Computer simulation to investigate separation of heavy metal ions by sand/graphene oxide column

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Abstract

In this study, computer simulations were performed on ionic solutions containing heavy metal ions Pb(II), Cd(II) and As(III). The situation where these aqueous ions are retained through the sand/graphene oxide column is simulated. The sand/graphene oxide separation column is formed by the aggregation of constructed sand particles and graphene oxide (GO) molecular clusters. The process of ion aqueous solution flowing through the column is investigated and the mobility of each ion is evaluated. The simulation shows that adding GO to the sand can separate the heavy metal ions more effectively. The sequence of the mobility of the simulated heavy metal ions in the column is: As(III) > Cd(II) > Pb(II), which is consistent with the experimental results reported in the literature. We use simulation methods to study the electrostatic interaction between heavy metal ions and GO sheets. It is found that this interaction is an important factor in the separation of sand/GO column.

Keywords

graphene oxide, computer simulations, heavy metal ions, mobility, GO column, separation

Introduction

Harmful chemicals in water resources can cause major problems to human health. Among the chemical pollutants in the water, metal pollution is considered very dangerous. Most types of heavy metals are highly toxic, persistent and non-biodegradable (Cai et al., 2019; Dong et al., 2017; Sheet et al., 2014). Therefore, the separation of these metals from water is considered a key issue. Many methods have been proposed to remove heavy metals from water, including ion exchange (Alyüz and Veli, 2009), coagulation and flocculation (El Samrani et al., 2008), chemical precipitation (Ghosh et al., 2011), reverse osmosis (Cséfalvay et al., 2009) and adsorption (Yanagisawa et al., 2010). Among these reported methods, adsorption is a feasible and low-cost separation method that can be widely used in different ways (Li et al., 2013). Various adsorbents of different materials have been used to separate heavy metal substances. Experimental results showed that carbon-based materials such as activated carbon, carbon nanotubes (CNTs), graphene oxide (GO) had good chemical stability and high adsorption capacity (Gupta and Bhattacharyya, 2012; Tangjuank et al., 2009). Recent reports showed that GO is an effective adsorbent for removing inorganic and organic contaminants, especially effective for removing heavy metal substances (Gupta and Bhattacharyya, 2012; Jiang et al., 2018). GO has been tested as an absorbent for removing heavy metal ions, including Pb(II), Cd(II), Co(II), Cr(VI), As(III), Cu(II) and Eu(III) (Fan et al., 2012; Sun et al., 2012; Wu et al., 2013; Zhang et al., 2010; Zhao et al., 2011). Since GO is highly mobile, this will reduce the separation efficiency, so sand is often used to immobilize GO. Gong et al. investigated the adsorption of Pb (II) and methylene blue in the fixed-bed column filled with GO coated sand (Gong et al., 2015). They found that the adsorption capacity of the column increased greatly by GO. The Sand/GO column could be used to remove heavy metals including Pb(II) and Cu(II) from aqueous solutions. Experiments have shown that increasing the amount of GO in the column can improve the removal efficiency; on the other hand, the increase in
the flow rate in the porous medium leads to a decrease in the adsorption of heavy metals. Abbasi et al. (2021) reported their experiment for the enhanced absorption of heavy metal ions in groundwater using sand columns enriched with GO. They concluded that the mixed medium of GO and sand can effectively reduce the mobility of heavy metals. The order of separation efficiency of sand/GO column for metal ions is: Pb(II) > Cd(II) > As(III). They proposed that the separation efficiency was attributed to the high adsorption performance of GO for metal ions, because of the specific physicochemical properties and high electronegativity of oxygen over carbon atoms (Abbasi et al., 2021; Peng et al., 2017).

In addition to experimental work, theoretical calculation research also helps to design new material media. The literature has reported some theoretical work to study the removal of heavy metal ions. For example, Abbasi et al. (2021) used the method of fitting experimental results to find the kinetic model of various metal ions adsorbed on GO. Azamat et al. (2015) used molecular dynamics (MD) simulation to investigate removal of heavy metal from water through armchair carbon and boron nitride nanotubes. Pacheco-Blas and Vicente (2019) applied MD simulation to investigate the removal of heavy metals with micelle in water, and extraction of Cd²⁺ by surfactant.

The current research proposes to use MD simulation in combination with other method to investigate the separation of metal ions by sand/graphene mixed media. Our goal is to understand the separation process and influence factors by theoretical method. MD simulation, sometimes referred as computer experiment, was applied frequently in many different areas to assist experimentalist for the understanding of dynamical path and designation of new materials (Bruce et al., 2002; Khurana et al., 2006; Mackerell Jr, 1995; Rakitin and Pack, 2004; Shelley and Shelley, 2000; Tummala and Striolo, 2008; Yan et al., 2010). This powerful technique provides useful dynamical and statistical information at atomic level. We hope that this study will help predict the separation ability of complicated sand/GO column for metal ions.

## Experimental Methods

### Molecular dynamics simulations

MD simulations with UNIVERSAL force field (UFF) were carried out for all the investigated systems (Rappe et al., 1992). The potential energy in UFF can be expressed as

\[ E = E_g + E_α + E_φ + E_w + E_{vdw} + E_{el} \]  

(1)

The interaction energy consist of bond stretching \(E_g\), bond angle bending \(E_α\), dihedral angle torsion \(E_φ\), inversion terms \(E_w\), van der Waals interactions \(E_{vdw}\) and electrostatic terms \(E_{el}\) respectively. UFF force field contains necessary parameters for all elements in periodic table.

### Reference simulations

In each MD simulation, the time step for the numerical integration was set to one femtosecond and temperature was 300 K respectively. In order to simulate the separation of a sand-filled column, sand grains must be constructed first. The reported empirical formula of sand was SiO₂ with density of 1442 kg/m³ for loose-packed sand. According to the literature, the structure of sand is made up of silicon and oxygen atoms. Each silicon atom is bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms. However, the empirical formula of silica is also SiO₂ with density of 2.65 g/cm³, about twice as large as that of sand. The crystalline structure of silicon dioxide has perfect diamond structure and tetrahedral arrangement. This indicates that the possible structure in sand is that the linkages between silicon atoms and oxygen atoms are similar to that in silicon dioxide, but the structure is not perfect diamond-linked array. In real, sand is a loose, fragmented, naturally-occurring material consisting of very small particles. Base on this, in the current simulation, we treated sand as loosely bonded SiO₂ particles in spherical shape. Each sand particle contains 300 Si atoms and 600 O atoms confined into a sphere with radius 3 nm and the density of sand particle matched to the reported density of sand, 1.442 g/cm³. Initially, the positions of all atoms were randomly generated in the sphere.

MD simulation was carried out to equilibrate this system. After the system reached to its thermal equilibrium, the closed pair of Si and O atoms (Si-O distance within 3.5 Å) were linked to form a Si-O bond. Each of Si atoms can form maximum of four bonds with its closed neighboring O atoms, and each of O atoms can form maximum of two bonds with its neighboring Si atoms. After the linkage, MD simulation was then executed to equilibrate the system and the Si-O linkage was restarted. The above processes, equilibrate the system followed by the connection of closed Si-O pairs were repeated until all silicon atoms and oxygen atoms were properly connected to their neighbors. We found that about 90% of silicon atoms having 4 bond connections with neighbored O atoms, and 95% of oxygen having 2 bond connections with neighbored Si atoms. Only small portion of Si and O in our particles had imperfect connections and we believe this will not affect the result for the subsequent simulations. Fig. 1 illustrates the procedure for the construction of our “sand” bead.

The reported structure of GO (Nasrollahzadeh et al., 2015) was adopted in our simulations. The GO molecule
is the oxidation product of graphene with a unique structure containing hydroxyl, epoxy, carboxyl, and carbonyl functional groups. **Fig. 2** shows the structure of optimized GO molecule. The molecule is not planar with certain curvature as literature reported. In addition to single GO sheet, we also simulated the blocks gathered by GO sheets. First stack ten GO pieces in a cubic box with edge length 45 Å, and then optimize the structure of these 10 GO pieces. GO and the optimized GO aggregation block were used in later simulations. The optimized configuration of GO and 10-GO lump were shown in **Fig. 2**.

In our subsequent simulations, both sand and GO were treated as “rigid” bodies. The relative configurations of all composed atoms of them were fixed and the movement of the particle only considers the translation of the center of mass and the rotation of the entire body.

### Sand columns reference simulations

In the current study, three types of sand columns were constructed: 1. ten sand beads (referred as sand system), 2. ten sand beads and ten separate GO molecules (referred as sand_10/GO_10 system), and 3. ten sand particles and two 10-GO aggregated lumps (referred as sand_10/GO_2(10) system). For comparison, another two systems, corresponding to sand_10/GO_10 and sand_10/GO_2(10), with zero atomic charges of GO were also simulated. These two zero-charged-GO systems were referred as sand_10/GO(0)_10 and sand_10/GO(0)_2(10) respectively. To construct sand and sand/GO columns, the pre-generated sand beads and GO molecules were packed into a cubic region with dimensions 150 Å × 150 Å × 150 Å. This region is bounded by the He atomic plane, confining sand particles and GO to the region. The He atomic plane is composed of He atoms fixed at a distance of 3 Å. First, put the target molecule (sand or GO) into the box in a random manner, and then optimize the configuration of the box by moving and rotating the particles sequentially. The optimization process was repeated until the energy was converged. We found that to relax the configuration of large molecules sequentially is an effective way to reach the energy minimum. In the optimization process, optimizing the structure of the \(i\)-th molecule requires calculating the force on the molecule,

\[
\vec{F}_i = -\frac{\partial U}{\partial \alpha} \quad \alpha = x_i, y_i, z_i, \theta_i, \psi_i, \chi_i
\]

**Fig. 1.** Illustration of the process to construct a “sand” bead.

**Fig. 2.** (a) Configuration of optimized Graphene oxide molecule. (b) Optimized configuration of a lump of 10-graphene oxide-sheets molecules.
In which, $\vec{F}_i$ is the force, $x_i, y_i, z_i$ are the center-of-mass coordinates; $\theta_i, \varphi_i, \chi_i$ are the Euler angles of the $i$-th molecule respectively. Based on the calculated force, the new position and orientation can be predicted,

$$a' = a^0 + \vec{F}_i \delta a$$

where $a'$ and $a^0$ refer to the new and old coordinates respectively. For each of the simulated system, we collect one hundred low-energy configurations of sand columns. Ten lowest-energy-configuration columns of each system were used for the later computations. During the subsequent simulations, the configurations of columns were fixed and periodically repeat in z direction (Liu et al., 2018) as shown in Fig. 3. The figure illustrates 3 repeating units configurations of sand, sand_10/GO_2(10) and sand_10/GO_10 columns.

Results and Discussion

| Radial distribution function |

Given in Fig. 4a are the radial distribution functions (RDF, $g(r)$) of O in water to the cations (O-M). The figure shows intense peaks around $r = 2.3$ Å for Cd$^{2+}$, $r = 2.7$ Å for As$^{3+}$ and $r = 2.9$ Å for Pb$^{2+}$. These strong peaks indicate that the positively charged ions are surrounded by the water molecule solvent through the interaction between the ions and the oxygen in the water. The peak height indicates the number of water molecules surrounding nearby, so-called “hydration number”. It can be seen from the figure that the order of the hydration number of cations is: As$^{3+}$ > Cd$^{2+}$ > Pb$^{2+}$. The figure shows that the Cl$^-$ ion has a lower number of hydration because it has a negative charge. This indicates that anions move more freely in water than cations.

The diffusion constant of the ion can be obtained from the calculation of the mean square displacement (MSD),

$$MSD = \langle \vec{r}_i(t)^2 - \vec{r}_i(0)^2 \rangle$$

The bracket indicates the ensemble average, and $\vec{r}_i$ is the position vector of the $i$th ion. The slope of the MSD versus time gives the diffusion constant.

$$MSD = 6Dt$$

$$D = \frac{1}{6t} MSD$$

| Mean square displacements |

Given in Fig. 4b are the calculated mean square displace-
ments of ions vs. time. The MSD plots showed that the diffusion constant of water is larger than ions, indicating that water moves faster than anion and cations. The diffusion constants of ions are in the order: Cl\(^-\) ≫ As\(^{3+}\) > Pb\(^{2+}\) ~ Cd\(^{2+}\). The mobility of anions is greater than that of cations. This may be due to the lowest level of hydration of Cl\(^-\) among the ions, which causes the anions to move more freely in the water. The mobility of an ion depends on its mass, charge, and degree of hydration. The magnitude of the cation diffusion constant indicates that the mobility of cations in water is similar. Although there are differences in hydration distance, number of hydration, ion mass, and ion charge, the similar cation mobility indicates that the ion moves with the water molecule that it hydrates.

<table>
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<tr>
<th>Mobility of cations</th>
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<td>After removing the boundary He-plate at the bottom of the solution box, the molecules and ions in the previously pre-equilibrated ion solution can flow into the separation column naturally. According to the low-energy configuration of the sand (sand/GO) system constructed by the previous calculations, the MD simulation of the flow of ions and water molecules into the sand (sand/GO) column is performed. In each MD simulation system, 10 configurations corresponding to the lowest energy of the sand column or sand/GO column are used. The distribution of ion movement distance is obtained by taking the average value of these MD simulation calculations. <strong>Figure 5</strong> is a schematic diagram of analyzing ion current in the simulation.</td>
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</table>

**Figure 5** shows the average distribution of Pb\(^{2+}\) in the Sand_10/GO_2(10) system along the column direction at different time stages. In the figure, the blue area is the

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**Fig. 4.** (a) Radial distribution function g(r) of ions to O in water. (b) Mean square displacements of ions and water.

**Fig. 5.** Pb\(^{2+}\) flow at different stages in sand_10/GO_2(10) system.
distribution after 8,000 steps; the red area is the distribution of 10,000 steps, and the light green area is the distribution of 12,000 steps. The figure shows that the maximum travel distance of Pb\(^{2+}\) ions after flowing for 12,000 time steps is approximately 250 Å. Figure 6 compares the flow distribution of Cd\(^{2+}\) in the pure sand column and the GO-added sand_10/GO_10 column at different time periods.

Figure 6 shows that ion moves faster after adding GO into the system. Since system sand_10/GO_10 is more crowded than pure sand system, the increase mobility of Cd\(^{2+}\) in GO added sand column must due to the electrostatic interactions. The corresponding distribution of Cl\(^{-}\) in sand_10/GO_10 column is also shown in the figure. The figure shows that the maximum displacement of Cd\(^{2+}\) and its number increased for GO added system. The distribution of Cl\(^{-}\) (in both the moving distance and number of ions) is much larger than the corresponding Cd\(^{2+}\). In all other systems, we have found that Cl\(^{-}\) move much faster than cations. This consists with the experimental result (Abbasi et al., 2021) that sand (sand/GO) system has the very low absorption capacity of anions. Such ions can not be effectively removed by sand (sand/GO) column. In Fig. 7, we summarize the calculated ion currents in the three systems. The figure shows the distribution of 12,000 fs after the solution flows into the sand column. The maximum displacement of each ion is marked in the figure for clarity. We found that the mobility of cations in the three sand columns is different.

In general, mobility of all cations in GO-added columns is greater than those in pure sand column. Among the cations, the mobility of Pb\(^{2+}\) in three simulated system is not too much different. The Cd\(^{2+}\) moved slower than Pb\(^{2+}\) in the pure sand column but moved faster than Pb\(^{2+}\) in the GO-added other two systems. The mobility of As\(^{3+}\) is the largest among cations in three systems. In particular, As\(^{3+}\) ions move very fast on those systems where GO is added. The simulation results show that GO molecules or GO blocks increase the moving speed of As\(^{3+}\) and Cd\(^{2+}\) in the sand/GO system, but have little effect on Pb\(^{2+}\). This means that the retention effect of Pb\(^{2+}\) in the sand/GO system is greater than that of the other two cations. According to M. Abbasi et al (Abbasi et al., 2021), the retention trend in the sand/GO column experiment is Pb\(^{2+}\) > Cd\(^{2+}\) > As\(^{3+}\), which is consistent with our simulation conclusion. In addition to ions, the movement of water molecules in the column is also analyzed. We found that the water moves down very fast because of the large free space of the pillars. In those GO-added sand column systems, the water flow rate is even faster.
than that in the pure sand column system I. This may be caused by the repulsion between the water and the negative charge at the GO.

**Moving trajectories of cations**

Given in Fig. 8 is the trajectories of ions in a select sand_10/GO_2(10) system. The detailed moving trajectories are shown in the left plot. Figure 8 shows that ions flow in a curved ways, that is, not directly flow downward. This indicates that the flow of ions is not completely free, they are interacted with sand and GO. It has been reported that the electrostatic interaction between positively charged heavy metal ions and negatively charged GO sheets provides a driving force for the
absorption (Abbasi et al., 2021). To investigate the electrostatic attraction between ions and GO, two comparative MD runs were executed. In these comparative runs, the atomic charges in GO were set to zero. This eliminates the electrostatic interaction between GO and charged ions or water. As mentioned earlier, these two systems are named sand\textsubscript{10}/GO(0)\textsubscript{10} and sand\textsubscript{10}/GO(0)\textsubscript{2}(10). Table 1 shows the simulation results of the maximum displacement of cations in each system. The value in parentheses in the table is the maximum ion displacement in the uncharged GO system.

According to the Table 1, the simulation shows that ions moved much faster for zero-charged GO. The trend of mobility of ions is still As\textsuperscript{3+} > Cd\textsuperscript{2+} > Pb\textsuperscript{2+}, however, the amplitude of ion movement in the zero-charge GO system is much greater than that in the charged GO system. Oxygen-containing functional groups (epoxy and hydroxyl groups on its basal plane, and carbonyl and carboxyl groups at the edges of the nanosheets) on the GO surface and -electron system offer abundant binding sites for the adsorption of heavy metals and affect mobility of ions. This calculation shows that both GO molecules and GO blocks can effectively prevent the movement of ions. Our simulation clearly demonstrates the importance of the electrostatic interaction between ions and GO to retain cations. It has been reported that the electrostatic interaction between positively charged heavy metal ions and negatively charged GO sheets provides a driving force for the absorption. Gu et al (Gu and Fein, 2015) found that the affinity order of metal ions to GO has nothing to do with the ionic radius, but is closely related to the electronegativity of the metal. Their experiment showed the affinity order of ions on GO is: Pb(II) > Cu(II) \gg Cd(II) \approx Ni(II) \approx Zn(II) > Sr(II) \approx Ca(II). Our simulation agrees with this experimental result that the retention degree of ions in GO is Pb\textsuperscript{2+} > Cd\textsuperscript{2+}.

Table 1. Maximum displacements of ions (Å) at 12,000 steps

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Sand\textsubscript{10}/GO\textsubscript{10}</th>
<th>Sand\textsubscript{10}/GO\textsubscript{2}(10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb\textsuperscript{2+}</td>
<td>250</td>
<td>256 (290)</td>
<td>262 (297)</td>
</tr>
<tr>
<td>Cd\textsuperscript{2+}</td>
<td>246</td>
<td>260 (447)</td>
<td>280 (505)</td>
</tr>
<tr>
<td>As\textsuperscript{3+}</td>
<td>258</td>
<td>462 (750)</td>
<td>302 (593)</td>
</tr>
</tbody>
</table>

Values in parentheses are calculated with zero-charged GO.

Conclusions

In this study, MD simulation was used to investigate the flow behavior of cations from the aqueous solution to the sand/GO column. Special technique was adopted to construct sand particles, separate sheets and lump of GO were added into sand column. We use a special simulation method to construct sand bead and block GO. After that, separate GO sheets and block GO are mixed into the sand column to form separation columns. The simulation results show that in all sand/GO systems, except for Pb\textsuperscript{2+}, the mobility of cations is greater than that in the pure sand column. This means that the addition of GO can increase the flow rate of cations. In all sand/GO systems the order of cation mobility is: Pb\textsuperscript{2+} \textless Cd\textsuperscript{2+} \textless As\textsuperscript{3+}. This order agrees well with experimental result. In addition, a comparison of the cation flow rates in charged GO and zero-charged GO systems can prove that the main driving force for cation flow in the sand/GO column is the electrostatic interaction with GO. Our research proposes a method to estimate the metal ion removal efficiency of the sand/GO column using computer simulation. This study successfully estimated the separation efficiency of the sand/GO separation column for metal ions, and provided a reference for the future design of metal ion separation columns.

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References


Dong, J., Li, B. and Bao, Q. (2017) In situ reactive zone with modified Mg(OH)\textsubscript{2} for remediation of heavy metal polluted groundwater: Immobilization and interaction of Cr(III), Pb(II) and Cd(II). J. Contam. Hydrol. 199, 50–57. https://doi.org/10.1016/j.jconhyd.2017.02.005