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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).

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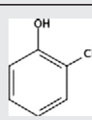
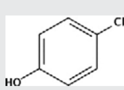
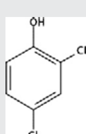
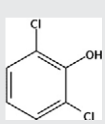
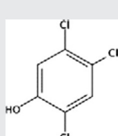
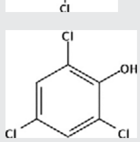
Adsorption is a widely used method to remove chlorophenols from wastewater (Kuleyin, 2007). Different adsorbents, such as powdered activated carbon (PAC), zeolite and clay, have been developed and their efficiency has been extensively studied (Ahmaruzzaman, 2008; Mihoc et al., 2014; Morenocastilla et 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.