

A Study of Effects of Different Surface Modifications of MWCNTs on their Adsorption Capacity of Benzene and Toluene

Pourfayaz, Fathollah*⁺

Department of Renewable Energies and Environment, Faculty of New Sciences and Technologies, University of Tehran, P.O. Box 14395-1561 Tehran, I.R. IRAN

Ahmadi-Avval, Parviz

Farayand Chemical Research Group, ACECR, Faculty of Engineering, University of Tehran, I.R. IRAN

Haji Tarverdi, Mohammad Sadegh

Technology Development Institute, ACECR, Tehran, I.R. IRAN

Maleki, Akbar

Department of Renewable Energies and Environment, Faculty of New Sciences and Technologies, University of Tehran, P.O. Box 14395-1561 Tehran, I.R. IRAN

Ahmadi, Mohammad Hossein*⁺

Faculty of Mechanical Engineering, Shahrood University of Technology, Shahrood, I.R. IRAN

ABSTRACT: Multi-Walled Carbon Nanotubes (MWCNTs) surfaces were serially modified by the annealing treatment under Helium flow at 1000°C, the nitric acid treatment and again the annealing treatment under same conditions and their maximum adsorption capacities for benzene and toluene were measured and analyzed. The unmodified and modified MWCNTs were characterized by Fourier Transform InfraRed (FT-IR) and Raman spectroscopy techniques and Brunauer–Emmett–Teller (BET) specific surface area measurements. The results revealed that the nitric acid treatment leads to form the functional groups and defects on the MWCNTs surfaces and increase their specific surface areas while the annealing treatments remove the functional groups and defects and therefore improve the structural integrity of the MWCNTs and enhance the π - π interaction between the MWCNTs and the toluene/benzene. According to the measurements of the maximum adsorption capacities, both acid and annealing treatments increased the adsorption capacity of the MWCNTs for both the benzene and toluene. It can be finally concluded that the adsorption capacity of the carbon nanotubes for the aromatic organic adsorbates such as benzene and toluene not only depends on their specific surface area but also is influenced by the structural integrity of the carbon nanotubes.

KEYWORDS: Surface modification; Carbon nanotubes; Adsorption; Aromatic contaminants.

* To whom correspondence should be addressed.

+ E-mail: pourfayaz@ut.ac.ir ; mohammadhosein.ahmadi@gmail.com
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INTRODUCTION

Volatile Organic Compounds (VOCs) can influence the ecosystem and potentially threaten the human health. Therefore, removal of them from the atmosphere is an important issue in the environmental fields [1-2]. Depending on their amounts, flow rate and temperature, the approaches such as adsorption, condensation, thermal oxidation and catalytic oxidation are employed to eliminate VOCs [3]. The adsorption process is one of promising and cost-effective approaches for removal of VOCs pollutants especially while their concentration is low [4]. In this method, VOCs pollutants (adsorbates) are chemically or physically adsorbed on adsorbents. In fact, the application of the solid adsorbents for the capturing of VOCs contaminants is one of the most convenient approaches that widely employed to monitor VOCs in ambient air [5]. Since in physical adsorption process, the solid adsorbents can be reduced and reutilized, it has fascinated more attention [6].

Adsorbent selected influences the adsorption and removal process of VOCs dramatically because various adsorbents have different abilities. An ideal adsorbent must have chemical and thermal stability, high adsorption capacity, rapid and easy regeneration ability, no catalytic activity, hydrophobic property and etc. [7-8]. Conventional adsorbents such as activated carbon have disadvantages. For example, activated carbon is faced with problems such as combustion risk, the block of its pores due to polymerization of some VOCs catalyzed by ashes present on its surface, little selectivity, high-temperature regeneration and adsorption of moisture. Therefore, researchers are increasingly trying to find new adsorbents for the elimination of VOCs for environmental samples. Carbon NanoTubes (CNTs) are a promising candidate due to their unique properties [1-2, 8-10].

Recent advances in the field of nanotechnology have led to developing its applications in various industries [11-15]. Therefore, in recent years a great attention has been paid to the nanomaterials such as the CNTs. Because of their unique chemical, mechanical, electrical and thermal properties, CNTs have found applications in various fields such as pollutants adsorption, nanoelectronics, nanocomposites, catalysis, sensors and biosensors [16-22]. CNTs have the high surface area, the hydrophobic property and chemical and thermal stability. Therefore, they can be suitable adsorbent for VOCs [1-2]. *Li and et al.* [5]

have used CNTs for eliminating VOCs and concluded that the CNTs are a potentially useful adsorbent. They have also shown that CNTs have much higher adsorption capacity than that of Carbopack B, a graphitized carbon black.

In this study, Multi-Walled Carbon Nanotubes (MWCNTs) were employed for trapping benzene and toluene. Aromatic compounds such as benzene and toluene are the most harmful matters among VOCs. They are carcinogen even at very low concentrations. In order to improve adsorption capacity of benzene and toluene and complete our previous works [23-24], surfaces of MWCNTs was modified with different methods [25]. The unmodified and modified MWCNTs were characterized by Fourier Transform InfraRed (FT-IR), Raman spectroscopy and Scanning Electron Microscopy (SEM) techniques and their specific surface areas were also measured using the Brunauer–Emmett–Teller (BET) method.

EXPERIMENTAL SECTION

Surface modification of MWCNTs

MWCNTs were provided by Research Institute of Petroleum Industry (RIPI) in National Iranian Oil Company (NIOC). Raw MWCNTs surfaces were successively modified for thrice.

The first modification: 1 g of raw MWCNTs was put into a quartz tube and exposed to a flow of Helium (He) and then heated to around 1000°C at a rate of 5°C /min and hold at same temperature for 30 minutes. The temperature was then reduced to room temperature under He gas flow. This annealing treatment causes the removal of the most of the functional groups formed on the surfaces of the CNTs during synthesis and purification processes. The treated MWCNTs are called annealed MWCNTs and denoted by A-CNTs.

The second modification: 1 g of A-MWCNTs and 200 mL of nitric acid (10 M) was poured into a round bottom flask. The flask was heated to boiling temperature and the mixture of CNTs and nitric acid was stirred under refluxing condition for 2 h. the CNTs were then centrifuged; washed with the deionized water until the solution pH reached about 7; and centrifuged again. The CNTs finally were dried at about 100°C for 48 h. The nitric acid-treated A-MWCNTs are denoted as Acid-A-CNTs.

The third modification: acid-A-MWCNTs were again annealed at 1000°C under He flow. The annealed acid-A-MWCNTs are denoted by A-Acid-A-CNTs.

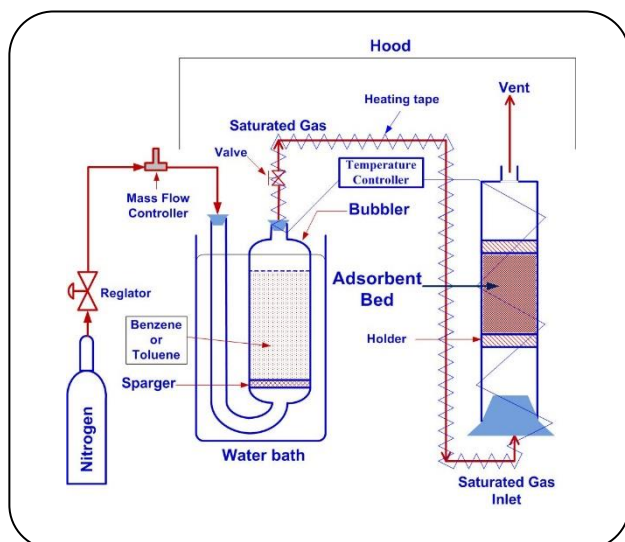


Fig. 1: Schematic of the set-up used to measure maximum adsorption capacity of benzene and toluene on MWCNTs.

Characterization of MWCNTs

Morphology and size of the CNTs were determined using field emission scanning electron microscopy (FESEM, Hitachi, S-4160). Surface areas of the samples were measured using a ChemBET-3000 chemisorption apparatus manufactured by Quantachrome. In order to identify the type of functional groups formed on the CNTs surfaces, FT-IR was performed using a Bruker Vector 27 spectrometer with a resolution of 5 cm^{-1} . The samples were mixed with KBr powder and compressed into pellets for FT-IR measurements. The infrared spectra were recorded in the transmittance mode. Raman spectra of the CNTs were also obtained on an Almega Thermo Nicolet Dispersive Raman Spectrometer by the second harmonic at 532 nm of a Nd:YLF laser.

Measurement of adsorption capacity

Fig. 1 presents the schematic of the set-up used to measure maximum adsorption capacity of benzene and toluene on MWCNTs. A controlled flow rate of nitrogen gas was saturated with benzene or toluene at a certain temperature (here 25°C) while it was passed into a saturator containing benzene or toluene. The saturated exit gas was then passed through the adsorption bed containing 0.5 gr of MWCNTs for 2 h. The temperature of the saturated gas was held at 25°C through path passing (from bubbler outlet to vent). It was experimentally found that the CNTs are surely saturated after 2 h of exposure to benzene/toluene-saturated nitrogen.

The saturated CNTs were then mixed with carbon disulfide (CS_2). In order to extract benzene/toluene by CS_2 , this mixture was well stirred and maintained overnight at 0°C . The amount of benzene/toluene dissolved in CS_2 were determined using Gas-Chromatography (GC). Finally, the maximum adsorption capacity of benzene/toluene on the CNTs was calculated and reported as milligrams of adsorbate per grams of adsorbent (mg/g).

RESULTS AND DISCUSSION

Morphology of the MWCNTs

The structure order, mesh, and size of the CNTs can considerably effect their adsorption capacity [20-21]. Therefore, in order to investigate the structural order of the MWCNTs and their mesh and also approximate their sizes, FESEM images of the samples were acquired and analyzed. Fig. 2 presents the FESEM images of the MWCNTs with different resolution. The scale bars in A (left image) and B (right image) are 500 and 300 nm, respectively. These images show that the diameter of the MWCNTs is about 39 nm. As is observed, the MWCNTs have an entangled structure and a random arrangement. This random arrangement causes microcavities and even macrocavities in the bulk of the MWCNTs. This size distribution of the cavities and the avoid spaces between the MWCNTs bundles can increase the adsorption capacity of the MWCNTs. Generally, the geometry and morphology of the MWCNTs bundles can influence on the adsorption properties of the CNTs [20-21, 26].

FT-IR spectra of the MWCNTs

FTIR spectra of the modified and unmodified MWCNTs are presented in Fig. 3. Several peaks are observed in spectra of Raw-CNT and Acid-A-CNT, while any peak is not seen in spectra of A-CNT and A-Acid-A-CNT. This showed that the annealing treatment of the CNTs under the He flow at 1000°C led to removing the functional groups and defects from the CNTs surfaces. The peaks at near 1580 cm^{-1} point to C=C stretching mode, indicative of the presence of the functional groups and defects on the CNTs surfaces. The functional groups and defects on the Raw-CNT surface may be formed the duration of the synthesis and purification processes of the CNTs. The peaks observed at around 1190 cm^{-1} are attributed to the C-O single bond of the functional groups

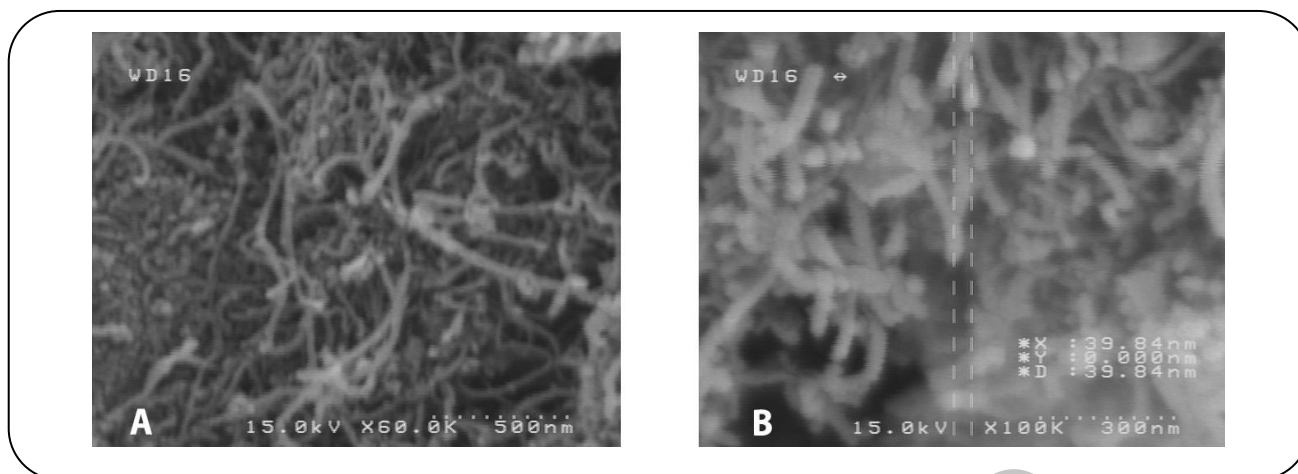


Fig. 2: FESEM images of the MWCNTs with different resolution. The scale bars in (A) 500 nm and (B) 300 nm.

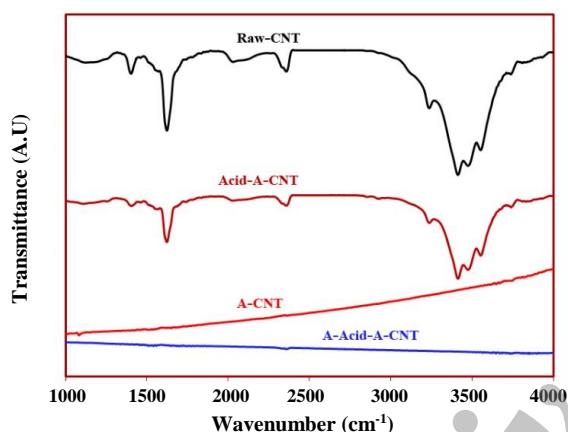


Fig. 3: FT-IR spectra of the treated and untreated MWCNTs.

such as lactone. The peaks at near 1720 cm^{-1} , ascribed to C=O stretching mode, can be indicative of the presence of the oxygen-containing groups such as lactone, quinone, and a carboxylic anhydride. The multiple peaks at $3200\text{--}3500\text{ cm}^{-1}$ are also assigned to the hydroxyl groups. The peaks assigned to the carbonyl (1720 cm^{-1}) and the hydroxyl ($3200\text{--}3500\text{ cm}^{-1}$) groups can usually indicate the presence of carboxyl groups on the CNTs surfaces [27-28].

Raman spectra of the MWCNTs

Fig. 4 exhibits the Raman spectra of the modified and unmodified MWCNTs. In all spectra, three peaks at about 1335 , 1575 and 2695 cm^{-1} are seen which so-called D, G and G'-bands, respectively. The G-band is associated with the tangential stretching mode of the carbon-carbon bonds with sp^2 hybridization in graphitic structures and D-band is related to the disordered or sp^3 -hybridized

carbons in the CNTs walls. Finally, the G'-band (also called 2D-band) is attributed the first overtone of the D mode, is often assigned to the crystallinity degree of the carbon nanotube [27-30]. The intensity of D-band is usually considered dependent on the presence of defects and functional groups on the surfaces of the CNTs. The $I_{\text{D}}/I_{\text{G}}$ ratio is the ratio of the D band intensity to the G band intensity. The $I_{\text{D}}/I_{\text{G}}$ ratio can be used to investigate the graphitic structure of the CNTs. This ratio is commonly proportional to a number of defects on the CNTs surfaces. The higher $I_{\text{D}}/I_{\text{G}}$ ratio, more defects on the carbon nanotubes surfaces [27-29]. The $I_{\text{D}}/I_{\text{G}}$ ratios in the Raman spectra of the modified and unmodified MWCNTs are exhibited in Fig. 5. As is seen in this figure, the $I_{\text{D}}/I_{\text{G}}$ ratios for A-CNT, Raw-CNT, A-Acid-A-CNT and Acid-A-CNT are $0.78 < 0.98 < 1.2 < 1.27$, respectively. According to these results, the $I_{\text{D}}/I_{\text{G}}$ ratio reduces as a result of the annealing treatment of the CNTs. This reveals that the annealing treatment not only cuts the functional groups from the CNTs surfaces but also improves the defects on the surfaces of the CNTs [27-28]. Moreover, the $I_{\text{D}}/I_{\text{G}}$ ratio for Acid-A-CNT with a value of about 1.27 is larger than that for A-CNT with a value of about 0.78, indicating the creation of the functional groups and defects on the surfaces of the CNTs due to the nitric acid treatment of the CNTs [27].

BET specific surface areas of the MWCNTs

Since the specific surface area of an adsorbent importantly influence on its adsorption capacity, BET specific surface areas of the modified and unmodified MWCNTs were measured that are reported in Fig. 6.

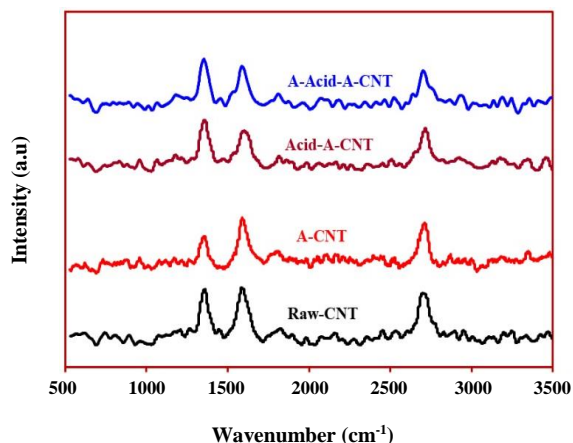


Fig. 4: Raman spectra of the treated and untreated MWCNTs.

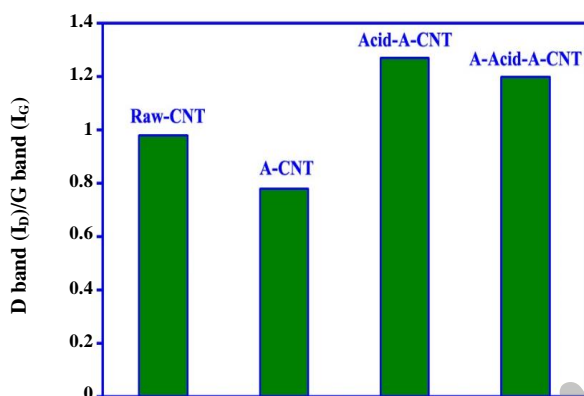


Fig. 5: The I_D/I_G ratios in the Raman spectra of the various MWCNTs.

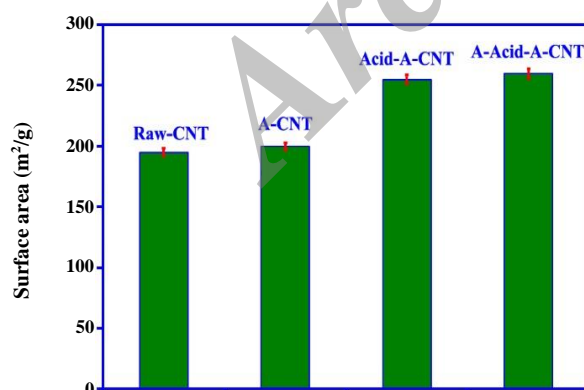


Fig. 6: BET specific surface areas of the modified and unmodified MWCNTs.

BET specific surface areas of Raw-CNT, A-CNT, Acid-A-CNT, and A-Acid-A-CNT were 195, 200, 255 and 260 m^2/g , respectively. As is observed, the nitric acid treatment has led to a significant increase in the specific surface area of the MWCNTs so that after the acid treatment of the MWCNTs, their BET surface area has increased from 200 to 255 m^2/g . It has been discovered that increase of the number of structural imperfections on the CNTs surfaces (particularly after processes such as the acid treatment) can enhance the specific surface area of the CNTs. It seems that the nitric acid surface modification can damage the graphical structure of the CNTs, form narrow micropores on their surfaces and therefore, enhance their specific surface areas [26, 31]. However, the annealing treatment of the MWCNTs did not considerably change their BET surface area.

Adsorption capacities of the MWCNTs

The maximum adsorption capacities of Raw-CNT, A-CNT, Acid-A-CNT, and A-Acid-A-CNT for benzene and toluene are shown in Fig. 7. For both benzene and toluene, the adsorption capacity of A-CNT is larger than those of Raw-CNT. Moreover, the nitric acid treatment of A-CNT caused a significant increase in its adsorption capacity for both benzene and toluene. It can rationally be said that for all adsorbents, the more specific surface area, the more adsorption capacity [26]. In fact, it can be concluded that the acid treatment led to an increase in adsorption capacity of the CNTs because it increased their specific surface area according to Fig. 6. The annealing treatment of Raw-CNT and Acid-A-CNT under the He flow at 1000°C also led to a considerable increase of their adsorption capacities for both benzene and toluene.

Other researchers [32] have shown that the structural defects and functional groups on the CNTs surfaces can act as active sites for physical/chemical adsorption of the adsorbate molecules. Therefore, the enhancement of the structural defects and functional groups can rationally result in an increase in the adsorption capacity of the CNTs. However, some researchers [1] have experimentally revealed that CNTs with low structural defects and high crystallinity can more efficiently adsorb the aromatic compounds such as benzene and toluene as compared with CNTs with high structural defects and low crystallinity. It looks that the π - π interaction between the CNTs and benzene rings of these aromatic compounds,

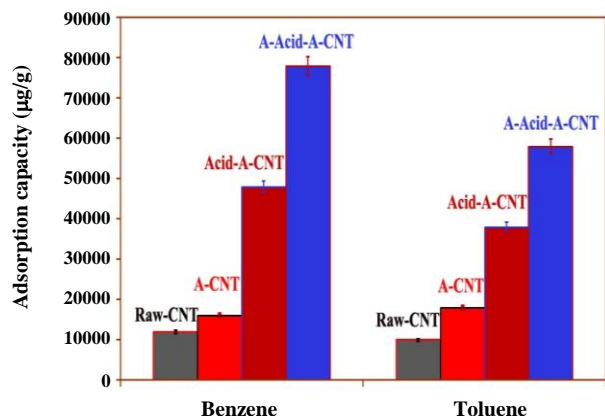


Fig. 7: The maximum adsorption capacities of the modified and unmodified MWCNTs for benzene and toluene.

can improve their adsorption capacity on the CNTs surfaces [1]. Since the improvement of structural integrity of the CNTs leads to improve their graphitic structure, it can enhance the π - π interaction between the CNTs and the aromatic VOCs and therefore increase their adsorption capacity for these aromatic VOCs [20, 33-35]. As mentioned above, I_D/I_G ratio for both A-CNT and A-Acid-A-CNT reduced as a result of the annealing treatment of the CNTs. It seems that the annealing treatment under He flow at 1000°C can lead to a decrease in defects on the CNTs surfaces and thus an increase in their adsorption capacity for the aromatic VOCs such as benzene and toluene due to the enhancement of the π - π interaction between the CNTs and these VOCs. Therefore, it can be accepted that the adsorption capacity of the CNTs for the aromatic VOCs such as benzene and toluene depends on both their specific surface area and structural integrity. Moreover, the acid treatment can more considerably improve the adsorption capacity of the nanotubes as compared to the annealing treatment [36]. Also, the annealing treatment is an energy-consumed process although it can improve the adsorption capacity adsorption of the CNTs.

CONCLUSIONS

MWCNTs surfaces were sequentially modified for thrice and the adsorption of toluene and benzene on the surfaces of the unmodified and modified carbon nanotubes was investigated. The results of the FT-IR and Raman spectra and the measurements of BET specific

surface areas of the unmodified and modified MWCNTs showed that the nitric acid treatment led to form the functional groups and defects on the carbon nanotubes surfaces and increase their specific surface areas. According to the results of the FT-IR and Raman spectra, the annealing treatments removed the functional groups and defects from the carbon nanotubes surfaces and therefore improved the structural integrity of the MWCNTs. The improvement of the structural perfection of the MWCNTs can also enhance the π - π interaction between the carbon nanotubes and the toluene/benzene.

Measurements of the maximum adsorption capacities of the unmodified and modified MWCNTs revealed that both acid and annealing treatments lead to an increase in the adsorption capacity of the carbon nanotubes for both the benzene and toluene adsorbates. It can be rationally concluded that the adsorption of the aromatic organic adsorbates such as benzene and toluene on the CNTs surfaces is influenced by not only the specific surface area but also the structural integrity of the CNTs. Additionally, the acid treatment can more efficiently enhance the adsorption capacity of the CNTs as compared with the annealing treatment. Also, the annealing treatment is an energy-consumed process although it can enhance the adsorption capacity adsorption of the carbon nanotubes.

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