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Review Article

Graphene-Based Membrane Technology: Reaching Out to the Oil and Gas Industry

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This paper presents a critical review and the state of the art of graphene porous membranes, a brand-new technology and backdrop to discuss its potential application for efficient water desalination in low salinity water injection (LSWI). LSWI technology consists in injecting designed, adequately modified, filtered water to maximize oil production. To this end, desalination technologies already available can be further optimized, for example, via graphene membranes, to achieve greater efficiency in water-oil displacement. Theoretical and experimental applications of graphene porous membranes in water desalination have shown promising results over the last 5-6 years. Needless to say, improvements are still needed before graphene porous membranes become readily available. However, the present work simply sets out to demonstrate, at least in principle, the practical potential graphene membranes would have in hydrocarbon recovery processes.

1. Introduction

In many ways, the history of science has been the history of manipulation—understood as the act of utilizing something skillfully—and it is precisely in this sense that manipulation has entered the "nanotechnology" era. Broadly speaking, nanotechnology is about understanding and manipulating materials and their properties at dimensions of 1 to 100 nanometers. It is sometimes referred to as a general purpose technology because of the impact it could have in almost every industry and area of society. In fact, the application of nanotechnologies in different fields—from healthcare to aeronautics—has proven to be extremely useful for quite some time now; one of the most appealing features being the real possibility of manipulating the behavior of the nanomaterials employed. However, one of the main challenges of finding applications of nanotechnologies to the oil and gas industry is that nanotechnology specialists are seldom familiar with the technicalities of hydrocarbon production and vice versa.

The "nano" knowledge acquired so far in other fields has certainly triggered the imagination of some folks at oil and gas exploration and production. Efforts have been made to transfer the knowledge to the oil and gas industry over the last couple of decades. Ongoing researches for the application of nanomaterials to address an array of issues that arise in oil and gas exploration have given promising results. Among the research worth mentioning is the use of nanomaterial-based sensors for reservoir monitoring and surveillance [1], nanotechnology for enhanced oil recovery (EOR) process [2], and for mitigating the environmental footprint of the oil industry [3, 4]. Though ground has been covered, there

is still a lot to pursue and achieve. In particular, the development of graphene-based membranes will be reviewed to support their potential application in oil recovery processes.

Improved oil recovery (IOR) and EOR processes are designed on studies of fluid behavior at macro- and microscales, taking into account, and to some extent with the aim of manipulating, rock fluid interaction properties in order to mobilize, displace and produce the maximum possible volume of hydrocarbon. To this end, the industry has been exploring the possibilities of low salinity water injection (LSWI), a method that consists in injecting adequately modified filtered water by following a specifically designed procedure to maximize the displacement at both macro- and microscales. Thus, the question arises on whether the experience gained in the field of graphene-based membranes can provide possible solutions (or improvements) to water treatment for LSWI purposes. The following paper gives an overview of graphene-based membrane technology to then discuss its potential use in LSWI.

In addition, the paper itself is also an attempt to inform the readership about the need to share oil and gas industry problems with scientists working on technologies which could palliate them. Groundbreaking work is that which can transcend its own field to the benefit of other fields.

2. Materials and Methods

2.1. Low Salinity Water Injection to Maximize Oil Recovery. Historically speaking, water flooding represents one of the most popular and effective methodologies adopted by the oil industry to recover additional amounts of oil from a reservoir that has already been subject to primary recovery mechanisms. Water flooding consists in injecting water (reason why it is also known as water injection) into the reservoir to push more oil towards the producing wells and maintaining reservoir pressure slightly above the bubble point (i.e., pressure at which the oil releases the first gas bubble) in order to maximize the mobility of the oil at reservoir conditions. A proper water flooding process must be designed with both economic and technical parameters in mind; for example, the evaluation of reservoir behavior, including primary production performance, selection of potential flooding plans, and estimation of injection and production rates [5].

The practice of water injection expanded rapidly after the 1920s and has only grown since then. However, and despite being a nearly 100-year-old practice, conventional water injection processes have been largely designed without taking into account the composition of the injected brine. Offshore fields and many onshore fields use seawater for injection, which is often treated to ensure no solids are present and thus minimizing possible damage and permeability reduction due to plugging of the pore throats. Other fields may use ground water produced from water supply wells [6]. In optimal displacing conditions, the process can provide an oil recovery factor that can reach 40% and thus a significant amount of oil still remains trapped in the porous medium after water flooding operations. The value of residual oil saturation trapped behind the water front is strongly affected by the interaction between rock surface and the fluid phases confined to the pore spaces and, in particular, by the wettability and capillary effects. On the other hand, rock-fluid interaction properties are strongly affected by chemical and physical interaction between the native components of the system (i.e., rock, hydrocarbon, and connate water) and the injected water. Lately, the oil industry has been showing a renewed interest in water injection processes in which the chemical composition of the injected brine is manipulated, or designed, to improve the efficiency of the displacement process by reducing the residual oil saturation.

A process that has caught the attention of researchers from both academia and industry is low salinity water injection (LSWI), classified by different authors as either an enhanced oil recovery (EOR) or an improved oil recovery (IOR) technique. LSWI acts at microscopic scale by reducing the residual oil saturation through the sought interaction between the composition of the injected brine, the connate water, the properties of the oil, and the composition of the reservoir rock. The technique is effective when applied to mixed-oil-wet sandstone reservoirs. According to the available literature [7–9], flooding with low salinity (LS) water causes desorption of petroleum heavy ends from the clays present on the pore wall resulting in a more water wet rock surface, a lower remaining oil saturation, and higher oil recovery [7]. In spite of the research, both at laboratory and reservoir scales, a full understanding and recognized explanation of the chemical and physical phenomena behind the technique is not yet available, and studies are still ongoing. However, authors agree that the methodology provides significant improvement in oil recovery. One of the main appeals of LS flooding is that it is operationally identical to conventional water flooding and does not require expensive or toxic chemicals [7]. Further advantages associated with LSWI are the mitigation of the reservoir scaling and souring risks, improvement of injectivity due to lower suspended solid content, and reduction of corrosion [10].

Even if the incremental oil recovery depends on the salinity of the brine, the relationship appears not to be simply proportional. Results of studies discussed in the technical literature have shown that above a certain threshold, recovery does not depend on salinity, and below a certain level of salinity, some issues can be encountered. According to Jerauld et al. [11], significant low salinity effects have been seen for a salinity range of 1000 to 2000 ppm; therefore they concluded the threshold must be above and below the indicated range. Other findings have shown that the injected concentration must be below 25% of the connate water salinity with approximately 3000 to 5000 ppm as upper salinity threshold and 0 to 1000 ppm as lower salinity threshold [12]. However, Alzayer and Sohrabi [6] argue that very low salinity (less than 1000 ppm) may cause other issues such as fine migration and clay swelling. Ayirala and Yousef [9] report that threshold salinity lower than 5000 ppm is desired to achieve an incremental oil recovery of 5 to 6% with respect to conventional water flooding. Rotondi et al. [10] summarize some basic requirements for LS water flooding that must be associated with the salinity of the injected water. In particular, the injected source water should have a salinity of less

than 6000 ppm with an optimal range of 1000 to 2000 ppm; formation rock should contain water sensitive minerals and should not be strongly water-wet; formation water should contain divalent ions; and reservoir oil should contain polar components. Consequently, most of the available literature seems to point out that a water salinity threshold of 5000 ppm should be considered for an effective LSWI process.

2.1.1. Current Solution and Technologies. Ayirala and Yousef [9] presented an extensive review of the desalination technologies already available and under development for LSWI (they call the process smart water flooding). They highlight the requirements of injected water for carbonates indicating a reduction of monovalent ions, such as sodium and chlorides, and sufficient concentration of sulfates calcium and magnesium. In their work, Ayrala and Yousef divide the desalination technologies into two main categories: chemical precipitation and chemical-based salt extraction. As emerging alternative technologies, they mention and discuss forward osmosis, membrane distillation, carrier-gas extraction, and dynamic vapor distillation. Finally, they mention and briefly discuss the application of graphene-nanosheet in a list of potential desalination technologies for the future.

Therefore, according to Ayirala and Yousef [9], the application of graphene membranes in the oil industry is considered as a novel technology over the long term. However, in other fields, scientific and technical communities are already working hard on a number of applications of graphene membranes. One of these applications is the desalination of water for different purposes.

The following sections focus on a critical review of the state of the art of graphene porous membrane with the aim of evaluating its potential application to efficient water desalination for low salinity water injection.

2.2. Graphene-Based Membranes

2.2.1. Current Technologies. In desalination, as well as in other separation fields, polymeric membranes have gained an important role and are now commonly used in micro- and ultrafiltration. A membrane can be defined simply as a discrete, thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for instance, containing holes or pores of finite dimension or consisting of some form of layered structures. In anisotropic membranes the transport rate of a species is inversely proportional to membrane thickness. High transport rates across membranes are highly desirable in separation processes for economic reasons. Thus, the membranes should be as thin as possible. Conventional film manufacturing technology restricts the fabrication of mechanically robust, defect-free films down to about 20 μm thicknesses; therefore, anisotropic membranes consist of an extremely thin layer on the surface of a thicker porous substrate. The permeation rates and separation properties of the membrane are dependent exclusively by this surface layer and its substructure while the porous support only acts as mechanical substrate [13].

Membranes work as semipermeable barriers, allowing a species (e.g., water) to pass quickly while partially or completely retaining other species (e.g., salts and other contaminants) [14]. Thin-film composite membranes with active layers made of polyamide (with a thickness of approximately 100–300 nm and characterized by large roughness) are the current gold standard for desalination and other high-end applications of membrane technology [15].

Since the proposal of the first prototype of thin-film membrane nearly 40 years ago, no other chemistry or structure has surpassed the performance of this particular arrangement [16]. Nevertheless, polyamide membranes have a number of drawbacks which represent the main limiting factors to decreasing the cost and energy demand of desalination and wastewater reclamation as well as partially hindering their applicability in some separation fields. The main weaknesses of polyamide membranes are (1) their roughness, which greatly enhances fouling; (2) their susceptibility to chemical oxidants, impeding the appropriate pretreatment of feed streams; and (3) their relatively high thickness, reducing water permeability [17]. Finally, polyamide membranes are intrinsically subjected to the common permeability-selectivity trade-off [18, 19].

Current research is directed towards finding innovative materials, not necessarily polymeric, or increasing the performance of standard polyamide layers [20, 21]. Interesting results have been obtained by working with inorganic nanomaterials used as fillers of the polymeric layer to allow the formation of composite thin films with enhanced permeability. Alternative structures and materials with respect to polyamide membranes have also been reported such as layer-by-layer assembled active layers, zeolite-based thin films [22–28], and graphene-based nanomaterials [29, 30] which perform separation by size exclusion of hydrated ions.

Graphene is an excellent starting material for developing size selective membranes because of its atomic thickness and high mechanical strength, thus the growing interest in mass transport properties across graphene-based membranes. Graphene membranes are nowadays produced as single layer and stacked multilayers. Figure 1 summarizes the main applications of these innovative membranes considering the separation mechanisms. Graphene and other 2D materials may ideally act as an absolute barrier, preventing the diffusion of any gas species and molecule [31, 32]. Several works outlined the enhanced oxygen-atom corrosion resistance of few-layer graphene and graphene oxide-based materials [33, 34] and successfully demonstrated their potential use as protective coatings for anticorrosion applications. On the other hand, two possibilities are foreseen for separation purposes: (1) exploiting nanopores, which can exclude larger molecules allowing smaller molecules to pass through, that can be introduced into the graphene single layer by a variety of techniques and (2) exploiting nanochannels present in stacked graphene membranes obtained starting by graphene oxide flakes.

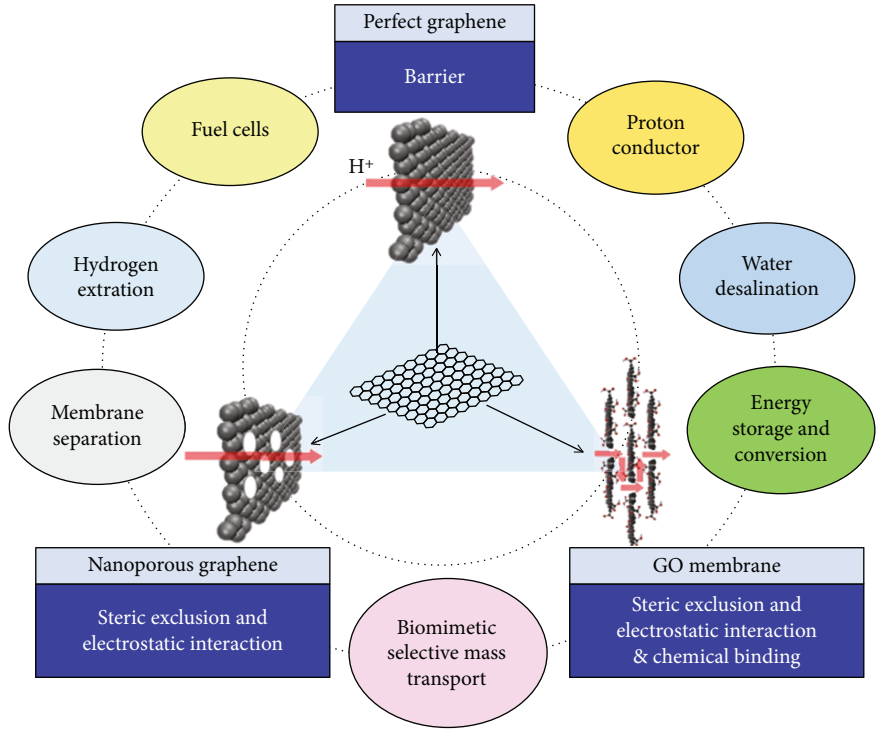


Figure 1: Applications and filtration mechanisms of graphene-based membranes. Reprinted with permission from [35]. Copyright John Wiley & Sons.

Both these technologies have emerged only recently in the academic world, and some patents have been registered in the last five years [36–38]. Although some companies have started to sell graphene single layer and stacked graphene multilayer for several applications, there are still no commercial separation membranes based on graphene in the market. Technological transfer and scale-up of these materials and related technologies for separation applications seem of the essence considering their enormous potential.

2.2.2. Single-Layer Graphene Membranes. The fabrication of separation membranes based on 2D materials represents one of the most challenging applications for water desalination at present. In this sense, pristine single-layer graphene has gained lots of attention due to its one-atomic-layer thickness, coupled to unique mechanical properties and excellent chemical stability. In general, water flux across a membrane scales inversely with respect to the corresponding thickness. Therefore, the strongly reduced thickness of graphene ($d \sim 0.34$ nm for single-layer graphene) might enable greater water permeability than those of conventional membranes [39], resulting in fast water transport and low filtration pressures. The single-layer graphene membranes generally consist of a porous support with single-layer graphene suspended over the pores of the substrate. Then, nanopores with controlled geometry, density, and chemistry are formed within the graphene structure, thus obtaining nanoporous graphene (NPG). In this sense, the working principle of NPG separation membranes is often based on reverse osmosis, where salt ions and other molecules can be rejected while water molecules may pass through the nanopores. However, it should be noted that most of the results so far come from theoretical models while few results have been experimentally obtained mostly because it is very difficult to make graphene single-layer membranes suspended on a porous support and to accurately control pore dimension at nanometer/subnanometer scale. In fact, modeling results demonstrate the correct pore dimension for water filtration must be lower than 2 nm [40]. This strongly limits the technology able to reach this patterning resolution. However, superior water permeability and ideal salt rejection found by ab initio calculations strongly motivate the experimental efforts to produce such membranes.

Graphene is usually obtained by following top-down synthetic approaches, like the mechanical exfoliation [41], or bottom-up synthesis methods, such as the epitaxial growth [42] and catalytic chemical vapor deposition (C-CVD) [43]. Several supports with different porosities have been proposed and combined to graphene single layer for fabricating NPG membranes, like silicon-based chips [44] and porous polymeric membranes [45]. In most of the cases, the as-grown graphene single layer exhibited intrinsic defects like single holes, tears, and wrinkles. The transport properties across such intrinsic defects of the NPG membranes were investigated for water desalination, resulting into insufficient salt rejection properties due to their large size [46]. Therefore, regardless of porous support, the introduction of the nanopores of different but uniform size within the graphene active layer was achieved by several techniques as block copolymers lithography [47], optimized thermal treatments, and/or

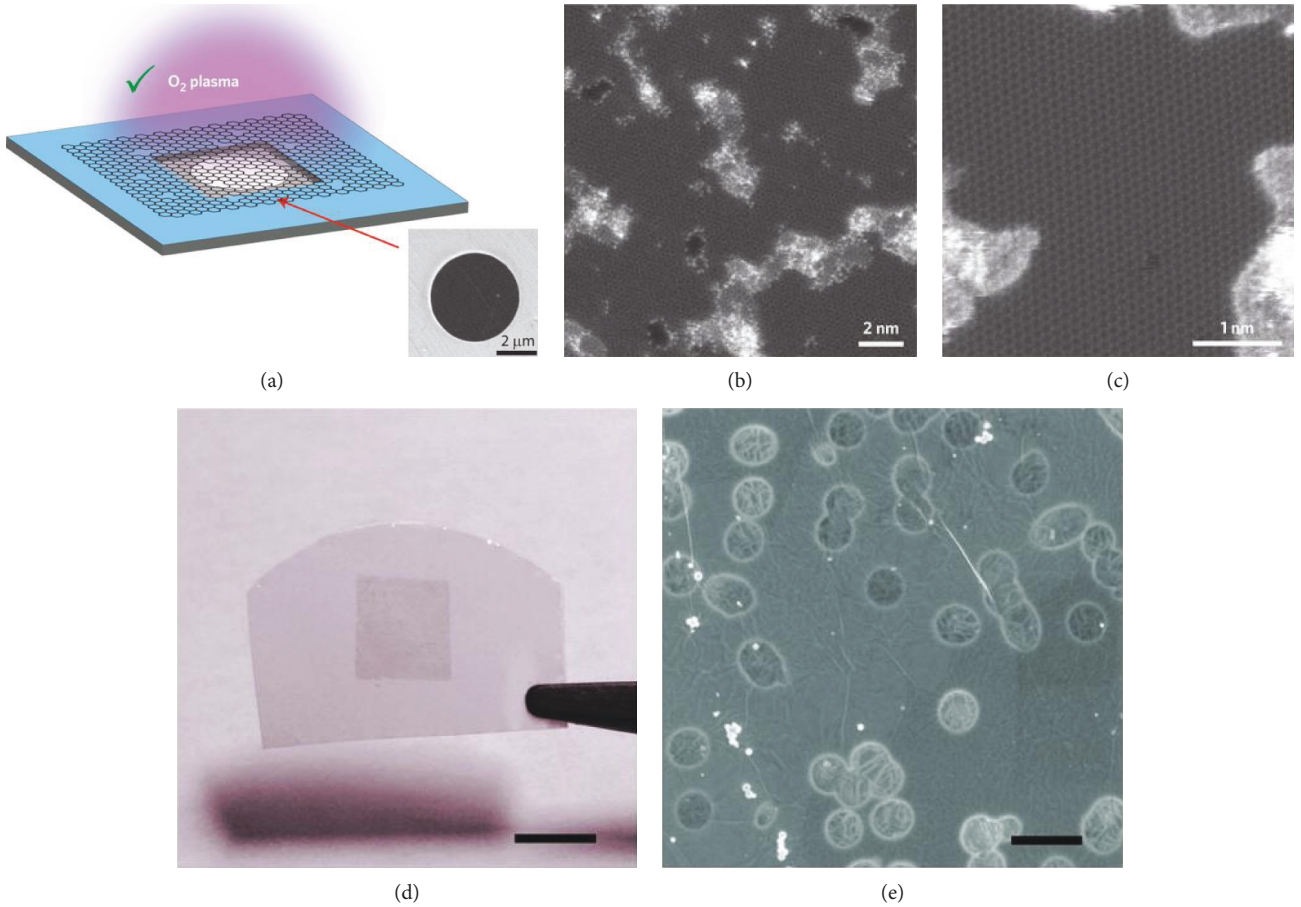


Figure 2: (a) Sketch of NPG membrane successfully tested for water desalination. (b, c) Scanning transmission electron microscope images of graphene with dimension of pores of ~1 nm. Reprinted with permission from [44]. (d) Graphene single-layer transferred onto a porous polymeric support. (e) Field emission scanning electron microscope image of graphene single layer suspended over the pores of the polymeric support. Reprinted with permission from [46].

via high-energy irradiation techniques such as ultraviolet-induced oxidative etching [48], ion bombardment [25], electron beam, and oxygen-plasma etching methods [44]. Depending on the experimental approach, the formation of pores in a continuous and wide size range, between approximately 0.5 and 10 nm, was achieved. A sketch of NPG membrane successfully tested for water desalination is represented in panel (a) of Figure 2. In this case, the nanopores (0.5-1 nm in diameter, panels (b) and (c) of Figure 2) were opened within the graphene layer by O_2 plasma etching. On the other hand, ions bombardment coupled to chemical etching were exploited to open nanopores (average diameter of 0.40 nm) within graphene single layer, to fabricate NPG on porous polymeric supports (panels (d) and (e) of Figure 2) [25, 49].

The first theoretical studies demonstrating the feasibility of NPG membranes for water desalination started to appear in 2012 and were based on molecular dynamic (MD) simulations. The ability of graphene single layer to withstand strong pressure regimes up to 57 MPa, that is, about ten times higher than the typical pressure in seawater reverse osmosis plants, was effectively demonstrated, either for graphene alone or when supported on substrates with porosities of up to 1 μm [50]. To evaluate the transport properties, a saltwater feed solution was simulated and forced to pass across the NPG membrane by applying pressure with a rigid piston. For a fixed pore density of $\sim 1 \times 10^{13}$ cm^{-2}, the NPG showed excellent water permeability per nanopores of $\sim 10^3$ L/m^2·h·bar, high flow rates and promising salt rejection, approaching nearly 100% when controlled subnanometer-sized pores were introduced into the graphene layer. Such ultrahigh water permeability was demonstrated also for low pressures closer to the realistic values applied in real reverse osmosis systems. Another MD simulation study also predicted that, for NPG membranes, tripling in water permeability would result in 44% less pressure requirement or 15% less energy consumption for a seawater reverse osmosis plant [51]. Other MD studies also highlighted that the filtration mechanism and salt rejection properties of the NPG are mainly governed by three parameters, that is, the size and geometry of the pores and the chemical functional groups terminating the edge of the nanopores. In terms of pore size, and theoretically speaking, nanopores with diameters as small as 0.75 nm allowed water molecules to pass through the NPG while effectively rejecting salt ions [52]. The chemistry of the pores, that is, the chemical functional groups terminating the edge of the pores, also influenced salt rejection of NPG

membranes. Theoretical analyses showed that higher ion exclusion rather than a change in the permeability of the membrane was obtained when specific terminating groups were present [40, 53]. MD simulations also showed selectivity of NPG against salt rejection, since it is permeable to specific solvated ions and impermeable to others [54, 55]. Finally, MD simulations evidenced that the water permeability of NPG membranes also depended on the density of nanopores per unit area [39].

Different mechanisms describing water transport and salt rejection across NPG may be outlined. The first one is based on the steric exclusion of bare ions or their hydration shells. The hydrated radius of ions in water is larger than the effective size of a water molecule. This would allow for full salt rejection if nanopores with appropriate diameter are present in the graphene layer. For example, the critical nanopore diameter for rejecting NaCl was estimated to be in the range 0.6–0.8 nm [56]. Another important mechanism is charge repulsion between salt ions and the chemical groups at pore edges [55, 57]. Finally, the rejection of salts is also favored by limiting the number of physical configurations, that is, geometrical orientations that would allow for salt ions to pass through the nanopores. This aspect was proven by MD simulations, where hydrogenated nanopores exhibited a higher salt rejection than hydroxylated ones. This was due to the restricted number of allowed geometrical orientations for hydrated salt ions when attempting to cross the hydrogenated nanopores [39, 40].

2.2.3. Multilayer Graphene Membranes. Graphene oxide (GO) is made up of graphene layers with many defects (holes, cracks, wrinkles, vacancy, edges, etc.) filled by oxygen atoms, hydroxyl, epoxy, carbonyl, and carboxyl groups. The presence of these groups gives GO different properties to those of pure graphene. In a typical preparation, GO is synthesized from natural graphite powder by a modified Hummers method [58].

GO is hydrophilic and it is not conductive. Hydrogen bonds link the different layers of GO together; dimensions can vary greatly depending on the preparation process. GO is found in the form of a brownish powder, highly electrostatic due to negative charges on its surface.

It is possible to increase the conductivity of GO and its hydrophobicity by reducing the amount of oxygen (and, therefore, defects) in the material, obtaining the so-called reduced graphene oxide (rGO), which shows a behavior between pure graphene and graphene oxide.

Due to its intrinsic hydrophilicity, GO can be easily dispersed in a water solution. This dispersion can be used to deposit GO films on different surfaces following different procedures. From water dispersion of GO it is possible to obtain a GO membrane by spin coating [59], vacuum filtration [60], drop casting [61], and self-condensation at the liquid/air interface [62]. The membrane can be used as it is (on a porous support, as shown in Figure 3(a)), or the deposited GO can be detached and used as a self-standing membrane (Figure 3(c)) if thick enough (several micrometers can be easily reached). In this way, it is possible to obtain GO membranes known by their filtering properties.

Figure 3(b) shows the top view obtained by electron microscope imaging of the rGO membrane suspended onto an anodic-aluminum oxide filter, while Figure 3(d) shows the cross sectional image of a self-standing GO membrane in which it is possible to appreciate the vertical stacking of the GO flakes.

Details on the preparation of GO membranes as well as several examples reporting the filtering properties of GO membranes can be found in the literature [35], showing their high selectivity to small and polar molecules, while rejecting nonpolar molecules like oils [63].

GO membrane structure is a multilayer stack of GO flakes; due to the presence of many defects and holes, these membranes are expected to let water flow through. Indeed, the presence of spacing between flakes, together with holes, results in a combined horizontal and vertical flux of the molecules as schematically depicted in Figure 3(e). Han et al. [64] link the high flow rate through the GO membrane to the slip flow theory. Han et al. also assess the presence of -OH and -COOH groups strongly enhance the transport of water through both holes (vertical direction) and channels (horizontal direction). Therefore, the filtration properties of GO membranes can be linked to both the size of pores, holes, and channels (blocking larger molecules) as well as to the high selectivity of GO membranes to water.

3. Results and Discussion

3.1. Experimental Cases of Desalination via Graphene-Based Membranes

3.1.1. Experimental Desalination by Single-Layer Graphene Membranes. As previously mentioned, water desalination across NPG membranes is generally obtained by placing graphene single-layer onto a porous support and then opening nanopores with controlled size within the graphene layer. One of the first attempts to experimentally validate the potentiality of graphene for water desalination dealt with the study of the molecular and ionic transport properties across intrinsic defects of graphene single-layer suspended onto a porous polymeric support [46]. In this case, opening of the pores into the graphene layer was not intentionally performed. Actually, the presence of intrinsic defects on the as-grown graphene single-layer, that is, single-pore defects, cracks, and tears, was exploited to investigate the selective transport of molecules across the membrane. The membranes were tested in a side-by-side diffusion cell by using a 0.5 M KCl solution. The permeability of the graphene-based membranes was first evaluated by measuring the diffusion of KCl ($d_{KCl} \sim 0.66$ nm). It was observed that intrinsic defects like holes and tears with average sizes smaller than 50 nm provided some resistance against the flux of the solution, while bigger defects allowed for the solution to permeate across the graphene membrane.

To check the size-selective transport of molecules across intrinsic defects of the graphene single-layer membranes, other solutions with molecules bigger than KCl (tetramethylammonium chloride (TMAC, $d_{TMAC} \sim d_{KCl}$), Allura red dye ($d_{AR} \sim 1.0$ nm), and tetramethylrhodamine dextran (TMRD,

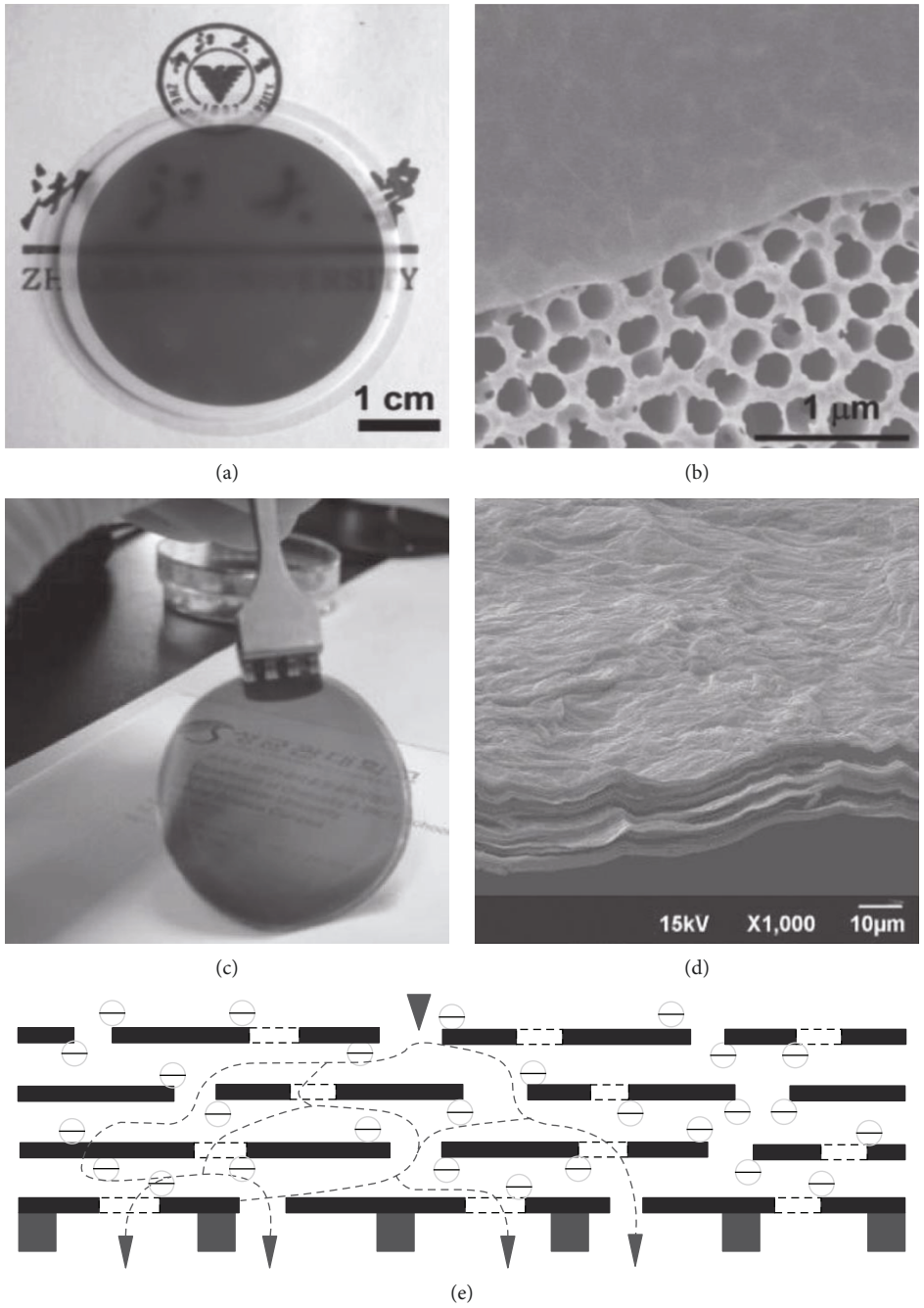


Figure 3: Digital photo of an rGO membrane coated on an AAO disk (a); SEM image (top view) of the coating of an rGO membrane on an AAO disk. The top half of the image shows the uniform and smooth coating of rGO sheets, whereas the bottom half shows the porous structure of the bare AAO disk. Reprinted with permission from [64]. Digital photo (c) and SEM (cross-sectional view) image (d) of self-standing GO membrane. Reprinted with permission from [65]. In (e), a schematic view for possible permeation route is shown: water molecules go through the nanochannels of the rGO membrane and the holes on the graphene sheets and at last reach the pores of supporting membranes. The blank squares present the holes on the graphene sheets (black line). The edges of the rGO and the periphery of the holes are negatively charged. Reprinted with permission from [64].

$d_{TMRD} \sim 12$ nm) were also tested, and the corresponding flux across the membranes was evaluated as well. It turned out that intrinsic pore defects were sufficiently small to attenuate the graphene permeability against the biggest TMRD molecules, while the smallest ones, that is, KCl and TMAC, were able to permeate across the membranes, as shown in panels a and b of Figure 4. In particular, the flux rate of the biggest molecules TMRD was reduced to ~80–85% with respect to the corresponding one estimated for the PCTE membrane alone. As expected, no selectivity was observed for the porous polymer support (Figure 4(c)) while the permeability of the graphene membrane was strongly dependent on the size of

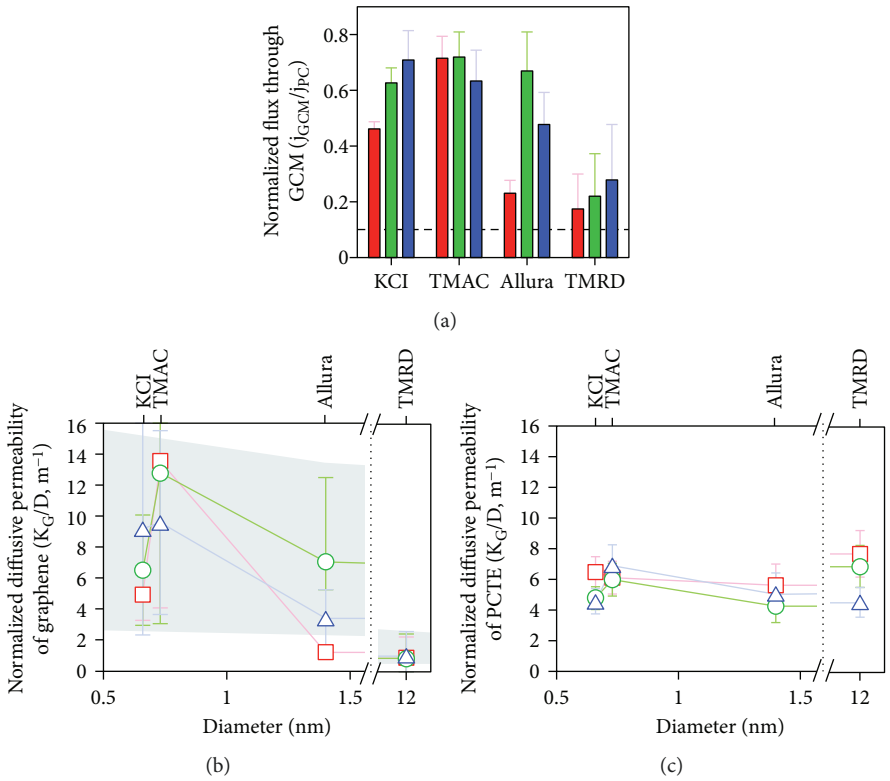


FIGURE 4: (a) Diffusive flux of molecules through graphene-PCTE membranes normalized by that through the bare PCTE support. (b) Permeability of graphene single layer normalized by the diffusivity of the different molecules. The transport of the 12 nm diameters TMRD molecule was significantly attenuated compared to the smaller molecules. (c) Measured permeability of the PCTE support normalized by the diffusivity. Reprinted with permission from [46].

the fluxed molecules (Figure 4(b)), due to the presence of the intrinsic defects. Based on the abovementioned results, it is possible to conclude that intrinsic defects of graphene have limited selectivity not suitable for salt rejection.

Therefore, to overcome the missing selectivity and salt rejection of the intrinsic defects, high-density, subnanometer-sized pores were intentionally opened into graphene single-layer membranes by ion bombardment coupled to chemical etching [25]. To investigate the transport properties of the NPG membranes, the diffusive flux of KCl and AR dye molecules was evaluated in a side-by-side diffusion cell. According to the mean pore size, that is, on the etching time, selectivity against K^+ and Cl^- ions was successfully obtained, allowing for salt ions to permeate across the NPG membrane while preventing the passage of bigger AR dye molecules, as sketched in Figure 5(a). More interestingly, selectivity of the NPG membrane against K^+ and Cl^- ions was achieved. This was due to the presence of different functional groups terminating the edges of the nanopores, which in turn modified the overall membrane potential (Figure 5(b)). The observed selectivity was due to electrostatic interactions with the negative charges arising from the functional groups terminating the edge of the pores. However, as the pore size increased, membrane potential slowly decayed to zero, indicating loss of selectivity between the potassium and chloride ions. This represented the decreased influence of electrostatic effects on ion selectivity, while steric hindrance effects started to become dominant over transport behavior.

Other experimental studies successfully demonstrated that sealing the intrinsic defects of graphene together with the reduction of pore dimension up to the subnanometer range strongly improved the efficiency of NPG membranes for water desalination [49]. The transport properties of the corresponding optimized NPG membranes were investigated under forward osmosis conditions by testing four different solutes: NaCl (0.716 nm size), $MgSO_4$ (0.86 nm size), AR dye, and dextran (~3.7 nm size). As shown in Figure 5(c), the membranes exhibited ~70% rejection for $MgSO_4$, ~90% rejection for AR, and ~83% rejection for dextran. On the contrary, NaCl exhibited a negative rejection, indicating that the rate at which NaCl transports across the membrane exceeded the transport rate expected for nonselective convective flow. This particular behavior was attributed to some criticality of the procedure followed to seal intrinsic defects of the graphene single layer, which still allowed for monovalent ions to pass through the membrane.

Despite achieving promising results concerning molecule separation and selectivity, the strategies described so far still present some major limitations, mainly due to the difficulty in sealing the intrinsic defects of graphene single layer and in the opening of uniform, subnanometer-sized pores. Some of these limitations have been successfully overcome by changing the strategy followed to fabricate the NPG

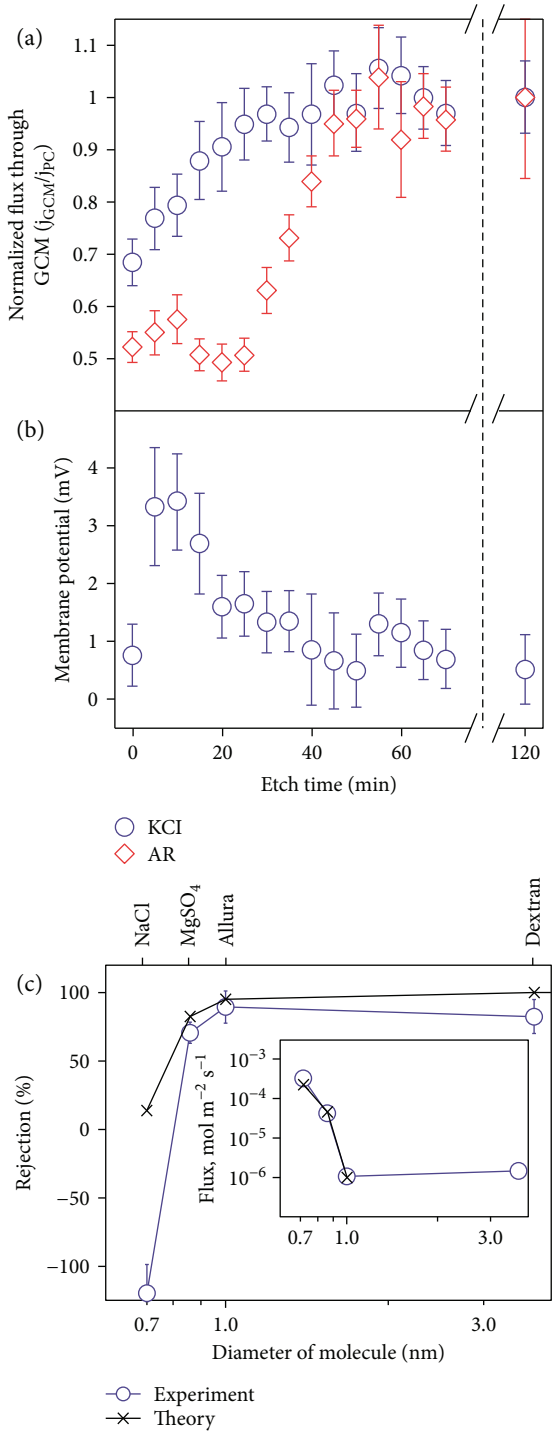


FIGURE 5: (a) Diffusive flux of KCl and AR dye molecules across the NPG membrane with subnanometer-sized pores. (b) NPG membrane potential measurements. Reprinted with permission from [47]. (c) Experimentally measured rejection and molar flux (inset) of the four different solutes tested across the NPG membranes. Reprinted with permission from [49].

membrane. Recently, it was reported that a single-layer graphene transferred onto SiN chips with a single 5 μm diameter hole successfully showed salt rejection properties for water desalination. The subnanometer-sized pores were opened in a strict controlled way by exposing the suspended graphene layer to a gentle O_2 plasma treatment [44]. The nanoporous SLG suspended over the single-hole SiN microchip was tested for water transport and salt rejection measurements, by using the experimental assembly of Figure 6. Desalination experiments with aqueous KCl solution (6 mM) confirmed the ability of the developed NPG to act as water desalination membrane, approaching nearly 100% rejection for 0.5–1 nm pores.

An overview of the specific characteristics of NPG membranes which have been experimentally investigated for water desalination and molecules separation is provided in Table 1.

3.1.2. Experimental Examples of Desalination by Stacked GO and rGO Membranes. As far as water purification is concerned, GO membranes are appealing not only because of their low cost and simple preparation method (compared to single-layer graphene membranes) but also because they are suited for many applications, like water desalination and oil/water separation. Ganesh et al. [67] tested GO membranes with different loads of graphene oxide for water desalination. They reported a rejection rate of 72% for Na_2SO_4 salt, while a rejection slightly below 60% for NaCl. Wang et al. [68] used graphene oxide dispersed in a basic solution to assembly GO membranes. They filtered more than 99% of dyes like Congo red and methyl blue, while obtaining a good result also for $MgSO_4$ (92.6%). Smaller ions, however, pass more easily through the GO membrane, achieving retention of 43.2% for NaCl. This behavior is confirmed by Joshi et al. [69], who tested the permeation of different salts through a GO membrane. Their results confirmed that some salts (like NaCl) are able to pass through the membrane, while for other salts (like $K_3[Fe(CN)_6]$), a high retention is observed. This behavior finds an explanation if the interaction between the ions in solution and the negative charged surface of the GO membrane is taken into account together with the fact that the membrane is able to block ions and molecules having a hydrated radius larger than the pores and channel dimension. Kim et al. [70] tested a Sulfonated poly(arylene ether sulfone) membrane coated with a structure of many GO and aminated GO layers, showing a high salt rejection (above 98%), higher than the membrane without GO (94% salt rejection). This work confirms that the presence of a GO coating on a support membrane can further enhance the filtration properties of the support membrane. Hu and Mi [71] cross-linked the GO layers using a layer-by-layer deposition that allowed obtaining a self-assembled membrane. The cross-linking was obtained by using 1,3,5-benzenetricarbonyl trichloride and a polysulfone membrane as support. This choice was justified by the necessity to enhance the water flux, while the self-assembly technique was used to have a fine control on the alignment of the GO flakes and, therefore, on the overall structure. In this study, salt rejection was investigated as a function of the number of layers and of salt concentration (see Figure 7). Huang et al. [72] investigated the effect of pH, pressure, and salt concentration on the filtration properties of GO

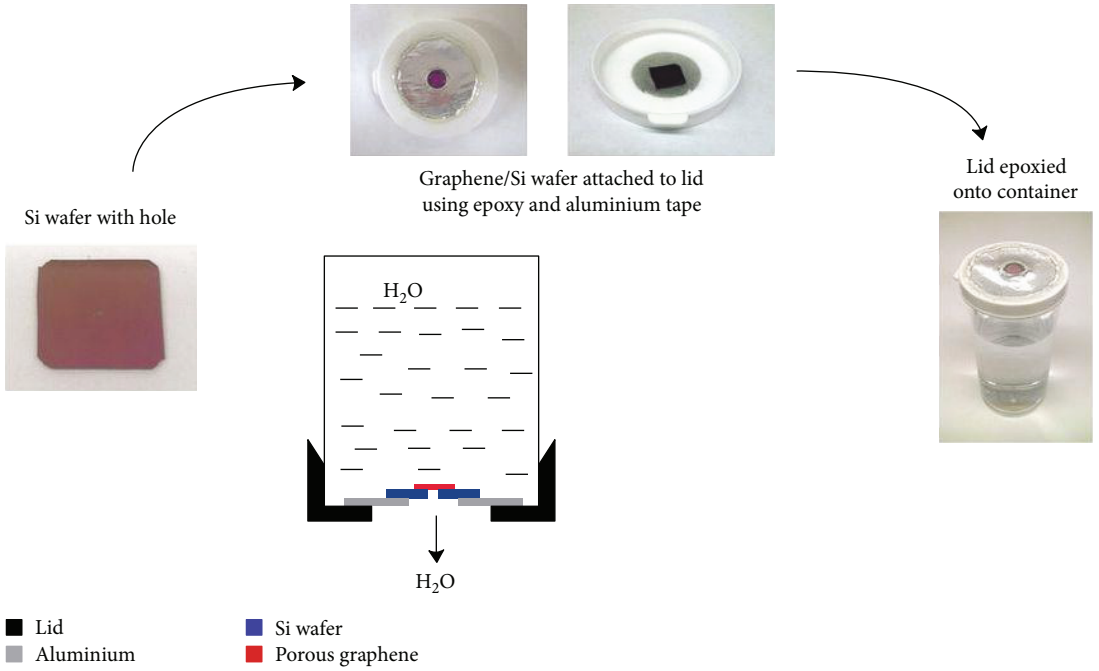


Figure 6: Experimental assembly for water transport measurements and desalination experiments. Reprinted with permission from [44].

Table 1: Overview of the main characteristics of single-layer graphene membranes experimentally investigated for water filtration.

Membrane	Porosity control	Mean pore size (nm)	Rejection (%)	Ref.
Single-layer graphene on porous polymeric supports	Intrinsic defects of SLG	1–15	46–71 (KCl, AR, TMAC, TMRD)	[46]
	Ion bombardment + chemical etching	0.40	65–100 (KCl, AR)	[25]
	Sealing of intrinsic defects + ion bombardment + chemical etching	0.16	70–90 ($MgSO_4$, AR, TMRD)	[49]
	Sealing of intrinsic defects	N/A	~67 (KCl)	[66]
		N/A	~84 (KCl)	
Single-layer graphene on SiN chip	O_2 plasma etching	0.5–1	~100 (KCl)	[44]

membranes. The surface of GO flakes is intrinsically negative charged. Therefore, tuning the pH of the solution, it is possible, for example, to reduce the repulsion of the GO flakes and so the interlayer distance (low pH values). Similarly, the concentration of salts in solution plays a role in charge screening, affecting the filtration properties.

4. Conclusions

An oil and gas industry issue, namely low salinity water injection (LSWI), was described in the attempt of identifying which technology would be better suited to address the matter; a realistic option was selected from different available nanotechnologies. It should be noted that authors are aware of the many obstacles to overcome, but both theoretical and experimental results prove that the possibilities of success nanotechnologies have are more than just a leap of faith. In fact, an array of ongoing studies corroborates the aforementioned out of which the development of graphene-based membranes for desalination separation stands out for a number of reasons, among others:

(1) Experiments on the subject have confirmed that the presence of stacked graphene oxide (GO) flakes or nanoporous graphene (NPG) can further enhance the filtration properties of the support membrane.

(2) The use of such membranes in the desalination process would prove essential in the "manipulation" of injection water for LSWI.

(3) GO membranes are cheap and the method for their preparation is rather simple, while the more complex procedure for NPG membranes could be compensated by their almost ideal filtration efficiency.

In authors' opinion these are three solid reasons to pursue the application of the technology by the oil industry. Ultimately, the desalination of water for LSWI via graphene membranes would tackle the issue of reaching a water salinity

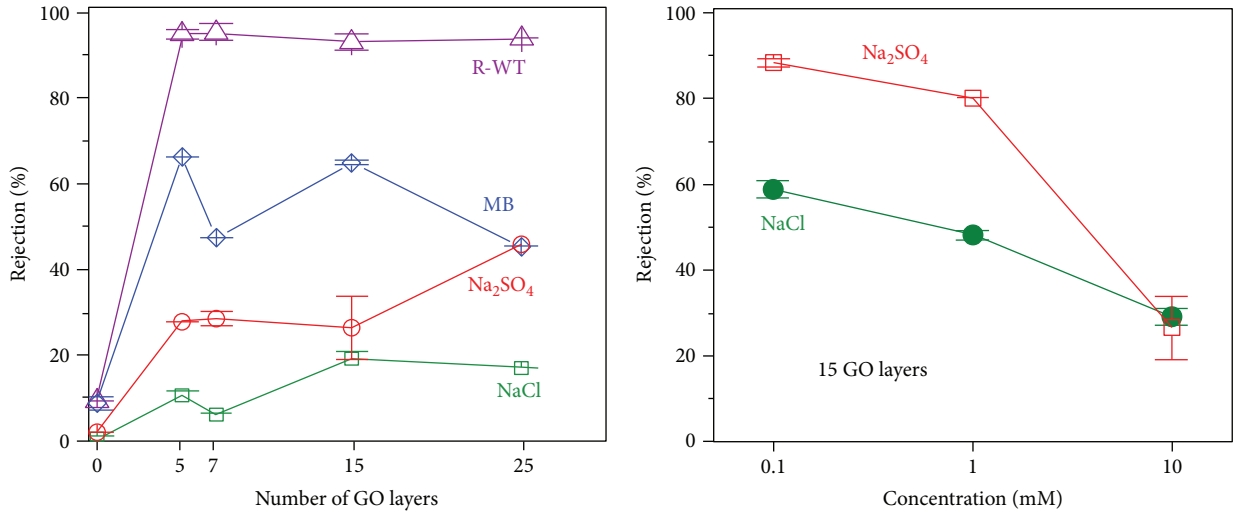


FIGURE 7: Various filtration results using GO membranes: rejection of salts and organic dyes with different numbers of GO layers (a) and effect of salt concentration on the rejection by the 15-layered GO membrane (b). The data at 0 layer are those of the polydopamine-coated membrane. All rejection tests were performed under 50 psi (0.34 MPa) and the rejection tests in (a) were performed with 20 mM NaCl, 10 mM Na2SO4, 7.5 mg/L MB, and 7.5 mg/L R-WT solutions, respectively. Reprinted with permission from [71]. Copyright (2013) American Chemical Society.

threshold—we have suggested 5000 ppm based on the current literature—for effective LSWI. Furthermore, the learning gain from the proof of concept (PoC) is an opportunity to build the future foundations of an oil recovery methodology that can help extend the life of mature fields beyond their economic limit.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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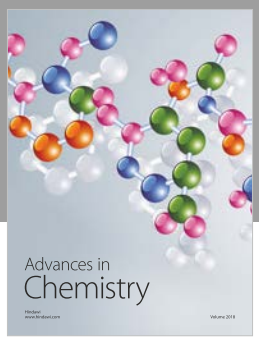
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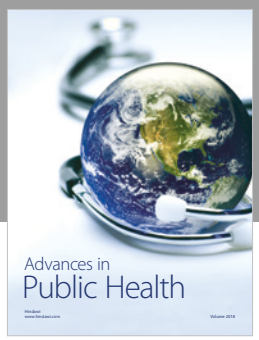
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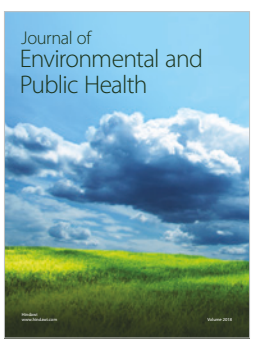


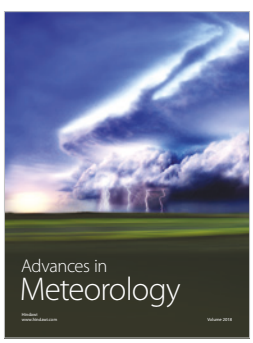








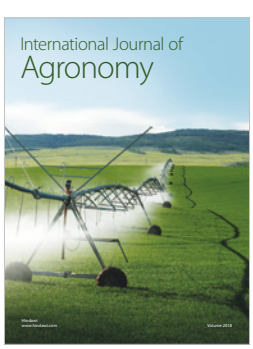






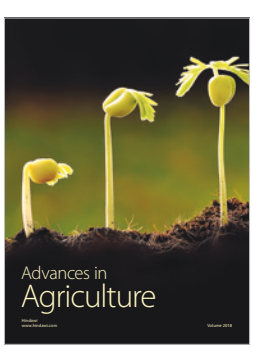




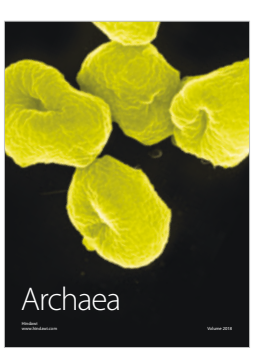




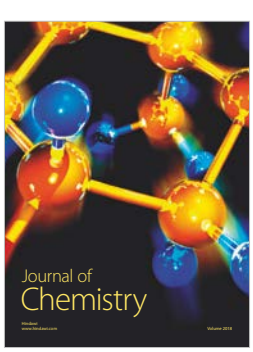















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