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Graphene-based nanofiltration membranes for improving salt rejection, water flux and antifouling–A review

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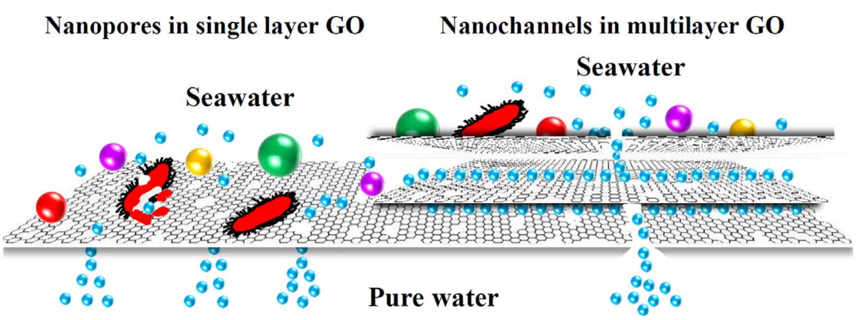
GRAPHICAL ABSTRACT



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ABSTRACT

Increasing water consumption and diminishing fresh water resources have created the need for new water treatment technologies to supply safe water for domestic and industrial needs. The development of polymeric nanofiltration (NF) membrane technology led to water treatment at lower operating pressures than that of reverse osmosis. NF membranes reject particles and multivalent ions, however, monovalent ions pass through them along with water molecules. Factors such as selectivity and permeability, and fouling also limit their application. Incorporating suitable nanomaterials with polymer membranes has solved major problems, such as biofouling, scaling, low flux rate, selectivity, and degradation. Recent studies reveal that nanoporous single layer graphene and stacked graphene oxide (GO) membranes with desired spacing between layers are capable of rejecting monovalent ions, and are promising materials for future nanofiltration-based desalination. GO has antifouling properties that are highly advantageous for improving membrane properties. The basic understanding of the mechanism of graphene-based nanofiltration have been reported mainly based on computational studies. Hence, a great deal of experimental research is essential to develop efficient graphene membrane-based desalination methods for practical use. In this review, we highlight various properties of graphene and its derivatives that are essential for improving salt rejection, flux, and antifouling.

1. Introduction

Water is one of the basic necessities for the existence of life on Earth. With the increasing world population and changing climate, the scarcity of fresh water resources has become a critical issue. It has been predicted that due to climatic variations, the possibility of frequent

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droughts will increase five-fold by 2050 [1]. Reduced rainfall and decreased soil moisture will lead to the reduction of groundwater and streams. Population growth and the nuclear family system increase water consumption, and stress the need for fresh water management at the household level, which includes rainwater harvesting, water saving devices, and grey-water recycling. The consumption of water has increased not only for drinking and sanitation, but also for agriculture and industrial uses. Exploitation of fresh water for increasing industrial applications, pollution of water resources by industries, release of household wastewater to the environment and decreasing groundwater levels contribute to the contamination of fresh water resources that has led to the search for alternative water sources such as aquifers, groundwater remediation, and seawater desalination. Since 97% of the world's available water is confined to the oceans, desalination has become an important method for augmenting the fresh water supply [2]. Many purification techniques have been implemented for the treatment of water, including distillation, ion exchange, and membrane filtration. Conventional water purification methods like distillation, are effective for removing bacteria, minerals, water-hardening substances such as calcium and magnesium, and harmful metals, such as lead, arsenic, and mercury from water. Although distillation removes drinking water contaminants, it does not remove chlorine and some volatile organic compounds. The resulting mineral-free water, due to its acidic nature, affects the human health [3]. Furthermore, the energy consumption required for distillation is very high [4]. Hence, membrane-based water purification technologies, such as reverse osmosis (RO), forward osmosis (FO), electrodialysis, electrochemical filtration [5], microfiltration, ultrafiltration, and nanofiltration (NF) have dominated over other technologies and are versatile for drinking water production, desalination, water reuse, and wastewater treatment [6].

RO is widely accepted as an effective and environmentally friendly method for desalination of many types of water, such as groundwater, water from lakes and rivers, brackish water, and seawater. RO membranes, operating under the influence of the osmotic pressure difference between saltwater and pure water, are suitable for softening water with a salt rejection rate of 99% when operated under standard conditions [7,8]. However, water recovery in seawater desalination plants varies from 35–85% which depends upon the composition and salinity of feed water, pretreatment, and concentrate disposal. To achieve higher recoveries, high pressures (> 60 bar) are needed, and therefore energy consumption increases accordingly [8,9]. Because the RO process is carried out by semipermeable membranes that are nonporous, these membranes can effectively remove not only particles, but also bacteria, organic contaminants, molecules such as dyes, and both monovalent and multivalent ions [10,11]. The advances in polymer science and technology has reduced the energy requirement for the RO of seawater in recent years. Although the polymeric membranes used in RO systems are highly selective, they are less resistant to high temperature and pressure [12]. As a result, they undergo rapid degradation when exposed to those conditions. Therefore, polymer membrane-based filtration needs further improvement in order to increase its flux, antifouling properties, and resistance to chemicals. Forward osmosis is also very effective in removing ions for producing drinking water [13]. A non-pressure driven process, such as electrodialysis, is a low-energy water purification process in which the ions are separated from the water and transported through parallel membranes under the influence of an electric field [14]. However, they are confined to desalination of water containing a low total dissolved salts, such as brackish water.

Other than semipermeable membranes, polymer thin film membranes having pore sizes in the sub-nanometer range, called NF membranes, allow solvent molecules and/or monovalent ions to pass through them and block particles and multivalent ions by NF mechanism. NF is a promising alternative to conventional filtration techniques, and is a pressure-driven membrane process employing with pore sizes of < 0.001 μm, and has rejection ability between RO and ultrafiltration [15–18]. For efficient NF for water purification applications, NF membrane must have a thin and porous structure with a narrow pore size distribution to ensure high selectivity and permeability. Studies have shown that the salt rejection via NF membranes is due to the combined steric, Gibbs–Donnan, and dielectric effects [19–22]. Therefore, salt rejection and water flow depend on various factors, such as the pore size, size of the ions, interaction of ions and hydration at the nanopores and the polymer membrane surface. The type of solution also alters the surface properties of the membranes. For example, aromatic polyamide active layer on polysulfone substrate in contact with an aqueous solution are slightly charged, due to the ionization of functional groups on the surface or the adsorption of charged solute [23]. Also, a weak ion exchange property of the NF membrane allows the exchange of ions that also results in the modification of the membrane charge [23]. NF has advantages over RO that include low operating pressures, high water fluxes, high rejection of divalent ions and it has disadvantages such as low rejection of monovalent ions [22,24,25]. Recent advances in nanofiltration technology improved the efficiency of NF membranes for removal of salts, including monovalent anions, even from highly concentrated desalination brines [26]. However, polymer NF membranes have limitations such as fouling, and trade-off between permeability and selectivity due to their dependency on pore size. Many commercial NF membranes are available for salt removal applications, and a detailed review and comparison of their transport properties and performances have been reported by Mohammad et al. [27]. In this review, we mainly focus on NF through graphene oxide and its composites rather than pure polymeric membranes.

With the ultrafast growth of nanoscience and the invention of nanomaterials with desired pore sizes, good chemical resistance, sufficient mechanical strength, and superior antifouling properties, thin-film nanocomposites have attracted great attention towards their application in salt rejection by NF. Thin film nanocomposites have good separation ability, wide pH tolerance, low energy consumption, and low operational costs [28]. Incorporating nanomaterials with polymeric membranes or using nanomaterial thin-films as the active filtration layer, has been identified as a promising technique, and has increased the hope for developing low-energy, small-scale desalination systems. The nanoporous structure allows fast flow of water across well-defined channels in which the flux across the membrane depends on the pore density and the thickness of the membrane [29,30]. A wide range of nanomaterials have been reported as potential candidates for applications in NF [31–36]. Considering the low toxicity, flexibility in storage and handling, easy processing and modification, graphene-based membranes are of great interest for NF, including water desalination [37]. Most of the reports on qualitative and fundamental aspects of graphene for desalination application are based on computational studies [29,38–40]. However, some recent studies on the salt rejection by nanofiltration reveal the potential of graphene-based membranes for future seawater desalination applications [41–44]. Goh et al. have reported a comprehensive review on the various aspects of preparation and application of graphene-based nanomaterials for nanofiltration [45]. Other review articles mainly discussed the synthesis of graphene and their derivatives or composites, and their applications in various water treatment processes [46–50]. However, the discussions on desalination through nanofiltration in most of the review articles were based on molecular dynamics simulation studies and a few experimental research reports and they generally concluded that the synthesis and practical application of such graphene membranes were a technical challenge. Moreover, recent reports suggest that surface modification of graphene oxide, such as functionalization and thermal reduction, mechanical stretching, can highly alter the ion transport mechanism [41,51,52], which enhances the performance of graphene based nanofiltration membranes.

In this review, we discuss the important chemical and physical features of graphene and its derivatives that are influential in enhancing the parameters of desalination by nanofiltration such as salt