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Adsorption of Cations Using Graphene Oxide Loaded with Ionic Liquid: A Molecular Dynamic Simulation

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Abstract **-** Sea water desalination is the process of separating salts from water to produce potable water. It is a very important process for countries that lack fresh water sources such as UAE. Many techniques are used in this process, but the most common one is the reverse osmosis (RO) process, which uses semipermeable membranes. Although this technique is widely used, it has a major drawback which is membrane fouling. Membrane fouling is caused due to inorganic salt deposition. This problem decreases the efficiency of the process and increases the costs. To solve the problem of inorganic salts fouling on the water filtration/desalination membranes, a proposed solution is to treat saltwater using a new adsorbent called GO-IL before sending it to the desalination process. GO-IL is an adsorbent made of graphene oxide nanosheets loaded with an ionic liquid called propylammonium nitrate. Treating saltwater using GO-IL aims to adsorb significant amounts of salts (e.g. Na^+ and Mg^{2+}) present in water before starting the desalination process. This pretreatment process reduces desalination membrane fouling, enhances the desalination process, and reduces cleaning and maintenance costs. The purpose of our work is to simulate the water pretreatment process using GO-IL on a molecular level scale using the computational power of Molecular Dynamics (MD) Simulations to test its efficiency.

Keywords**:** Graphene oxide, Ionic Liquid, Adsorption, Desalination, Reverse Osmosis, Molecular Dynamic Simulation

1. Introduction

Sea water desalination is mainly the separation of salts from sea water to produce usable water. It is a very important process specially for countries that lack fresh water sources and have many coastal areas. Many techniques are used in this process such as thermal evaporation and membrane separation [1]. One of the most common techniques that uses membrane separation is the Reverse Osmosis process. In this process the salt is separated from water using a semi-permeable membrane with pressure as the driving force. Naturally, water will move from the less salt concentrated side (fresh water) to the more salt concentrated side (salt water), this process is called osmosis. In the reverse osmosis process, pressure is used to force the water molecules to move from the saltwater side to the freshwater side while the salts cannot cross because of the semi-permeable membrane.

During the RO process, the semi-permeable membrane is exposed to inorganic salt deposition which is called membrane fouling. This deposition highly reduces the efficiency of the membrane and increases the costs of the process as the membranes must be periodically replaced. Inorganic salts include calcium and magnesium salts. This problem can be solved if a pre-treatment step of adsorbing salt cations is proposed for the RO process.

Many adsorbents have been experimentally tested for cations adsorption. One of those adsorbents is the Graphene Oxide Loaded with Ionic liquid adsorbent (GO-IL). It has shown great results experimentally for adsorbing salt cations such as Calcium ions (Ca^{2+}) and Magnesium ions (Mg^{2+}). Many studies have shown that GO is a good adsorbent for many metals such as Co^{2+} and Cd^{2+} [2]. However, GO alone tend to agglomerate in the presence of Ca^{2+}, Mg^{2+} and Na^+ which are the main salt cations in sea water. This problem can be solved by inserting a spacer material between the GO layers, which in our case is chosen to be the Ionic Liquid (IL). The chosen IL to be used is Propylammonium Nitrate (PAN). This made GO-IL a potential adsorbent for the salt cations in the pretreatment step for RO.

Molecular Dynamic (MD) is a type of simulation that imitates how atoms behave in a certain system based on the given conditions. The motion of the atoms is determined based on the classical Newtonian dynamic equation's numerical solution. MD not only provide the user with the predicted motion of atoms, but it also can provide thermodynamic data that can be used in further studies [3]. The first step and the most important one in MD is to define the interaction potential and

molecular topology for the system to be simulated. The interaction potential is basically some parameters that defines the interactions between the types of atoms present in the system and also the bonds that can be formed between them. The molecular topology is the initial coordinates and type of each atom in the system. The second step is to define initial position and initial velocities for each atom. After that the software computes interatomic forces and move the atoms according to the equation of motion. The molecular geometry is then changed and thermodynamic data is computed. These computations are done repeatedly depending on what the user had defined to the software. Many softwares are used for MD simulation such as LAMMPS, Quantum, Gromacs and NAMD. The software that is being used in this project is LAMMPS. This software was chosen because of its strong capabilities and great flexibility.

2. Modelling Details

2.1. Modelling molecular structures

In this section, we present a summary of the steps we performed to replicate the GO-IL adsorption process on a molecular level. Our work is all on the nano-scale because larger scales require massive hardware power.

The first step is to model the graphene oxide sheets. **Error! Reference source not found.**Fig.1 (A) shows a hexagonal graphene oxide sheet of radius 30 Angstroms (Å). We used the Make-Graphitics building tool [4] to build the sheet, where we specified its size and the C/O ratio. Fig.1 (B) shows a smaller sheet of radius 15 Angstroms (Å) that we built as a sample to experiment with because it takes shorter time and requires less hardware power to run molecular dynamics simulations. The modelled graphene oxide sheets contain hydroxyl, carboxyl, and epoxy functional groups.

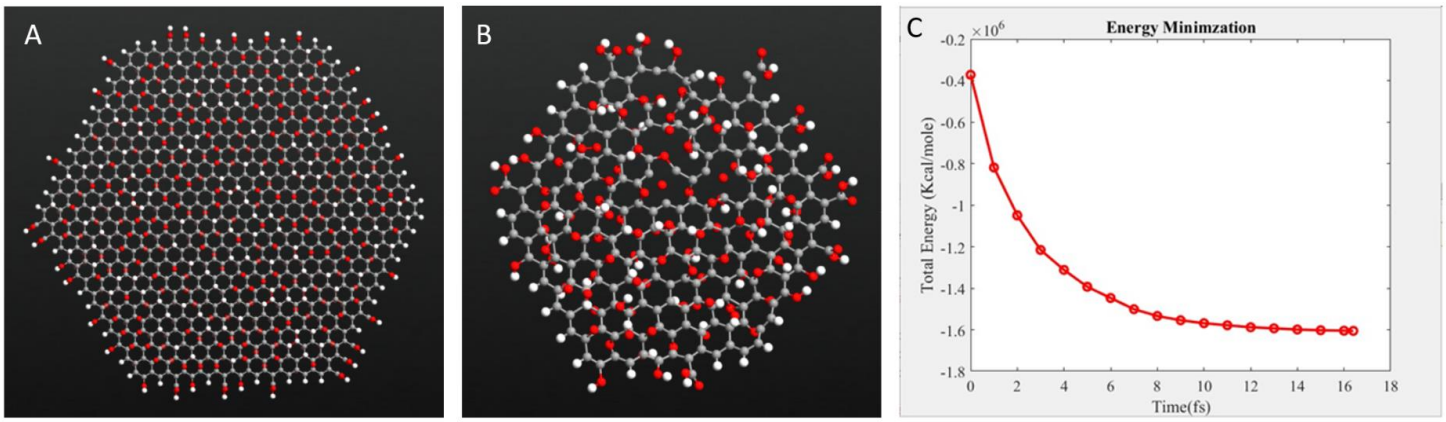

Fig. 1: (A) Graphene oxide sheets of radius 30Å, (B) Graphene oxide sheets of radius 15Å. (C) Energy minimization plot.

Fig. 1 (C) shows how energy minimization is done in LAMMPS. The energy is reduced until it reaches stability, and the tolerance value is achieved. This assures that the simulated system is approximately near the real one and is mimicking it. The data used in this curve were exported from LAMMPS and imported in MATLAB for plotting. After minimization, relaxation has to be done for the system to release any tension between the atoms. These two steps are crucial for any simulation process before implementing any further steps. In reality, graphene oxide sheets contain some impurities. So, we manually added sulfur and potassium impurities to the sheet randomly using QuantumATK and then performed a short minimization to position the impurities in a reasonable place with the correct bonds.

After modelling the graphene oxide sheet, we modelled the ionic liquid molecule that should be attached to the sheet. The ionic liquid molecule consists of two parts, a cation which is propylammonium and an anion which is nitrate. We built the molecule manually then performed a short minimization to get the structure shown in Fig. 2. The next thing that should be modelled is a water bulk that resembles the saline water that is to be treated. Fig. 2 shows a water bulk that we created using Lammps by adding random H_2O molecules. The bulk shown contains ions such as Mg^{2+} and Na^{+}.

2.2. Defining force fields

After modelling the system, we should specify for the simulator how each atom behaves naturally and how it interacts with its surroundings. In molecular dynamics, this is done by inputting force field files along with the system structure. A force field file includes tables of numbers that define pair interactions, bond lengths, angles, dihedrals, and much more. There are many types of force fields, some are based on calculations and others are based on experimental data. Each type of force field approximates specific types of interactions. For example, Lennard-Jones (LJ) potential defines interatomic forces between atom pairs [5] while Reactive Empirical Bond-Order (REBO) potential defines bonds and interatomic forces between atoms. All force fields are approximations that serve different goals, and one should choose the force field that best describes/simulates the desired phenomena. In our case, the adsorption process involves bond breakage and bond formation. So, we used the Reactive Force Field (ReaxFF) potential. ReaxFF has been used to simulate graphene oxide systems in [6], [7], and [8]. This potential defines bonds of different orders (single, double, and triple), hydrogen bonds, Coulomb interactions and van der Waals interactions [8].

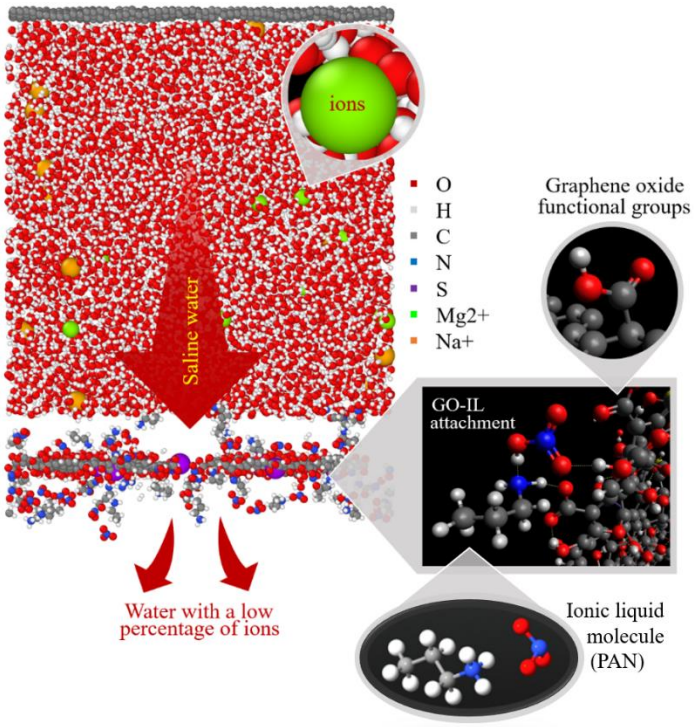

Fig. 2: An illustrative figure of the modelled system

3. Simulation and Observations

After modelling the system and defining the potentials, we started the simulation by performing a quick minimization and a short relaxation at constant temperature (300K) to allow the atoms to be in reasonable positions (not overlapping, for example). Then, the first thing we should notice is the ionic liquid getting attached to the graphene oxide sheet. To do so, the sheet should be deprotonated. So, we removed some hydrogen atoms from the carboxyl functional groups in the sheet, where the ionic liquid molecules should get attached. Fig. 3 (A) shows a carboxyl group after removing a hydrogen atom and Fig. 3 (B) shows a carboxyl group before removing a hydrogen atom.

By removing hydrogens, the functional group becomes negatively charged and ready to get attached to the cation of the ionic liquid molecule. After minimization and short relaxation, new bonds formed as shown in Fig. 3 (C). Yellow dashed lines represent hydrogen bonds, grey particles: carbon, red: oxygen, white: hydrogen, blue: nitrogen. As mentioned in [9], the negatively charged group is expected to get attached to the positively charged NH_3. Fig. 3 (D) shows the attachment from [9]. Fig. 3 (C) shows this attachment that was simulated successfully. After loading the graphene oxide sheet with ionic liquid, the adsorbent is ready to catch the salt ions present in water. Fig. 3 (E and F) shows the attachment of Mg^{2+} and Na^{+} cations to the negatively charged nitrate ion from the ionic liquid molecule.

The prelimenary results of our project are shown in Fig. 3 (C, E, and F). However, the main purpose of the project is to simulate the cations attachment to the adsorbent in a water bulk. The whole modelled system to achieve this purpose, as presented in section 2.1, is illustrated in Fig. 2. The wall shown on the top of the water bulk applies pressure to move the bulk downwards towards the adsorbent (GO-IL). Due to the large number of molecules in the system, this movement takes considerable hardware power and time, especially when performing test trials. Therefore, the final results of this project are not yet finalized. The final results are expected to show cations attachment to the adsorbent by a specific percentage that we are looking for. High attachment percentage means the proposed solution is efficient in removing cations from saline water and reducing membrane fouling in the Reverse Osmosis process.

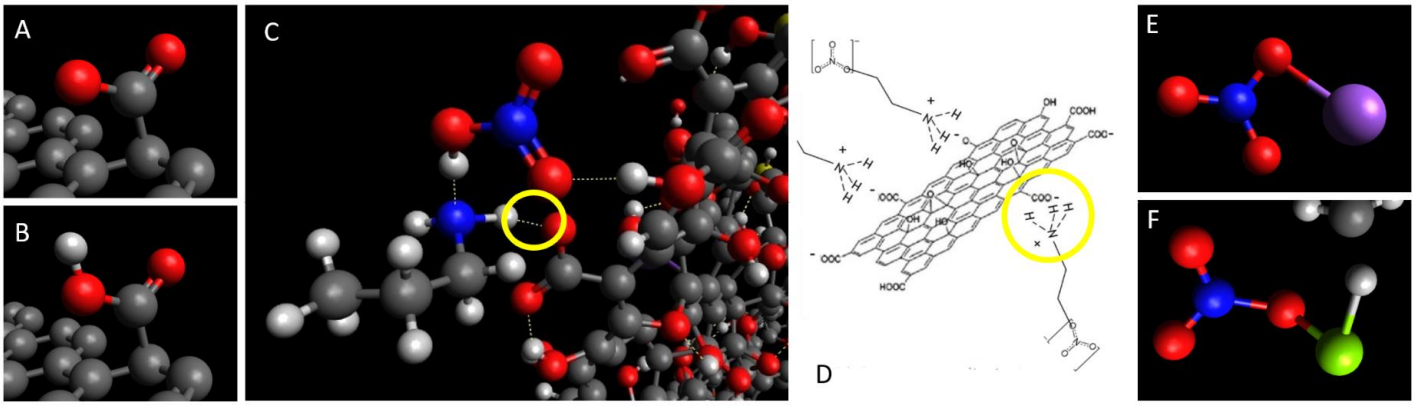

Fig. 3: (A) a carboxyl group after deprotonation (B) a carboxyl group before deprotonation (C) simulated ionic liquid attachment to the GO sheet (D) its chemical representation from [9]. (E) and (F) Attachment of Mg^{2+} and Na^{+} ions to the negatively charged part of the ionic molecule (NO_3).

4. Conclusion

The objective of this project is to simulate the GO-IL adsorption process and assess its efficiency. The GO-IL adsorption process is a pretreatment process that saline water goes through before it gets desalinated. This pretreatment process helps minimize the fouling that the cations present in water cause to the Reverse Osmosis membranes. Using the Molecular Dynamics Simualtion method to simulate the proccess helps reduce the cost and efforts needed to conduct experimental work. It further allows to perform sensitivity analysis and find the process optimum working conditions.

Acknowledgements

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