Two-Dimensional Nanomaterials and its Application as a Reverse Osmosis Membrane: An Overview

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Abstract. With increased rate of global population and energy needs the clean water crisis aggravating all over the world continuously. Membranes based Reverse osmosis (RO) desalination technology is a promising solution to the shortage of safe drinking water as it has a high water recovery with low energy consumption compared to other separation techniques at minimum cost. Two dimensional (2D) nanoscale materials such as graphene with sub-nanopores have potential to excel as a RO membrane. Recent developments in 2D nanomaterials addressed the capability of RO membrane in terms of both mechanical strength and desalination performance. Developing the 2D materials with controlled pore (vacancy defect) sizes, pore chemistry and applied pressure is attracted vast interest in synthesizing such type of materials as a RO membrane. In this article, authors reviewed various 2D nanomaterials and its performance as a membrane in RO process.

1. Introduction

The past decade has witnessed the remarkable success of membrane based RO desalination plants with effective utilization of the polymeric membranes for water treatment. As of now, polymer based membranes dominated the RO desalination plants commercially, due to their matured technology. However, the polymeric membrane designs were developed three decades ago and do not have resistance against fouling. This could be the reason for low water flux of the polymeric membranes in the past two decades and the performance of RO membrane in terms of water permeability and salt rejection rate has not improved significantly [1-3].

Recent development in the field of nanotechnology and nanomaterials help the researchers to overcome the above mentioned issues. Particularly, the application of 2D nanomaterials in RO desalination as a membrane becomes an attractive approach to address the fouling and sustainability issues of existing polymeric membranes. Actually, the performance of these membrane used in RO desalination can be measured in terms of quantity of water permeation level obtained in the permeate side while holding back the salt ions. But water permeability and rejection of salt ions are function of pore (vacancy defect) size, applied pressure and pore chemistry of the membrane. Hence developing the 2D nanomaterials such as graphene and its analogues with controlled defect sizes are urgently needed to increase the performance as a RO membrane.

This paper first covers the study related to RO desalination. Next, the study on 2D nanomaterials and its performance as a membrane using computational method (Molecular Dynamics simulation) is presented. Finally, the study is concerned about the effect of defects (vacancy and Stone-Thrower-Wales) on the mechanical properties of 2D nanomaterials.
2. Reverse Osmosis (RO) Desalination

At present, more than one third of people in the world facing water crisis. Some study [4] indicates that by 2025, two third of global population will face water crisis due to huge demand on clean water along with increased rate of population in global level and more use of households and industrials. Desalination is suitable remedy for water scarcity which isolates pure water from seawater. Reverse Osmosis (RO), a membrane based technology is favoured over other desalination technologies due to its promising high efficiency provided high water flux and ion separation ability. As compared to thermal based desalination techniques such as multi-effect distillation and multistage flash distillation, the membrane based RO desalination technique has low energy requirement and low energy cost [5-10]. To date, more than 18000 desalination plants have been installed worldwide, among them half of which are RO desalination plants [11, 12]. In the RO process, the salt contaminant is removed by applying the external pressure (larger than osmotic pressure) in the feed side and then water is passed through a semi-permeable membrane into water permeate side as shown in Figure 1.

![Figure 1. Schematic representation of RO Process](image)

Water transport across the membrane caused by solution–diffusion mechanism [13, 14]. The semi-permeable membrane such as biological or polymeric membrane utilized in RO technique is generally termed as RO membrane, which excludes certain amount of particles or ions to pass through it by diffusion mechanism [15]. Water and ion permeation are the two key parameters for RO membranes and these have been relatively slow in the past decade. The recent development in 2D materials science could offer an engaging backup to polymeric materials.

3. Two-Dimensional (2D) Nanomaterials for Desalination

Foulants such as organic substances and micro-organisms reduces the durability of the polymeric membranes with increased maintenance cost of the membranes. The chemical expense to clean the membranes also increased periodically [16] resulting decreased rate of water flux and permeability. Novel 2D materials with nanopores were proposed as a replacement for conventional RO membranes to rectify this problem. With well-defined pore sizes, the porous membrane can provide water permeation by fast convective process. Computational study (Molecular Dynamics simulation) on 2D nanomaterials elucidates the performance as a membrane in RO desalination.

3.1. Molecular dynamics (MD) simulation study on 2D nanomaterials

The electron density of the graphene in its aromatic rings are capable of drive back the atoms and molecules that are trying to pass through these rings resulting pristine form of graphene mono layer sheet is impermeable to liquid or gases. Hence creating the nanopores (defects) in single layer graphene sheet is an essential to create water pathways. The major breakthrough for desalination application using mono layer graphene sheet with nanopores was experimentally demonstrated by
Surwade et al. [19] and further he proved the theoretical predictions [17-19]. Graphene with controlled nanopores is anticipated to shine as a possible candidate with the following characteristics such as single atomic thickness, angstrom sized pores can be obtained by oxidative etching method and ion bombardment with high precision, higher flux rate and 100% salt rejection rate compared with zeolite-based membranes, diversified desalination performance by adding functional groups at the hole[20-24]. David Cohen-Tanugi et al. [18] first revealed the concept of monolayer graphene with nano size pores based membrane in a RO system for seawater desalination through MD study and its performance as a membrane was established closely related to size of the pore, chemistry at the edge of pore and pressure applied to the membrane. Figure 2 is simulation model snapshot of RO system where salt ions and water particles in the feed side are forced through the pores of the membrane by applied pressure and only water molecules are collected in the permeation side.

![Graphene sheet with nanopores](image)

**Figure 2.** High pressure water molecules pass through the one atomic thick nanoporous graphene sheet while holding back salt ions [25].

Followed by many researchers have attempted to study the water transport mechanism through nanoporous graphene using MD simulations. Konnatham et al. [26] examined the water transport and ion selective through nanoporous graphene. Gaoquanshi et al. [27] have proved the mechanisms of molecular separation using nanoporous graphene. Joshi et al. [28] demonstrated the ion separation mechanism using graphene and graphene oxide membranes. Their studies emphasized the importance of pore size, chemistry at the hole and pressure applied to the membrane. Zhang et al. [29] examined the multilayer porous graphene membrane performance and their studies showed that improved salt rejection rate when the number of layers increased. Liu et al. [30] dispensed the complete review of recent happening of graphene-analogous 2D nanomaterials in terms of different properties, modelling studies and its suitable applications. Prompted by the great declaration of graphene-based membranes for RO process, new studies also engaged to inquiring other graphene-analogous 2D nanomaterials such as monolayer MoS$_2$ with nanopores tested as RO membrane by Heiranian et al.[31] using MD simulation. Obtained results showed that the water flux through the MoS$_2$ membrane was larger than the graphene nanopores. Followed by Li et al. [32] examined the open and close filtration states of porous monolayer MoS$_2$ at critical strain of 6% by applying tensile strain to the membrane and this study gives a hope to use as a controllable filtering RO membrane. Recently, Yang et al. [33] demonstrated the monolayer carbon nitride (C$_2$N) by MD simulation shown in Figure 3 and proposed that C$_2$N could be a potential candidate to excel as a RO membrane. Based on the above literature studies, it is undoubtable that the application of 2D nanomaterials as a membrane in RO system improves its performance. However, the generated defects (pores) in the 2D nanomaterials, particularly graphene based materials may reduce its mechanical strength and affect its performance.
3.2. Effect of defects (Pore generations) on mechanical properties of 2D nanomaterials

Despite advancements on the methods of creating pores in the graphene sheet for water pathways, the created high density holes in the graphene may reduce the mechanical properties or failure of the whole structure. A mechanical property of 2D materials depends upon the presence of defects such as point, line defects and their evolution during deformation. G. Rajasekaran et al. [34] have provided complete review an effect of defects on graphene sheets on the mechanical properties and they have examined that tailoring specific properties depends upon controlling the point and line defects. Further they reported the orientation of the Stone-Thrower-Wales (STW) defects in the graphene sheet and direction of load applied plays a vital role for altering its strength under axial compression [38]. M. Terrones et al. [35] discussed the new perspectives of tailoring the mechanical properties of graphene, MoS$_2$ and phosphorene based on defect control engineering. Figure 4 shows the formation of vacancy defect by removing one carbon atom from the layer of graphene sheet whereas Figure 5 shows the formation of STW defects by rotating the covalent bond connected to the two carbon atoms.

**Figure 3.** RO Desalination water model with carbon nitride filtration membrane [33].
Figure 4. Atomistic view of graphene sheet with (a) removal of carbon atom highlighted, (b) created pore (mono vacancy) [36,37].

Figure 5. Atomistic view of graphene sheet with a) STW1 and b) STW2 defects loaded in zigzag and armchair directions [38].

It was predicted from the above simulation studies literature that the effect of vacancy defect created in the 2D nanomaterials is more sensitive to its mechanical strength compared to STW defects.

4. Conclusion
In summary, we conclude that the generations of vacancy defect (pore) in 2D nanomaterials are essential, particularly in graphene and its derivatives for water passage because of its impermeable nature to gases and liquids. But the impact of vacancy defects can deteriorate the mechanical strength of this materials due to removal of atoms from the lattice structure, resulting the reduced performance of these materials as a membranes. However the impact of STW defects on 2D nanomaterials are less compared to vacancy (pore) defects due to no removal of any atoms in the lattice structure while formation of STW defects. It can be concluded that there is a future scope of research on 2D nanomaterials with STW defects for water passage in RO desalination.

5. References
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