Adsorption of chlorophenols from aqueous solutions by pristine and surface functionalized single-walled carbon nanotubes

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ABSTRACT

The adsorption of six kinds of chlorophenols on pristine, hydroxylated and carboxylated single-walled carbon nanotubes (SWCNTs) has been investigated. Pseudo-first order and pseudo-second order models were used to describe the kinetic data. All adsorption isotherms were well fitted with Langmuir, Freundlich and Polanyi–Manes models, due to surface adsorption dominating the adsorption process. The close linear relationship between $\log K_{ow}$ and $\log K_d$ suggested that hydrophobicity played an important role in the adsorption. The SWCNTs' adsorption capacity for chlorophenols was weakened by addition of oxygen-containing functional groups on the surface, due to the loss of specific surface area, the increase of hydrophilicity and the reduction of π–π interaction. The best adsorption capacity of pristine SWCNTs, SWCNT-OH and SWCNT-COOH for six chlorophenols varied from 19 to 84 mg/g, from 19 to 65 mg/g and from 17 to 65 mg/g, respectively. The effect of pH on the adsorption of 2,6-dichlorophenol (2,6-DCP), was also studied. When pH is over the pK_a of 2,6-dichlorophenol (2,6-DCP), its removal dropped sharply. When ionic strength increased (NaCl or KCl concentration from 0 to 0.02 mmol/L), the adsorption capacity of 2,6-DCP on pristine SWCNTs decreased slightly. The comparison of chlorophenols adsorption by SWCNTs, MWCNTs and PAC was made, indicating that the adsorption rate of CNTs was much faster than that of PAC. The results provide useful information about the feasibility of SWCNTs as an adsorbent to remove chlorophenols from aqueous solutions.

Introduction

Chlorophenols are widely used as intermediates to produce pesticides, dyes and biocides (Colella et al., 1998; Dominguez-Vargas et al., 2009; Morenocastilla et al., 1995). The presence of chlorophenols in industrial effluents is of increasing environmental concern due to their toxicity and carcinogenicity (Okolo et al., 2000). Chlorophenols have been regulated as priority pollutants by US Environmental Protection Agency (Adam and Al-Dujaili, 2013). The disinfection of drinking water with chlorine may also produce chlorophenols in case the water resource is contaminated by phenol (Ahmaruzzaman, 2008). The existence of chlorophenols in drinking water causes unpleasant taste and odor even at concentration as low as 0.1 mg/L (Suffet et al., 1999).

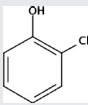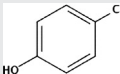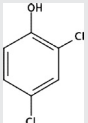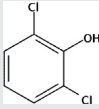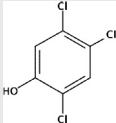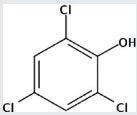* *Corresponding author*. E-mail: chen_water@tsinghua.edu.cn (Chao Chen).

Adsorption is a widely used method to remove chlorophenols from wastewater (Kuleyin, 2007). Different adsorbents, such as powdered activated carbon (PAC), zeolite and clay, have been developed and their efficiency has been extensively studied (Ahmaruzzaman, 2008; Mihoc et al., 2014; Morenocastilla et al., 1995). Carbon nanotubes (CNTs), as a new kind of adsorbent, have been proved to be very efficient in removing many organic pollutants from water (Chen et al., 2007; Iijima, 1991; Liu et al., 2013; Machado et al., 2011; Pyrzynska et al., 2007). They have large specific surface area and the ability of π–π electron coupling interaction with aromatic compounds (Ji et al., 2009; Pan and Xing, 2008; Shi et al., 2010). These characteristics make the application of CNTs in water treatment highly potential. To improve the adsorption capacity, functionalization of CNTs has attracted increasing interest (Das et al., 2014; Lu et al., 2005; Ma et al., 2011). Theoretically, the addition of oxygen-containing functional groups on the surface of CNTs can reduce the aggregation of CNT bundles, thus the available adsorption sites will increase (Pan and Xing, 2008). These functional groups also make the adsorption of polar contaminants more favorable (Liu et al., 2013). However, recent studies indicate that oxidation will depress the adsorption of some organic compounds (Cho et al., 2008; Sheng et al., 2010; Yu et al., 2014; Zhang et al., 2009).

Recently, most adsorption studies have focused on multi-walled carbon nanotubes (MWCNTs), due to their cheaper price than single-walled carbon nanotubes (SWCNTs) (Apul and Karanfil, 2015). However, SWCNTs generally have higher adsorption capacity than MWCNTs, due to their larger specific surface area (SSA) and smaller diameter (Apul and Karanfil, 2015; Pan and Xing, 2008). For example, Chen et al. (2011) found that SWCNTs have higher adsorption capacity for perfluorooctane sulfonate than MWCNTs, which is consistent with their SSA. Kim et al. (2014) found that SWCNTs have stronger ability to adsorb lincomycin, sulfamethoxazole and iopromide than MWCNTs and activated carbon. Liao et al. (2008) also found that the adsorption capacity of MWCNTs for chlorophenols was very low. In addition, no information about adsorption of chlorophenols on SWCNTs has been found, as far as the authors know. Considering these facts, the ability of SWCNTs to remove chlorophenols from aqueous solutions is worth investigating.

In the present work, we investigated the adsorption of chlorophenols on pristine and functionalized SWCNTs (hydroxylated SWCNT (SWCNT-OH) and carboxylated SWCNT (SWCNT-COOH)). The impact of surface functionalization on the adsorption of chlorophenols was analyzed. Six kinds of chlorophenols (2-CP, 4-CP, 2,4-DCP, 2,6-DCP, 2,4,5-TCP and 2,4,6-TCP) were selected as adsorbates for the adsorption experiment. Three commonly used adsorption isotherm models (Langmuir, Freundlich and Polanyi–Manes) were applied to fit the experimental data. The kinetic study of chlorophenols on pristine SWCNTs was performed and the

Table 1 – Selected properties of chlorophenols [a].

Chlorophenols	Structure	MV [b] (cm^3/mol)	C_s (g/L)	LogK_{ow}	pK_a
2-CP		99.8	2.40	2.220	8.50
4-CP		99.8	2.10	2.418	9.47
2,4-DCP		111.7	0.47	3.095	8.05
2,6-DCP		111.7	0.52	2.896	7.02
2,4,5-TCP		123.7	0.085	3.835	7.10
2,4,6-TCP		123.7	0.091	3.769	6.59

[a] All properties of chlorophenols were obtained from SciFinder. https://scifinder.cas.org.
[b] MV: molar volume.

results were analyzed with conventional theoretical methods. The effects of pH and ionic strength on the adsorption behavior of chlorophenols were studied to reveal the impact of environmental conditions. The comparison of chlorophenol adsorption by SWCNTs, MWCNTs and PAC was also made to evaluate the adsorption ability of SWCNTs. Our work may provide useful information for further research and practical applications of SWCNTs in the removal of chlorophenols from wastewater.

1. Materials and methods

1.1. Materials

2-Chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), and 2,4,6-trichlorophenol (2,4,6-TCP) were purchased from Sigma Aldrich. They all had purity above 98%. The selected properties of chlorophenols are listed in Table 1. Pristine SWCNT, SWCNT-OH and SWCNT-COOH were supplied by Chengdu Organic Chemicals Co., China. Their basic structural characteristics are listed in Table 2. Stock solutions were prepared by dissolving specific amount of chlorophenols in ultrapure water produced by Milli-Q Academic water purification system. They were diluted to get desirable concentrations in experiments. NaCl and KCl (Sigma Aldrich, >99.5%) were used to adjust ionic strength.

1.2. Adsorption experiments

A batch adsorption technique was conducted at 25 ± 3 °C to obtain adsorption isotherms. In each adsorption experiment, stock solutions of chlorophenols were diluted to 2 mg/L with ultrapure water in a series of 500 mL glass flasks. SWCNTs with mass ranging from 8 to 22 mg were put in each flask to contact with sample solutions. The flasks were then shaken in a self-made rotary shaker for 2 hr to reach adsorption equilibrium. The adsorption time was determined by our kinetic studies. After equilibration, the suspensions were filtered through a 0.45-μm filter membrane to remove the SWCNTs for further sample analysis. For ionic strength experiments, the adsorption isotherms were obtained in the same way except for adding NaCl or KCl in the solution to change the ionic strength.

To investigate the effects of pH on chlorophenols adsorption, 10 mg SWCNTs were placed in a 500 mL glass flask to contact with 2,6-DCP solution for 2 hr under different pH values. The removal rates of 2,6-DCP were measured by comparing the initial and final carbon concentrations. 0.1 mol/L NaOH and HCl were used to adjust the pH values of the sample solutions.

Kinetic experiments were conducted by using 500 mL glass flasks with 10 mg SWCNTs and 500 mL sample solutions of chlorophenols. The final concentrations of chlorophenols were measured at regular time intervals. The initial concentrations of chlorophenols were measured at the beginning of experiments.

The pH drift method (Rivera-Utrilla et al., 2001) was carried out to determine the pH_{pzc} (point of zero charge) of pristine SWCNTs. Several 500 mL flasks were filled with 0.01 mol/L NaCl solution. The pH was adjusted to a value between 4 and 10 by addition of 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. 10 mg pristine SWCNTs were added into the solution and after 4 hr the final pH was measured and plotted against the initial pH. The pH where the curve crossed the line $pH_{initial} = pH_{final}$ was regarded as the pH_{pzc}.

1.3. Chemical analysis methods

The concentrations of chlorophenols were measured by a UV–Vis detector (UV-2700, Shimadzu, Japan). The pH values of solutions were measured by a pH meter (PB-21, Sartorius, Germany). The carbon concentrations of 2,6-DCP were measured by a total organic carbon analyzer (TOC-V$_{CPH}$, Shimadzu, Japan).

1.4. Data analysis

The amount of chlorophenols adsorbed on SWCNTs was calculated by using the following Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, q_e (mg/g) is the amount of chlorophenols adsorbed on SWCNTs, C_0 (mg/L) is the initial concentration of chlorophenols, C_e (mg/L) is the equilibrium concentration of chlorophenols, m (g) is the adsorbent mass, and V (L) is the volume of sample solution.

The pseudo-first order model (Eq. (2)) and pseudo-second order model (Eq. (3)) were used to describe the adsorption kinetic data of chlorophenols:

$$q_t = q_e(1 - e^{-K_1 t}) \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where, q_e (mg/g) and q_t (mg/g) are the adsorbed amounts of chlorophenols at adsorption equilibrium and at time t (hr), respectively; K_1 (hr^{-1}) and K_2 (g/(mg·hr)) are the adsorption rate constants for the two kinetic models, respectively.

Table 2 – Selected properties of three different kinds of SWCNTs.					
Adsorbent	Diameter [a] (nm)	Length [a] (μm)	BET surface area [b] (m^2/g)	Purity [a] (%)	O% [a] (wt.%)
SWCNT	1–2	5–30	625	>90	/
SWCNT-OH	1–2	5–30	526	>90	3.96
SWCNT-COOH	1–2	5–30	552	>90	2.73

SWCNTs: single-walled carbon nanotubes.
[a] Property data were offered by the producer.
[b] BET surface area was measured by the Analytical Center of Tsinghua University using TriStar 3020 II.
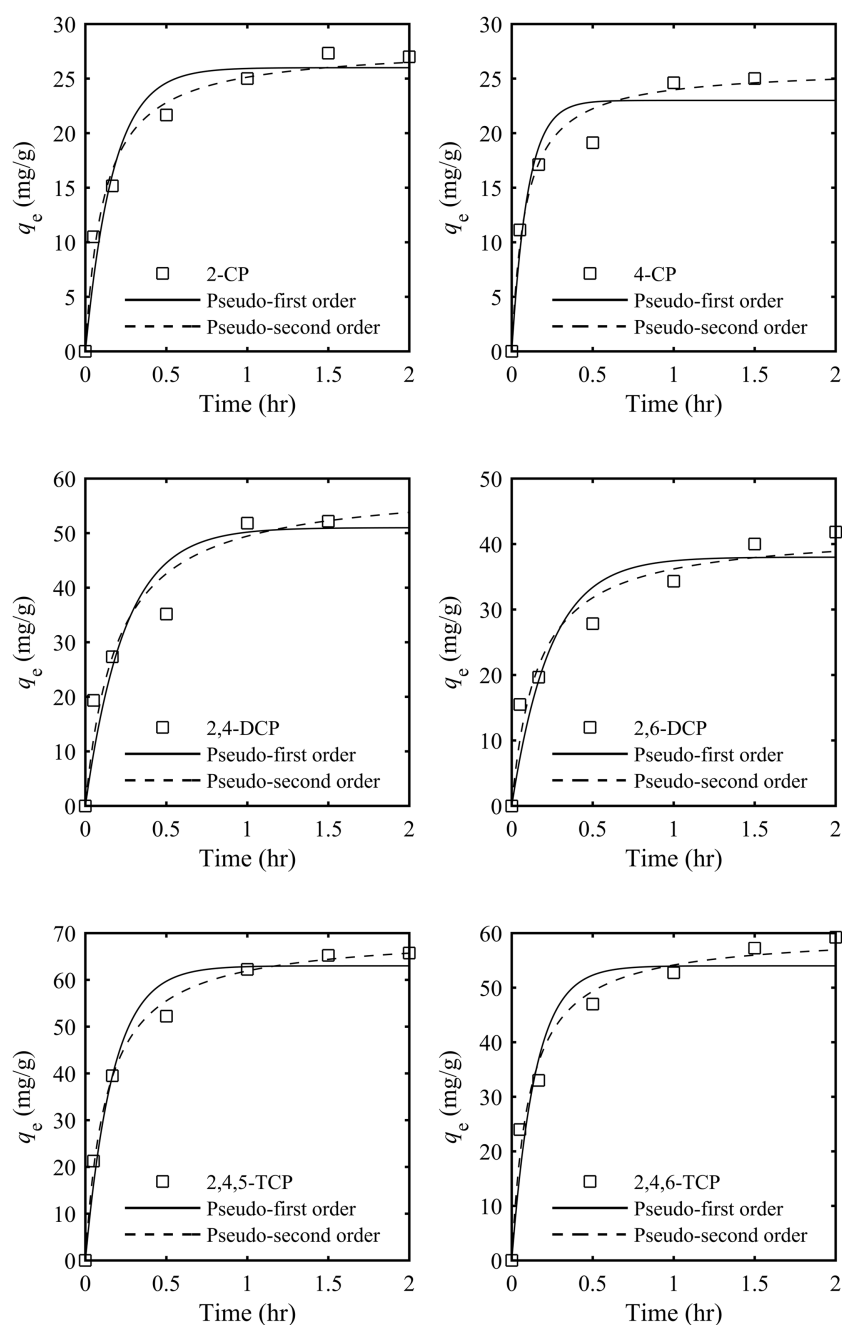
Fig. 1 – Kinetic adsorption curves for six kinds of chlorophenols.

The Langmuir equation (Eq. (4)), Freundlich equation (Eq. (5)), and Polanyi–Manes (PM) equation (Eq. (6)) were applied to fit the adsorption isotherms data. These three models are widely used to fit the adsorption isotherm data of different adsorbates on SWCNTs (Apul et al., 2013; Kim et al., 2014; Yang et al., 2006; Zhou et al., 2013). The Langmuir model is suitable for monolayer adsorption and the Freundlich model is commonly applied to heterogeneous adsorption (Jaroniec, 1975; Langmuir, 1918). The PM model has been reported to fit the aqueous adsorption isotherms well (Yang and Xing, 2010).

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \tag{4}$$

$$q_e = K_F C_e{}^n \tag{5}$$

$$\log q_e = \log Q + a \left(\frac{\varepsilon_{sw}}{V_s} \right)^b \tag{6}$$

$$\varepsilon_{sw} = RT \ln \left(\frac{C_s}{C_e} \right) \tag{7}$$

where, q_m (mg/g) is the maximum adsorption amount, K_L (L/mg) is the adsorption equilibrium constant for Langmuir equation; K_F (mg^{1-n} g^{-1} L^n) is the adsorption affinity coefficient for Freundlich equation, and n indicates the nonlinearity of isotherms; Q (mg/g)

Table 3 – Kinetic parameters of pseudo-first order and pseudo-second order model for six kinds of chlorophenols.

Adsorbates	C_0 (mg/L)	Pseudo-first order			Pseudo-second order		
		q_e (mg/g)	K_1 (hr^{-1})	R^2	q_e (mg/g)	K_2 (g/(mg·hr))	R^2
2-CP	1.7	26	5.85	0.954	28	0.31	0.985
4-CP	1.7	23	10.07	0.939	26	0.45	0.972
2,4-DCP	1.7	51	4.13	0.904	59	0.09	0.944
2,6-DCP	1.7	38	4.22	0.905	42	0.15	0.951
2,4,5-TCP	1.7	63	5.90	0.975	70	0.11	0.996
2,4,6-TCP	1.7	54	6.91	0.946	60	0.15	0.982

is the maximum adsorption capacity for PM equation, ε_{sw} (kJ/mol) is effective adsorption potential, V_s (cm^3/mol) is molar volume of adsorbates, a ((cm^3)$^{b+1}$/(kg·J^b)) and b are fitting parameters, R (8.314 × 10^{-3}kJ/(mol·K)) is universal gas constant, T (K) is absolute temperature, C_s (mg/L) is the solubility of adsorbates.

Single point adsorption coefficient K_d (L/g) (Eq. (8)) was calculated based on the fitting results of Langmuir model at $C_e = 0.002C_s$.

$$K_d = \frac{q_e}{C_e}. \qquad (8)$$

2. Results and discussion

2.1. Kinetic studies

Fig. 1 shows that adsorption amount increased very quickly in the first 30 min and adsorption equilibrium was reached within 2 hr. The time needed to reach adsorption equilibrium for chlorophenols onto SWCNTs was much shorter than onto activated carbons (Colella et al., 1998; Varghese et al., 2004). The disparities of adsorption equilibrium time may be attributed to the different adsorption mechanisms between these two adsorbents. Intraparticle diffusion dominates the adsorption process of activated carbons, while SWCNTs adsorb organic compounds mainly by external mass transfer (Zhang et al., 2012).

The kinetic parameters of pseudo-first and pseudo-second order models are listed in Table 3. The pseudo-second order model fitted the kinetic data much better than pseudo-first order model with higher R^2 values. Ho and McKay (1999) reported that pseudo-second order model achieved highest correlation coefficients when applied to sorption process, which is consistent with our results. The K_1 and K_2 values of

chlorophenols with one chlorine group are much greater than those of the other chlorophenols. The higher solubility and smaller molecular volume of one-chlorine-group chlorophenols may be the reasons for the observed difference in K_1 and K_2 values. These properties facilitate the diffusion of molecules in water thus accelerate the adsorption process.

2.2. Adsorption isotherms

The fitting parameters of three different models are listed in Table 4. All of the three models fitted the isotherms well. There are three kinds of adsorption sites present in the closed-ended SWCNT bundles: grooves, external surface and interstitial channels (Ren et al., 2011). The interstitial channels of SWCNT bundles are too small for the adsorbate molecules to fit into, thus grooves and external surface area are the major adsorption sites (Pan et al., 2008). As a result, surface adsorption dominates the adsorption process. Since Langmuir model and PM model were both derived from surface adsorption (Langmuir, 1918; Yang and Xing, 2010), and Freundlich model is a special form of PM model (Yang et al., 2006), it is reasonable that our adsorption data were well fitted by these three models.

In other reports (Yang et al., 2006; Zhou et al., 2013), Langmuir model was not suitable to fit the isotherms. In our study, we considered the low concentration during the adsorption process in our experiment and the homogeneity of SWCNTs to be the main reasons for this conflict. The Langmuir model is based on these assumptions (Langmuir, 1918): the adsorption is caused by forces typically chemical; the adsorbed film is monolayer; all adsorption sites are energetically equivalent; no interactions exist between adsorbate molecules. Low concentration of adsorbate can reduce the interactions between adsorbate molecules. In our study, the concentrations of chlorophenols were kept below 0.015 mmol/L, and the SWCNTs used were highly pure. Thus

Table 4 – Fitting parameters of three different models for six kinds of cholorophenols and single point adsorption coefficient.

Chlorophenols	Freundlich			Langmuir			Polanyi–Manes				LogK_d
	K_F (mg^{1-n} g^{-1} L^n)	n	R^2	q_m (mg/g)	K_L (L/mg)	R^2	a	b	Q (mg/g)	R^2	
2-CP	24.95	0.3995	0.976	24.9	5.916	0.983	−422.70	4.829	31.62	0.987	2.220
4-CP	24.92	0.3684	0.958	29.0	4.096	0.974	−1829.00	5.760	31.62	0.979	2.418
2,4-DCP	54.85	0.3349	0.946	59.9	6.263	0.966	−3763.00	5.379	63.10	0.959	3.095
2,6-DCP	45.61	0.4508	0.994	55.3	3.198	0.989	−39.33	2.260	125.89	0.995	2.896
2,4,5-TCP	102.0	0.4187	0.991	107.7	4.763	0.988	−99.22	2.524	158.49	0.994	3.769
2,4,6-TCP	122.9	0.6507	0.992	166.8	1.765	0.992	−139.50	2.482	251.19	0.993	3.835

the assumptions of Langmuir model were well met under our experiment conditions.

The Freundlich model fitted the isotherms well with values of nonlinearity index n varying from 0.3349 to 0.6507. With n value approaching 1, the nonlinearity of the isotherm decreases. There is no clear correlation between the properties of chlorophenols and n values. This indicates that nonlinearity of Freundlich model is decided by multiple factors. Two factors are reported to have influence on the nonlinearity: the molar volume of adsorbate and electrostatic repulsion between the adsorbed and dissolved adsorbate ions (Chen et al., 2011; Sun et al., 2012). Smaller molar volume facilitates the adsorbate molecules getting into the grooves and interstitial regions which contains more heterogeneous sites (Sun et al., 2012). As a result, the molar volume is negatively correlated with nonlinearity of isotherms. The electrostatic repulsion will also increase the nonlinearity. As shown in Table 1, chlorophenols with larger volume size dissociate more easily. With the two factors acting together, the nonlinearity has no clear tendency.

2.3. Comparison of adsorption capacity among different chlorophenols

The adsorption capacity of different chlorophenols onto pristine SWCNTs varies with the number of chlorine groups. As shown in Fig. 2, chlorophenols with more chlorine groups have higher adsorption capacity on SWCNTs. This is also reflected by the parameters of q_m and Q in Table 4. We suggest that hydrophobicity is the main reason for the difference in adsorption capacity. A linear relationship between $\log K_{ow}$ and $\log K_d$ is shown in Fig. 3, which confirms that adsorption capacity is positively correlated with hydrophobicity.

The linear relationship indicates that hydrophobicity plays a very important role in the adsorption of chlorophenols on SWCNTs. However, other reports (Chen et al., 2007; Pan and Xing, 2008; Wang et al., 2010b) found that adsorption capacity of
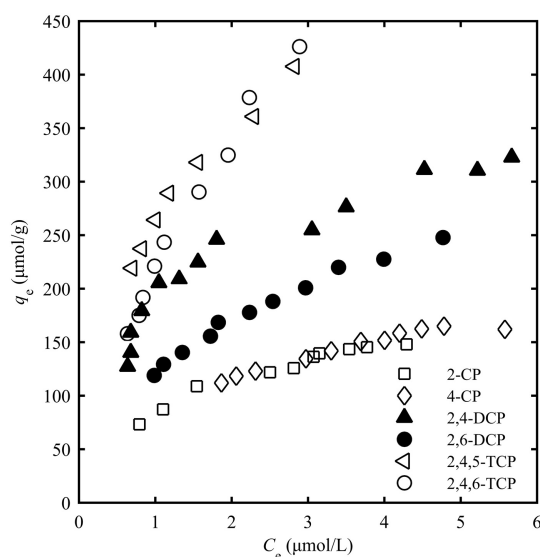
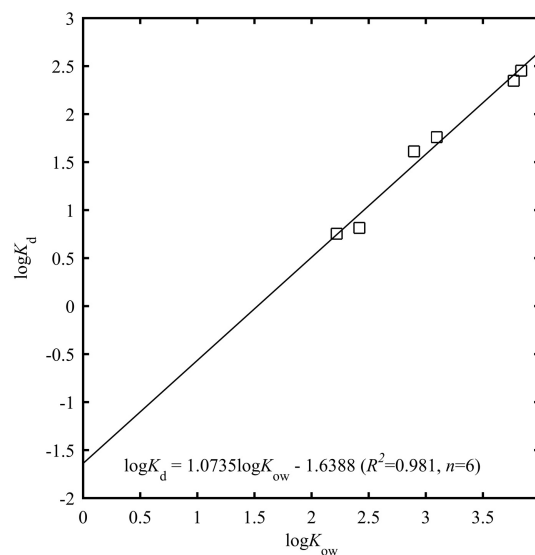$$\log K_d = 1.0735 \log K_{ow} - 1.6388 \ (R^2 = 0.981, \ n=6)$$

Fig. 3 – The relationship between $\log K_{ow}$ and $\log K_d$.

some aromatic compounds on pristine SWCNTs correlates poorly with hydrophobicity, which suggested that non-hydrophobic interactions contribute greatly to adsorption. Comparing our result with those reports, we contend that hydrophobic interaction dominates the adsorption process of chlorophenols and other non-hydrophobic interactions are relatively weak.

In Fig. 2, the disparity between adsorption capacities of 2,4-DCP and 2,6-DCP is obvious. Since their $\log K_{ow}$ values are close to each other, it should be non-hydrophobic interactions that attribute to the difference. The benzene ring of chlorophenols can form π–π electron–donor–acceptor (EDA) interaction with the surface of SWCNTs (Apul and Karanfil, 2015; Lin and Xing, 2008; Wang et al., 2010a). The strong electronegativity of Cl atom decreases the electron density of benzene ring and makes chlorophenol a π–electron acceptor. The π–π EDA interaction will be enhanced by the decrease in electron density of benzene ring. For chlorophenols, the electron density of benzene will be affected by the position of chlorine groups. As shown in Figs. 4, 2,4-DCP has a more positively charged benzene ring than 2,6-DCP. As a result, the electron density of 2,4-DCP is lower than 2,6-DCP and the π–π EDA interaction between 2,4-DCP and SWCNTs is stronger. The

Fig. 2 – Adsorption isotherms for six kinds of chlorophenols on pristine SWCNTs. SWCNTs: single-walled carbon nanotubes.
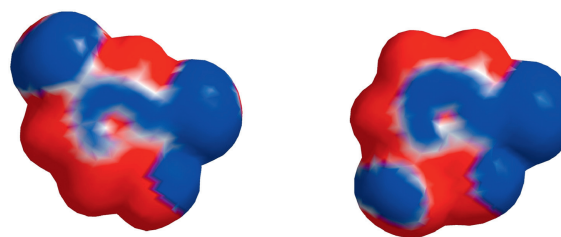
Fig. 4 – Total charge density of 2,4-DCP (left) and 2,6-DCP (right). The red color indicates area positively charged and the blue color represents area negatively charged. Results were calculated by ChemBioOffice 2010 using Extended Huckel method.

higher adsorption affinity between 2,4-DCP and SWCNTs contributes to the higher adsorption capacity of 2,4-DCP on SWCNTs.

2.4. Comparison of adsorption capacity on different SWCNTs

As a hydrophobic adsorbent, CNTs are easily to aggregate in water due to strong van der Waals interaction along the longitudinal direction of nanotubes (Chen et al., 2004). The purpose of deliberate surface functionalization is to improve the

dispersion of CNTs in water thus increase the available adsorption sites (Zhang et al., 2009). In our experiment, the best adsorption capacity of SWCNTs, SWCNT-OH and SWCNT-COOH for six chlorophenols varied from 19–84 mg/g, 19–65 mg/g and 17–65 mg/g, respectively. Fig. 5 shows that adsorption capacities of chlorophenols on different SWCNTs decrease in the following order: SWCNTs > SWCNT-OH > SWCNT-COOH. This is in accordance with the results of other reports (Cho et al., 2008; Sheng et al., 2010; Yu et al., 2014; Zhang et al., 2009) which found that the
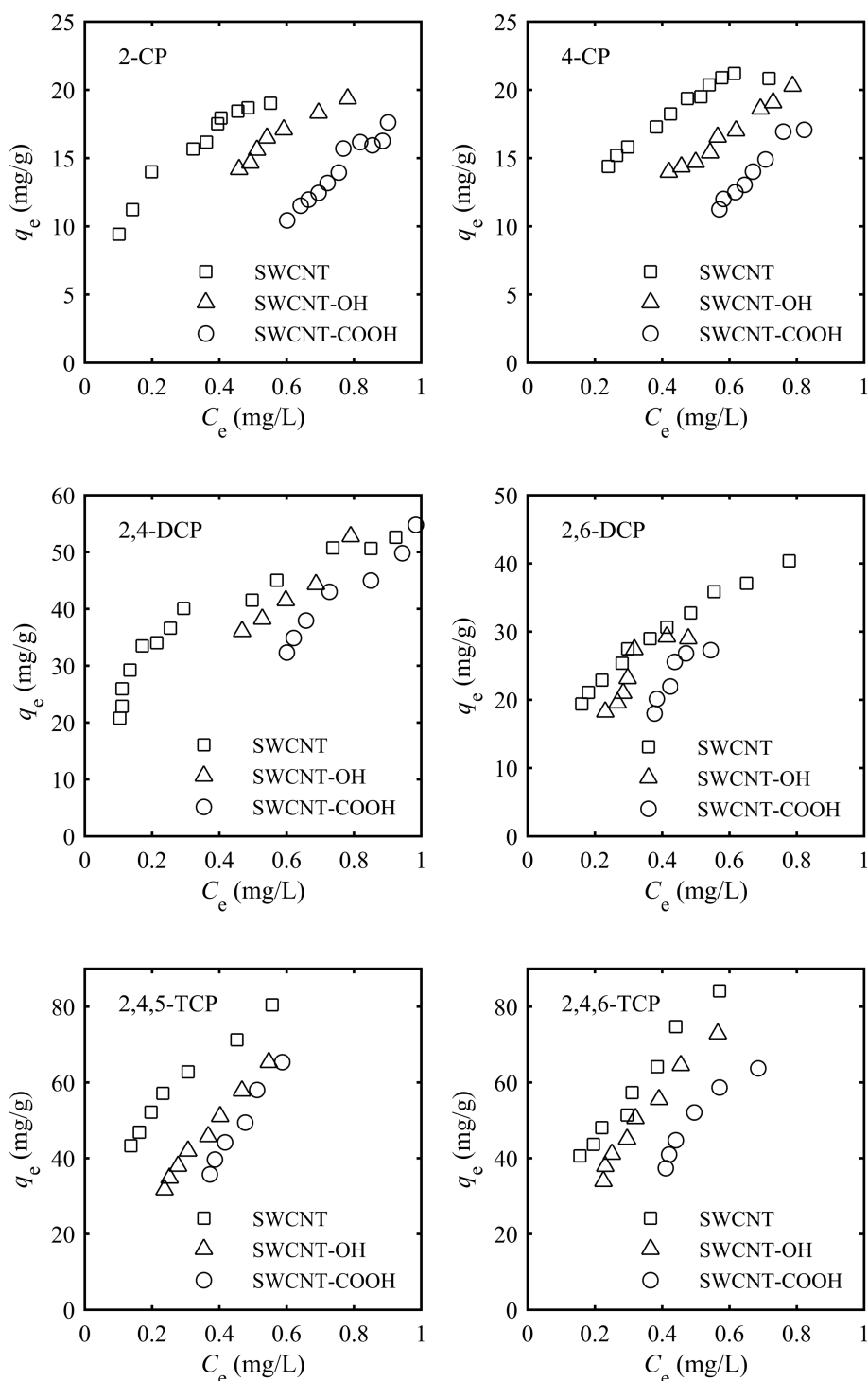
Fig. 5 – Adsorption isotherms of chlorophenols on three kinds of SWCNTs (pristine SWCNTs, SWCNT-OH and SWCNT-COOH).

increase in oxides concentration would decrease the adsorption capacity of CNTs greatly.

Several mechanisms have been proposed to explain this phenomenon. First, the oxygen-containing functional groups will create polar region that facilitates the formation of water clusters, which occupy adsorption sites and inhibit adsorbate molecules from being adsorbed (Cho et al., 2008; Zhang et al., 2009). Second, the specific surface areas of SWCNTs are reduced significantly by oxidation (Zhang et al., 2009). As shown in Table 2, the oxygen-containing groups caused about 10% loss in specific surface area for both SWCNT-OH and SWCNT-COOH. This will reduce the adsorption sites of SWCNTs and in turn depress the adsorption of adsorbate molecules. Third, oxides on the surface of SWCNTs can withdraw electrons from π system of SWCNTs, which decreases the ability of SWCNTs as an electron donor (Sheng et al., 2010). As a result, the π–π EDA interaction is reduced and the adsorption capacity is decreased.

The SWCNT-OH has smaller specific surface area and higher oxides concentration than SWCNT-COOH (Table 2). However, the former one has higher adsorption capacity. We propose that the repulsion between chlorophenol anions and dissociated carboxylic groups is the main reason. To those adsorbates which are not ionizable, oxygen-containing groups may have little impact on the adsorption capacity. Zhang et al. (2009) also reported that adsorption capacities of phenanthrene on SWCNT-OH and SWCNT-COOH were close to each other.

2.5. Effect of pH on the adsorption of 2,6-DCP

For organic acids, the fraction of dissociated (f_d) and nondissociated (f_n) species can be estimated by $f_d = (1 + 10^{pKa-pH})^{-1}$ and $f_n = (1 + 10^{pH-pKa})^{-1}$, respectively (Yang et al., 2008). Fig. 6a shows the distribution of dissociated and nondissociated species of one representative chlorophenol, i.e. 2,6-DCP, as a function of pH. The removal of 2,6-DCP varied with pH as shown in Fig. 6b. The maximum removal of 2,6-DCP occurred at pH 4.8. With the pH increasing from 3.7 to 10.2, the removal decreased from 47.9% to 12.9%. When pH was below the

2,6-DCP's pK_a, the removal varied slightly, indicating that the effect of pH on the adsorption of 2,6-DCP was not very obvious. However, when pH was above the pK_a, the removal decreased sharply. Dissociation of 2,6-DCP at higher pH may be the main reason for the decrease. As shown in Fig. 6a, the dissociated species is dominant in the solution when pH > pK_a. Because chlorophenol anions are hydrophilic, the hydrophobic interaction between SWCNTs and 2,6-DCP molecules will be reduced greatly. As a result, the adsorption of 2,6-DCP is hindered and the removal is decreased.

Electrostatic repulsion between deprotonated chlorophenol and negatively charged SWCNTs' surface is another factor that affects the removal. The pH_{pzc} of pristine SWCNTs was 8.1. When pH > pH_{pzc}, the overall surface of SWCNTs is negatively charged. The adsorption of 2,6-DCP anions will be depressed because of the electrostatic repulsion force. This adds to the reduction of adsorption capacity of 2,6-DCP on SWCNTs. With pH increasing, more sites on the surface of SWCNTs get negatively charged, leading to further decrease in removal.

In our experiment, we observed that the highest removal was not obtained at the lowest pH. This indicates that decrease in pH will not always increase the adsorption capacity of 2,6-DCP. A similar result was reported by Yao et al. (Yao et al., 2011). We propose that interaction between hydronium ions and 2,6-DCP molecules reduces the adsorption capacity of 2,6-DCP on SWCNTs. As pH decreases, more hydronium ions are formed and interact with the benzene ring of 2,6-DCP molecule through cation-π interaction (Ma and Dougherty, 1997). This cation–π interaction will make 2,6-DCP molecules more hydrophilic and hinder the adsorption of 2,6-DCP molecules on the surface of SWCNTs.

2.6. Effect of ionic strength on the adsorption of 2,6-DCP

The effect of ionic strength on the adsorption of one representative chlorophenols, i.e. 2,6-DCP, is shown in Fig. 7. The adsorption amount of 2,6-DCP decreased slightly with the
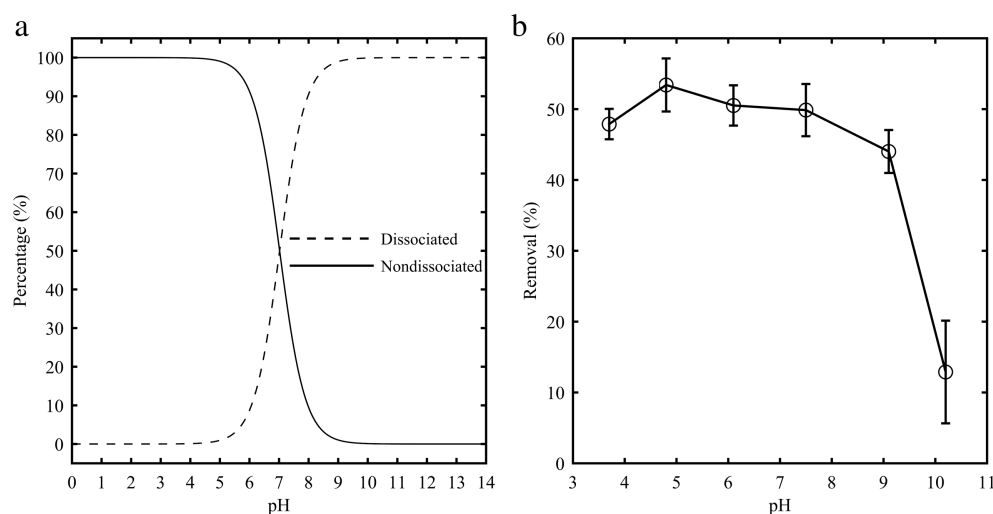

Fig. 6 – (a) Species distribution of 2,6-DCP as a function of pH values. (b) Effects of pH values on the removal of 2,6-DCP by pristine SWCNTs. Conditions: initial concentration of 2,6-DCP was 0.987 mg/L; 10 mg pristine SWCNTs were used as adsorbent; the temperature was fixed at 298 K. Error bars represent the standard deviation of duplicate measurements (n = 3).

NaCl concentration increasing from 0 to 0.03 mmol/L (Fig. 7a). A similar result was reported by Yu et al. (2014). The impact of KCl on the adsorption capacity of 2,6-DCP was negligible (Fig. 7b). Theoretically, NaCl and KCl both have a "salting-out" effect on the adsorption of hydrophobic organic compounds (Zhang et al., 2010). This effect can enhance the hydrophobicity of 2,6-DCP and the effect of NaCl is stronger than that of KCl (Xie et al., 1997). However, the adsorption capacity of 2,6-DCP did not increase with the addition of NaCl or KCl as expected. This implies that some factors other than ionic strength play an important role in the adsorption process.

It could be proposed that cation–π interaction among SWCNTs, cation ions and 2,6-DCP molecules is the main reason for the reduction of adsorption capacity. Because the binding energy of benzene-benzene is much weaker than that of K^+-benzene (Cabarcos et al., 1998), the K^+ ions will interact with the surface of SWCNTs and occupy the adsorption sites instead of 2,6-DCP molecules. The K^+ ions can also interact with the benzene ring of 2,6-DCP molecule. Finally, a complex, as shown in Fig. 8, will form through cation–π interactions. However, this complex is not stable because water molecules compete with 2,6-DCP on interaction with K^+. This competition weakens the adsorption affinity of 2,6-DCP on SWCNTs. The loss of adsorption sites and adsorption affinity will decrease the adsorption capacity of 2,6-DCP on SWCNTs. This mechanism is also suitable for Na^+. The only difference is that the binding energy of Na^+-benzene is weaker than that of K^+-benzene (Kumpf and Dougherty, 1993), which further weakens the adsorption affinity of 2,6-DCP on SWCNTs.

The reduction of 2,6-DCP adsorption amount with addition of NaCl indicates that the effect of cation-π interaction overwhelmed the salting-out effect in the adsorption of 2,6-DCP. The two effects were equivalent to each other with the addition of KCl, which was reflected by the negligible change of 2,6-DCP adsorption capacity. These results indicate that SWCNTs may not be suitable for the removal of chlorophenols from salting wastewater.

2.7. Comparison of chlorophenols adsorption by different adsorbents

The comparison of chlorophenol adsorption by SWCNTs, MWCNTs and PAC were made to further evaluate the
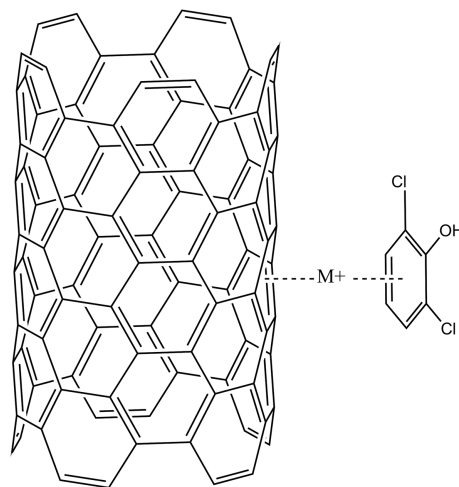

Fig. 8 – A complex of SWCNT-M⁺-2,6-DCP. M⁺ represents K⁺ or Na⁺.

application potential of SWCNTs. To compare the adsorption capabilities of different adsorbents, the K_d values at three different concentrations (0.1, 1 and 10 mg/L) were calculated with data from this study and published reports (Colella et al., 1998; Kragulj et al., 2015; Kuśmierek and Świątkowski, 2014; Strachowski and Bystrzejewski, 2015; Tseng et al., 2010). The K_1 and K_2 values were gathered to compare the adsorption rate of chlorophenols onto different adsorbents.

As shown in Table 5, the K_d values of the three adsorbents decrease in the following order: PAC > SWCNTs > MWCNTs. The K_d values of PAC are 1–3 orders of magnitude higher than those of MWCNTs. The adsorption capacity of MWCNTs is significantly lower than that of the other two adsorbents, largely due to the small SSA of MWCNTs, suggesting that MWCNTs may not be suitable for the removal of chlorophenols. As concentration increases, the K_d values of SWCNTs became more comparable to that of PAC, indicating that the adsorption of chlorophenols on SWCNTs became more favorable at higher concentrations.

The rate constants for MWCNTs and SWCNTs are much higher than those of PAC (Table 5). The rate constants of pseudo-second order model (K_2) for PAC are 1–2 orders of magnitude lower than those of SWCNTs. This indicates that adsorption equilibrium can be achieved much faster by
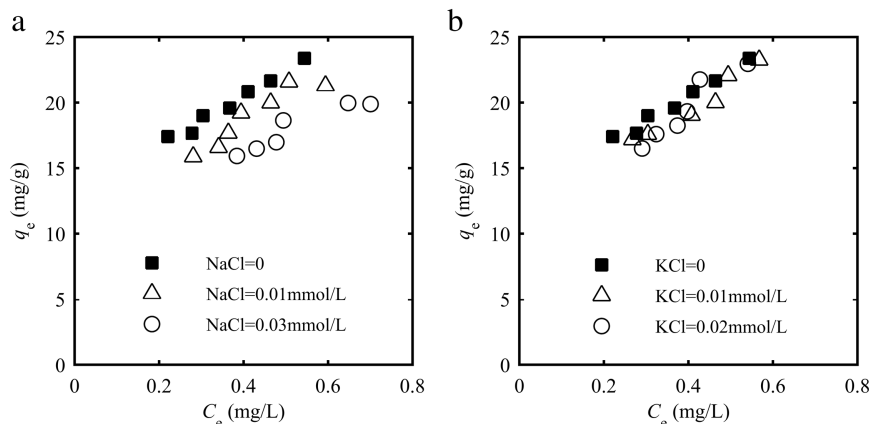

Fig. 7 – Effect of ionic strength on the adsorption of 2,6-DCP: (a) NaCl; (b) KCl.

Table 5 – Comparison of K_d, K_1, and K_2 values for chlorophenols adsorbed onto different adsorbents.

Adsorbates	Adsorbents	K_d (L/g)			K_1 (hr^{-1})	K_2 (g/(mg·hr^{-1}))	Reference
		0.1 mg/L	1 mg/L	10 mg/L			
2-CP	SWCNTs	99.44	24.95	6.25	5.85	0.31	This study
	MWCNTs	0.64	0.63	0.59	NA[a]	>6	Strachowski and Bystrzejewski (2015)
	PAC	1377.32	195.45	27.73	NA[a]	0.016	Strachowski and Bystrzejewski (2015); Colella et al. (1998)
4-CP	SWCNTs	106.70	24.92	5.82	10.07	0.45	This study
	MWCNTs	13.54	3.79	1.06	3.42	0.23	Kuśmierek and Świątkowski (2014)
	PAC	187.47	46.86	11.71	0.96	0.0037	Kuśmierek and Świątkowski (2014)
2,4-DCP	SWCNTs	253.67	54.85	11.85	4.13	0.09	This study
	MWCNTs	52.63	42.00	33.51	NA[a]	NA[a]	Kragulj et al. (2015)
	PAC	1092.27	287.10	75.46	2.46–2.86	0.02–0.036	Tseng et al. (2010)

[a] NA: not available.

SWCNTs than by PAC. The faster kinetic adsorption rate on CNTs may be attributed to the external surface and grooves of CNTs are highly available to adsorbate molecules (Chen et al., 2011), while the adsorption sites of PAC are within the pore structure thus increasing the contact time (Strachowski and Bystrzejewski, 2015).

3. Conclusions

This study investigated the adsorption of six kinds of chlorophenols on three kinds of SWCNTs. The adsorption equilibrium was reached within 2 hr, and the pseudo-second order model well described the adsorption kinetics. All adsorption isotherms of chlorophenols on pristine SWCNTs were fitted well by Langmuir, Freundlich and Polanyi–Manes models. Chlorophenols with more chlorine groups had higher adsorption capacity. The linear relationship between $\log K_{ow}$ and $\log K_d$ was observed, suggesting that hydrophobicity played an important role in the adsorption of chlorophenols. The adsorption capacity of chlorophenols on three kinds of SWCNTs decreased as the following order: SWCNTs > SWCNT-OH > SWCNT-COOH, indicating that oxidation of SWCNTs' surface reduced the adsorption capacity significantly. The adsorption capacity of 2,6-DCP decreased significantly when pH value exceeded the pK$_a$. With the addition of NaCl, reduction in adsorption capacity of 2,6-DCP was observed. However, the effect of KCl was negligible. We proposed that cation-π interaction is another factor which affects the adsorption of 2,6-DCP other than ionic strength. Through the comparison of SWCNTs, MWCNTs and PAC, we found that CNTs adsorbed chlorophenols much faster than PAC. Our work provided useful information about adsorption of chlorophenols on SWCNTs. It also indicated that surface oxidation of SWCNTs and solution environments had significant effects on the adsorption of chlorophenols onto SWCNTS.

Acknowledgments

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