Comparison with as-grown and microwave modified carbon nanotubes to removal aqueous bisphenol A

Chao-Yin Kuo *

Department of Safety Health and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Rd., Sec. 3, Douliou, Yunlin 640, Taiwan

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ABSTRACT

This study utilized carbon nanotubes (CNTs) to remove bisphenol A (BPA) from aqueous solution. The surfaces of CNTs were modified by $SOCl_2/NH_4OH$ under microwave irradiation. The surface characteristics of as-grown and modified CNTs were analyzed by measuring zeta potential, and using a scanning electron microscope, a surface area analyzer and a Fourier transform infrared spectroscope. The specific surface area of modified CNTs exceeded that of as-grown CNTs. The pH_{iep} values of as-grown CNTs and modified CNTs were determined to be 4.3 and 6.5, respectively. Some amine functionalities were formed on the surface of modified CNTs; therefore, the surface of the modified CNTs contained more positive charges than that of the as-grown CNTs. The adsorption kinetics were examined using pseudo first- and second-order models, intraparticle diffusion and Bangham's models. The equilibrium data were simulated using Langmuir, Freundlich, Dubinin and Radushkevich (D–R) and Temkin isotherms. The results reveal that the pseudo second-order model and Langmuir isotherm fit the kinetics and equilibrium data, respectively. The adsorption capacity of BPA on the surface of CNTs fluctuates very little with pH in the range of 3–9, suggesting the high stability of CNTs as an adsorbent for BPA over a rather wide pH range. The values of ΔH^0 and ΔS^0 were calculated to be -11.7 kJ/mol and 46.1 J/mol, respectively. The isotherm and thermodynamic simulations indicate that the adsorption of BPA onto as-grown CNTs proceeds by physisorption process.

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1. Introduction

Some chemicals such as hormones in the living body are suspected to have serious effects on internal secretion; these are called endocrine-disrupting chemicals (EDCs), and have recently become a social issue. The removal of EDCs from wastewater is considered to be important for environmental protection. Bisphenol A (BPA), one of these EDCs, is used as an intermediate in the manufacture of polycarbonate, epoxy, resins and polysulfone. Accordingly, BPA has been reportedly observed in waste landfill leachates, rivers, seas and soils [1]. Although rapid biodegradation of BPA can be observed in river water [2–4], BPA presents a risk to humans and animals. Therefore, BPA was studied as the model compound herein.

Adsorption is used in water treatment for the heavy metal, EDCs, the control of taste, odor and color. Therefore, various adsorbent is widely employed for research [5–7] for example carbon nanotubes (CNTs). CNTs are relatively new adsorbents of trace pollutants from water, because they have a good specific surface area, and small, hollow and layered structures. CNTs have been demonstrated to exhibit good potential as superior adsorbents for removing numerous

organic and inorganic pollutants, such as Procion Red MX-5B [8], natural organic matter [9], trihalomethanes [10], 1, 2-dichlorobenzeze [11], Cd^{2+} [12–14], Zn^{2+} [13–15], Pb^{2+} [13,14,16,17], Ni^{2+} [18] and Cu^{2+} [13,14,18–20]. Hence, CNTs would be also expected to have good potential for removing BPA from aqueous solutions. However, no relevant work has been published.

As-grown CNTs contain various impurities, such as amorphous carbon and catalytic metal particles. The transformation of the surface chemistry of CNTs typically depends on the functional groups attached to the surface. The oxidation of carbon surfaces is known to generate not only more hydrophilic surface structures, but also more oxygen-containing functional groups, increasing the adsorption capacity [21]. The surface of CNTs can be modified by thermal oxidation [9], chemical oxidation [10,12,14–18,22–24] and microwave-assisted heating [25,26]. The frequently used approach is to combine thermal and chemical oxidation by adding $NaOCl$, HNO_3, HCl, H_2O_2, $KMnO_4$ and H_2SO_4. Obviously, different treatments influence the surface chemical properties of CNTs and thereby modify their adsorption capacities. Thionyl chloride, $SOCl_2$, is a liquid organic solvent that has been often applied in the end-group derivatization of single-wall carbon nanotubes [27,28]. The increase in the oxygen concentration by $SOCl_2$ treatment can be associated with generation of new species [28]. However, the effects of microwave-assisted chemical oxidation by $SOCl_2$ on the adsorption of CNTs have not yet

* Tel.: +886 5 534 5601x4423; fax: +886 5 531 2069.
  E-mail address: kuocyr@ms35.hinet.net.

been reported. In addition, through $SOCl_2/NH_4OH$ modification, some hydrophilic amine groups could generate in CNTs surface which contain more positive charges than that of the as-grown CNTs, and provide various organic adsorption sites.

This work evaluated the effects of $SOCl_2/NH_4OH$ modification by microwave irradiation for CNTs on the removal of BPA. This study elucidates the kinetic, equilibrium and thermodynamics of the adsorption of BPA by CNTs. The objectives of this investigation were (i) to identify and compare the surface characteristics of as-grown and modified CNTs; (ii) to determine the effects of pH on the adsorption of BPA by as-grown and modified CNTs; (iii) to evaluate the adsorption capacity of BPA by as-grown and modified CNTs, and (iv) to determine changes in the thermodynamic parameters, enthalpy (ΔH^0) and entropy (ΔS^0), during adsorption.

2. Materials and methods

2.1. Materials and modification procedures

As-grown CNTs were generated by the pyrolysis of methane gas on particles of Ni in chemical vapor deposition (CVD). The as-grown CNTs employed herein were multi-walled carbon nanotubes (CBT and MWNTs-2040). $SOCl_2$ and NH_4OH were the surface-modification reactants of as-grown CNTs. The pH of the solution was adjusted by adding NaOH and $HClO_4$. All solutions were prepared using deionized water (Milli-Q) and reagent-grade chemicals.

In the modification procedures, as-grown CNTs were heated at 350 °C for 30 min to remove the impurities and the amorphous carbon. 0.1 g as-grown CNTs were mixed with $SOCl_2$ (1 M and 3 ml) in a Telfon vessel and then placed in a microwave oven (BERGHOF, MWS-2). The microwave power was 800 W and the irradiation time was 10 min. The $SOCl_2$-modified CNTs were purified repeatedly using Milli-Q deionized water until the pH of the solution reached pH 7. The obtained CNTs were dried at 120 °C for 24 h. Following $SOCl_2$ modification, 0.1 g $SOCl_2$-modified CNTs were mixed with NH_4OH (1 M and 3 ml) in a Telfon vessel and heated in a microwave oven according to the above experimental conditions and following the aforementioned procedures. After cleaning and drying, the obtained particles were modified CNTs used herein.

2.2. Adsorption experiments

All adsorption experiments were performed in a closed 200 ml glass pyramid bottle that contained 0.025 g of as-grown or modified CNTs and an appropriate concentration of BPA; the solution was placed in a water bath, which was shaken at 150 rpm. In experiments on the effect of pH, the control conditions were an initial BPA concentration of 10 mg/l and a CNT concentration of 0.125 g/l. Then, the pH of the solution was adjusted to between 3 and 9 by adding 0.1 M $HClO_4$ and 0.1 M NaOH during the experiments. In the experiments on the effect of temperature, the control conditions were the same as those in the experiments on the effect of pH. Then, the temperature was maintained at 7, 27 and 47 °C and the pH was fixed at 6.0 during the experiments. At the end of the equilibrium period, the suspensions were centrifuged at 3500 rpm for 10 min, and the supernatant was filtered through 0.2 μm filter paper (Gelman Sciences) for the subsequent analysis of the concentration of BPA.

2.3. Analytic methods

The zeta potentials of the as-grown and modified CNTs were measured using a Zeta-Meter 3.0 (Zeta-Meter Inc., U.S.A.). The acidity or basicity of the CNTs surface and the isoelectric point of pH (pH_{iep}) were determined by measuring the zeta potential as a function of pH. Scanning electron microscope (SEM) analysis (JEOL and JSM-T330A) was employed to observe the morphology of as-grown and modified

CNTs. The specific surface area of CNTs was measured using the BET method, using a Model ASAP 2010 surface area analyzer (Micromeritics, USA). The functional groups of CNTs were identified by Fourier transform infrared spectroscopy (FTIR) analysis using a Spectrum One and an Autoimagic system (Perkin Elmer, USA) and the KBr pressed disc method. The concentration of BPA was determined by high-performance-liquid chromatography (HPLC, Agilent Technologies, HPLC-1200 Series). All detailed analyses were conducted strictly by the QA/QC method to ensure the accuracy of the results.

3. Results and discussion

3.1. Characteristics of as-grown and modified CNTs

The specific surface areas of as-grown and modified CNTs were measured as 78.2 and 94.8 m^2/g, respectively. The specific surface area of modified CNTs exceeded that of as-grown CNTs, indicating that the modification of CNTs using $SOCl_2/NH_4OH$ is an effective approach for removing the amorphous carbon and carbon black that was introduced by the CVD preparation, and for probing the inner cavities of the CNTs, exposing their internal surface area, and thereby increasing the specific surface area. Several studies have also demonstrated that the specific surface area of modified CNTs exceeds that of as-grown CNTs after treatment with different acids and/or oxidants [10,12,15,18–20,22].

Fig. 1 presents SEM images of as-grown and modified CNTs. It reveals that the CNTs are cylindrical. Although the magnification was 50,000, significant morphological difference was not observed between the as-grown and the modified CNTs. The inter-molecular force causes the isolated CNTs of different sizes and directions to yield an aggregated structure. The diameters of both as-grown and modified CNTs were approximately 50 nm and the lengths ranged from hundreds of nanometers to micrometers.

Zeta potential is a physical parameter, which can be employed to quantify the electrical potential of the solid particle surface. Fig. 2 plots the zeta potential of as-grown and modified CNTs. All of the zeta potentials of CNTs became more negative as the pH increased, probably because of the deposition of more OH^- on the surface of CNTs. The pH_{iep} values of as-grown CNTs and modified CNTs were determined to be 4.3 and 6.5, respectively. Upon surface modification with $SOCl_2$ and NH_4OH, the pH_{iep} shifts to higher pH values may due to the introduction of basic surface groups. Numerous investigations have demonstrated that the zeta potentials of acid-modified CNTs [12,16,17,23,24] and oxidant-modified CNTs [12,15,18,20] are more negative than those of as-grown CNTs. Lu and Su [9] demonstrated that the pH_{iep} values of as-grown CNTs and heated CNTs were nearly the same. However, the surface charge of as-grown CNTs is more positive than that on heated CNTs at pH < 5.0, but is more negative at pH > 5.0. This study suggests that the surface charge of modified CNTs depends on the species of acid and/or oxidant and the treatment procedure used for modification.

FTIR is utilized to characterize the functional groups absorbed by CNTs. Fig. 3 displays the FTIR spectra of as-grown and modified CNTs. The as-grown CNTs yielded peaks at near 1370, 1550, 2800–3000 and 3300–3600 cm^{-1}, which can be attributed to carboxyl groups [23,29], carboxylate anion stretching [9], CH stretching [30,31] and OH stretching [15,17,30,31], respectively. These oxygen-containing functional groups caused the surface of as-grown CNTs to contain more negative charges than that of the modified CNTs. The modified CNTs yielded several peaks, which were associated with OH stretching at 1100 cm^{-1} [32]; 2400 cm^{-1} [30] and 3300–3600 cm^{-1} [15,17,30,31], carboxyl group stretching at 1370 cm^{-1} [17,23,29], NH stretching at 1530 cm^{-1} [33,34], C=O stretching at 1750 cm^{-1} [15,17,31,33] and CH stretching at 2800–3000 cm^{-1} [30,31]. Breza [28] indicated that $SOCl_2$ treatment induces significant changes in the composition of
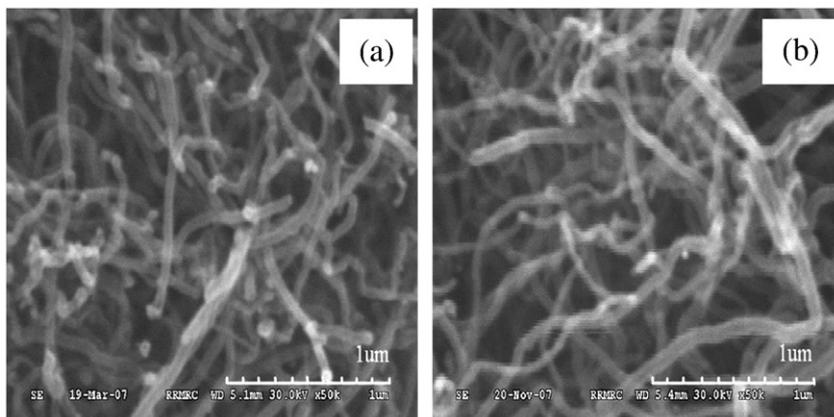
Fig. 1. SEM images of CNTs (a) as-grown CNTs and (b) modified CNTs (magnification: 50000).

CNTs. The oxygen-related functional groups can be assigned to the modified carbon sites, –COH, –C=O and –COOH groups; hence, the oxygen content increases. Misra et al. [35] stated that the strong peaks at 1250 and 1372 cm^{-1} are consistent with C–N and N–CH$_3$ stretching vibrations and the associated presence of intercalated N atoms between the graphite layers in the inner parts of the nanotube walls. OH and NH stretches could be also assigned to 3200–3600 cm^{-1} [36]. Moreover, Wu et al. [34] and Xie et al. [34] indicated that the peaks at 3319 cm^{-1} and 2070–3100 cm^{-1} are associated with the presence of NH stretching. These adsorption peaks clearly show that some hydrophilic amine groups were generated in the modified CNTs surface herein. Ammonia has been regarded as an effective precursor for introducing amine functionalities to the CNTs, increasing their hydrophilicity [37]. Since some amine functionalities were formed on the surface of modified CNTs, the surface of modified CNTs contain more positive charges than that of the as-grown CNTs. Evidently, various functional groups were generated on the surface of modified CNTs, providing various adsorption sites.

3.2. Kinetic analyses

Fig. 4 displays the kinetic analysis of the removal of BPA by as-grown CNTs. The adsorption is initially (contact time <0.5 h) rapid, and then slows, perhaps because many vacant surface sites were available for adsorption during the initial stage, and then, the remaining vacant surface sites were difficult to occupy because of the repulsive forces between the BPA molecules on the CNTs and the bulk phase. Pseudo first- and second-order models and intraparticle

diffusion and Bangham's models were adopted to test the experimental data and thus elucidate the kinetic adsorption process. The pseudo first-order model can be expressed as

$$\ln(q_e - q) = \ln(q_e) - k_1 t \tag{1}$$

where q_e and q are the amounts of BPA adsorbed on CNTs at equilibrium and at various times t (mg/g) and k_1 is the rate constant of the pseudo first-order model of adsorption (1/h) [38]. The values of q_e and k_1 can be determined from the intercept and the slope of the linear plot of $\ln(q_e - q)$ versus t. The pseudo second-order model is

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_e and q are defined as in the pseudo first-order model, and k_2 is the rate constant of the pseudo second-order model for adsorption (g/mgh) [39]. The slope and intercept of the linear plot of t/q as a function of t yielded the values of q_e and k_2. Furthermore, the initial adsorption rate h (mg/gh) can be determined from $h = k_2 q_e^2$. Since neither the pseudo first-order nor the second-order model can identify the diffusion mechanism, the kinetic results were analyzed using the intraparticle diffusion model to elucidate the diffusion mechanism, which model is expressed as

$$q = k_i t^{1/2} + C \tag{3}$$

where C is the intercept and k_i is the intraparticle diffusion rate constant (mg/gh$^{0.5}$), which can be evaluated from the slope of the linear plot of q versus $t^{1/2}$[40]. Kinetic data were further utilized to
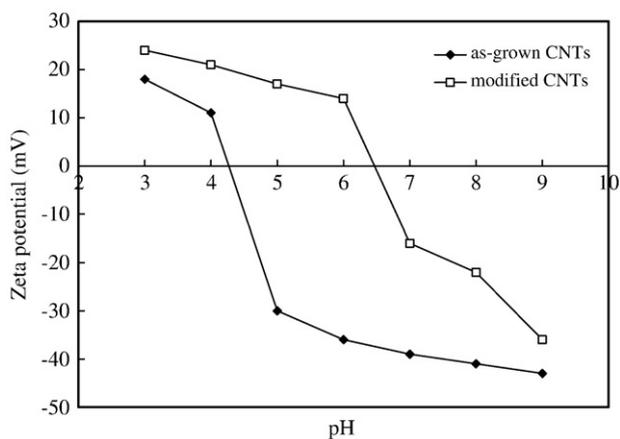

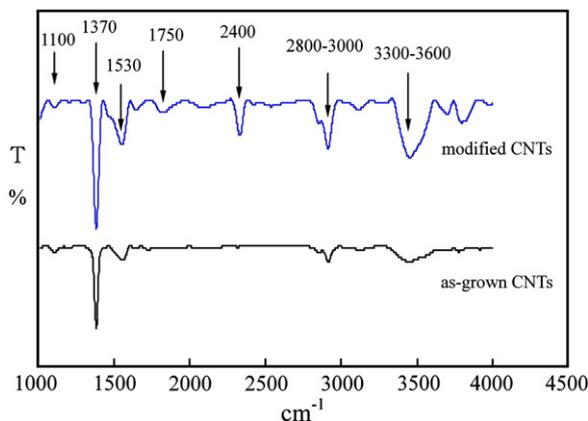Fig. 2. Zeta potential analysis of as-grown and modified CNTs.

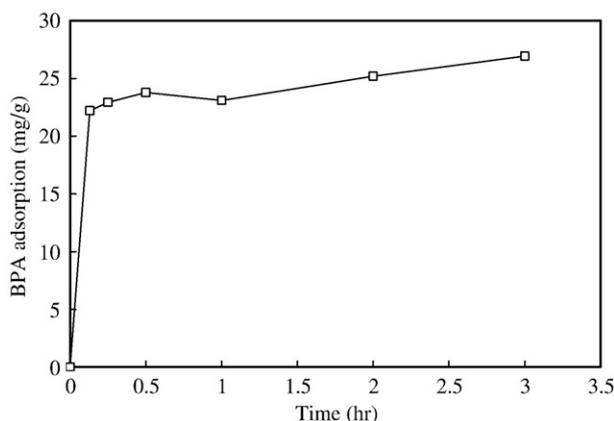Fig. 3. FTIR spectra of as-grown and modified CNTs.

Fig. 4. Kinetic analysis of the removal of BPA by as-grown CNTs (BPA = 10 mg/l, pH = 6, CNTs dose = 0.125 g/l and T = 27 °C).

elucidate the slowness of the step in the present adsorption system, based on Bangham's model [38,39].

$$\log\left(\frac{C_0}{C_0-qm}\right) = \log\left(\frac{k_0 m}{2.303 V}\right) + \alpha \log t \qquad (4)$$

where q and t are defined as in the pseudo first-order model; C_0 is the initial concentration of BPA in solution (mg/l); V is the volume of solution (ml); m is the mass of CNTs per liter of solution (g/l) and k_0 and α are constants. Table 1 presents the kinetic parameters for the removal of BPA by as-grown CNTs. The R^2 value of the pseudo second-order model exceeded 0.99; moreover, the q value ($q_{e, \text{ cal}}$) calculated from the pseudo second-order model was consistent with the experimental q values ($q_{e, \text{ exp}}$). Hence, this study suggests that the pseudo second-order model best represented the adsorption kinetics.

Typically, various mechanisms govern the adsorption kinetics; the most limiting are the diffusion mechanisms, such as external diffusion, boundary layer diffusion and intraparticle diffusion [41]. Therefore, the intraparticle diffusion model was adopted to determine the rate-limiting step of the adsorption process. If the plot of q against $t^{1/2P}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [42]. Although the regression was linear, the plot did not pass through the origin, suggesting that adsorption involved intraparticle diffusion, but was not the only rate-controlling step. The double logarithmic plot of Bangham's model was not perfectly linear ($R^2 = 0.798$) so the diffusion of BPA into pores of CNTs is not the only rate-controlling step [43], as revealed above using the intraparticle diffusion model.

3.3. Equilibrium analyses

3.3.1. Effect of pH

Theoretically, the key factor that affects the adsorption of BPA on the sites of CNTs is pH. The dependence of adsorption on pH is due to the dependence of the surface charge of CNTs on pH, which was shown by zeta potential measurements. The relevant experiments demonstrated that the adsorption capacity of BPA on the surface of CNTs fluctuates very little over the pH range 3–9 (Fig. 5), indicating the high stability of CNTs as an adsorbent of BPA over a rather wide pH range. The experimental results were similar to those of Peng et al. [11] who removed 1, 2-dichlorobenzene using as-grown and graphitized CNTs; those of Liao et al. [24], who utilized CNTs to remove resorcinol and those of Chin et al. [23], who removed p-xylene by CNTs. The pK_a value of BPA was 9.6–10.2 [1]. The BPA will be the ionized form (negative charge) when the solution pH>pK_a. The pH$_{\text{iep}}$ values of as-grown CNTs and modified CNTs were determined to be 4.3 and 6.5, respectively. Academically, at acidic pH, the surface of CNTs is expected to have a net positive charge; in contrast, at pH values that exceed pH$_{\text{iep}}$, a net negative charge is present on the surface of the CNTs. However, the dependence of adsorption on pH is independent of the dependence of the surface charge of CNTs on pH. Additionally, the maximum adsorption capacity of modified CNTs exceeded that of as-grown CNTs. This work suggests that the surface of modified CNTs is not only more positively charged and hydrophilic but also provides various functional groups, which significantly promoted the adsorption of BPA by modified CNTs. The maximum adsorption capacity increased as the temperature declined, indicating that the adsorption of BPA onto CNTs was an exothermic reaction. The following section will thoroughly discuss thermal effects.

3.3.2. Isotherm simulations

Equilibrium data are important in developing an equation that accurately models the results and can be used to design adsorption systems. This study adopted the Langmuir, Freundlich, Dubinin and Radushkevich (D–R) and Temkin isotherms to describe equilibrium adsorption. The Langmuir isotherm assumes monolayer coverage of the adsorption surface and no subsequent interaction among adsorbed molecules. Hence, the adsorption saturates, and no further adsorption occurs. The expression for the Langmuir isotherm is

$$q_e = \frac{q_m K_L C}{(1 + K_L C)} \qquad (5)$$

where q_e is the amount of BPA that is adsorbed per gram of CNTs (mg/g); C represents the equilibrium concentration of BPA in solution (mg/l); K_L is the Langmuir constant (l/mg), which is related to the affinity of binding sites, and q_m is the theoretical saturation capacity of the monolayer (mg/g). Another important parameter, R_L, called the

Table 1
Kinetic parameters for the removal of BPA by as-grown CNTs (BPA = 10 mg/l, pH = 6, CNTs dose = 0.125 g/l and T = 27 °C).

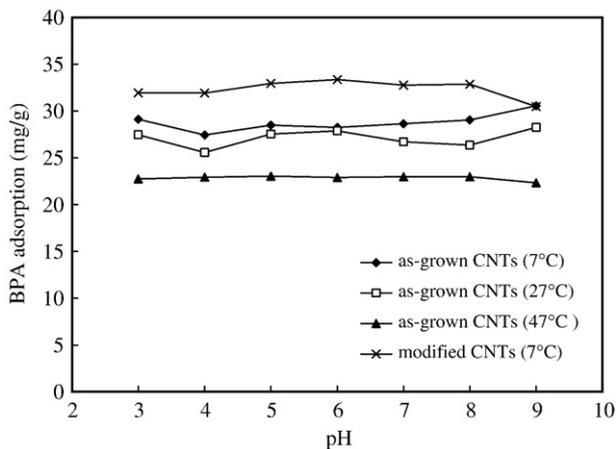| Pseudo first-order model	$q_{e, \text{ exp}}$ (mg/g)	k_1 (1/h)		$q_{e, \text{ cal}}$ (mg/g)	R^2
	26.94	1.32		7.88	0.798
Pseudo second-order model	$q_{e, \text{ exp}}$ (mg/g)	k_2 (g/mg h)	h (mg/g h)	$q_{e, \text{ cal}}$ (mg/g)	R^2
	26.94	0.49	357.12	27.03	0.997
Intraparticle diffusion model	k_i (mg/g h$^{0.5}$)		C (mg/g)	R^2	
	3.06		21.11	0.881	
Bangham's model	α		k_0 (l/(mg/l))	R^2	
	0.063		0.585	0.798	

Fig. 5. Effects of pH for the adsorption of BPA by as-grown and modified CNTs (BPA = 10 mg/l, CNTs dose = 0.125 g/l and reaction time = 24 h).

separation factor or equilibrium parameter, also evaluated herein, is determined from the relation,

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where K_L is the Langmuir constant (l/mg) and C_0 is the initial BPA concentration (10 mg/l). Ho and McKay [44] established (i) $0 < R_L < 1$ for favorable adsorption, (ii) $R_L > 1$ for unfavorable adsorption, (iii) $R_L = 1$ for linear adsorption and (iv) $R_L = 0$ for irreversible adsorption.

The Freundlich isotherm is derived to model the multilayer adsorption and the adsorption on heterogeneous surfaces. The Freundlich isotherm is

$$q_e = K_F C^{\frac{1}{n}} \tag{7}$$

where q_e and C are defined as for Langmuir isotherm and K_F and n are the Freundlich constants, which represent the adsorption capacity and the adsorption strength, respectively. The magnitude of $1/n$ quantifies the favorability of adsorption and the degree of heterogeneity of the surface of the CNTs. If $1/n$ is less than unity, suggesting favorable adsorption, then the adsorption capacity increases and new adsorption sites form [45].

The D–R isotherm describes adsorption on a single type of uniform pore. In this respect, the D–R isotherm is an analogue of the Langmuir type but it is more general because it does not assume a homogeneous surface or constant adsorption potential [46,47]. The D–R isotherm can be described as follows;

$$\ln(q_e) = \ln(X'_m) - K' \varepsilon^2 \tag{8}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C}\right) \tag{9}$$

$$E = (2K')^{\frac{-1}{2}} \tag{10}$$

where q_e is the amount of BPA that is adsorbed per unit mass of CNTs (mol/g); X'_m is the adsorption capacity (mol/g); K' is a constant that is related to the adsorption energy (mol^2/kJ^2); R is the gas constant (kJ/mol K); T is the adsorption temperature (K); ε is Polanyi potential, and E is the mean free energy of adsorption (kJ/mol).

The Temkin isotherm describes the behavior of adsorption systems on a heterogeneous surface and is represented as follows.

$$q_e = \frac{RT}{b_1} \ln(K_t C) \tag{11}$$

Eq. [10] can be expressed in linear form as,

$$q_e = B_1 \ln(K_t) + B_1 \ln(C) \tag{12}$$

where $B_1 = RT/b_1$, and B_1 is a constant that is related to the heat of adsorption. K_t is the equilibrium binding constant (l/mol) that corresponds to the maximum binding energy.

Fig. 6(a),(b),(c) and (d) displays the simulations of Langmuir, Freundlich, D–R and Temkin isotherms, respectively. Table 2 presents the isotherm parameters for different temperatures and CNTs. The adsorption capacities increased with BPA concentration, reaching a plateau, which represents the maximum adsorption capacity. The maximum adsorption capacity of as-grown CNTs at 7 °C, 27 °C and 47 °C was 60.98, 59.17 and 53.48 mg/g, respectively, and that of modified CNTs at 7 °C was 69.93 mg/g. Based on a comparison of the R^2 values in Table 2, in all cases of adsorption of BPA on CNTs, the Langmuir isotherm most closely fits the experimental data. K_L, K_F, B_1 and K_t decreased as the temperature increased, suggesting that the adsorption of BPA on CNTs fell as the temperature increased (Table 2). These results reveal that the affinity of the binding sites for BPA declines as temperature increases. Additionally, the adsorption affinity of BPA by modified CNTs was stronger than that of as-grown CNTs. Since R_L and $1/n$ are both less than unity, the adsorption of BPA onto CNTs was favored. If the E value is between 8 and 16 kJ/mol, the adsorption proceeds by some surface reaction for example ion exchange [46,47]. The E values were calculated to be 11.32–12.31 kJ/mol (Table 2); therefore, this work suggests that the adsorption of BPA onto CNTs is explained by surface reaction. Fig. 6(a),(b),(c) and (d) display the simulations of Langmuir, Freundlich, D–R and Temkin isotherms, respectively. Table 2 presents the isotherm parameters for different temperatures and CNTs. The adsorption capacities increased with BPA concentration, reaching a plateau, which represents the maximum adsorption capacity. The maximum adsorption capacity of as-grown CNTs at 7 °C, 27 °C and 47 °C was 60.98, 59.17 and 53.48 mg/g, respectively, and that of modified CNTs at 7 °C was 69.93 mg/g. Based on a comparison of the R^2 values in Table 2, in all cases of adsorption of BPA on CNTs, the Langmuir isotherm most closely fits the experimental data. K_L, K_F, B_1 and K_t decreased as the temperature increased, suggesting that the adsorption of BPA on CNTs fell as the temperature increased (Table 2). These results reveal that the affinity of the binding sites for BPA declines as temperature increases. Additionally, the adsorption affinity of BPA by modified CNTs was stronger than that of as-grown CNTs. Since R_L and $1/n$ are both less than unity, the adsorption of BPA onto CNTs was favored.

3.3.3. Thermodynamic simulation

The thermodynamic parameters offer in-depth information on inherent energetic changes that are associated with adsorption. Changes in the enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption were calculated to predict whether the adsorption is endothermic or exothermic. The thermodynamic parameters were calculated from Eq. [13]:

$$\Delta H^0 - \Delta S^0 T = -RT \ln K_L \tag{13}$$

where K_L is the Langmuir equilibrium constant (l/mol); R is the gas constant (8.314×10^{-3} kJ/mol K), and T is the absolute temperature (K). ΔH^0 and ΔS^0 were determined from the slope and intercept of the van't Hoff plots of $\ln(K)$ versus $1/T$ (Fig. 7). The values of ΔH^0 and ΔS^0 were calculated as -11.7 kJ/mol and 46.1 J/mol, respectively
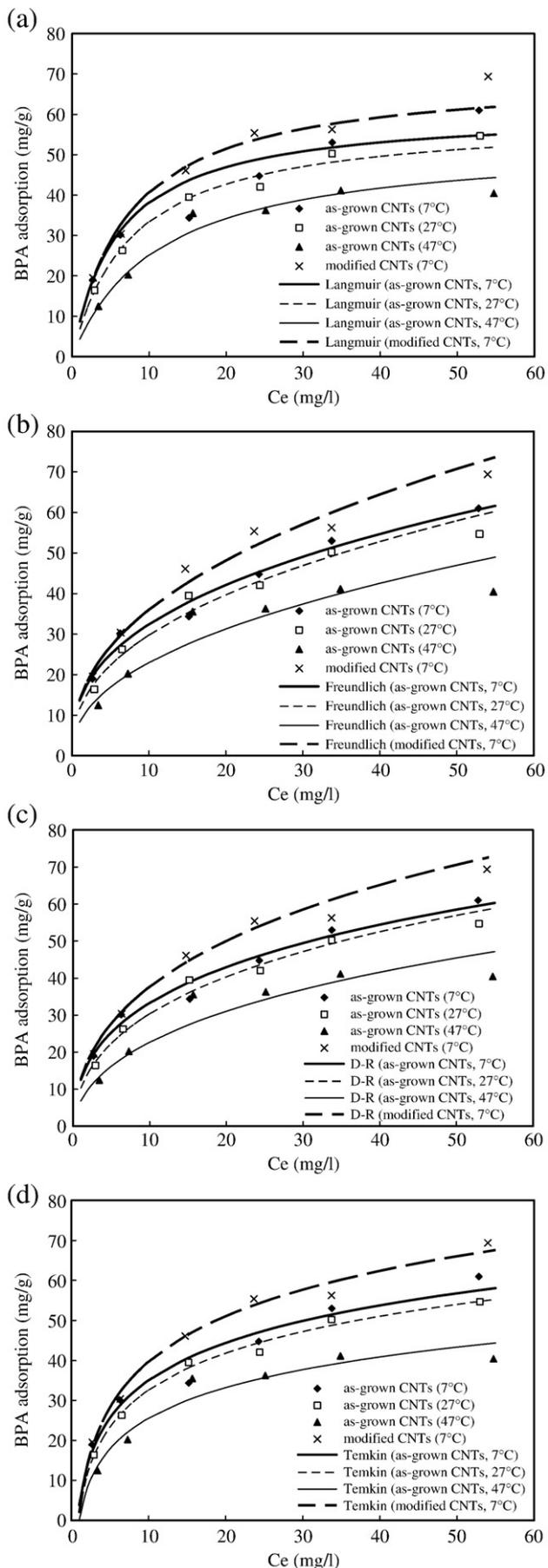
Table 2
Isotherm parameters for removal of BPA by CNTs (BPA = 10 mg/l, pH = 6, CNTs dose = 0.125 g/l and reaction time = 24 h).

Langmuir constants	K_L (l/mg)	q_m (mg/g)	R_L	R^2
As-grown CNTs (7 °C)	0.167	60.98	0.375	0.990
As-grown CNTs (27 °C)	0.130	59.17	0.436	0.995
As-grown CNTs (47 °C)	0.089	53.48	0.530	0.990
Modified CNTs (7 °C)	0.139	69.93	0.418	0.989
Freundlich constants	K_F	n	R^2	
As-grown CNTs (7 °C)	13.59	2.65	0.974	
As-grown CNTs (27 °C)	11.43	2.41	0.971	
As-grown CNTs (47 °C)	8.25	2.25	0.903	
Modified CNTs (7 °C)	13.67	2.38	0.979	
D–R constants	X'_m (mol/g)	E_a (kJ/mol)	R^2	
As-grown CNTs (7 °C)	9.86×10^{-4}	11.95	0.972	
As-grown CNTs (27 °C)	1.12×10^{-3}	12.13	0.982	
As-grown CNTs (47 °C)	1.05×10^{-3}	12.31	0.924	
Modified CNTs (7 °C)	1.39×10^{-3}	11.32	0.988	
Temkin constants	B_1	K_t (l/mol)	R^2	
As-grown CNTs (7 °C)	13.53	1.33	0.946	
As-grown CNTs (27 °C)	13.33	1.15	0.990	
As-grown CNTs (47 °C)	11.05	1.01	0.931	
Modified CNTs (7 °C)	16.41	1.12	0.986	

($R^2 = 0.977$). Although no certain criterion that is related to the ΔH^0 values define adsorption, the heats of adsorption between 20.9 and 418.4 kJ/mol, which are the heats of chemical reactions, are commonly assumed to be similar to those associated with chemisorption [47]. The value of ΔH^0 suggests that the adsorption of BPA onto as-grown CNTs may proceed by physisorption. The negative ΔH^0 value reveals that the adsorption of BPA onto as-grown CNTs is exothermic, which fact is supported by the decline in the adsorption of BPA with an increase in temperature. Moreover, the positive ΔS^0 indicated that the number of degrees of freedom at the solid–liquid interface increased with the adsorption of BPA onto as-grown CNTs. Based on the equation $\Delta G^0 = \Delta H^0 - T\Delta S^0$, all values of ΔG^0 in this work were negative. Since ΔG^0 is negative and accompanied by positive ΔS^0, the adsorption is spontaneous with high affinity for BPA. Zeng et al. [48] also indicated that the adsorption of BPA on sediments is an exothermic reaction ($\Delta H^0 = -5.735$ kJ/mol) and could be categorized as a physical adsorption.
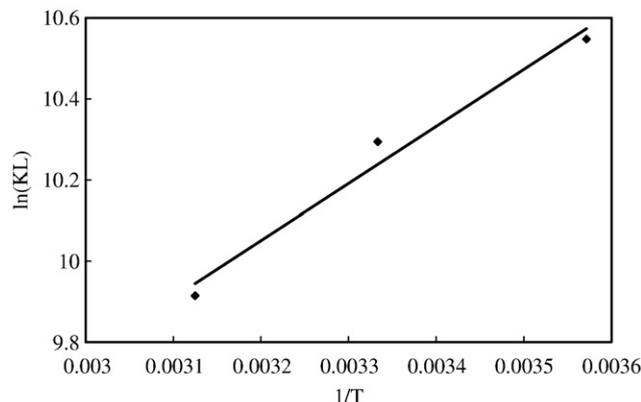

Fig. 6. Adsorption isotherms of BPA (a) Langmuir plots; (b) Freundlich plots; (c) D–R plots and (d) Temkin plots (CNTs dose = 0.125 g/l, pH = 6 and reaction time = 24 h).

Fig. 7. Van't Hoff plot for the adsorption of BPA onto as-grown CNTs.

4. Summary

This work examined the adsorption potential of as-grown and modified CNTs for removing BPA. The specific surface areas of as-grown and modified CNTs were measured as 78.2 and 94.8 m^2/g, respectively, suggesting that the modification of as-grown CNTs using $SOCl_2/NH_4OH$ under microwave irradiation is effective. The FTIR results indicated that some hydrophilic amine groups were generated in the surface of modified CNTs. The kinetic analyses suggested that the adsorption of BPA onto CNTs involved intraparticle diffusion, but that this process was not the only rate-controlling step. The adsorption capacity of BPA on the surface of CNTs fluctuates very little over the pH range 3–9. The maximum adsorption capacity of as-grown CNTs at 7 °C, 27 °C and 47 °C was 60.98, 59.17 and 53.48 mg/g, respectively, and that of modified CNTs at 7 °C was 69.93 mg/g. The mean free energy of adsorption was calculated to be 11.32–12.31 kJ/mol; hence, this investigation suggested that the adsorption mechanism of BPA on CNTs could be though a surface reaction.

Acknowledgements

References

[1] C.A. Staples, P.B. Dom, G.M. Klecka, S.T. Oblook, L.R. Harris, Chemosphere 36 (1998) 2149–2173.
[2] B.P. Dorn, C.S. Chou, J.J. Gentempo, Chemosphere 16 (1987) 1501–1507.
[3] J.H. Kang, F. Kondo, Chemosphere 49 (2002) 493–498.
[4] J.H. Kang, F. Kondo, Chemosphere 60 (2005) 1288–1292.
[5] M. Sciban, M. Klasnja, B. Skrbic, Desalination 229 (2008) 170–180.
[6] B.H. Hameed, L.H. Chin, S. Rengaraj, Desalination 225 (2008) 185–198.
[7] A. Al-Sarawy, I.G. Rashed, M.A. Hanna, F.K.M. Wali, Desalination 186 (2005) 129–153.
[8] C.Y. Kuo, J. Hazard. Mater. 152 (2008) 949–954.
[9] C.S. Lu, F.S. Su, Sep. Purif. Technol. 58 (2007) 113–121.
[10] C.S. Lu, Y.L. Chung, K.F. Chang, Water Res. 39 (2005) 1183–1189.
[11] X. Peng, Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian, Z. Jia, Chem. Phys. Lett. 376 (2003) 154–158.
[12] Y.H. Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu, Carbon 41 (2003) 1057–1062.
[13] A. Stafiej, K. Pyrzynska, Sep. Purif. Technol. 58 (2007) 49–52.
[14] A.H. El-Sheikh, Talanta 75 (2008) 127–134.
[15] C.S. Lu, H.S. Chiu, Chem. Eng. Sci. 61 (2006) 1138–1145.
[16] Y.H. Li, Y. Zhu, Y. Zhao, D. Wu, Z. Luan, Diamond Relat. Mater. 15 (2006) 90–94.
[17] H.J. Wang, A.L. Zhou, F. Peng, H. Yu, L.F. Chen, Mater. Sci. Eng. A 466 (2007) 201–206.
[18] M.I. Kandah, J.L. Meunier, J. Hazard. Mater. 146 (2007) 283–288.
[19] C.H. Wu, J. Colloid, Interface Sci. 311 (2007) 338–346.
[20] C.Y. Kuo, Desalination (2008)(submitted).
[21] J.W. Shim, S.J. Park, S.K. Syr, Carbon 39 (2001) 1635–1642.
[22] C.S. Lu, Y.L. Chung, K.F. Chang, J. Hazard. Mater. 138 (2006) 304–310.
[23] C.J.M. Chin, L.C. Shih, H.J. Tsai, T.K. Liu, Carbon 45 (2007) 1254–1260.
[24] Q. Liao, J. Sun, L. Gao, Colloids Surfaces A 312 (2008) 160–165.
[25] A.R. Harutyunyan, B.K. Pradhan, J. Chang, G. Chen, P.C. Eklund, Carbon 106 (2002) 8671–8675.
[26] F. Ko, C. Lee, C. Ko, T. Chu, Carbon 43 (2005) 727–733.
[27] M. Breza, Chem. Phys. 330 (2006) 224–230.
[28] M. Breza, J. Mol. Struct. 767 (2006) 159–163.
[29] C. Yang, X. Hu, D. Wang, C. Dai, L. Zhang, H. Jin, S. Agathopoulos, J. Power, Sources 160 (2006) 187–193.
[30] W.M. Davis, C.L. Erickson, C.T. Johnston, J.J. Defino, J.E. Porter, Chemosphere 38 (1999) 2913–2928.
[31] X. Xie, L. Gao, J. Sun, Colloids Surfaces A 308 (2007) 54–59.
[32] S.J. Kim, C.K. Lee, Y.M. Lee, I.Y. Kim, React. Funct. Polym. 55 (2003) 291–298.
[33] D. Xie, J.G. Park, M. Faddah, J. Zhao, H. Khanijoun, J. Biomat. Appl. 21 (2006) 147–165.
[34] Z. Wu, Y. Xu, X. Zhang, G. Shen, R. Yu, 2007Talanta 72 (2007) 1336–1341.
[35] A. Misra, P.K. Tyagi, M.K. Singh, D.S. Misra, Diamond Related Mater. 15 (2006) 385–388.
[36] K. Tomihata, Y. Ikada, Biomaterials 18 (1997) 189–195.
[37] B.N. Khare, P. Wilhite, R.C. Quinn, B. Chen, R.H. Schingler, B. Tran, H. Imanaka, C.R. So, C.W. Bauschlicher, M. Meyyappan, J. Phys, Chem. B 108 (2004) 8166–8172.
[38] S. Lagergren, K. Sven, Vetenskapsakad. Handl., Band 24 (1898) 1–39.
[39] G. Blanchard, M. Maunaye, G. Martin, Water Res. 18 (1984) 1501–1507.
[40] W.J. Weber Jr., J.C. Morris, J. Sanit, Eng. Div. ASCE 89 (1963) 31–59.
[41] E. Guibal, P. McCarrick, J.M. Tobin, Sep. Sci. Technol. 38 (2003) 3049–3073.
[42] A. Ozcan, A.S. Ozcan, J. Hazard. Mater. 125 (2005) 252–259.
[43] E. Tutem, R. Apak, C.F. Unal, Water Res. 32 (1998) 2315–2324.
[44] Y.S. Ho, G. McKay, Chem. Eng. J. 70 (1998) 115–124.
[45] A.S. Ozcan, B. Erdem, A. Ozcan, J. Colloid Interface Sci. 280 (2004) 44–54.
[46] A. Kilislioglu, B. Bilgin, Appl. Radiat. Isotopes 58 (2003) 155–160.
[47] N. Unlu, M. Ersoz, J. Hazard. Mater. 136 (2006) 272–280.
[48] G. Zeng, C. Zhang, G. Huang, J. Yu, Q. Wang, J. Li, B. Xi, H. Liu, Chemosphere 65 (2006) 1490–1499.