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Separation of nitrate ion from water using silicon carbide nanotubes as a membrane: Insights from molecular dynamics simulation

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ABSTRACT

Molecular dynamics (MD) simulations were performed to investigate the separation of nitrate ion as contaminant from aqueous solution by means of armchair silicon carbide (SiC) nanotubes. The (7,7) and (8,8) SiC nanotubes embedded in a silicon nitride (SiN) membrane as a membrane immersed in an aqueous solution of $NaNO_3$. An external electric field was applied to the system along the *z* axis of the simulation cell. In order to investigate these systems, we calculated the ion current, the radial distribution function of water-nanotube and ion-water, the retention time of ions, water density, the hydrogen bond of water, and the autocorrelation function of the hydrogen bond. The results showed that the considered armchair SiC nanotubes can be used for separating nitrate ion from water. The results revealed that nitrate ions were separated successfully using the (8,8) SiC nanotube, though these ions did not pass through the (7,7) SiC nanotube.

1. Introduction

Water covers approximately 70% of Earth's surface. However, lack of clean, safe drinking water has been a major global problem to humanity for many years [1]. Surface water and groundwater can become contaminated in many ways. Industrial, municipal, and agricultural pollutants are the main sources for reducing water quality in the water resources which can, in turn, significantly reduce the supply of freshwater for human use [2]. Nitrate is a major nutrient required for plant growth. Nitrate is also used as nitrogenous fertilizer which is applied to agricultural lands in order to increase crop production. However, when the nitrate reaches the surface and ground waters, concentrations of nitrate in surface and ground waters increase. This is the main reason of water contamination by means of nitrate. The other reason for water contamination is the disposal of untreated municipal and industrial wastes [3]. Nitrate contaminated water resources, can lead to serious problems including eutrophication, and cause potential hazards for human health through methemoglobinoma in children, hypertension, thyroid malfunctioning, and stomach cancer in adults. Also, it can endanger animals' health [4,5].

Due to its high stability and solubility, nitrate has a low tendency for precipitation and adsorption, and, therefore, it is difficult to remove this ion from water using conventional water treatment technologies [6]. Researchers have used several physicochemical and biological methods to remove excessive nitrate from water including adsorption [7], ion exchange, reverse osmosis, electrodialysis [8,9], denitrification [10], algae growth, disposal of the harvest, a combination of ozonation and sand/activated carbon filtration [3].

In this regard, one of the most promising and developing methods is the application of nanotechnology. High energy and costs requirement of existing treatment technologies are major problems. Progresses in nanotechnology suggest new ways to overcome these problems by increasing energy efficiency and decreasing costs related to water treatment. To date, researchers have successfully designed and fabricated water and ion selective nanostructures including boron nitride nanotubes and carbon nanotubes [11–14]. These nanostructures have been able to remove contaminants from the water [15,16].

Silicon carbide (SiC) nanotubes are a new class of nanotubes, first synthesized in 2001 by Pham-Huu et al. [17]. There are many theoretical studies focusing on the geometry, electronic structure, and properties of SiC nanotubes [18]. For example, Mavrandonakis and Froudakis [19] investigated the structural and electronic properties of SiC nanotubes using ab initio method. They tested SiC nanotubes with different Si to C ratios and the incline towards C-rich to Si-rich. They showed that SiC nanotubes lose stability when the ratio of Si over C increases. They also reported that the SiC nanotubes remain stable until the ratio reaches 50:50.

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Table 1
The Lennard-Jones parameters for silicon carbide nanotube.

Atoms	ε (kJ/mol)	σ (Å)
Si	1.9619	3.736
C	0.3598	3.4

Because of ion selective properties, many investigations were done on SiC nanotubes. Aside from ion selective property of SiC nanotubes, bulk silicon carbide has other important physical and electronic properties such as high strength and high thermal conductivity which make SiC nanotubes applicable in many mechanical and electronic fields [20–22]. Therefore, SiC nanotubes hold promise as alternate nanotubes to carbon and boron nitride nanotubes due to some advantages. For example, SiC nanotubes have demonstrated improved hydrogen storage compared to pure carbon nanotubes [23]. Zhao and Ding demonstrated that SiC nanotubes can act as chemical sensors for detecting carbon dioxide while carbon nanotubes cannot detect this gas [24]. In another research, Jia et al. studied the possibility of (5,5) SiC nanotubes in the presence of an external electric field as a potential gas sensor for detecting SO_2 [25]. They found that (5,5) SiC nanotube could effectively adsorb SO_2 molecules and finally achieve the geometry of $(SO_2)_{10}$/SiC nanotube. Wong and Liew demonstrated the ability of SiC nanotubes to act as a formaldehyde detection sensor. They found that significant charges were transferred from SiC nanotube to HCOH molecules, which led to changes of conductance of SiC nanotubes and rendered this kind of nanotubes suitable for HCOH detection [26]. Zhao et al. showed that the SiC nanotube could act as a catalyst. They demonstrated for the first time that the pure SiC nanotubes might act as a novel kind of metal-free N–H bond or O–H bond splitter [27].

However, to the best of our knowledge, there is no study on the application of armchair SiC nanotubes on water treatment processes such as the removal of nitrate ions from aqueous solution [28]. Thus, we studied the removal of nitrate ions from aqueous solutions using armchair SiC nanotubes under induced electric field using molecular dynamics (MD) simulations method. The length of SiC nanotubes was 20 Å and their diameter were about 12.26 Å and 13.89 Å, for (7,7) and (8,8) nanotubes respectively. We performed MD simulations because of their powerful ability in simulating molecular structures. MD method has advantages compared to other numerical methods. In the next sections, we first explain the procedure of building initial models for MD simulations and then demonstrate the results of our investigations.

2. Simulation modelling and method

In this research, we used SiC nanotubes with the (7,7) and (8,8) chirality. The geometries of these nanotubes were optimized using the density functional theory (DFT) method to obtain their atomic charges and optimized structures. The DFT calculations were performed using GAMESS at the B3LYP level of theory using 6-311G (2d, 29) basis sets [29]. The partial charges of atoms were calculated by CHelpG (Charges from Electrostatic Potentials using a Grid based method) scheme. The optimized Si–C bond distance was obtained 1.814 Å, which was consistent with other article data [18]. The Lennard-Jones parameters for silicon and carbon atoms of SiC nanotube were summarized in Table 1. For the parameterization of nitrate ion, we used Mayne method [30]. This is a rapid parameterization method of small molecules using the force field toolkit in VMD [31].

The MD domain consisted of a SiC nanotube with a length of 20 Å embedded in a silicon nitride (SiN) membrane, water molecules, and $NaNO_3$ aqueous solution (Fig. 1). The SiN membrane was generated with VMD inorganic membrane builder [32]. In this builder the pores were cut at a default position which is centred at $(X,Y,Z = 0)$ in the membrane. This means that the holes are always centred such that the crystals would alternate between N-pore, Si-pore as the nanotube diameter increases. In the current system designed, the nitrogen atoms of the SiN membrane surrounded the (7,7) SiC nanotube and the silicon atoms of the SiN membrane were around the (8,8) SiC nanotube. Consequently, this position of nitrogen and silicon atoms of membrane around the nanotubes allowed system to separate ions through the SiC nanotube, selectively. In order to insert nanotubes inside the membrane, we can drill the centre of membrane in the desired size. Therefore, nitrogen and silicon atoms of SiN membrane can surround the (7,7) and (8,8) nanotubes and vice versa. But ion selectivity phenomenon does not happen in all these cases. In cases where the distance between the last layer of the pore of the membrane (nitrogen or silicon atoms) and the wall of nanotubes is large, ion selectivity does not occur. Two reasons can be happen for this phenomenon. First, when the size of pore is large, the effects of positive and negative charges of nitrogen and silicon atoms of SiN membrane cannot be felt on the wall of nanotubes and any

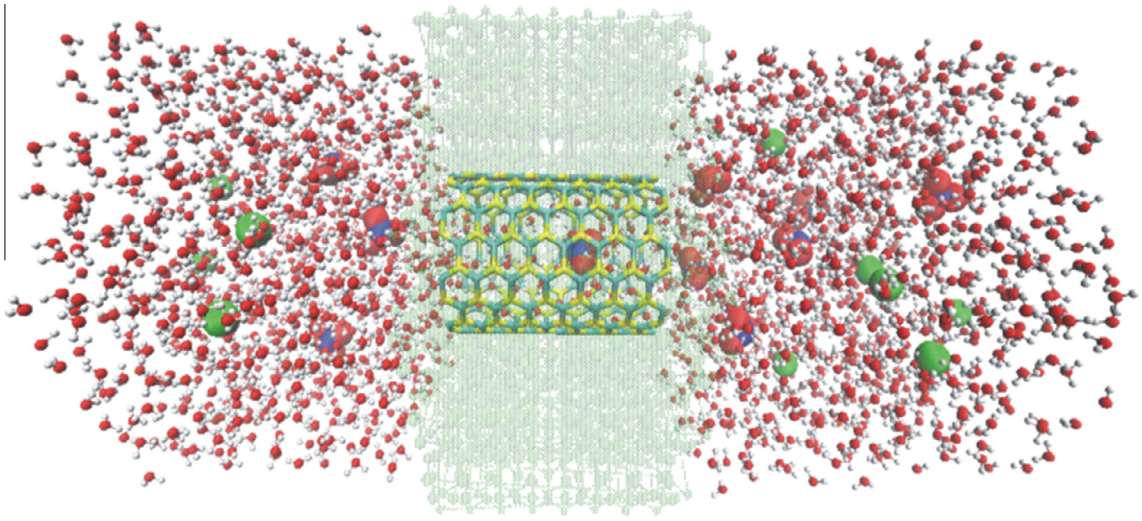

Fig. 1. The (8,8) SiC nanotube surrounded by SiN membrane which connected two reservoirs containing water and ions (sodium: green, nitrogen: blue, yellow: silicon, cyan: carbon, oxygen: red, and hydrogen: white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)