

Are carbon nanotubes promising adsorbents for water treatment?

Ting Shao, Shujuan Zhang, and Tanju Karanfil

Department of Environmental Engineering and Earth Sciences,
Clemson University, Anderson, SC 29625

Introduction

Adsorption is one of the most commonly used technologies to remove organic contaminants from aqueous solution in water treatment. The most conventional adsorbent is activated carbon (AC) – a substance which is extremely porous. However, in several recent studies, carbon nanotubes (CNTs) have been observed to be more efficient carbonaceous adsorbents than conventional ACs, with higher adsorption capacity [1-3], shorter equilibrium time [4, 5] and less weight loss in reactivation [2]. CNTs, as newly emerged carbonaceous materials, have attracted considerable interests as potential adsorbents for water treatment application due to their high specific surface area, distinct structure and modifiable surface chemistry. Therefore, a fundamental comparison between CNTs and ACs is critical and necessary in evaluating the potential environmental application of CNTs and selecting the optimal carbonaceous adsorbents in water treatment.

In this review, we first summarized the physiochemical properties of CNTs and ACs, and then compared the adsorption behaviors between them in terms of adsorption capacity and kinetics.

Structural Characteristics of CNTs

CNTs are novel nanomaterials that consist of one or more micron-scale graphite layers rolled into a seamless cylinder of nanoscale diameter with both ends usually "capped" with half of a fullerene-like molecule. Typically, the outer diameters and lengths of CNTs are in the nanometer range (ca. 1 – 100 nm) and up to several tens of micron, respectively. On the basis of their structures, CNTs can be categorized as single-walled (SWNTs) and multi-walled carbon nanotubes (MWNTs) (Fig. 1).

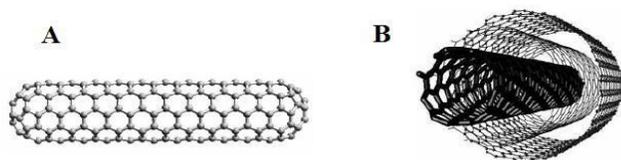


Fig. 1 The structure of CNTs. (A) SWNT; (B) MWNT.

Aggregation is an important physicochemical attribute of CNTs that differentiate them from other carbonaceous adsorbents (e.g., ACs). Due to the strong van der Waals forces along the tube length axis, CNTs are prone to form bundles, which would alter the size, shape, and surface area of CNTs. In addition, aggregation (bundling) may impact adsorption properties of CNTs by reducing the surface area, but generating interstitial channels between nanotubes and grooves on the periphery of CNTs. Additionally, the

adsorption sites on MWNTs include the concentric channels between nanotubes layers; however, the channels are believed to be too narrow (0.34 nm) to be accessible to a majority of adsorbate molecules. Thus, the external surface, inner cavities, interstitial channels, and external grooves constitute the four possible sites for adsorption.

Structural Characteristics of ACs

ACs are porous adsorbents with high degree of porosity and extensive internal surface area (e.g., 800-1000 m²/g). They can be produced from a variety of carbonaceous materials including wood, coal, and coconut shells and can be fabricated in the form of fine powders, large sized granules, pellets and fibers. Among these forms, the most common forms are the powder like (PAC) and the granular one (GAC), which consist of a varying pore structure characterized by wide pore size distribution (Fig. 2). As compared to GAC, activated carbon fibers (ACFs) usually have uniformly sized (< 2 nm, micropore), slit shaped pores oriented along the longitudinal axis (Fig. 2). In addition, for GACs, the micropores are branched from macropores and mesopores while the micropores of ACFs are on the surface of the carbon, which suggests shorter transport pathway of ACFs from carbon surface to the micropores and faster adsorption kinetics than those of GACs.

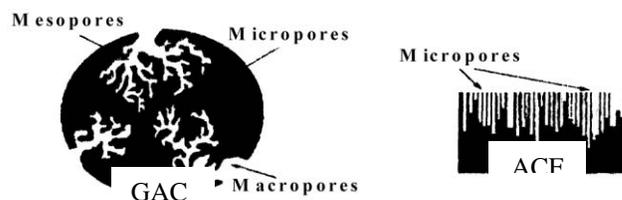


Fig. 2 Schematic pore structure of GAC and ACF.

Adsorption Comparison between CNTs and ACs

Adsorption of organic compounds by carbonaceous sorbents is controlled by the characteristics of adsorbents, the nature of adsorbates, and the background solution chemistry. In terms of adsorbents, the criteria of their applicability for water treatment are generally based on adsorption capacity and kinetics.

The reported specific surface area of CNTs used as adsorbents normally ranges from 55 to 541 m²/g and is generally lower than those of ACs (Fig. 3). Several studies concluded that surface area was a critical factor determining the higher adsorption capacity of ACs than that of CNTs. For example, Chin et al. [6] observed that ACs showed a higher adsorption capacity of o-xylene and p-xylene than SWNTs due to the higher surface area of ACs. Similar observation has also been reported by Cho et al. [7] that AC had a greater adsorption affinity of naphthalene than CNTs because of its larger surface area. However, it should be noted that some organic compound adsorption on CNTs (especially on SWNTs) is comparable to or even higher than that on ACs. Su and Lu [2] attributed the higher adsorption of dissolved organic matter (DOM) on CNTs to larger average pore diameter and volume. Similarly, molecular sieving effect has been observed by Yang

and Xing [1] in the adsorption of fulvic acid by CNTs and PAC, and they postulated that fulvic acid could not access some micropores on PAC surface. Ji et al. [3] also reported that CNTs exhibited higher sorption affinity of tetracycline (bulky organic molecule) than an AC but weaker adsorption of naphthalene (small molecule). Most ACs are microporous (< 2 nm), whereas CNTs form porous interstices with large pore sizes (mesopores and macropores) along with inner cavities (Fig. 3). Therefore, surface area may not be the only parameter controlling the adsorption behavior of carbonaceous sorbents, pore size distribution of various sorbents with respect to the molecular size and configuration of organic compounds is the other important criterion to select an optimal adsorbent in water treatment. In addition, CNTs can be engineered or modified specifically to enhance their selectivity to specific target contaminants.

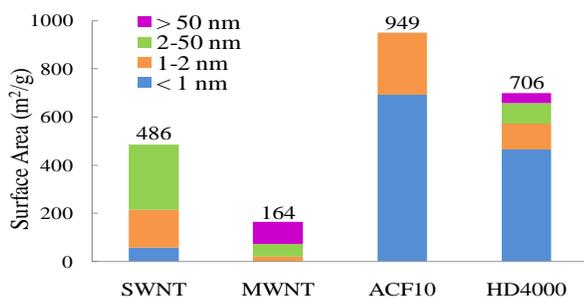


Fig. 3. The surface area fraction of carbonaceous adsorbents in each pore size range (ACF10: a phenol formaldehyde-based ACF; HD4000: a coal-based GAC) [8]

Several previous studies have investigated the adsorption kinetics of organic compounds by CNTs and ACs with similar surface chemistry but different surface areas and pore structures. For example, Lu et al. [5] reported that a shorter equilibrium time was needed for adsorption of trihalomethanes (THM) on CNTs than that on PACs. They attributed this observation to the pore structure of PAC in which small adsorbate (THM) has to move from the exterior surface to the inner surface of the micropores to reach equilibrium, as shown in Fig. 2. On the other hand, for CNTs, the interstitial pore spaces and inner cavities (mesopores) are usually effective for adsorption of low molecular weight small sized adsorbates, which suggests a smaller adsorbate mass transfer resistance on CNTs than that on PACs. Similar finding has also been reported in previous study of uraemic toxin adsorption by CNTs and an AC [9]. Results showed that the adsorption equilibrium time for adsorption of uraemic toxin on the AC was 5 times more than that on the CNTs as a result of the higher ratio of mesopores/macropores to micropores and the higher pore volume of CNTs. In addition, because of the strong chemical resistance and stiff structure, CNTs could be used for a longer time than ACs, which has been demonstrated by Su and Lu that CNTs had less weight loss after ten cycles of water treatment and reactivation than ACs [2].

It should be noted that the presence of NOM exhibited different suppressing impact on adsorption of small organic compounds by CNTs and ACs. Wang et al. [10] reported that

the effects of NOM coating on adsorption of phenanthrene and naphthalene by MWNT were weaker than those on ACs, which was consistent with our observation. This observation implied that once employed into water treatment plant which has NOM, CNTs will still adsorb a considerable amount of organic compounds. All these studies suggest that CNTs could be a potential adsorbent for water treatment.

Conclusions

Experimental observations in previous studies indicate that the surface area, pore structure and pore size distribution are three important factors controlling the adsorption of organic compounds by carbonaceous porous adsorbents. For the low molecular weight small sized organic compounds, the conventional ACs of highly microporous usually have stronger adsorption affinities than CNTs. However, due to the large mesopore and macropore volumes and high surface area (which does not subject to molecular sieving effect), CNTs are expected to be able to adsorb large size molecules (e.g., NOM). Furthermore, in terms of adsorption kinetics, CNTs are dominated with cylindrical mesopores in which no diffusion of adsorbate molecules into deeper secondary pore regions occurs, indicating the higher mass transfer rate and faster adsorption kinetics of CNTs than that of ACs.

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