

An Evaluation of the Adsorption Potential of MWCNTs for Benzene and Toluene Removal

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Abstract:

In order to evaluate the adsorption potential of multi-walled carbon nanotubes (MWCNTs) for benzene, toluene and xylenes (BTX), the adsorption capacities of benzene and toluene on two different MWCNTs were measured using a gas-chromatography (GC) and then compared with each other. Fourier transform infrared (FTIR) was employed to investigate the presence of functional groups on the carbon nanotubes surface. The MWCNTs were also characterized by Raman spectroscopy and scanning electron microscopy (SEM) techniques and their specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method. FTIR spectra proved the presence of functional groups on the surface of both two different MWCNTs. Generally, the results revealed that the MWCNTs with larger specific surface area and higher crystallinity have higher adsorption capacities for both benzene and toluene. Moreover, as compared with conventional adsorbents like the activated carbon, the carbon nanotubes have the advantages such as selectivity to aromatic volatile organic compounds such as BTX.

Keywords: Removal of BTX, MWCNTs, Nano-adsorbent, Adsorption capacity, Specific surface area.

1. INTRODUCTION

Removal of volatile organic compounds (VOCs) especially benzene, toluene and xylenes (BTX) is an important issue in fields of environmental conservation and health because of their influence on ecosystems and their potential for human health threat [1-3]. Depending on concentrations, flow and temperature of these contaminants, methods such as adsorption, condensation, thermal oxidation and catalytic oxidation are used to remove VOCs [4]. Adsorption process is one of promising

and economical methods for eliminating VOCs pollutants particularly at low concentrations [5]. In this method, VOCs pollutants (adsorbates) are chemically or physically adsorbed on adsorbents. Physical adsorption process has attracted more interest because adsorbents can be reduced and reused in this process [6].

Conventional adsorbents such as activated carbon have disadvantages. For example, activated carbon is faced with problems such as combustion risk, blocking of its pores due to polymerization of some VOCs catalyzed by ashes present on its surface,

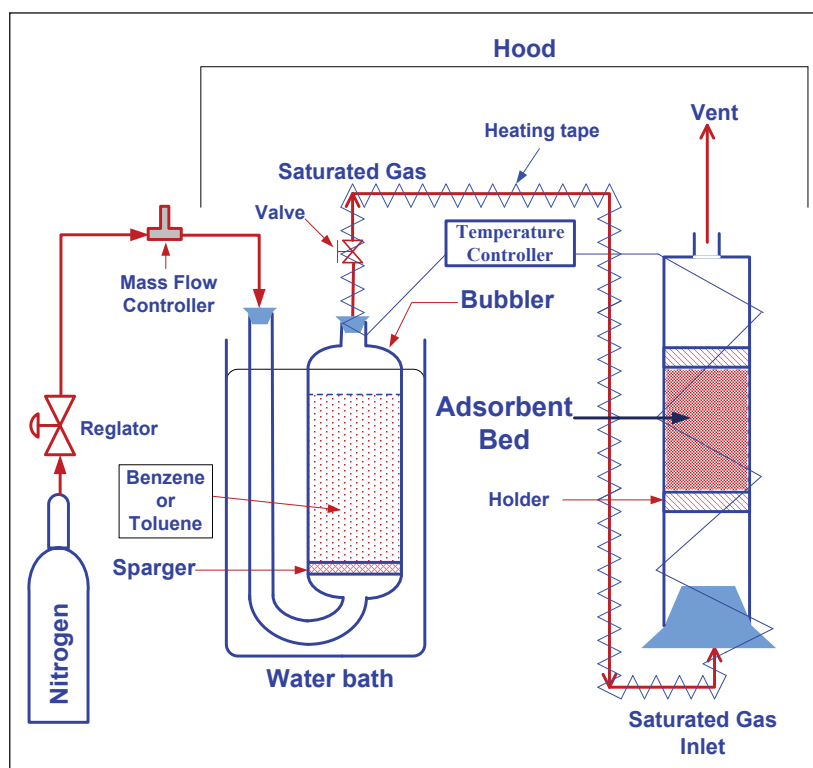


Figure 1: Schematic diagram of the experimental setup used to measure maximum adsorption capacity of the MWCNTs.

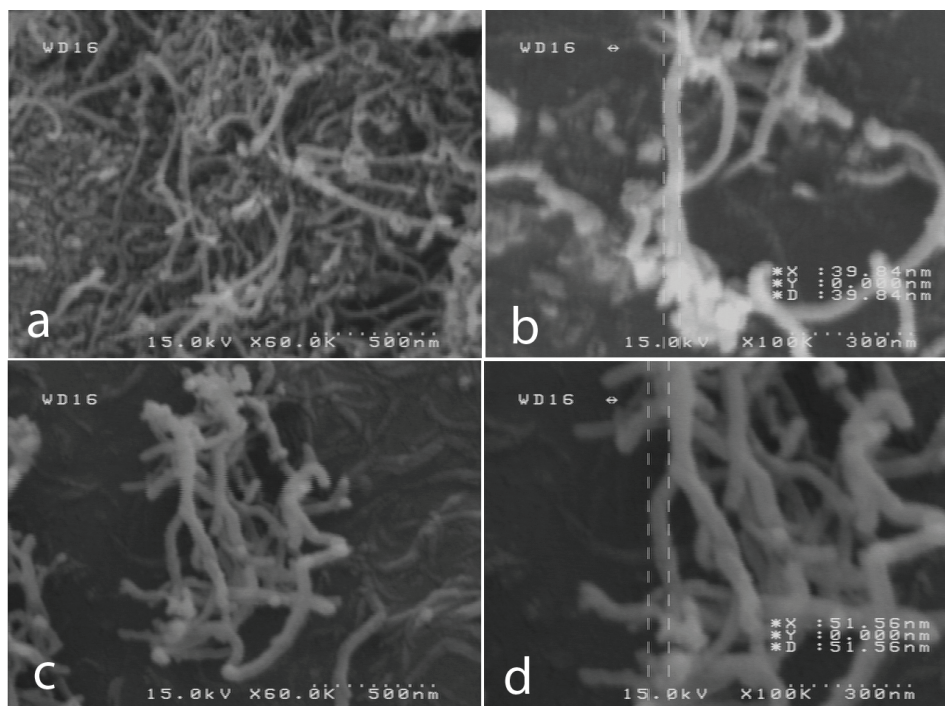


Figure 2: FESEM images of (a) MWCNT-Ir; (b) MWCNT-Ir with high resolution, (c) MWCNT-Ch and (d) MWCNT-Ch with high resolution.

little selectivity, high-temperature regeneration and adsorption of moisture. Therefore, researchers are increasingly trying to find new adsorbents for elimination of VOCs from environmental samples. Carbon nanotubes (CNTs) are promising candidate due to their unique properties [2-3, 7-9].

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 [10-11]. CNTs have high surface area, hydrophobic property and chemical and thermal stability. Therefore, they can be suitable adsorbents for VOCs [2-3, 12].

In this study, two types of multiwall 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. The MWCNTs were characterized by Raman spectroscopy and scanning electron microscopy (SEM) techniques and their specific surface areas were also measured using the Brunauer–Emmett–Teller (BET) method. Adsorption capacities of benzene and toluene on the

MWCNTs were measured and then compared with each other.

2. EXPERIMENTAL

2.1. Characterization of MWCNTs

MWCNTs were purchased from Research Institute of Petroleum Industry (Iran) and Shenzhen Nanotech Port Co. Ltd (China) which hereafter are denoted as MWCNT-Ir and MWCNT-Ch, respectively. Field emission scanning electron microscopy (FESEM, Hitachi, S-4160) was used to investigate morphology and size of the nanotubes. Measurements of surface areas of the MWCNTs were performed by a ChemBET-3000 chemisorption apparatus manufactured by Quantachrome. An Almeg Thermo Nicolet Dispersive Raman Spectrometer with the second harmonic of a Nd:YLF laser (532 nm) was also employed to obtain Raman spectra of the MWCNTs.

2.2. Measurement of adsorption capacity

Schematic diagram of the experimental setup

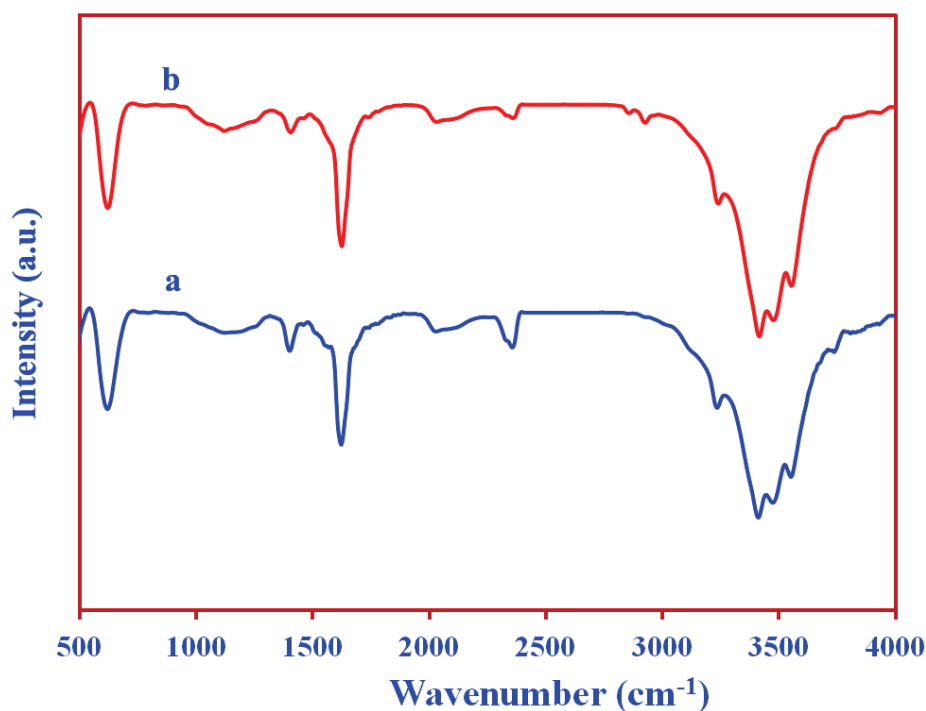


Figure 3: FTIR spectra of (a) MWCNT-Ir and (b) MWCNT-Ch.

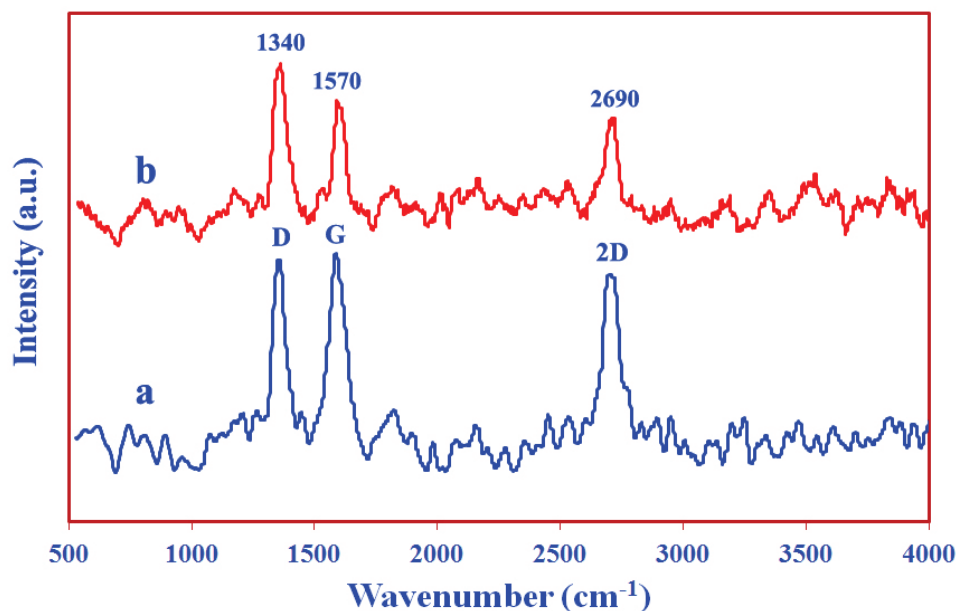


Figure 4: Raman spectra of (a) MWCNT-Ir and (b) MWCNT-Ch.

utilized to measure maximum adsorption capacity of benzene and toluene on the MWCNTs are shown in Figure 1. A flow of nitrogen gas with a controlled certain flow rate, was saturated with benzene/toluene at certain temperature (here 25°C) using a saturator containing benzene/toluene. In order to adsorb benzene/toluene on the MWCNTs, the outlet gas saturated was then passed through the adsorption bed containing 0.5 gr of MWCNTs for 2 h. In this case, it has been experimentally proved that the MWCNTs are saturated with benzene/toluene after 2 h of exposure to the saturated nitrogen.

The temperature of the saturated nitrogen was held at 25°C through path passing (from bubbler outlet to vent). In order to measure the quantities of benzene/toluene adsorbed on the MWCNTs, the saturated MWCNTs were mixed with carbon disulfide (CS₂) and then this mixture was well stirred and maintained overnight at 0°C. Thus, the benzene/toluene adsorbed on the MWCNTs were extracted in CS₂ and their quantities were determined using gas-chromatography (GC). Lastly, the maximum capacity of the MWCNTs for adsorption of benzene/toluene, was estimated and reported as micrograms of adsorbate per grams of adsorbent (µg/g).

3. RESULTS AND DISCUSSION

3.1. FESEM images of the nanotubes

FESEM technique was employed to study the structural order of the nanotubes and their mesh and also estimate their sizes. Figure 2 presents the FESEM images of the different MWCNTs with various resolutions. According to these images, the average diameters of MWCNT-Ir and MWCNT-Ch were about 39 and 51 nm, respectively. The sizes of MWCNT-Ir and MWCNT-Ch were also 30-45 and 42-55 nm, respectively. As it is observed, both MWCNT-Ir and MWCNT-Ch have an entangled structure and a random arrangement. This random arrangement leads to microcavities and even macrocavities in the bulk of the nanotubes. Generally, the structure order, mesh, and size of the nanotubes can dramatically influence on their adsorption capacity [13].

3.2. FTIR Spectra of the nanotubes

In Figure 3, FTIR spectra of MWCNT-Ir (a) and MWCNT-Ch (b) are presented. The peak at about 1580 cm⁻¹ is attributed to C=C stretching mode. This peak is indicative of presence of the

functional groups and defects on the MWCNTs surface that have probably formed the duration of the synthesis and purification processes [14-15]. The peak observed 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 C=O stretching mode, indicative of the presence 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 the MWCNTs can indicate the presence of carboxyl groups on the nanotubes surface [14-15].

3.3. Raman Spectra of the nanotubes

Figure 4 shows the Raman spectra of the MWCNTs. Three peaks at about 1340 , 1570 and 2690 cm^{-1} are observed in both spectra which called D-band, G-band and 2D-band, respectively. The G- and D-bands are attributed to the tangential stretching of sp^2 -bonded carbon atoms in graphene-like structures and the vibrations of sp^3 -hybridized carbons or carbon atoms with dangling bonds at disordered sites, respectively. The D-band appears in Raman spectrum as a result of the presence of defects and functional groups on the surface of the nanotubes. Therefore, the ratio of the intensity of D band over that of G band (I_D/I_G) is widely exploited to characterize the quantities of defects in the nanotubes [14, 15]. As it is observed, the

I_D/I_G ratio of MWCNT-Ch with value of around 1.2 is larger than that of MWCNT-Ir with value of around 0.98, indicating that the quantity of the defects on the surface of MWCNT-Ch is higher than that on the surface of MWCNT-Ir. Finally, the 2D-band corresponded to the first overtone of the D mode, is often associated with the degree of nanotube crystallinity [14, 15].

3.4. BET specific surface areas of the nanotubes

Since the specific surface area of an adsorbent has a significant influence on its adsorption capacity, the measurement of this parameter for the adsorbents used here, was vital to study their adsorption properties [13]. In Figure 5, BET specific surface areas of MWCNT-Ir and MWCNT-Ch are exhibited. As it is seen, the specific surface areas of MWCNT-Ch and MWCNT-Ir are $125 < 195\text{ m}^2/\text{g}$, respectively. The BET surface of MWCNT-Ir was larger than that of MWCNT-Ch because the external diameter of MWCNT-Ir was smaller than that of MWCNT-Ch (see Figure 2).

3.5. Adsorption capacities of nanotubes

Figure 6 shows the maximum adsorption capacities of MWCNT-Ch and MWCNT-Ir for benzene and toluene. As it is observed in this Figure, the adsorption capacities of MWCNT-Ch and MWCNT-Ir for benzene are 8000 and $12000\text{ }\mu\text{g/g}$ and for toluene are 6000 and 10000

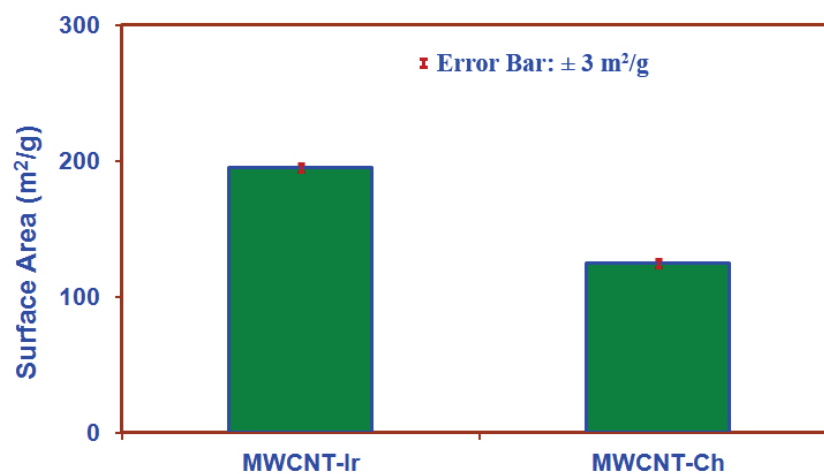


Figure 5: BET specific surface areas of the MWCNTs (Error Bar: $\pm 3\text{ m}^2/\text{g}$).

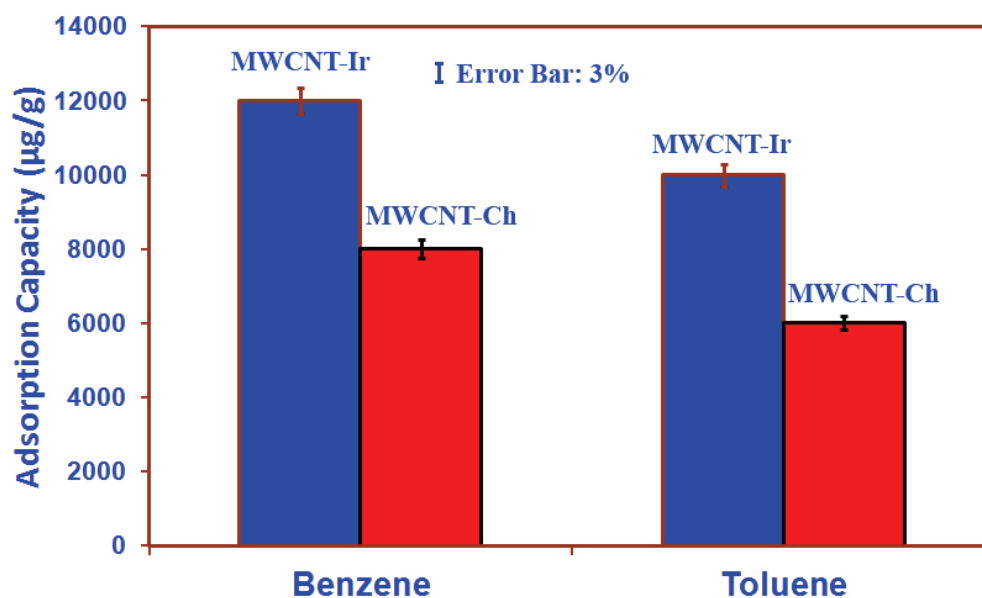


Figure 6. Maximum adsorption capacities of MWCNT-Ch and MWCNT-Ir for benzene and toluene (Error Bar: 3%).

µg/g, respectively. For both benzene and toluene, the adsorption capacity of MWCNT-Ir is higher than that of MWCNT-Ch. As mentioned above, the specific surface area of MWCNT-Ir is larger as compared with that of MWCNT-Ch. It has completely been accepted that for the nanotubes, the more specific surface area, the more adsorption capacity [13]. However, the higher adsorption capacity of MWCNT-Ir not only can be ascribed to their higher specific surface area but also it may be attributed to their higher crystallinity and more structural integrity as compared with those of MWCNT-Ch [2, 13].

According to other researchers [16], the structural defects of the nanotubes act as active sites for adsorption of contaminants and even the adsorbate molecules can chemically be adsorbed on these active sites. Therefore, the presence of the structural defects on the surface of the nanotubes often leads to an increase in their adsorption capacity. However, for the adsorption of the aromatic VOCs on the nanotubes, the structural imperfections reversely cause the decrease of the adsorption capacity [2]. Sone and et. al. [2] have experimentally shown that the carbon nanotubes with high structural crystallinity and integrity can efficiently adsorb

the aromatic VOCs such as benzene and toluene. It seems that the π - π interaction between the nanotubes and the aromatic VOCs like benzene and toluene, enhances the adsorption of these adsorbates on the nanotubes [2]. The structural integrity and crystallinity of the nanotubes lead to a perfect graphitic structure, improving the π - π interaction between the nanotubes and the aromatic VOCs [17-18]. Moreover, it seems that the π - π interaction between the nanotubes and toluene is weaker than that between the nanotubes and benzene because toluene has a methyl group. Therefore, the adsorption capacity of toluene was lower than that of benzene for both MWCNT-Ir and MWCNT-Ch (Figure 6).

According to above discussion, the I_D/I_G ratio in Raman spectrum corresponds to the quantity of the structural defects on the surface of the nanotubes. MWCNT-Ir had higher crystallinity and more structural integrity because the I_D/I_G ratio of MWCNT-Ir was larger than that of MWCNT-Ch. Therefore, it can be concluded that the perfect graphitic structure and high specific surface area led to the higher adsorption capacity of MWCNT-Ir as compared to that of MWCNT-Ch for both benzene and toluene.

4. CONCLUSION

To evaluate the adsorption potential of MWCNTs for benzene, toluene and xylenes (BTX), the maximum adsorption capacities of two different MWCNTs for benzene and toluene were measured and then compared with each other. MWCNT-Ir and MWCNT-Ch were characterized using SEM, FTIR and Raman spectroscopy techniques and their BET specific surface areas were also measured. The FESEM images revealed that both MWCNT-Ir and MWCNT-Ch had an entangled structure and a random arrangement, leading to microcavities and even macrocavities in the bulk of the nanotubes.

FTIR results indicated the presence of the functional groups on the surfaces of both MWCNT-Ir and MWCNT-Ch. According to Raman spectra, the I_D/I_G ratio of MWCNT-Ch was higher than that of MWCNT-Ir, resulting in that the number of the structural defects on the surface of MWCNT-Ir was less than that on the surface of MWCNT-Ch.

The measurements of specific surface areas showed that the BET surface of MWCNT-Ir with value of $125 \text{ m}^2/\text{g}$ was larger than that of MWCNT-Ch with value of $195 \text{ m}^2/\text{g}$. For both benzene and toluene, the maximum adsorption capacity of MWCNT-Ir was higher than that of MWCNT-Ch. It seems that the perfect graphitic structure and high specific surface area are two important parameters for the adsorption of benzene and toluene, so that the MWCNTs with larger specific surface area and higher crystallinity (MWCNT-Ir) had higher adsorption capacities.

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