



Different effects of surface heterogeneous atoms of porous and non-porous carbonaceous materials on adsorption of 1,1,2,2-tetrachloroethane in aqueous environment



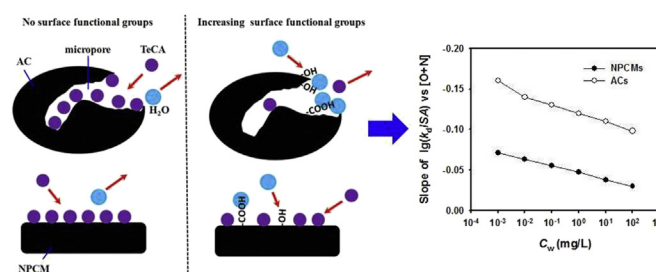
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HIGHLIGHTS

- The increasing surface [O + N] caused a sharper decrease of TeCA adsorption to ACs than NPCMs.
- The water cluster blocked the micropores of ACs and decreased TeCA adsorption dramatically.
- The less effect of water cluster on TeCA adsorption to NPCMs with no micropores.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface heterogeneous atoms of carbonaceous materials (CMs) play an important role in adsorption of organic pollutants. However, little is known about the surface heterogeneous atoms of CMs might generate different effect on adsorption of hydrophobic organic compounds by porous carbonaceous materials — activated carbons (ACs) and non-porous carbonaceous materials (NPCMs). In this study, we observed that the surface oxygen and nitrogen atoms could decrease the adsorption affinity of both ACs and NPCMs for 1,1,2,2-tetrachloroethane (TeCA), but the degree of decreasing effects were very different. The increasing content of surface oxygen and nitrogen ($[O + N]$) caused a sharper decrease in adsorption affinity of ACs (slope of $\lg(k_d/SA)$ vs $[O + N]$: $-0.098 \sim -0.16$) than that of NPCMs (slope of $\lg(k_d/SA)$ vs $[O + N]$: $-0.025 \sim -0.059$) for TeCA. It was due to the water cluster formed by the surface hydrophilic atoms that could block the micropores and generate massive invalid adsorption sites in the micropores of ACs, while the water cluster only occupied the surface adsorption sites of NPCMs. Furthermore, with the increasing concentration of dissolved TeCA, the effect of surface area on adsorption affinity of NPCMs for TeCA kept constant while the effect of $[O + N]$ decreased due to the competitive adsorption between water molecule and TeCA on the surface of NPCMs, meanwhile, both the effects of micropore volume and $[O + N]$ on adsorption affinity of ACs for TeCA were decreased due to the mechanism of micropore volume filling. These findings are valuable for providing a deep insight into the adsorption mechanisms of CMs for TeCA.

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1. Introduction

Carbonaceous materials (CMs) such as activated carbons, carbon nanotubes, and graphenes etc, have received growing research attention in environmental remediation. Owing to their unique physicochemical properties (e.g. high specific surface area, superior hydrophobicity, and porous structure), CMs as superb adsorbents have been widely used in water purification, soil and sediment remediation to sequester organic contaminants and reduce the bioavailability of organic contaminants (Zimmerman et al., 2004; Lohmann et al., 2005; Ji et al., 2009; Petersen et al., 2009; Amstaetter et al., 2012; De La Torre-Roche et al., 2013). Furthermore, multiple adsorption mechanisms, such as hydrophobic driving forces, electrostatic interactions, hydrogen bonding, π - π interactions and micropore volume filling, have been proposed to control adsorption of organic compounds by CMs (Li et al., 2002; Chen et al., 2007, 2008; Yang et al., 2008; Pan and Xing, 2008; Hyung and Kim, 2008).

The adsorption affinity of CMs is closely related to their physicochemical properties. Different types of CMs exhibit very different adsorption affinity to the same organic compound due to their variation in physicochemical properties and morphological structures (Lu and Sorial, 2004; Zhang et al., 2010; Apul et al., 2013; Cai and Larese-Casanova, 2014). There are two very different adsorption mechanisms for activated carbons (ACs) — porous carbonaceous materials (PCMs) and carbon nanotubes (CNTs) — non-porous carbonaceous materials (NPCMs) toward aromatic organic compounds. The adsorption capacity of ACs was controlled by micropore structure and molecular sieving effects, while the adsorption capacity of CNTs depended on their surface area (Zhang et al., 2010). Micropore structure improved the adsorption capacity of ACs mainly via two mechanisms (Li et al., 2002; Karanfil and Dastgheib, 2004): (1) effective adsorption sites on adsorbent surface for adsorbate increased, and (2) adsorption potentials between opposing pore walls begin to overlap once the micropore width was less than about twice the adsorbate diameter. Surface area improved the adsorption capacity of CNTs only depend on the number of the adsorption sites (Zhang et al., 2010).

Except for the micropore structure and surface area, furthermore, the surface heterogeneous atoms also play a very important role in adsorption of organic compounds by CMs (Yang and Xing, 2010; Rivera-Utrilla et al., 2011). The heterogeneous atoms (e.g. oxygen and nitrogen) on the surface of CMs are mainly presented in the forms of carboxyl groups, phenolic hydroxyl groups, lactone groups, amino-groups, nitro groups, and acylamino-groups, etc (Pan and Xing, 2008; Zhang et al., 2011; Yang et al., 2014). And most of these functional groups are polar and hydrophilic (Pan and Xing, 2008; Yang and Xing, 2010; Rivera-Utrilla et al., 2011). With the increasing content of the surface hydrophilic functional groups of CMs, the adsorption of some polar organic compounds such as phenol and aniline on CMs would be enhanced due to the formation of hydrogen bond and electron donor-acceptor (Li et al., 2002; Yang et al., 2008, 2014). However, the adsorption of hydrophobic non-polar organic compounds such as trichloroethene and aromatics on CMs would be inhibited due to the competitive adsorption between the adsorbates and water clusters that were formed by the interaction between the surface hydrophilic functional groups and water molecules (Ahnert et al., 2003; Ania et al., 2007). Adsorption of hydrophobic non-polar organic compounds by activated carbons mainly depends on the micropore volume, while adsorption of hydrophobic non-polar organic compounds by NPCMs mainly depends on the surface area (Li et al., 2002; Zhang et al., 2010). However, it is unclear the effect of the water cluster that formed by the surface hydrophilic functional groups and water molecules on the adsorption of a hydrophobic non-polar organic

compounds by micropore structure and surface area. To date, though several researches have comparatively studied the adsorption capacities and mechanisms of different kinds of CMs (including graphenes, CNTs, and ACs) toward the environmental pollutants (carbamazepine, aromatic organic contaminants, ciprofloxacin, bisphenol, and 2-chlorophenol, etc) from aqueous solution (Zhang et al., 2010; Cai and Larese-Casanova, 2014; Li et al., 2015), the effects of surface heterogeneous atoms of CMs on the adsorption affinity of ACs and NPCMs for a hydrophobic organic pollutant were not compared systematically. Thus, a comprehensive comparison of the effect of surface heterogeneous atoms of CMs on the adsorption affinity of ACs and NPCMs for a hydrophobic organic pollutant is quite necessary for understanding the adsorption mechanisms and selecting the proper adsorbents for certain adsorbates.

TeCA is a kind of common halogenated aliphatic contaminant and usually selected as a target adsorbate due to its carcinogenicity, wide application (used as organic solvent, solubilizer, and synthetic agent, etc), and frequent occurrence in groundwater (Arnold et al., 2002; Mackenzie et al., 2005; Huang et al., 2014). In this study, the effects of surface heterogeneous atoms of CMs on the adsorption affinity of porous carbonaceous materials (ACs) and non-porous carbonaceous materials (NPCMs) for 1,1,2,2-tetrachloroethane (TeCA) were systematically compared by dividing sixteen different types of CMs into porous carbonaceous materials (containing five different types of pristine activated carbons and three different functionalized activated carbons) and non-porous carbonaceous materials (NPCMs) [containing powdery graphite and oxidized graphite, four different functionalized multi-walled nanotubes, graphene oxide (GO) and reduced graphene oxide (rGO)]. Furthermore, different effects of the concentration of dissolved TeCA on adsorption processes of ACs and NPCMs were analyzed. The results of this study will provide a better and thoroughly understanding of the adsorption mechanism of hydrophobic organic compounds by CMs and help to select the proper adsorbents for a certain adsorbate (e.g. TeCA).

2. Methods and materials

2.1. Materials

Table S1 summarized the sources of CMs and preparation methods of the sixteen kinds of CMs that used in this study. Powdery graphite (purity was greater than 99.9%, and particle size was less than 45 μm) was purchased from Sigma Aldrich Co. (Shanghai, China). Oxidized graphite was obtained by oxidizing the powdery graphite with sulfuric acid, hydrogen peroxide and potassium permanganate (Wang and Hu, 2011), the details of oxidized procedure are presented in supplementary material. Functionalized and graphitized MWCNTs were purchased from Organic Chemicals Co. (Chengdu, Sichuan Province, China). Based on the information provided by the manufacturer, G-MWCNT was obtained by treating high-purity MWCNT in inert gas at 2800 $^{\circ}\text{C}$ for 20 h; OH-MWCNT and COOH-MWCNT were obtained by oxidizing high-purity MWCNT with KMnO_4 in H_2SO_4 solutions, at different acid concentrations and temperature; NH_2 -MWCNT was obtained by first covalently amidating COOH-MWCNT with ammonium hydroxide and then decarboxylating the product at high temperature. G-MWCNT contained more than 99.9% (wt:wt) MWCNT and less than 0.1% impurities (mainly ash); OH-MWCNT, COOH-MWCNT, NH_2 -MWCNT contained more than 95% MWCNT and less than 5% impurities. The outer diameters of the MWCNTs ranged from 8 to 15 nm, and the average length was approximately 50 μm .

Both graphene oxide (GO) (>99%) and reduced graphene oxide (rGO) (>99%) were purchased from Nano Materials Tech Co.

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