Short Communication

Modeling of Benzene Adsorption in the Gas Phase on Single-Walled Carbon Nanotubes for Reducing Air Pollution

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Abstract:
Air Pollution has always been a major problem in metropolises. Volatile organic compounds are one of the major pollutants that are caused by incomplete combustion of fuels in vehicles and gasoline evaporation, especially in fueling stations. Removing these pollutants through traditional methods has always been considered. The paper investigates and studies chemical adsorption behavior of benzene on single-walled carbon nanotubes (9, 9) and (7, 7) in the gas phase by the Gaussian 09 program and using quantum chemical calculations and density functional theory method (DFT). First, carbon nanotubes were generated by a nanotube modeler, and then benzene was passed through the inside and outside of the nanotubes. After that, the absorption energies were calculated using the B3LYP calculation method and 6-31G basic set at different time intervals. Next, the amount of structure energy for carbon nanotube and benzene was separately calculated by the Gaussian 09 program. Using the existing equations, the absorption energy at different time intervals was obtained as follows: For 0.5, 1, 1.5, and 2 angstrom outside the nanotube (7, 7), 14.25, 11.22, 3.32, and 0.78 electron volts (eV); for the nanotube (9, 9), -776.34, -807.12, -817.16, and -844.62 electron volts (eV); for the inside of the nanotube (7, 7), 14.66, 7.76, 7.30, and 7.27 electron volts (eV); and for the nanotube (9, 9), -813.69, -813.97, -816.68, and -819.33 electron volts (eV), respectively. As the results show, when the diameter of the nanotube increases, the energy absorption decreases. Therefore, the carbon nanotube (7, 7), which has a smaller diameter than the carbon nanotube (9, 9), will be more effective in absorbing and removing benzene from the air.
Keywords: *Air pollution, Carbon nanotubes, Volatile organic Compounds, Benzene.*

1. INTRODUCTION

Air pollution is one of the phenomena in the modern life caused by pollutants from human circadian activities. These pollutants are resulted from the production of foods, industrial goods, various commodities and energy. Perhaps the main cause of air pollution is incomplete combustion due to a lack of full fuel delivery or improper air-fuel ratio [1].

One of the major pollutants is volatile organic compounds caused by the incomplete combustion of fuels in vehicles and evaporation of petrol, especially in the refueling stations [2]. Industrial processes are the main sources of benzene in the environment. Benzene levels in the air can be elevated by emissions from burning coal and oil, benzene waste and storage operations, motor vehicle exhaust, and evaporation from gasoline service stations. Once in the air, benzene reacts with other chemicals and breaks down within a few days. Benzene in the air can also be deposited on the ground by rain or snow [3].

It is a known human carcinogen, with a substantial number of case reports and epidemiological studies providing evidence of a causal relationship between occupational (chronic) exposure and various types of leukaemia [4].

Concurrent with the development of human knowledge about materials at the nanoscale and increased ability to work with nanostructures, nanotechnology gradually expands and global investment in this field also increases. Today, engineered nanomaterials and nanotechnologies are rapidly growing, and nanotechnology has positive impacts on many aspects of people's everyday life [5].

Carbon nanotubes have outstanding mechanical, structural and electrical properties. Due to their special electronic properties, superior mechanical strength, high flexibility, and dimensions, they have various applications in different fields. Moreover, new applications are increasingly added to carbon nanotubes [6].

These nanomaterials have been proven to possess good potential as environmental sensors or superior adsorbents for removing many kinds of organic pollutants such as dioxin and volatile organic compounds from air streams [9].

Adsorption of aromatic compounds such as benzene, poly aromatics, xylenes, chlorophenols, 1,2-dichlorobenzene, phenolic compounds, amino acids, natural organic materials, and dyes on carbon nanotubes have been studied theoretically and experimentally [7].

Extensive research has been performed in the world and Iran on the adsorption of volatile organic compounds such as benzene and toluene by carbon nanotubes from aqueous environments. Some examples are as follows: Benzene and toluene removal by carbon nanotubes from aqueous solutions by Bina Bijan et al. (2012) [8]; Adsorption of benzene, toluene, ethylbenzene and p-xylene by NaOCl-oxidized carbon nanotubes by Fengsheng Su et al. (2010) [9]; studies of Fei YU et al. (2012) [10]; and Thermodynamics of benzene adsorption on oxidized carbon nanotubes - experimental and simulation studies by Marek Wiśniewsk et al. (2012) [11].

Studies have also been done on the relationship between adsorption energy, diameter, length and other characteristics of carbon nanotubes. For example, Javad Beheshtian et al. (2009) studied the hydrogen adsorption energy on zigzag nanotubes (0, 5) and chiral (5, 5). They concluded that among these two types of nanotubes, zigzag ones (with lower diameter) have more adsorption energy [12]. M. Madani et al. (2012) studied CO adsorption on carbon nanotubes (4, 4) and (5, 5). They concluded that the amount of energy absorbed in nanotube (5, 5) with a greater diameter is lower than nanotube (4, 4) [13]. Bahram Shirvani Boroujeni et al. (2010) studied the adsorption behavior of an ammonia molecule on the outer surface of single-walled carbon nanotubes (0, 5), (0, 8), (5, 5) and (6, 6) using the density functional theory (DFT).

The calculated binding energies clearly show that the adsorption level depends on the nanotube diameter and the energy level is reduced by increasing the diameter [14]. H. Kataura et al. (1999), or the Kataura plot illustrates the relationship between the increase in adsorption energy and reduction of diameter in carbon nanotubes [15].

So far, several methods have been proposed to remove these pollutants from the air. By modeling

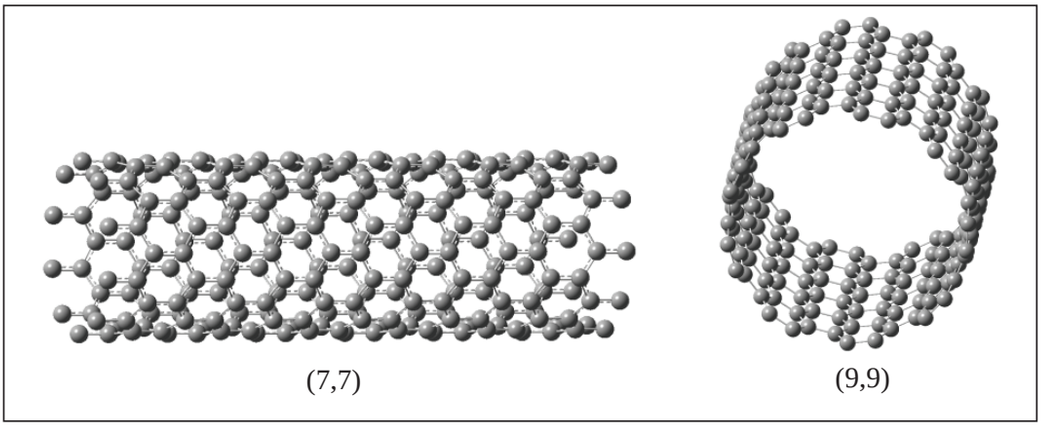

Figure 1: *Carbon nanotubes simulated by Nanotube modeler*

two types of carbon nanotubes with different inner diameters, this paper attempts to examine the possibility of benzene adsorption by carbon nanotubes from the ambient air.

2- MATERIALS AND METHODS

Today the DFT method is the standard model in many Gamess and Gaussian computational chemistry software systems. For modeling, this study used an 8-core computer system with 500GB of memory and a 2.3 GHz processor running Windows 7. Calculations were performed by Gaussian09.

Calculations were based on the density functional theory (DFT) because this method has a higher calculation speed compared to other methods with the same accuracy. The B3LYP method and the basic set of 6-31G (# B3LYP/6-31G) were used for optimization of structures and calculation of interaction energy. The energy adsorption level were calculated in different intervals for molecular structures of benzene, carbon nanotube (7, 7) with a diameter of 9.6°A, carbon nanotube (9, 9) with a diameter of 12.4°A and the combination of carbon nanotubes with molecular structures of benzene.

BELYP is a hybrid method in which the electron correlation energy is calculated from equation (1) [16]:

The Gaussian software was used to prepare input data and perform computing. Using a series of graphics software including Nanotube Modeler, HyperChem and GaussView, first the desired molecular geometry structure was plotted. Then, necessary commands for determining the needed calculations were entered. Finally, as the input file, it was introduced to Gaussian09, and in the next Gaussian step, calculations were presented as numbers by solving the Schrödinger electron equation.

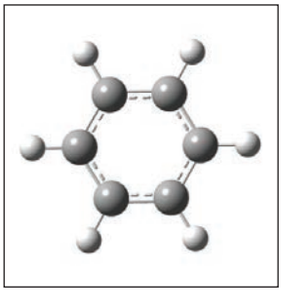

Figure 2: *Molecular structure of benzene plotted by Hyper Chem*

Figure (1) shows the carbon nanotubes simulated by Nanotube modeler and Figure (2) shows the geometry structure of the benzene molecule drawn by Hyper Chem and they were delivered to the main

$$E_{\mathrm{xc}}^{\mathrm{hybr}} = a_0 E_x^{\mathrm{HF}} + (1 - a_0) E_x^{\mathrm{LDA}} + a_{\mathrm{x}} \Delta E_x^{\mathrm{B88}} + E_c^{\mathrm{LDA}} + a_c \Delta E_c^{\mathrm{GGA}} \qquad (1)$$

$$a_0 = 0.2;\ a_x = 0.72;\ a_c = 0.81$$

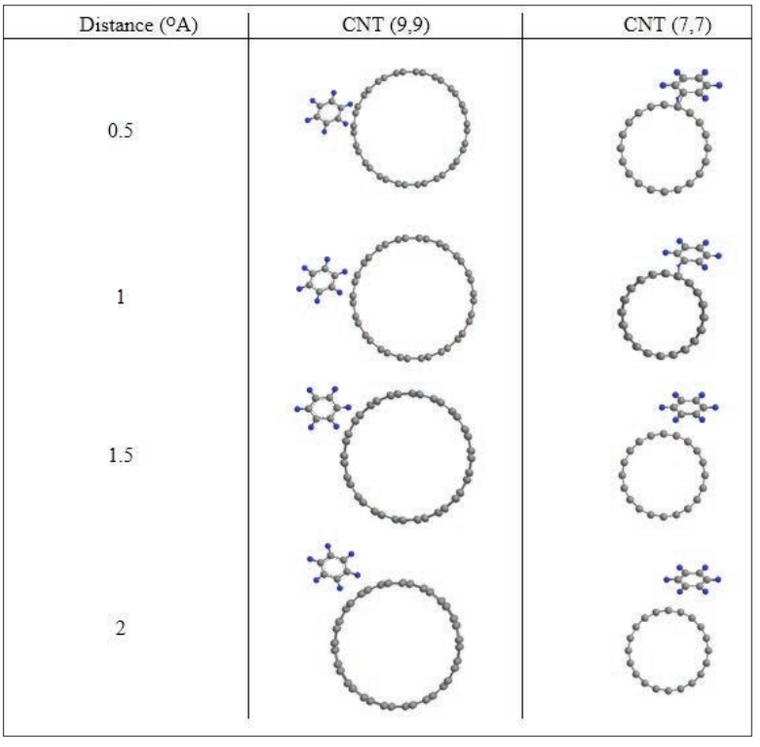

Figure 3: *Different modes of benzene adsorption by carbon nanotubes (outside of nanotube)*

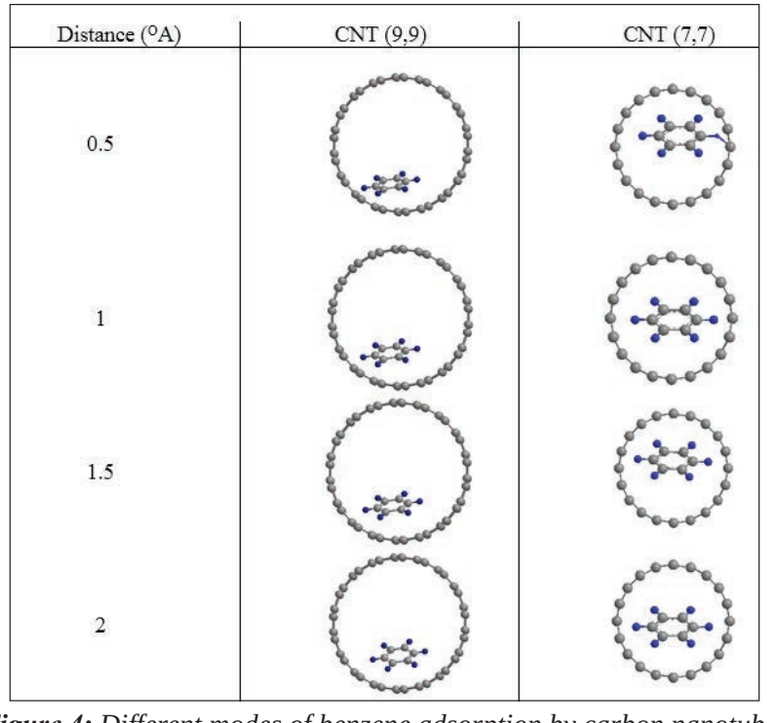

Figure 4: *Different modes of benzene adsorption by carbon nanotubes (inside of nanotube)*

Table 1: *Results of energy adsorption at different intervals and modes*

Optimized systems	*dt (°A)*	*Distance (°A)*	*Eads (eV) **
Outside of (7,7) – C6H6	9.6	0.5	14.25
		1	11.22
		1.5	3.23
		2	0.79
Inside of (7,7) - C6H6	9.6	0.5	14.66
		1	7.77
		1.5	7.30
		2	7.27
Outside of (9,9) – C6H6	12.4	0.5	-776.34
		1	-807.12
		1.5	-817.16
		2	-844.62
Inside of (9,9) - C6H6	12.4	0.5	-813.69
		1	-813.97
		1.5	-816.68
		2	-819.33

*1 hartree = 27.2107 eV

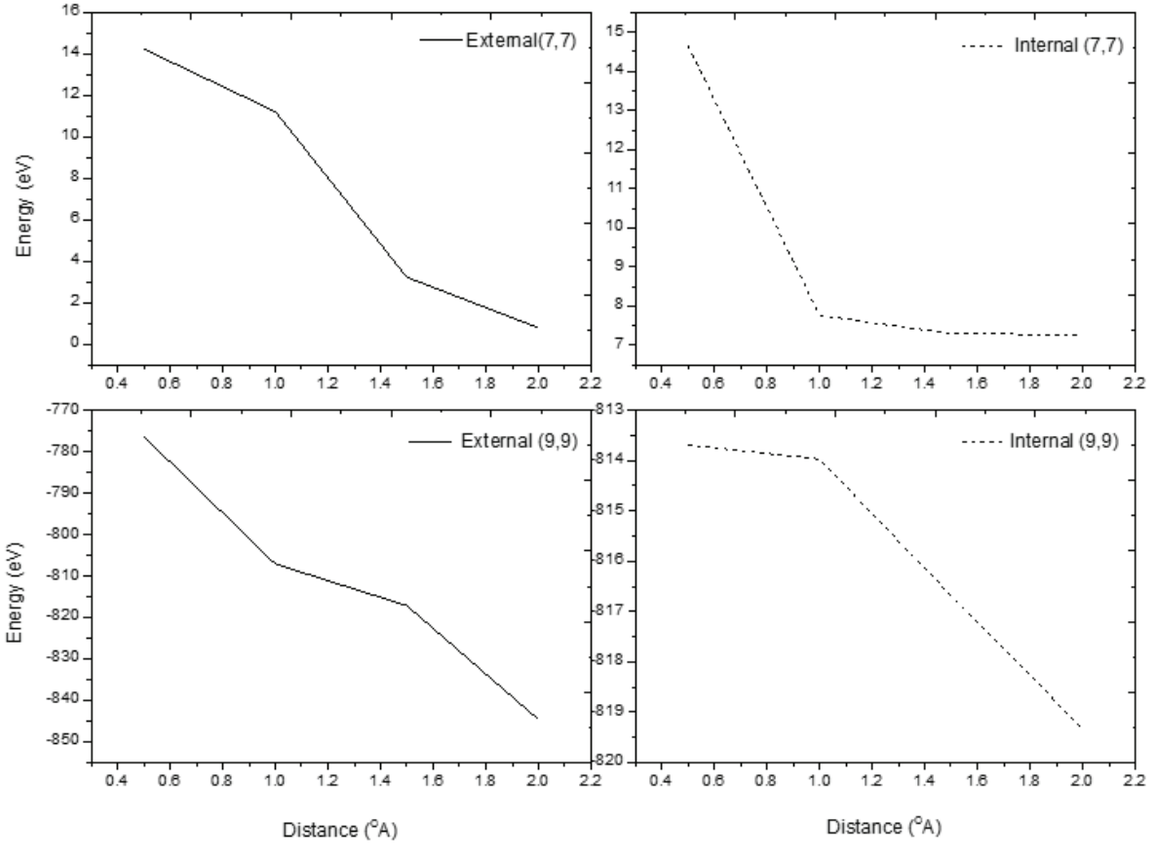

Chart 1: *Results of energy adsorption outside and inside of carbon nanotubes (7, 7) and (9, 9)*

program. Figures (3) and (4) show different modes of benzene passing at different distances, from inside and outside of the mentioned nanotubes for energy calculation.

In the next step, the structural energies for benzene and carbon nanotubes (9, 9) and (7, 7), were measured individually. Finally, adsorption energies were calculated using equation (2) [17] where Eads is adsorption energy, EB/CNT is total energy of nanotube and benzene, EB is benzene energy and ECNT is nanotube energy as the hartree unit.

$$Eads=EB/CNT-[ECNT+EB] \quad (2)$$

The calculation results of energy adsorption are presented in Table 1 and Chart 1.

3- DISCUSSION AND CONCLUSION

As observed in Table 1 and Chart 1, calculation of adsorption energy shows the adsorption of benzene on interior and exterior walls in both types of the modeled carbon nanotubes. Based on the calculations, the amount of energy absorbed at different intervals of 0.5, 1, 1.5, and 2 Å was 14.25, 11.22, 3.32, and 0.79 eV for outside of nanotube (7, 7); 776.34, -807.12, -817.16, and -844.14 eV for outside of nanotube (9, 9); 14.66, 7.77, 7.30, and 7.27 eV for inside of nanotube (7, 7); and -813.69, -813.97, -816.68, and -819.33 for inside of nanotube (9, 9), respectively.

The energy absorption increases with decreasing diameter .These results are in agreement with previous results indicating that gaseous molecules binding energy decreases as the diameter of (n,0) and (n,n) CNTs increases [18].The most favorable adsorption distances from the molecule to outside and inside of (7,7) and (9,9) CNTs are 0.5 Å, respectively.

Therefore, despite the fact that both types of the modeled nanotubes can absorb and remove the benzene pollutant from gas environments, CNTs (7, 7) with a lower diameter is more efficient than CNTs (9, 9).

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