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Separation of copper and mercury as heavy metals from aqueous solution using functionalized boron nitride nanosheets: A theoretical study

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ABSTRACT

Molecular dynamics simulations were performed to investigate the separation of copper and mercury ions as heavy metals from aqueous solution through the functionalized pore of a boron nitride nanosheet (BNNS) membrane. The considered system was comprised of a BNNS with a functionalized pore located in the centre of a simulation box containing an aqueous ionic solution of copper chloride and mercuric chloride. An external voltage was applied along the simulated system in order to produce a separation of heavy metals using pore of BNNS. A functionalized pore of BNNS was obtained by passivating each nitrogen and boron atoms at the pore edge with a fluorine and hydrogen atom, respectively. Our results show that the voltage caused the Cu^{2+} and Hg^{2+} cations to pass selectively through the functionalized pore of the BNNS. This selective behaviour of the BNNS is due to the potential of the mean force of each ion. The potential of the mean force of the heavy metals shows that the heavy metals ions met an energy barrier and could not pass through the functionalized pores of the BNNS. By applying a voltage to the system, they overcame the energy barrier and crossed the pores. We calculated the radial distribution function of ion-water and its integrations; the ion retention time; the hydrogen bond; and the auto-correlation function of the hydrogen bond. Using these parameters, the structure of the water molecules and ions were investigated in the system.

1. Introduction

Heavy metals can cause water pollution, which has attracted the attention of scientists around the world in recent decades. Some of these heavy metals in water can be harmful to human life. Their entry into water occurs through industrial effluents—some of these industrial effluents contain large amounts of toxic heavy metals. In nature, circulation of mercury vapour has a significant influence on the content of the soil and water. Elemental mercury in the rain water creates compounds by oxidation to divalent mercury. Both the chemical reaction, and under the influence of biological factors, and especially the activity of bacteria in the sediments of water bodies methyl and dimethyl mercury compounds are formed. Copper is generally found in the earth's crust, usually in the form of sulphides. Municipal and industrial waste waters are an important source of pollution of rivers and water reservoirs. Copper accumulating plants may be the cause of poisoning. Copper is present in all types of water, and its content is subject to large variations. Copper is an essential nutritional element being a vital part of several enzymes. It is one of the components of human blood. Although copper is an essential metal, it can, in some circumstances, lead to toxic effects including liver damage and gastrointestinal disturbances.

Mercury and copper are two heavy metals that should be removed from wastewater. For this purpose, different strategies can be used. Techniques for eliminating heavy metals include electrochemical operation and biological treatment [1,2], agricultural and industrial wastes as adsorbents [3], precipitation, flocculation, ion exchange, reverse osmosis [4–6], adsorption on modified natural materials [7], adsorption on industrial by-products [8], membrane filtration [9], photocatalysis [10], and electrodialysis [11] processes.

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Other techniques, including the use of nanosheet membranes, can also be considered. Nanosheet membranes have the ability to separate ions and molecules. Ion separation using nanosheet membranes is achieved through a pore created in the membrane.

A boron nitride nanosheet (BNNS) is a nanostructured membrane that has properties such as excellent sorption capacity, good electrical insulation, ultimate thinness, strong resistance to oxidation and chemical inertness, lubricity, ultraviolet photoluminescence, anisotropic properties, heat resistance, high thermal conductivity, and excellent resistance to thermal shock [12–17]. A BNNS structure is almost similar to a graphene structure in which equal numbers of boron and nitrogen atoms substitute for carbon atoms [18]. BNNS, also called white graphene, is comprised of a few layers of hexagonal boron nitride sheets. These structures can be synthesized by various methods [19–24]. The thermal and chemical stability of BNNS is better than that of graphene. BNNS has a large band gap of 5.5 eV, whereas graphene is conductive.

BNNS has many applications including the manufacturing of nanocomposites [25]. the functionalizing the BNNSs by amine molecules for homogeneous dispersion in organic solvents and water [26], and being used as an adsorbent with a high specific surface area and excellent sorption performances [27]. In addition, BNNSs provides a broad range of membrane applications due to their aforementioned properties. 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, it is required to drill pores in the BNNS. Functionalized BNNS pores are obtained by passivating each nitrogen and boron atom at the pore edge using chemical functional groups, such as a fluorine atom and hydrogen atom (Fig. 1). A functionalized BNNS can be used for the separation of heavy metals from water.

To the best of our knowledge, no study has been reported in the literature on heavy metal separation by BNNS using experimental or theoretical methods. Hence, in the present study, molecular dynamics (MD) simulation method was used to investigate the separation of Cu^{2+} and Hg^{2+} ions as heavy metals from aqueous solution by a BNNS with a functionalized pore in its centre. We studied an ion separation mechanism based on the voltage applied to the system. Boron nitride nanosheets were used by experimental methods for other purposes such as for effective sorption for a wide range of oils, solvents and dyes in order to water cleaning [27] or hydrogen storage [28]. BNNS has the intrinsic tensile strength of 102 GPa and the Young's modulus of 145 Gpa [25]. So, we believe that BNNS membrane will be stable and the use of external high voltage does not affect its membrane. We expect that our findings can be used to aid the design of energy efficient BNNS materials for the separation of heavy metals for water purification and treatment.

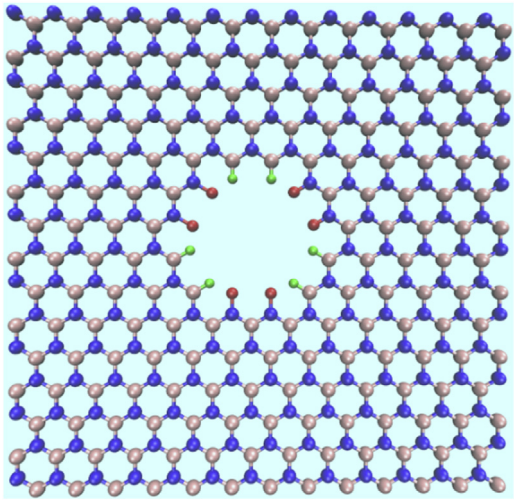

Fig. 1. Functionalized BNNS membrane with a pore in its centre (blue is nitrogen, silver is boron, red is fluoride, and green is hydrogen). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Methodology and simulation details

The full geometric optimization of a functionalized BNNS was calculated by using the density functional theory (DFT) method to obtain atomic charges and the optimized structure. The partial charges for BNNS atoms were determined using CHelpG (Charges from Electrostatic Potentials using a Grid based method) scheme developed by Breneman and Wiberg [29]. The optimized geometries of the functionalized BNNS were determined using the GAMESS-US software package [30] at the B3LYP level of theory using 6-311G basis sets. The dimensions of the BNNS membrane are 3×3 nm^2. There are 183 nitrogen, 183 boron, 6 fluorine, and 6 hydrogen atoms in the BNNS.

The diameter of the pore is about 0.8 nm. The pore diameter was obtained from the open pore area measurements using the formula$d = 2A/\pi$. This diameter of the pore was 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. When the large pore was used, there was no the selection of ion and all type of ions crossed the pore. Versus ions did not pass from small pore, even with very high voltages; 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 effective potential energy (U_{eff}) of the intermolecular interactions is given by the sum of Lennard–Jones potentials 12-6 (U_{vdw}) and Coulomb potentials (U_C) for short range and long range interactions, respectively [31], as follows:

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

where r_{ij} refers to the distance between atoms i and j; ε_i and σ_i represent the Lennard–Jones parameters that are related to atom i; and q_i and q_j represent the partial charge assigned to atoms i and j, respectively. The Lorentz-Berthelot combining rules were used for the cross interaction parameters between species:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \cdot \varepsilon_j} \quad (2)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

where ε_{ij} and σ_{ij} are regarded as the usual empirical Lennard–Jones parameters between the i and j sites. The particle mesh Ewald scheme [32] was used to calculate electrostatic interactions.

Fluorine and hydrogen atoms were used to passivate nitrogen and boron atoms, respectively, in the pore of the BNNS membrane. MD simulations were performed using the NAMD 2.9 [33] as in previous works [34–39]. 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