Dissertation for the Degree of Doctor of Philosophy

Synthesis and Application of Graphene Oxide Based Lamellar Membranes for Water Purification

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The Dissertation for the degree of Doctor of Philosophy
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Preamble

This thesis is submitted for partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Mechatronics Engineering at Jeju National University, Republic of South Korea. All the research work presented here was established in Advanced Micro-Mechatronics Lab at Jeju National University. No content or segment of this thesis has been submitted for any degree at any other institution or university. This thesis work is original according to the best of the author's knowledge unless reference is taken from related work published. Content from this thesis has already been published in 3 research articles in international peer-reviewed journals listed below.

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This thesis is dedicated to My Beloved Father

Master Ghullam Sarwar Memon (A.K)

&

My Beloved Mother

Head Mistress Shamshad Begum

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Synthesis and Application of Graphene Oxide Based Lamellar Membranes for Water Purification

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Abstract

Sufficient efforts have been carried out to fabricate highly efficient graphene oxide (GO) lamellar membranes for heavy metal ion separation and desalination of water. However, selectivity for small ions remains a major problem. Herein, GO-based bio-inspired membranes are fabricated by green method and used for selective separation of heavy metal ions and water desalination. The GO is modified with Onion extractive (OE) and fabricated into GO/OE composite membranes. The GO/OE composite membrane (350 nm) shows an excellent rejection efficiency for several heavy metal ions such as Cr^{6+} (~87.5%), As^{3+} (~89.5%), Cd^{2+} (~93.0%), Pb^{2+} (~99.5%), and good water permeance ~460±20 Lm-2h-1 bar-1. In addition, GO/Quercetin (GO/Q) membrane is also fabricated from quercetin for comparative studies. Quercetin is an active ingredient of onion extractives. The GO/Q composite membranes show good rejection up to ~78.0%, ~80.5%, ~88.0% and 95.2% for Cr^{6+}, As^{3+}, Cd^{2+}, and Pb^{2+} respectively with DI water permeance ~150±10 $Lm^{-2}h^{-1}bar^{-1}$. Further, both membranes are used for water desalination by measuring rejection of small ions such as NaCl, Na_2SO_2, $MgCl_2$, and $MgSO_4$. The resulting membranes show >70% rejection for small ions. In addition, both membranes are used for filtration of Indus River water and GO/Q membrane shows remarkable high separation efficiency and making river water suitable for drinking purposes. Furthermore, the GO/QE

composite membrane is highly stable up to ~25 days under acidic, basic, and neutral environments as compared to GO/Q composite and pristine GO-based membranes.

1. Objectives of Thesis

This thesis key objectives are classification of graphene-based membranes, and characterization rGO with critical literature survey about graphene and its composite membranes and their applications specially water purification from heavy metals and water Desalination. The research methodology together with materials and reagent, washing of glassware, instrumentation, samples synthesis for characterizations, synthesis procedure GO and rGO membranes, and their application for water purification are experimentally achieved. Furthermore synthesis, characterization, and application of GO and rGO membranes are classified and experienced and finally the conclusions, future direction and recommendations are given. The increasing water demand is attributed to industrial development and human activity. Because of several factors, including wastewater releases, anthropogenic activities, extreme storms, and heavy rain, endanger human and aquatic life because water supplies are more polluted daily. A critical problem in water quality is water pollution, and there is a severe threat to the ecosystem because of it. Other pollutants, such as heavy metals and various kinds of waste, have proven toxic to life, and this is why GO composite membranes GO have been invented to help purify drinking water of these dangerous toxins. It is cheap and straightforward to use.

2. Introduction

GO is a 2D Nanomaterial having domains of sp2 hydrogen bonding across some of the oxygen-containing functions, giving it structural stability. sp2 hybridized domains held in a laminar structure[1]. There has been considerable interest in graphene oxide, for example novel 2D-dimensional substance through a thickness sub-Nanometer, in water purification matrix membranes as a membrane structure and functional coating. A membrane structure made of this novel 2-D material, it improves membrane performance in a variety of ways including higher permeance water , reduced stain and enhanced antibiotic valuable, therefore ultimately prime less efficiency uses, a higher lifespan and lesser preservation costs in the long run It is possible to use the nano-channels and structural defects within GO as a means of transport on subtract polyethylene sulphone (PES) membrane material pure Graphene oxide, using remedy coatings methods on suitable porous substrates, lamellar structures are created. Additionally, Additives and methods of quality containing Go may increase water permeability, hydrophilicity, and chemical resistance. In this work, GO membrane water filtration applications are examined and possible concerns are mentioned., which focuses on the most recent studies. As a result, water treatment membranes that include GO may be manufactured in a variety of ways. The GOM microstructure includes nanochannels between two GO sheets, inter-edge gaps, and wrinkles. Water movement across this complicated microstructure has been studied using molecular dynamics. Water transport is rapid in the sp2 domains of GO, but sluggish in the sp3 domains[2]. Water is thought to move through the GOMs through large channels generated at wrinkles and inter-edge areas. In Filtration as well as treatment, combustion or ion sieve and water desalination, GOMs with tunable nano-sized pores or interlayer channels are of interest. Excellent selectivity and rejection efficiency are required in an ideal membrane[3]. Heavy metals are metallic elements that are harmful or toxic in low amounts. Salt ions contain Mg, Cd, As, Cr, and Pb. Heavier ions are found in the crust. They can't be cleaned up or deteriorated. They enter our bodies via food, water, and breathing[4]. Copper, selenium, and zinc are trace elements necessary for the human body's metabolism. Due to lead pipes, high ambient air concentrations, or food chain consumption (among other things), heavy metal poisoning is a common problem[5].

2.1 Water desalination

Clean water scarcity seriously affects around 1200 million people across the globe, with predictions that this figure would rise to 3900 million in the next three decades due to population growth, increased industrialization, and increased energy consumption[6]. Desalination of saltwater may help alleviate water scarcity and provide a reliable source of freshwater for both emerging and industrialized nations. It is seen as the most viable method for increasing freshwater access to millions of people across the globe. Desalination facilities have continued to expand from the 1960s to the present day[6] [7]. Plant-wise, construction and procedure, especially the past three decades have witnessed exponential development. Desalination facilities provide water to many nations and an estimated three hundred million people. Desalination by heat techniques as are membranes that are propelled by pressure[8]. The two most used desalination procedures. Other techniques, Thermal membrane separation and electrodialysis, on the other hand, are less common and less successful in large-scale applications. Thermal energy is used in A concentrated solution may be separated since saline seawater using evaporating for water technique MED is directly proportional of numbers of effects, MSF also using desalination application. Membrane-based desalination uses a variety of porous membranes. Salts are removed from high-salinity water by using pressure or temperature differences[9]. Reverse Osmosis (RO) membrane separation is the dominant membrane-based technique. For 86 percent of existing facilities, seawater desalination is now primarily accomplished via MSF and RO 3, 4 combined. Present 7% of MED and 3% electrodialysis, Nanofiltration are some of the other techniques utilized (2%). The RO method, which accounts for more than 60% of current desalination capacity[10], involves passing a vast capacity in water encompassing ions of salt in solution between two layers of semi-permeable barrier using hydraulic pressure that is higher than the osmotic pressure but not equal to it. From an energy standpoint, RO is considered an efficient method for saltwater desalination. Some other desalination process may be compared to it. Reverse osmosis energy consumption decreased during the last 4th decades five due to technical advancements, most notably the adoption of more excellent permeability[10].

2.2 Membrane technology

Depending on the membrane's and species' qualities, a layer acts as a discriminating barrier, allowing certain species to cross while prohibiting others from doing so (Figure 2)[11]. Membrane technology is the science and technology of moving components, species, or substances over or through membranes. Membrane technology describes mechanical separation procedures for gas and liquid streams. These are molecules, ions, or other small particles[12]. At the same time, membrane processes consist of permeate, retentate, and feed (Figure 2). Permeate is a species that passes through the membrane. On the other hand, the retentate does not pass through the membrane. The feed of the membrane is it is influent. Membrane separation is usually determined by two parameters: permeability and selectivity. Both criteria must be evaluated at the same time. To enhance the expense of the membrane. Permeability refers to the rate at which water vapors pass through a membrane. It assesses inflows or permeance (expressed by the unit $L^{-1}m^{-2}h^{-1}$). Permeability refers to higher membrane production, whereas selectivity corresponds to the efficiency with which a membrane separates a component from a mixture. Its retention factor, often known as the separation factor, is a metric used to quantify selectivity. Higher molecule mass particles are extracted using membrane technology from a weak black liquid fraction. The pore size of black fluid concentration membranes is categorized. Inside the papers industry, the following membrane technologies are the most utilized[13]. Membrane technology is used in various applications related to the environment, energy, natural resources, and medical science[13]. Over classic processes including adsorption, extraction, absorption, filtering, and distillation, this technique has various benefits such as energy savings, acceptable cost, high selectivity, compactness, ease of fabrication and maintenance, and environmental friendliness[14]. A few microns to 0.1 meters are the size range of holes in a microfiltration membrane (MF). Pores in this material range in size from 0.1 microns to 0.01 microns. Membranes for nanofiltration (NF) have a thickness ranging from 0.01 mm to 0.001 mm. Membrane thickness: 0.001 m. For the first time, the huge pressure drops (10–100 MPa) allowed water molecules to pass through RO membranes, unlike prior membrane technologies[15]. Membrane separation effectiveness stands powerfully effect via the structure, extent, besides form of the pores, as well as the membrane's chemical and physical properties.

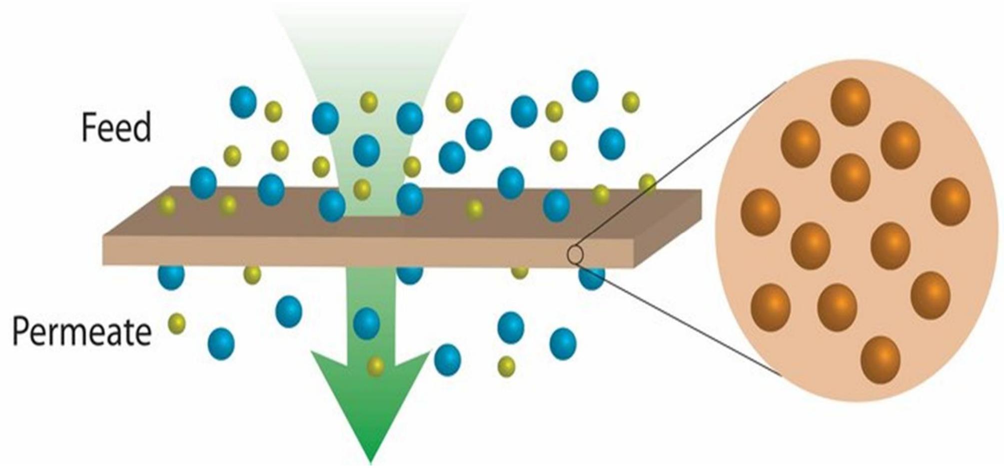

Figure 1. Schematic diagram of membrane separation

2.3 Classifying of Membrane

It is possible to categories membranes based on their material composition, geometry, properties, and separating uses[16]. Prior to being created, membranes might be inorganic or organic, straight, or wacky, symmetrical, or asymmetrical, porous, or nonporous (dense), across or else tinny membrane are all possibilities. They can also be neutral or charged. This categorization, however, is not restricted to these groups. They can be classified as inorganic, organic (polymeric), or composite membranes based on their substance[17]. Organic membranes are primarily polymeric membranes, while inorganic membranes usually comprise carbon, silica, zeolites, ceramics, and metal compounds[18]. These membranes might be porosity or non - porous in origin. Porous membranes include carbon, zeolites, silica, and specific polymeric membranes, whereas metals / ions transfer membrane are examples of nonporous membranes (dense). Several chemicals have been used onto membranes to enhance the performance of different separation processes, including forwarding osmosis (FO), osmosis, filtration (RO), ultrafiltration (UF), and gas extraction. Due to their varied microstructural characteristics, it is difficult to choose one of them as the ideal material. Because of its excellent packing density, low cost, and large-scale uses, the creation of polymeric membranes was seen as a breakthrough. However, their uses are limited because of swelling in organic solvents and poor stability at high temperatures[19]. Pore metallic, oxide, and carbons were the most effective mineral laminates for overcoming certain limitations, nevertheless they are brittle, have excessive manufacture expenses, then have difficulties with low temperature increase. Carbon nanotubes (CNTs) are intensively examined for nanofiltration applications with excellent separation capability as their adjustable micro-structural characteristics. However, due to their limited permeability, such membranes cannot get further attention[20]. It has been challenging to create atomic size nanochannels inside the nano membranes that properly permit separating the components in a mixture until now. As a result, there is constantly a desire for new types of materials with exceptional qualities to improve existing processes.

2.4 Nanofiltration (nf) membrane

NF membranes are semipermeable membranes by inlet diameters by the nanoscale range enable substances containing solvents and perhaps anion ions to pass over while blocking particles then multivalent ions. With pore sizes of 0.001 millimeters, the nanofiltration process has the capacity to distinguish between reserve osmosis and extremely-filtrations[21]. It is a feasible substitute for existing filtering methods. To achieve excellent selectivity and permeability, Nanofiltration membranes are essential that have narrow and pores' shape with a limited porous area issuing for water purification applications. According to studies, salt rejection across nanofiltration laminate is due to a combination of steric, Gibbs–Donnan, and dielectric processes[22]. As a result, salt rejection and water flow are influenced by a variety of variables, including pore size, ion size, ion interaction, and hydrate in nanopore and polymer sheet surfaces. It surfaces characteristics of the membranes are also affected by the type of solution used. It is possible for functionalities of molecules at surface to be ionized or charged solutes to be adsorbed for this, Poly-sulfone substrates in interaction to the water solution exhibit mildly charged aromatic polyamide active layers[23]. The nanofiltration membrane's weak ion exchange permits ion exchange to occur, resulting in a change in membrane charge[24]. Short effective compressions, higher water permits, and strong bivalent ion rejection are all benefits of NF over RO, but it has drawbacks such as low monovalent ion rejection[25]. Even from highly concentrated purification salt-water, recent advancements in nano-filtration technology enhanced the effectiveness of nanofiltration membranes for the separation of heavy metals, with univalent negative ion[26].

2.5 Graphene Based-Membrane

Graphene is the world's thin substance, containing a few layers of carbon atoms organized with honeycomb matrix. Due to its intriguing features such as solid carrier mobility, lightweight, and high mechanical and electrical properties, graphene has been extensively researched in electronic, optoelectronic, thermoelectric, bio-medical, and environmental applications[28] since its discovery. The mono-atomic thickness and 2D shape with attractive automatic energy and synthetic inactive, notably, have ushered in a new era in the field of separation membranes. Freshwater demand for drinking and farming is one of our greatest issues of our century. There is a lot of possibility in graphene oxide (GO) membranes both water desalination and purification. Increasing water permeability without reducing separation efficiency is difficult with GO membranes, as delamination occurs rapidly in aqueous solutions[29].

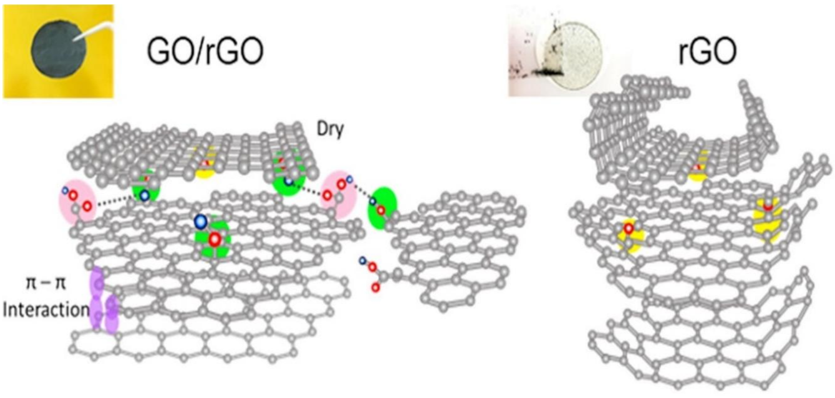

Figure 2. Schematic of graphene, GO, rGO, major in development of membrane technology.

Recently, graphene has been investigated as a separating membrane for different NF applications in the form of nano porous and layered structures, with numerous benefits over other conventional materials[32] [33]. Based on their microstructural characteristics, graphene-based membranes are divided into three categories: (a) porous graphene membranes, (b) graphene laminates, and (c) graphene-based composite membranes (Figure 4)[31]. GBSMs are potentially highly efficient membranes for desalination. The applications and performances of GBSMs are compared and analyzed. The defects of GBSMs were briefly mentioned. GBSMs have promising potential as pressure-driven membrane and electric-driven membrane. Membrane desalination has become an important solution to global water problems. Graphene-based materials have excellent advantages in the desalination process due to their intriguing features, including single atomic layer structure, large specific surface area, hydrophobic property, rich modification approaches, etc. After an introduction of membrane, graphene, and graphene oxide (GO), this review systematically summarizes the current progress and gives an insight into the graphene-based separation membranes (GBSMs). The applications of the pressure-driven graphene-based membranes are introduced and their performances are listed and analyzed. By molecular dynamics simulation (MDS), the researchers predict the excellent performances of GBSMs, including high water flux, good salt rejection, etc. which have been verified in subsequent experiments. We believe that the application of graphene-based materials in pressure-driven membrane is worthy of further exploration. Several researchers have prepared electric-driven membranes with graphene-based materials, since they have good stability and water-retention. However, graphene is not efficient in forward osmosis membrane area for now.

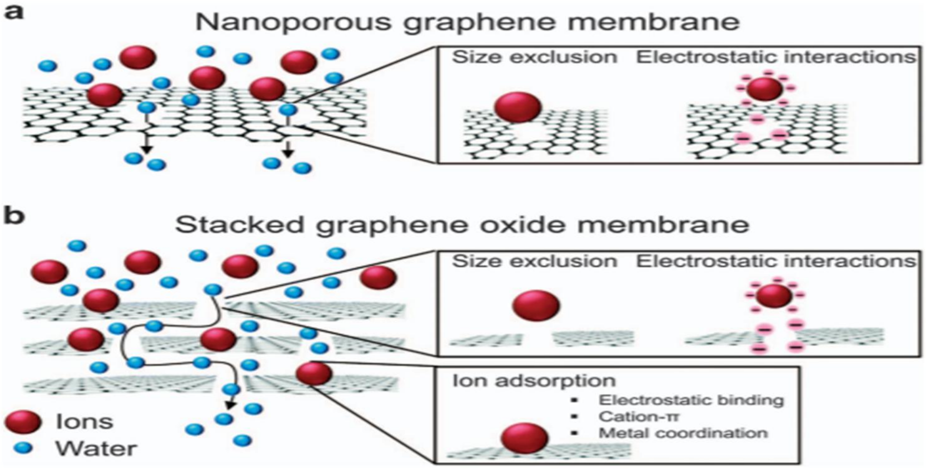

Figure 3. Schematic of the separation mechanism of (a) a monolayer graphene membrane with nanopores of controlled size and (b) a multilayer graphene membrane composed of stacked GO sheets.

2.6 Manufacture in synthesis technique of membrane

The outstanding qualities of graphene-based membranes make them ideal for a wide range of separation procedures. Along with its exceptional properties, GO is an excellent tool for fabricating precise laminar nanostructures. Laminating 2D laminates using Graphene oxide nanosheets, for example, was formerly considered to be an effective and scalable technique of creating 2D laminates[32]. Processes that use wetting chemicals like electrophoretic deposition and the Langmuir–Blodgett assembly, dip coating, through evaporating, droplet forming, as well as rotation coating & sprinkle layer, can be used to directly assemble GO nanosheets into laminar membranes because of their several advantages, because of its high aspect ratio construction & water-dispersible[32].

2.7 Ionic and molecular separation

The global water shortage, like other challenges we face, is a significant concern[44 45]. Many researchers are working on developing membrane technology that can use ocean water to recycle manufacturing effluent at a reasonable cost. One of the most promising approaches to finding a viable solution for the worldwide water issue is to employ nanotechnology in water filtration membranes[46]. Despite its many advantages, it has a major flaw: fouling, which reduces the membrane's lifespan[47]. As a result, a significant portion of membrane technology research has concentrated on creation, so it’s termed antifouling nano membrane sheet. Yet to, significant effort has been made in investigate new substance such as polymers, zeolites, silica, ceramics, and carbon-based membranes to address these problems[11]. Such substances and techniques helped to alleviate the problems to certain extent, but further research is needed to develop the optimal membrane material with excellent permeability, separation efficiency, and fouling resistance for practical applications.

2.8 Membrane and stability

GOM stability in aqueous solutions is a significant problem for their successful separation in many solution-based applications like ion or molecular sieving. Due to the presence of numerous oxygen functional groups that easily engage with water molecules via hydrogen bonding and may quickly degrade GOMs in aqueous solution[49], GOMs have limited structural and physicochemical stability. As a result, there is a pressing need to improve the design and self-assembly process of GOMs to increase their stability under various circumstances. GOMs have only been used to separate small ionic species in a few experiments. Mechanical stability of GOMs and chemical stability are critical for many industrial processes that operate in high-pressure environments. As a result, further efforts to increase the mechanical stability of graphene-based membranes should be addressed. It will be pretty advantageous to operate without using differential pressure.

2.9 Separation and permeability

An ideal membrane would be ultrathin to achieve maximal permeability and selectivity while maintaining high stability in hostile environments. Developing an optimal membrane for such an application with high rejection and excellent permeability is difficult. Creating regulated nanopores with graphene sheets and regulating d-spacing is a critical problem in porous graphene[50]. In the case of GOMs, however, swelling is a significant issue that substantially impacts the membrane's separation ability. Furthermore, one of the serious issues is the antifouling efficiency of GOMs.

2.10 Membrane Swelling

GOMs using an aqueous medium must be carefully swollen to obtain the desired selectively. The abundance of oxygenated functional groups on GO makes it extremely hydrophilic, giving it a solid proclivity to absorb water and swell in humid or watery conditions, significantly degrading its intended performance. The natural tendency of a layer-stacked GOM to swell, that is, absorb water into the GO channel and produce an increased interlayer gap, can substantially impact its aqueous-phase separation performance[51].

2.11 X-ray Diffraction (xrd)

One of the most extensively used non-destructive methods for studying crystalline materials is X-ray diffraction (XRD). It may also be used to determine how the inter-layer spacing of GO sheets in membranes changes over time. Interlayer spacing of laminated membranes may be determined using XRD. Bragg's law was used to accurately characterize the XRD diffraction position, allowing the interlayer spacing to be reflected on the crystal face information. Additionally, the wider peaks in the FWHM (full width at half maximum) data indicate a more disorganized structure. A graphite monochromatic XRD diffractometer, the D-MAX/2400, was used in our research to detect the XRD pattern using Cu Ka radiation at a wavelength of 1.541 Å.

2.12 Scanning Electron Microscopy

SEM was used to create pictures to examine membrane surface morphology and cross-section morphology inside layers of membranes on specific locations. SEM equipment (Nova Nano SEM 430, 15 kV/10 kV/5 kV) was used to examine the surface morphologies and structures of GOMs in this study. GOMs samples were attached to polymeric and AAO substrates using a sticky carbon tab to create SEM samples. Images with various magnifications were obtained using working energy of 5–7 k eV.

2.13 Fourier transform infra-red spectroscopy (ftir)

FTIR is a commonly used method for determining functional groups in compounds based on atom vibrations. This work investigated the chemical structure of GO laminates using an FTIR spectrophotometer (FTIR, Bruker Tensor 27) across the 400-4000 cm1 range. Our research utilized FTIR to detect oxygen-containing functional groups inside membranes and establish that thermal or chemical reductions had eliminated these groups. It is also used to double-check cross-linking bonds between GO sheets and other cross-linking reagents.

3. Research Background

Here GO, a 2D graphene derivative, is an excellent nano membrane sheet substance used in analysis water treatment due to have great hydrophilicity, greater water permeation, as well as extraordinary ionic/molecular filtering capabilities. In this part, we introduce GO. GOMs may be valuable in a variety of applications, but here we focused on their potential multifunctional value.

3.1 Graphene-based membrane

Graphene-based membranes have recently emerged as a promising research and development area for separating molecules and ions (Table 1). According to research, a precise mono-sheet of graphene is impermeable to minor species such as hydrogen and helium are two types of gases[51]. The graphene's- orbitals, its formation of a thick, dispersed cloud closes the space between its aromatic rings. There is space where material may enter the electron density near the closed rings[52]. Molecular dynamic (MD) simulations currently indicate it has a responsible microstructure of graphene-based membranes. They have laminated and porous for a variety of water penetration processes[53]. attributed enhanced water flow throws by GOMs to unrivaled permeable micro-structures, demonstrating it is impacts on side-edge caused by additional linkages might form among oxidized areas with H_2O molecules prevent H_2O carriage in GO a single continues layer and with enhanced H_2O move remained attributed such as nanostructures with pores. As a result, enhanced H_2O flux, smaller flakes, a high density of inter-edge gaps, and broad layers are selected in graphene membrane production. Adding or cross-linking chemicals may also change the size of interlayer sheets. investigated the ability of monolayer graphene to filter sodium chloride from a feed solution. Due to size exclusion[8], tiny hydrophobic pores and low pressure effectively impede NaCl salts, while the greater adequate bulk in the charged atoms also lack of (H) bonds may (Pb) to a significant energy path to the ionic route. Graphene and GOMs compared fabrication of polymeric as well as different materials premised membranes were conclusion with respect improved liquid and barrage transference permeability. These following parts provide additional details of membranes, focusing on three main types of structure:

Nanocomposite Monolayer (2) Multi-layer stacking GO structures (3) GO layers in complicated membrane.

3.2 Potential application

Water treatment, apart from other issues, water scarcity is currently the world's most pressing issue[27 54 20 55 56]. Many scientists are developing membrane technology to repurpose industrially polluted water and saline water at reasonable costs. One of the most promising approaches to finding a viable solution for global water scarcity is nanotechnology in water treatment membranes. Despite its numerous advantages, it has one major disadvantage: fouling, which reduces membrane life[47]. As a result, creating a fouling-resistant membrane necessitates more thought in membrane-based technologies. Many attempts have been made to address these difficulties using novel materials such as zeolites, silica, polymers, ceramics, and carbon-based membranes[57] [20] [20] [20]. These physical and technological advancements helped to overcome the problem, but further research is needed to find the ideal membrane material with excellent permeability, filtration performance, and antifouling properties for practical applications. Based on Graphene oxide has recently emerged in the exciting new area of study, development used molecular as well as ionic filtration. Because oxygen functions were current in the boundary's basic planer of GO, The fascinating feature in water treatment and filtration applications[58]. It may be pressed into laminates right away or used as a simple composite with inorganic minerals or polymers[59] [32] [60]. Furthermore, the nano capillaries seen in GO flakes can act as a molecular screen by obstructing larger species[61]. The GOMs that followed had exceptional filtering abilities. According to the distortion in sp^3 C–O bonds, nanoscale crinkles and physical flaws occur in the basal plane of GO flakes, allowing major routes for water penetration. Furthermore, oxygen functionalities provide many reaction sites for various outward modification Designs, Graphene Oxide-Based Composite Nanofiltration Membranes Synthesis and Properties, which can be used to create GOM fabrication sequences with significantly improved filtration efficiency. GO lamellar membranes may be made in various ways, each with their microstructural characteristics and transport routes. GOMs have been widely studied both theoretically and experimentally for their uses in ionic and molecular filtration up to this point. Nonetheless, several critical issues such as regulated interlayer space, aqueous solution stability, and fouling characteristics must be addressed for these membranes to function well in salt removal did the groundwork[62]. GOMs have been demonstrated to enhance the permeability of water vapor in the dry state while entirely blocking the penetration of other liquids and gases. The lower friction nanochannels formed between the non-oxidized regions of GO flakes are responsible for the increased water vapor penetration. When GOMs are immersed in water, the d spacing of GOMs grows, making it easier for smaller molecules with less than 0.45 nm in diameter to go across the membranes used a vacuum filtration method to formed nano channels using graphene oxide with enhanced interlayers numerous nano capillaries by thicknesses of 3–5 nm. The concentration of GO dispersion deposited was used to regulate the diameter of the membrane. Many probe molecules have been used to evaluate the membrane's separating capabilities. Gold nanoparticles (5 nm diameter) were rejected entirely by these membranes, which had a high permeability of 460±30 $Lm^{-2}h^{-1}bar^{-1}$. However, there is practically no clearance of a tiny molecule with a molecular size of 1 nm in the as-prepared membrane. Furthermore, according to slip flow theory, it aids water movement. Water first flows via a hydrophilic gate for aggregation, then through a sliding mechanism to hydrophobic nano capillaries. (See Figure 5 for a theoretical design)[63]. The newest research on mass transfer using (GO) fabricated membranes, Graphene oxide sheets, nanosized graphene, and flawless graphene structure are all considered in terms of their potential applications. An overview and prognosis on the potential and difficulties in this emerging subject are also offered. Through view of these, researchers may be able to better understand material transfer as optimize the fabrication for graphene-based membranes towards huge production for a range of purposes. Despite the shortcomings like weak mechanical strength of single layer graphene, difficult to prepare nanopores on graphene film and hard to integrate with polymer, we hold the opinion that graphene-based films still have great research value especially in the membrane separation technology.

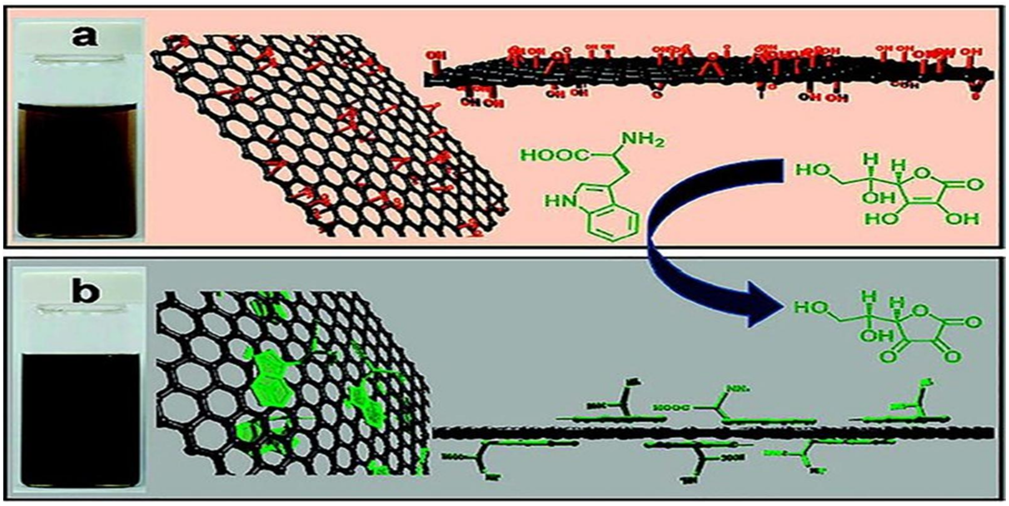

Figure 4. Schematic illustration of the reduction process, including photographs of (a) the graphite oxide aqueous solution and (b) the stably dispersed graphene aqueous dispersion.

Despite retaining excellent water media stability. First showed that thick reduce graphene oxide membrane size (0.5–1.0 m) has been water impermeable. However, by changing the width of the membranes, the permeance of these membranes may be improved. rGO membranes were afterward described by numerous studies for various NF applications[65] used a vacuum filtering approach to make too much smallest reduce graphene oxide-based membrane 53 to 22 nanometer thickness containing two-D nano capillaries, which they successfully used purposed purifications of water. The nanosheet had purest H_2O permeates of likely 22.5 $Lm^{-2}h^{-1}$ bar^{-1}, by good repudiation below 99% in condition of organic dyes and standard rejection (20 to 60%) for ion salts as it was produced. Smaller molecules, such as NaCl were rejected well by these rGO-based membranes (thickness 100 nm). The narrower nanochannels between rGO nanosheets account for the more excellent NaCl rejection. Whereas important progress ware made in GOMs used for salt separation from aquatic as well as water analysis processes, there are still many problems that need to be addressed, with the ideal fabrication of graphene oxide-based membrane, comparable by means of composition the oxidization ranges, pore diameter, D-space adjustment, and the number of graphene sheets, among others. Although the pore size was more significant formerly 0.8 nm, graphene oxide-based membrane had higher solvent permeability later carbon nanotube membranes due to the faster speed in the core. Various techniques have been used to adjust the d spacing in this regard. By adding large nanomaterials or crosslinking bulky and stiff species, membrane selectivity and permeance can be enhanced. Reduced graphene oxide-based membranes can reduce d-spacing quickly, making them impermeable to all gases, fluids, and other species. Despite owning this filtration constant, it remained more challenging to reduce the d-spacing due to GOMs' tendency the swelling after stuck into liquid. Ionic species can no longer be rejected by these membranes throughout an even wider range of sizes because of this. The instability of GO membranes in water pertains to both breakdown and expansion, which is frequently overlooked. Swell not having decomposition can cause separation without unstable (rejection rate). As a result, controlling swelling is crucial in resolving the instability of GO membranes in water. Recently developed the interlaminar narrow molecular bonding approach produces a strong graphene oxide surface resist swelling, to improve the membrane's mechanical strength, an interfacial long-chain molecular bridge holds the GO laminate to the porous substrate. The stabilized GO membranes display exceptional endurance under demanding working circumstances, such as crossflow, high-pressure, and long-term storage, to the logical creation and adjustment of the molecular bridges. Furthermore, this technique works on a variety of porous substrates, including ceramics, nylon, and mixed-cellulose acetate. Furthermore, this method is scalable. This adaptable technique will expand the range of applications for GO membranes in aquatic conditions. Because rGO plays such a critical role, the impact of the GO reduction degree or the additional quantity of rGO on the performance of the resulting membrane should be thoroughly examined. Prepared GO/rGO membranes with varying lamellar distances and examined the impact of lamellar distance on the stability of the produced GO/rGO membranes by regulating the concentration of oxidized groups by modifying the reducing conditions[67].

3.2.1 Pervaporation

To separate water from solvent mixes and organic fluids, pervaporation (PV) is an energy-efficient and high-tech approach[67]. The PV approach uses a specified range to separate both aqueous and gaseous states, therefore indicates reason either membrane is used [68] [69] and the vaporization approach[70] [71] make it easier for chosen species in a liquid media to travel through a membrane. PV has been successfully utilized to remove water from several organic components; nevertheless, it still faces several obstacles, including the larger size of organic compounds in contrast to water, which makes penetration of organic components across membrane difficult. Furthermore, the membranes' stability in aqueous solutions is a significant concern. These include membranes made from inorganic, polymer-based and composite materials, have been investigated for use in PV to overcome these challenges. However, these membranes have reduced flow too limited innovation in the organic type. As a result, there is a constant demand for higher-performing membranes with superior filtration, flow as well as performance have discovered a new pathway for GOMs in organic mixes' PV dryness. GOMs for selective liquid filtering from organic mixtures such as ethanol, methanol, propanol isomers, butanol isomers, ethyl acetate, and dimethyl carbonate have been recently stayed described in a few papers. GOMs have much potential in PV separation because of their high hydrophilicity and quick water transfer between graphene layers[67]. As a result, it may be viewed as an ideal material for designing hydrophilic membranes when combined with polymers. These features improved the interfacial interaction between the polymer solution and the GO, allowing for GO composites with excellent thermal and mechanical properties. This type of manufactured GO can remove water since it has various active oxygen-based capabilities. Ionized areas of manufacture form fast interactions with water molecules, resultant is increasing permeance[76] and selectivity. These membranes have recently been used to selectively dehydrate methanol, ethanol, isopropyl alcohol, butanol, and other organic solvents from an aqueous medium.

3.2.2 Gas separation

Over the last few decades, membrane-based gas separation methods have become more popular. Because of their inherent advantages, such as minimal energy consumption, no chemical usage, and fewer moving components, they may have cheaper operating and maintenance expenses. Fujifilm created a unique gas separation platform technology based on key technologies from our photography background. Custom membranes can be developed using the framework for such a variety of applications. Hydrogen, methane (CH_4), CO_2 capture (CO_2/air, CO_2/H_2), volatile organic molecules, and hydrocarbons (alkene/alkane) separation and purification are important for sustainable resource uses[73] [74] The combination of gas molecules is of comparable size, making possessions more challenging to distinguish. Traditional separation methods were expensive to implement and resulted in many environmental difficulties. Membrane-based technology is regarded as a more prosperous and efficient gas separation method than older methods, with various advantages[75]. Through nanocomposites related to silicon zeolite to carbon, researchers have been studying this topic for more than forty years[76]. Despite these shortcomings, they nonetheless have a higher permeability rate, a worse selective, as well as poor stability. Researchers must continue to focus on developing materials with improved permeability, specificity, and stability. Because of its superior molecular level thickness and low mass transfer hurdle, graphene oxide has been recently regarded as an excellent dynamic phase for gas partition over a (membrane) graphene oxide nanosheet. There are many derivatives of graphene like as GO is a new material that has been extensively studied for gas separation several investigations have recently demonstrated the capacity of thin graphene oxide-based membrane such vapor penetration through changing the support behaviors of graphene oxide (GO) nano flake.

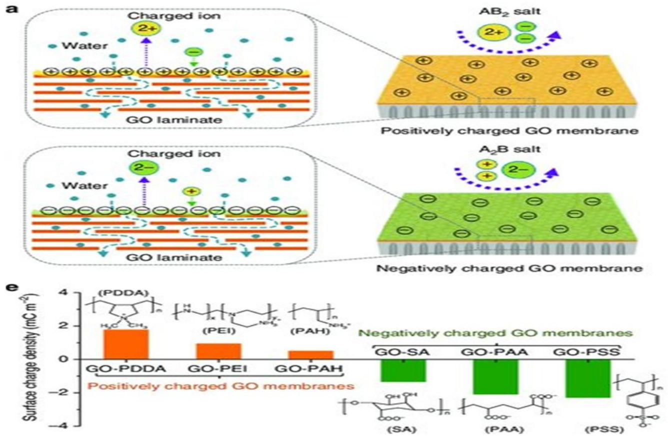

Figure 5. GO membranes may be made by depositing polyelectrolytes.

On the surface of GO laminates to achieve regulated ion transport. Coating polycations like poly diallyl dimethyl ammonium, polyethyleneimine (PEI), and polyallylamine hydrochloride. GO membrane to reject A 2 B-type salts. The fabrication of surface-charged GO membranes is depicted in this diagram. To make the surface-charged GO laminates, filter a GO aqueous suspension on porous polyacrylonitrile. Substrate using a pressured-assisted filtration-deposition process, then dip-coat a dilute polyelectrolyte solution on the surface of pre-stacked GO laminates[61].

It was computed the gas separation of mono and mixed gases. GOMs with a thickness of 18 nm were used to study mono gas separation for He, H_2, CH_2, O_2, N_2, CO_2, and CO molecules, and it was discovered that the H_2 transport rate was roughly 300 times larger than CO_2. After that, the membrane's selectivity for mixed gases (H_2/CO_2 and H_2/N_2) was tested, and it showed 3400 and 9000, respectively. Though, as the thickness of the membrane grows, the penetration rate of H_2 and He decreases, which is caused by a fault in the molecular passageways on the GO sheets. Furthermore, this research suggests that ultrathin GOMs may be used extensively to recover H_2 for NH_3 products and CO_2 collection prior to combustion. After that, used a spin coating approach to create a CO_2 selective graphene-based membrane and vacuum filtering to create hydrogen-selective GOMs on a porous substrate. They discovered that having water molecules on the surface of GOMs improves CO_2 transport significantly more than other lighter gases. They also demonstrated that gas penetration occurs across the interlayer spacing of pilled GO flakes, which varies depending on the synthesis technique[78]. During the membrane design, the interlayer spacing between GO flakes and the volume of interpolated water molecules significantly altered the gas transport properties.

Furthermore, the number of functionalities present in the basal plane influences the stacking of GO flakes and the interlayer spacing. Most GO flakes have oxygen functions on the basal plane, whereas the edges have carboxy and carbonyl. Furthermore, the carboxy groups' highly ionized oxygen atoms act as a negatively charged species that aids in the assembly of GO flakes. Recently manufactured a GO composite membrane from GO and PEBA with different thicknesses (6 - 15 nm) on a PVDF substrate (Figure 5). Gas selectivity and penetration of various gases were studied using GO laminates. These membranes allow for more CO_2 gas permeability while allowing for less movement of other gases. $CO_2>H_2>CH_2>N_2$ is the sequence of transit. Furthermore, it has been discovered that increasing the number of GO nanoflakes improves the selectivity and permeance rate of the membrane for CO_2. CO_2 permeates 100 barriers and CO_2/N_2 selectivity of 91. (Figure 5). In addition, continuous CO_2 and N_2 penetration were achieved for up to 6000 minutes. Following that, GOMs exhibit no flaws, indicating that these membranes are highly stable for use[79]. Better membrane materials, on the other hand, would encourage quicker development. We examine the status of membrane materials, including polymers and hybrid materials, as well as existing difficulties and barriers, and lastly, we propose future research priorities in membrane science in this Perspective. A multidisciplinary approach including the broad domains of chemical, and materials engineering, polymer science, and materials chemistry will be required to develop novel membrane materials for large-scale separations.

4. Methodology

This includes research methods, chemicals and reagents, glassware cleaning, instruments, sampling fabrication for Characterizations, GO and rGO membrane manufacturing, and their use in water purification.

4.1 Experimental work

The Green method was used to fabricate GOMs after a modified Hummer's approach was employed to manufacture graphene oxide. We discussed novel methodologies and methods for determining the crystalline structure, morphology, contact angle, and stability of GO composite materials by adding ginger extract in this chapter. FTIR, SEM, XRD, XPS, and Contact angle goniometer were used to analyze the crosslinking mechanism, morphology, d-spacing, degree of reduction, and hydrophilicity/hydrophobicity of the GO composite material. The membranes were then employed for a variety of applications, including molecular separation and ionic separation.

4.2 Washing of glassware

All apparatus were adequately cleaned with tape water, then submerged in Royal water for a few hours, and then washed three to four times with DI water before being dried in an oven at 1000 C and chilled before creating GO composite material.

4.3 Sample collection

extract of onion was collected according to Fig. 1. First 6.0 g pieces of fresh onion was added into 150 mL of DI water in 250 mL beaker and keep it on the 70 °C for overnight. Finally, the solution was filtered through Whatman (Grade 1) filter paper.

4.4 Extraction procedure

Extract of onion was collected according to (Figure 1). First 6.0 g pieces of fresh onion was added into 150 mL of DI water in 250 mL beaker and keep it on the 70 °C for overnight. Finally, the solution was filtered through Whatman (Grade 1) filter paper.

4.5 Material and reagents

Natural flake graphite (35 mesh, Sigma Aldrich Co., Ltd.), concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium per manganate ($KMnO_4$), hydrogen per oxide (H_2O_2) (30%), hydrochloric acid HCl, and onion were all acquired at the Jamshoro fruit market.

3.6 Synthesis of GO nanosheet

3.6.1 Synthesis of GO

4.0 g of 35 mesh graphite powder was added to 98.0 mL of concentrated sulphuric acid (H_2SO_4) and 2.5 g of sodium nitrate ($NaNO_3$) in ice bath with continuous magnetic stirring. Further, 15.0 g of Potassium permanganate ($KMnO_4$) was added to the above mixture at below 20°C and stirred up to 90 min. After that 138 mL of de-ionized (DI) water slowly added to reaction mixture to avoid overheating and followed addition of 400 mL of DI water with 5.0 mL of 30% hydrogen peroxide (H_2O_2) to obtained graphite oxide suspension. As-prepared product was washed with 3% aqueous HCl and dialysis for 5 days to remove metallic impurities. Furthermore, as-obtained graphite oxide was exfoliated into GO suspension with help of tip sonication (280 W, 120 min). Then GO dispersion was centrifuged at 8000 rpm for 20 min to remove additional contamination such as thick multilayer flakes etc. Finally, the as-prepared dispersion was dried using vacuum freeze dryer and used for fabrication of membranes.

4.6.2 Preparation of go/oe dispersion Synthesis of GO

Further, to prepare the GO/OE dispersion, the 0.2 g of GO powder was added to extraction of onion (150 mL) and keep on heating overnight (70°C) with continuous stirring. The color of GO dispersion changes from yellowish/ golden to black.

4.6.3 Go/oe composite membrane

The GO/OE-based composite membrane was prepared according to reported method[53]. 15 mL of GO/OE dispersion was diluted up to 60 mL in beaker and sonicated for 40 min. As-prepared GO/OE dispersion was filtered through vacuum filtration assembly using Nylon as substrate. The obtained GO/OE membrane was dried at room temperature overnight before use. The thickness of membrane is controlled by varying volume and concentration of dispersion during filtration.

4.6.4 Go/q composite membrane

0.2 g of Quercetin powder and 0.2 g of GO nanosheets were added into 150 mL of DI water and kept at 70°C overnight in a closed environment. As-obtained black GO/Q dispersion is used for fabrication of GO/Q composite membrane. 10 mL of GO/Q dispersion was further diluted with 50 mL of DI water and filter on Nylon support. As-prepared GO/Q membrane was dried at room temperature overnight before used. The thickness is also controlled by the same method. For comparative studies, we also prepared pristine GO membranes with similar methods.

Figure 6. Modification of GO with onion extractive and Quercetin powder, and fabrication of GO/OE, and GO/Q composite membranes respectively.

4.7 Material and membrane characterization

The scanning electronic microscope (SEM, Nova Nano SEM 430) was used to observe the morphologies of GO-based membranes. X-ray diffraction (XRD) spectra were measured with X-ray diffractometer to observe the structural information with Cu Kα radiation (λ=0.154, D-MAX/2400). The chemical composition of material and membranes were determined with X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI). The FTIR spectra was recorded with Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700). The thicknesses of membranes were measured with help of Bruker DekaXT Profiler (Germany). The rejection of heavy metal and small ions was confirmed with ionic conductivity meter (Mettler Toledo, M400) and atomic absorption spectrometer (Thermo Scientific – iCE 3300).

4.7.1 Permeation test

All experiments were performed at room temperature and operating pressure 1.0 bar. The DI water permeance and salt rejection of GO membranes were measured using vacuum filtration method.

The salt rejection (R) was measured according to Equation -1

$$\mathrm{R}\ (\%) = 100\ x\ (1 - CP/Cf)\ (1)$$

Where Cp and Cf are the concentration of permeate and feed solution respectively. While the permeance (J) of the membrane is calculated according to Equation–2.

The permeance of the membrane is calculated in Lm-2h-1bar-1.

$$\mathrm{J} = \mathrm{VA\Delta TP}\ (2)$$

Where V, A, P, and ΔT are the volume in liter, area of membrane in cm2, pressure in bar, and permeate time in hour respectively.

4.7.2 Stability performance

As-prepared membranes were cut into 1.5 x 1.5 cm2 pieces and immersed into different pH solution such as DI water (pH~7), HCl (pH~2) and NaOH (pH~12) respectively. The stability of each membrane was recorded at different times.

4.7.3 Degree of swelling

The swelling studies of the membranes were carried out in DI water at pH~7. The membrane was immersed into 10 mL of DI water for 48 h at room temperature. After 48 h, the membranes were dried. The weight of membrane was noted after and before dipping into water. The swelling degree was evaluated according to the following formula.

$$\mathrm{DS} = (Ww - Wd) \,/\, Wd \; x \; 100$$

Where Ww and Wd show the weights of wet and dry membranes respectively.

5. Results and Discussion

Present the conclusion as well as an explanation. The preparation, characterization, and use of GO and rGO membranes are part of such research.

5.1 Physiochemical characterization of go based membrane

Synthesis and description of GO-based membranes. According to their modified method, the Despite a thickness of less than ~1 nanometer. Graphene oxide nanosheets were created having diameter size between 0.25 and 1.5 micrometers[80]. Then GO was partially reduced with extractive of onion (Figure 6). The several molecules containing different oxygen and nitrogen functional groups are present in the onion extractive to be easily reduced. (Figure 6d) the vacuum filtration method synthesized the GO/OE membranes with different thicknesses (Figure 6). Pristine GOMs were also prepared with a similar method for comparative studies: GO's cross-sectional view and surface morphology (Figure 7c, and 7b) and GO/OE membranes (Figure 7e and 7f) were characterized by SEM. It illustrates that the surface morphology of GO is non-uniform, rough, and cloudy in appearance, with dense GO layers (Figure 7c). After reduction with Onion extractive (OE), the reduced membrane (GO/OE) represents smooth and uniform morphology (Figure 7e). Our prepared GO/OE membranes visibly show the laminated structures with a significant interlayer distance (~0.95 nm) compared to new GO membranes. As industrial liquids, GO has a considerably variable membrane characteristics than in liquid. O_2 dissolution with chemical fluids was considerably inhibited owing to the comparatively limited charge absorption capacity. The volume of distribution of carboxyl group, particularly representing the primary supply of negative ions of GO, rises dramatically in polar solvents. Due to classical Established concept for ionic solvation, such a pKa shift is directly proportional to the inverse of the organic solvent's dielectric constant. Many synthetic solvents have lower dielectric constants than liquid. To summarize, a neutral or weakly negatively charged of GO in several organic solvents may be seen.

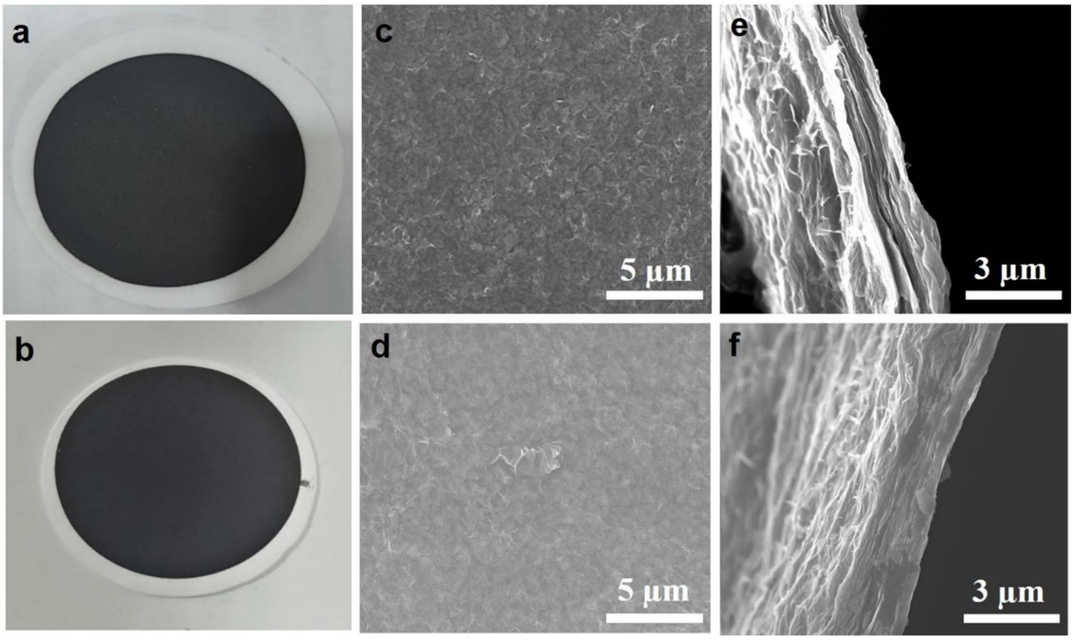

Figure 7. The structural and surface morphology of GO/OE and GO/Q membranes. (a, b) Digital photos of GO/OE (a) and GO/Q (b) membranes. (c, d) Surface morphology and (e, f) cross-sectional studies of GO/OE and GO/Q membranes respectively.

The XRD studies of dry pristine GO membrane (Figure 7a) suggests a diffraction peak present at 11.5° conforming at the interlayer space of 0.77 nm, which is almost similar as reported in literature for dry GO membranes[81 82]. After modification with extractive of

Onion, the interlayer spacing increased up to 0.85 nm (10.5°), which is possibly due to presence of several molecules within onion extractive, which successfully cross-link the GO sheets and results interlayer spacing increased. On the other side, the interlayer spacing in GO/Q membrane decreased from 0.77 nm to 0.35 nm (26.4°), which is due to reduction of GO sheets with quercetin molecule. The resulting membrane clearly shows the reduced peak at 26.5° by interlayer distance of 0.34 nm (Figure 7a). Membranes' chemical structure and elemental content were assessed using XPS. Pristine GO membrane confirmations related XPS ranges by way of described in literature as shown in figure 7b. It deconvolved into four peaks, indicating the existence of epoxy, carboxyl hydroxy, and carbonyl groups (Figure 7b). The peak at 284.2 eV dedicated to C-C / C=C due to presence of aromatic rings in GO sheets, peak at 286.3 eV ascribed to 1,2 alkoxy and epoxide groups, peak at 287.1 eV assigned to C=O group and peak at 288.6 indicated the epoxy (C-O-C) group as shown in Fig. 3b. After modification of GO with OE and Q. Graphene oxide-based membranes are moderately compact. Figure 7c, d illustrations the decrease in oxygen content and epoxy peak almost disappear. The O/C ratio of GO/OE and OE decreases from 0.44 to 0.32 and 0.28 respectively, that proves reduction of GO, also confirmed physically change in color.

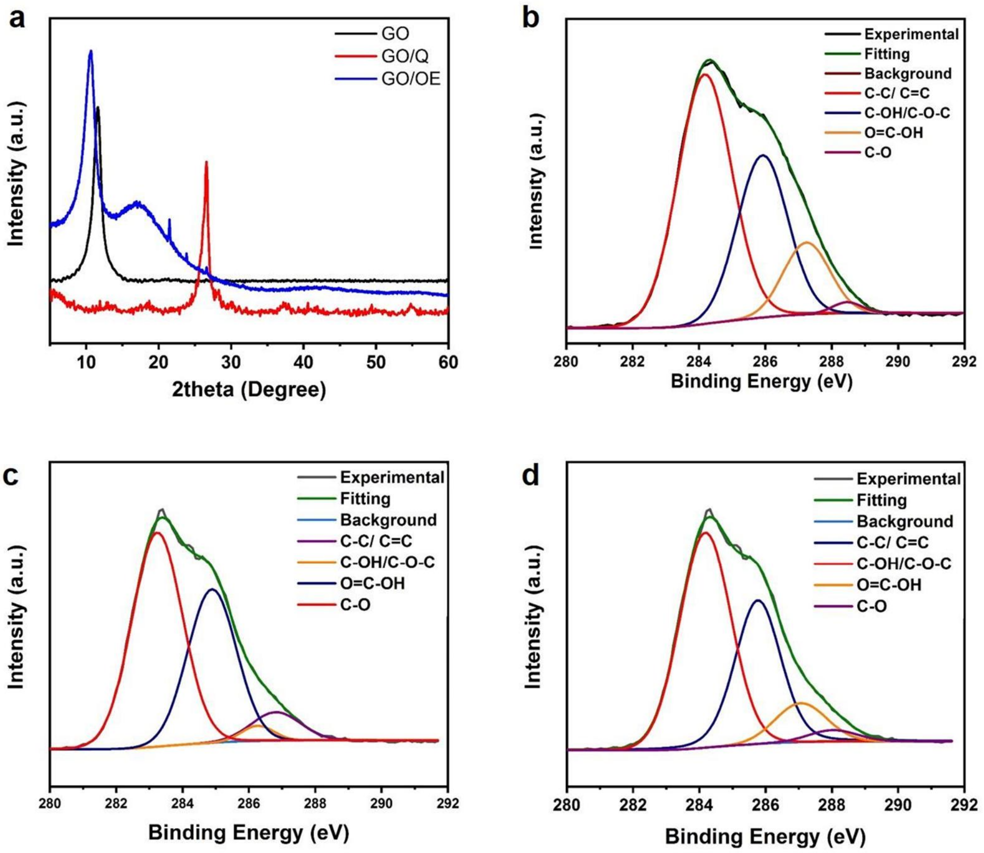

Figure 8. (a) XRD patterns of GO, GO/OE and GQ membranes. (b-d) C 1s XPS spectra of GO (b), GO/OE membrane (c), and GO/Q membrane (d) respectively.

FTIR was used to characterize the bonding mechanism. Shows characteristics four prominent spectrum of graphene oxide (GO), the acquired indicate spectrum at 3432, 1680, 1280 and 1053 cm^{-1} show the O-H stretching, carbonyl (C=O) stretching, epoxy (-C-O-C-), and alkoxy (C-O) groups, respectively, while GO/OE shows three peaks obtained but less intense as compare GO peak its means reeducation occur another composite GO/Q shows two disappeared peaks of epoxy and alkoxy validate the interaction of GO with GO/Q (Figure 8). Further Fourier- transform infra-red spectroscopy (FTIR) interpretation spectrum of compound bonding of onion using with graphene oxide through hydrogen bonding/π–π contact with alkoxy and epoxy groups instant in graphene oxide. Along with that, a lower penetrating spectrum of the carbonyl group and an enlargement spectrum of the O-H group proves the removal of the oxygen content of GO. Onion has numerous active compounds such as Many onion types have yellow or brown skins due to flavanols such as quercetin and its derivatives, which are rich in hydroxy functional groups, and anthocyanins, which give certain kinds their red or purple color[84]. As a result, they operate as both a stabilizing agent and just a reduction reaction, preventing the aggregation of decreased GO sheets.

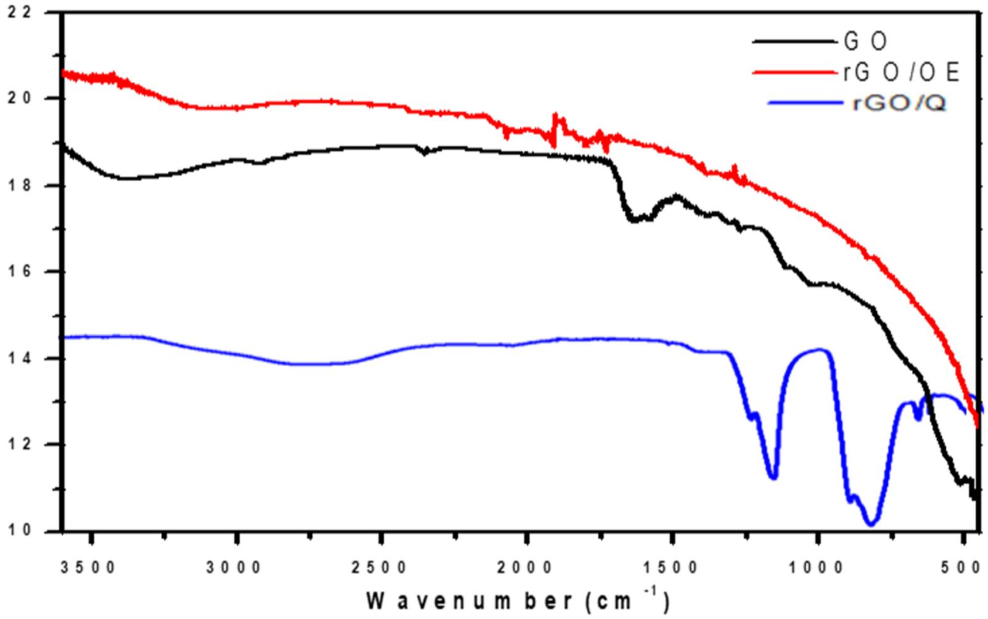

Figure 9. FTIR spectra of GO and rGO.

5.2 Filtration efficiency of go based Membrane

The as-prepared membranes were used to measure the DI water permeance. The pristine GO membrane shows very less permeance ~37 $Lm^{-2}h^{-1}bar^{-1}$ with thickness (~290±20 nm) as reported in previous work[17]. While GO/OE composite membrane (~350±10 nm) modified throw environmentally friendly exhibits great water permeance ~460±5 $Lm^{-2}h^{-1}bar^{-1}$, that is numerous periods higher than pristine GO membranes with similar thicknesses (Figure 7a). Besides his, the 300 nm-thick GO/Q membrane shows 150±5 $Lm^{-2}h^{-1}bar^{-1}$ as shown in Fig. 4b. Further, we studied the water permeance behavior of both GO/OE and GO/Q composite membranes with variable thickness (Figure 7a, 7b). The membrane generally shows the same trend, the water permeance is reduced drastically as increases the thickness of membranes. As-prepared 350 nm thick GO/OE membrane exhibits water permeance 460±5 $Lm^{-2}h^{-1}bar^{-1}$. Whereas the thicker GO/OE membrane (1050 nm) shows much less flux ~76±5 $Lm^{-2}h^{-1}bar^{-1}$, which is also five times higher than pristine GO membranes. This is due to mass transference and defect produced during separation process are enclosed by higher and lower layers of GO/OE. Hence, water moves slowly through thick membranes, which is also consistent with theory reported by previous work. While the same trend was also observed for 1120±10 nm-thick GO/Q membranes, which exhibit water permeance up to 35±5 $Lm^{-2}h^{-1}bar^{-1}$. The permeability observed almost five to seven times decreased in permeability observed compared to 300 nm-thick GO/Q membranes.

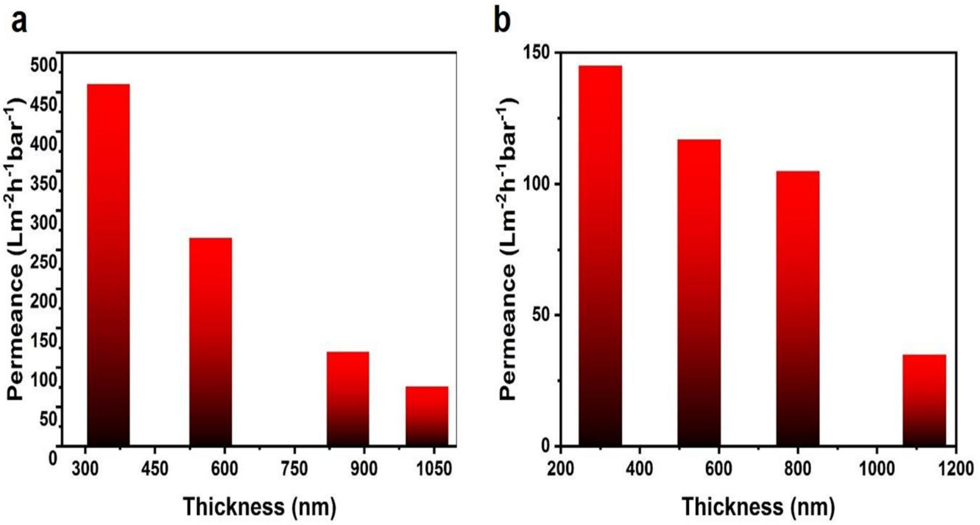

Figure 10. DI water permeance of (a) Q/OE, and (b) GO/Q membranes with different thicknesses.

The newly developed GO, GO/OE and GO/Q membranes were further tested against heavy metal ions. Here we employed Pb $(NO^3)_2$, $CdCl_2$, $K_2Cr_2O_7$ and As_2O_3 with different sizes and charges using 1.0 bar pressure and 1.0 M concentration for each ion respectively (Figure 4). The 290 nm thick pristine GO-based membrane demonstrate >90% rejection for Pb^{2+}, Cd^{2+}, As^{3+}, and Cr^{6+} ions, which consistent with reported data in literature. The GO/OE membrane shows good separation ~99.5% and ~93.5% for Pb^{2+} and Cr^{6+} ions respectively. The separation sequence of ions i.e., Pb $(NO_3)^2$> $K_2Cr_2O_7$ >$CdCl_2$>As_2O_3 is achieved for GO/OE membranes as shown in Fig.5a. While GO/Q membrane shows little less separation up to 98.2% and 97.0% for Pb^{2+} and Cr^{6+} ions respectively as shown in Fig. 5b. The separation of heavy metal ions by GO membranes is achieved using different mechanisms. Usually, it takes place by size exclusion, dehydration effect (steric exclusion of the hydration shell), subtler effect which involve specific interaction with pore, charge repulsion, entropic differences, and interaction of solutes with specific chemical structure of pore. As we know, pristine GO membranes are negatively charged, therefore, they show less rejection for cations. However, our fabricated GO/OE and GO/Q composite membranes are highly positive at neutral pH. Therefore, such membranes can repel the positively charged species and show remarkable high rejection for ions. Similar mechanisms were observed for separation of Pb^{2+} and Cr^{6+} heavy metal ions. Further, the presence of these counter ions that could attach with surface might decrease as well as repulsive force and generating higher rejection for metals ions such as Pb^{2+} and Cr^{6+} compared to other divalent ions.

Therefore, the rejection order for such ions is observed as Pb $(NO_3)^2$> $K_2Cr_2O_7$ >As_2O_3>$CdCl_2$. It in summary, our fabricated GO/OE membranes show better heavy metal ions rejection and high water permeance than GO/Q and pristine GO membranes.

Figure 11. (a, b) Permeability and separation efficiency of GO/OE (a) and GO/Q (b) membranes for heavy metal ions respectively. (c, d) Salt separation of GO/OE (c) and GO/Q (d) membranes against small ions respectively.

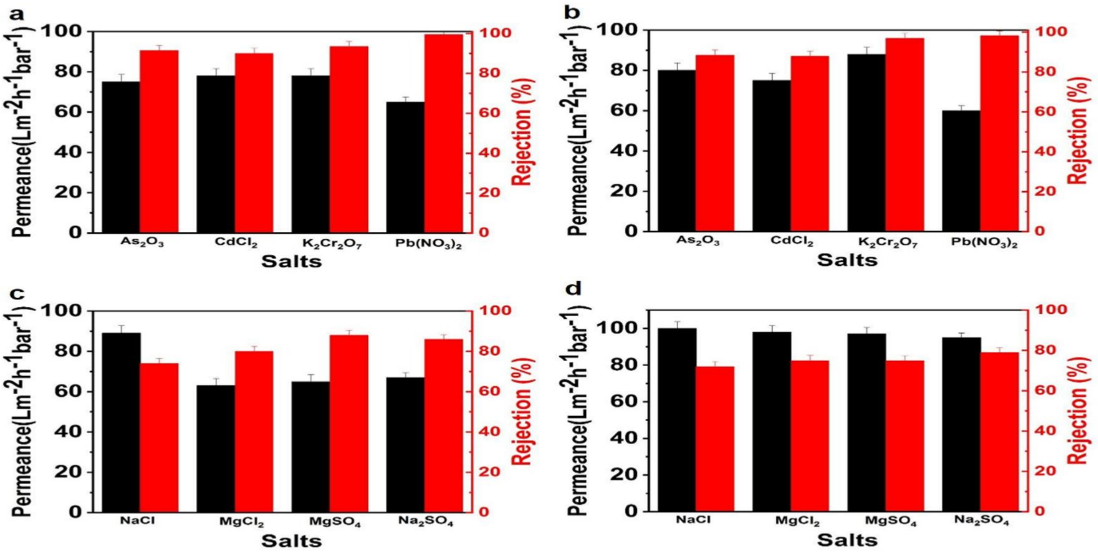

Table 1. Separation Performances of GO based membranes

Heavy Metal Salts	MW	Pristine GO membrane (290±10 nm)		GO/OE membrane (350±10 nm)		GO/Q membrane (300±10nm)	
		Rej. (%)	Perm. (LMBH)	Rej. (%)	Perm. (LMBH)	Rej. (%)	Perm. (LMBH)
NaCl	58.44	45±1	29±1	74±1	89±5	72±1	100±5

$MgCl_2$	95.11	55±1	28±2	80±1	63±5	75±1	98±5
MgSO4	120.36	55±1	25±1	88±1	65±5	75±1	97±5
Na_2SO_4	142.04	57±1	28±2	86±1	67±5	79±1	95±5
As_2O_3	197.84	67±1	24±2	91.5±1	75±5	80.5±1	80±5
$CdCl_2$	183.32	75±1	22±2	90.0±1	78±5	88.0±1	75±5
$K_2Cr_2O_7$	294.18	70±1	14±1	93.5±1	78±5	97.0±1	88±5
$Pb\ (NO_3)^2$	331.2	74±1	11±1	99.5±1	65±5	98.2±1	60±5
MW, molecular weight; DW, deionized water; GO, graphene oxide; OE, Onion extractive; Q,Quercetin.							

Table 2. DI water Permeability with variable thicknesses

S. No	Thickness (nm)	GO/OE membrane (LMBH)	Thickness (nm)	GO/Q membrane (LMBH)
01	350±10	460±5	300±10	150±5
02	570±10	265±5	550±10	117±5
03	865±10	120±5	800±10	105±5
04	1035±10	76±5	1120±10	35±5

In addition, we have also evaluated the desalination properties of pristine GO, GO/OE, and GO/Q membranes to separate small salt ions such as NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ using pristine GO, GO/Q, and GO/OE membranes with almost similar thicknesses using 0.95 bar pressure as shown in Table 1. The pure graphene oxide membranes using width 300±10 nanometers indicate a higher 57% and 55% rejection for small ions, i.e., Na_2SO_4 and $MgSO_4$, respectively. Thus, constant by reported data in the literature. Due to the lower ion sizes, they have a low rejection for NaCl salt. While GO/OE membranes show good rejection, almost 88% and 86% for $MgSO_4$ and Na_2SO_4 salts. The rejection sequence of the salt $MgSO_4 > Na_2SO_4 > MgCl_2 > NaCl$ was achieved for GO/OE membrane. While the GO/Q is a completely reduced membrane, these showed higher rejection, 79% for Na_2SO_4 and 75% for $MgSO_4$. The rejection sequence of the salt $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$ was achieved for the GO/Q membrane. The higher rejection of Na_2SO_4 and $MgSO_4$ salts is explained with the help of the Donnan exclusion effect[84]. According to Donnan's exclusion theory, the rejection rate is related to the valences of the ions, following the order of Zco-ions / Z counter-ions (Z refers to the valence). Potential zeta studies confirm that GO/SAA composite membranes are cationic selective membranes, can effectively repel the cationic ions, and show good separation efficiency for Na_2SO_4 and $MgSO_4$ salts. Besides this explanation, the counter-ions can bind the part of the surface charge, further weakening the repulsive force and resulting in higher retention for the divalent ions (Mg^{2+}) and other ions. There is a significant difference in salt rejection rates and permeability between the GO-based membranes shown in Table 2 and those reported for the "pristine" GO-based membrane.4.3 Stability of pristine GO, GO/OE, and GO/Q membranes.

The stability GO-based membrane plays a vital role in separation performance, so achieving higher stability requires time. Pristine GO membrane is easily delaminated due to its hydrophilic nature. GO can lead to strong repulsive forces to separate GO sheets from each other due to the presence of epoxy, hydroxy, carboxyl, and carbonyl at the edges and basal planes, respectively. Furthermore, GO sheets can delaminate in water due to the hydration effect of the carboxyl group that repulsive force between GO sheets. So, it is essential to control functional groups present in GO to enhance stability in water. Further to know the stability of both GO/OE and GO/Q membranes were used stability test using different pH. (Figure 11). As-fabricated GO/OE membranes show up to ~40 days' stability in water at pH-7 and more than almost one-month stability in both acidic and basic media (Figure 11 a and c). Due to the presence of functionalities in onion extractives that are cross-linked GO nanosheets strongly. Additionally, the stability of GO/Q membranes was measured in static mode. These membranes show higher stability in an aqueous medium up to 30 days, as shown in Fig. 5b.

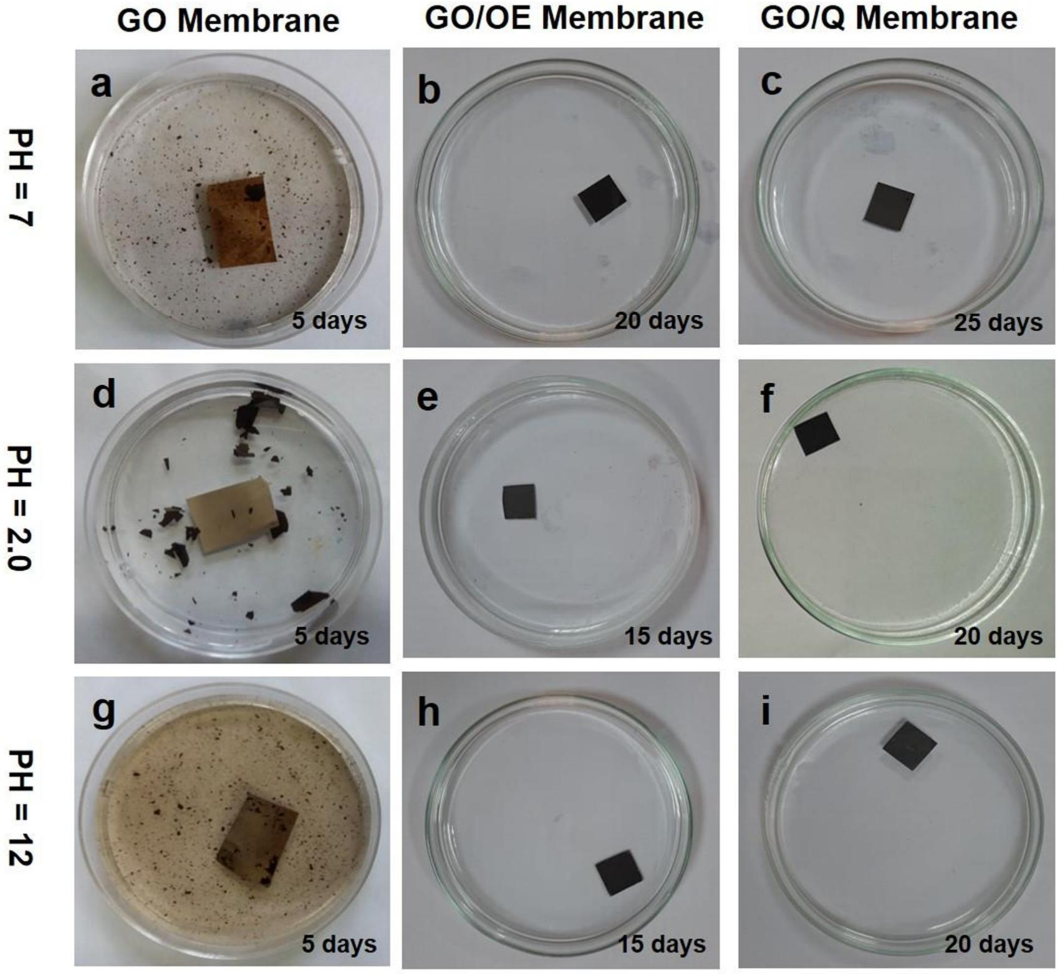

Figure 12. Photograph of stability of GO (a, d, g), GO/OE (b, e, h), and GO/Q (c, f, i) membranes. (a, b, c) Stability in neutral medium (water, pH ~7), (d, e, f) in acidic medium at pH ~2 and (g, h, i) in basic medium (pH~12) respectively at room temperature.

6. Conclusion and Future Perspectives

Herein, GO/OE and GO/Q-based composite membranes were prepared with a simple and green approach. The GO/OE membrane (350 nm) showed a high water permeance ~460±5 Lm-2h-1bar-1 and better separation efficiency for heavy metals such as 99.5% rejection for Pb $(NO_3)^2$ compared to pristine GO and GO/Q composite membrane with similar thicknesses. In addition, the desalination properties of membranes were also measured, and both GO/OE and GO/Q composite membranes exhibited >70% rejection for small ions such as NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$. Further, GO/Q membrane exhibited high stability in neutral environment (~25 days), and 20 days in both basic and acidic media compared to pristine GO and GO/OE composite membrane. Our fabricated membranes have versatile benefits as compared to GO and rGO membranes reported in literature due to ideal pore size achieved by green strategy and have great potential for different separation application in prospect.

6.1 Innovative Mechanisms of Membrane Fabrication

Membranes having well patterns might presently be produced using modern membranes preparation methods. Which includes vacuum filtering. Such, on other hand, take a long duration so were generally suitable for large-scale manufacturing. Composite membranes are also common; however, they're often supported by flaws. Organizing the manufacture of ultra-thin, free-standing GOMs with fewer imperfections is preferable as economic GOM applications since it can be scaled up.

6.2 Future improvement on the membrane preformation

Even though several graphene based composite membranes have been produced for ionic and molecular separation, such morphology of those same barriers still has not been improved. It is possible to increase permeability by reducing membrane thickness, however this might also result in a drop in separation efficiency. Surface roughness, pore size, and pore size distribution all have an impact on the integrity of the membranes, which is well established. As a result, future membrane performance will benefit from improvements in both membrane thickness and substrate structure. Low pressure and low concentration of feed were commonplace when GOMs were being employed for the separation of ions and organic compounds in aqueous solution. GOMs that can withstand high pressure should be able to filter feed solutions with high concentrations.

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Synthesis and Application of Graphene Oxide Based Lamellar Membranes for Water Purification

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Abstract

중금속 이온 분리 및 담수화를 위한 고효율 그래핀 산화물(GO) 라멜라 막을 제조하기 위한 충분한 노력이 수행되었습니다. 그러나 작은 이온에 대한 선택성은 여전히 주요 문제로 남아 있습니다. 여기서 GO 기반의 생체모방막은 친환경 공법으로 제작되어 중금속 이온의 선택적 분리 및 담수화에 사용된다. GO는 양파 추출물(OE)로 변형되어 GO/OE 복합 멤브레인으로 제조됩니다. GO/OE 복합 멤브레인(350nm)은 Cr6+(~87.5%), As3+(~89.5%), Cd2+(~93.0%), Pb2+(~99.5%), 우수한 투수성 ~460±20 Lm-2h-1 bar-1. 또한 비교 연구를 위해 GO/Quercetin(GO/Q) 멤브레인도 케르세틴으로 제조됩니다. 케르세틴은 양파 추출물의 활성 성분입니다. GO/Q 복합 멤브레인은 DI 수분 투과율이 ~150±10 Lm-2h-1bar-1인 Cr6+, As3+, Cd2+ 및 Pb2+에 대해 각각 ~78.0%, ~80.5%, ~88.0% 및 95.2%의 우수한 거부율을 나타냅니다. . 또한 두 멤브레인 모두 NaCl, Na2SO2, MgCl2 및 MgSO4와 같은 작은 이온의 거부를 측정하여 담수화에 사용됩니다. 생성된 멤브레인은 작은 이온에 대해 70% 이하의 거부율을 나타냅니다. 또한 두 멤브레인 모두 Indus River 물의 여과에 사용되며 GO/Q 멤브레인은 현저하게 높은 분리 효율을 나타내며 강물을 식수로 적합하게 만듭니다. 또한 GO/QE 복합 멤브레인은 GO/Q 복합 및 깨끗한 GO 기반 멤브레인과 비교하여 산성, 염기성 및 중성 환경에서 최대 ~25일 동안 매우 안정적입니다.