Journal of Molecular Graphics and Modelling 57 (2015) 70–75

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Removal of trihalomethanes from aqueous solution through armchair carbon nanotubes: A molecular dynamics study

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ARTICLE INFO

Article history:
Accepted 23 January 2015
Available online 3 February 2015

Keywords:
Carbon nanotube
Graphene
Nanostructured membrane
Trihalomethane
Molecular simulations

ABSTRACT

Molecular dynamics simulations were performed to investigate the removal of trihalomethanes (THMs) including CH_3Cl, CH_2Cl_2 and $CHCl_3$ from aqueous solutions by armchair carbon nanotubes (CNTs) under induced pressure. The studied system involved the armchair CNTs embedded between two graphene sheets with an aqueous solution of THMs in the simulation box. An external pressure was applied to the system along the *z*-axis of the simulation box. Six types of armchair CNTs with different diameter were used in this work, included (4,4), (5,5), (6,6), (7,7), (8,8) and (9,9) CNTs. The results of molecular dynamics simulation display that the armchair CNTs behave differently relative to THMs and water molecules. The permeation of THMs and water molecules through the armchair CNTs was dependent on the diameter of CNTs and the applied pressure.

1. Introduction

Drinking water supply is one of the main concerns in countries. The drinking of low quality water causes health hazards in the community. Chlorination of water is one of the disinfection treatment methods [1–3]. This method is one of the most widely used disinfection processes because of low cost, easy utilization and good efficiency [4]. The main objective of chlorination is to kill microorganisms in the water. Water chlorination was started in 1908 in New Jersey and it remains a widely used method of disinfection [5]. Trihalomethanes (THMs) are formed as a by-product predominantly when chlorine is used to disinfect water for drinking. They represent the group of chemicals generally referred to as disinfection by-products (DBPs). These molecules are halogen-substituted single-carbon compounds with the formula CH_nX_m, where *X* can be fluorine, chlorine, bromine or iodine. THMs are formed in the water chlorination process when the chlorine is reacted with humic and fulvic acids [6–9]. THMs have been detected in different aqueous solutions such as: ground and mineral water, tap and swimming pool water, snow, rain, sea and river water [10]. The formation rate of THMs in aqueous solutions increases as a function of the chlorine and humic acid concentration, contact time, pH, dissolved organic carbon, and temperature [11]. THMs are tasteless, odorless, and high volatility but harmful and potentially toxic. They can cause cancer, miscarriage, reproductive problems, and birth defects [12]. Chaidou et al. [13] have shown that chlorination DBPs cause problems in different parts of the human body such as the kidney, liver, and nervous system. In another work, the effect of DBPs on DNA damage at quite low levels in human derived hepatoma line was studied by Zhang et al. [14]. Therefore, removal of chlorination disinfection by-products such as trihalomethanes from water is important.

Up to the present time, many researches have been carried out different methods to reduce THM concentration in water, such as reverse osmosis, and adsorption on activated carbon [15–17]. One of the wastewater treatment methods is membrane technology. Over the past decade, separation processes by membrane have been developed for industrial applications [18,19]. Carbon nanotubes (CNTs) are one of the membranes that can be used in the removal of THMs form aqueous solutions. CNTs with their nano scale diameters, can lead to potential applications in the desalination process [20–26] and diseases treatment [27–30]. The CNTs are characterized by a pair of indexes (*n*,*m*). The indexes *n* and *m* are the number of unit vectors of graphene sheet. Depending on the values of these two indexes, there are three types of CNTs including zigzag ($m = 0$), armchair ($n = m$) and chiral ($n \neq m$).

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http://dx.doi.org/10.1016/j.jmgm.2015.01.008
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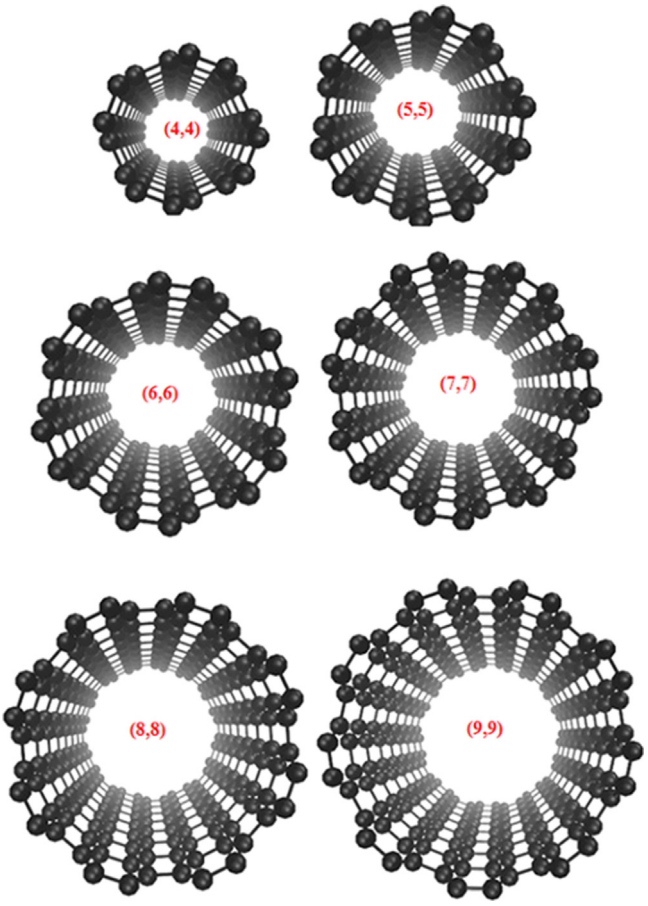

Fig. 1. Schematic layout of the nanotubes studied in this work. CNT (4,4), CNT (5,5), CNT (6,6), CNT (7,7), CNT (8,8), CNT (9,9) with diameters of: 5.49 Å, 6.83 Å, 8.18 Å, 9.53 Å, 10.88 Å and 12.24 Å, respectively.

To the best of our knowledge, no study was reported about the removal of THMs (CH_3Cl, CH_2Cl_2 and $CHCl_3$) from aqueous solution using the armchair CNTs. Therefore, in this work, we studied the removal of THMs from aqueous solutions using armchair CNTs as a membrane under induced pressure using molecular simulation method. Molecular dynamics (MD) simulation is one of the main fields of nanotechnology. Design, production and scale up of various processes can be simulated by this method. In this work, CH_3Cl, CH_2Cl_2, and $CHCl_3$ were used as THMs molecules. The reason for choosing these species was due to their presence in water, after the chlorination process.

2. Simulation methodology

In this research, six types of CNTs with a length of 22 Å were selected, including (4,4), (5,5), (6,6), (7,7), (8,8) and (9,9) CNTs (Fig. 1). A full geometric optimization of the electronic ground state of CNTs and THM molecules was obtained by applying density functional theory (DFT) method. These computations were done at the B3LYP level of theory using 6-311G (2d, 2p) basis sets. All calculations were carried out using GAMESS-US package [31]. The results of DFT for the THMs are given in Table 1. For the CNTs, all carbon atoms are assumed to be electrically neutral [32].

The MD domain was consisted of an armchair CNT embedded between two graphene sheets, with an aqueous solution of THM molecules (Fig. 2). THM molecules used in the simulation were a solution containing equal proportions of all three molecules $CHCl_3$, CH_2Cl_2 and CH_3Cl. The concentration of THM molecules was 0.3 mol/L and the number water molecules in the box were

Table 1
The results of the DFT calculations for THMs.

Type of THMs	CH_3Cl	CH_2Cl_2	$CHCl_3$
Charge of carbon	−0.66	−0.476	−0.351
Charge of hydrogen	+0.248	+0.267	+0.285
Charge of chlorine	−0.083	−0.029	+0.022
Bond length of C—H (Å)	1.089	1.087	1.086
Bond length of C—Cl (Å)	1.804	1.792	1.788

1700 molecules. The simulation box for all runs was ($x \times y \times z$) 30 Å × 30 Å × 80 Å. The periodic boundary conditions with the minimum image convention were used in all three directions to mimic system with an infinitely large area. The short-range interactions for atomic species were described with the Lennard–Jones potential. The water–CNT, water–THMs and THMs–CNT interaction parameters were derived using the Lorentz–Berthelot combining rules. We performed MD simulations with NAMD2.9 [33] similar to previous works [34–37] with a 1 fs time step using a Particle Mesh Ewald (PME) summation for electrostatic interactions calculations [38]. Also, all analysis scripts were composed locally using the VMD1.9.2 [39] and Tcl commands. The empirical CHARMM force field was used for the atoms [40] to describe inter-atomic interactions. Parameters for carbon atoms in the CNTs and graphenes were taken as the parameters for carbon in the CHARMM27 force field [41,42]. To represent water molecules, the intermolecular three point potential (TIP3P) model [43] was employed. Three site models have three interaction points corresponding to the three atoms of the water molecule. Each site has a point charge, and the site corresponding to the oxygen atom also has the Lennard–Jones parameters. Since three site models achieve a high computational efficiency, these are widely used in MD simulations. Most of the models use a rigid geometry matching that of actual water molecules. One of these models is the TIP3P model, which assumes an ideal shape. The potential energy (U_{eff}) for the non-bonded interactions was given by the sum of Lennard–Jones (U_{vdw}) and Coulomb (U_C) potentials through Eq. (1).

$$U_{eff} = U_{vdw} + U_C = 4\sqrt{\varepsilon_i \varepsilon_j}\left[\left(\frac{\sigma_i + \sigma_j}{2r_{ij}}\right)^{12} - \left(\frac{\sigma_i + \sigma_j}{2r_{ij}}\right)^{6}\right] + \frac{q_i . q_j}{4\pi\varepsilon_0 r_{ij}} \quad (1)$$

where r_{ij} is the distance between the fragments i and j; ε_i and σ_i are the Lennard–Jones parameters related to atom i; q_i and q_j are the partial charge assigned to atoms i and j. In this work, the armchair CNT embedded between two graphene sheets was placed in the

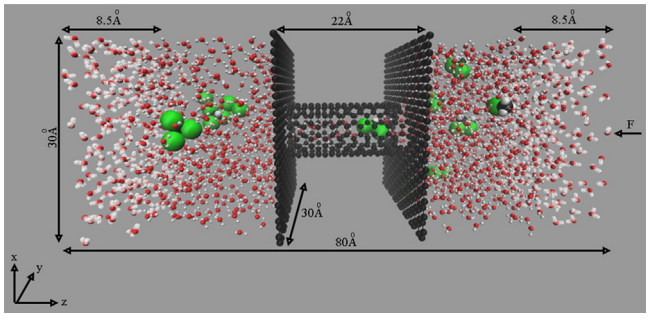

Fig. 2. A snapshot of the simulated system. The simulation box is 30 Å × 30 Å × 80 Å (black color represents carbons atoms; green color represents chlorine atoms; red and white colors represent the oxygen and hydrogen atoms of water molecules, respectively. Two water reservoirs are attached to each side of the box. In the glass region, external forces are applied on water molecules to create a pressure drop across the membrane). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)