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Removal of a hazardous heavy metal from aqueous solution using functionalized graphene and boron nitride nanosheets: Insights from simulations

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ABSTRACT

A computer simulation was performed to investigate the removal of Zn^{2+} as a heavy metal from aqueous solution using the functionalized pore of a graphene nanosheet and boron nitride nanosheet (BNNS). The simulated systems were comprised of a graphene nanosheet or BNNS with a functionalized pore containing an aqueous ionic solution of zinc chloride. In order to remove heavy metal from an aqueous solution using the functionalized pore of a graphene nanosheet and BNNS, an external voltage was applied along the *z*-axis of the simulated box. For the selective removal of zinc ions, the pores of graphene and BNNS were functionalized by passivating each atom at the pore edge with appropriate atoms. For complete analysis systems, we calculated the potential of the mean force of ions, the radial distribution function of ion–water, the residence time of ions, the hydrogen bond, and the autocorrelation function of the hydrogen bond.

1. Introduction

A hazardous material is any agent that has the potential to harm humans, or the environment, if it is used or released improperly. Heavy metals (e.g., zinc ions) are considered hazardous materials. Zinc ions are discharged by electroplating, metalworking, galvanization, paint, batteries, smelting, fertilizers and pesticides, pigments, and the mining and steel processing industries [1]. A high level expression of zinc can cause human health disorders such as stomach cramps, skin irritations, vomiting, nausea, and anemia. The current regulation of wastewater and drinking water standards require that heavy metal contamination be reduced to a few parts per million [2].

Chemical precipitation, coagulation, ion exchange, adsorption, and reverse osmosis have been used for the removal of heavy metals [3–6]. Nanosheet membranes have also been used for the removal of various heavy metals [7]. Nanosheet membranes have the ability to separate ions and molecules. Ion separation using nanosheet membranes is done via pores created in them [8]. Graphene and boron nitride nanosheet (BNNS) are examples of nanostructured membranes.

Graphene is a two-dimensional (2-D) carbon-based nanomaterial with layers of carbon atoms densely packed in a honeycomb crystal lattice composed of two equivalent carbon sub-lattices [9]. Graphene offers a wide range of possible membrane applications because of its ultimate thinness, flexibility, chemical stability, and mechanical strength [10]. Since its recent isolation [11], graphene has been the subject of many exciting experimental [12–16] and theoretical studies [17]. The interaction of a graphene surface with target molecules results in an interesting material for water treatment applications.

Recently, ion permeation and gas separation through graphene membranes via the molecular dynamics (MD) simulation method have been performed [18–21]. MD simulations demonstrate that single-layer graphene with sub-nanometer-sized pores can be efficiently utilized for ion, gas, and hazardous ion separation [22–24].

In this work, along with graphene nanosheet, BNNSs were used for the removal of zinc ions. A BNNS with a very high specific surface area exhibits excellent sorption performance for a wide range of oils, solvents, and dyes from water [25]. This nanostructured material has unique properties compared to graphene, including a wide energy band gap, electrical insulation, ultraviolet photolumines-

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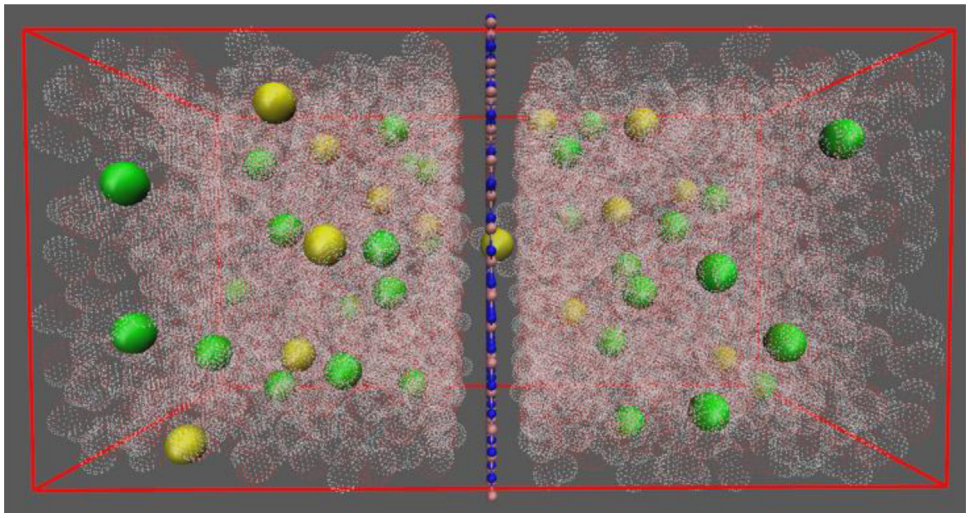

Fig. 1. The simulated system. The size of the box is $30 \times 30 \times 60$ Å^3. The BNNS membrane is located in the middle of simulation box (red represents O, white is H, yellow is Zn^{2+}, and green is Cl^-). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cence, high thermal conductivity and stability, and high resistance to oxidation and chemical inertness [26–31]. The reusability of a saturated BNNS by burning in air, due to its high resistance against oxidation, is one of its important characteristics. This easy recyclability makes porous boron nitride nanosheet a good candidate for water treatment processes [25]. Perfect BNNS is impermeable to ions because there are no pores, and the electron density of its aromatic rings is enough to repel ions trying to pass through it. To pass ions through a BNNS, the drilling of pores is required. Functionalized pores in a BNNS are obtained by passivating each nitrogen and boron atom at the pore edge using chemical functional groups such as fluorine and hydrogen atoms. A functionalized BNNS can be used for the separation of heavy metals from water.

In this research, a molecular dynamics simulation of zinc ion separation from an aqueous solution using a graphene nanosheet and BNNS with a functionalized pore in its center was performed. We investigated a mechanism for ion separation based on the external voltage applied to the simulated system. To the best of our knowledge, no study has been reported in the literature on the removal of zinc ions by functionalized graphene nanosheet and BNNS. We expect that our findings can be used to aid the design of nanostructured membranes for the removal of hazardous materials for water treatment.

2. Simulation model and method

We used the MD simulation method to study the removal of heavy metals through the pores of graphene nanosheet and BNNS with various patterns. The MD simulation method is a valuable tool that is used to study of the permeation phenomenon if the permeation barrier is low enough to allow a sufficient number of crossings within the simulation time frame [32]. Fig. 1 shows an image of the simulation system. The size of the simulation box was $30 \times 30 \times 60$ Å^3. The box contained 1600 water molecules, with 0.5 M $ZnCl_2$ and a graphene nanosheet and BNNS as a nanostructured membrane in the middle of the box. The full geometric optimization of a functionalized graphene nanosheet and BNNS was calculated by using the density functional theory (DFT) method to obtain atomic charges and their optimized structures. The DFT method was performed using the GAMESS-US package [33] at the B3LYP level of theory using 6-311G basis sets. A repeated nanosheet unit was used for optimization of the functionalized membranes by the DFT method. The results from DFT calculations for the functionalized membranes are given in Table 1.

The dimensions of the membranes were 30×30 Å^2. There were 377 carbon atoms and 9 fluorine atoms in the graphene, and 183 nitrogen, 183 boron, 6 fluorine, and 6 hydrogen atoms in the BNNS (see Fig. 2). During the simulations, these membranes were held fixed. Graphene one of the the strongest materials with an intrinsic tensile strength of 130 GPa and a Young's modulus (stiffness) of 1 TPa [34]. Also, BNNS has the intrinsic tensile strength of 102 GPa and the Young's modulus of 145 Gpa [35]. So, we believe that graphene and BNNS membranes will be stable and the use of external high voltage does not affect their membranes.

The diameter of the pores in the graphene nanosheet and BNNS were about 6 and 8 Å, respectively. The pore diameter was determined from the open pore area measurements using the formula $d = 2\sqrt{A/\pi}$. These diameters of the pores were the most appropriate for our purpose. In this study, variants of the functionalized pores with different sizes were evaluated. But they did not have the desired selectivity. In addition to fluorine and hydrogen atoms used in this work, other atoms were investigated for pore functionalization. In this case, the best choice with a high-performance was functionalized pore with fluorine and hydrogen atoms.

The system was subjected to a zero-temperature energy minimization for 1 ns, and then the system temperature was increased to 298 K. After these steps, MD simulations were performed for 5 ns at 298 K under applied voltage before data collection. The voltage range from 0 to 35 V was used in this study. In the experimental works, many methods have been used for the removal of heavy metals; such as chemical precipitation, ion exchange, adsorption, and membrane filtration [36]. The range of voltage used in our MD study is similar to other experimental studies in which the voltage is used to remove heavy metals [37,38].

Table 1
Results obtained from DFT calculations for partial charges of graphene and BNNS atoms.

Atom type	Charge
Nitrogen	−0.4
Boron	0.4
Nitrogen bonded to fluorine	0.25
Boron bonded to hydrogen	0.05
Fluorine of BNNS	−0.25
Hydrogen of BNNS	−0.05
Carbon	0
Carbon bonded to fluorine	0.29
Fluorine of graphene	−0.29