Removal of Cd(II) from water using carbon, boron nitride and silicon carbide nanotubes

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Abstract.   Molecular dynamics simulations were used to study the removal of Cd(II) as a heavy metal from wastewater using armchair carbon nanotube, boron nitride nanotube and silicon carbide nanotubes under applied electric field. The system contains an aqueous solution of $CdCl_2$ as a heavy metal and a (7,7) nanotube as a nanostructured membrane, embedded in a silicon nitride membrane. An external electric field was applied to the considered system for the removal of Cd^{2+} through nanotubes. The simulation results show that in the same conditions, considered armchair nanotubes were capable to remove Cd^{2+} from wastewater with different ratios. Our results reveal that the removal of heavy metals ions through armchair carbon, boron nitride and silicon carbide nanotubes was attributed to the applied electric field. The selective removal phenomenon is explained with the calculation of potential of mean force. Therefore, the investigated systems can be recommended as a model for the water treatment.

Keywords: heavy metal; Cd(II); ion separation; nanotube; PMF

1. Introduction

Removal of ions using nanostructured membranes such as nanotubes are now highly related to industrial processes, and have attracted great attention in recent years as important research issues (Furukawa *et al.* 2010). Moreover, development of low-cost the removal of heavy hazardous metals from wastewater is of high significance. Disappointingly, the majority of the methods proposed for removing heavy metals contains complex procedures, and make it difficult to completely understand the transport properties. Heavy metal separation from wastewater in a structurally controllable modeling system, where the controllable parameters of system can be modified by experimental methods, has been a target of many studies in this area. The presence of toxic heavy metals ions in water can cause many serious problems in human body and also water treatment plays an important role in the global challenge for sustainable water supply in the recent century. Hence, removal of these ions from water and wastewater is considered to be a critical issue (Gao *et al.* 2014, Huang *et al.* 2013). A number of methods have been proposed for removing heavy metals, including ion-exchange (Alyüz and Veli 2009), ion electrodialysis (Chen 2004), photocatalysis (Zhang and Itoh 2006), coagulation and flocculation (El Samrani *et al.* 2008), chemical precipitation (Ghosh *et al.* 2011), reverse osmosis (Cséfalvay *et al.* 2009), adsorption (Yanagisawa *et al.* 2010), membrane filtration (Chen *et al.* 2005), and flocculation (El Samrani *et al.* 2008) processes.

Also, membrane-based treatment technologies have a key role in water treatment. The membrane-based water treatment processes can be categorized according to membrane pore size and rejection mechanism.

Ion selectivity is defined as the ability of a membrane to pass or reject ions. Nanotubes are capable of acting as a selective membrane to replicate this property. Accordingly, in this research, we use three types of armchair nanotubes, namely carbon nanotube (CNT) and boron nitride nanotube (BNNT) and silicon carbide nanotubes (SiCNT). Due to their nano scale diameters, the use of CNTs is considered as a controversial issue in the water treatment industry. It can be hypothesized that separating ions and transporting water across CNTs is a complex issue. Nanotube diameter is regarded as an effective parameter in ion separation phenomenon. Related studies indicate that specific ions are allowed to pass through CNTs and water molecules with different arrangements can pass through them (Das *et al.* 2014).

BNNTs are also widely used by researchers due to their unique properties (Golberg *et al.* 2007) and also for designing ion-selective devices (Tang and Kim 2014). Won and Aluru considered the ionic selectivity of BNNTs in relation to chloride and potassium ions (Won and Aluru 2009). They immersed a (10, 10) BNNT in a reservoir of potassium chloride solution to investigate its ionic selectivity. They found that this nanotube was capable of conducting chloride ions but potassium ions were not.

SiCNTs first synthesized in 2001 by Pham-Huu *et al.* (2001). Because of ion selective properties, many investigations were done on SiCNTs. Aside from ion selective property of SiCNTs, 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 (Bai 2011). Therefore, SiCNTs hold promise as

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alternate nanotubes to CNT and BNNT due to some advantages. For example, SiCNTs have demonstrated improved hydrogen storage compared to pure carbon nanotubes (Mpourmpakis *et al.* 2006). Zhao and Ding demonstrated that SiCNTs can act as chemical sensors for detecting carbon dioxide while CNTs cannot detect this gas (Zhao and Ding 2009). In another research, Jia *et al.* studied the possibility of (5,5) SiCNTs in the presence of an external electric field as a potential gas sensor for detecting SO_2 (Jia *et al.* 2012). They found that the (5,5) SiCNT could effectively adsorb SO_2 molecules and finally achieve the geometry of $(SO_2)_{10}$/SiC nanotube.

Regarding ion selectivity through CNT, BNNT, and SiCNT several parameters, such as size exclusion, dehydration and charge repulsion, can be effective (Thomas *et al.* 2014). In the case of size exclusion parameter, it should be mentioned that if the size of ions is larger than the diameter of nanotubes, they will not be able to enter the nanotubes. The cations or anions tend to be surrounded by a hydration shell that makes powerful interaction between ions and water. In larger nanotubes, ions are able to pass nanotubes with their full solvation shell. In contrast, if nanotube diameter becomes smaller than the size of ion solvation shell, some water molecules should be removed from ion hydration shell. In this case, the ions will be able to pass through the nanotube. The removal of water molecules from ion hydration shell requires spending energy which is a factor for ion rejection. As the nanotube diameter decreases or increases, ion rejection rate rises or falls, respectively (Richards *et al.* 2013).

Progress in the manufacturing of membranes occurs very slowly. Ideally, it is preferred to design the molecular characteristics of a membrane in order to increase the ion removal rate. Therefore, it is better to study the structural properties of membranes via computer simulation methods before fabrication. On this based, we used molecular dynamics (MD) simulations to study the removal of Cd^{2+} from wastewater using an armchair CNT, BNNT or SiCNT as a membrane. MD simulation is a powerful computational method that solves Newton's equation of motion for a system of particles interacting with a given force field. Since MD method calculates the movement of particles at the molecular level, it can be used to predict macroscopic properties based on generated primary data via statistical mechanics and also it provides a controlling instrument for studying the permeation, selective separation of nanotubes. To study ion separation by nanotubes under an electric field in this paper, nanotubes should be arranged to form a membrane that can separate two reservoirs. In line with this objective, we used CNT, BNNT and SiCNT with (7,7) chirality. Then, as shown in Fig. 1, we fixed them in a silicon nitride (SiN) membrane and immersed all of them in a mixture of 0.5 M $CdCl_2$ aqueous solution. All of the atoms in the membrane (nanotube+SiN) were held fixed during the simulations while water molecules and ions are allowed to move freely. The length of the used nanotubes was 1.5 nm. The results of the present study not only contribute to understanding heavy metal separation through nanotubes but also show the structure of water molecules inside nanotubes.
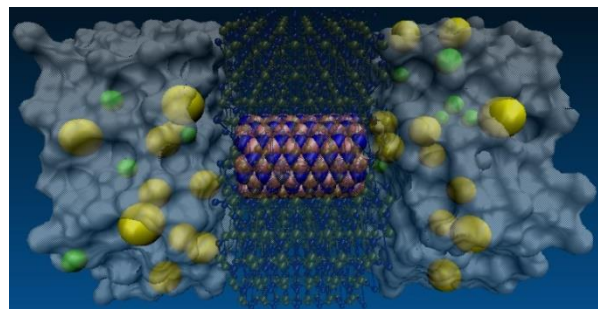

Fig. 1 A snapshot of the simulated system (yellow: Cl⁻, green: Cd^{2+}, red: Oxygen and white: Hydrogen)

2. Simulation methodology

MD simulations were performed to separate ions by means of different nanotubes in different voltages. In line with this purpose, the (7, 7) CNT, BNNT and SiCNT were selected. The geometries of the selected nanotubes were optimized in the GAMESS (Schmidt *et al.* 1993) at the B3LYP level of theory using the 6-31G basic set. In the experimental works, nanotubes are often embedded in SiN membrane (Holt *et al.* 2004, 2006) or polystyrene film matrices (Hinds *et al.* 2004, Majumder *et al.* 2005). Therefore, in this work we assume that it is possible to manufacture SiN membranes with considered nanotubes, too. The SiN membrane with appropriate pore for these nanotubes was generated with VMD inorganic membrane builder. Then, teach of these nanotubes were embedded in it. Nanotubes embedded in the SiN membrane were placed in the center of the box at the position of x, y, z = 0. The water molecules and the desired ions were also added to the system. The number of water molecules in the simulation box was approximately 1100. The axes of the nanotubes were parallel to the z-axis of the box. For nanotubes atoms, the Lennard-Jones parameters were adopted from reference (Hummer *et al.* 2001, Menon *et al.* 2004, Won and Aluru 2007). The Lennard-Jones parameters for heavy metal were obtained from reference (Li *et al.* 2013). In this study, the carbon atoms in the CNT were assumed to be uncharged Lennard-Jones particles,(Shim *et al.* 2011) and the partial charges for BNNT and SiCNT were determined by DFT method. The partial charges obtained from DFT method that used in the MD simulation were -0.4, +0.4, +0.6 and -0.6 for nitrogen, boron, silicon and carbon atoms, respectively. Also, the interaction parameters between different species of the system were obtained using Lorentz-Berthelot combining rules. MD simulations were carried out at temperature 298 K using the Langevin dynamics method for temperature coupling, and the Nose-Hoover Langevin piston was used to maintain the pressure at 1 bar.

All MD simulations were performed in the canonical (NVT) ensemble with periodic boundary conditions in all the three-directions with the NAMD 2.11 (Phillips *et al.* 2005) with a 1 fs time step and VMD1.9.3 (Humphrey *et al.* 1996) was used to visualize the simulations, as in our previous works (Azamat 2016 Azamat *et al.* 2016b, c, Barzegar *et al.* 2016). The TIP4P water model was used to represent water molecules (Jorgensen *et al.* 1983). The van der Waals interactions were truncated by a 12 Å cutoff. The

Particle Mesh Ewald method (Darden *et al.* 1993) was used to treat long-range electrostatic calculations. The simulation box for all runs was $3.6 \times 4 \times 5$ nm^3, and the system was subjected to a zero-temperature energy minimization for 1 ns and then for each choice of voltage, the MD simulation was run 6-10 times within 5 ns at 298 K with different and uncorrelated starting configurations in order to produce more accurate averages. The simulation time of entire study is about 1 μs. An electrical field was applied in the z direction of the system for all considered systems within the whole simulation period. Due to the applied electric field, the Cd^{2+} ions were passing through the nanotubes. As a result of this phenomenon, system current could be measured. The current versus voltage curve was obtained for the respective systems at an ionic concentration of 0.5 M. The amount of current (*i*) was calculated by Equation, $i = n.q/t$, where *n* refers to the average number of heavy metal that cross the considered nanotubes, *q* stands for the charge of the ion, and *t* refers to the simulation time, respectively.

The ion permeation through the nanotubes was investigated by calculating the potential mean force (PMF) (Kjellander and Greberg 1998) along the *z*-axis of the simulation box. Umbrella sampling method was used to measure the PMFs of the ions and the data were analyzed using the WHAM (Roux 1995). The ions were moved from the position -7.5 Å to the position 7.5 Å in 0.5 Å increments. Each sampling window was simulated for 1 ns. In each simulation, the *z* coordinate of ions was held constant using a 15 kcal/mol.Å^2 harmonic constraint while the ion was free to move radially.

3. Results and discussion

According to the water treatment perspective, it is important to understand the separation properties of heavy metals and the transport of water molecules through nanotubes. Although remarkable advances have been recently made on this research issue, understanding the effects of nanotubes on heavy metal separation still remains to be an open question. With this research gap in mind, we performed MD simulations in this study to investigate the separation of Cd^{2+} as a heavy metal from wastewater across (7,7) CNT, BNNT and SiCNT. To this end, some properties of the simulated system including ionic current, water flow rate, normalized transport rate of water, and ion retention time were investigated. Although the (7,7) CNT, BNNT and SiCNT have spaces that are big enough for all ions to go through them, our results indicate that only cations (Cd^{2+}) enter the nanotubes and chlorine ions cannot enter these nanotubes. The ability of nanotubes to separate ions was investigated by calculating PMF for ions. Fig. 2 shows the PMF curves for the experiments ions. As it can be observed in Fig. 2, a deep potential well was produced for Cd^{2+} ion in the (7, 7) nanotubes.

Water molecules can spontaneously get into nanotubes with diameters greater than 8.1Å (Azamat *et al.* 2016a). Water molecules can remain inside nanotubes or get out of them (Corry 2008). However, in the case of narrower nanotubes such as (5,5) nanotubes, water molecules partially enter them (Won and Aluru 2007). Since large
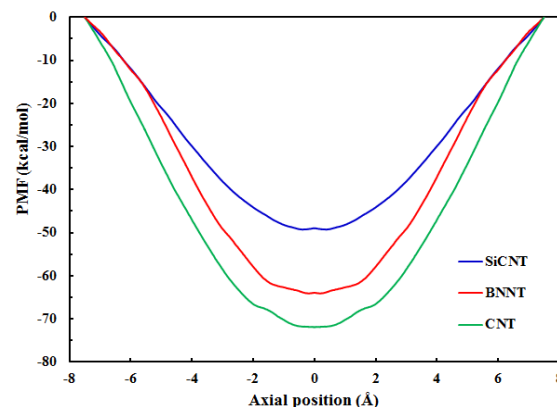

Fig. 2 The potential of mean force for Cd^{2+} in (7,7) CNT, BNNT and SiCNT
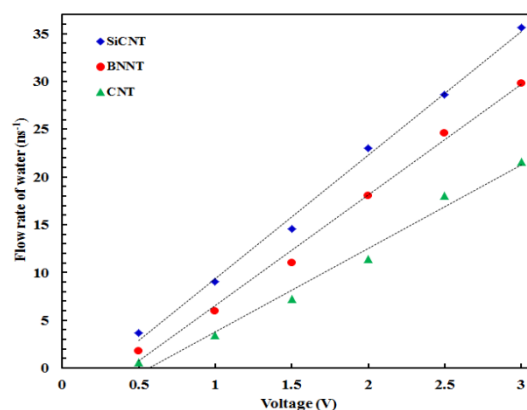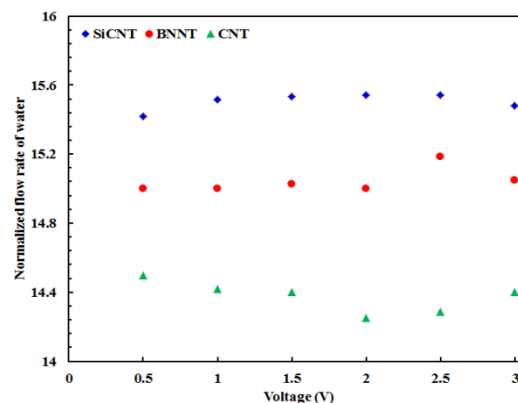

Fig. 3 Flow rate of water in the (7,7) nanotubes

Fig. 4 Normalized flow rate of water in the studied systems

nanotubes were used in the present study, water molecules could pass through them. If the pressure was applied on system, water molecules pass under pressure, but in this study, water transport is due to the ion transport. Water flow rate was defined as the total number of water molecules moving through the nanotube from -z to +z per unit of time. Fig. 3 demonstrates the flow rate of water molecules.

As can be seen in this figure, due to the partial charges of the (7,7) SiCNT and the BNNT, amount of water flow rate through these nanotubes was higher than that of the (7,7) CNT. Each carbon atom of (7,7) CNT was assumed to be neutral in MD simulations, but atoms of BNNT and SiCNT had partial charges which caused the amount of

water flow rate through them be higher than that of the CNT. Also, as it can be observed, by increasing the applied voltage to the system, the amount of passing water is also enhanced.

Fig. 4 shows the normalized flow rate of water molecules with respect to the number of transported Cd^{2+} ions. The results indicate that the normalized flow rate of water (transported water for one permeated ion) is independent of the applied electric field. Moreover, although there are not significant differences between nanotubes in terms of normalized water flow rate, there are still differences between them.

The water network structure inside the nanotubes resulted in the hydrogen bonds between water molecules. The water density inside nanotubes (inner water molecules) increased with increasing the applied voltage because of the high transport of ions at the high voltage; hence, the number of hydrogen bonds will also increase. We counted the number of hydrogen bonds during 5 ns MD simulation and then we reported the average number of hydrogen bonds in Fig. 5.

The results of the study indicated that the transport properties of (7,7) CNT, BNNT and SiCNT can be used for removing water contaminants. Thus, in the present study, the heavy metal separation from water via them was studied. The results of this study revealed that ion separation was accomplished successfully in the system. Fig. 6 depicts the current-voltage profile, where the current increases as the voltage increases.

This trend indicates that the number of Cd^{2+} and water molecules passing through the (7,7) nanotubes increases as the applied voltage increased (Fig. 7). The number of Cd^{2+} ions passing through the (7,7) nanotubes is SiCNT>BNNT>\CNT. This behaviour is related to the difference in their PMFs.

Incidentally, when no electric field was applied to the system, the ions were not able to pass from them. However, when the electric field was applied, the ions overcame the potential barrier and could get out of the nanotubes. Fig. 8 illustrates the retention time for the Cd^{2+} (the time required for the cations to pass across the (7,7) nanotubes) in systems as a function of the applied voltage.
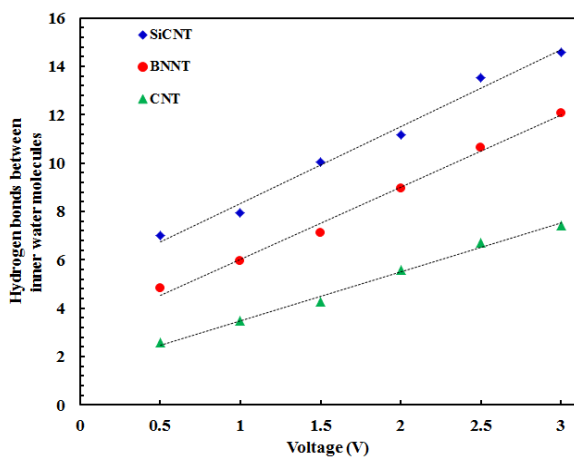

Fig. 5 Hydrogen bonds between inner water molecules of nanotubes
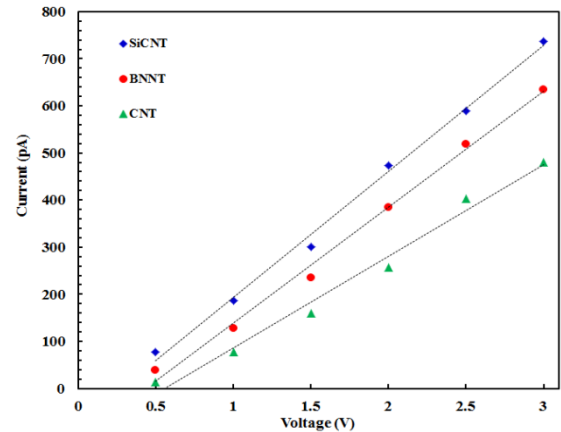

Fig. 6 Current-voltage curves for ions in the (7,7) nanotubes. Each data point represents the average of ten sets of simulations. Lines were obtained from linear regression
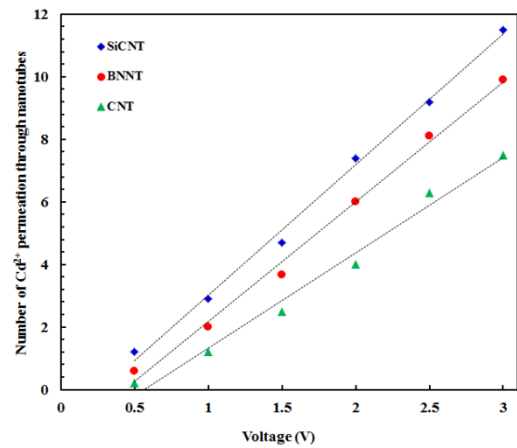

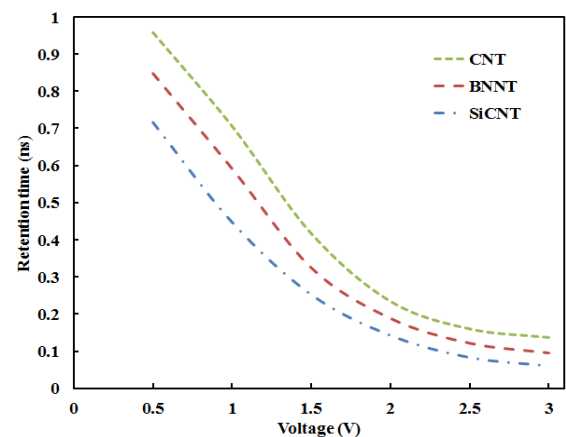Fig. 7 The number of ions passing through the nanotubes

Fig. 8 Retention time for Cd^{2+} ions in the (7,7) nanotubes at applied voltages

As Fig. 8 shows, the retention time decreases with increasing the voltage. Hence, it should be noted that the retention time is lower for the SiCNT. This trend is consistent with the previous parameters such as PMF and current. It can thus be argued that it is easier for the cations to pass through the (7,7) SiCNT than the (7,7) CNT and BNNT. Moreover, under the application of low electric
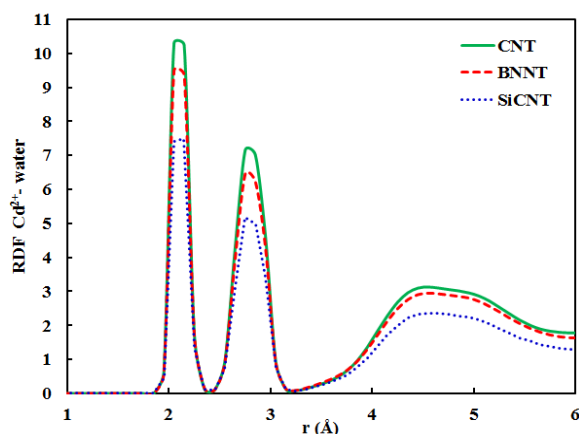
Fig. 9 Ion-water radial distribution functions in the simulation box of (7,7) CNT, BNNT and SiCNT

fields for three nanotubes, there is an overlap between the retention times of cations inside the nanotubes. Nevertheless, there is no overlap when a high electric field is applied. In other words, it can be observed that in low electric field one cation enters the nanotube and would not exit until a second cation gets into the nanotube. However, cation permeates into the nanotube regardless of any support from another cation under the application of a high electric field.

To clarify the structure change of Cd^{2+} ion in the simulation box, we calculated the RDF of ion-water in all type systems from the trajectory files. RDF is defined as

$$RDF = \lim_{r \to 0} \frac{p(r)}{4\pi\rho r^2 dr} \qquad (1)$$

where r and ρ are the distance from the centre of the ion and the number density of water molecules in the system, respectively. $P(r)$ is the number of water molecules around the ions found at a specified distance. This parameter can explain the atomic density of water molecules around a specific ion. Fig. 9 shows the RDF for Cd^{2+}- water.

It can be noted that RDF is zero for a short distance which is due to strong repulsive forces. For Cd^{2+} ion, the position of the first maximum and the magnitude of peaks in three nanotubes are different, which indicates that the hydration number of the Cd^{2+} ion is different. However, for Cd^{2+} under different voltages, the locations of the maximum and minimum peaks were similar. Fig. 9 shows that trend of the magnitude of the Cd^{2+} peaks is SiCNT < BNNT < CNT.

4. Conclusions

MD simulations were used to investigate the selective transport properties of the (7,7) CNT, BNNT and SiCNT. The results indicate that Cd^{2+} with different ratios cross these nanotubes. The simulation results showed that the separation of ions across the selected nanotubes was related to the applied voltage. It can be concluded that by applying an electric field, it has an impact on properties of the systems such as PMF, flow rate of water, the ionic current and retention time of ions. Finally, it can be maintained that the results of the study highlight the significant capability of

the CNT, BNNT and SiCNT in removing heavy metal from wastewater. Thus, carefully fabricated nanotube membranes can act as heavy metal separator which needs to be addressed and investigated by future researchers.

Acknowledgments

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