Computational Materials Science 128 (2017) 8–14

Contents lists available at ScienceDirect

Computational Materials Science

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

Molecular dynamics simulations of removal of cyanide from aqueous solution using boron nitride nanotubes

Jafar Azamat [a], Alireza Khataee [a,b,*]

[a] Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran
[b] Department of Materials Science and Nanotechnology, Near East University, 99138 Nicosia, North Cyprus, Mersin 10, Turkey

ARTICLE INFO

Article history:
Received 7 August 2016
Received in revised form 13 October 2016
Accepted 28 October 2016

Keywords:
Boron nitride nanotube
Cyanide
Water pollutant
Molecular dynamics

ABSTRACT

Cyanide is a highly toxic chemical compound in all forms and used in many metallurgical and chemical synthesis methods. A huge amount of cyanide is discharged in effluents from different industries. Therefore, the removal of cyanide from aqueous solution by boron nitride (BN) nanotube as a membrane was investigated through molecular dynamics simulations. The considered system comprised a BN nanotube inserted between two graphene nanosheets and water containing cyanide ions. External pressure and electric fields were used for the removal of cyanide ions. Four types of armchair BN nanotubes were used with different diameter from 6.90 Å to 11.07 Å. Nanotubes performance relative to permeation of cyanide and water was different and the amount of species passing was dependent on the applied pressures, electric fields and the diameter of nanotubes.

1. Introduction

Recently, the water sources are contaminated by the various industries which are using cyanide. To protect the water sources, wastewater containing cyanide needs to be treated before discharging into the environment. Accordingly, environmental contamination by harmful compounds considered as a challenge in the world. Cyanide is a chemical compound which has a cyano group and is highly toxic in all forms to humans and aquatic organisms. This compound can be found in organic and inorganic forms. Only 0.5–3.5 mg of cyanide per kilogram of body weight can cause death in humans [1]. Skin contact with liquids containing cyanide may produce irritation and sores. Short term contact to cyanide causes tremors and rapid breathing and at long term exposure, cyanide cause thyroid effects, weight loss, nerve damage, and finally death [2].

Cyanide in the form of salt or complex is used in many metallurgical and chemical synthesis methods. A huge amount of cyanide is discharged in effluents from different industries particularly in metallurgical processes and plating and surface finishing such as, steel plant, electroplating, textiles, petrochemical, metal cleaning, metal processing, photography, pharmaceuticals, and ore leaching [3–5]. The acceptable level of cyanide at the effluent outlet lies between 4 and 40 μM. The environmental pollution resulting from cyanide will lead to ecological balance being destroyed, agriculture reduced sharply, as well as cause human and livestock poisoning or stop living [6]. It should be noted that in spite of its toxicity, cyanide is found in the different life forms including photosynthetic bacteria, plants, fungi, foods, algae, and some animals [7].

Up to the present time, several chemical and biological strategies such as chemical, photolytic, catalytic, ultrasonic, biological, ion-exchange, activated carbon adsorption, coagulation, and oxidation methods have been developed for the removal of cyanides from wastewater [8–12]. However, many of these methods are not environmentally friendly. For example, caustic chlorination leads to the formation of carcinogens, cyanogens, and toxicants harmful to aquatic life. Therefore, the removal of cyanide from aqueous solutions to a safe level through green route and cost effective processes are the current interest.

Besides the above-mentioned methods for removal of cyanide, nanostructure membranes can also be used. To ensure accuracy and to save costs, it is better to approve performance of nanostructure membranes for removal of cyanide via computational chemistry. Boron nitrite (BN) nanotube [13,14] is a nanostructure that can be used for this purpose. Many studies were done on the synthesis of BN nanotubes [15–17], therefore their production for industrial applications seems convenient. These nanotubes have a tubular structure, and accordingly divided into three categories that are denoted by a pair of indexes (i, j), including chiral (i ≠ j), zigzag (i = 0) and armchair (i = j) nanotubes. Index *i* and *j* are the

* Corresponding author at: Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran.

E-mail addresses: a_khataee@tabrizu.ac.ir, ar_khataee@yahoo.com (A. Khataee).

http://dx.doi.org/10.1016/j.commatsci.2016.10.040
0927-0256/

number of unit vectors of two dimension hexagonal BN sheet. Due to the different properties of these nanostructures, scientists are commonly using from them [18–23]. In the phenomenon related to transportation and purification materials, BN nanotubes can be effective [24–27]. BN nanotubes with (7,7) and (8,8) chirality were used for removal of heavy metals from aqueous solutions [28] in the presence of electric field. The results obtained from our previous study [28] showed that BN nanotubes are selective to removal of cations and anions using computational methods. In our systems, a BN nanotube fixed in a silicon-nitride membrane immersed in $ZnCl_2$ aqueous solution. Selected BN nanotubes had a large radius to accept cations and anions. However, the results showed that the (7,7) nanotube was selective to cations, while the (8,8) nanotube was selective to anions. Cations and anions were encountered with an high energy barrier in the (8,8) and (7,7) BN nanotubes, respectively. In another study, Nanok et al. were considered the structure of water molecules inside BN nanotubes [29] with diameters ranging from about 9 Å to about 24 Å using molecular dynamics (MD) simulations. They studied the effect of the nanotube wall on the water density and represented that water self-diffusion didn't extend much beyond the layer of molecules adsorbed to the nanotube wall. Won et al. reported the selectivity of (10,10) BN nanotube relative to Cl^- and K^+ ions [30]. They showed that the (10,10) BN nanotube was selective to chloride ions. Their results were confirmed with potential of mean force calculations for considered ions. This parameter showed that chloride ions encountered a lower energy barrier than the potassium ions at the (10,10) BN nanotube. The electrostatic interactions arising from BN nanotube caused the selectivity of chloride ions. According to their results, a (10,10) BN nanotube could be used as an ion sensor. Also Won and Aluru showed that the (5,5) BN nanotube had superior water permeation properties while a (5,5) carbon nanotube did not conduct water. The van der Waals interactions between the nitride atoms and water molecules cause the wetting behavior of the BN nanotubes [31]. Their results recommended that a small BN nanotube could be a candidate for synthetic water channel. In other study, using MD simulations, Suk et al. were investigated the ability of reverse osmosis BN nanotubes and compared the results with the ability of carbon nanotube and a polymethyl methacrylate [32]. The variation of water flux was clarified by a theoretical method and also with potential of mean force calculations. Based on their results, they suggested that the water flux in BN nanotube was more than other membranes.

To the best of our knowledge, there is not a comprehensive study on the separation of cyanide from water using the BN nanotubes. Therefore, in this research we investigated the removal of cyanide from aqueous solutions using BN nanotube as a noncytotoxic nanostructure membrane [33] under induced pressure and electric field by computational chemistry. MD simulation technique is one of the computational methods that can be used for design, creation and simulation of the processes.

2. Simulation methodology and details

For removal of cyanide by BN nanotube, four types with a length of 2.1 nm including (5,5) to (8,8) BN nanotubes was used (see Fig. 1). The geometric optimization of these nanotubes and potassium cyanide was done by density functional theory (DFT) method using GAMESS [34] at the B3LYP level of theory using 6-311G basis sets. Partial charges for all type of atoms are given in Table 1.

The size of simulation cell was $3 \times 3 \times 8$ nm^3. In each cell, a BN nanotube is located in the middle of the box that it embedded between two graphene nanosheets; both of these were fixed during the simulation. This setup immersed in 0.3 mol/L aqueous solution of potassium cyanide as shown in Fig. 2. The coulomb potentials were used for description of the long range electrostatic interactions by the particle mesh Ewald (PME) [35] and Lennard-Jones potential was used for the short range interactions. Van der Waals interactions were truncated with a 1.2 nm cutoff. The cross interaction Lennard-Jones parameters between water-nanotube, water-graphene, water-ion, ion-graphene and ion-nanotube were obtained by the Lorenz-Berthelot combining rules [36]. The MD simulations were carry out by GPU enabled version of NAMD 2.10 [37] scalable MD simulation code with a 1 fs time step, similar to the previous studies [38–41] and the VMD 1.9.2 [42] was used for data analysis and visualizations.

The Lennard-Jones parameters for BN nanotube and cyanide were taken from literature [25,43]. Also for carbon atoms of graphene we used parameters from Ref. [44]. The TIP4P model [45] was employed for water molecules and aromatic carbons parameters in the CHARMM force field [46] was used for the graphene atoms. The simulation box was minimized 2 ns with NAMD at 0 K, and equilibrated for 1 ns via NVT ensemble at 298 K and finally 6 ns MD simulations were performed by using the Langevin dynamics [47] to keep the temperature at 298 K.

External pressure and electric field were used for cyanide removal through nanotubes. A constant force was induced to the oxygen atom of water molecules in a selected region of the system [48] for applying pressure to the system, as $P = n.F/A$, where n, F, P and A are the number of water molecules in the considered layer of system, the value of induced force (pN), the hydrostatic pressure difference (Pa) and the cross sectional area of the system (m^2), respectively. The selected area is within a fixed distance of the left or right boundary of the system. The applied forces acted as a pressure gradient in system. The applied pressures were up to 150 MPa and they were applied to approximately 460 water molecules.

3. Results and discussion

MD simulation was carried out to study the separation of cyanide using BN nanotubes. The permeation of water molecules and cyanide ions through each type of the nanotubes were considered. MD results showed that cyanide ions could not pass through the (5,5) BN nanotube due to its small diameter, but water molecules passed through it by applying external pressure. From one perspective this type of nanotubes can be used to separate cyanide from water, if we want to keep cyanide in one side of the membrane. But it should be noted that in the case of (5,5) BN nanotube, the flow rate of water molecules was low, because of the structure of water molecules inside it (the reason will be explained later). Therefore, it is not appropriate for cyanide separation.

On the other hand, water molecules and cyanide ions passed through the (6,6), (7,7) and (8,8) BN nanotubes by applying pressure or the electric field. It might seem that in these nanotubes were not appropriate for separation of cyanide due to letting the both species (water and cyanide) to pass. But it should be noted that the amount of outgoing water through nanotubes along with cyanide ions was not noticeable. Therefore, they can be used to remove cyanide. However, the amount of passing ions and water in the presence of pressure and electric field were different.

Water passing through these nanotubes in the presence of pressure was performed with different structures. Arrangement of water molecules inside BN nanotubes is shown in Fig. 3. In each case, water molecules had different arrangement. The radial distribution function (RDF) that was obtained from trajectory files with VMD, was used to demonstrate this phenomenon. The RDF between inner water molecules and BN nanotubes was calculated. RDF is the probability of finding a species at a distance of d away from the given reference species, which is shown in Fig. 4. The