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Functionalized graphene as a nanostructured membrane for removal of copper and mercury from aqueous solution: A molecular dynamics simulation study

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ABSTRACT

The purpose of the present study was to investigate the removal of copper and mercury using functionalized graphene as a nanostructured membrane. The molecular dynamics simulation method was used to investigate the removal ability of these ions from aqueous solution using functionalized graphene membrane. The studied systems included a functionalized graphene membrane which was placed in the aqueous ionic solution of $CuCl_2$ and $HgCl_2$. An external electrical field was applied along the *z* axis of the system. The results indicated that the application of electrical field on the system caused the desired ions to pass through the functionalized graphene membrane. The Fluorinated pore (F-pore) terminated graphene selectively conducted Cu^{2+} and Hg^{2+} ions. The calculation of the potential of mean force of ions revealed that Cu^{2+} and Hg^{2+} ions face a relatively small energy barrier and could not pass through the F-pore graphene unless an external electrical field was applied upon them. In contrast, the energy barrier for the Cl^- ion was large and it could not pass through the F-pore graphene. The findings of the study indicate that the permeation of ions across the graphene was a function of applied electrical fields. The findings of the present study are based on the detailed analysis and consideration of potential of mean force and radial distribution function curves.

1. Introduction

The pollution of water by heavy metals is considered to be a serious concern around the world throughout the past decade. Some heavy metals can be toxic and harmful for human life. Some of industrial wastewater may contain toxic heavy metals. Elements which are toxic for humans and the environment range from copper, mercury, chromium, lead, manganese, cadmium, nickel, zinc to iron. In case the concentration of such heavy metals increases beyond the permitted limit in wastewater, they must be eliminated from wastewater since these heavy metals in water can cause many worrying problems. Hence, different technologies and measures should be taken to prevent the increase of such metals. The experimental procedures which might be applied to get rid of heavy metals include precipitation, flocculation, ion exchange, reverse osmosis [1–3], electrochemical operation and biological treatment [4,5]. One more technique which might be considered is to make use of the technology of nanostructured membranes. Nanostructured membranes offer some technologies for separating ions. The flux across a membrane increases based on the size of a pore created in the membrane. One nanostructured membrane is graphene which has unique properties such as ultimate thinness, flexibility, chemical stability, and mechanical strength [6–8]. Thanks to these outstanding properties, graphene can be considered as a highly appropriate choice for removing ion. Since the isolation of graphene [9], it has been a research agenda for many theoretical [10] and empirical research studies [11]. Specifically, functionalized graphene membranes as well as nanoporous membranes [12–15] have unique properties and applications [7,16–23]. Nanoscale pores can be introduced in graphene with unsaturated carbon atoms at the pore edge which are passivated by chemical functional groups. Recently, several experimental studies have been developed to create pores in graphene, [24–26]. Although numerous studies have found many applications of graphene in several areas such as DNA sequencing and gas separation [27,28], the role and significance of this material for removing heavy metal

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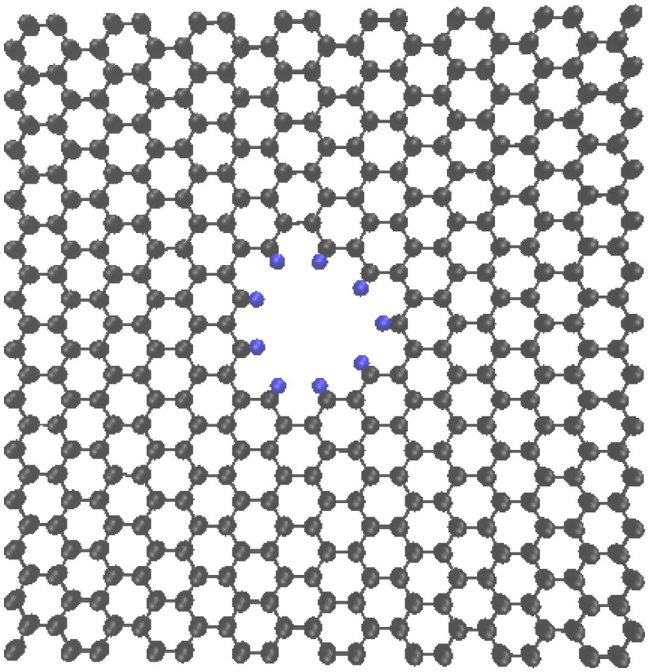

Fig. 1. Functionalized graphene membranes as a nanostructured membrane (black: carbon; blue: fluoride). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

from aqueous solutions remains unexplored and is considered to be a research gap. Therefore, it may be speculated that this membrane can potentially act as a filter for ion separation. Graphene is assumed to show high selectivity through molecular size exclusion effects and at the same time it has high permeability due to its very little thickness. A graphene without any defects does not have any pores and hence is not permeable to gases [29]; this is attributed to the fact that the electron density of its aromatic rings is enough to repel atoms trying to pass through this membrane. Hence, to achieve ion permeability, it is necessary to drill pores in the graphene by a chemical or thermal treatment [30,31]. It has been acknowledged that cavitary graphenes are highly efficient membrane materials for ion, gas and nanoparticle separation [32,33].

To the best of researchers' knowledge, no studies have been conducted on removing copper and mercury ions by functionalized graphene. Thus, the researchers intended to address this research lacuna in the present study. That is, molecular dynamics (MD) simulations of functionalized graphene was used to remove heavy metals from aqueous solution under the application of electrical field. How ion removal changes based on pore chemistry and applied electrical field was investigated in this paper. In this study, a functionalized graphene was designed and it was found that this grapheme can effectively separate heavy metals from water. The researchers expect that the findings of the present study can be used as a research initiative and framework for designing energy-efficient graphene-based tools for heavy metal separation.

2. Computational methods and details

The full view of the functionalized graphene as a nanostructured membrane is shown in Fig. 1. A full geometric optimization of functionalized graphene was obtained by applying Density Functional Theory (DFT) method. DFT method was employed to obtain the optimized structure and atomic charges of functionalized graphene. These computations were done at the B3LYP

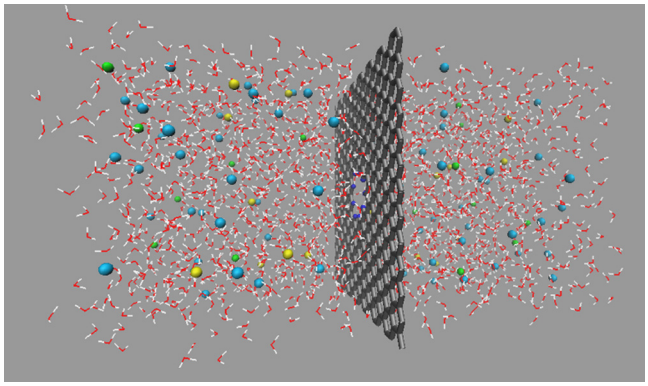

Fig. 2. A snapshot of the simulated system (black: carbon; blue: fluoride; green: Cu^{2+}; yellow: Hg^{2+}; cyan: Cl^{-}; red: O; white: H).

level of theory using 6-311G (2d, 2p) basis sets. All calculations were carried out using GAMESS-US package [34]. DFT has recently become the preferred method for systems, because it has some static correlation and suitable computational cost. Suitable computational cost term arises from the fact that DFT method depends on just three variables (x, y, z) while wave function theory for an n-electron molecule depends on $4n$ variables, three spatial coordinates and one spin coordinate, for each electron [35]. The definitions of exchange and correlation energies in DFT at least in current implementations are local or short-rang since they depend on the density at a given point and its immediate vicinity, *via* its derivatives [36]. But because of the nature of the exchange and correlation functional, DFT suffers the self-interaction error (SIE) of the electrons. SIE by exchange part for commonly used functionals simulates static correlation effects cannot be covered by single determinant wave function theory methods which is an advantage. Therefore DFT correlation includes only dynamic correlation and DFT exchange includes not only local exchange but also some static correlation, although the latter is present in an unspecified and uncontrolled way (SIE).

Long-range interactions for atomic species have been characterized with the Lennard–Jones potential [37,38]. Lennard–Jones parameters for carbon atoms included $\varepsilon = 0.2897$ kJ/mol and $\sigma = 3.39$ Å [39]. The water–graphene, water–ion and ion–graphene interaction parameters are derived by using Lorentz–Berthelot combining rules where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = (\varepsilon_{ij} \cdot \varepsilon_{ij})^{0.5}$. In this rule, ε_{ij} and σ_{ij} are regarded as the usual empirical Lennard–Jones parameters. The chemical agent which was used in this study to passivate each carbon in the graphene was a fluorine atom. Fluorinated pore (F-pore) was obtained by passivating each carbon at the pore edge with a fluorine atom. The researchers performed MD simulations with NAMD molecular dynamics package developed at the University of Illinois at Urbana-Champaign [40] as a previous work [41]. In this work, there was a 1 fs time-step with a 12 Å cut-off for van der Waals interactions and a Particle Mesh Ewald (PME) scheme [42] was used for electrostatic calculations; all the analysis scripts were composed locally using VMD, a visualization package available from UIUC visualized using VMD [43]. As it is illustrated in Fig. 2, the MD domain consisted of a functionalized graphene, water, and heavy metals (copper and mercury). The simulation box for all runs was 3 nm × 3 nm × 6 nm. Dimension of graphene sheet is 3 nm × 3 nm. The number atoms of graphene are 377 carbon atoms and 9 fluorine atoms. A repeated unit of graphene sheet was used for optimization of the functionalized graphene by DFT method.

In all the simulation period, an electrical field was applied in a direction which was perpendicular to the graphene membrane.