THE ADSORPTION OF BENZENE, TOLUENE AND XYLENES (BTX) ON THE CARBON NANOSTRUCTURES: THE STUDY OF DIFFERENT PARAMETERS

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ABSTRACT

In this study, the adsorption of benzene, toluene and xylenes (BTX) as appropriate representatives of volatile organic compounds (VOCs) on seven types of different carbon nanostructures were investigated. In this research, multi-walled carbon nanotubes (MWNT1 and MWNT2), single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), carbon nanofibers (CNF), nanoporous carbon and MWNT-COOH, as well as activated carbon as a conventional sorbent for organic contaminant were studied. Nanostructures morphologies were studied by both Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The structure and surface properties of carbon nanostructures including surface area and pore volume were characterized by nitrogen adsorption isotherm at 77K using an ASAP 2010 analyzer accelerated surface area and BET method. Adsorption studies were conducted by passing air samples through the adsorbents in the glass column at an adjustable flow rate and finally trapping any adsorbed species which are not retained by the adsorbents in the column to a charcoal sorbent tube and analyzed by a GC system. The carbon nanofiber (CNF) demonstrated the highest capacity for adsorbing all BTX compared to the SWCNT, MWNT, nanoporous carbon, and MWNT-COOH, respectively. Different effective factors on the adsorption of organic compounds on the carbon nanostructures including pore characteristics, surface area, surface defects, and functional groups have been discussed. It was observed that, carbon nanostructures except MWNT-COOH had higher values of adsorption for BTX, compared to the activated carbon in spite of lower surface area.

KEYWORDS: Carbon nanotube (CNT); carbon nanofiber (CNF); nanoporous carbon; Volatile Organic Compound (VOCs); adsorption capacity.

1. INTRODUCTION

Carbon nanostructures are a relatively new class of synthesized carbonaceous material. They are considered to be promising candidates for many areas of applications including environmental applications such as membrane structures for water treatment, sensing, energy storage, targeted delivery of remediation agents, as well as special adsorbents for removal of hazardous contaminants [1,2]. The huge potential for production and industrial applications of carbon nanostructures have raised serious concerns over the potential environmental and health impact of these materials [3,4]. However, study and characterization of the adsorption properties of contaminants adsorbed on the carbon nanostructures may help on both potential environmental applications and understanding of the environmental impact of these new materials [2,5,6].

VOCs are a class of chemical pollutants in the environment that could cause severe health problems. Some of these pollutants like benzene, toluene, and xylene (BTX) are even known or suspected carcinogens and therefore, development of effective control strategies is needed [7-9].

Adsorption of contaminants on the different sorbents is the most important method for controlling VOCs emissions [10-12]. Activated carbon is used as a conventional sorbent which has received a great deal of attention in the field of environmental control. Such a sorbent has high removal efficiency with low cost as well as the ability to be regenerated. However, activated carbon is unable for selective adsorption of aromatic compounds [13]. It has amorphous structure and has complex physicochemical properties too [14]. Also, the adsorptive capacity of activated car-
carbon is adversely affected by the density of surface active sites, the activation energy of adsorptive bonds, the slow kinetics and non-equilibrium of sorption in heterogeneous systems, and the mass transfer rate to the sorbent surface as well as its large dimensions [1].

To overcome above restrictions, new carbon materials have been proposed as appropriate candidates for controlling VOCs emissions.

Several studies have been conducted to evaluate the adsorption of organic contaminants by carbon nanostructures [2, 6, 13-35]. For example, Sone et al. [13] showed that, CNTs can be used as efficient adsorbents for selective eliminating aromatic VOCs. Liu et al. [17] found that, SWCNTs have a large surface area and high adsorption and desorption efficiencies for collecting VOCs with low boiling points and strong volatility.

Different studies have provided experimental evidences that, CNTs have high surface area to volume ratio, controlled pore size distribution, peculiar morphology, and the ability to manipulate the surface chemistry, which overcomes many of the above mentioned intrinsic limitations [31, 33, 36, 37]. Carbon nano-adsorbents have more adsorption capacity than activated carbon [15, 16]. Sorption of VOCs on CNTs can provide a better understanding of the relationships between sorption potential and carbon structures, because of its well-defined structures [14].

Nevertheless, most of these studies have been performed on the removal of organic pollutants from water [23-35]. A few of them have concentrated on the removal of contaminants from air [3, 14, 18-22]. Moreover, in most studies, carbon nanotubes (CNTs) have been used as adsorbents and other carbon nanostructures like carbon nanofiber as well as carbon nanoporous have been studied very limited [19-21]. On the other hand, as carbon nano-structures can vary significantly in shape, size, morphology, and impurity (e.g., metal, amorphous carbon and O-containing groups), which can influence their adsorptive properties, more studies are still required for a better understanding of the molecular interactions of carbon nanotubes and organic contaminants with different properties.

This study has been concentrated on testing the adsorption of BTX as a representative of VOCs to six types of different carbon nanomaterial with the ultimate goal of their applicability in a respirator cartridge for volatile organic vapours. Through this study, a comparison of different kinds of carbon nanomaterials including MWNTs, SWCNTs, CNFs, and carbon nanoporous have been compared to activated carbon as a conventional sorbents for organic contaminants.

For generation of model air samples, 84 microliter of the BTX mixture injected into a 5-L tedlar-bag using a 100 ML syringe previously filled with hydrocarbon free air under ambient pressure. Then, the bag injection valve was immediately closed and heated at 80 °C in an oven for 1h.

### 2.2. Carbon nanostructures preparation

Throughout this study, different types of the carbon nanostructures including; multi-walled carbon nanotube (MWNT1 and MWNT2), DWCNT, SWCNT, CNF, Nano-porous carbon, and MWNT-COOH were used as adsorbents. Adsorption of BTX on the carbon active (CA) was also measured to show a comparison between different adsorbents with carbon nano-structures and without it.

Carbon nanostructures used in this study were manufactured by the Research Institute of Petroleum Industry (RIPI). Pure CNTs were prepared through the chemical catalytic vapor deposition (CCVD) method as described elsewhere [38].

Purity of nanotubes is an important factor that influences their overall adsorptivity. These impurities could also be highly adsorbent materials and ignoring their presence could greatly misrepresent the adsorption properties of nanotubes [19]. So, two-steps purification was used for removal of the catalytic particles and the carbonaceous impurities such as amorphous carbon, carbon nanoparticles, graphitic carbons, and the other forms of carbon that are unavoidable by-products of the synthesis processes.

The purity of the CNTs was about 95%, with diameters and lengths ranging between 30–50 nm and 5–15 nm, respectively. The difference between two kinds of MWNT1 and MWNT2 was in their diameter which were 10-20 and 5-10 nm, respectively.

Carbon nanofiber was produced by methane decomposition over monometallic Ni and bimetallic Ni-(Cu, Mo) catalysts based on the nanoporous MgO support at 570°C flowing a gas mixture of CH₄/N₂ over the catalyst samples [40].

Carbon nanoporous was produced by “host and guest” technique. For this work, sucrose was carbonized inside the pores of the MCM-41 template at 900 °C and then MCM-41 template was completely removed by HF solution [39].

### 2.3. Characterization of carbon nanostructures

The structure and surface properties of carbon nanostructures including surface area, dimensions (diameter and length), pore volume, and surface carbon properties were characterized by the following instruments and techniques:

Scanning Electron Microscope (SEM, Cambridge S-360 operated at 16 kV and 2.5 A) and high resolution transmission electron microscope (HRTEM, LEO-912-AB operated at 120kV) were used for studying the morphologies and microstructures of resulted nanostructures.

Pore size distribution and specific surface area were determined by nitrogen adsorption isotherm at 77K using...
a Micromeritics ASAP 2010 analyzer accelerated surface area and BET method.

Situation of disordered carbon and defects on carbon nanomaterials were evaluated by determining the intensity ratios of D- to G-bands through Raman spectroscopy.

2.4. Adsorption experiments

Figure 1 shows the schematic of the experimental set up for adsorption experiments. Adsorption study was conducted using a set up similar to that of Sone et al [13]. Before doing the adsorption study, two-step purification was used for removal of the catalytic particles and the carbonaceous impurities such as amorphous carbon, carbon nanoparticles, graphic carbons, and the other forms of carbon that are unavoidable by-products of the synthesis processes.

![Schematic of the experimental set up for adsorption experiments](image)

Then, the adsorbents were placed into a 9 cm length glass column (internal diameter 10 mm) with homogeneous packing. For holding adsorbents in place, silane-treated glass wool and propylene filter were used at the two ends of the column. The final mass of adsorbents in each column was approximately 60 mg. The inlet end of the adsorbents-column was connected to the sample bag. The other end was connected to the charcoal sorbent tubes for air sampling (Sorbent Tube, Anasorb CSC, SKC) to trap any un-retained adsorbents.

The outlet end of the sorbent tube was connected to a SKC low flow pump and the air samples were passed through the adsorbents in column at an adjustable flow rate.

To measure the amounts of BTX adsorbed on the charcoal, the tube was extracted by CS2. Analyses of BTX were performed by a Shimadzu GC system. The BTXs adsorbed on the adsorbents were estimated by subtraction of the BTX retained on the charcoal from the initial quantities injected into the sample bag. Adsorption experiments were conducted in quadruplicate for each sample.

3. RESULTS AND DISCUSSION

3.1. Characteristics of carbon nanostructures

Table 1 shows the physical characteristics of carbon nanostructures used in this study including their dimensions (diameter and length), ID/IG (ratio of amorphous carbon to crystalline carbon), pore volume and morphology information. Figure 2 and 3 show typical SEM and TEM images of the carbon nanostructures used in this study, respectively.

3.2. Adsorption of BTX on different carbon nanostructures

Average values for adsorption (g BTX/g adsorbents) are shown in Figure 3. The carbon nanofiber (CNF) demonstrated the highest capacity for adsorbing all BTX including benzene, toluene, o-xylene, m-xylene and p-xylene. The adsorption capacity of the CNFs for adsorbing benzene, toluene, o-xylene, m-xylene and p-xylene were 0.04143, 0.05288, 0.05826, 0.05825, and 0.05825 g/g, respectively. Thus, the CNF showed an affinity order of m, p-xylene>o-xylene > toluene > benzene and for other carbon nanostructures their affinity order were o-xylene>m-xylene>p-xylene>toluene > benzene and this order was the same as in the study of Sone [13].

For benzene, the adsorption capacity order was as: CNF > SWCNT > CA > nanoporous carbon> MWNT1 > MWNT2 > MWNT-COOH and for toluene and xylenes, the capacity order was as: CNF > SWCNT > MWNT1 > MWNT2 > CA > nonporous carbon> MWNT-COOH.

![TABLE 1 - Specific surface area and pore volume of studied carbon nanostructures](image)
FIGURE 2 - Typical SEM (Left) and TEM (Right) image of carbon nanostructures.

MWNT

SWCNT

CNFs

FIGURE 2 - Typical SEM (Left) and TEM (Right) image of carbon nanostructures.
Adsorption of a particular compound by a particular adsorbent depends on a number of factors including pore characteristics, molecular size, vapour pressure, or volatility of the compound being adsorbed, surface area of adsorbent, surface defects, and surface treatment (functional group on the adsorbent surface).

3.3. Pore characteristics and molecular size

Pore characteristics and molecular size play a key role in the efficient adsorption. If the molecule is too big to fit into the micropore, the adsorption capacity is reduced. Since the molecular sizes of all adsorbed species were smaller than 1 nm, probably micro porosity seems to be one of the most important parameters affecting the performance of adsorbents to the adsorption of BTX.

As it can be seen form Figure 4, on contrary to the activated carbon with a wide pore size distribution, in all studied nanostructures, the pores have been controlled in the range of mesopore (2–50 nm). So, in carbon nanofiber, SWCNT, and MWNT with micropore volume of 0.0049, 0.00343 and 0.000505 cm³/g respectively, there is an effective surface area and pore volume for selective adsorption of BTX with molecular size smaller that 1 nm.

Some studies showed that, SWNT has a microporous nature unlike to the mesoporous nature of MWNT [37, 41, 42]. Meanwhile, in this study both MWNTs and SWNCTs were more mesoporous than microporous. Finally, in the most studies, CNTs porosity could not be applied to explain its high adsorption [5].

3.4. Specific surface area

Surface areas of carbon nanostructure including CNFs (188.9), SWCNT (303 m²/g), MWN Ts (133 m²/g), and carbon nanoporous (704 m²/g) are generally lower than that of ACs (1150), but, the adsorption capacity of all carbon nanostructures, except for functionalized MWNT with COOH are higher than activated carbon (with micropore volume of 0.04450 cm³/g). Thus, surface area may not be a direct parameter to predict organic chemical-CNT interactions [5]. Therefore, the effect of surface area may be negligible.

3.5. Surface defect

Raman spectroscopy is a very valuable tool for the characterization of carbon-based nanostructures. All carbon forms contribute to the Raman spectra consists of two characteristic bands, namely, the G-band at 1583 cm⁻¹ and the D-band at 1345 cm⁻¹. The D-band is usually attributed to the presence of amorphous or disordered carbon due to finite or nano-sized graphitic planes and other forms of carbon, such as rings along with defects on the nanotube walls. The G-band originates from in-plane tangential stretching of the carbon–carbon double bonds in the graphene sheets [43, 44]. The intensity ratio (R) of the D-band to G-band is used to evaluate the defects of CNTs. Also, relatively lower values of intensity ratio means less defects and higher quality CNTs [45].

As it can be seen from Figure 5, the intensity ratios of D- to G-bands are 0.1, 0.46, and 1.17 for SWCNT, MWNT and CNFs, respectively. Therefore, the higher adsorption of CNFs can attribute to the higher ratio of ID/IG, revealing large amount of disordered carbon and defect on CNFs. On the other hand, in another study [14] mentioned that selectivity/affinity for adsorbing the aromatic VOCs decreased and finally disappeared as the ratio of the crystalline to amorphous carbon is decreased.

However, the balance between these two opposite effects deserves further study. The higher R (ID/IG) ratio of
FIGURE 4 - Pore size distribution for MWNTs, SWCNTs, CNFs and Activated carbon
FIGURE 5 - Raman spectra of (a) SWCNT (b) RBM of SWCNT (c) MWNT (d) Oxidized MWNT (e) CNF
multwall carbon nanotubes compared to the single walled carbon nanotubes indicates more structurally disordered walls and defects on the MWNTs. In spite of this, adsorption of SWCNT was higher than MWNTs, probably because the slightly higher surface area and supermicropores volume is dominant to the structural defect on MWNTs wall. Meanwhile, smaller adsorption capacity of MWNT could be due to the fewer ratio of the crystalline (G-band) to amorphous carbon (D-band), contrary to the SWCNT.

3.6. Surface treatment

Diaz et al [48] showed that mineral impurities play a positive key role in the adsorption of alkenes, chlorinated compounds, and benzene on activated carbon. As mentioned earlier, all adsorbents were pre-treated through two step purification and all impurities such as amorphous carbon, carbon nanoparticles, soot as well as the other forms of by-products were removed from the surface of nano adsorbents. So, it seems that, lower adsorption capacity of adsorbents obtained in this study, in comparison with another study [14], is probably due to existence of such impurities.

Functionalization of CNTs was aimed for surface treatment and easy processing; however at the same time, their adsorption properties with organic chemicals can be altered greatly [5].

In this study, functional group of -COOH was intentionally added via oxidation through the method described elsewhere [43]. As it can be seen, from Figure 3, adsorption capacity of functionalized MWNT with -COOH has been decreased in comparison with pristine MWNT and MWNT-COOH. Among the studied adsorbents, functionalyzed CNTs have the lowest adsorption capacity.

The reason behind this reduction in adsorption capacity is that, adding functional group to CNTs will lead to the increased oxygen content, decreased surface area, increased diffusion resistance, reduction of the accessibility, affinity of CNT surfaces for organic chemicals, and finally reduced adsorption of nonpolar hydrocarbons due to reduced hydrophobicity [5].

3.7. Effect of diameter

Comparison of adsorption capacity of MWNTs showed that, MWNT1 (16 nm) had slightly higher capacity than MWNT2 (5 nm), showing that adsorption increases with the increased diameter. For molecules with planar structures like benzene, this can be attributed to the better contact of CNTs and chemicals [49, 50].

4. CONCLUSION

This study showed that, carbon nanostructures including carbon nanofiber, SWCNT, and MWNTs have higher values of adsorption capacity for BTX compared to the activated carbon, except for functionalized MWNT with COOH functional group.

This is in agreement with some other studies showing that, CNTs especially SWCNTs have the higher adsorption capacity [15, 16, 26]. In spite of having a lower surface area, they are more efficient adsorbents than activated carbon. Meanwhile, if in some studies there are some opposite findings in which activated carbon has higher adsorption capacity than CNFs or CNTs; it is probably due to the mesoporous structure of that specific type of activated carbon.

Higher BET surface area of SWCNTs (303 m²/g in comparison with 133 m²/g for MWNT) and its slightly higher micropore volume as well as higher crystallization ratio of SWCNT can be contributed to its higher adsorption capacity.

It seems that, both CNT surface area and porosity, not just diameter alone, could be used to explain CNT adsorption characteristics completely. The balance among different mechanisms (sometimes opposite effects) for adsorption of organic compounds on the carbon nanostructures needs further study.

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REFERENCES


