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Short Communication

Effect of Acid Treatment of Carbon Nanotubes on Their Adsorption Capacities of Benzene and Toluene

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Abstract
Toluene and benzene were eliminated using multi-walled carbon nanotubes (MWCNTs). In order to investigate influence of acid treatment on the MWCNTs adsorption capacities, the MWCNTs were functionalized by nitric acid (10 M) under reflux conditions for 2 h. Fourier transform infrared (FTIR) and Raman spectroscopy were employed to confirm the formation of functional groups on the nanotubes surface. Specific surface areas of the nanotubes were also measured using the Brunauer–Emmett–Teller (BET) method. Adsorption capacities of the functionalized and unfunctionalized MWCNTs were obtained and then compared with each other. FTIR and Raman spectra proved the formation of functional groups on the MWCNTs surface as a result of this acid treatment. Adsorption capacities measurements revealed that the functionalized MWCNTs have large adsorption capacities of toluene and benzene as compared with the unfunctionalized MWCNTs. This enhancement of adsorption capacities was ascribed to an increase in the specific surface area of the nanotubes due to this acid treatment.
Keywords*: Acid treatment,, Carbon nanotubes, Functionalization, Nanoadsorbent.*

1. INRODUCTION

Volatile organic compounds (VOCs) can risk ecosystem and human health. Approaches such as adsorption, condensation, thermal oxidation and catalytic oxidation are employed to eliminate VOCs such as toluene and benzene [1]. Adsorption approach is a capable method which can be employed to eliminate these organic contaminants [2]. In this approach, VOCs materials as adsorbates are chemically or physically adsorbed on solid adsorbents. The physical adsorption process has attracted more interest because in this process, the solid adsorbents can be more easily reduced and reused [3].

Current adsorbents such as activated carbon have some disadvantages and consequently scientists are studding new adsorbents such as carbon nanotubes (CNTs) for removal of VOCs. CNTs are promising alternative because their unique chemical and physical properties [4-5]. The CNTs consist of one or several graphene layers wrapped into cylindrical tubes that are closed at each end by

hemispherical caps [6]. The CNTs show an exceptional combination of chemical, thermal, mechanical and electrical properties. The CNTs have found applications in different fields such as pollutants adsorption, nanocomposites, nanoelectronics, sensors, biosensors and catalysis [7-10]. They have high surface area, chemical and thermal stability and hydrophobic property that make them suitable adsorbents for these organic pollutants [4-5, 11]. For example, Q. L. Li et al. [4] used CNTs to trap VOCs from environmental samples. They showed that multiwall carbon nanotubes (MWCNTs) have higher adsorption capacity as compared with Carbopack B, a graphitized carbon black. Moreover, H. Sone et al. [5] employed highly crystalline MWCNTs to eliminate aromatic VOCs.

In previous work, the adsorption capacities of two types of MWCNTs for benzene and toluene were measured and compared with each other. In this investigation, the influence of the functionalization of MWCNTs by nitric acid on their adsorption capacities for both benzene and toluene were studied. First, MWCNTs were functionalized by nitric acid treatment. They were then characterized using Fourier transform infrared (FTIR) technique and their specific surface areas were measured by the Brunauer–Emmett–Teller (BET) method. Finally, Adsorption capacities of the functionalized and unfunctionalized MWCNTs were measured and then compared with each other.

2. EXPERIMENTAL

2.1. Functionalization of MWCNTs

MWCNTs were provided by Shenzhen Nanotech Port Co. Ltd (China). Prior to measurement of adsorption capacities, the raw MWCNTs were annealed under a flow of Helium at 1000^{o}C for 30 minutes. The annealed MWCNTs are denoted as unfunctionalized MWCNTs. This heat pretreatment lead to eliminate defects and functional groups formed on the nanotubes surface during synthesis and purification processes. In order to functionalize the MWCNTs, a mixture of the nanotubes and nitric acid (10 M) was heated to boiling temperature and stirred under refluxing condition for 2 h. The MWCNTs were then centrifuged; washed with the deionized water, and dried at about 100^{o}C for 48 h. Surface areas of the nanotubes were measured using a ChemBET-3000 chemisorption apparatus manufactured by Quantachrome. FTIR was performed using a Bruker Vector 27 spectrometer with a resolution of 5 cm^{-1}. Raman spectra of the MWCNTs were acquired by an Almeg Thermo Nicolet Dispersive Raman Spectrometer by the second harmonic at 532 nm of an Nd:YLF laser.

2.2. Measurement of adsorption capacity

In Figure 1, schematic diagram of the experimental setup employed to measure maximum adsorption capacity of benzene and toluene on the MWCNTs are shown. According to this Figure, in order to measure the adsorption capacities of the MWCNTs, first a flow of nitrogen gas was saturated from benzene/toluene by passing from a saturator containing benzene/toluene and then passed through the adsorption bed containing MWCNTs for 2 h. It has been experimentally shown that after 2 h exposure of the MWCNTs to the saturated nitrogen, they get saturated with benzene/toluene.

To measure the quantities of benzene/toluene adsorbed on the MWCNTs, The saturated MWCNTs were mixed with carbon disulfide (CS_2) and then this mixture was well stirred and maintained overnight at 0^{o}C. Thus, the benzene/toluene adsorbed on the MWCNTs was extracted in CS_2 and their quantities were determined using gas-chromatography (GC). Finally, the maximum capacity of the MWCNTs for adsorption of benzene/toluene estimated

and reported as micrograms of adsorbate per grams of adsorbent (µg/g).

3. RESULT AND DISCUSSION

3.1. FTIR Spectra of the nanotubes

In Figure 2, FTIR spectra of the functionalized (upper) and unfunctionalized (lower) MWCNTs are presented. As can be observed, the nitric acid treatment led to the appearance of several peaks in their FTIR spectrum. The peak at about 1580 cm^{-1} is attributed to C=C stretching mode. The presence of this peak showed that the functional groups and defects were created on the MWCNTs surface as a result of the acid treatment [5].

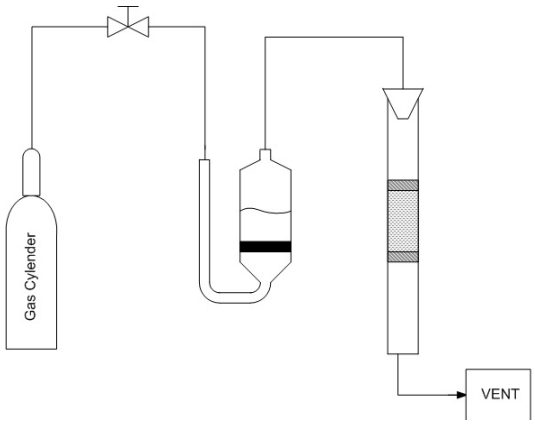

Figure1. *Schematic diagram of the experimental setup employed to measure maximum adsorption capacity of the carbon nanotubes.*

The peak observed at near 1190 cm^{-1} can be ascribed to functional groups containing C–O single bond, e.g. lactone. The peak around 1720 cm^{-1} corresponds to C=O stretching mode, indicative of the formation of acidic carbonyl groups. Finally, the peak at about 3400 cm^{-1} is assigned to the hydroxyl groups. Generally, the presence of the peaks assigned to the carbonyl (1720 cm^{-1}) and the hydroxyl (3400 cm^{-1}) groups in the spectrum of functionalized MWCNTs can indicate the formation of carboxyl groups as a result of the nitric acid treatment [12-14].

3.2. Raman spectra of the nanotubes

Figure 4 shows the Raman spectra of the functionalized and unfunctionalized MWCNTs. Three peaks at about 1345, 1573 and 2693 cm^{-1} are seen in spectra of both the functionalized and unfunctionalized MWCNTs which named D-band, G-band and 2D-band, respectively. The 2D-band attributed to the first overtone of the D mode is often related to the degree of nanotube crystallinity [9, 12, 16]. The G- and D-bands are ascribed to the tangential stretching mode of sp^2-hybridized carbons into graphene-like structures and the vibration mode of sp^3-bonded carbon atoms with dangling bonds at disordered sites, respectively. The D-band is revealed in Raman spectrum due to the presence of functional groups and defects on the carbon nanotubes surface. The ratio of the intensities of D and G bands (I_D/I_G) is commonly used to characterize the quantities of the functional groups and defects in the carbon nanotubes [9, 12, 16]. As can be seen, the I_D/I_G ratio of the functionalized MWCNTs with value of near 1.4 is larger than that of the unfunctionalized MWCNTs with value of near 1.1, confirming the formation of the functional groups on the nanotubes surface as a result of the nitric acid treatment of the MWCNTs.

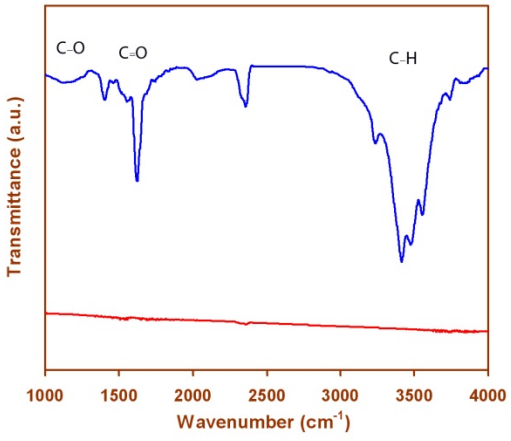

Figure2*. FTIR spectra of the functionalized (upper) and unfunctionalized (lower) MWCNTs*

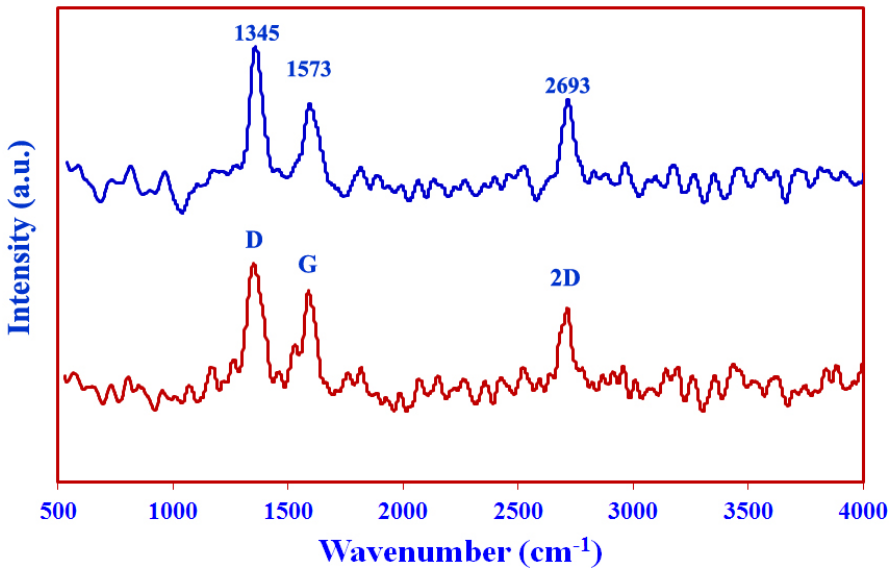

Figure3*. Raman spectra of the functionalized (upper) and unfunctionalized (lower) MWCNTs.*

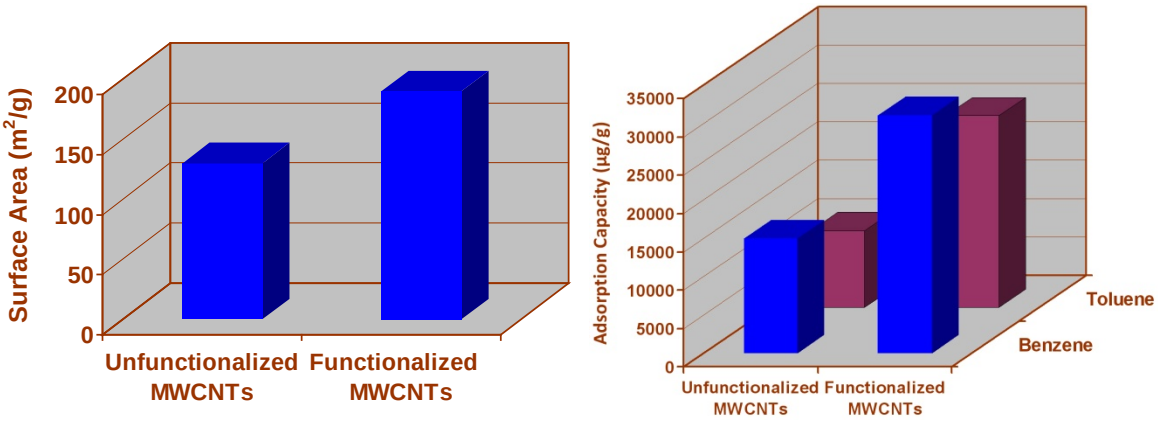

Figure4. *BET specific surface areas of the functionalized and unfunctionalized MWCNTs.*

3.3 BET specific surface areas of the nanotubes

Figure 4 shows BET specific surface areas of the functionalized and unfunctionalized MWCNTs. As can be seen, the specific surface areas of the functionalized and unfunctionalized MWCNTs are 190 and 130 m^2/g, respectively. The specific surface area of an adsorbent significantly influences its adsorption capacity. It has been revealed that increase of quantity of structural imperfections on the nanotubes surface (particularly after processes such as acid treatment) can increase specific surface area of the nanotubes. It looks that the nitric acid functionalization can damage the graphical structure of the nanotubes, form narrow micropores on their surfaces and therefore, increase their specific surface areas [15-17].

3.4. Adsorption capacities of nanotubes

In Figure 5, the maximum adsorption capacities of the functionalized and unfunctionalized MWCNTs for benzene and toluene are exhibited. The adsorption capacities of the functionalized and unfunctionalized MWCNTs are 31000 and 15000 µg/g for benzene and 25000 and 10000 µg/g for toluene, respectively. For both benzene and toluene, the adsorption capacity of the functionalized MWCNTs is higher than that of the unfunctionalized MWCNTs. As pointed out, the specific surface area of the functionalized MWCNTs is larger as compared with that

of the unfunctionalized MWCNTs. It has been widely accepted that for the nanotubes, the more specific surface area, the more adsorption capacity [18]. It can be concluded that the increase of the specific surface area of the nanotubes as a result of the nitric acid functionalization leads to an increase in their maximum adsorption capacities.

4. CONCLUSION

Effect of nitric acid treatment of MWCNTs on their adsorption capacities of benzene and toluene was investigated. First MWCNTs were functionalized by nitric acid (10 M) under reflux conditions for 2 h. Then, Adsorption capacities of the functionalized and unfunctionalized MWCNTs were compared with each other. FTIR results indicated the formation of functional groups on the MWCNTs surface as a result of the nitric acid treatment. According to BET measurements, the specific surface area of the functionalized MWCNTs was larger as compared with that of the unfunctionalized MWCNTs. Adsorption capacities measurements showed that for both benzene and toluene, the maximum adsorption capacity of the functionalized MWCNTs was higher than that of the unfunctionalized MWCNTs. It was concluded that higher adsorption capacities of the functionalized MWCNTs can be attributed to the increase of the specific surface areas of the nanotubes as a result of the nitric acid functionalization.

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