphene surface of MWCNTs is expected to be highly polarizable and is likely to act as an electron donor, when in contact with strong electron acceptors such as NACs. Acceptor strength of the NAC depends on the electron-withdrawing ability and the number of substitutes on the NAC. Among the four NACs studied, DNB had more $-\text{NO}_2$ groups than any others, so its acceptor strength would be stronger and consequentially DNB should have a greater sorption affinity

Fig. 4. Sorption isotherms of DNB, mNT, pNP, and NB onto MWCNTs at (■) 283 K, (○) 293 K, and (▲) 308 K. Lines represent the model fitting of Freundlich equation.

Table 4

Coefficients of Langmuir and Freundlich model fittings for sorption of NACs on as-grown and oxidized MWCNTs at different temperatures.

NACs	Temperature (K)	Langmuir model				Freundlich model			
		Q_m^c (mg/g)	Q_{m-SA} (mg/m ²)	K_L^c (mg/L)	R^2	K_F^c (mg/g) (L/mg) ^{1/n}	K_{F-SA} (mg/m ²) (L/mg) ^{1/n}	$1/n^c$	R^2
DNB	283 ^a	44.0 ± 2.04	0.275	1.76 ± 0.35	0.977	18.1 ± 1.45	0.113	0.30 ± 0.033	0.969
	293 ^a	41.4 ± 1.69	0.259	2.07 ± 0.35	0.983	15.8 ± 1.48	0.099	0.31 ± 0.038	0.963
	308 ^a	40.4 ± 2.87	0.253	3.64 ± 0.90	0.967	11.8 ± 0.91	0.074	0.37 ± 0.030	0.984
	283 ^b	53.1 ± 2.43	0.194	2.14 ± 0.35	0.981	18.9 ± 0.98	0.069	0.33 ± 0.021	0.987
	293 ^b	48.7 ± 1.52	0.178	2.72 ± 0.35	0.954	16.0 ± 0.33	0.058	0.34 ± 0.008	0.993
	308 ^b	44.2 ± 1.92	0.161	3.57 ± 0.50	0.986	12.7 ± 0.76	0.046	0.37 ± 0.023	0.987
mNT	283 ^a	43.9 ± 2.52	0.273	2.49 ± 0.61	0.977	13.9 ± 1.14	0.087	0.34 ± 0.034	0.983
	293 ^a	41.4 ± 3.04	0.259	4.36 ± 0.99	0.982	10.9 ± 0.88	0.067	0.41 ± 0.033	0.988
	308 ^a	37.3 ± 2.60	0.234	5.46 ± 1.11	0.985	8.4 ± 0.82	0.053	0.43 ± 0.037	0.986
	283 ^b	48.5 ± 1.66	0.177	2.65 ± 0.32	0.991	15.9 ± 1.33	0.058	0.35 ± 0.033	0.973
	293 ^b	47.8 ± 1.35	0.175	3.35 ± 0.31	0.995	13.5 ± 1.21	0.049	0.39 ± 0.034	0.992
	308 ^b	41.0 ± 1.43	0.150	4.92 ± 0.52	0.993	9.8 ± 0.80	0.036	0.41 ± 0.030	0.983
pNP	283 ^a	32.2 ± 0.83	0.201	2.59 ± 0.27	0.993	10.9 ± 1.30	0.068	0.33 ± 0.047	0.948
	293 ^a	31.7 ± 0.91	0.198	3.95 ± 0.38	0.995	8.9 ± 0.97	0.055	0.38 ± 0.042	0.969
	308 ^a	30.6 ± 0.99	0.192	6.25 ± 0.57	0.996	6.4 ± 0.93	0.040	0.44 ± 0.054	0.962
	283 ^b	45.8 ± 1.87	0.167	2.21 ± 0.32	0.984	14.8 ± 1.33	0.054	0.36 ± 0.036	0.964
	293 ^b	41.1 ± 1.59	0.150	4.00 ± 0.44	0.994	9.7 ± 0.55	0.035	0.45 ± 0.024	0.978
	308 ^b	39.9 ± 2.30	0.146	5.27 ± 0.88	0.982	8.7 ± 0.62	0.032	0.43 ± 0.026	0.988
NB	283 ^a	28.3 ± 1.06	0.177	8.97 ± 0.99	0.992	5.5 ± 1.09	0.034	0.41 ± 0.064	0.936
	293 ^a	27.8 ± 1.01	0.174	11.63 ± 1.12	0.995	4.3 ± 0.79	0.027	0.45 ± 0.058	0.956
	308 ^a	24.0 ± 1.41	0.151	11.40 ± 1.80	0.986	3.9 ± 0.91	0.024	0.44 ± 0.075	0.927
	283 ^b	38.1 ± 1.67	0.139	8.85 ± 1.00	0.992	5.2 ± 0.34	0.019	0.47 ± 0.022	0.990
	293 ^b	37.5 ± 2.32	0.137	11.45 ± 1.68	0.988	4.1 ± 0.24	0.015	0.50 ± 0.019	0.989
	308 ^b	35.1 ± 2.49	0.128	15.02 ± 2.32	0.989	3.8 ± 0.31	0.014	0.54 ± 0.027	0.992

Q_{m-SA} and K_{F-SA} were coefficients of Q_m and K_F normalized by surface area.

^a As-grown MWCNTs.

^b Oxidized MWCNTs.

^c Mean ± standard deviation.

than the other NACs considered. For these reasons, π - π electron donor acceptor interactions may be the most important interaction between NACs and MWCNTs where the number of nitro groups becomes a significant factor affecting and controlling the sorption.

Since nitric acid oxidation removed a large amount of impurities, including amorphous carbon and metal particles allowing the formation of bundles, the surface area and pore volumes of MWC-

NTs were consequently increased by ~70% compared to the as-grown MWCNTs (Table 2), and the sorption capacity of MWCNTs (Q_m and K_F) was increased for all the NACs studied (Table 4). In order to distinguish the effect of surface area and pore volume on the sorption of NACs from that of oxygen-containing groups, the sorption capacity (Q_{m-SA} and K_{F-SA}) was normalized on the basis of surface area, and Q_{m-SA} and K_{F-SA} compared between the ni-

Fig. 5. Plots of $\ln K_0$ versus $1/T$ of sorption of DNB, mNT, pNP, and NB on MWCNTs.

tric acid-oxidized and as-grown MWCNTs. This comparison showed that Q_{m-SA} and K_{F-SA} of the nitric acid-oxidized MWCNTs were consistently lower than those of as-grown MWCNTs for all the NACs studied (Table 4). The existence of oxygen functional groups on the nitric-oxidized MWCNTs, which increased the hydrophilicity of MWCNTs, had already been identified (Fig. 2). Numerous studies demonstrated that the oxygen functional groups depressed the sorption of organic chemicals on carbon materials [27,30] via water adsorption, dispersive/repulsive interactions, and hydrogen bonding. A recent study [8] also revealed that incorporated surface oxides created polar regions that reduced the surface area available for naphthalene sorption, and as little as a 10% increase in surface oxygen concentration resulted in a decrease of the maximum adsorption capacity of naphthalene by roughly 70%.

3.4. Thermodynamic analysis

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during sorption. To assess the thermodynamic parameters, the sorption isotherms of DNB, mNT, pNP, and NB onto MWCNTs were measured at 283, 293, and 308 K and the changes in thermodynamic parameters of free energy of sorption (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated from the variation of the thermodynamic equilibrium constant K_0 with the change in temperature. The constant K_0 for the adsorption reaction can be defined as

$$K_0 = \frac{a_s}{a_e} = \frac{v_s q_e}{v_e C_e}, \quad (9)$$

where a_s is the activity of adsorbed NACs, a_e is the activity of NACs in solution at equilibrium, q_e is the surface concentration of NACs on MWCNTs (mg/g), C_e is the concentration of NACs at equilibrium solution (mg/L), v_s is the activity coefficient of the adsorbed NACs, and v_e is the activity coefficient of NACs in solution. As the concentration of NACs in the solution approaches zero, the activity coefficient approaches unity, reducing Eq. (9) to the following form:

$$K_0 = \frac{a_s}{a_e} = \frac{q_e}{C_e}. \quad (10)$$

Values of K_0 were therefore obtained by plotting $\ln(q_e/C_e)$ versus q_e , and extrapolating q_e to zero. The straight line obtained was fit using least-squares analysis where the intercept of the vertical axis was $\ln K_0$.

Free energy changes ΔG for any interaction can be calculated using the relationship

$$\Delta G = -RT \ln K_0, \quad (11)$$

Table 5

Thermodynamics parameters of NACs sorbed on MWCNTs.

MWCNTs	NACs	ΔG (kJ/mol)			ΔH (kJ/mol)	ΔS [J/(mol K)]
		283 K	293 K	308 K		
As grown	DNB	−10.57	−9.59	−8.07	−34.10	−84.64
	mNT	−8.85	−7.44	−6.01	−36.71	−100.02
	pNP	−7.68	−6.57	−4.74	−37.69	−107.00
	NB	−3.60	−2.33	−1.52	−25.05	−76.82
Oxidized	DNB	−10.19	−9.80	−8.33	−27.08	−60.75
	mNT	−8.64	−7.63	−6.29	−28.99	−71.91
	pNP	−9.74	−8.67	−6.27	−41.77	−113.80
	NB	−4.57	−3.67	−2.65	−22.64	−64.49

where R is the universal gas constant and T is the temperature in Kelvin. Rearrangement and substitution give

$$RT \ln K_0 = T \Delta S - \Delta H, \quad (12)$$

$$\ln K_0 = -\Delta H/RT + \Delta S/R, \quad (13)$$

where Eq. (12) describes how the equilibrium constant K_0 varies with absolute temperature T for an equilibrium system and Eq. (13) predicts a linear plot of $\ln K_0$ versus $1/T$ for reversible sorption of NACs on MWCNTs. The slope of Eq. (13) is $-\Delta H/R$, and the intercept is $\Delta S/R$ (Fig. 5) [31]. ΔG (kJ/mol), ΔH (kJ/mol), and ΔS [J/(mol K)] values are given in Table 5.

The ΔG values were negative for all four NACs at all three temperatures, confirming that the sorption of NACs onto MWCNTs was spontaneous and thermodynamically favorable. The observed negative ΔH suggested an exothermic sorption, which was supported by the observation that sorption of NACs onto MWCNTs decreased with increasing sorption temperature (Fig. 4). Kara et al. [32] suggested that the ΔH of physisorption was less than 40 kJ/mol, implying the sorption of NACs onto MWCNTs was a physisorption process [33] except for the sorption of pNP on the oxidized MWCNTs ($\Delta H = 41.77$ kJ/mol). The negative ΔS indicated decreased randomness at the solid–liquid interface during sorption as might be expected from acceptor donor complex formation.

The values of ΔH and ΔS , for the sorption of NACs onto oxidized MWCNTs and as-grown MWCNTs, decreased after nitric acid oxidation except for pNP. The value of ΔH for pNP increased remarkably after nitric acid oxidation. The significantly higher thermodynamics adsorption constants observed for pNP in the oxidized MWCNTs may be due to specific interactions between pNP and the oxidized MWCNTs. One such specific interaction is the formation of hydrogen bonds and pNP is the only dissociable compound among the four NACs studied that has a hydroxy functional

group (–OH) capable of forming H-bonds with the surface oxygen groups of the MWCNTs. Some authors have also identified the existence of H-bonds between the phenol and carboxyl groups of activated carbon, although water can compete with phenol [14,34]. It is well known that adsorption of phenolic compounds to carbon materials is partly physical and partly chemical [11]. While physisorbed phenol compounds can be desorbed by using different solvents or by heat treatments in inert atmosphere, the chemisorbed compounds cannot be desorbed, even at high temperatures, due to the strong chemical bond between phenolic compounds and the carbon surface formed. In general, since the ΔH of a chemical reaction is much larger than the ΔH for a physical reaction the large change of enthalpy for sorption of pNP onto oxidized MWCNTs is most likely attributable to chemical sorption of pNP via hydrogen bonding.

4. Summary

The kinetics and thermodynamics of NAC sorption onto as-grown and nitric acid-oxidized MWCNTs were investigated. The sorption followed a pseudo-second-order kinetics law. The sorption of NACs onto MWCNTs was exothermic and spontaneous where both the Langmuir and the Freundlich models described the sorption data well. Molecule size and the number of nitro groups of the NACs were the main factors that affected sorption kinetics and the equilibrium. Nitric acid oxidation increased the surface area and pore volume of the MWCNTs and introduced oxygen functional groups to MWCNTs which depressed the sorption rate and sorption capacity of NACs onto MWCNTs.

References

- [1] R.Q. Long, R.T. Yang, *J. Am. Chem. Soc.* 123 (2001) 2058.
- [2] X. Peng, Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian, Z. Jia, *Chem. Phys. Lett.* 376 (2003) 154.
- [3] C. Lu, Y.L. Chung, K.F. Chang, *Water Res.* 39 (2005) 1183.
- [4] K. Yang, L. Zhu, B. Xing, *Environ. Sci. Technol.* 40 (2006) 1855.
- [5] C.J.M. Chin, L.C. Shih, H.J. Tsai, T.K. Liu, *Carbon* 45 (2007) 1254.
- [6] Q. Liao, J. Sun, L. Gao, *Carbon* 46 (2008) 553.
- [7] W. Chen, L. Duan, D. Zhu, *Environ. Sci. Technol.* 41 (2007) 8295.
- [8] H.H. Cho, B.A. Smith, J.D. Wnuk, D.H. Fairbrother, W.P. Ball, *Environ. Sci. Technol.* 42 (2008) 2899.
- [9] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, *Carbon* 46 (2008) 833.
- [10] L.R. Radovic, I.F. Silva, J.I. Ume, J.A. Menéndez, C. Leon, A.W. Scaroni, *Carbon* 35 (1997) 1339.
- [11] C. Moreno-Castilla, *Carbon* 42 (2004) 83.
- [12] R.W. Coughlin, F.S. Ezra, *Environ. Sci. Technol.* 2 (1968) 291.
- [13] J.A. Mattson, H.B. Mark, M.D. Malbin, W.J. Weber, J.C. Crittenden, *J. Colloid Interface Sci.* 31 (1969) 116.
- [14] S. Haydar, M.A. Ferro-Garcia, J. Rivera-Utrilla, J.P. Joly, *Carbon* 41 (2003) 387.
- [15] F. Villacafias, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, *J. Colloid Interface Sci.* 293 (2006) 128.
- [16] S.B. Haderlein, K.W. Weissmahr, R.P. Schwarzenbach, *Environ. Sci. Technol.* 30 (1996) 612.
- [17] S.B. Haderlein, R.P. Schwarzenbach, *Environ. Sci. Technol.* 27 (1993) 316.
- [18] C. Lu, Y.L. Chung, K.F. Chang, *J. Hazard. Mater.* 138 (2006) 304.
- [19] C.H. Wu, *J. Hazard. Mater.* 144 (2007) 93.
- [20] Y.S. Ho, G. McKay, *Water Res.* 34 (2000) 735.
- [21] Z. Aksu, A. Tatlı, Ö. Tunc, *Chem. Eng. J.* 142 (2008) 23.
- [22] S. Azizian, *J. Colloid Interface Sci.* 276 (2004) 47.
- [23] S. Azizian, B. Yahyaei, *J. Colloid Interface Sci.* 299 (2006) 112.
- [24] X. Yang, B. Al-Duri, *J. Colloid Interface Sci.* 287 (2005) 25.
- [25] Z. Li, *Langmuir* 15 (1999) 6438.
- [26] S. Agnihotri, J.P.B. Mota, M. Rostam Abadi, M.J. Rood, *Carbon* 44 (2006) 2376.
- [27] M. Franz, H.A. Arafat, N.G. Pinto, *Carbon* 38 (2000) 1807.
- [28] P.A.M. Mourão, P.J.M. Carrott, M.M.L. Ribeiro Carrott, *Carbon* 44 (2006) 2422.
- [29] D. Zhu, S. Kwon, J.J. Pignatello, *Environ. Sci. Technol.* 39 (2005) 3990.
- [30] D. Zhu, J.J. Pignatello, *Environ. Sci. Technol.* 39 (2005) 2033.
- [31] E.A. Ghabbour, G. Davies, M.E. Goodwillie, K. O'Donoghue, T.L. Smith, *Environ. Sci. Technol.* 38 (2004) 3338.
- [32] M. Kara, H. Yuzer, E. Sabah, M.S. Celik, *Water Res.* 37 (2003) 224.
- [33] B. von Oepen, W. Kordel, W. Klein, *Chemosphere* 22 (1991) 285.
- [34] O.P. Mahajan, C. Moreno-Castilla, P.L. Walker, *Sep. Sci. Technol.* 15 (1980) 1733.