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Application of graphene, graphene oxide, and boron nitride nanosheets in the water treatment

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Abstract. In this research, we study recent advances in the use of graphene, graphene oxide, and boron nitride nanosheets for the water treatment processes. The perfect nanostructured membranes are impermeable to ions or molecules. Therefore, for using them in the selective separation processes, they should be drilled and so, the created pores will be functionalized using appropriate chemical functional groups. Up to now, numerous research articles have been done on the use of functionalized chemical groups on the nanostructured membranes but the results of those works have not been compared with each other. Therefore, a comprehensive review of the structural property and application of functional groups at the edge of membranes pores was performed. To the best of our knowledge, no review study has been reported in the literature on the effect of functionalized groups on the separation of molecules or ions by nanostructured membranes. This review paper aims to draw the attention of the theoretical as well as the experimental researchers working on the functionalized materials towards the recent developments probing the permeation of various species such as atoms, ions, and small molecules through graphene, graphene oxide, and boron nitride nanosheets.

Keywords: boron nitride, graphene, graphene oxide, membrane, water treatment

1. Introduction

In the functionalization process of membranes, some functional groups added to the surface or edge pore of material to prepare new materials with new physical and chemical properties (Majumder *et al.* 2005, Sasidharan *et al.* 2011). Functionalization of material changes the chemistry of material so that the functionalized material used in the separation process have efficient selectivity. Functional groups could be added to the surface of materials or to the edge of pores by covalent bonds. By creating an appropriate pore on the membrane and adding chemical groups to the edge pore, it acts selectively for the particles, so that some of the material passes through the pore, and the rest stay behind the pore (Zornoza *et al.* 2011).

The selective separation of ions from aqueous solutions using two-dimensional nanostructured materials has become an advanced technology for solving enormous challenges such as limited resources and environmental problems. Compared with conventional separation methods, the separation process with the two-dimensional nanostructured membrane is an energy-efficient and environmentally benign technology, which occupies less space and can be operated in a continuous mode (Azamat and Khataee 2018, Khataee *et al.* 2017, Sardroodi *et al.* 2012). The pristine two-dimensional nanostructured membranes such as graphene, graphene oxide, and boron nitride are impermeable to ions. These nanosheets are currently, without any doubt, the most intensively studied materials. Therefore, for using them in selective separation processes, firstly they should be drilled and then, the edge of created pores functionalized using appropriate chemical functional groups such as –F, –H, –OH, –N, –O, –COOH, –CO, –Fe, –Si and etc. These chemical groups have the most important influence on the selective separation process of ions. It should be noted that some of these functional groups, in different membranes, show different behaviors. This treatment depends on the type of pore, pore size, and even the number and type of functional groups on the edge pore of membranes.

By decorating the two-dimensional nanostructured membranes with different functional chemical groups, they can be used to selectively permeate cations, or anions. Also, functionalized groups can be effective in hydrophilicity or hydrophobicity of considered nanosheets (Azamat *et al.* 2016d). This behavior of nanosheets plays an important role in the separation process. Ion separation using functionalized two-dimensional membranes has been influenced by the simplicity and selectivity of the systems. A comprehensive overview on recent advances in ion separations based on functionalized membranes can be useful for future research and it can lead to intelligent choices of chemical functionalized groups. Functionalizing nanostructured membranes pores with various chemical groups could be very useful in order to selectively separate ions. Sint *et al.* (2008) for designing selective membrane for ion separation, functionalized graphene pores with fluorine, nitrogen and hydrogen atoms. They used fluorine and nitrogen atoms as functional groups because of their

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negative charges to attract positive charged ions like Na^+ and K^+, on the other hand, they functionalized graphene pore with hydrogen atoms because of its positive charge for being selective in front of negative charged ions like Cl^- and Br^-.

Fluorine as most electronegative atom is highly reactive so it could be very useful as a functional group for functionalizing a membrane pore. Fluorine atom because of its electronegative nature could form hydrogen bond with water molecules, as a result, when this atom is used as a functional group for functionalization of a membrane pore, it could increase water flux. Hydrogen bonding between fluorine and water molecules is connected the network of water molecules at two sides of the membrane. The hydrogen bond in water molecules is a dynamic attraction between neighboring water molecules involving one hydrogen atom located between the two oxygen atoms (Azamat *et al.* 2016d). V-shaped water molecules in the both sides of membrane have chain structure due to hydrogen bonds between water molecules. Because, the hydrophilic groups at the pore edge attract the water molecules and thus, the water molecules in both sides of membrane can be close together that leads to create the chain structure of water molecules inside the pore. Also, water molecules can easily permeate through the pore with chain structure by applying an external pressure on the system.

Jahanshahi *et al.* (2018) used from fluorinated graphene nanosheet for removing nitrate ions from water molecules. It is represented that fluorinated graphene pore passed more water molecules than hydrogenated graphene pore. This phenomenon was occurred because the fluorine atoms at the edge of the graphene pore formed hydrogen bond with water molecules. Li and coworkers (Li *et al.* 2017) used three different functionalized graphenes for the separation of heavy metal ions by reverse osmosis process. The behavior of these functionalized membranes according to their functional groups and pore sizes were different from each other. The pore diameter of graphene functionalized with boron, nitrogen and hydrogen and hydroxyl group was 10.24 Å, 8.14 Å, and 6.5 Å, respectively. By increasing the pore size of the graphene, the water flow rate increased too. Potential of mean force (PMF) calculations indicated that in all membranes, water molecules passed easier than ions because of their lower free energy barrier in the graphene pores. However, because of different size of functionalized pore, the influence of functional groups on ion rejection could not precisely compared with each other in this work.

In a similar work for separating copper and mercury as heavy metals, functionalized graphene pore with fluorine atoms was used (Azamat *et al.* 2014). Fluorine atoms played a key role in this research. Because of its negative charge attract heavy metals to pass through the graphene. Azamat (2016) investigated the selective behavior of fluorinated and hydrogenated functionalized graphene for water desalination. For this, two different functionalized graphene nanosheets were used and saline water was confined between them and external electric fields were applied to the system. Hydrogenated pore (H-pore) attracted chlorine ions and at the other side, fluorinated pore (F-pore) attracted sodium ions. By studying the PMF of the ions, it shown that the energy barrier of Cl^- was high at the F-pore so this ion could not pass across it and the energy barrier of Na^+ was high at the H-pore and make it hard for sodium to pass through it. Carboxyl group (-COOH) is a part of an organic compound turns it to a carboxylic acid. Important characteristics of carboxyl functional group as appropriate functional group for functionalization of membranes, are polarity and its hydrophilic nature. As a result, compounds with carboxyl group have polarity, because carboxyl group is either hydrogen bond acceptor or hydrogen bond donor. Consequently, carboxylation is an efficient method for overcoming low water flux of some membranes.

For example, polysulfone is a hydrophobic polymer which is used as a membrane and by carboxylation it, hydrophilic characteristic is given to hydrophobic polysulfone (Khataee *et al.* 2013, Möckel *et al.* 1998). Klaysom *et al.* (2013) by functionalizing of polysulfone membrane with carboxyl group, prepared an appropriate support membrane which was more efficient than unfunctionalized polysulfone. Their functionalized support membrane had advantages over unfunctionalized polysulfone with carboxyl group such as lesser internal concentration polarization and higher water flux due to given hydrophilic property to polysulfone. So, carboxyl is a functional group that could influence on its host material and change its nature in an appropriate way.

Carboxyl group by losing its hydrogen atom turns to negatively charged carboxylate ($-COO^-$). Carboxylate as a functional group could be used in membrane for desalination and ion separation because of its negative charge. So, by adding carboxyl and carboxylate groups to membranes such as polymeric membranes or carbon-based membrane, their abilities to selective separation were enhanced. Yuan and coworkers (Yuan *et al.* 2017) showed that functionalized graphene oxide with carboxyl have higher water flux than unfunctionalized graphene oxide, because of formation of hydrogen bonds between carboxyl group and water molecules. Also, it shown that this membrane has better salt rejection because of repulsive electrostatic interactions with ions. Mishra and Ramaprabhu (2011) were functionalized graphene with carboxyl, carbonyl and hydroxyl groups for giving it hydrophilic characteristic. They used these functionalized graphenes as an electrode for removing arsenic and sodium ions from water. By functionalizing surfaces of graphene, they prepared better adsorption sites than pristine graphene. Functionalized graphene sheets had better performance in ions removal than pristine graphene, because of interactions between functional groups with ions and water molecules. So, performance differences between functionalized and pristine graphene shows us that functionalization is a very good method for enhancing membrane abilities or adding new characteristics to it.

Konatham and coworkers (Konatham *et al.* 2013) theoretically investigated the influence of functionalizing graphene pore by functionalization of pristine graphene with different functional groups includes COO^-, NH_3^+, and OH^- groups with different pore size. They compared performances of pristine and functionalized graphenes by calculating PMF for ions and water molecules and showed the effect of functional groups on the water permeability and salt rejection. In the 0.025 M $CaCl_2$ solution, carboxylated graphene pore with 10 Å pore size showed a good performance in repelling chlorine ions due to 45 kcal/mol energy barrier. While in pristine graphene with 10.5 Å pore size, chlorine ions had 4 kcal/mol energy barrier, and in hydroxylated graphene with 7.5 Å pore size, chlorine ions had 18 kcal/mol. So that with decreasing energy barrier the salt rejection performance of membrane was decreased. On the other hands, in 0.25 M solution, hydroxylated graphene pore showed better performance than pristine and carboxylated graphene pore. Whereupon functionalized graphene pores due to creating electrostatics interactions with ions act better than pristine graphene pore. In the case of water molecules, in low concentration solution, carboxylated graphene pore acted as a block in front of the water molecules despite of this fact that in salt rejection was very good. In high concentration solution, water molecules had the same PMF values in the functionalized graphenes and pristine graphene with 10.5 Å pore size. This is due to in the low concentrations, carboxyl groups in the graphene pore could interact electrostatically with ions but in high concentration solution, electrostatic effect could be weakened. Density distribution of oxygen atoms of water molecules inside carboxylated graphene pore showed that the oxygen atoms attracted by carboxylate functional groups because of the electrostatic interactions and no oxygen atom exist in the center of the pore, however, by increasing the salt concentration, sodium ions accumulated near the graphene pore and water molecules occupied center of the carboxylated graphene pore as well as other places of the pore which is near to the functional groups.

Functionalization of materials enable us to encounter critical problems that sometimes we could not solve them with conventional methods. For instance, lithium batteries are a good option for electric device’s power sources. For preparing pure lithium it is required to remove other residues from resources of the lithium such as salt lake brine and one of these residues are magnesium which has approximately same properties with lithium, consequently separation process of Li^+ from Mg^{2+} is very difficult but nanostructured membranes like graphene could be a good choice for being membrane for magnesium removal from lithium (Azamat *et al.* 2016a, Ruan *et al.* 2016).

Zhu *et al.* (2017) used two functionalized graphenes as membranes for removal of Li^+ from Mg^{2+} and showed that specific interactions between functional groups such as carboxylate and carbonyl with ions beside of the unique properties of the ions are important factors which help functionalized graphene to behave selectively relative to the different species of the ions. Their results revealed that both carboxylated and carbonylated graphene pores are selective to Mg^{2+}. Their PMF results indicated that Li^+ ions encountered higher PMF than Mg^{2+} at functionalized graphene pore and high energy barrier is the reason of the lithium ions could not pass through the functionalized graphene pore. This high energy barrier is related to the structure of the first and second hydration shells around ions which contains different number of water molecules that by electronegative interactions surround ions and these electronegative interactions according to the ionic radii of the ions have various values of strengths. It could be seen that carboxylated pore passed more magnesium ions through itself and blocked more lithium ions than carbonylated pore. But the main reason of the selective approach of the functionalized graphene pores was possibility of replacing of removed water molecules which formed second hydration shell around the ions by oxygen atoms of carbonyl and carboxyl functional groups that are attached to the pore edges of the graphenes. Either Mg^{2+}or Li^+ lost almost same number of water molecules from their second hydration shell at the entry of the graphene pore. Functional groups replaced removed water molecules of the hydration shell of the Mg^{2+}. Hence, its structure remains stable and this ion passed across the functionalized pore. Every functionalized pore in this work had 5 functional groups which attached to the pore edge and results of the molecular dynamics (MD) simulation shows that oxygen atoms of the functional groups (either carbonyl or carboxylate) participated in the forming second hydration shell of the Mg^{2+}. On the other hand, when water molecules of the hydration shells of the Li^+ were removed, were not replaced by the functional groups and state of coordinative unsaturation was the reason of the higher energy barrier for Li^+ at the entrance of the pore. Another reason of this selective separation was due to the weak electronegative interactions of the Li^+ ion and its hydration shell and then, easily disturbed them by functional groups and Li^+ ions dragged to the regions which are closer to the edges of pore. In the case of Mg^{2+}, due to the stronger electrostatic interactions with water molecules of their hydration shells, filled the center of the pore and passed it easier than Li^+ ions. This research shows nanostructured membranes by functionalizing enable to act selectively.

2. Graphene nanosheet

2.1 Graphene nanosheet

Pristine graphene is a two-dimensional carbon-based nanosheet which has been the subject of many exciting theoretical and experimental studies (Hossain *et al.* 2012, Wu *et al.* 2011) since its recent isolation (Girit *et al.* 2009), and offers a wide range of opportunities for molecules or ions separation (Tsetseris and Pantelides 2014) due to its special properties such as ultimate thinness, flexibility, chemical stability, and mechanical strength (Geim 2009, Zhang *et al.* 2014). A pristine graphene sheet is impermeable to molecules as small as He (Bunch *et al.* 2008). Thus, to achieve permeability, drilled pores in the graphene is required. Then, the created pore on the surface of graphene was functionalized with various chemical groups. Functionalized graphene nanosheets can have unique properties (Georgakilas *et al.* 2012, Pei *et al.* 2010). In scientific literatures, the remarkable field of application has emerged for graphene nanosheet, that is water purification (Balapanuru *et al.* 2019, Boretti *et al.* 2018, Jafarzadeh *et al.* 2018, Taherian *et al.* 2013). In the following sections, we will investigate this research areas and some works done in this area.

2.2 Graphene in desalination

Considering the properties of graphene nanosheet in the water treatment industry, a lot of studies have been done using this membrane. In the water desalination process, ion rejection and water permeability are the two significant factors describing the performance of nanostructured membranes. To do this, we need to manipulate the graphene membrane with drilling and designing and functionalization appropriate pores on the surface of membrane. Hence, for efficient ion separation from water using a graphene, functionalization of created pores in the membranes must be done, so that the ion rejection should be 100%, while water molecules pass through the pore of membrane with the high-water flux. Hydroxyl group because of its hydrophilic characteristic has been used as a functional group for functionalizing graphene pore. In fact, compounds with hydroxyl group can form hydrogen bond with water molecules due to its electronegative oxygen atom. Cohen-Tanugi and Grossman (2012) performed some excellent MD simulation studies on the water desalination. They used two functionalized graphene, hydroxylated graphene pore (hydrophilic pore) and hydrogenated graphene pore (hydrophobic pore). Their system included one functionalized graphene as membrane at the center of the system and saline water at the feed side of the membrane and then, hydrostatic pressure was implied to the system (see Fig. 1).

Interactions between functional groups on the edge pore and molecules at the feed side of box were very vital. For example, in the hydroxylated pore, water flux was approximately two times more than that of hydrogenated pore. They used three different pore sizes of each functionalized pore for desalination and by increasing the pore size, water flux increased too, but in the large pore, ions could pass through it that was not good. So, the pore size of functionalized graphene is as important as the pore chemistry. The area of the hydroxylated pore was 25% larger than that of the hydrogenated pore, while the water flow rate of hydroxylated pore was 69% to 113% higher than hydrogenated one. So, the higher water flow rate of hydroxylated pore was not only due to its pore size. By studying on results of the oxygen density maps and angular distribution function, they realized that water molecules passed across the hydrogenated pore with an organized order. Hydrogen atoms which were attached to the pore edge disrupted the hydrogen bonding network of the water molecules and when these molecules tend to pass across the hydrogenated pore, their unity are affected by hydrophobic interactions. By comparing hydrogenated and hydroxylated pore with approximately the same sizes, hydroxylated pore let more ions pass across it, because hydroxyl group formed hydrogen bonds with ions as well as water molecules. So, hydrogenated pore had better performance in salt rejection and more water molecules passed through hydroxylated pore.

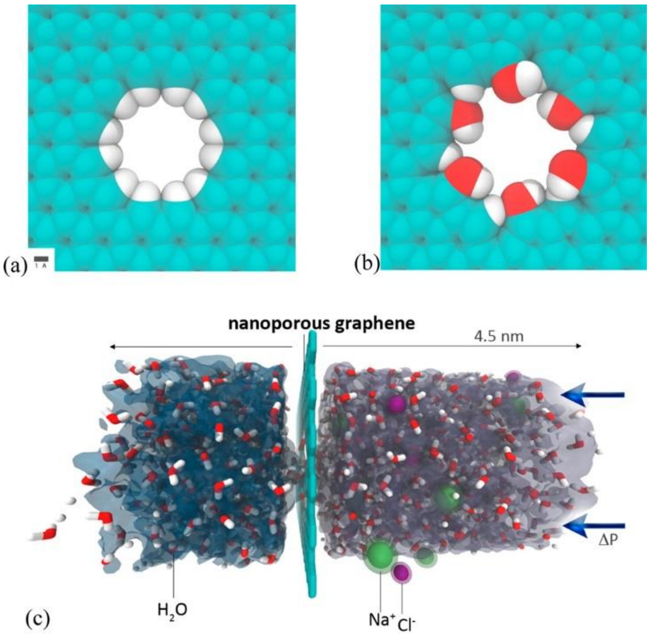

Fig. 1 Hydrogenated (a) and hydroxylated (b) graphene pores, and (c) side view of the computational system. Reproduced with permission from reference (Cohen-Tanugi and Grossman 2012) Copyright 2012 American Chemical Society

In a similar research on the water desalination by Wang *et al.* (2017), six graphene membrane with different pore size and pore chemistry were investigated. Water molecules and ions were under external hydrostatic pressure. In hydrogenated and hydroxylated pore which had larger pore diameters, water flux was higher in hydrogenated pore despite of its hydrophobic nature. This phenomenon was due to the larger size of hydroxyl group than hydrogen atoms. Hydroxyl group has two atoms and take more space from pore area relative to hydrogen atoms as functional group. In smaller functionalized pores, water flux of hydroxylated pores was higher than hydrogenated one, because hydrophilic nature of hydroxyl was influential and its effect was superior to largeness of cross-sectional of the graphene pores. Hydroxylated pore because of negative charges of hydroxyl groups attract positive charged sodium ions, on the contrary, hydrogenated pore passed negative charged chlorine ions, due to its positive charges. Ions could not pass across the smaller pore size, because of their hydration shell around them.

2.3 Graphene in ion separation

Ruan *et al.* (2016) and Zhu *et al.* (2017) in two MD simulation studies investigated the separation of Mg^{2+} from Li^+ using graphene as a membrane under induced electric field as motivator for ions movements toward the pore of membrane. In their first study (Ruan *et al.* 2016), a graphene with a pristine pore (see Fig. 2) and in their second study (Zhu *et al.* 2017), two different functionalized graphene (carbonyl and carboxylate groups) were used. Results of MD simulation of three graphene with pore diameter 0.24 Å showed that more Mg^{2+} (400 Mg^{2+}) passed

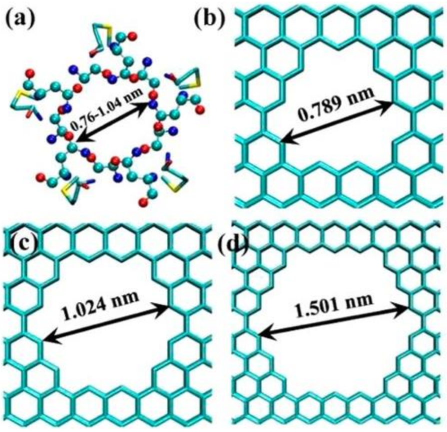

Fig. 2 (a) Selectivity filter structure of Mg^{2+} channels viewed from the top. (b) Graphene nanopores with pore diameters of 0.789, (c) 1.024, and (d) 1.501 nm. Reproduced with permission from reference (Ruan *et al.* 2016) Copyright 2016 American Chemical Society

through carboxylate pore under electric field of 1 V/nm in comparing to carbonylated pore (300 Mg^{2+}) and unfunctionalized graphene (150 Mg^{2+}), which could be result of negatively charged carboxylate groups which could attract positively charged cations. Functionalized pores, in addition to their higher ionic current through themselves showed higher selectivity for Mg^{2+} over Li^+ (carboxylated pore and carbonylated pore had selectivity equal to 5 and 3.5, respectively), in comparing to unfunctionalized graphene with 2.5 selectivity. In these systems, Li^+ encountered with higher energy barrier than Mg^{2+} for passing through pores. This is due to the second hydration shell of these cations.

Smaller second hydration shell of Mg^{2+} in comparing to larger second hydration shell of Li^+, in addition to Mg^{2+} stronger coulombic interaction with the graphene resulted in Mg^{2+} ability in occupying of the pore center of the graphene which helped Mg^{2+} to pass through the pore easier than Li^+ and this occupation caused to forming of repulsive interaction between Mg^{2+} and Li^+ which resulted in lithium cations difficult passing through the pore. Lithium cations for overcoming high energy barrier had to diminishing some water molecules by breaking more hydrogen bonds between water molecules of their first and second hydrations shells in comparing to magnesium cations and this effort caused to encountering higher energy barrier. According to hydrogen bond number of water molecules in first and second hydration shell of both cations in these studies, water molecules of second hydration shell of magnesium cation could easier than water molecules of second hydration shell of lithium cation separated from water molecules of first hydration shell which resulted in magnesium cations encountering lower energy barrier than lithium cations.

Functionalized graphene pores could compensate the effect of magnesium cations dehydration which caused in unstabling these cations in comparing to their state in the bulk, by acting as a water molecule in their second hydration shell and consequently their easier passage through the pore rather than lithium cations which remain unsaturated after dehydration which resulted in high energy barrier for their passage through the functionalized pores. Increasing of electric field amount caused to increasing of ionic current but not in selectivity for magnesium cation over lithium cation in both studies.

In an experimental work, O'Hern *et al.* (2014) in order to separate potassium cation from chlorine anion fabricated a one-layered graphene nanosheet. For fabricating graphene nanosheet with appropriate pores with diameter sizes from 1 to 4 Å, a pristine one-layered graphene was bombarded by gallium ions and appropriate pores were created in the graphene nanosheet. After bombarding, the graphene was immersed in a solution which resulted in enlarging and oxidation of the created pores. Time of the remaining of the graphene nanosheet was a crucial factor on the size of the created pores and if remaining time was short, carbon atoms of the pore edges which were functionalized with negatively charged functional groups could have pore diameter sizes which helped graphene nanosheet to separate potassium from chlorine anions, because of attractive interactions. But if remaining time and oxidation time was long, the pore diameter sizes became larger and graphene could not separate ions from each other. Dehydration process of different ions could result in different energy barrier for breaking hydrogen bonds of water molecules in first and second hydration shells and consequently, these differences in separation process by a graphene-like membrane could be influential factor on ions passage through the pore of the membrane.

Sahu *et al.* (2017) in a MD simulation study investigated the separation of potassium cations from chlorine anions using graphene nanosheet under applying electric field. They reported dehydration of potassium cations required less energy than dehydration of chlorine anions. Hence, chlorine anions encountered with higher energy barrier than potassium cations for passing through a pore with diameter of 2.1 Å and then, a selective separation process was occurred for potassium cations over chlorine anions. By increasing of electric field, potassium cations current was increased in comparing to chlorine anions current. Because by increasing of electric field, oxygen atoms of water molecules became more polarize (more negative) and positively charged potassium cations attracted by these negatively charged molecules and could easier than chlorine anions which had negative charges pass through the graphene's pore.

Kommu *et al.*(2016) studied some heavy metals removal by functionalized graphene. They used three different functional groups (fluorine, nitrogen and hydroxyl) for functionalization of graphene pore. Hydroxylated pore with 12 Å dimeter was larger than the rest pore with 9 Å and 8 Å, so specific influence of functional group on salt rejection could not be examined. Nitrogenated pore because of its smaller size showed better salt rejection rather than other ones. But water flux through fluorinated pore was higher than nitrogenated pore and hydroxylated one. By comparison of interaction energies between functional groups and water molecules, the lower water flux of hydroxylated pore was due to the stronger hydrogen bonding

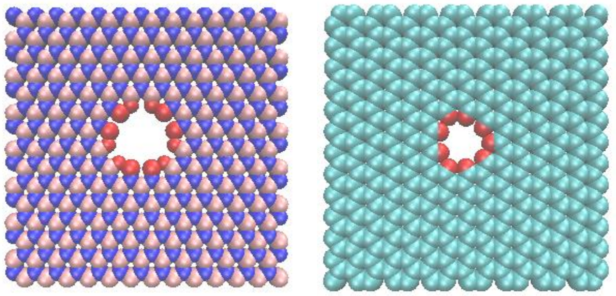

Fig. 3 Functionalized pore of membranes, Left: BNNS and right is GNS (blue represents nitrogen, silver is boron, cyan is carbon and red color is fluoride)

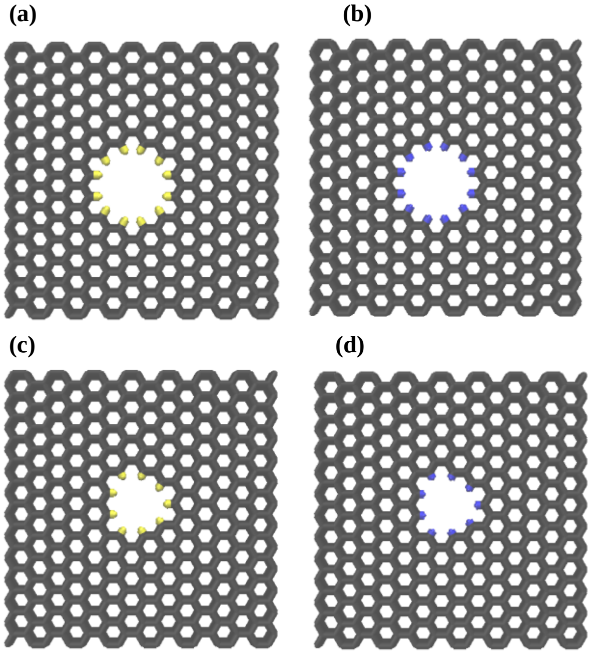

Fig. 4 Functionalized graphene membranes: (a) large F-pore, (b) large H-pore, (c) small F-pore, and (d) small H-pore, Reprinted from reference (Azamat *et al.* 2015a), with permission from Elsevier, License Number: 4997210365768.

of water molecules and hydroxyl groups on the edge pore. So, despite this fact which hydroxylated pore had larger diameter, its water flux was lower than other functionalized pores, because of its pore chemistry (Azamat and Khataee 2017a).

Azamat with MD simulations studied the removal of nickel cations from aqueous solution under applying electric field, using functionalized graphene and boron nitride nanosheets (see Fig. 3). After drilling a pore in each of nanosheets, their pores were functionalized by fluorine atoms but their pore areas were different from each other (fluorinated graphene had 6 Å pore diameter size and fluorinated boron nitride had 8 Å pore diameter size) (Azamat 2017).

This system was consisted of a membrane which in its feed side was a nickel (II) chloride solution. The purpose of this paper was letting nickel cations to pass across the considered membrane. The attractive interaction between negatively charged fluorine atoms and positively charged nickel ions was formed which made easy passage for nickel ions through the pores. Nickel cations encountered with very lower energy barrier for passing of pore, which results showed that nickel cations could overcome this energy barrier and pass through both of nanosheets. An influential factor on increasing of nickel cations passage was magnitude of electric field which by increasing of the electric field amount, the number of cations which could pass across the membrane was increased. For all runs, to avoid vertical displacement of the membrane, the atoms at the edge of the membrane were fixed, while other atoms of membrane were free to move, that is, the membrane was flexible during the MD runs. Also, water molecules and ions had motions in all directions of the simulation box. This method is a more realistic condition than a fully fixed membrane.

2.4 Graphene in removal of trihalomethane

Azamat *et al.* (2015a) in two papers by MD simulation studied removal of trihalomethane from water in order to keep trihalomethane molecules at feed side of the system and let water molecules pass through the pore of membrane and go to the permeate side (pure water side) of the system, in one of these papers, functionalized graphene was used as membrane and in the other one functionalized boron nitride was used as membrane (Azamat *et al.* 2016b). Both papers had a system which was consisted of a membrane and solution of trihalomethane with 0.4 mol/L concentration and an external pressure was applied to systems in order to moving molecules toward the membrane. In the graphene membrane, four different functionalized group was added to the edge pore (Azamat *et al.* 2015a) to study the effect of functional groups and pore size on the separation process (see Fig. 4).

The fluorine and hydrogen atoms were used for functionalization of pores. In each case, two pores with the dimeter of 6Å and 8Å were designed and MD simulation results of this study showed that the fluorinated graphene could pass more water molecules through itself because fluorine atoms had electronegative natures and could form hydrogen bonds with water molecules which resulted in more water molecules passing.

In the other work (Azamat *et al.* 2016b), Azamat et al. designed two different functionalized boron nitride nanosheets which had different functionalization’s and pore sizes (one was functionalized with fluorine and hydrogen atoms which had 8Å pore diameter and the other was functionalized with hydroxyl groups and hydrogen atoms which had 5.7 Å pore diameter: see Fig. 5).

For each selected applied pressure, more independent MD simulations with uncorrelated initial configurations were performed to reach a certain result. MD simulation results showed that either water molecules or trihalomethane molecules could pass through large functionalized pores. So that in 200 MPa applied pressure, 3000 water molecules could pass through large pore of boron nitride which was more passing water molecules than hydrogenated

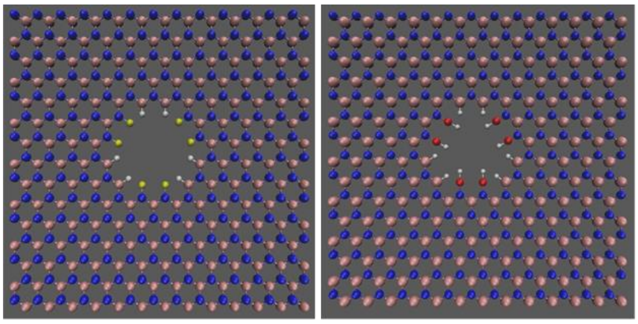

Fig. 5 Functionalized boron nitride nanosheet membrane with a large (left) and small (right) pore, blue nitroge silver boron, yellow fluoride, white hydrogen, red oxyge Reprinted by permission from Springer Nature: Springe Journal of Molecular Modeling (Azamat *et al.* 2016b License Number: 4997210787120

pore. These results indicate that functionalized graphene and boron nitride had similar performance in separation process. Functionalized graphene which had pore diameter sizes with 6 Å and functionalized boron nitride with 5.7 Å did not let any trihalomethane molecules pass through them but water molecules with smaller number in comparing to large pore could pass through the membrane.

In the case of using functionalized graphenes with small pore diameter sizes when applied pressure was in range of 10 to 100 MPa, water molecules passing by increasing of the applied pressure was increased too, but when applied pressure was in range of 100 to 200 MPa, by increasing of the applied pressure water molecules passing number was decreased. This is due to by increasing applied pressure, more water and trihalomethane molecules accumulated in front of the functionalized graphene pore and blocked passage of water molecules. On the other hand, functionalized boron nitride which was functionalized with hydroxyl groups and hydrogen atoms with 5.7 Å diameter size, could by increasing of applied pressure from 5 to 200 MPa passed water molecules through itself. Also, by increasing of applied pressure water molecules passing number was increased and this phenomenon indicates that functionalized boron nitride which was functionalized with hydroxyl groups and hydrogen atoms in applied pressure in the range of 100 to 200 MPa had better performance in water flow than hydrogenated and fluorinated graphenes. On the other hands, when applied pressure was in range of 5 to 100 MPa, fluorinated and hydrogenated graphenes, because of a little bit larger pore diameter could more water molecules pass through themselves. Generally, according to MD simulation results, both functionalized graphene and boron nitride had similar performances in the separation process of trihalomethane molecules from water molecules.

3. Graphene oxide nanosheet

3.1 Graphene nanosheet

Another carbon-based nanomaterial is graphene oxide nanosheet which is prepared by oxidization of graphene sheets with chemically modified with oxygen-containing functional groups on the graphene basal plane (Bagri *et al.* 2010). Graphene oxide was first prepared by Brodie (1859). The preparation method of graphene oxide was then improved by Staudenmaier (Staudenmaier 1898) and Hummers (Hummers and Offeman 1958). Therefore, the conventional method for synthesis of graphene oxide is oxidization of natural graphite by strong oxidants (An *et al.* 2016). Graphene oxide is cheaper than graphene and it has a high mechanical resistance (single layer of graphene oxide has a Young's modulus of up to 0.2 TPa) (Perreault *et al.* 2015).

The advantage of graphene oxide with respect to graphene and MoS_2, is its surface with functional groups that gives the hydrophilic property to the surface. Also, chemical functionalization of graphene oxide can enhance its permeability. Although graphene is one of the toxic materials, its chemical modification leads to a nontoxic graphene oxide nanomaterial. The two-dimensional structure and physicochemical properties of graphene oxide offer an exciting opportunity to make a fundamentally new class of sieving membranes by stacking graphene oxide nanosheets.

3.2 Graphene oxide in desalination

Graphene oxide nanosheets have been considered promising membrane materials, because they are only one carbon atom thick and thus, may form separation membranes that minimize transport resistance and maximize flux. In recent years, graphene oxide has become one of the most studied nanomaterials (Kuila *et al.* 2013, Smith *et al.* 2014) and generated interest for energy-related applications (Dreyer *et al.* 2010). According to experimental studies, the minimum oxygen concentration in the graphene oxide nanosheet is about 20%. More reduction leads to a lower concentration of oxygen (12.5-0.04%) in the reduced graphene oxide. Moreover, the 20% O/C ratio is common in the theoretical studies in graphene oxide nanosheet and this ratio is useful for comparing results with the experimental works.

In a MD simulation study, Hosseini *et al.* (2018) investigated the ability of functionalized graphene oxide in desalination process. They used four functionalized graphene oxide as a membrane in order to evaluate the effect of the pore size and chemistry on the water desalination (see Fig. 6). The functional groups were hydrogen atoms and hydroxyl groups.

Water flux as a function of applied pressure revealed that hydroxylated graphene oxide with larger pore had higher water flux in all applied pressure because of its hydroxyl hydrophilic nature and its pore largeness. So, the importance of pore chemistry was obvious. In their research, for better understanding of abilities of functionalized graphene oxide, its performance compared with functionalized graphene as a highly successful membrane. Graphene oxide because of its hydrophilic surface had higher water flux than graphene, because water molecules could permeate through the graphene oxide distribute on the surface of the graphene oxide but when

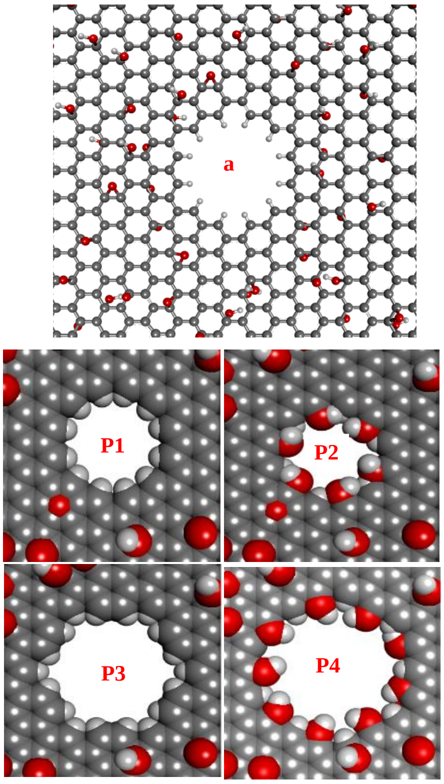

Fig. 6 Graphene oxide and different pore architectures (a) Hydrogenated GO with epoxy and hydroxyl groups on the surface, (P1) Hydrogenated GO pore, pore radius ~2.9 Å, (P2) Hydroxylated GO pore, pore radius ~3.1 Å, (P3) Hydrogenated GO pore, pore radius ~4.5 Å, and (P4) Hydroxylated GO pore, pore radius ~4.1 Å (gray, red and white colors are carbon, oxygen and hydro-gen atoms, respectively), Reprinted from reference (Hosseini *et al.* 2018), with permission from Elsevier, License Number: 4997211050020

water molecules pass across the graphene sheet, they accumulate near the pore and block passage of water molecules which want to go through the pore. Hydroxylated graphene oxide membranes were good at water flux but salt rejection as an important factor for evaluating a membrane was not good enough. Hydroxyl groups at pore edges of graphene oxide sheets formed hydrogen bonds with Cl^- ions so chlorine ions could pass across the sheet especially when applied pressure was increased as well as pore diameter increasing. So, choosing functional group for functionalizing nanostructured pore and this pore's diameter size are very important factor for having high water flux and salt rejection.

Sun *et al.* (2013a) by drop casting method synthesized membrane based on graphene oxide nanosheets and then studied the selective ion permeation through this synthesized membrane. Sodium ions permeation through the created nanochannel from the graphene oxide nanosheets. Sodium ions because of the presence of H^+ in the environment did not interact with nanosheets and passed through the membrane, while copper ions strongly interacted with graphene oxide nanosheets and adsorbed on their surfaces and could not pass across the membrane. So, interaction of hydroxyl and epoxy groups of the graphene oxide nanosheets with ions determined which ion pass through the membrane and which ions could not pass across it.

Chen *et al.* (2017) experimentally and theoretically studied the water purification through graphene oxide membrane. They focused on the diameter of nanochannels consisted of graphene oxide nanosheets as an important factor on the water purification. Water molecules radii and diameter of ions hydration shell are very crucial in all separation process, because when we have a nanosheet with a pore or a nanochannel with diameter smaller than ions hydration shell diameter, water molecules could pass across the membrane or nanochannel while ions could not pass through these, so by controlling of diameter of nanochannels or membranes pore a successful separation was happen. Chen *et al.* by intercalating potassium ion between graphene oxide layers tended to have nanochannels with specific diameter sizes. By intercalating potassium ions between graphene oxide nanosheets they controlled desalination process, because ions due to their hydration shells diameter could not pass through the intercalated graphene oxide layers while water molecules easily passed through them.

Giri *et al.* (2019) in a MD simulation study investigated the ability of a nanochannel consisted of two graphene oxide nanosheets in desalination process. They investigated the influence of oxidation degree of graphene oxide nanosheet and nanochannel diameter as important influential factors on the separation process of water molecules from sodium and chlorine ions. Oxidation degree of a graphene oxide nanosheet is defined as ration of oxygen atoms of the graphene oxide nanosheet to carbon atoms of the graphene oxide nanosheet. The simulation box was consisted of four pristine graphene nanosheets as blockers against molecules inside the feed side and permeate side of the system and also two graphene oxide nanosheets which were roof and floor of the nanochannel. They studied various nanochannels which their difference was in their diameters (6 Å to 10 Å) and oxidation degree of graphene oxide nanosheet (0 to 40). Results of the simulations showed that by increasing of nanochannel diameter, water permeation increased, however, salt rejection was decreased. For example, either water molecules or ions could pass across the nanochannel and these results were not good for a membrane which its duty was to produce purified water.

Sodium and chlorine ions could not pass across nanochannel with diameter of 6 Å and only few ions could pass through the nanochannel with 8 Å (some ions could enter to the nanochannel but because of interaction between their water molecules in their hydration shell and hydroxyl groups on the graphene oxide nanosheet, they lost some water molecules and consequently, their movement was interrupted), while ions could pass across the nanochannel with 10Å diameter. Increasing of oxidation degree resulted in decreasing of water and ions permeance. Water molecules formed hydrogen bond with hydroxyl groups on the graphene oxide nanosheets and their chain was broken.

In other similar work, Devanathan *et al.* (2016) reported that the water flux in the graphene oxide nanochannels was slow. These researchers by experimental investigation and MD simulation proved that water molecules because of their hydrogen bonding to hydroxyl groups on the graphene oxide nanosheet had slow flow along a graphene oxide nanochannel. Hosseini *et al.* (2019) in another paper studied different functionalized graphene oxide. In their previous work they functionalized graphene oxide nanopore rim's with hydrogen atoms and hydroxyl groups and in their latter work they functionalized graphene oxide nanopore edge's with hydrogen atoms and fluorine atoms. Both papers used applied pressure as a force drive for molecules movement toward the membrane. Beside functionalized graphene oxide, they studied functionalized pristine graphene as membrane for desalination in order to comparing these nanosheets ability in desalination and reported that water molecules permeance through functionalized graphene oxide was higher than water molecules permeance through functionalized pristine graphene. This is due to water molecules by interacting with hydroxyl and epoxy groups on the graphene oxide could easily with encountering lower energy barrier go toward the graphene oxide nanosheet and more accumulated on the graphene oxide nanosheet and consequently, water molecule's chance for passing through the nanosheet was higher than when they wanted pass across the functionalized pristine graphene. So, interaction of hydroxyl and epoxy groups with passing molecules could influence on the separation process and water flux.

For example, Kaleekkal *et al.* (2017) by adding functionalized graphene oxide nanosheets to their mixed matrix membrane's structure enhanced hydrophilicity of their membrane which was result of interactions between water molecules and functionalized graphene oxide nanosheets. Results of both papers showed that the water permeance through both, hydroxylated and fluorinated, graphene oxide nanosheets was the same, so, both functional groups had positive influence on the water flux. As mentioned earlier hydroxylated nanopore made hydrogen bonds with chlorine ions and these ions encountered with low energy barrier at the hydroxylated pore center and finally could pass across it. On the other hand, fluorinated nanopore because of its negatively charged fluorine atoms on its edge rejected chlorine ions by strong electrostatic interactions. In conclusion of both papers fluorinated graphene oxide nanosheet had better performance in high water flux and salt rejection than fluorinated pristine graphene and hydroxylated graphene oxide nanosheets.

3.3 Graphene oxide in solvent separation

Liu *et al.* (2019) studied the separation of ethanol-water mixture from each other by graphene oxide nanosheet as a membrane. They investigated two influential factors on the separation process, the pore size and oxidation degree of graphene oxide nanosheet. Their system was consisted of a graphene oxide as a membrane and an ethanol-water mixture behind it. Hydrostatic pressure was applied to the system as molecules force drive. By increasing of oxidation degree, water flux was increased because water molecules by having strong interactions and larger adsorption energy could get themselves closer to the graphene oxide nanosheet and finally pass across it more than ethanol molecules. On the other hand, increasing pore size increased both water and ethanol permeation, so, for having high water flux and 100% ethanol rejection, researchers introduced a graphene oxide nanosheet with oxidation degree of 0.49 and 2.4 Å pore size.

Fang *et al.* (2018) studied permeation of water and ethanol molecules through a functionalized graphene oxide with MD simulation. Their system was consisted of a functionalized graphene oxide nanosheet with carboxyl groups and a mixture of water and ethanol was above it. They tended to study on the effect of ionization of carboxyl group of the graphene oxide pore edge on the separation process. MD simulations results showed that ionization of carboxyl groups resulted in increasing of water flux and selectivity for water molecules over ethanol molecules even in system which its graphene oxide had large pore area (it is required to mention this that ethanol molecular diameter is 4.5Å and water's molecular diameter is 2.6Å). Water molecules interacted with COO^- functional group on the graphene oxide's pore rim. Also, in this pore, size of pore was small enough and blocked ethanol molecules passage for going to the permeate side of the system.

Yu *et al.* (2018) by MD simulation studied the ability of carboxylated graphene oxide in permeating of water and ethanol molecules. Their system was consisted of a functionalized graphene oxide (two different functionalized graphene oxide were studied, one was functionalized with carboxyl COOH groups and the other was functionalized with carboxylate COO^- groups) which was immersed in an equimolar water and ethanol mixture. Both functionalized graphene oxide nanosheets had hydroxyl and epoxy groups on their both sides and both of them had same pore area. Density profile of both molecules near the functionalized pore with carboxyl groups showed that both molecules were around the pore (either water molecules or ethanol molecules could form hydrogen bonds with COOH groups and pass through it) while density profile of molecules around the functionalized graphene oxide with carboxylate groups showed that only water molecules were near the pore and no ethanol molecule could be around it. Results of the MD simulation showed that either water molecules or ethanol molecules could pass through functionalized graphene oxide with carboxyl groups, on the other hand, only water molecules could pass through functionalized graphene oxide with carboxylate groups and ethanol molecules were rejected and could not pass through it. So, COO^- groups caused to selective permeation of water molecules.

The reason of happening of this selective behavior of functionalized graphene oxide with carboxylate groups was not pore area, because both functionalized graphene oxide nanosheets had equal same area, however interaction between water molecules and COO^- groups which resulted to forming of hydrogen bonds between them and occupying region around the pore and blocking ethanol molecules for reaching near the functionalized pore with COO^- groups (high adsorption energy of water molecules caused to accumulation of these molecules around the pore with COO^- groups). Water molecules could pass more through functionalized graphene oxide with carboxylate groups rather than the other functionalized graphene oxide because of stronger interactions between water molecules and COO^- groups.

4. Boron nitride nanosheet

4.1 Boron nitride nanosheets

Hexagonal boron nitride nanosheet as a one atom thick nanostructure material could be used in separation process as an efficient membrane. Two-dimensional boron nitride nanosheet because of its similar structural geometry with graphene was considered as a separator but its chemical properties is different than graphene. A boron nitride nanosheet with a very high specific surface area exhibits excellent sorption performance for a wide range of oils, solvents, and dyes from water (Azamat *et al.* 2021a, b, Saadat Tabrizi *et al.* 2020). This nanostructured material has unique properties compared to graphene, including a wide energy band gap, electrical insulation, ultraviolet photoluminescence, high thermal conductivity and stability, and high resistance to oxidation and chemical inertness (Lei *et al.* 2014, Mortazavi and Rémond, 2012, Sun *et al.* 2013b).

The reusability of a saturated boron nitride nanosheet by burning in air, due to its high resistance against oxidation, is one of its important characteristics. This easy recyclability makes porous boron nitride nanosheet a good candidate for water treatment processes (Lei *et al.* 2013a). Perfect boron nitride nanosheet is impermeable to ions, because there are no pores and the electron density of its aromatic rings is enough to repel ions trying to pass through it. To pass ions or molecules through a boron nitride nanosheet, the drilling of pores is required. After drilling pore, functionalized pore in a boron nitride nanosheet is obtained by passivating each nitrogen and boron atom at the pore edge using chemical functional groups such as fluorine and hydrogen atoms. Hexagonal boron nitride is a stable form of boron nitride which is a chemical compound consisted of boron and nitrogen that covalently bonded together and be crystalized. Multi-layered hexagonal boron nitride is consisted of several layer of boron nitride nanosheet which by van der Waals interaction stick to each other. Various methods have been used for separating layers of hexagonal boron nitride from each other for having a nanosheet. One of these methods is exfoliation, for example Yin *et al.* (2019) used this method in order to producing boron nitride nanosheets and using them in thein nanofiber membrane's structure. Results of their experiments showed that presence of boron nitride nanosheets in the structure of the membrane caused to increasing of mechanical strength and thermal conductivity.

Jia and Wu (2018) also used exfoliation method for having boron nitride nanosheets. It is required to mention that exfoliation is not a fixed approach with constant procedure which caused multilayered nanomaterial like boron nitride and graphene be exfoliated by very different manners, furthermore, through the exfoliation be functionalized with different functional groups, such as ammonia group, which lead to having nanosheets with different abilities because of their nature of functional groups. Jia and Wu (2018) used ultrasonic exfoliation and showed that presence of boron nitride nanosheets caused to creating stable nanochannels which eased proton conductivity through the membrane. One important difference between boron nitride and graphene is boron nitride's wide band gap. Beside of mechanical strength, boron nitride showed many other extraordinary properties which convince scientists and researchers to do many experimental and theoretical studies for introducing it, as a new emerging nanomaterial which could improve performances in various fields from pharmaceutical to electronica one (Azamat and Khataee 2016, 2017b).

4.2 Boron nitride nanosheet in ion separation

In a MD simulation research, graphene and boron nitride nanosheets were used for separation of Zn^{2+} and Cl^- ions from water molecules (Azamat *et al.* 2015b). Graphene was functionalized by fluorine atoms with 6 Å diameter pore size and boron nitride was functionalized by hydrogen and fluorine atoms with 8 Å diameter pore size. Because of both membranes pore chemistry with negative charges, Cl^- ions encountered with high energy barrier and could not pass across the membrane's pores. On the other hand, Zn^{2+} ions attracted by negative charge pores and could pass across the pore according to driven force that electric field prepared for ions and molecules movements. More Zn^{2+} ions could pass across the boron nitride than graphene because the energy barrier for zinc ions in the boron nitride pore was lower than that of graphene pore and consequently, lower retention time was occurred for Zn^{2+} ions when they passed across the pore of boron nitride nanosheet.

In a similar work (Azamat *et al.* 2016c), ability of functionalized boron nitride nanosheet was studied in the removal of copper and mercury as heavy metal ions from aqueous solution. In this work like previously reviewed research, functional group has an important effect on separation process. Boron nitride nanosheet was functionalized by fluorine and hydrogen atoms to gain negatively charged characteristic and because of this, chlorine ions could not pass across the boron nitride pore but positively charged copper and mercury by help of electric field crossed functionalized boron nitride nanosheet pore.

4.3 Boron nitride nanosheet in desalination

Although boron nitride nanosheet has hydrophobic nature because of water molecule's contact angle (hydrophilic < 90° > hydrophobic) on the boron nitride's surface, but studies showed that bond between boron and nitrogen is polar and consequently, could interact with water molecules (Xiao 2016). Tang *et al.* (2019) used boron nitride nanosheets in their mixed-matrix membrane's structure and reported that by adding boron nitride nanosheets to their membrane and increasing its wt%, contact angle of water was decreased (although it could be expected that contact angle of water should be increased because of the hydrophobic nature of boron nitride nanosheets but as mentioned earlier interaction between water and polar sites of the boron nitride nanosheets create a hydrophilic relationship between them). Results of their experiments showed that by increasing loading of the boron nitride nanosheets in the membrane's structure, pure water flux was increased, so presence of boron nitride nanosheets was introduced as most important factor on water flux. Tang et al. mentioned that porosity and pore size of the membrane were influential on water flow through their mixed-matrix membrane beside of the boron nitride nanosheets loading.

Today process of synthesizing nanostructured materials like boron nitride nanosheets is not completely organized and there is no a conventional and worldwide method for fabricating them, so researchers and scientists' study different approaches for producing stable nanomaterials such as porous nanostructures in order to better understanding of the synthesizing processes of various approaches and evaluating their advantageous and drawbacks. Lei *et al.* (2013b) reported that their experimental investigation showed that multi-layered hexagonal boron nitride nanosheets could be synthesized by templating technique which is an approach for synthesizing unique porous nanostructured materials like boron nitride nanosheets. Their multi-layered boron nitride nanosheets were synthesized during a process which boron and nitrogen atoms from different origins were bonded to each other and formed crystallized multi-layered boron nitride nanosheets which were in the shape of white powder. Different analyzing techniques showed that the boron nitride nanosheets were fabricated with pores in nanometrical scale (pores diameter from 20 to 100 nm). The aim of this experimental study was the removal of contaminants like oils and solvents from water by relying on absorptive characteristic of multi-layered boron nitride nanosheets. They tended to remove different kinds of oils like used engine oils and various organic solvents such as ethanol in order to study different parameters which had influence on separation process.

When they put multi-layered boron nitride nanosheets in contaminated water realized that after two minutes, multi-layered porous boron nitride nanosheets could absorb contaminants, thirty three times more than their own weight, from water which is better performance than other conventional absorbents and also they could absorb contaminants more than two times in comparison to non-porous multi-layered boron nitride nanosheets which importance of porous structure could be understood from this fact. They observed that this porous structure by increasing absorption capacity of contaminants helped to better absorbing contaminants from water and keep them in the structure. Multi-layered boron nitride nanosheets could reject water molecules while absorb contaminants and consequently by removing saturated multi-layered boron nitride nanosheets from water after purification by removing nanosheets from water they had clean water. During absorption process of contaminants into multi-layered boron nitride nanosheets which mainly capillarity phenomenon helped them for diffusing into the multi-layered nanosheets, they adsorbed in the pores of the nanosheets and on their surfaces and this adsorption process enhanced absorption capacity of the contaminant molecules, on the other hand, mechanical strength of the nanosheets revealed as the most important influential factor on the separation process because without mechanical strength of the boron nitride nanosheets, their structure ruined by molecules which were placed into them between layers of nanosheets and into their pores (intercalation process) but boron nitride nanosheets could stand and absorb molecules and keep them into themselves and swallow thirty three times more than themselves.

In conclusion, porous structure of boron nitride nanosheets and spaces between them increased surface area and probability of occurring adsorption process and subsequently intercalation was increased. After removing saturated multi-layered boron nitride nanosheets from water, they could be burned, without oxidation, and reused for separation process which is an excellent characteristic for an absorbent. So, we could rely on boron nitride nanosheet as a strong nanomaterial in the separation process.

Chen *et al.* (2018) in an experimental study fabricated a membrane which contained of hexagonal boron nitride nanosheets in its structure in order to be used for water purification. Boron nitride nanosheets in the membrane's structure made membrane stable in acidic and basic environments and created nanochannels which simplified molecules passage through the membrane with fast movements. This membrane could be selective to molecules size. An important characteristic of these nanochannels was their stable condition during the filtration process which were not destroyed by passing molecules. By increasing of molecules size they could not pass across the membrane while water molecules with an acceptable flow rate could pass across the membrane because of their smaller size. For example, dye molecules were removed from water because of their larger size than nanochannels in the membrane. Boron nitride has hydrophobicity, so is not dispersible in aqueous media, hence the researchers of this study for having a membrane based on boron nitride nanosheets used amino groups as functional groups for functionalization of boron nitride nanosheets in order to enhance their dispersibility and their stability too which able the membrane to be more stable in harsh conditions such as in solution with high concentration. So, functionalization compensated the inability of boron nitride nanosheet in dispersion in water. In addition to, molecules size influence on the separation process, membrane's thinness had great impact on it. Results of the experiments showed that by increasing thickness of the membrane, molecules permeance decreased, because each molecule in thick membranes had to pass longer nanochannels in comparison to molecule which pass through thin membranes and consequently, thin membranes had larger molecules permeance. Negatively charged membrane's surface had influence on separation process by attracting or rejecting

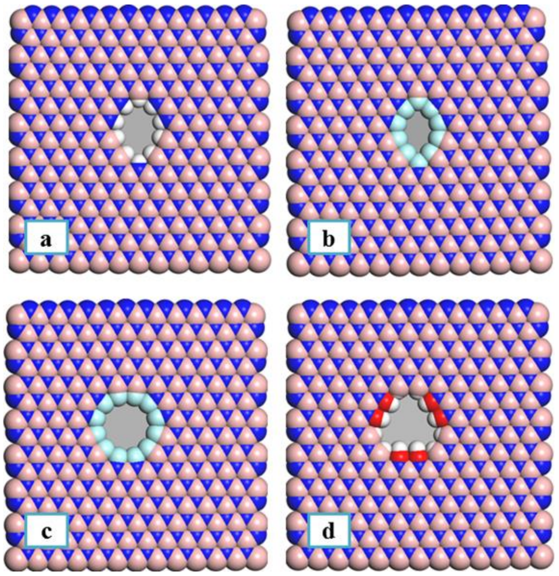

Fig. 7 Chemically functionalized boron nitride nanosheet membranes by (a) hydrogen (–H) (system 1), (b) fluorine (–F) with small pore size (system 2), (c) fluorine (–F) with large pore size (system 3), and (d) both hydrogen (–H) and hydroxyl (–OH) group (system 4) at the pore edge. (blue, silver, green, white and red colors represent nitrogen, boron, fluorine, hydrogen and oxygen atoms, respectively). Reprinted from reference (Jafarzadeh *et al.* 2019), with permission from Elsevier, License Number: 4997211326920.

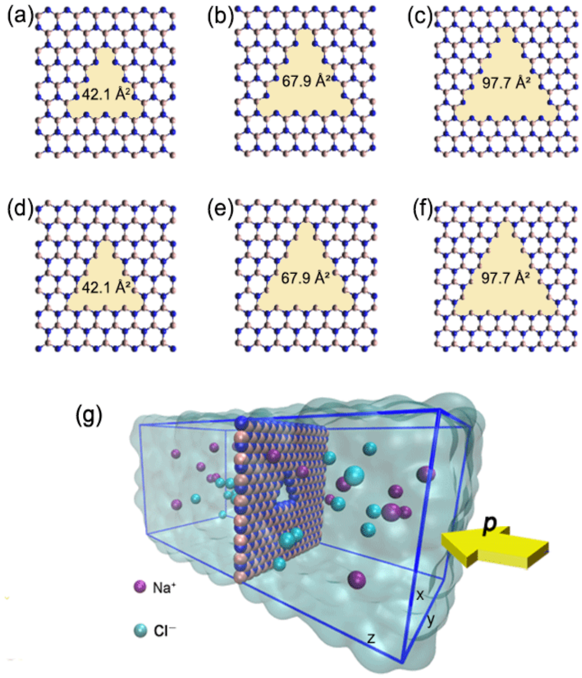

Fig. 8 Top views and diameters of the experiment-based (a) N3, (b) N4, (c) N5, (d) B3, (e) B4, and (f) B5 pores of the h-BN membranes. (g) Schematic diagram of a simulation cell for the N4-type membrane, in which the blue shade represents the water molecules. Reproduced with permission from reference (Gao *et al.* 2017), Copyright 2017 American Chemical Society

charged molecules and providing a selective separation process.

By considering these facts, some studies have been carried out for having efficient membranes based on boron nitride nanosheets. By MD simulation and designing boron nitride nanosheets, we could better understand and study ability of pristine and functionalized boron nitride nanosheets as membranes. In this section, we will compare two papers which were used of boron nitride nanosheet as membrane for desalination of water. Both papers had boron nitride nanosheet as membrane at their systems center. Both of papers used of applying external pressure as force drive for movement of molecules toward membrane. Jafarzadeh et al. (Jafarzadeh *et al.* 2019) designed four different boron nitride nanosheets (see Fig. 7) with functionalized pores (two fluorinated with different pore areas, one hydrogenated and one hydroxylated), while Gao *et al.* (2017) used of six boron nitride nanosheets which were different from each other by considering their pore edge atoms (full nitrogen or full boron) and their pore areas as it could be seen in Fig. 8.

Gao *et al.* (2017) nanosheets and their pore areas were larger than of Jafarzadeh *et al.* (2019) nanosheets and their pore areas. But we could draw some conclusions about influence of functionalization of pore rims of nanosheets on water flux and salt rejection of membranes by comparing results of these two papers.

Gao *et al.* (2017) reported that their boron nitride nanosheet with full-nitrogen pore was best performer membrane with 100% salt rejection, although, their water flux was smaller than the others in some cases. (see Fig. 9). They mentioned that nitrogen atoms of the pore edge made interaction with water molecules and interaction between them was important key in high water flux and their boron nitride nanosheet was better membrane rather than pristine graphene with a created nanopore into it because carbon atoms of the graphene's nanopore could not make strong interaction with water molecules.

Nitrogen atoms at the boron nitride nanosheet edge had negative charges and these charges attract hydrogen atoms of the water molecules to themselves and this led water molecules to keep their chain, which was created due to the hydrogen bonding of water molecules, and pass through the center of the pore by encountering lower energy barrier than when they want pass across the boron nitride nanosheet with full boron atoms at its pore edge which by their positive charges attract oxygen atoms of water molecules toward themselves and caused to breaking of hydrogen bonding between water molecules. Hence, the lower water flux than boron nitride nanosheet with full nitrogen atoms at its pore edge. So, hydrogen bonding between water molecules at feed side and permeate side of the membrane is an important key for having high water flux.

Jafarzadeh *et al.* (2019) also reported that their fluorinated boron nitride nanosheet (fluorine atom has negative charge) with 15.8 Å^2 pore area had higher water flux than other functionalized boron nitride nanosheets and calculated potential of mean force values for water molecules along all of their systems showed that water molecules encounter with lower energy barrier at the fluorinated pore and

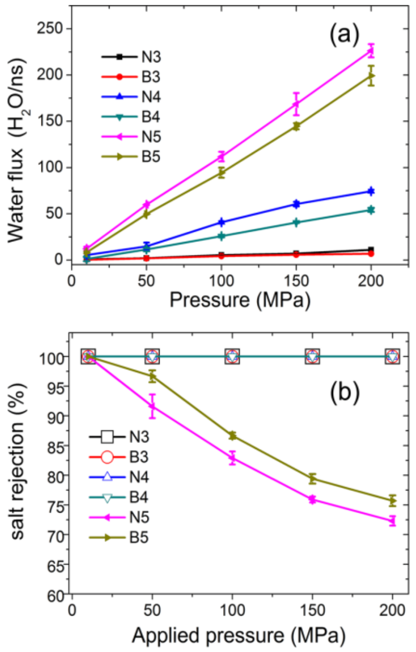

Fig. 9 (a) Water flux and (b) salt rejection with respect to pressure for the six h-BN membranes. Reproduced with permission from reference (Gao *et al.* 2017), Copyright 2017 American Chemical Society

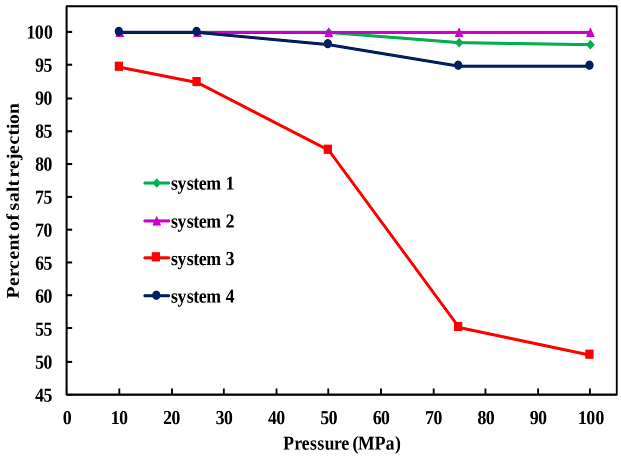

Fig. 10 The total salt rejection versus pressure for all of the systems. Reprinted from reference (Jafarzadeh *et al.* 2019), with permission from Elsevier, License Number: 4997220022295

consequently, could easily pass through the pore because of higher hydrophilic nature of their functionalized pore.

By comparing these two paper's best membranes we realize that although fluorinated boron nitride nanosheet had smaller pore area than boron nitride nanosheet with full nitrogen atoms at its pore edge but more water molecules under applying 50 MPa pressure in 5 ns passed across the fluorinated boron nitride than other unfunctionalized nanosheet under same conditions which indicate influence of appropriate functionalization of nanosheet pore. By increasing of applied pressure, water flux through both boron nitride nanosheets was increased, but salt rejection of boron nitride nanosheet with nitrogen atoms at its pore edge, under all applied external pressure values, remain 100% which was an excellent performance because main purpose of both papers was having pure water at their permeate sides of their membranes, on the other hand, by increasing of applied pressure to the system consisted of fluorinated boron nitride nanosheet as membrane, salt rejection drop from 95% at 10 MPa to 50% at 100 MPa (see Fig. 10). In conclusion, at the 50 MPa pressure, using of fluorinated boron nitrite nanosheet could be more efficient than unfunctionalized boron nitride nanosheet because of its higher water flux and its acceptable salt rejection percentage.

Finally, this question arises that how is that possible to bring the use of nano sheets for water purification in the real-life applications? What are the barriers and challenges and what are the promising points? In response to this question is to say, the applications of nanosheets in order to water purification, need firstly experimental working on them with guidance of theoretical simulations. Successful performance of nanosheets in water purification brings this question out that what is the situation of the using of nanosheets in experimental and industrial applications. First of all, it is required to say that the MD simulation method give us an insight into what is going on in the molecular and sub-nanometer scales during a process. Knowing information about a nanosheet performance as a membrane in a theoretical study will help to a better understanding its behavior in an experimental circumstance. Fabricating a single-layer nanosheet in an experimental environment will be challenging. Conventional synthesizing manners like mechanical and chemical exfoliations are restrictions of producing. During the last decade, several new synthesizing methods have been proposed and investigations in this area are underway. Reports about synthesizing structurally well-ordered with proper thickness nanosheets from these experiments are promising. New methods for synthesizing nanosheets, like the CVD process and sputtering deposition, should be economically viable, non-toxic, and stable (Wang *et al.* 2020). Despite the results of these experimental studies, there is still much to be done. Recent experimental studies on using multi-layer nanosheets in water treatment membranes show that these nanosheets require a substrate, a polymeric composite, or a mixed matrix membrane in order to be added into them. Synthesizing multi-layer nanosheets is practicable because of uncomplicated fabrication processes (Xu *et al.* 2019). However, synthesizing and producing single-layer nanosheets which could be used as a membrane in real harsh conditions is a real challenge. Therefore, besides further investigations on new and efficient ways for synthesizing stable, scaled-up, and defect-free nanosheet, it is required to fabricate suitable support for the two-dimensional single-layer nanosheet for having a well-organized membrane module. It can be said that more theoretical and experimental data are required to fully realize and evaluate the performance of nanosheets in industrial situations. In conclusion, bringing the use of nanosheets in real-life applications requires appropriate synthesizing methods on large scale for industry usage, commercializing nanosheets synthesis and fabricating it for water treatment applications, doing more experimental studies for creating sub-nanometer pores in nanosheets, and obtaining suitable and commercialize membrane module for the nanosheet.

5. Conclusions and future prospects

Herein, we investigate the performance of functionalized membranes on the water treatment processes. The selected nanostructured membranes were included graphene, graphene oxide, and boron nitride nanosheets. We have done a comprehensive overview of the chemical structure property and application of appropriate functional groups on the membranes. The results showed that the water treatment process with the nanostructured membranes is an energy-efficient technology. In this research, some theoretical and experimental works about the separation of various species such as atoms, ions, and small molecules by the functionalized materials were investigated. The chemical groups have the most important influence in the selective separation process of ions or water molecules. It should be noted that some functional groups, in different membranes, show different behaviors. Their treatment depends on the type of pore, pore size, and even the number and the type of functional groups on the edge pore of membranes.

By considering results of the theoretical studies on the nanosheets as a membrane to separate various molecules from each other, we understand that the physical and chemical characteristics of these kinds of nanostructured materials make them reliable tools for using them soon widely in water treatment because extraordinary physical and chemical characteristics allow us to have efficient energy consumption. On the other hand, theoretical studies showed that these nanosheets could be functionalized with appropriate functional groups and turn to totally different nanosheets by considering their new chemical and physical properties. Functionalization of membranes goal is having a selective separation process by rejecting undesired molecules and welcoming desired ones. Graphene and graphene-like nanosheets do not let molecules for passing through them, so we should prepare an appropriate pore in them and for having an efficient selective separation process we could functionalized our prepared pore with functional groups. Overall, by engineering and designing unique pores in nanosheets, we could have particularly determined membranes with functionalized pores that are ready to encounter with the specific situation, because these pores are unique by considering their shapes and sizes, their charges, and interaction between functional groups passivated to the edge pores which could be led to forming a hydrogen bond between some of the molecules and thus easy passage for these molecules through functionalized pores.

As a result, functionalized nanosheets in comparison to pristine nanosheets could be considered as a new nanostructured material because of their new chemical and physical properties. Graphene and its derivatives are subjects of many types of research for using them as membranes for water desalination because the mechanical strength of these nanosheets caused to have great flux in comparison to conventional membranes. Experimental studies should be done to have stable single-layer nanosheets with functionalized pores to achieve a reliable nanotechnological approach for having efficient separation processes. Theoretical studies should classification functionalized nanosheets by considering their charge density and pore diameter for giving precise data to experimental researchers to have specific goals for synthesizing and fabricating practical functionalized graphene and graphene-like nanosheets to use them as membranes for having 100% rejection of unwanted species and passing of wanted species with large flux.

Graphene oxide because of its oxidative nature act differently from pristine graphene and this difference could be an important influence on any separation process due to the various molecules and ions interactional behavior with an oxidative surface and consequently, these interactions lead to a pure selective separation process while pristine graphene often acts inactively when confronting with molecules and ions. Also, we saw that boron nitride could have larger adsorption energy than other nanostructured materials, especially when an electric field was applied to the system contained boron nitride nanosheet as adsorbent and adsorbates because of boron and nitrogen atoms positively and negatively charged respectively and could attract charged adsorbates, consequently in a separation process unwanted ion by adsorption process could be removed from the system. Besides these facts and different natures of reviewed nanosheets, we could understand that by functionalization and engineering nanostructured materials we could prepare them for specific tasks in separation processes.

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