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# Study of the effect of osmotic pressure on the water permeability of carbon-based two-dimensional materials

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ABSTRACT

Two-dimensional materials such as graphene and carbon nanotube have promising applications in the preparation of permeable membranes and the field of environmental protection due to their unique structures and components. This paper conducts a study on graphene and nanotubes in salt solution using molecular dynamics computational method, and ascertains the quantitative relations between the ionic concentration, water flux and reverse osmosis pressure by setting up theoretical porous models of the two materials. This fundamental research provides much guidance in the determination of critical parameters like pressure and water flux in the actual application of membranes.

## 1. Introduction

Water is becoming a scarce resource and this issue of water shortage has evolved into one that concerns the state economy, sustainable development and prolonged societal stability. To combat the above mentioned natural constraints, humans have turned to water purification techniques, the most popular of which are filtration and chlorination. Over the past two decades of water filtration research, a great deal of effort has been directed to the study of carbon nanotube (CNT) and graphene sheets as well as their potential applications in filtration devices [1,2]. This great interest by the scientific community on CNT and graphene sheets is due to their remarkable mechanical strength and stability [3–5], their flexibility [6] as well as their customizable permeability [7]. Besides the above mentioned superior properties, CNT and graphene membranes are also reported to be relatively easy and cost effective to manufacture, making them suitable for commercial upscaling [3,7]. Such properties render them a top material candidate for membrane applications, a means of water filtration which though effective and fast, is still energy expensive and with much room for improvement in its sieving capabilities. In this report, we focus on the method of filtration and in particular, the membrane which is at the core of water purification via filtration.

In the following study, we direct our attention to the balance between applied external pressure and osmotic pressure due to the concentration of sodium chloride (NaCl) ions in the saline solution. Filtration is possible due to the permeation of water molecules through the filtering membrane. Permeation refers to a process in which a solvent (water in this case) enters a solution through a semi permeable membrane or a dilute solution naturally infiltrates into a solution with a higher ion concentration. As long as an appropriate external pressure is exerted to the side with the dilute solution, the process of permeation can be stopped. This pressure should be equivalent to the osmotic pressure of the solution. That is to say, when the pressure exerted to the saline solution is higher than the osmotic pressure, fresh water can be acquired using a semi permeable membrane. This process which opposes the naturally occurring phenomenon is called reverse osmosis (RO). There are two necessary requirements for reverse osmosis process. The first is that there must be a semi permeable membrane which has high selectivity and permeability (usually water permeability) while the other is that the operating pressure must be higher than the osmotic pressure of the solution. RO is developing rapidly and gradually gaining more and more market share in the desalination industry [8]. In the field of reverse osmosis, graphene membranes and carbon nanotube (CNT) have become research topics of great interest to the scientific community since Iijima published the paper on carbon nanotubes [9]. Graphene is a two-dimensional crystal stripping from graphite materials. It consists of an atom-thick layer of carbon atoms and is the thinnest, strongest and most conductive nanomaterial ever found; carbon nanotube, or Bucky tube, is a one-dimensional quantum material with a special structure (its radial dimension is nanometer scale while the axial dimension is micrometer scale). Due to the special structure and characteristic, carbon nanotube and graphene have

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potential application values in biological molecular separation devices [10], molecular sensors [11], molecular storage and the packaging of targeted delivery medium [12,13] as well as serving as the channel for fast transport of fluids [14–16]. Because of the nanoscale properties of graphene and carbon nanotube, researchers have been experimenting with their applications as a membrane in the process of reverse osmosis. Through creating apertures with an appropriate size, one can potentially build a membrane/CNT which allows water to diffuse through while blocking NaCl ions. Compared against traditional RO method, carbon nanotube has great advantages. Firstly, its tiny aperture enables it to act as a "Molecule Filter"——getting smaller particles across while blocking larger ones. Moreover, when considering the permeability of CNT to small water molecules, it should be noted that the unique electrical and hydrophobic properties of the CNT will allow water molecules to pass through its apertures at an extremely high speed in an orderly and linear way, resolving one of the limitations facing RO technology. Despite its benefits, experimentalists in this field have yet to successfully apply CNT membranes to water purification in a satisfactory manner. The filtration effect of today's state of the art CNT filtration membranes are far from ideal due to the great difficulty researchers face in fabricating high-quality CNT membrane with good structural integrity and high density [16,17].

With that in mind, this study carries out a related research on membrane permeation based on the material characteristics of graphene membranes and CNT and studies those using molecular dynamics simulation techniques. Using an appropriate pore diameter which allows diffusion of water molecules while blocking NaCl ions, the study aims to investigate the relationship between the applied external pressure, diffusion rate of water molecules and the concentration of NaCl ions in the saline solution. We hope that this research will provide a theoretical basis for the application of graphene membranes and CNT in sea water desalination.

## 2. Physical model and simulation method

### 2.1. Modelling of carbon nanotube and graphene

In this study, a chirality of (40,40), 2 nm-long carbon nanotube with diameter 5.4 nm was established using visual molecular dynamics (VMD) molecular simulation software [18]. As is shown in Fig. 1, four holes are created in the middle of the nanotube. Different diameters were used for each hole in order to study the relationship between pore sizes, net osmotic pressure as well as water flux. The minimum diameter was defined to be the smallest possible size that allows water molecules (about 0.36 nm in length, which is around the size of one water molecule) to pass through the pore while the maximum diameter is defined to be slightly smaller than the dimension required for sodium and chloride ions to permeate through. Based on related research [19], 0.4 nm was set to be the pore diameter against which the subsequent studies will be compared. Upon building the carbon nanotube model, it was dissolved in sodium chloride (NaCl) solution with a NaCl concentration of 0.8 M to simulate seawater (salinity ~3.5%), with a box size of 7 nm × 7 nm × 6 nm. Two other sets of NaCl concentrations (0.5 M, 1.1 M) were modelled for comparison and solvated in the same simulation box. In order to simplify the real-life model, an equivalent model was built in this study where ions inside of the nanotube were removed and pressure difference was generated using ions initially residing outside of the nanotube.

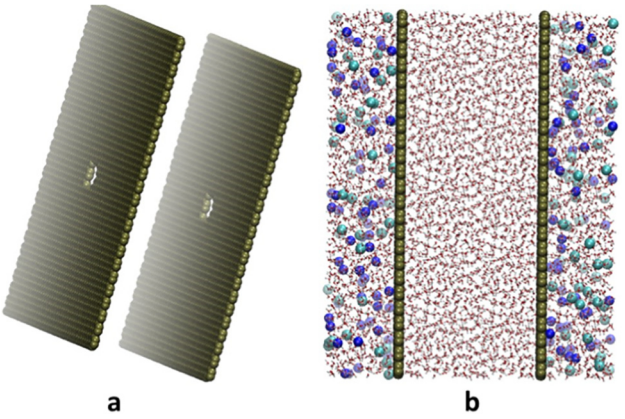


**Fig. 2.** Model of the graphene membrane (a) perspective view of the graphene membranes and its pore in the middle, (b) side view of the graphene membrane immersed in NaCl + water solution (the tan colored atoms are carbon; red and white dots are water molecules; green and blue atoms are chloride and sodium). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Carbon nanotube can also be regarded as curled graphene. To study the geometrically induced differences between them, a graphene model with the same parameters as the carbon nanotube was built for comparison. Using VMD, a two-layer graphene model with a separation of 4 nm was established. The dimension of each layer is 10 nm × 10 nm and a pore with the same diameter as that in the nanotube was created in the center of both layers, as depicted in Fig. 2. The graphene model was also dissolved in NaCl solution with box size 10 nm × 10 nm × 8 nm. Ions on the inner surface were removed and ions on the outer layer used to establish the osmotic pressure difference.

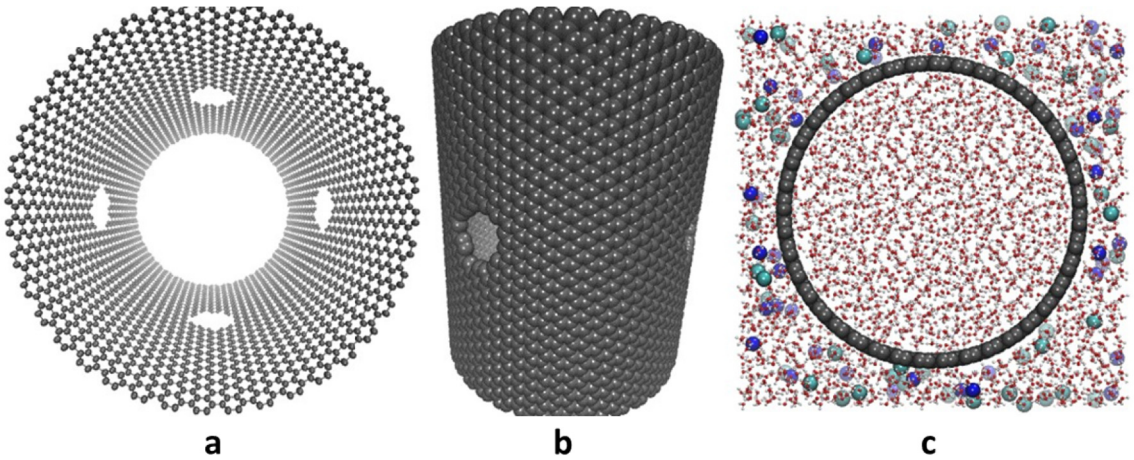


**Fig. 1.** Models of the carbon nanotube (a) top view of the CNT, (b) side view of the CNT, (c) top view of CNT immersed in NaCl + water solution (the grey colored atoms are carbon; red and white dots are water molecules; green and blue atoms are chloride and sodium). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)