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Review

Aqueous adsorption and removal of organic contaminants by carbon nanotubes

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HIGHLIGHTS

- We summarize the most recent research progress of CNTs for removal of organics.
- Adsorption mechanisms between CNTs and organics were elucidated in detail.
- The developing trends and prospects of CNTs for removal of organics were discussed.

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ABSTRACT

Organic contaminants have become one of the most serious environmental problems, and the removal of organic contaminants (e.g., dyes, pesticides, and pharmaceuticals/drugs) and common industrial organic wastes (e.g., phenols and aromatic amines) from aqueous solutions is of special concern because they are recalcitrant and persistent in the environment. In recent years, carbon nanotubes (CNTs) have been gradually applied to the removal of organic contaminants from wastewater through adsorption processes. This paper reviews recent progress (145 studies published from 2010 to 2013) in the application of CNTs and their composites for the removal of toxic organic pollutants from contaminated water. The paper discusses removal efficiencies and adsorption mechanisms as well as thermodynamics and reaction kinetics. CNTs are predicted to have considerable prospects for wider application to wastewater treatment in the future.

Contents

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1. Introduction

The disposal of large amounts of wastewater that contain potentially toxic organic solutes is a problem shared by many companies. The removal of toxic components in wastewater (e.g., metal ions, organic poisons, and harmful germs) prior to its disposal is crucial (Fu and Wang, 2011; Jagtap et al., 2012) because of general safety concerns and environmental consequences. Many technologies have been established for such removal, including chemical oxidation/reduction, biological treatment, coagulation/flocculation, adsorption, membrane separation, and ion exchange. Novel technologies are continuously being developed through the constant efforts of researchers (Ma et al., 2012a). One of the most effective of these methods is adsorption because processes based on this concept are simple, highly efficient, and easy to operate; therefore, adsorption processes are widely used (Jia et al., 2013; Liu et al., 2013; Sun et al., 2012).

Various adsorbents have been developed for the removal of organic pollutants (e.g., dyes, pesticides, pharmaceuticals/drugs, and phenols) from water (Alexander et al., 2012; Atul et al., 2013; Bond et al., 2012; Delgado et al., 2012). Activated carbon (AC) is the most commonly used commercial adsorbent because of its excellent adsorption capacity for organic contaminants (Demirbas, 2009; Hosseini et al., 2011). However, it has certain shortcomings that include limited availability, low adsorption capacity, and difficult recovery. Recently, a great deal of attention has been focused on the application of nano-structured materials as adsorbents to remove toxic and harmful organic substances from wastewater (Aditya et al., 2011; Mohmood et al., 2013). Carbon nanotubes (CNTs), which were discovered by Iijima in 1991 (Iijima, 1991), are one of the most widely studied carbon nanomaterials and can serve as excellent adsorbents (Brar et al., 2010; Herrero Latorre et al., 2012; Pyrzynska, 2010) because of their hollow and layered structure and large specific surface area, which is why CNTs are the most commonly used nano-materials for adsorbing toxic material (Sui et al., 2012b; Sweetman et al., 2012; Tan et al., 2012).

CNT adsorbents can be classified into three types: single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs), and functionalized CNTs (*f*-CNTs) (Bahgat et al., 2011; Ma et al., 2011b; Ruelle et al., 2012). Such materials have already played an important role in the effective removal of several organic contaminants from water (Ma et al., 2011b; Ren et al., 2011). For example, (MWCNTs) are much more effective in the removal of methyl orange (MO) (Hosseini et al., 2011), Eriodirome Cyanine R (ECR) (Ghaedi et al., 2011b), arsenazo(III), and methyl red (MR) (Ghaedi et al., 2011c) from wastewater than activated carbon (AC).

This paper reviews the recent progress in the application of CNTs in the removal of toxic organic pollutants from contaminated water. A total of 145 published studies (2010–2013) are reviewed, the current applications of various types of organic pollutants are presented, and several possible adsorption mechanisms and thermodynamics/kinetics are discussed. We conclude with a glimpse into future challenges for the wider application of CNTs and related materials in the field of environmental engineering.

2. Application of CNTs for adsorption

2.1. Removal of organic dyes

Organic dyes are one of the most hazardous materials in industrial effluents that are discharged from various industries (e.g., textiles, leather, cosmetics, and paper) and act as contaminants to the environment in general and water sources in particular. Many organic dyes have high levels of biotoxicity that cause potential mutagenic and carcinogenic effects in humans. For example, dyes such as Sudan red I, II, III, and VI, whose use in food is prohibited as a result of their toxicity or carcinogenicity at even low concentrations, are widely used in other industries. Most dye compounds contain complex aromatic structures (Fig. 1) that make them highly resistant to biodegradation and recalcitrant to conventional biological and physical oxidation treatments. Therefore, the targeted removal of such compounds has attracted a growing amount of attention (Jiao et al., 2013; Yang et al., 2013b).

A wide range of materials has been used for the removal of organic dyes from wastewaters, including AC, zeolite, clay, and polymers, to name but a few. The current priority is to develop novel adsorbent materials with high adsorption capacities and removal efficiencies to realize effective control of these environmental pollutants. CNTs could be one of the most promising absorbents for this purpose because of their large adsorption capacity for organic dyes. Indeed, MWCNTs have been shown to outperform cadmium hydroxide nanowire-loaded AC ($Cd(OH)_2$-NW-AC) with respect to their efficient removal of safranine O (SO) from wastewater (Ghaedi et al., 2012a). However, only a few reports on the application of CNTs for dye removal from aqueous solution have been published until now (Bahgat et al., 2011; Ghaedi et al., 2011a; Ghaedi et al., 2011b; Ghaedi et al., 2011c; Hu et al., 2011b; Machado et al., 2011) and the CNTs were typically directly used without further treatment (Ghaedi et al., 2011a; Ghaedi et al., 2011b; Ghaedi et al., 2011c; Machado et al., 2011) (Table 1).

Functionalization of CNTs has been undertaken because the introduction of various functional groups can provide new adsorption sites for organic dyes. Among such modifications, oxidation is an easy method of introducing hydroxyl and carbonyl groups to the sidewalls of CNTs. Oxidized MWCNTs have been shown to be effective in the removal of MR (Ghaedi and Kokhdan, 2012) and methylene blue (MB) from aqueous solutions (Ghaedi et al., 2012b). Another work has focused on the development of CNT-impregnated chitosan hydrogel beads (CSBs) for the removal of Congo red (CR). In Langmuir adsorption modeling, CSBs demonstrated a higher maximum adsorption capacity than normal chitosan CBs (450.4 vs. 200.0 $mg \cdot g^{-1}$; Chatterjee et al., 2010). A new generation of CSBs prepared by using sodium dodecyl sulfate (SDS) and MWCNTs to improve upon their mechanical properties has also demonstrated a high maximum adsorption capacity for CR (375.94 $mg \cdot g^{-1}$; Chatterjee et al., 2011).

Compared to MWCNTs and hybrid CNTs (HCNTs), SWCNTs can demonstrate better adsorption properties for organic contaminants because of their higher specific surface area. Indeed, SWCNTs are more efficient at removing benzene and toluene, and has shown maximum adsorption capacities of 9.98 and 9.96 $mg \cdot g^{-1}$, respectively (Bina et al., 2012). A maximum adsorption capacity of 496 $mg \cdot g^{-1}$ was achieved when reactive blue 29 (RB29) was removed from aqueous solution using SWCNTs (Nadafi et al., 2011).

Recently, a novel self-assembled cylindrical graphene-CNT (G-CNT) hybrid was developed, and it achieved a maximum adsorption capacity of 81.97 $mg \cdot g^{-1}$ for the removal of MB from aqueous solution, and the removal efficiency reached 97% for low (10 $mg \cdot L^{-1}$) initial MB concentrations (Ai and Jiang, 2012). Lastly, Zeng et al. (2013) proposed a new concept of using entangled CNTs as porous frameworks to enhance the adsorption of organic dyes. The composites obtained through polymerization with polyaniline (PANI) possessed large surface areas. At an initial malachite green (MG) concentration of 16 $mg \cdot L^{-1}$, the CNT/PANI composites exhibited a 15% higher equilibrium adsorption capacity of 13.95 $mg \cdot g^{-1}$ compared to neat PANI.