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Chapter

Graphene Oxide-Based Membranes as Water Separation: Materials, Preparation, Characteristics, and Applications

Aster Woldu

Abstract

Membrane-based separation technology has attracted great interest in many separation fields due to its advantages of easy-operation, energy-efficiency, and easy scale-up and environmental friendliness. The development of novel membrane materials and membrane structures is an urgent demand to promote membrane-based separation technology. Graphene oxide (GO), as an emerging star nano-building material, has showed great potential in the membrane-based separation field. In this review paper, it is briefly reviewed the preparation and characterization of GO. Then, the preparation method, characterization, and type of GO-based membrane are summarized. Before that the general concept behind membrane technology is presented.

Keywords: graphene oxide (GO), graphene, graphene-oxide membrane

1. Introduction

Unquestionably; water is the source of life and one of the most important material resources for human existence and advancement. Although 71% of the earth’s surface is covered with water; approximately 98% of our water is salty and only 2% is fresh. Of that 2%, almost 70% is snow and ice, 30% is groundwater and less than 0.5% is surface these are freshwater resources that can be directly used by humans, such as river water, freshwater lakes, and shallow groundwater [1]. Meaning; there is no surplus fresh water in the planet. In addition to this, modernization that demands the fast development of industries and increasing human activities, forced many harmful inorganic and organic pollutants to be released into water, which extremely jeopardizes the available freshwater resource and ecological environment. Today according to the world population clock, the population exceeds 7 billion and will reach 10 billion by 2050. These all indicates pure drinking water would be a major problem all over the world, especially for the developing countries [1].

As a kind of technology which can increase the amount of freshwater, desalination of the salty water and treating the polluted water have become a strategic choice to solve the crisis of water resources. Currently, the global volume of desalinated water
has exceeded 90 million m$^3$/day, alleviating water shortages which have affected over 200 million people [1, 2]. Reusable water obtained from treating the wastewater is not as such considerable [3, 4].

To desalinate water a number of process technologies are used. The mentioned techniques are (1) reverse osmosis (RO), distillation, freezing, hydration and solvent extraction, etc. or (2) ion exchange, electro-dialysis (ED), adsorption capacitance, pressure impregnation and forward osmosis (FO) technology [1–3]. Out of the mentioned technologies; three of the processes require the use of semipermeable membranes.

Literature indicated membrane technology has become a dignified separation technology over the past few decades [2] and from Figure 1 the polymer based membrane technology is in the forefront of water purification and desalination, owing to its advantages of low energy consumption (as compared to other technology, low investment cost, ease of operation and possibility for continuous operation and inherent simplicity) [3, 5], but is plagued with some bottlenecks like most of them tend to foul, have low resistance to chlorine, strong acids/alkaline, high temperature and organic solvents, and suffer from aperture shrinkage under high pressure [1, 3]. And despite large scale seawater desalination plants have already confirmed their much needed success, the widespread implementation of these plants is held back due to their high energy costs. One approach to resolve the mentioned problems is through enhancing a membrane used in separation process. A tremendous amount of effort has been paid to develop new membranes and develop novel membrane structures with greater chemical stability, thermal stability, water permeability, as well as high selectivity, which in turn yield less energy consumption [6–10].

Since 2004; researcher focused on carbon-based materials especially one material—graphene. Graphene and its derivative graphene oxide (GO) and carbon nanotubes

Figure 1.
Trends in global desalination by (a) number and capacity of total and operational desalination facilities and (b) operational capacity by desalination technology (https://www.desaldata.com/).
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(CNTs) have demonstrated notable potential in the field of membrane. The basic characters for their suitability are their strong mechanical strength, high resistance to strong acids/alkaline and organic solvents, and easy availability. Among them, GO selected for evolving nano-building materials for the manufacturing of novel separation membrane due to its high mechanical strength, high chemical inertness, nearly frictionless surface, its flexibility, suitability for large-scale production and its cost-effectiveness [5–10].

In this mini review first an introduction about membrane, graphene and graphene oxide (GO) are provided. Then it is tried shortly to discusses points on the preparation and characterization of GO. Finally the preparation method, characterization, and type of GO-based membrane are discussed.

2. Briefing on membrane separation

Membrane separation is a technology in which selectively materials are screened out via pores or minute gaps presented in the molecular arrangement of membrane structure. Membrane separations are basically classified by pore size and by the separation driving force. These classifications are: microfiltration (MF), ultrafiltration (UF), ion-exchange (IE), and reverse osmosis (RO), and forward osmosis (FO) [11].

Membrane separations are primarily used to separate solids (either particulate or in solution) from liquid. The technology also used in effect liquid-liquid separation and gas-to-liquid infusion processes. Reverse osmosis (RO), ultra-filters (UF), and micro-filters (MF) are membrane technologies that employ pressure across the membrane as the driving force for separation (a trans-membrane pressure or TMP). Basically UF practical in concentrating and purifying virus, bacteria, fermentation broths, colloids, and particles, as well as dissolved high molecular weight polymer. Since membrane separations can also be accomplished at below ambient temperatures; they are suitable in the manufacture of degradable materials such as pharmaceuticals and foods. MF is engaged for separation and purification of suspended solids, colloidal particles, and bacteria from liquids and it is also used in the screening of particles and bacteria from gases. Non-filtration membrane technologies are dialysis and electro dialysis. Dialysis uses concentration differences as the separating driving force and the electro dialysis uses electric potential differences as the separating driving force for the separation. An artificial kidney is a specific example of dialysis where blood impurities are effectively removed for renal failure patients.

3. Contribution of membrane technology for water treatment

Reverse osmosis (RO), forward osmosis (FO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), and particle filtration are working in water treatment process to treat the raw or wastewater depends on their pore sizes. Figure 2 summarizes the various membrane filtration processes related to common materials that would be filtered out through each process during water treatment. Figure 3 illustrates the application of FO and reverse osmosis process for water purification of sea water and wastewater.
Graphene - A Wonder Material for Scientists and Engineers

Figure 2.
Illustration of different membrane filtration spectrum.

Figure 3.
Examples of application of membrane technology for water treatment. (A) Diagram of an FO-RO system for integrated SWRO and wastewater recovery. Water from the wastewater is extracted by osmosis through the FO process and dilutes the seawater before entering the RO process. (B) OMBR (osmotic membrane biological reactor) system comprising a bioreactor containing submerged FO membranes and an RO unit that re-concentrates the draw solution and produces water.
4. Conventional membrane material

Almost all industrial membrane processes are carried by organic membranes made up of natural (wool, rubber (polyisoprene)) or synthetic (polyamide, polystyrene and poly-tetra-fluoro-ethylene (Teflon) polymers. (http://www.separationprocesses.com; [6]). Membranes can also be manufactured from other non-polymeric materials. Such membranes materials can be inorganic membranes (like metal, ceramic, carbon, and zeolites) and liquid membranes. But their application in water purification is not exhibited (http://www.separationprocesses.com).

For purification of water; currently the polymeric membrane governed the membrane market including real-world application and academic research due to its advantages of energy-efficiency, easy-operation, low-cost, and inherent simplicity. However, there are limitations related to the conventional membranes exhibited in most practical applications. Most of them tend to foul have low resistance to chlorine, strong acids/alkaline, high temperature and organic solvents, high contaminant permeation relative to stringent selectivity requirement and suffer from aperture shrinkage under high pressure [6]. The strong trade-off relation between membrane selectivity and permeability is a common challenge for all of polymeric membranes.

Because of the mentioned limitations the development of novel membrane materials is a major research thrust for academia, industry, and national laboratories. The desirable membrane properties, which are constantly searched by the researchers are good mechanical strength, superior chemical stability, thermal stability, water permeability, as well as high selectivity [6].

5. Graphene and graphene-oxide

5.1 Graphene

Since 2004, the Nobel Prize winning material, graphene is taken as one of the most wonderful achievements in the field of science and technology [7, 12]. Graphene is an atomically-thin (0.35 nm in thickness), it is a two-dimensional sheet with a honeycomb structure made up of sp² hybridization carbon atoms which are linked together with strong sigma keys [7]. Graphene has unique properties that make it a core of scientific research that many of them can be transformed into practical [5, 7–9]. These valuable properties includes (1) a highly specific surface area [5, 7], as reported by Zhu et al. [13]; specific surface area (SSA) values of carbon materials obtained from GO have been well below 2630 m²/g, but the specific surface area of common active carbon is only 1500 m²/g [12].

It has also a remarkable elasticity and mechanical strength; atomic force microscopy (AFM) measures the performance of freestanding monolayer graphene membrane based on Nano indentations; the result showed it has a breaking strength of 42 N·m⁻¹ and a Young's modulus of TPa 1.0. even if graphene is an extremely strong material, still an external mechanical load can change the electronic properties of graphene thus, it is possible to affect its field emission performance. graphene's capability to absorb pressure can also be affected by different degrees of axial compression. The varying sizes of buckling stress and strain are measured using a cantilever beam. When graphene is used as a membrane material, it can provide a stronger support force and adjustable sheet spacing. Therefore, the mechanical strength and controllability of the membrane
can be improved. Graphene also exhibited excellent molecular barrier abilities and superior thermal and electrical conductivity [8–11]. Frequently, graphene and its derivatives are used in super capacitor, fuel cells, capacitive deionization, desalination, and others [13]. Different literature also reported graphene derivatives which can be integrated with other materials such as inorganic nanostructures, organic crystal, polymers, organic framework, biological materials, and carbon nanotubes to improve specific properties of the materials (Yi [11]).

5.2 Graphene-oxide (GO)

The structure of GO similar to graphene but it also contains hydroxyl (–OH), alkoxy (C–O–C), carbonyl (C=O), carboxylic acid (–COOH), and other oxygen-based functional groups. GO has a non-stoichiometric general formula of the type \( C_xH_yO_z \). See Figure 4 it is a suitable nanoparticle to improve the hydrophobicity of the membrane. The functional groups making it more dispersed in the polymeric solution. That means, if it is incorporated in the membranes, it can be improve properties for water purification. GO-incorporated membranes consist of a high mechanical strength and thermal stability [11]. The GO-incorporated membrane can enhance water transport even in low-pressure applications [14].

The most important property of GO nano-sheets is antifouling during operation due to negative charge and high hydrophobicity [7, 11]. It is believed that the GO-incorporated membranes have improved fouling resistance by reducing surface roughness and increasing hydrophilicity [7]. The GO-incorporated membrane shows high water permeability in various applications such as NF, RO, FO, and PRO processes [11]. Although the benefits of GO has been reported many, the material is still

![Graphene and Graphene Oxide](image)

**Figure 4.** Depicted generic chemical and physical structures of graphene-based materials.
expensive and is relatively difficult to manufacture at a larger capacity. Therefore, the manufacture of the material expected to well develop to decrease the cost and complication of manufacturing [11, 12].

6. Preparation of graphene oxide

The preparation process of GO essentially comprise two steps: oxidation of graphite and exfoliation of graphite oxide. In literature different methods are reported for the preparation of GO [12]. Table 1 summarized different methods used for the preparation of GO.

<table>
<thead>
<tr>
<th>Year</th>
<th>Methods’ name</th>
<th>Oxidant</th>
<th>Acid used</th>
<th>Reaction time</th>
<th>Note: limitation and advantage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1859</td>
<td>Brodie</td>
<td>KClO₃</td>
<td>HNO₃</td>
<td>3–4 days</td>
<td>Time consuming and generated toxic gas (ClO₂), which was unsafe and harmful to the environment.</td>
<td>Smith et al. [12]</td>
</tr>
<tr>
<td>1898</td>
<td>Staudenmaier</td>
<td>KClO₃</td>
<td>H₂SO₄, HNO₃</td>
<td>1–10 days</td>
<td>Improved Brodie’s method by adding KClO₃ in multiple aliquots during the oxidation course and further acidifying the mixture by adding concentrated sulfuric acid (H₂SO₄) More practical and convenient for the production of GO with comparable oxidation degree Produced toxic gases (ClO₂, NOₓ) and is not environmentally friendly.</td>
<td>Smith et al. [12]</td>
</tr>
<tr>
<td>1937</td>
<td>Hofmann</td>
<td>KClO₃</td>
<td>H₂SO₄, HNO₃</td>
<td>4 days</td>
<td>A modification of Brodie’s method, it substituted fuming HNO₃ with non-fuming HNO₃ during the oxidation course Produced toxic gases (ClO₂, NOₓ) and is not environmentally friendly</td>
<td>Smith, et al. [12]</td>
</tr>
<tr>
<td>1958</td>
<td>Hummers and Offeman</td>
<td>KMnO₄</td>
<td>NaNO₃, H₂SO₄</td>
<td>2 h</td>
<td>More efficient and less time consuming Widely used in current research Toxic gas NOₓ, Mn⁺⁺ in GO</td>
<td></td>
</tr>
</tbody>
</table>
7. GO membrane fabrication

The final step in fabricating GO membranes involves integrating GO with the support. Different supports are used [11] for this purpose. After selecting the support, there are also various routes for this integration step. The vacuum filtration shown in Figure 5 is the most applied method [11, 12]. The process involves filtering a suspension of GO in a solvent (usually water) through the support structure, with the retained GO sheets stacking up on each other and effectively being deposited on its surface and forming a thin film on the support. This layering step determines the GO membrane performance. Similar to vacuum filtration in principle is drop casting,

<table>
<thead>
<tr>
<th>Year</th>
<th>Methods’ name</th>
<th>Oxidant</th>
<th>Acid used</th>
<th>Reaction time</th>
<th>Note: limitation and advantage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>Modified Hummers</td>
<td>KMnO4</td>
<td>K₃S₂O₅, P₂O₅, H₂SO₄</td>
<td></td>
<td>This included two oxidation procedures. Preoxidized the graphite in a mixing solution of concentrated H₂SO₄, K₃S₂O₅, and P₂O₅ at 80°C. Then the mixture was washed and dried at ambient temperature. After that, the mixture was ulteriorly oxidized by Hummers’ method Controlling the temperature is major factor. NOₓ, N₂O₅ generated, hazardous heavy metal Mn²⁺ introduced in the preparation process.</td>
<td>Peng et al. [15]</td>
</tr>
<tr>
<td>2010</td>
<td>Improved Hummers</td>
<td>KMnO4</td>
<td>H₂SO₄/H₃PO₄</td>
<td>12 h</td>
<td>Hybrid of H₂SO₄/H₃PO₄ with volume ratio of 9:1 was used as the mixed acid Simpler and higher yielding, and generated no toxic gas making it possible for large-scale production of GO. Hazardous heavy metal Mn²⁺ introduced in the preparation process.</td>
<td>Peng et al. [15]</td>
</tr>
<tr>
<td>2015</td>
<td>Iron-based green method</td>
<td>K₂FeO₄</td>
<td>H₂SO₄</td>
<td>1 h</td>
<td>Less time consuming (1 h) and enabled the recycle of H₂SO₄, which decreased the pollution to environment. Fe³⁺ in GO.</td>
<td>Peng et al. [15]</td>
</tr>
</tbody>
</table>

Table 1. Methods for the preparation of GO.
which deposits GO onto the support via droplets of concentrated solutions. Upon the evaporation of the solvent, a layer of GO is left behind [8, 9].

Another technique to form membranes from GO is dip coating, which involves dipping the support into a solution of GO where it is coated with a thin film [11]. The uses of spray-coating, spin-coating and chemical vapor deposition (CVD) methods are also reported to be applied for GO membrane manufacturing [11, 12].

8. Conclusion

Because of many advantage like easy-operation, energy-efficiency, and easy scale-up, and environmental friendliness; membrane-based separation technology attracted many separation fields. But the membrane fabricated afflicted with bottlenecks like- fouling, have low resistance to chlorine, strong acids/alkaline, high temperature and organic solvents, and suffer from aperture shrinkage under high pressure and high energy cost. One of the methods to resolve the mentioned problems is through enhancing a membrane castoff in separation process.

A tremendous amount of effort has been paid to develop new membranes and develop novel membrane structures with greater chemical stability, thermal stability, water permeability, as well as high selectivity, which in turn yield less energy consumption. Since 2004 researcher focused on carbon-based materials especially one material—graphene. Graphene, and its derivative graphene oxide (GO) and carbon nanotubes (CNTs). They have been demonstrated notable potential in the field of membrane. The basic characters for their suitability are: their strong mechanical strength, high resistance to strong acids/alkaline and organic solvents, and easy availability. Among them, GO selected for evolving nano-building materials for the manufacturing of novel separation membrane due to its high mechanical strength, high chemical inertness, nearly frictionless surface, its flexibility, suitability for large-scale production and its cost-effectiveness.
The Nobel Prize winning material, graphene is taken as one of the most wonderful achievements in the field of science and technology. It is an atomically-thin (0.35 nm in thickness), it is a two-dimensional sheet with a honeycomb structure made up of sp² hybridization carbon atoms which are linked together with strong sigma keys.

Preparation of GO from graphene essentially comprise two steps: oxidation of graphite and exfoliation of graphite oxide and is carried out by simply six different kinds of oxidation process. To get GO membranes it need only a final steps of integrating GO suspension with the support by vacuum filtration, dip coating or interfacial polymerization.

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