

GRAPHENE-BASED MEMBRANES FOR ENHANCED PERFORMANCE OF WATER PURIFICATION

BY

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In

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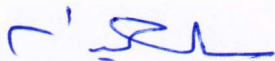
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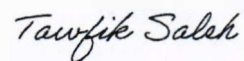
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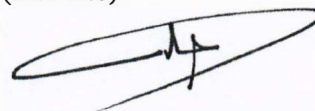
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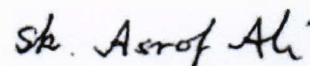
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| I dedicate my dissertation work to my parents and my wife |

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I am completely thankful to Almighty God who granted me this prestigious opportunity to be alive in good health and sound mind to accomplish this great feat if not for Him (God almighty), it would have ended in a gross failure... I am forever grateful.

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LIST OF ABBREVIATIONS

WHO : World Health Organization	1
MF Microfiltration	6
UF Ulter filtration	6
GO : Grahphene oixde	8
G-QDs : Graphene quantum dots.....	8
rGO : Reduced Graphene oixde.....	12
CIP : Ciprofloxacin	15
TC : Total carbon	18
CTC : Charge transfer complexes.....	20
OTC : Oxytetracycline.....	20
SMX : Sulfamethoxazole.....	21
SMC : Scanning electron microscopy.....	24
PRO : Retarded osmosis membrane	25
NMP : N-Methyl-2-pyrrolidone.....	25
BSA : Bovine Serum Albumin	27
TMC : 1,3,5-Benzenetricarbonyl trichloride	33
C ₁₀ H ₂₀ : Decene.....	33
C ₁₆ H ₃₄ : Hexadecane	33
C ₇ H ₈ : Toluene.....	33
HNO ₃ : Nitric acid.....	33
MgSo ₄ : Magnesium sulfate	33
MPD : phenylenediamine	33
N ₂ O ₆ Pb : Lead nitrate	33
NaCl : Sodium chloride	33
PSf : Polysulfone.....	33
CaCl ₂ ·2H ₂ O : Calcium chloride dehydrate.....	33
Ni(NO ₃) ₂ ,H ₂ O : nickel nitrate	33
Cr(NO ₃) ₃ : Chromic nitrate.....	33
DMF : Dimethylformamide	34
SOCl ₂ : Thionyl chloride	34

DTGS : Deuterated triglycine sulfate	35
EDX : Energy dispersive x-ray spectrometer	35
FESEM : Filed-emission scanning electron microscope	35
FTIR : Fourier Transform Infra-Red.....	35
HS-GCMS : Headspace Gas chromatography mass Spectrometer.....	35
XRD : X-ray diffractometer.....	35

ABSTRACT

Full Name : Ali Ibrahim Alkenani

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Water pollution from salts, organic and inorganic compounds makes the water unsuitable for use. Therefore, efficient pre-treatment and purification strategies shall be developed to simultaneously address many pollutants in water. The advancement in nanoscience and polymer science has made membrane technology a promising treatment method. This method is very effective for several applications such as purification of drinking water and treatment of wastewater. Consequently, it has received great interest. Polymer-inorganic composites-based membranes are powerful since they combine several properties such as chemical, mechanical and thermal stability. In this work, efficient membranes were prepared by integrating graphene modified with amines in polyamide of trimesoyl chloride and m-phenylenediamine. The surface structural morphology, chemical, elemental, and functional groups of the synthesized membranes were ascertained with Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray diffraction (XRD), and Fourier Transform Infra-red spectroscopy (FTIR).

The performance parameters of the newly prepared membranes including permeate flux, salt rejection, and hydrocarbons rejection were evaluated with optimization of the related experimental parameters. The proposed membranes showed high stability, high flux, salt rejection, and oil rejection. The prepared membranes showed enhanced performance high salt rejection, and about 100 % hydrocarbons rejection, and more than 96 % total removal of nickel, chromium, and lead metal ions. Due to their good performance, the prepared membranes are highly promising in practical applications. |

ملخص الرسالة

الاسم الكامل: علي ابراهيم محمد الكناني

عنوان الرسالة: الأغشية القائمة على الجرافين لتحسين الأداء في تنقية المياه

التخصص: كيمياء

تاريخ الدرجة العلمية: 2021-06

يؤدي تلوث المياه بالأملاح والمركبات العضوية وغير العضوية إلى جعل المياه غير صالحة للاستخدام. لذلك، يجب تطوير استراتيجيات المعالجة المسبقة والتنقية الفعالة لمعالجة العديد من الملوثات في الماء في وقت واحد. أدى التقدم في علم النانو وعلوم البوليمرات إلى جعل تكنولوجيا الأغشية طريقة علاج واعدة. هذه الطريقة فعالة للغاية في العديد من التطبيقات مثل تنقية مياه الشرب ومعالجة مياه الصرف الصحي. وبالتالي، فقد حظيت باهتمام كبير. تعتبر الأغشية القائمة على المركبات غير العضوية البوليمرية قوية لأنها تجمع بين العديد من الخصائص مثل الاستقرار الكيميائي والميكانيكي والحراري.

في هذا العمل تم تحضير أغشية فعالة من خلال دمج الجرافين المعدل مع الأمينات في بولي أميد من كلوريد تريميسويل و م-فينيلين ديامين. تم التحقق من التشكل الهيكلي السطحي والمجموعات الكيميائية والعنصرية والوظيفية للأغشية المركبة باستخدام المجهر الإلكتروني لمسح الانبعاث الميداني والتحليل الطيفي للأشعة السينية المشتتة للطاقة والأشعة السينية المشتتة وتحويل فورييه بالأشعة تحت الحمراء. - التحليل الطيفي الأحمر.

تم تقييم معاملات الأداء للأغشية المحضرة حديثاً بما في ذلك تدفق النفاذية، ورفض الملح، وإزالة الهيدروكربونات مع تحسين المعلمات التجريبية ذات الصلة. أظهرت الأغشية المقترحة ثباتاً عالياً وتدفقاً عالياً ورفضاً للملح ورفضاً للزيت. أظهرت الأغشية المحضرة أداءً معزراً في رفض الملح العالي، وحوالي 100% من الهيدروكربونات المستخدمة في هذه الدراسة، وأكثر من 96% من الإزالة الكلية لأيونات معدن

النكل والكروم والرصاص. نظرًا لأدائها الجيد، فإن الأغشية المحضرة ذات الثبات الممتاز والتدفق العالي

في تقنيه الماء من الاملاح والمركبات العضوية الخطرة وتعتبر من التطبيقات الواعدة للغاية في تقنية المياه

من الشوائب في التطبيقات العملية.

|

[CHAPTER 1]

INTRODUCTION

Water is essential for the survival of all living organisms. Safe and mineralized water is essential for healthy living. [1] During its mobility water carries solid suspended particles and dissolves impurities. It becomes impure and unsafe for human health due to the presence of heavy metals and imbalanced minerals. Metal contamination is due to atmospheric deposition, weathering, or release of agricultural, residential, or manufacturing runoff. Major drinking water in the world is obtained through pipes and hand pumps. According to WHO in total, there are 1400 million billion liters of water. However, most of this water is not used for drinking purposes because 97% of it is seawater and only 3% is freshwater. Out of which 2% is routed in the polar ice caps and glaciers, only 1% water is accessible for drinking purposes, whereas major water goes for irrigation than for drinking and all other use. In the present situation, only 80% of the population in case of urban areas and only 11% in case of rural areas have access to the piped water. [9] According to GWSSAR, 30% of diseases are waterborne and 40% of people die due to the unavailability of clean and safe water [2]. Many water resources are unhealthy because of imbalanced physical, chemical parameters and harmful biological agents. Due to industrialization and the unselective use of chemical fertilizers and pesticides in agriculture water becomes polluted and is hazardous for human health. Due to the use of contaminated

water, the human population is suffering from different types of water-borne diseases. The availability of pure water is an essential feature for preventing diseases and refining the quality of life.

At least 2.5 billion peoples in developing countries have a poor hygienic water system and over 780 million people have no access to safe drinking water. As a result across the world about 2.3 billion people suffering from water-related diseases. [3] Due to some important factors like increasing population, industrialization, urbanization, etc, the feasibility and quality of water either surface or ground, have been disintegrating. Many of the freshwater sources are contaminated by the use of pesticides in agricultural fields and other anthropogenic activities that completely change the physical, chemical, and biological processes related to water resources. [10]

The poor supply of water and the presence of a high concentration of chemicals may cause different diseases like goiter and cancer etc. [4] Due to lack of cleanliness and sewage treatment, improper processing, and use of dirty water many gastrointestinal illnesses being observed. [5] Dental fluorosis is caused by low or high levels of fluoride ions concentration in water. Goiter is mainly due to the low concentration of iodine in humans. [6] According to an estimate, there would be 200 million approximate cases of diarrhea and 2.1 million deaths caused by diarrheal illness each year if everyone had pure drinking water and satisfactory sanitation service. [7] Different acute and chronic health issues may cause because of toxic inorganic chemicals in water such as vomiting, nausea, dizziness, lung irritation, skin rash, and sometimes death. Cancer, birth defects, organ damage, and

some disorders of the nervous and immune systems have been reported as the chronic effect. [8]

1.1 Water pollution

The major pollutants of water are the organic and inorganic contaminants that arise from industrials, agriculture, and savages. In a recent study by Nadia and coworkers, a major factor of polluting the environment was considered to be the rapid development of the industries. Industrialization caused the rapid degradation of the ecosystem. In their study, they unveiled the water parameters and causes of pollution in Riyadh City. The city underwent rapid urbanization and industrialization in the last few decades with an increase in population and agricultural activities. Several pollution problems arise in Saudi Arabia due to the mass of industrial effluents discharged to nearby water bodies. Heavy metals were evaluated according to which the metals ranked in the order of increasing magnitude from Co to Zn as given $\text{Co} < \text{Hg} < \text{Cd} < \text{As} < \text{Ni} < \text{Cr} < \text{Pb} < \text{Cu} < \text{Zn}$. [11] The mean values from three locations in dry and wet seasons revealed the highest Cr concentration of 8.52 ppm and the lowest 0.05 ppm at different locations. The water samples were found most contaminated with the Zn with the highest concentration levels of 34.36 ppm. The water was also found contaminated with hazardous Pb, Ag, and Hg up to 8, 6, 2.1, and 1.1 ppm respectively. These values were too high than the standard permissible value of discharge effluents according to WHO that were 5, 0.04, and 0.002 ppm for Pb, As and Hg respectively. [11]

1.2 Water Treatment and purification

The process of removal of contaminants, particles, organic and inorganic materials, and biological agents from water is termed water purification. It involves both distillation and deionization. [18] The primary objective of the purification is to provide drinkable water to the mass of the population. It further meets the requirement of pharmaceutical, industrial, medical and chemical applications. In the process of purification contaminants being removed completely or it may reduce the concentration of contaminants such as the suspended particles, algae, fungi, and microbes. The purification process could be established domestically at a small level or on a large scale for the city.

Most water is treated at the plants specially established for water treatment in industrialized countries. These plants complied with the general regulation of national and international standards. In general, at the water treatment plants wastewater is treated chemical, physically, and biologically which is referred to as pretreatment. Chemical methods involve several mechanisms such as ion exchange, oxidation, and hydrolysis, etc as outlined in Figure 1. Water treatment and purification process below. The refinement is carried out after the pretreatment process. In the process of coagulation, chemicals are added that aggregate the suspended particles are soluble pollutants that can easily be settled on the bottom of the tanks. [16]

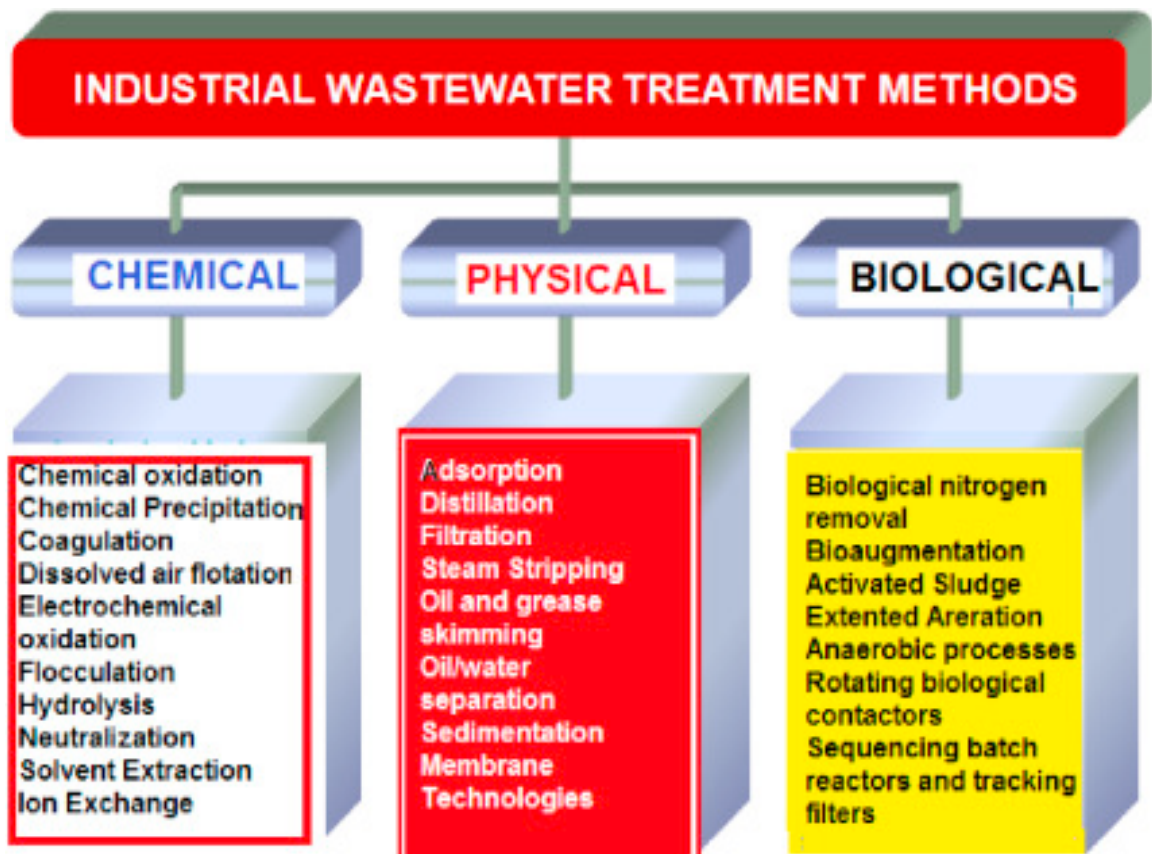


Figure 1. Water treatment and purification process

1.2.1 Water purification membranes

Several types of water filtration membranes have been employed for water purification. These membranes differ based on their pore size. The membranes allow the passage of certain species across it either passively or through active transport depending on the physical or chemical properties of species. The membranes can be classified into isotropic and anisotropic depending on their homogeneity. Isotropic membranes have homogenous in their chemical composition whereas the anisotropic ones are chemically heterogeneous as outlined in Figure 2 below. [17] The isotropic membranes could be microporous, nonporous, or electrically charged membranes. The pore diameter of the microporous membranes is in the range of 0.1 to 5 micrometers. These separate the solute particles based on the differences in size. They are just like commonly used filters. These membranes could be polymer-backed track-etched, stretched films of polymers or phase inversions.

The anisotropic membranes are of two types which are composite membranes and phase separation membranes. They could be coated films, thick films, or self-assembled structures. [18] The porosity and the pore size of the phase separation membranes vary across the thickness of the membrane. Its development began in early 1960 that brought breakthroughs the membrane technology. Composite membranes are heterogeneous that are made of different materials of polymers.

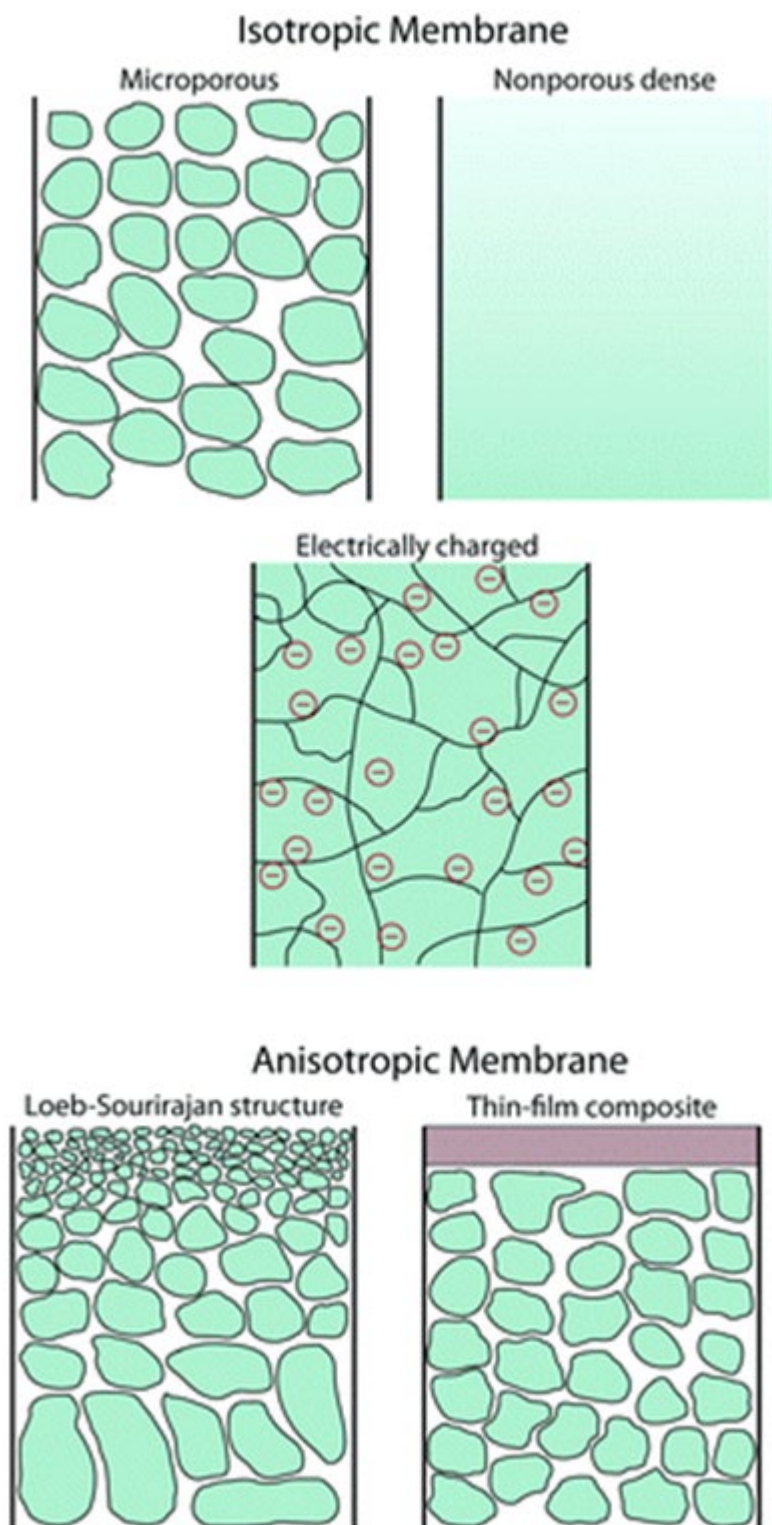


Figure 2. Homogeneous and heterogeneous membranes [17]

The various types of membranes used for the purification and treatment of water with varying pore sizes include nanofiltration, microfiltration, ultrafiltration and reverse osmosis. Each membrane separates different parts based on their size as demonstrated in Figure 3. The reverse osmosis membranes are considered non-porous because the pores are so dense only allowing the transportation of metal ions

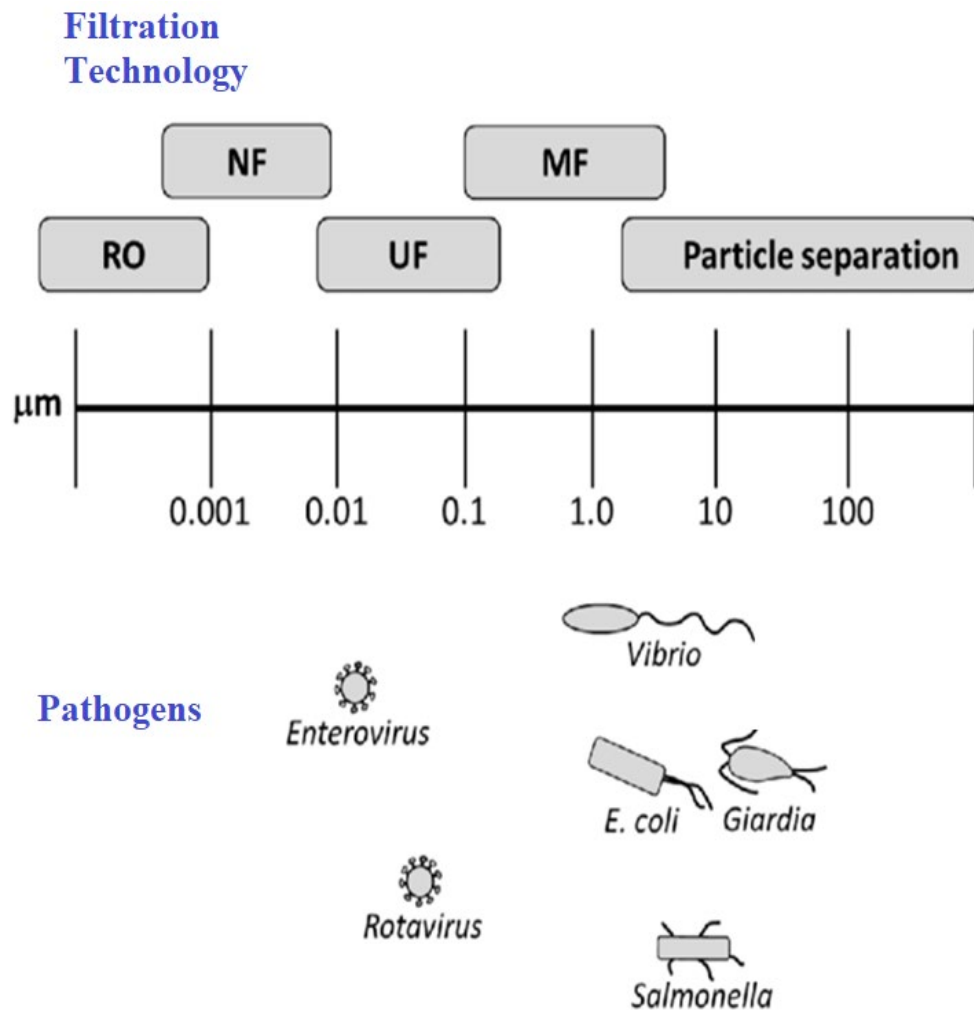


Figure 3. Membrane filtration spectrum [18]

MF and UF have large pores with the size of 0.1 to 5 micrometers approximately. These allow the passage of small molecules. UF can filter large biomolecules, proteins, viruses, and pathogens. The UF has various other applications such as the separation of proteins from biological fluids, surfactants in industrial cleaning. [20]

Several materials have been used for membrane design and fabrication. Among the inorganic materials, porous ceramics such as Al_2O_3 , ZnO_2 , SO_2 , and TiO_2 membranes were introduced. Further various composite materials were also employed for the designing of purification membranes e.g. TiO_2 - SiO_2 and Al_2O_3 - SiC etc. [21]

1.3 Graphene

Graphene is an allotrope of carbon that is a million times thinner than human hair, but 200 times stronger than steel. In general, carbon has five allotropes namely diamond, graphite, graphene, carbon nanotubes, and Buckyballs. These may take the form of the hollow sphere, ellipsoids, or tubes in nano-scale. The diamond and graphite are three-dimensional (3D) materials, graphene is two-dimensional (2D), carbon nanotubes are one-dimensional (1D) and Buckyballs are zero-dimensional (0D) materials. Graphene is 2D in the sense that it can conduct electrons in two dimensions but one direction is confined. It is crystalline and transparent material with hexagonal patterns. Graphene is considered as the basic element of other carbon allotropes like graphite, Buckyballs, and carbon nanotubes. It is called the mother of all carbon nano-materials because it can be transformed into other allotropic forms. Such as the stacking of carbon nano-sheets forms the

graphite. Carbon nanotubes can form through the rapping of the graphene sheets, and the rolling results in the formation of fullerenes. [12]

The single-layered graphene was theoretically unveiled by P. R Wallace. It was first isolated in 2004 at the University of Manchester by Prof. Kostya Novoselov and Prof. Andre Geim. For this pioneered work they received Noble Prize in physics. However, the experimental discovery of graphene was credited to Hanns-Peter-Boehm and his coworker who discovered it in 1962. [13] Boehm and their coworkers introduced the term graphene in 1986. [14]. The epitaxial layers were grown on the surface of the materials in 1970. The films were also obtained from the graphite and soot of chemical exfoliation. However, thinner than 50 to 100 layers produced after 2004.

Structurally, graphene is one carbon-thick planner sheet of hexagonal rings forming a densely packed honeycomb-like crystal lattice. The carbon atoms are sp^2 hybridized. It contains alternate single and double bonds just like benzene rings. Although graphene is composed of packed rings still it is non-fluorescent due to zero optical band gaps. Its surface area is the larger one among the known materials. It can be stretched like rubber. Although there are alternate single and double bonds. However, the C-C bond length of 0.142 nm.

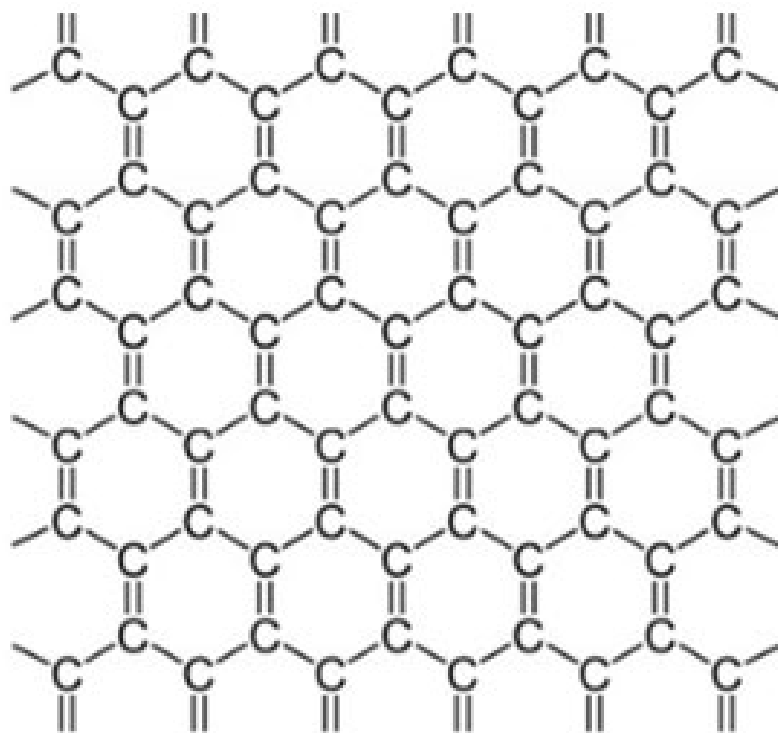


Figure 4. Graphene its chemical structure and skeleton

The graphene-based nano-materials include graphene, graphene oxide, graphene quantum dots, and reduced graphene oxide. Graphene its self composed of sp^2 hybridized carbon atoms however, due to the addition of functional groups the graphene-based materials such as graphene oxide (GO), graphene quantum dots (G-QDs), and rGOs comprised of a mixture of sp^2 and sp^3 hybridized carbon atoms.

The surface of graphene is functionalized with oxygen to form graphene oxide and GO is rich in oxygen-containing moieties. The partial reduction of the GO results in the formation of rGO. Both GO and GQs are inexpensive and compatible with biological applications due to water solubility, photostability, and environment friendly. [15]

1.3.1 Graphene oxide membranes

Graphene-based materials are the most advanced materials employed for membrane technology. Graphene oxide is the most common among other graphene-based materials. The surface of the GO is functionalized with various groups such as hydroxyl, carboxyl, epoxy, and carbonyl groups that made it hydrophilic. The stability, physicochemical properties, and porosity of GO make it a promising material to be used for the purification of water. [23] The water passed through the sheets of the GO layers leave behind several contaminants and becomes purified. Several modified GO-based membranes have been reported with ultrafiltration performance such as silane-modified on ceramic support with better adhesion of GO membranes etc. [24]

It was observed that from a mixture of ethanol and water the concentration enhancement of 30,92 wt% from 5 wt%, which is an indication of better performance of

small molecule separation. One of the properties of the GO membranes is the controlled ion transport where ions (KCl , FeCl_3 , etc) transport can be controlled by electro and magneto control systems. The migration of ions can be influenced by the applied electric and magnetic fields. The electric fields can further be used for the selective migration of ions through the GO membrane. Hence through several structural modifications, graphene oxide membranes with better per

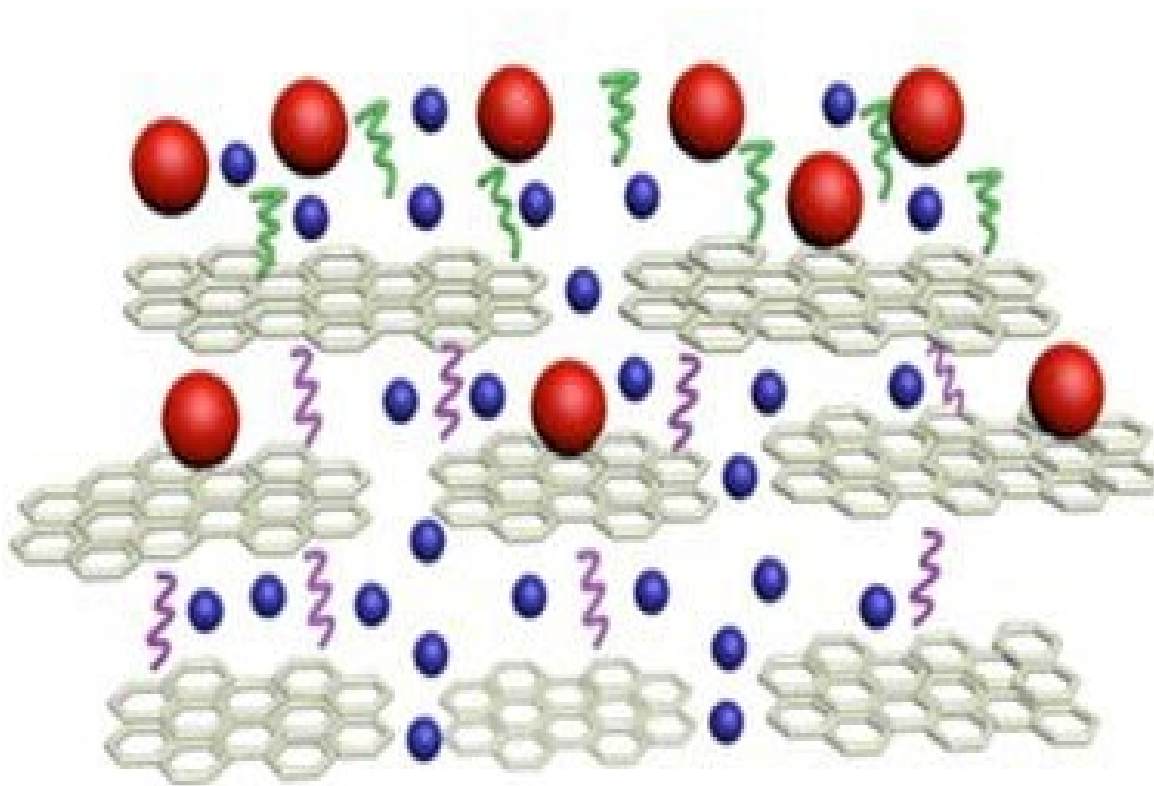


Figure 5. A multilayered graphene membrane.

1.4 Statement of Problem

Industrial wastewater is increasing and its reuse is highly recommended. Therefore, there is a need for wastewater treatment. Membrane technology is one of the most important methods for such treatment. The polymeric membrane has long been a promising methodology with a huge potential to develop the efficacy of water desalination and wastewater desalination. Nevertheless, the development of polymeric membranes with high permeates flux and ion rejection continued to remain the main challenge to researchers. Modification of polymeric membrane by graphene oxides is expected to enhance water purification.

1.5 Objectives

This research work aims to formulate nanomaterials that can be incorporated into polymeric membranes for application in water purification. The specific objectives are:

1. To synthesize graphene oxide from graphite.
2. To embedded graphene oxide in membranes
3. To test the membranes for water purification using Sterlitech Membrane Testing Instrument; cross-section system. Operational conditions and parameters including permeate flux, temperature, initial concentration, and salt rejection will be optimized
4. To evaluate the performance of the modified membrane in terms of permeate flux and ion rejection

CHAPTER 2 |

| LITERATURE REVIEW

2.1 Graphene and Graphene oxide-based membranes for antibiotic removal from water

The water pollutants are of a wide range. One of them is antibiotics. Due to the extensive applications and usage of antibiotics, these contaminate water. To remove the antibiotics from the water some strategies have been used based on the photocatalysis and adsorption of the pollutants. Graphene and its derivatives such as graphene oxides have been extensively used for the purification of water through the photocatalytic and adsorption-based removal of contaminants due to their unique structure and properties. These materials can degrade the antibiotics as well can be adsorbed on the surface that are the key mechanisms for the purification processes. Graphene as the thinnest material has a large surface area of 2630 m²/g. Its surface is rich in π -structures due to hexagonal rings of carbon with alternate single and double bonds. Its adsorption efficiency mainly depends on the π -structure.

Several organic pollutants can be adsorbed on the surface of graphene and its derivatives through the π - π stacking and van der Waal interactions. Several antibiotics such as glycopeptides, macrolides, quinolones, and aminoglycosides tend to be adsorbed on the graphene layers through π - π interactions because these compounds

possess aromatic rings such as piperazine units and morpholine groups. A problem encountered with graphene is its agglomeration in the aqueous media that becomes a problem with the limited capacity of adsorption and low efficiency of separation. Hence, it is required to functionalize the surface of the graphene with various functional groups such as hydroxyls, carbonyls, carboxylic acids, sulfonic groups, etc. Furthermore the self-aggregation of graphene losses its catalytic activity. [25]. The functionalization and structural modification of graphene also enhance the catalytic activity. Hence several materials have been synthesized by the modification and functionalization of graphene as outlined in Figure 6 [25].

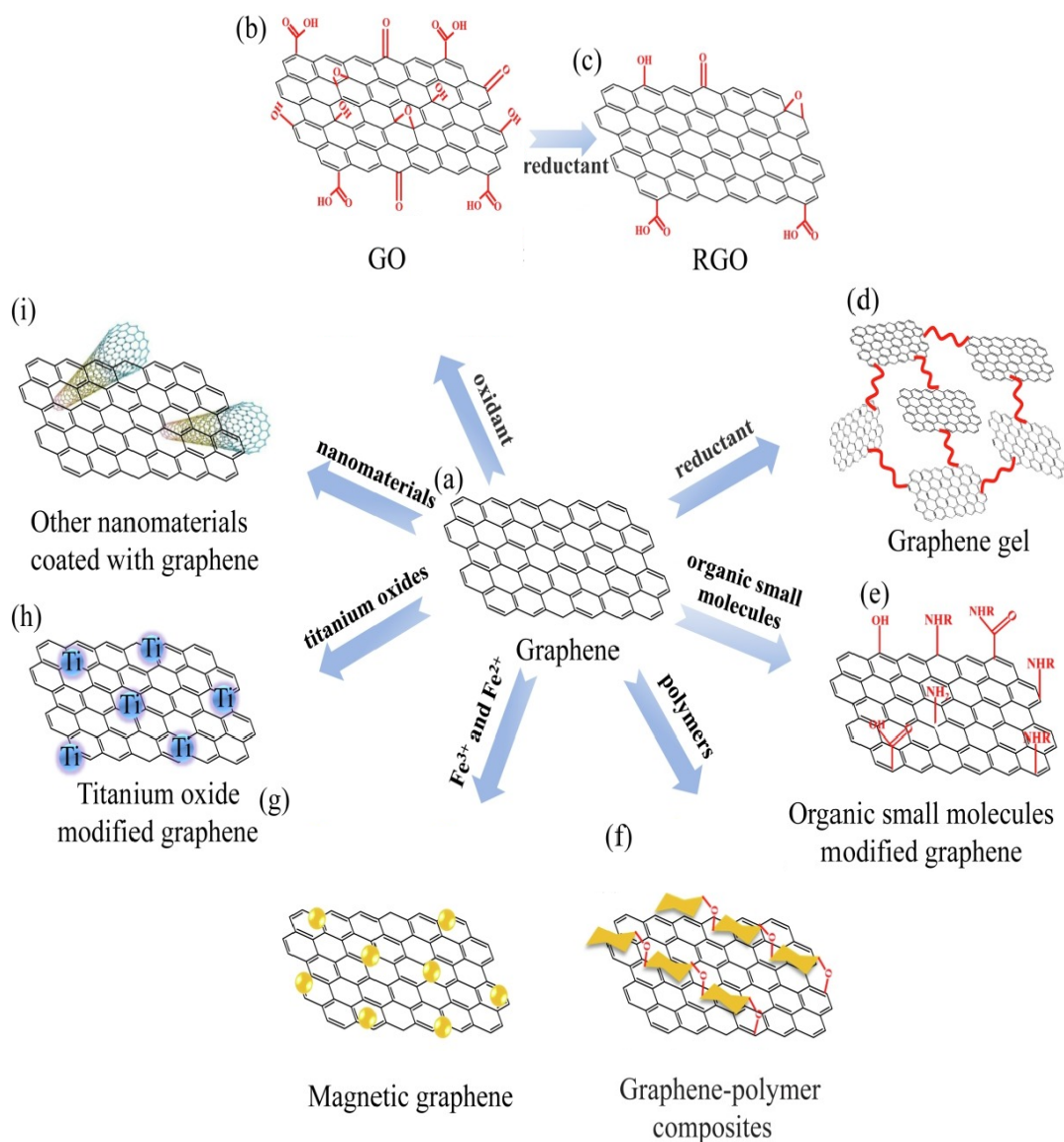


Figure 6. A schematic outline of the graphene derivatization for the formation of the GO, RGO, graphene gel, organic small molecules modified graphenes, and G-polymer composites [25]

2.2 Graphene and graphene oxide-based membrane Absorbents

As absorbent graphene possesses excellent potential as a purifier for the removal of antibiotic wastes from the water. The high porosity and greatest surface area of the graphene make it an ideal candidate as an adsorbent than the traditional ones due to surface reactions and faster diffusion of antibiotics. Several GO and rGO has been prepared from the graphene to enhance adsorption properties. Such materials have been prepared by Chen and coworkers for the adoption of sulfamethoxazole and ciproflaxine with a maximum sorption capacity of 240 and 379 mg/g respectively at pH 5.0. [28] Further, the graphene oxide membranes have been prepared for the removal of tetracycline from water through pi-pi interactions. [29] Based on these literature reports it is clear that GO and rGO have high potential as adsorbents for the removal of antibiotic contaminants from water.

The poor solubility and aggregation phenomenon of 2D graphene limits its applications for the removal of antibiotic contaminants from water. However, this problem has been encountered by the design and synthesis of three-dimension graphene materials. These are macroscopic in structure and prevent the stacking and aggregation of graphene layers. These 3D graphene materials have been categorized into hydrogels and aerogels. The 3D network structure of these materials enables them to be used as antibiotics adsorbents. The most commonly used preparation method of 3D graphene materials is the addition of reductants in hot water. This method is simple and operation requires a short time and low cost. Some researchers employed small molecular organic materials to load on the graphene and GO surfaces to prepare exfoliated sheets of modified graphene. These small molecular groups enhance the adsorption sites on the surface of the graphene for the antibiotics. Several mechanisms for the adsorption of

antibiotics on graphene materials have been reported which include noncovalent interactions such as hydrogen bonding, pi-pi interactions, cation pi-bonding, electrostatic interactions, amidation reactions, hydrophobic interactions, pore filling, and ion exchange mechanisms as outline in the Figure 7 below.

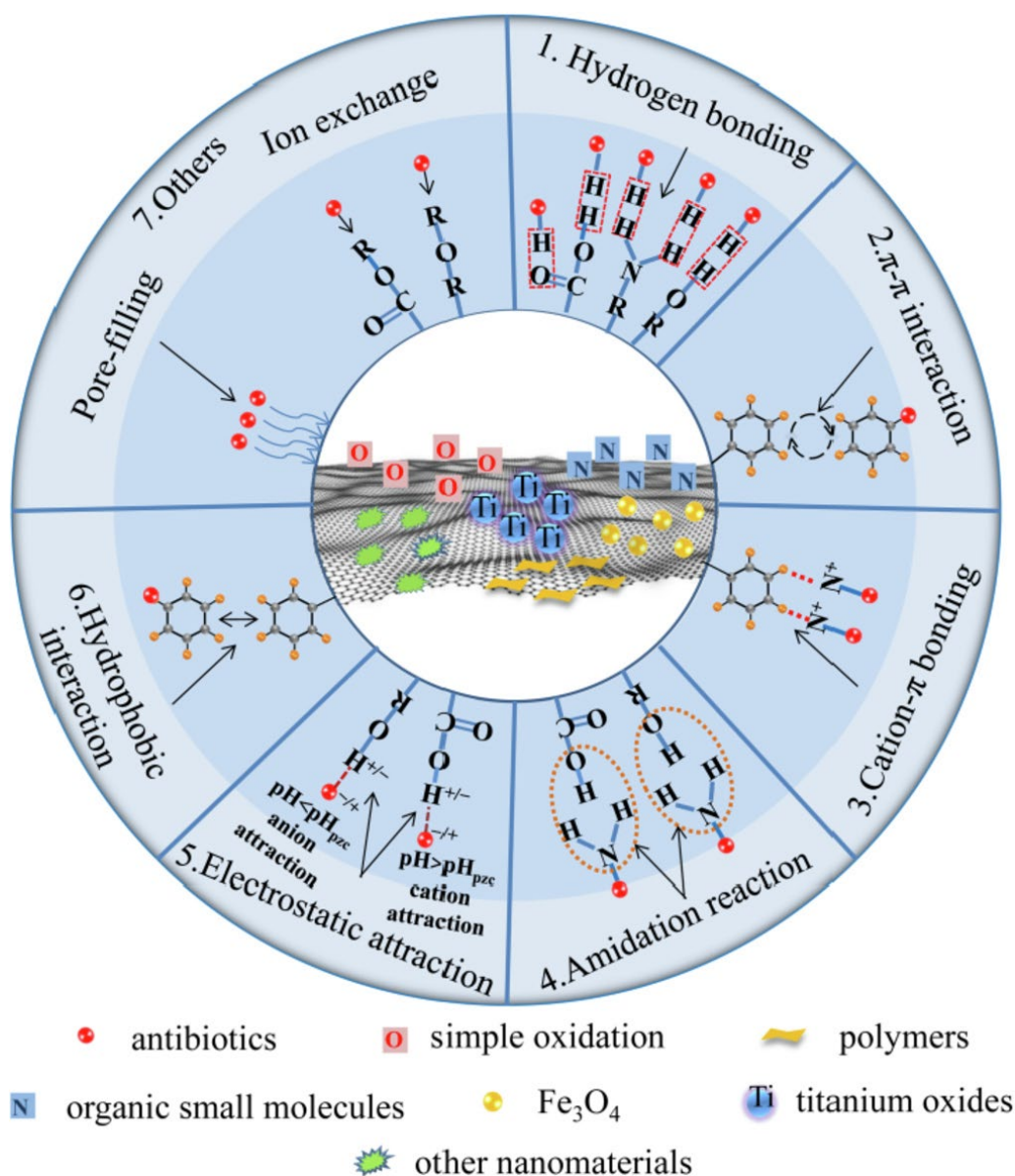


Figure 7. A schematic for the removal of antibiotics on graphene-based materials.

2.3 Photocatalytic Degradation of Antibiotic Removal

Besides adsorption, an alternate way of removing antibiotic contaminations from the wastewater is photocatalytic degradation. In this process, active photocatalysts are used to break down and degrade the antibiotic pollutants into non-toxic small molecules under the action of active groups produced by the light sources, such as sunlight, ordinary visible light, or UV radiations, etc. Graphene requires a low cost for large-scale production and its optical band gap is narrow which makes the graphene materials as the best photocatalyst for antibiotic degradation. [30]

To improve the capacity of degradation of antibiotic pollutants, several attempts have been made to design and fabricate the graphene-based photocatalyst. These include single semiconductors, metal-doped single semiconductors, and coupled semiconductors, etc.

Several types of organic frameworks and metal compounds such as titanium oxide, zinc oxide, bismuth-based oxides, silver phosphate, tungsten oxide, and MIL-68(In)-NH₂ have been employed for the construction of photocatalytic devices for the photodegradation of pollutants. [31]. However, these inorganic and organic frameworks encounter several issues such as low efficiency of catalytic conversion, photobleaching, and photo-corrosion, the poor performance of adsorption, and low separation efficiencies. These issues hinder the applications of these materials in photocatalytic degradation. Among the photocatalyst, titanium oxide is being widely used for the degradation of antibiotics and other bioorganic and organic pollutants. It has the highest photocatalytic activity and oxide of the materials with strong potential. Furthermore, titanium oxide is the

transparent material in the visible region. Despite this, they encounter several disadvantages as mentioned before.

The disadvantages encountered by the metal oxide-based photocatalyst can be overcome by the improved semiconductors constructed on the nanosheets of graphene. The large specific area of the graphene-based membranes riched with several surfaced functional groups enhances the photocatalytic properties and improves the adsorption efficiency. One another advantage of graphene-based materials is that they prolong the electron transfer and accelerate the operation of electron-hole pairs through photon absorption [32].

2.4 GO/Bi₂WO₆ For CIP Removal from Water

Li and their coworkers synthesized a composite material using reduced graphene oxide and Bi₂WO₆. This material has been used for the removal of CIP from water through photon stimulation using visible light as a source. In their work, they unveiled the excellent photocatalytic properties of the material. RGO/BiWO₆ exhibited a photocatalytic degradation rate of about 89.2% for the degradation of CIP. The higher rate of degradation is due to the RGO loading capacity, increased adsorption on the surface, enhancement in the catalytic sites, and the reduction in the rate of electron-hole recombination. The conduction band electrons and valance band holes of BiWO₆ serve as the electron-hole pair. When the composite is irradiated with visible light the electron from the conduction band of BiO₂WO₆ promotes the reduced GO. This results in the lifetime of the pair of electron-hole pair extend. [32] These excited electrons simultaneously undergo a quick reaction with the oxygen to produce oxygen-free radicals in the photodegradation system. The electron-hole pairs and the newly produced oxygen-free radicals undergo further

reaction with water molecules to degrade the CIP as demonstrated in Figure 8 below. This study revealed that the composite material of Bi_2WO_6 and reduced graphene oxide show excellent photocatalytic activity through accelerating the separation of electron-hole pair induced by photons, and higher electrical conductivity. Thus it is enhancing the efficacy of CIP degradation.

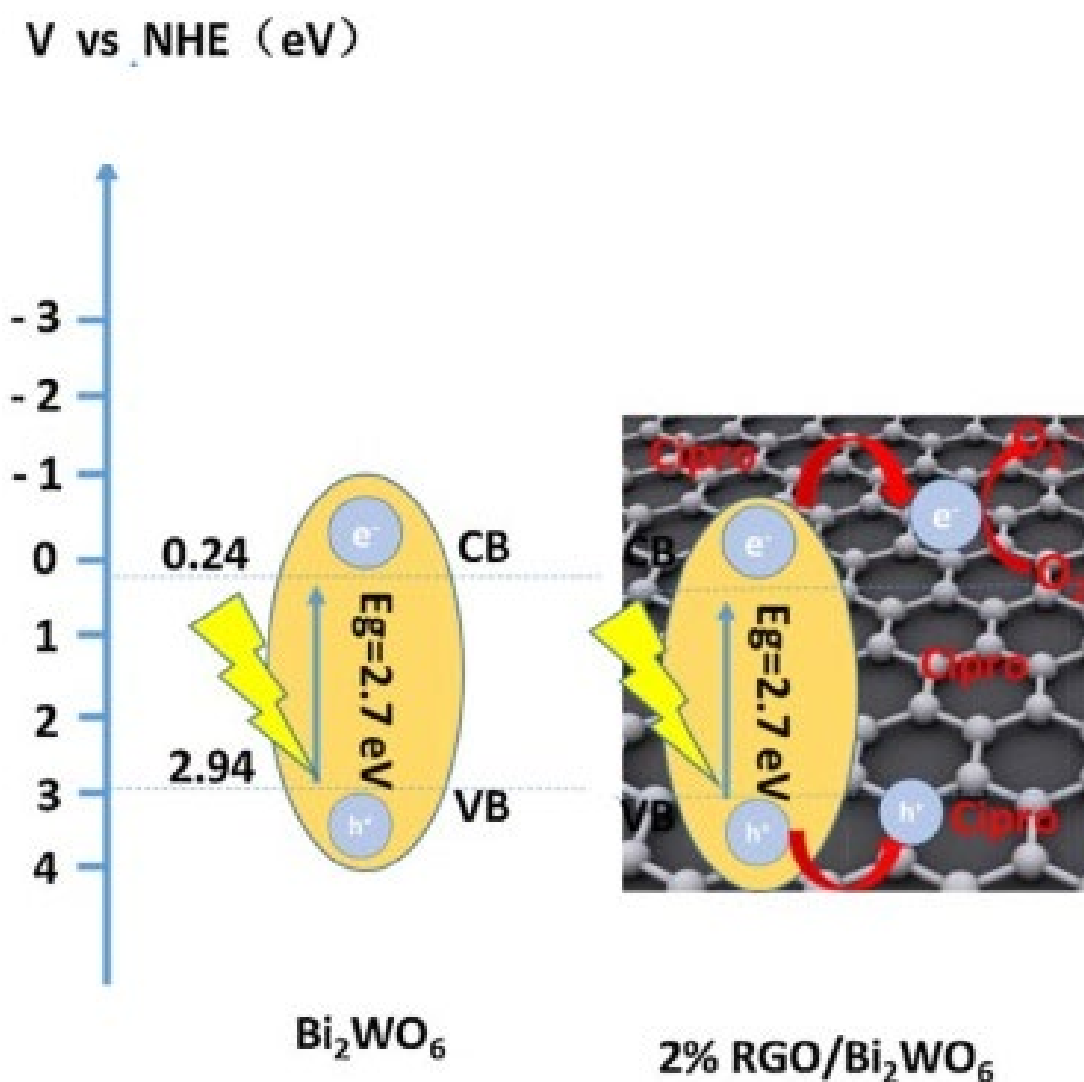


Figure 8. The mechanism of photocatalytic reaction by RGO/ Bi_2WO_6 composites [32].

In the past few decades, composite materials bring great advancement and improvement in the performance of photodegradation of pollutants through charge separation, active sites, surface area enhancement, and photostability, and electrons transfer mechanisms for the removal of antibiotics contaminations. Hence the modification in the design and fabrication of the graphene-based photocatalyst is an explicit way to improve the photocatalytic activity of graphene.

In a similar consequence of composite materials development, Anirudhan and his coworkers designed and prepared a new zinc oxide doped graphene oxide/nano-cellulose material (ZnO-GO/NS). This material has been employed for the degradation of CIP. The bandgap energy found for the ZnO was 3.37 eV and UV radiation is required for the irradiation because this is a wide bandgap. A change in the bandgap from a wide range to the value of 2.4 eV was found on the introduction of ZnO in GO. This enables irradiation in the visible region. When the composite is bonded with the cellulose the surface area of the newly designed material (ZnO-GO/NC) increased along with the increase in the porosity. An increase in the bandgap value was found to be 2.8 eV.

The conduction holes and valence band electrons formed in the composite material of CIP-ZnO-NC on irradiation with the light in the visible range. These further produce the singlet oxygen or oxygen radicals by reacting with oxygen and produce hydroxyls in reaction with oxygen. These highly reactive oxygen species degrade the CIP molecules through oxidation or reduction. After the degradations, the generated electrons trap at the defect sites and prevent the recombination of charge carriers as demonstrated in Figure 9. The efficiency of the degradation increased to 98% on irradiation with visible light. This

increased efficiency is due to the enhanced photocatalytic activity due to the incorporation of ZnO that triggers the electron transfer between ZnO-GO/NC and CIP in visible light.

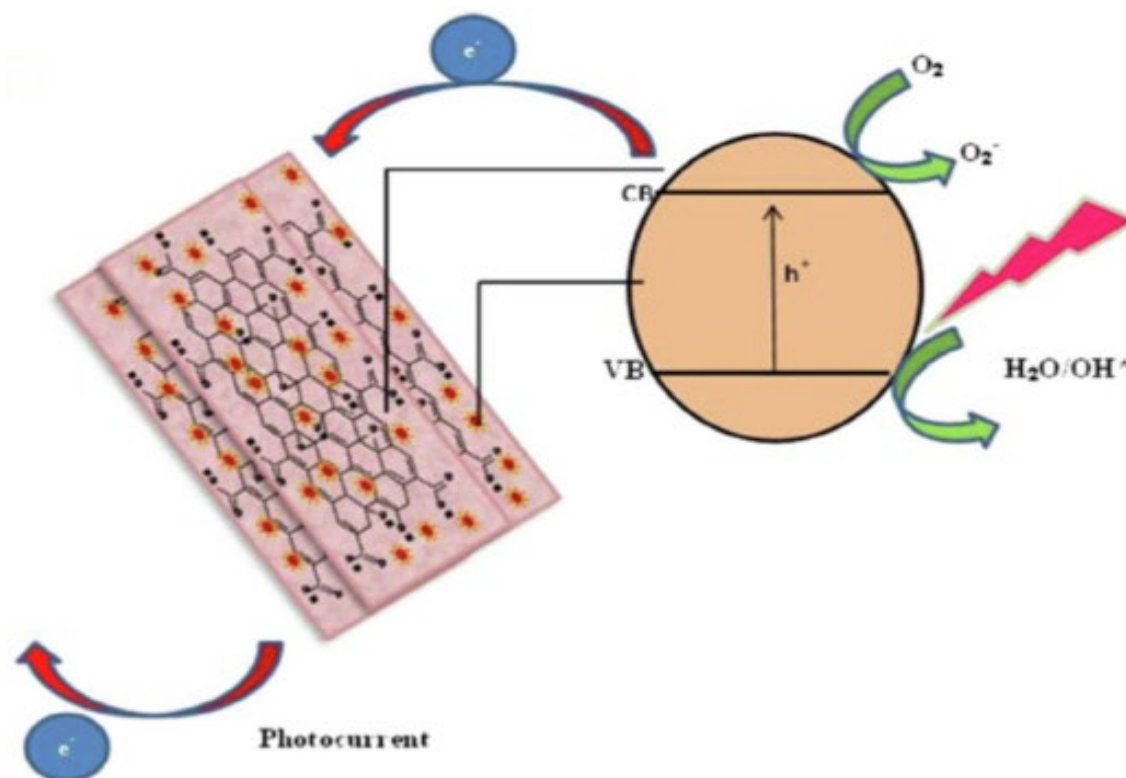


Figure 9. The reaction mechanism for the degradation of antibiotics on ZnO-GO/NC and CIP. [33]

Chen together with his team prepared a composite material of silver phosphate, bismuth vanadium oxide, and reduced graphene oxide ($\text{Ag}_3\text{PO}_4/\text{BiVO}_4/\text{RGO}$) to employ as a photocatalyst for the removal of TC from water. On irradiation with visible light, the catalyst revealed the photocatalytic efficiency of 90% for the removal of TC as demonstrated in Figure 10. This catalytic efficacy was far greater and much improved than that of BiVO_4 which was 56% and for $\text{Ag}_3\text{PO}_4/\text{BiVO}_4$ the efficiency was reported to be 82% and that for RGO/BiVO_4 was 78%. The coupled semiconductors' performance in

terms of photocatalytic efficiency and photodegradation ability is much better and improved than the single semiconductors and graphene composites. The improvement in the performance suggests developing new coupled semiconductor/graphenes composite photocatalysts for the degradation and removal of antibiotics from water. The studies are needed to explore the mechanism of interaction between the constituents of the photocatalytic system to understand the mechanism of degradation.

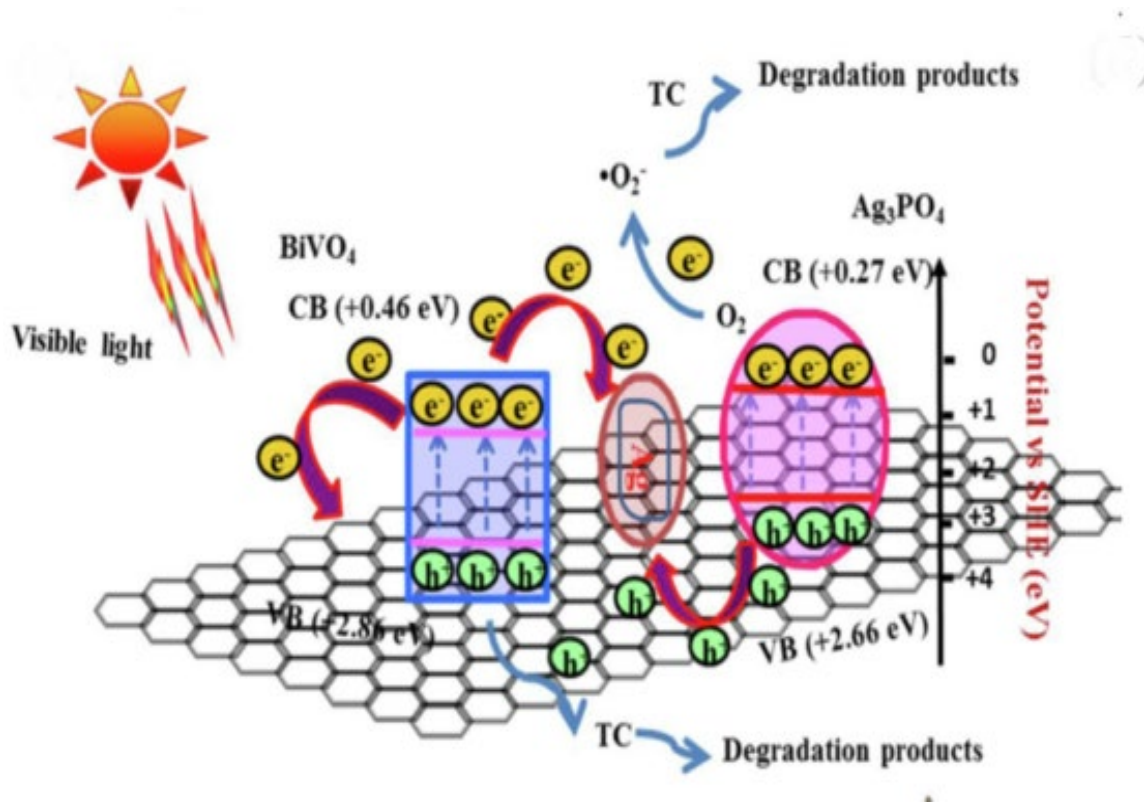


Figure 10. A schematic illustration of the process and mechanism of photocatalytic degradation of antibiotic TC at the surface of $\text{Ag}_3\text{PO}_4/\text{BiVO}_4/\text{RGO}$ on irradiation of Visible light.

2.5 Nanoparticles Doping in Graphene Oxide Membranes

One another approach to enhance photocatalytic performance is the doping metal nanoparticles that reduced the rate of recombination for photogenerated electrons and holes. Such as the doping of gold, platinum, nickel, and silver on the catalyst surface. A recent study revealed that TiO₂ decorated with Pt on the graphene oxide aerogel (TiO₂-NS/Pt/GO) exhibited the enhanced performance of photocatalytic degradation under the irradiation with visible light for CTC. The performance is far better than that of TiO₂ and TiO₂/GO aerogel for pristine. Furthermore the coupling of TiO₂ and platinum further improve the response of TiO₂-NS/Pt/GO aerogel on the irradiation with visible light. [38]

It is revealed in further studies that the doping of silver could improve the electron transfer capability from Ag₃PO₄ to graphene. It enhances the photocatalytic stability of Ag₃PO₄ to hinder the electron-hole pair recombination. A new type of Z-scheme heterojunction has been designed by reducing the silver on the surface of Ag₃PO₄/BiVO₄/RGO. [25] The electrons induced by the photon triggering of BiVO₄ and holes by Ag₃PO₄ would quickly transfer to silver. Some of the electrons generated by the photon are transferred to RGO from BiVO₄ and stored on RGO. This process promoted the charge separation to a greater extend. Hu and his team synthesized a TiO₂ loaded zeolite and graphene-based composite material for the degradation of OTC as demonstrated in Figure 11. It was reported in their study that the zeolite was the porous material with a pore size of 2.4 nm so-called small ZSM-5. It further has a large surface area revealing higher adsorption capacity for OTC. Furthermore, fast intramolecular transfer was revealed by the small predried mesoporous ZSM-5 channels.

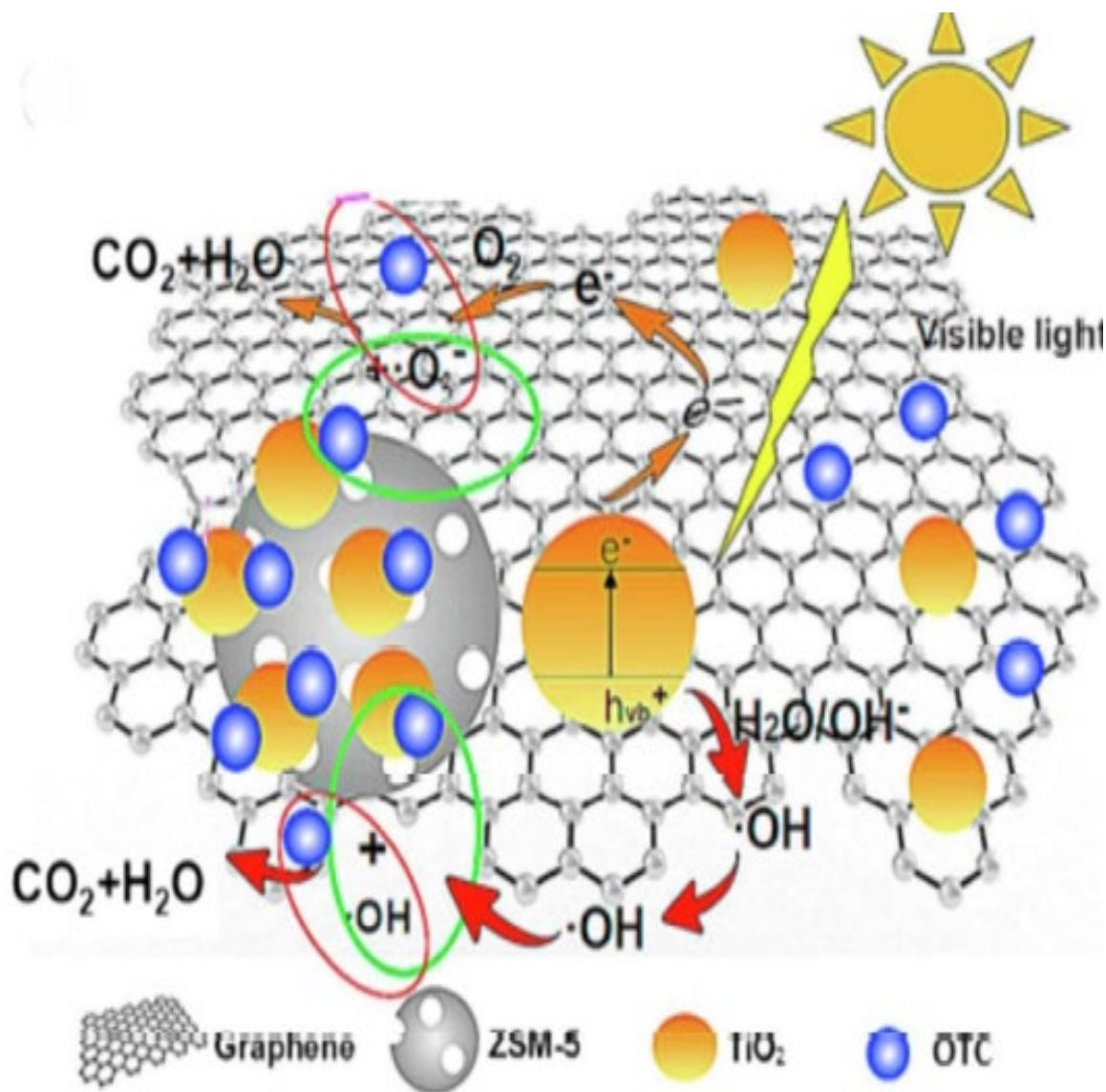


Figure 11. A schematic illustration of TiO₂/GO composite for the degradation of OTC through the photon-induced electron transfer process

The efficiency of photocatalytic degradation of antibiotic pollutants mainly depends on the light source and its intensity being used for the irradiation. The commonly used light sources for the degradation of antibiotics are sunlight, UV, Visible light, and simulated sunlight sources. Lin and coworkers studied the light source effects on the efficiency of degradation. For this purpose, they used two types of light sources that are

UV and visible light for the degradation of SMX employing a composite photocatalytic material of TiO₂-RGO. It was observed that as compared to the visible light the rate of photon utilization of SMX improved dominantly on the irradiation of TiO₂-RGO with UV light source. The rate of recombination of photoexcited electron-hole pair was reduced which was assumed to be the reason for enhancement in the efficiency of photocatalysis by TiO₂-RGO. Besides the type of light, the intensity of the light also revealed a great influence on the efficiency of photodegradation. The higher rate of degradation of the antibiotic contaminants was reported in the higher intensity of light. Some reports have been found that revealed the effect of conditions of irradiation on the photodegradation processes.

Several mechanisms for the photocatalytic degradation of antibiotics by the graphene-based photocatalyst have been proposed as outlined in Figure 12. When the graphene-based composite material is irradiated with the source of light the electron-hole pairs are separated on the surface of graphene with graphene nanomaterials. The electrons from the valence band are excited to the conduction band with the hole formed in the valence band. These free electrons are available in the conduction band of the graphite material transformed to graphene. [32] These electrons are reacting with the triplet oxygen and produce oxygen free radicals which participate in the degradation of antibiotic contaminants.

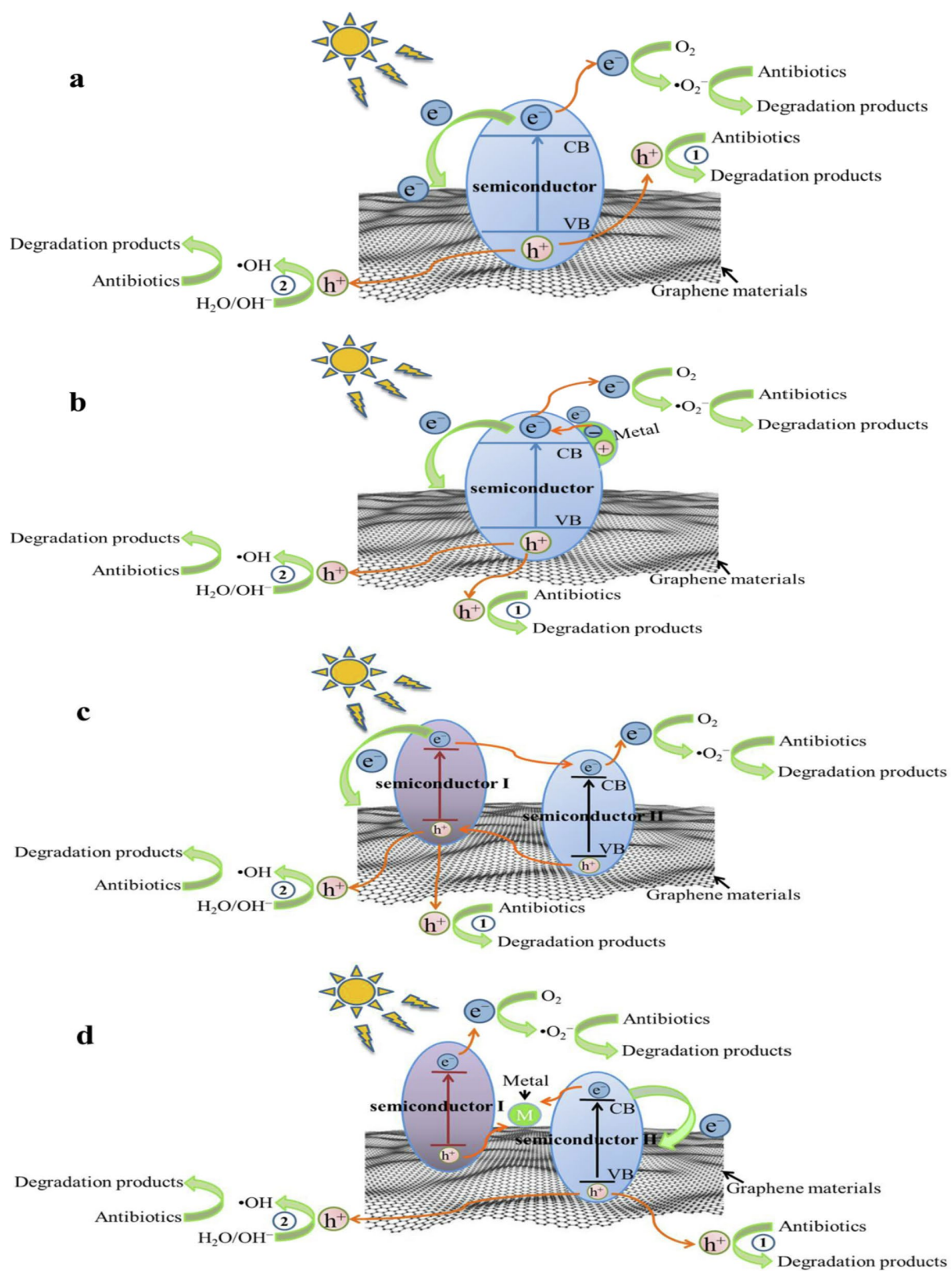


Figure 12. The pictorial representation of the mechanisms obeys by the graphene-based materials for photodegradation of antibiotics

2.6 Ti-GO Incorporated polyamide Membranes for Water Purification

In water treatment and purification plants, membrane-based separation techniques are widely used to obtain drinkable and deionized water. One among such membranes is the reverse osmosis membranes formed by the composites of polymers inorganic materials. These membranes have unique photophysical and mechanical properties such as chemical and thermal stability, flexibility, and processability like that of organic polymers. In this context, modified membranes with aromatic polyamide surfaces that were doped with the TiO_2 and GO composite have been prepared that revealed the enhanced performance of salt rejection and filtration. The protocol of the membrane includes the polymerization of 1,3,5 benzene tricarboxylic chloride, phenylenediamine, and TiO_2 -GO composite on the surface of the polysulfone porous support. The structure of the membrane was characterized by FTIR, X-ray diffraction technique, and X-ray photoelectron spectroscopy.

The structural characterization confirmed the surface of the membrane was riched with TiO_2 -GO composite. The surface morphology was unveiled further by using scanning electron microscopy (SMC) that exhibited the smooth surface of the modified membrane. The membrane performance for the salt and oil rejection was found enhanced with the incorporation of TiO_2 -GO composite on the matrix of the membrane. The salt rejection efficiency was reported to be 97% and hydrocarbon rejection was noticed at 100%. This higher rejection performance was due to the change in roughness, charge, and hydrophilicity of the membrane surface. The parameters of filtration for the membrane were evaluated at STP conditions. The outline of the membrane filtration system has been demonstrated in Figure 13.

The system has a membrane cell that has an area of 35 cm². Teflon and stainless steel tubes have been used to connect the cell with the feed tank and pump. The water flux has been recorded after compacting the membranes with different coatings in five-liter of deionized water for three hours at the pressure of 10 bar. The salt rejection performance was monitored by adding 2000 ppm NaCl and 1500 ppm Na₂SO₄. [26]

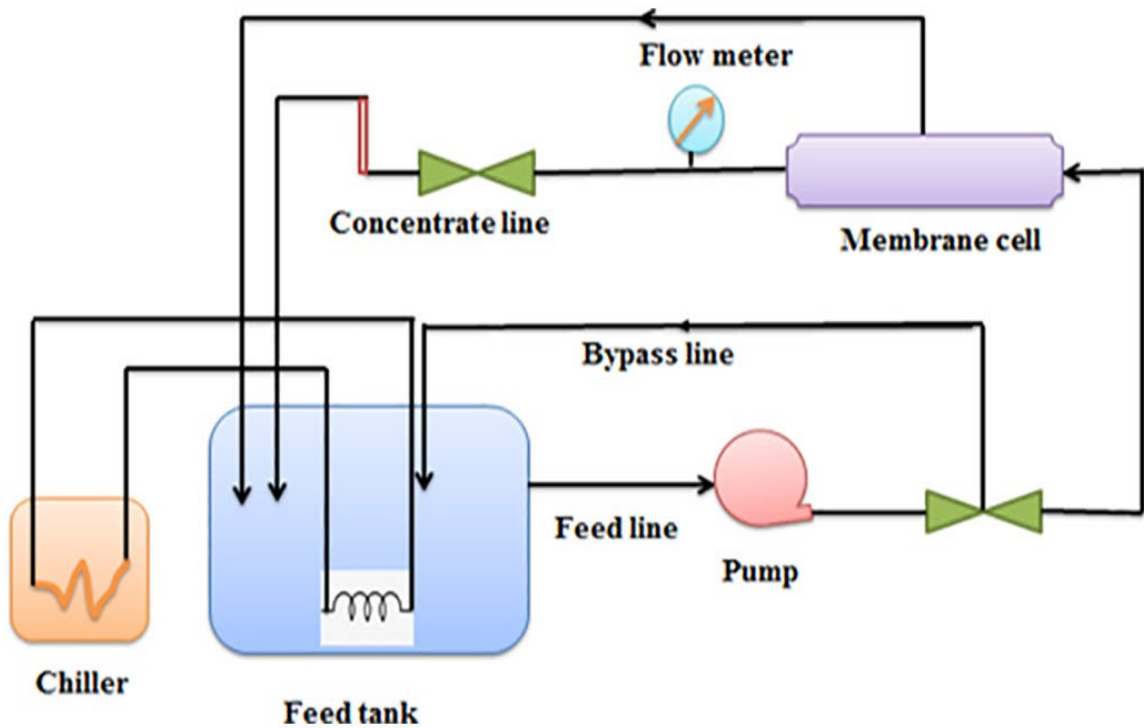


Figure 13. A schematic representation of the lab-scale strip of membrane filtration system for water purification. [26]

2.7 Retarded Osmosis membrane Based on GO-Polysulfone.

As a consequence of membrane development pressure, retarded osmosis membrane (PRO) of GO incorporated on the substrate of polysulfone has been designed and fabricated that revealed enhancement in the generation of osmotic power. For this reason, numerous

membranes have been fabricated with different percentage compositions of GO using the method of phase inversion. For pore formation polyethylene glycol has been used as a pore-forming agent. Among the various compositions, the membrane with TFN-0.25 GO exhibited the highest water flux, increased porosity, and microvoids morphology as compared to the membranes taken as control. TFN-0.25 revealed the highest power density of 8.36 Wm^2 at the pressure of 15 bar. The mechanical and intrinsic properties of the membrane have been drastically improved by the incorporation of graphene oxide on the matrix of the polymer.

The method of non-solvent-induced phase separation has been adapted for the preparation and fabrication of TFN-GO membranes. Furthermore, various ratios of graphene oxides have been homogeneously dispersed through ultrasonication on the NMP for the period of 10 hrs at the temperature of 40 C. To this solution, about 18 weight percent of PSF is added and thoroughly mixed to make the homogenous solution. Before membrane fabrication, the moisture and air were removed by employing the vacuum desiccator. An automatic crash Machine is used to dope solution homogeneously across the glass plate. The deionized water with a non-solvent batch was used to soak the glass plate for five minutes duration to allow the process of phase-inversion immersion precipitation.

The residual solvent was removed and polymerization is done. The interfacial polymerization allowed the formation of a dense membrane layer of polyamide on the top of the substrate. After passing through further dew steps the final dried membrane was denoted as TFN-GO with various compositions of GO. The scheme of the membrane synthesis is outlined in Figure 14 below.

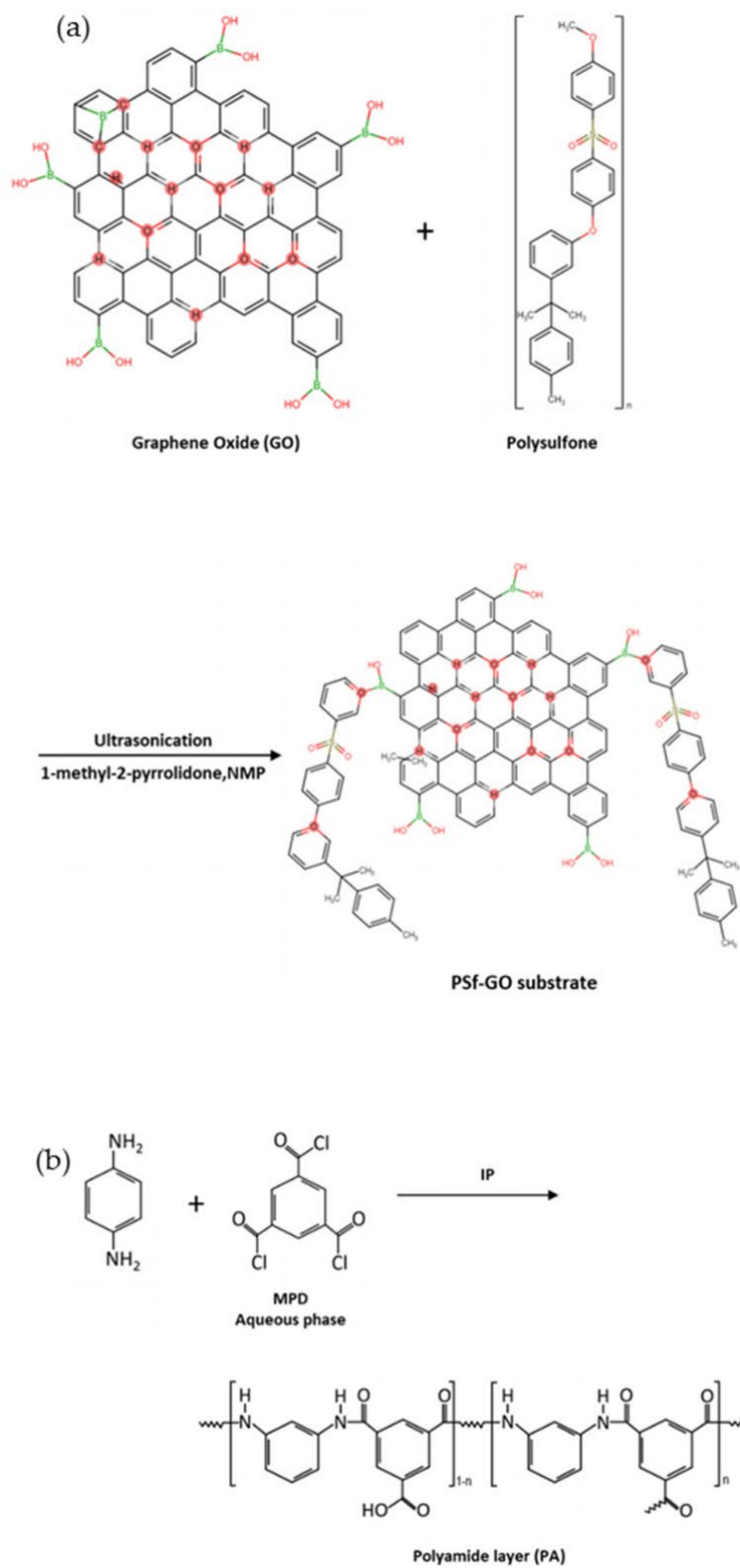


Figure 14. A schematic of GO interaction with polysulfone in NMP and formation of polyamide layer through interfacial polymerization on the substrate. [27]

2.8 Polyamide-GO/Polysulfone Ultrafiltration Membrane:

In a consecutive study of membrane development, researchers utilized different materials to fabricate the membranes to enhance the purification efficiency and alter mechanical properties, photostability, and other desired properties. In this context, a novel ultrafiltration membrane has been synthesized and fabricated by using polysulfone incorporating on the GO functionalized with the polydopamine (RGO-PDA) [38]. Several characterization techniques such as FTIR, Raman spectroscopic analysis, X-ray photon spectroscopy, and scanning electron microscopy has been utilized for the confirmation of membrane functionalization and investigation of morphology. The phase inversion techniques have been utilized to perhaps the membranes of PSF/RGO-PDA and pristine PSF, PSF-GO composites. [38]

Scanning electron microspore studies of the membranes show that the distribution of RGO-PDA was homogenous and the aggregation of the pristine graphene oxide particles block the pores. The addition of RGO-PDA increased the water flux. However, it didn't influence those rejection properties. The decrease in the flux was observed on the addition of pristine GO particles. The study conducted by Lin et al. PSF/RGO-PDA-0.1 showed the highest permeability of the pure water that was about two times greater than that of pristine PSF and PSF-GO. The fabricated membranes revealed the excellent rejection efficiencies of BSA, HA, and various sorts of dyes. The percent rejection of 57.8% and 78.7% has been reported for the BSA and HA respectively.

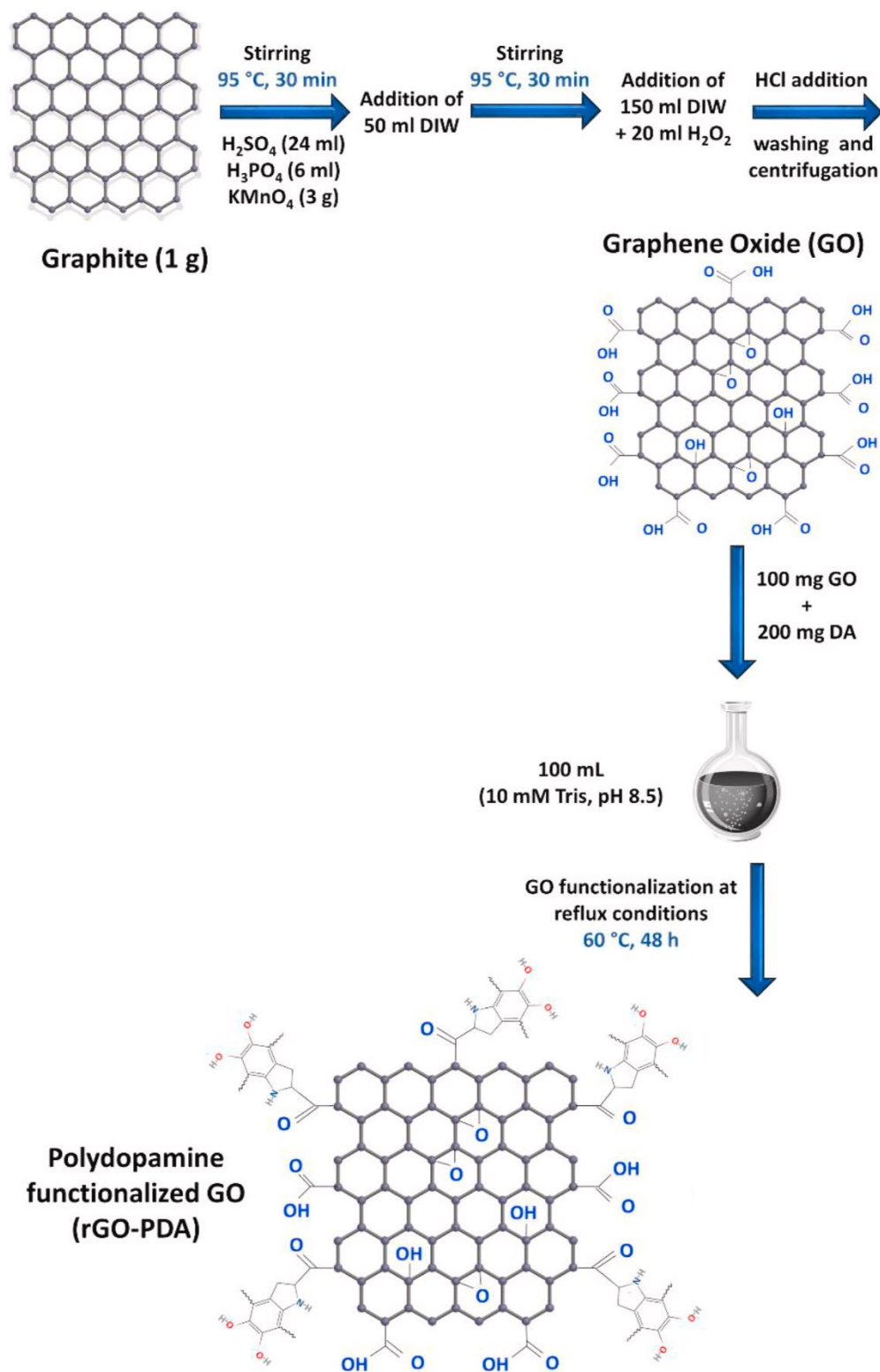


Figure 15. The synthetic scheme for the fabrication of polydopamine GO (rGO-PDA) [38]

In similar studies the phase inversion technique has been used for the synthesis of membranes of pristine PSF, PSF/RGO-PDA and PSF/GO composite. [39]. As outlined in figure-16, GO. RGO-PDA was added to the solvent of NMP and sonicated for 1 hour. After that PVP and PSF are added to the sonicated solution and PSF pellets were obtained. The solution is stirred overnight. In the set of different solution PSF, 0.02 wt% Go and 0.02 wt% rGO-PDA was added to make casting solutions. The casting machine is used to obtain a membrane. The membrane is processed through the method of phase inversion in deionized water. And finally PSF MMMs we obtained to used for further application.

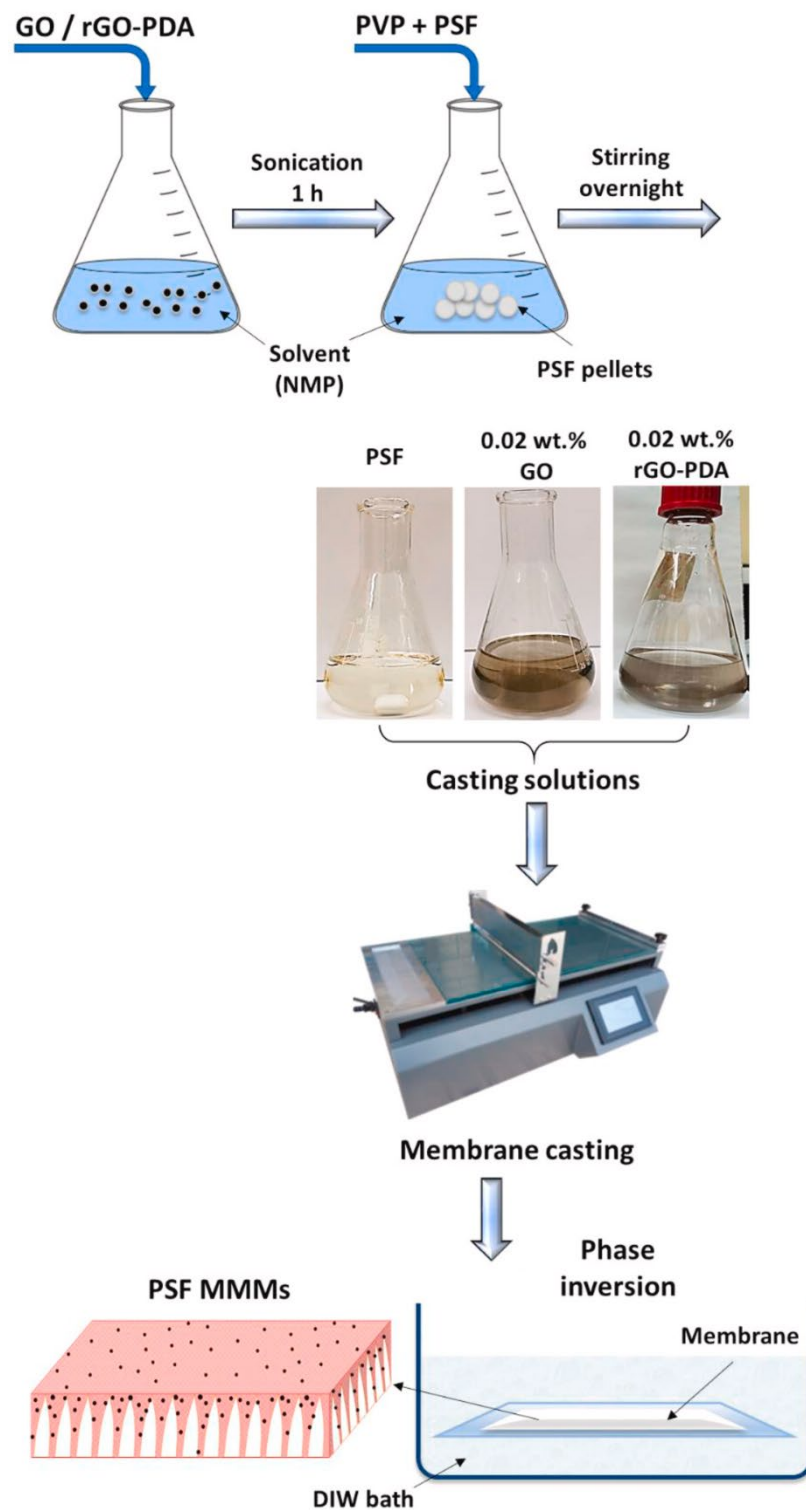


Figure 16. Schematic of the protocol for the fabrication of PSF-MMMs [38]

2.9 Photocatalytic PSF-TiO₂/GP Non-hybrid Membranes.

In a study conducted by Tutuk and his team, membranes for the degradation of organic contaminants have been prepared by utilizing PSF, TiO₂, and GO [39]. The enhancement in photocatalytic efficiency is one of the promising criteria through antifouling membranes. The incorporation of the single photocatalyst into the membrane layers revealed a low degradation capacity of organic pollutants. Researchers reported the insertion of two photoactive materials into the polysulfone membranes. These materials are nano-TiO₂ and GO has acted as fillers.

These membranes were further employed for the degradation of rubber waste in natural water sources contaminated with rubber waste. The degradation was monitored in dark and UV light irradiation. The variable compositions were tested and the best performance was revealed by the TiO₂ loaded at the are of 1.5 wt%. It provided the 16.29 permeability flux with the removal efficacy of 79.27%. Some of the membranes prepared by loading 1.0 wt% of graphene oxide revealed a permeability flux of 8.15 of 70.73%. On the addition of the mixture of TiO₂ and graphene oxide on the matrix of the PSF membranes. The mixture as filler remarkably enhanced the permeable flux. It showed the removal efficiency of 60.98% and 91.27% for the removal of organic and ammonia. This membrane (PSF-TiO₂/GO) exhibited the fastest photocatalytic degradation efficiency. It was confirmed that with the incorporation of the mixture of titanium oxide and graphene oxide the capacity and stability of the membrane improved due to the synergic effect of the membrane.

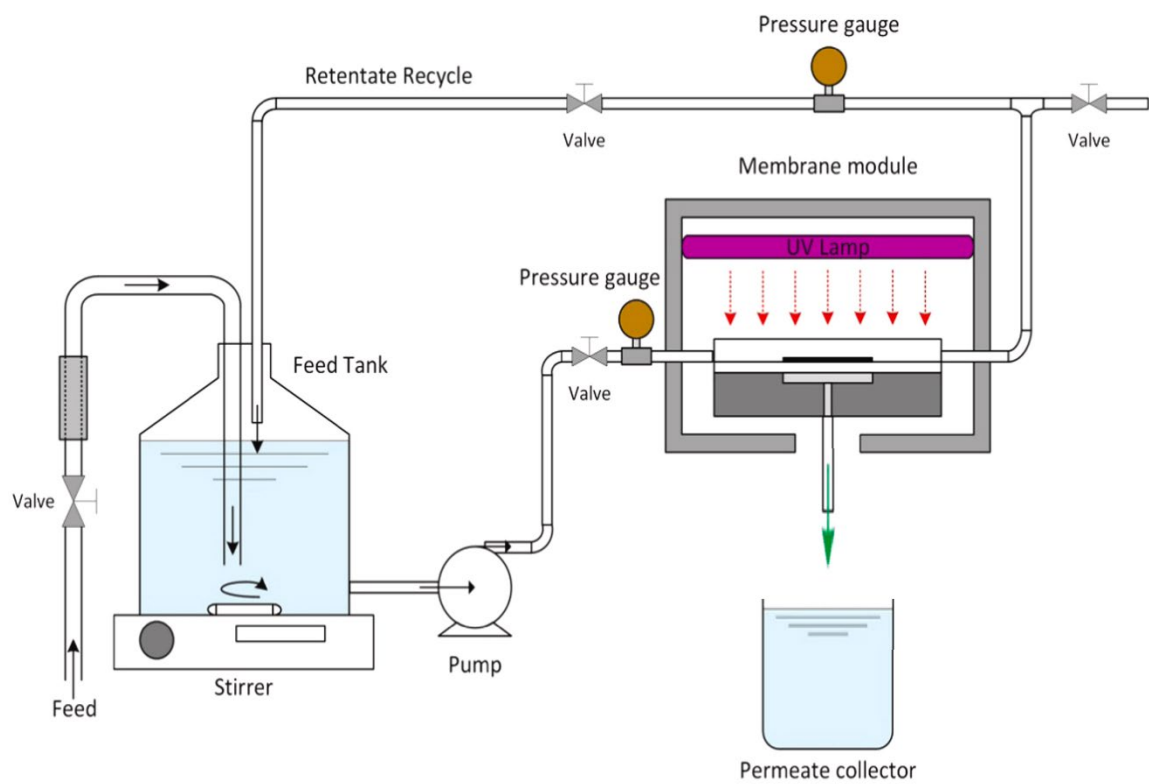


Figure 17. Schematic representation of membrane filtration system. [39]

2.10 Arsenate Rejection from Water by Polysulfone-GO Nanocomposite Membrane.

Razz and his researchers prepared a filtration membrane for the removal of arsenite from water. The membrane was fabricated by using the materials polysulfone and graphene oxide. The designed membrane was PSF/GO. The membrane was rich with the hydrophilic functional groups on its surface. The surface morphology is characterized by FTIR techniques [40]. It was observed that with the increase in the content of graphene oxide the structure of the sublayer was enhanced.

The pores on the membrane of pure PSF that were dropping like voids were changes into microvoids in the membrane of PSF-GO. It indicates the increase in the porosity. The modified membranes exhibited a low degree of roughness as compared to the membrane of pure PSF. The water flux for the modified membrane was also found to be increased with the increase in the GO up to 1 weight %. The pure water flux of 50 L/m²h at the pressure of 4 bar was calculated for the PSF-GO-1 composite membrane. The rejection efficiency of 83.65% was obtained for the PSF-Grapheneoxide-2 at the pressure of 4 bar. It was found the rejection rate of arsenate was dependent on the pH of the solution. The rate of rejection increased with the increase in the pH of the solution.

In brief, the study revealed that PSF as an additive on the graphene oxide enhanced the hydrophilicity, flux, and rejection rate for arsenate. The wet phase inversion method gave efficient membranes of PSF/GO nanocomposite. The membranes revealed excellent performance for arsenate rejection and water flux.

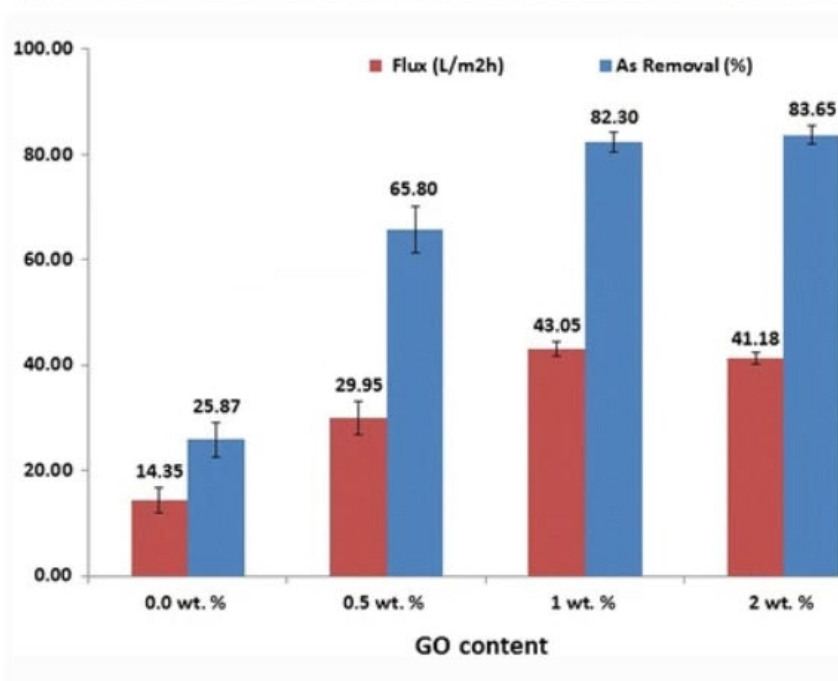
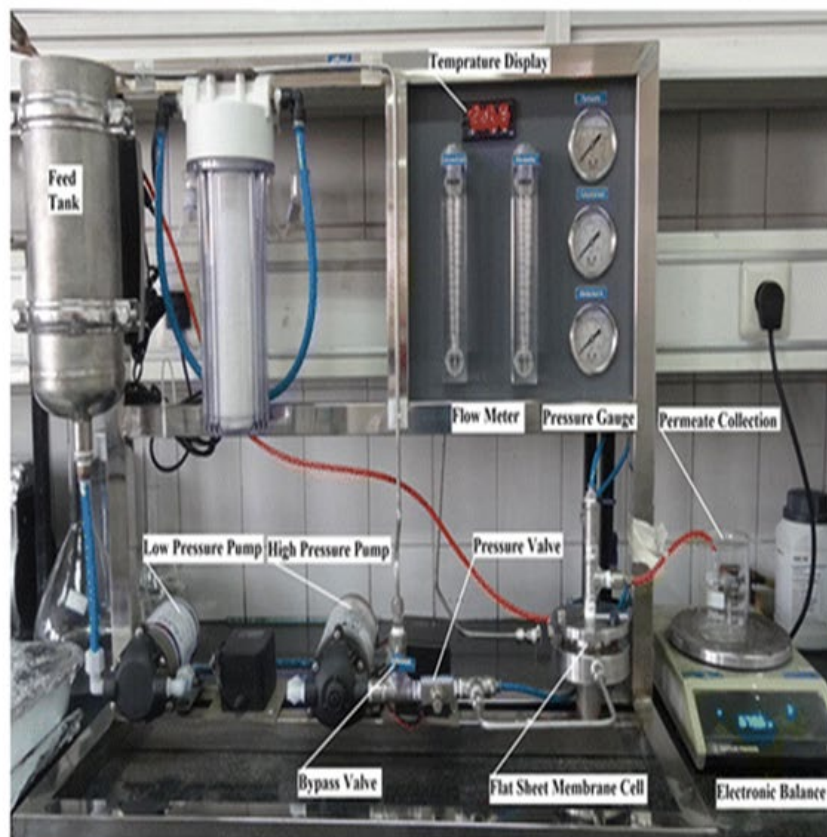


Figure 18. A schematic representation of the membrane filtration system for arsenic rejection [40]

CHAPTER 3

Experiments and Methods

3.1 Experimental

3.1.1 Material

Graphite powder, nitric acid (HNO_3) with purity 70% and molecular weight MW 63.01 g/mol, sodium chloride (NaCl) has purity $\geq 99.0\%$, MW 58.44 g/mol, calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) with purity 99.0%, MW 147.01 g/mol, Lead nitrate ($\text{N}_2\text{O}_6\text{Pb}$), purity $\geq 99.0\%$, MW 331.2 g/mol and Magnesium sulfate (MgSO_4) have purity $\geq 99.0\%$, MW 120.3 g/mol were brought from Fisher scientific company . Chromic nitrate ($\text{Cr}(\text{NO}_3)_3$) with purity 99.0%, MW 238.01 g/mol and nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ with purity 99.0% MW 290.80 g/mol were obtained from BDH LAB .Toluene (C_7H_8) purity $\geq 99.75\%$, MW 92.14 g/mol, Decene ($\text{C}_{10}\text{H}_{20}$) with purity $\geq 97.0\%$, MW 140.27 g/mol, Hexadecane ($\text{C}_{16}\text{H}_{34}$) purity $\geq 99.0\%$, MW 226.44 g/mol and 1,3,5-Benzenetricarbonyl trichloride (TMC) ($\text{C}_6\text{H}_3(\text{COCl})_3$) have purity 98% MW 265.48 g/mol, m-phenylenediamine (MPD) purity 99%, MW 108.14 g/mol were obtained from Sigma Aldrich and Polysulfone (PSf) support was obtained from Sterlitech and were utilized as received. All materials and chemicals used in the process were with high purity and used directly without any further purification.

3.1.2 Synthesis of graphene oxide modified with amines

Graphene oxide was synthesized using graphite following modified Hummer's method (Cristina Botas et.al. 2018). A mixture of 5g graphite and 5g NaNO₃, was prepared and kept in a flask in an ice bath at 0 °C. After 30 min, around 200 mL concentrated H₂SO₄ was slowly added at different intervals and under stirring then. After 1h, KMnO₄ (25 g) was added slowly in doses for 1h to keep the reaction temperature < 20 °C. The mixture was heated to 30-35 °C under stirring for 180 min. Then, 3% H₂O₂ (>1L) was added slowly until the yellowish color was observed. The temperature was observed to rise due to the exothermic process. The mixture was kept under stirring for 30 min. Then, the graphene oxide was separated and washed by centrifuge (7000 rpm for 1h) until the pH was neutral.

For the chemical grafting of the amines on the prepared graphene nanosheets, graphene oxide was dispersed in DMF via sonication (0.18 mg / 1 mL). Into the dispersed graphene, SOCl₂ was added in the argon atmosphere. The system was refluxed at 70 °C for 24 h to activate the carboxylic groups at the edges of nanosheets. Excess SOCl₂ was removed through reduced pressure. Diethylenetriamine was then added under argon and the system was stirred for 3days at 75 °C. The resultant suspension was separated by centrifuge and purified thoroughly by several washing cycles and dried under vacuum at 40 °C temperature to obtain graphene modified with amines. This was then used for the preparation of membranes

3.2 Preparation of membranes

Several 7 × 7 cm² rectangular pieces of a microporous polysulfone (PSf) support layers with approximately 100 µm thick, were immersed in nitric acid (HNO₃) solution, 1M.

After one day, the activated supports were dried for 3 h. Then, TMC 0.01% was introduced into membranes and kept for five minutes. After that, the polysulfone support was submerged in a bath of sonicated solution of MPD and amine-modified graphene at ambient temperature for one day in a way that allows the polymerization to complete. Finally, it was cured and vacuum dried, and kept on a glass plate until use. The previous procedures were used to prepare different membranes with different layers.

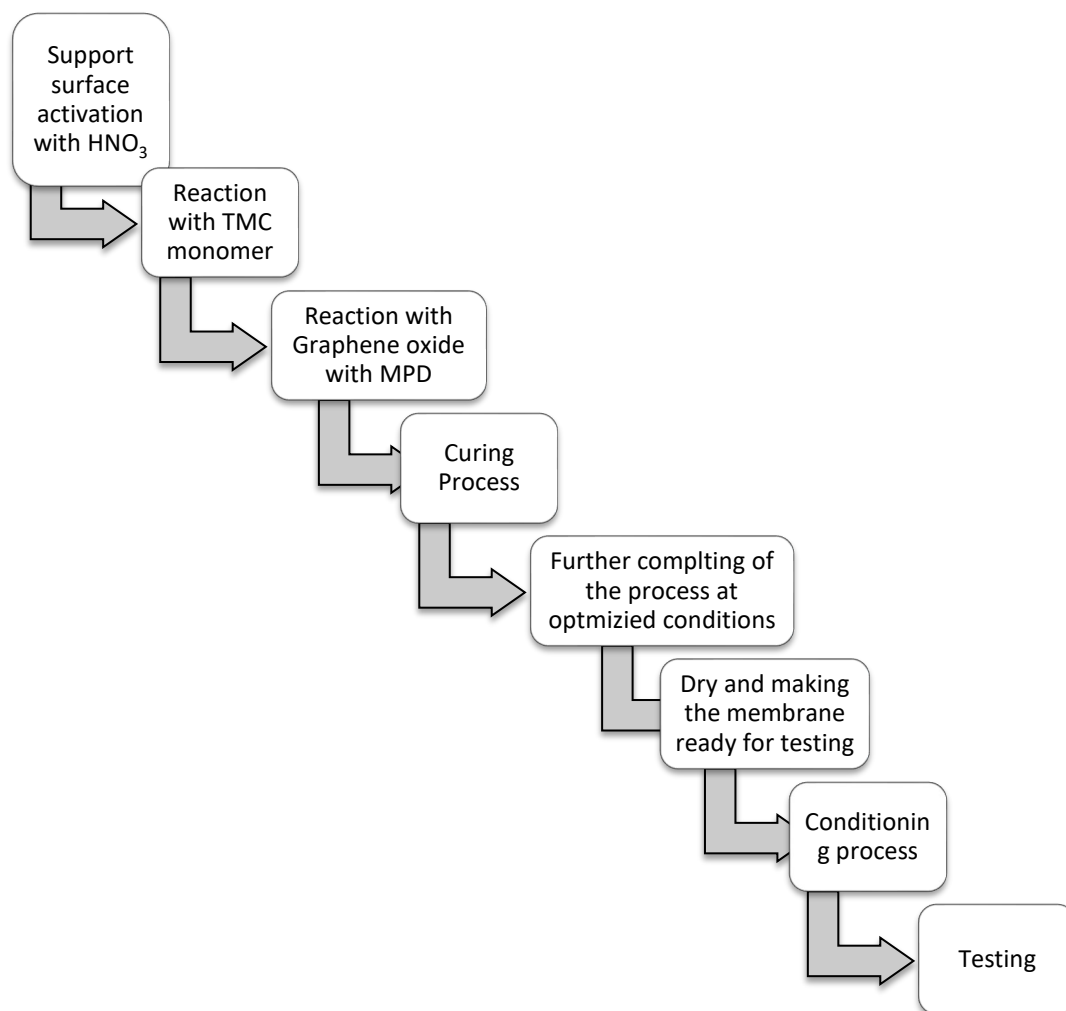


Figure 19. A schematic diagram of the synthesis process of the membranes.

3.3 Characterization instruments

Different instrument characterization methods were utilized to analyze modified GO membrane. (FTIR) Fourier Transform Infra-Red spectroscopy manufactured by Thermo Scientific™ model (Smart iTR NICOLET iS10) in 400-4000 cm^{-1} wavelength range was applied and with detector (DTGS) deuterated triglycine sulfate was requested to characterize the chemistry of the prepared materials. Before start the membrane characterization, background correction was done by scanning the empty stage. Therefore, the collected spectra were identified by the intensity of the functional group. The XRD (X-ray diffractometer) was obtained from Bruker model 2D PHASER by detectors SSD160-2 (Si-strip detector with 160 channels) to characterize the crystalline phase also the average crystalline size of synthesized Go nanocomposite membrane. As the samples nanosheet, small size is taken and taped on a microscope slide. For analyzing the effect of surface modification on the membrane morphology, FESEM (field-emission scanning electron microscope Tescan Lyra-3, dual beam, Tescan) attached with energy dispersive x-ray spectrometer (EDX, Oxford instrument) was utilized. Before starting the analysis, different specimens were coated with a thin layer of gold using a sputtering process to make them electrically conductive. In order to check the performance of the membrane, the filtrate solutions have been analyzed by HS-GCMS Gas chromatography headspace quipped with mass Spectrometer manufactured (5975C with triple-axis detector) by Agilent (7890A). first start with calibration of the instrument by Draw 1 mL of calibration which contains (Toluene, Hexadecane, and Decene)solution in deionized water from a micropipette and transfer to the headspace vial. Calibration points to be prepared are 0,2.5,5,10 and 20 mg/L

then cover the said vial and put it in headspace heating chamber with incubation temperature 60°C and 10 minutes of incubation time with Agitation speed 300 rpm, after the headspace the samples move to the front inlet with 280°C to evaporate the water and make the target volatiles after that move to column type (: 5% Phenyl Methyl Siloxane) and length (30m×250um×0.25um) for separation which located inside the oven with program 40°C hold for 5 minutes then increased to 15°C per minute to 280°C and hold for 4 minutes after separation done the compounds move toward to MS through the transfer line with temperature 290 °C and the MS acquisition Parameters (MS source 230°C and MS quad 150°C).

3.4 Membrane performance tests

The filtration system of the membrane was tested after each surface treatment and the membranes were tested at room temperature and constant pressure 1000 kPa through the filtration system (cross-flow permeation) which was provided by Sterlitech. The membrane filtration system has a membrane cell with an area of 35 cm connected to the feed tank and the pump by Teflon and the stainless steel tubes Figure 13. Membrane with different layers of the coating first compacted in 2 L of deionized water for 4 hours with increase the peruse to 1000 kPa gradually to keep the flux constant before adding the testing solution. Then the 2 L of target solution of mixed pollutants of metals, salts, and organic compound which was considered as a model for testing the performance of membranes was added to the feed tank. The solution was prepared of 2000 ppm of metals and salt and then was spiked with 1ml of concentrated hexadecane, toluene, and decane to reach 250 ppm. Finally, the breakthrough of the membrane was investigated by studying the effect of feed

concentration on analytes rejection at concentration. The effect of layers coating of the analytes rejection was analyzed by a different instrument. Salt concentration measure by Ion chromatography and conductivity meter and metals measure by ICP while organic compound monitoring by GC-headspace. The system was running for 1 h to equilibrate before measuring the permeate water flux and rejection. Then the permeate flux was collected of 10 ml at the graduated cylinder to measure the required time.

CHAPTER 4

RESULTS AND CONCLUSION

4.1. Characterization

4.1.1. Characterization of the membrane composite MDP with Graphene.

The FTIR (Fourier Transform infra-red) was presented to identify the major functional group found in the synthesis membrane. FTIR of MDP with GO membrane shows a wide absorption peak in Figure 20 around 3373 cm^{-1} indicated to the O-H stretching vibrations of this group, which allows for the composite to diffuse in water. Another small peak appears approximately at 2850 cm^{-1} that indicates C-H stretching vibrations. Also at 1629 cm^{-1} , the peak is linked with stretching vibration of carbonyl C=O and C=C groups. Therefore, found a weak peak at 1050 cm^{-1} can be related to C-O stretching vibrational. The wide peak absorptions at low frequencies at 600 cm^{-1} might be related to the vibration of some bonds with the composite structure.

The XRD is required to identify the crystal structure of the synthesized MDP and GO composite. The peaks of XRD are illustrated in Figure 21. The first peak in the XRD pattern shows at 14.5° . Another sharp peak appears at 21.2° and the last peak has been shown at 29° .

The field-emission scanning electron microscope (FESEM) was performed to investigate the morphology of MDP and GO composite membrane. the SEM image in Figure 22 shows the formation of Graphene oxide with MDP of nanosheet before the treatment. And the graphene structure shows how the graphene minimizes the pore size of the nanosheet. EDX (energy-dispersive X-ray) was performed for GO composite to prove the presence and well dispersion of graphene on Psf membrane. While the EDX in Table 1. EDX composite for the membrane before treatment shows the high peak of carbon by 69% while for Nitrogen is 19.97 % and about ten percent for oxygen. Figure 24 illustrates the morphology of synthesis membrane after the treatment can be observed the metals have been rejected and change in the morphology, this confirmed the performance of the membrane. On the other hand, the results of EDX Table 2. EDX spectrum of the prepared membrane after the use in water treatment Table 1. EDX composite for membrane after treatment show different composition that before the treatment starting with Carbon by 47 % following that 17% of nitrogen, third in oxygen by 16 % and total metals by 20 % which that indicate the high rejection of the membrane

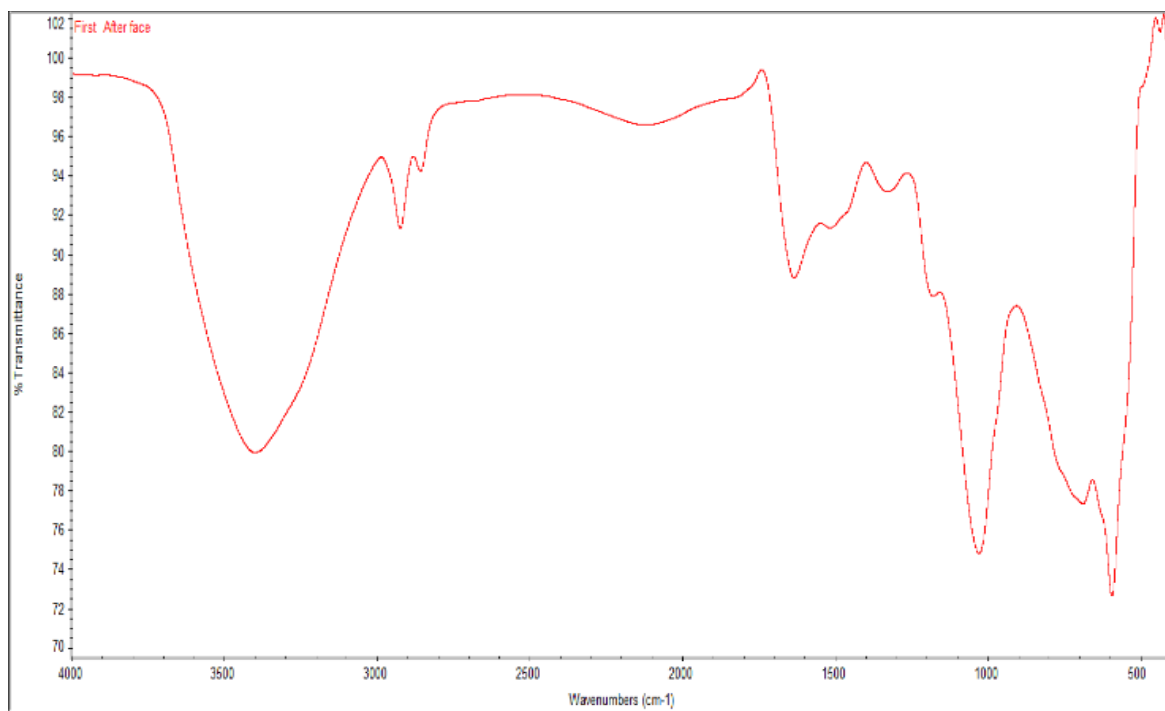


Figure 20. FTIR spectrum of the prepared membrane

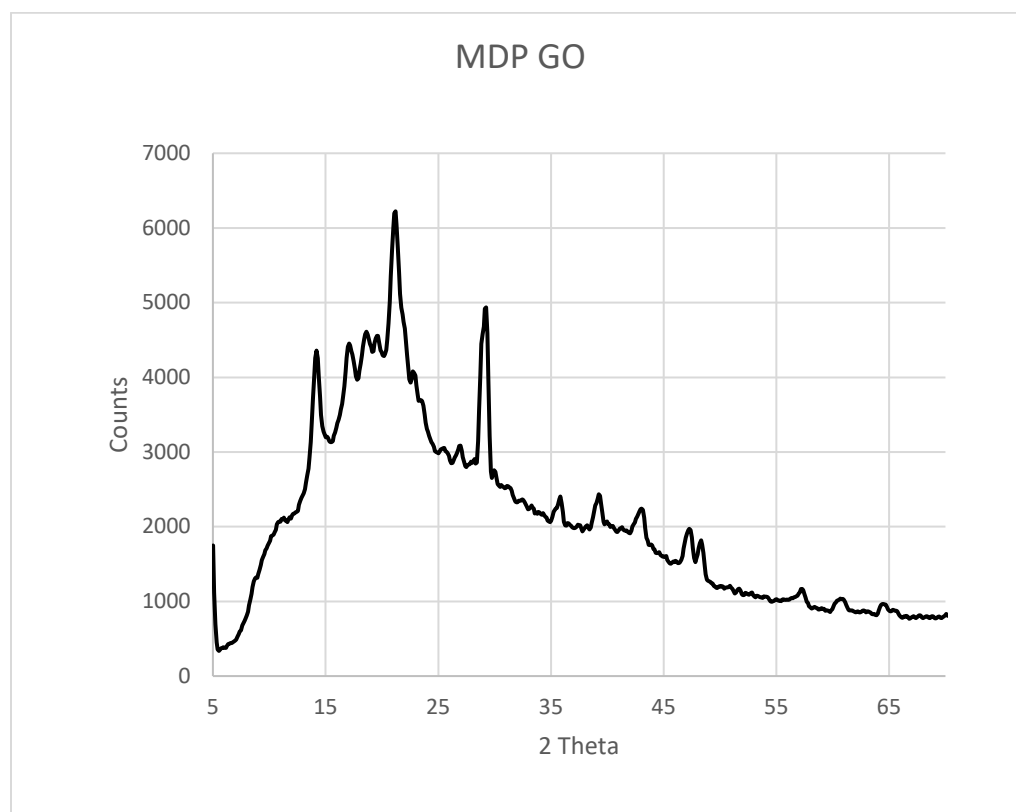


Figure 21. XRD pattern of the prepared membrane

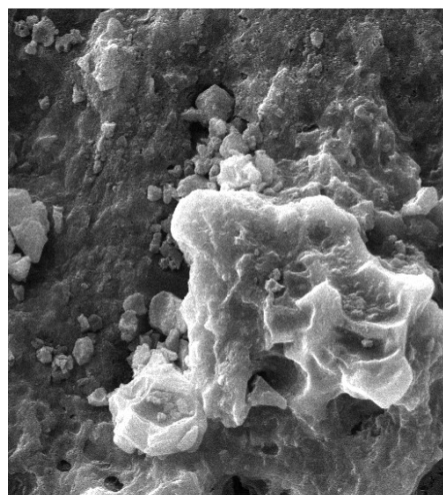
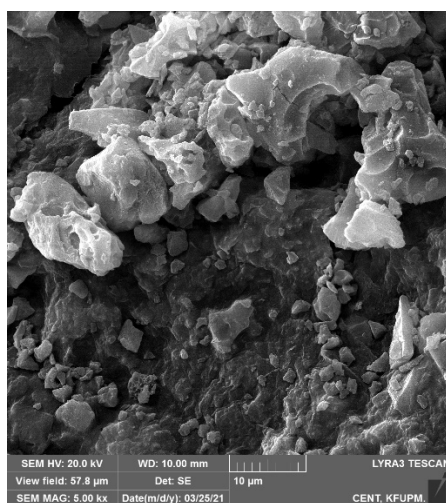
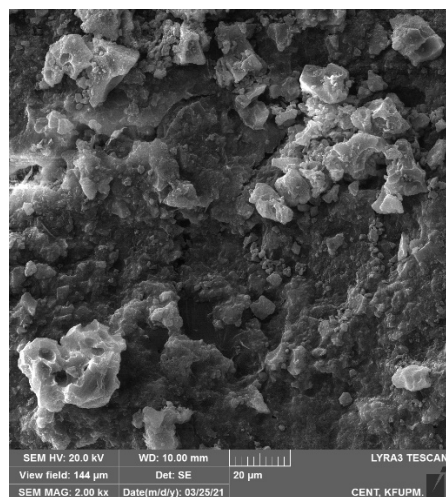


Figure 22. SEM images of the prepared membrane

Table 1. EDX composite of the new prepared membrane

Element	Weight%	Atomic%
C K	63.30	69.12
N K	21.33	19.97
O K	12.26	10.05
Cl K	1.37	0.51
Cu K	1.73	0.36
Total	100	

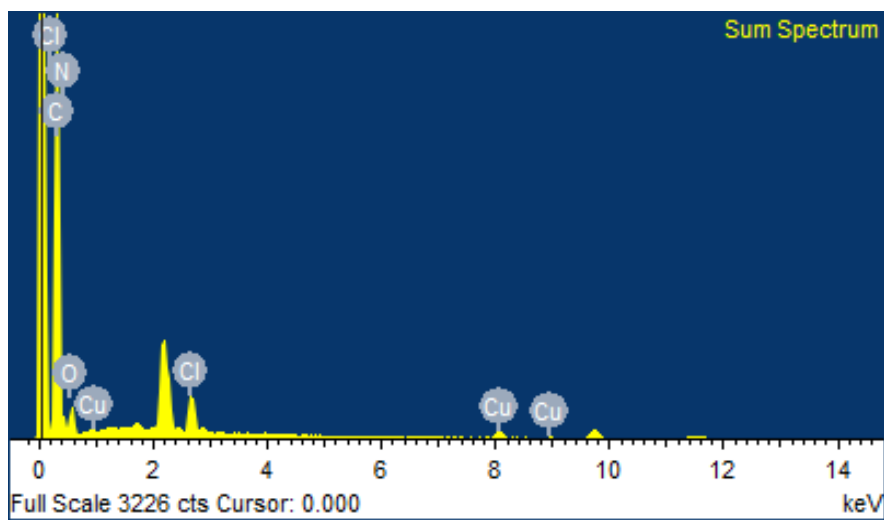


Figure 23. EDX spectrum of the prepared membrane

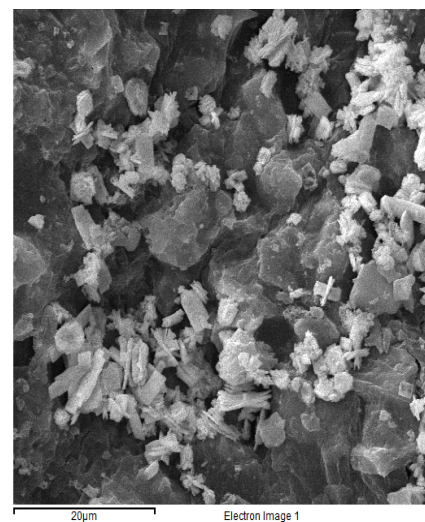
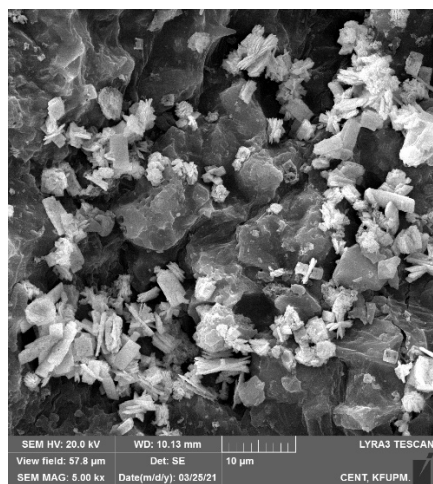
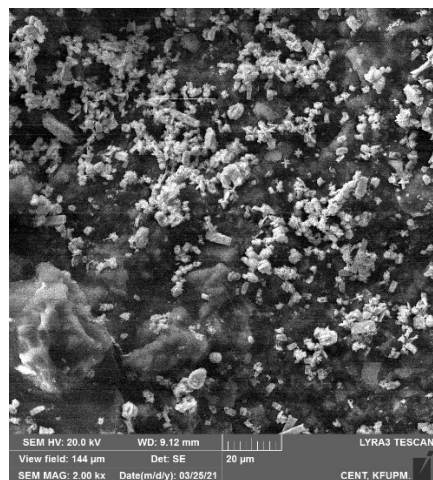


Figure 24. SEM images of the prepared membrane after treatment

Table 2. EDX spectrum of the prepared membrane after the use in water treatment

Element	Weight%	Atomic%
C	47.37	61.61
N	17.28	19.28
O	16.38	15.99
Na	0.20	0.14
S	2.00	0.98
Cl	0.32	0.14
Ca	0.08	0.03
Cr	0.17	0.05
Ni	0.18	0.05
Cu	3.08	0.76
Pb	12.92	0.97
Total	100	

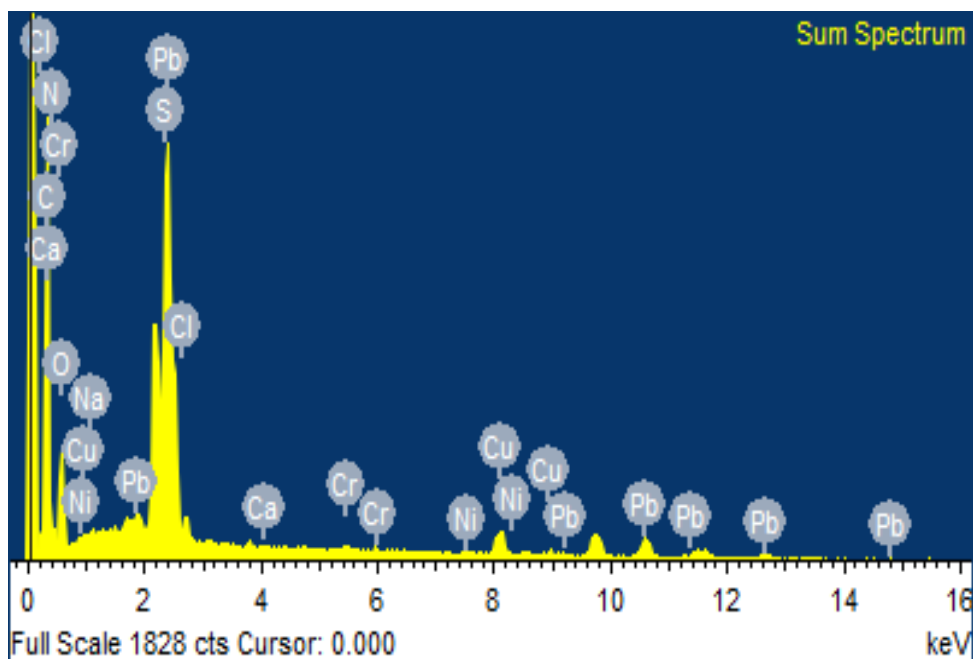


Figure 25. EDX spectrum of the membrane after the use in water treatment

4.1.2. Characterization of the GO membrane

The membrane consists of polymer and graphene without amines was prepared for comparison purposes. XRD performed to identify the structure of the synthesized GO composite Figure 26 shows the weak peak at 14.5° while a sharp peak was observed at 22° . another peak is shown up at 29.9° .

The FTIR Required to identify the major functional group. As shown in Figure 27, a peak can be observed at 2973.55 cm^{-1} , which indicate the C-H stretching vibrational. Then minor peak shows up at 2915 cm^{-1} and refer to N-H stretching mode. Moreover, high peak at 1606 cm^{-1} which indicate C=C group, following that small peaks range at 1533

cm^{-1} , 1442.22 cm^{-1} , 1369 cm^{-1} and 1249 cm^{-1} which indicates the N-O, C-H, S=O, and C-N respectively.

SEM was performed to check the morphology (surface and cross-section) of the modified membrane. The surface SEM images are depicted in Figure 28. The SEM images illustrated the uniform and porous nature of the polysulfone layer. Energy-dispersive X-ray Table 1 spectroscopy was utilized to analyze the nanoparticles on the surface of the membrane. The composite of the membrane contains 65% carbon and 35 % oxygen.

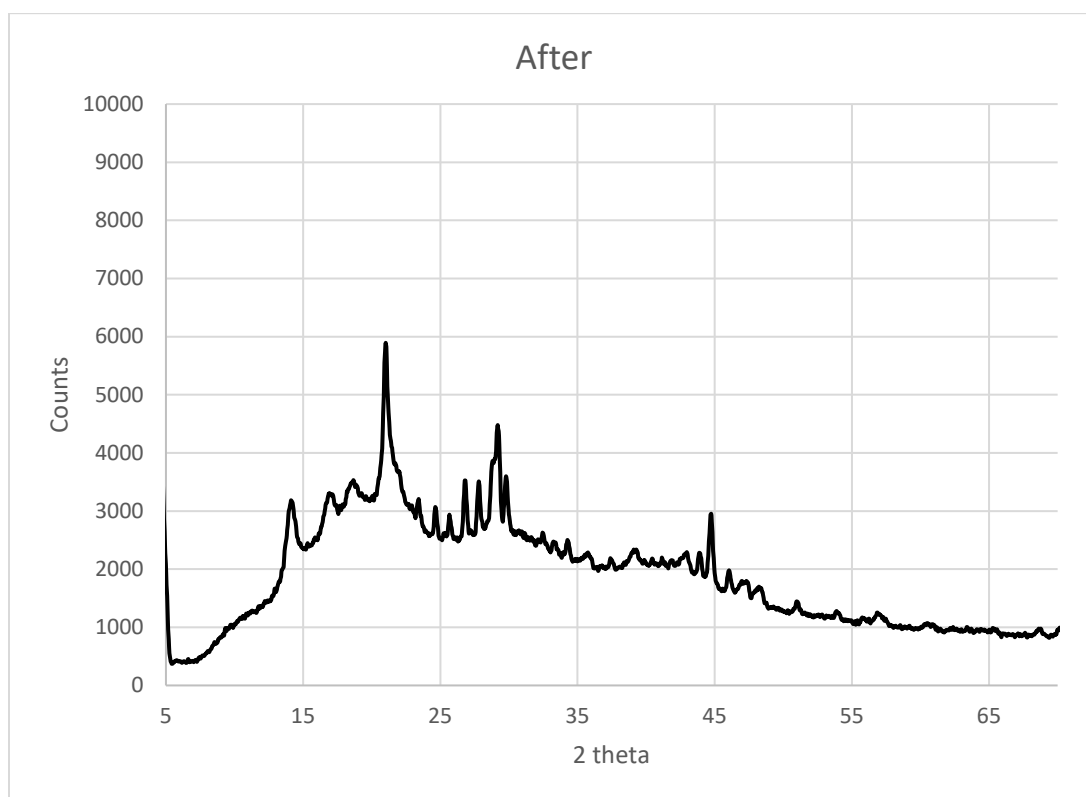


Figure 26. XRD Pattern of the membrane prepared with graphene without amine

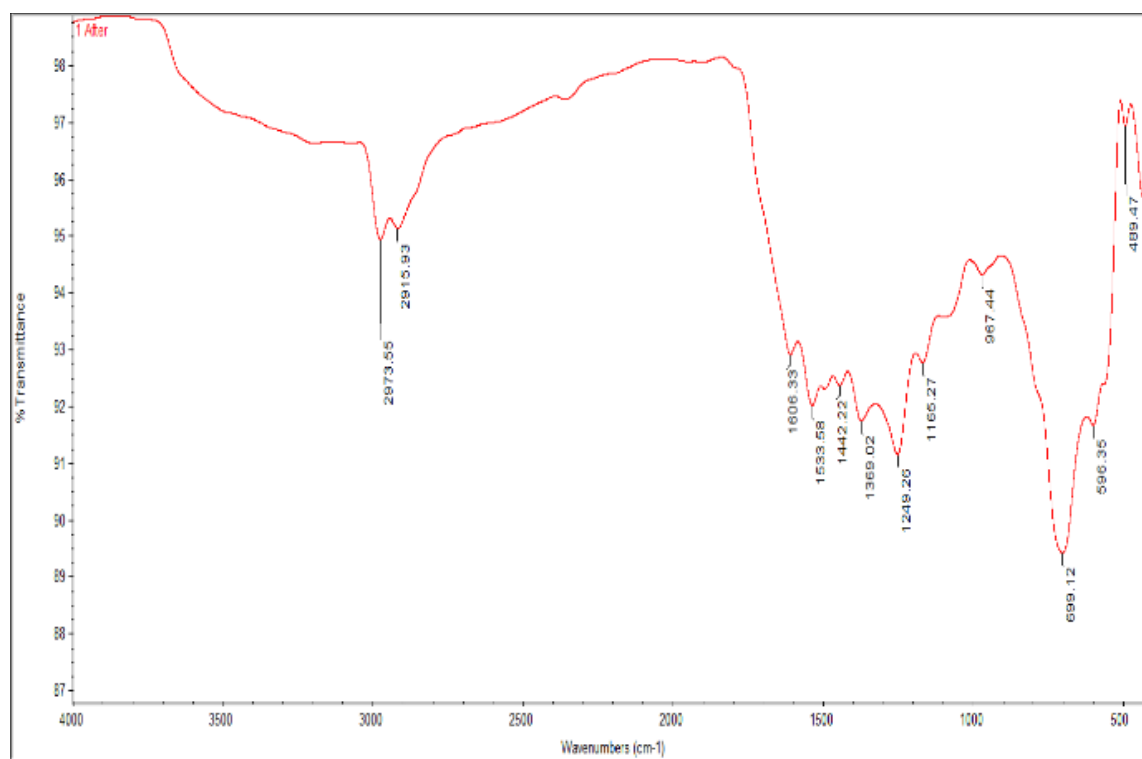


Figure 27. FTIR spectrum of the membrane prepared with graphene without amine

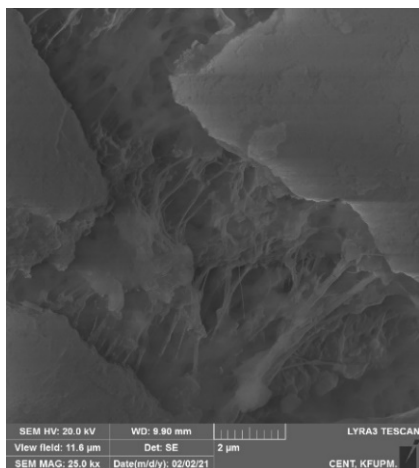
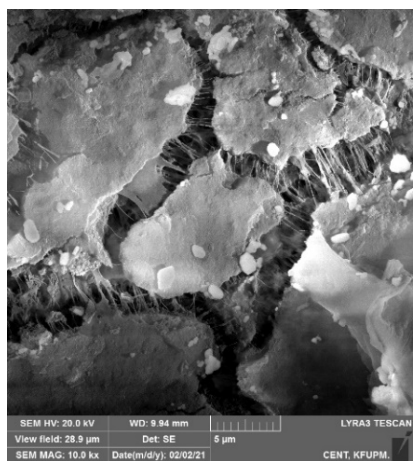
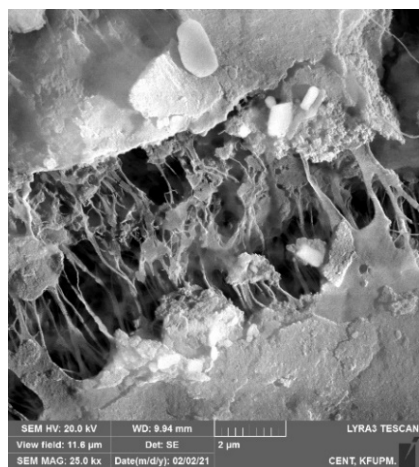


Figure 28. SEM images of the membrane prepared with graphene without amine

Table 3. EDX spectrum of the membrane prepared with graphene without amine

Element	Weight%	Atomic%
C K	65.01	71.28
O K	34.98	28.76
Si K	0.001	0.004
Totals	100.00	

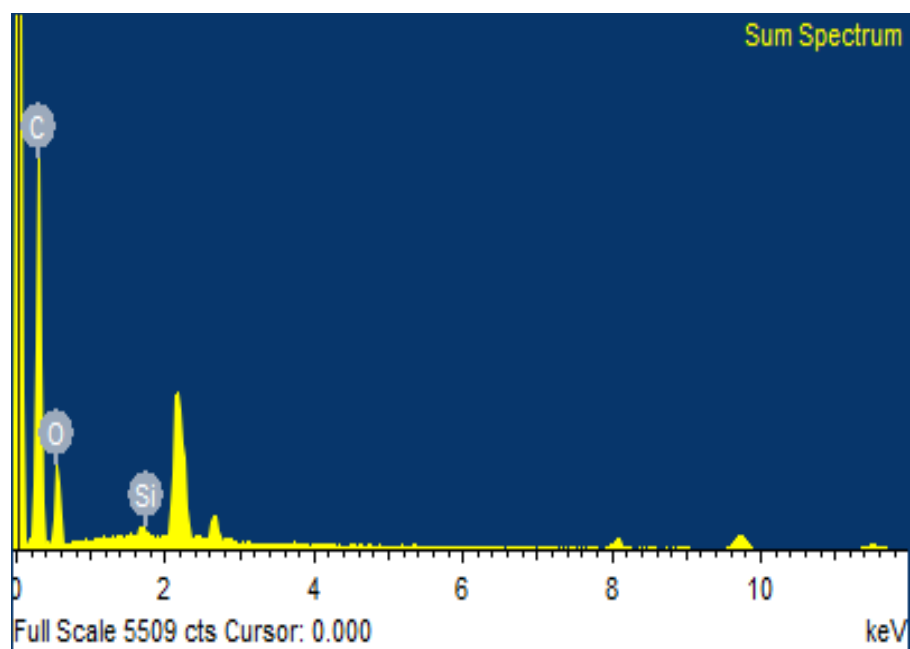


Figure 29. EDX spectrum the membrane prepared with graphene without amine

4.2. Performance Optimization of the membranes

In order to study the effect of layers and pressure, several membranes have been prepared. The membrane (A) has been synthesized by TMC with amine-modified GO on Psf nanosheet and three layers with constant pressure, Figure 30. It can be observed that the flux starts by 13 minutes with a huge reduction in conductivity then the flux fluctuated with increased conductivity, which indicates that the efficiency of the membrane is reduced and the penetration of the target has increased. For membrane (B), Figure 31, which was prepared with one more layer gives similar results as the membrane (A) with little improvement. The membrane (C) was prepared with different composite, by adding TMC then MPD with amine-modified GO in one layer. As shown in Figure 32, this membrane displays better flux with time, and the conductivity was also reduced. To improve its performance, another membrane was prepared by adding more layers. As shown in Figure 33, membrane D that has the same composite of the membrane (C) but with two layers showed better-enhanced stability in the flux. The conductivity also was reduced with a good flux. After some time, there was an increase in conductivity, which indicates that the high pressure affected to have a faster breakthrough. Thus, the salts and metals have penetrated through the membrane. On the other side, membrane (E) which was formed with the same composite as membrane C but with three layers of polymer and amine-modified graphene show the best results among all membranes from membrane A to membrane D. The conductivity was reduced while the flux was good at 1000kPa, Figure 34. The membrane E was also evaluated at various pressures, from 1000 upto 6000 kPa. The membrane showed also a good reduction in conductivity with good flux, Figure 35. However, the conductivity was reduced when the pressure was increased upto 6000 kPa.

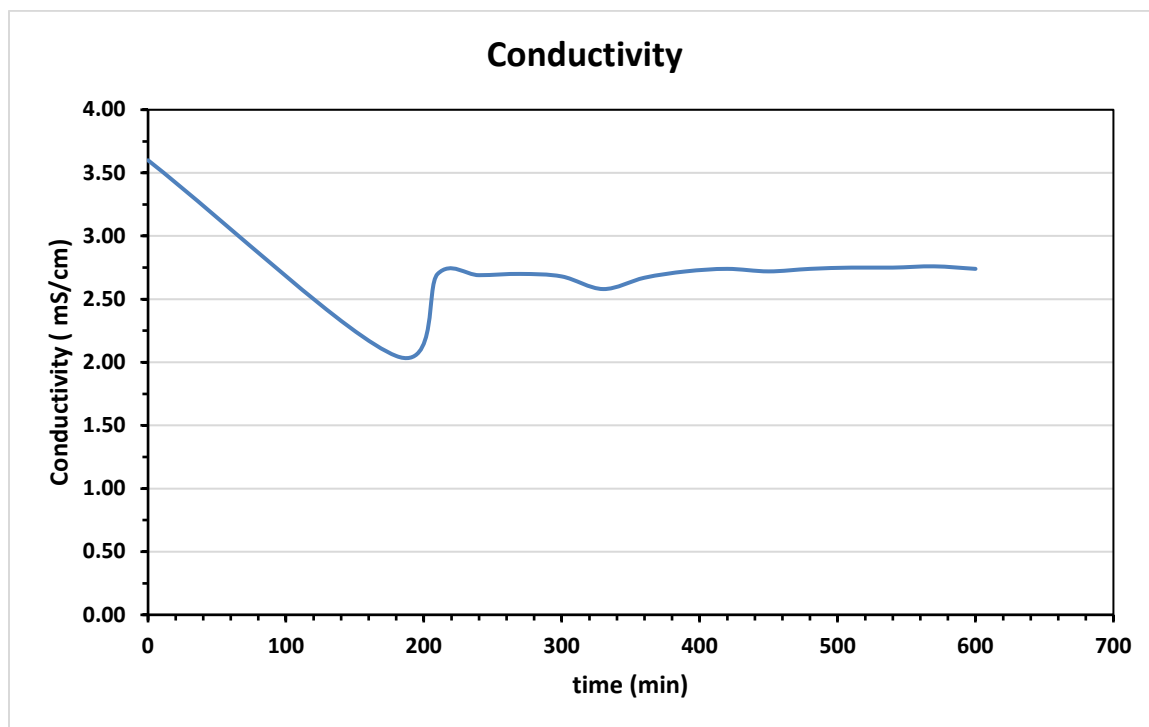


Figure 30. Performance of membrane A

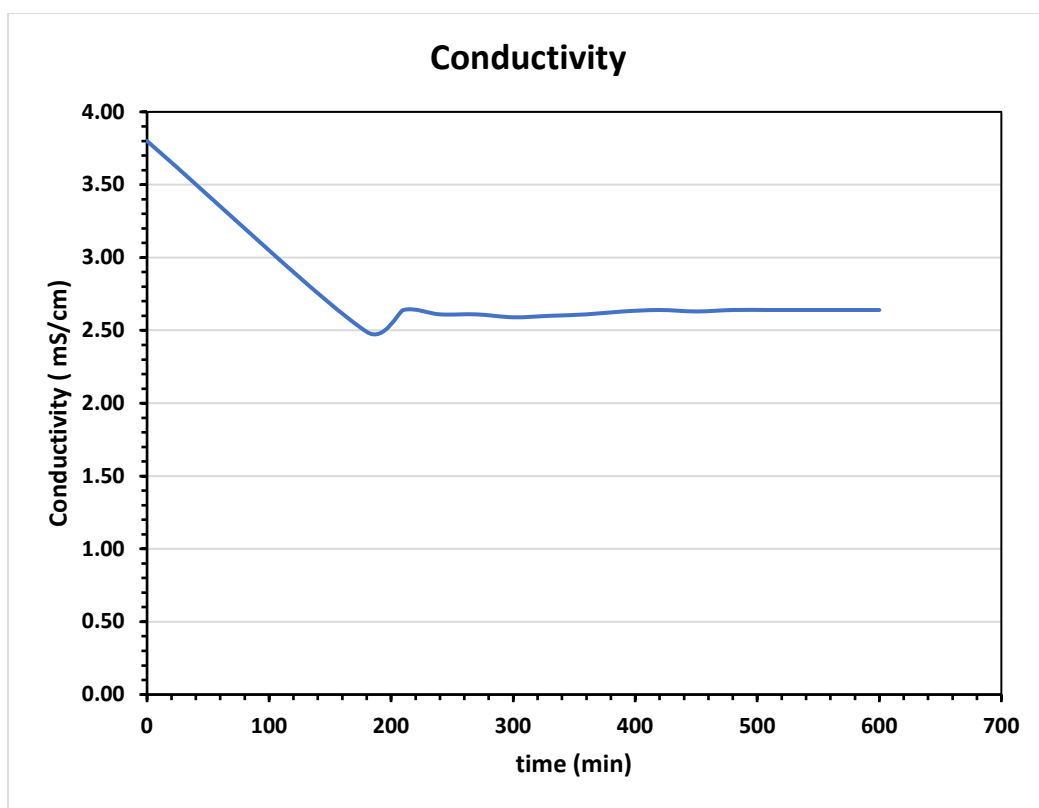


Figure 31. Performance of membrane B

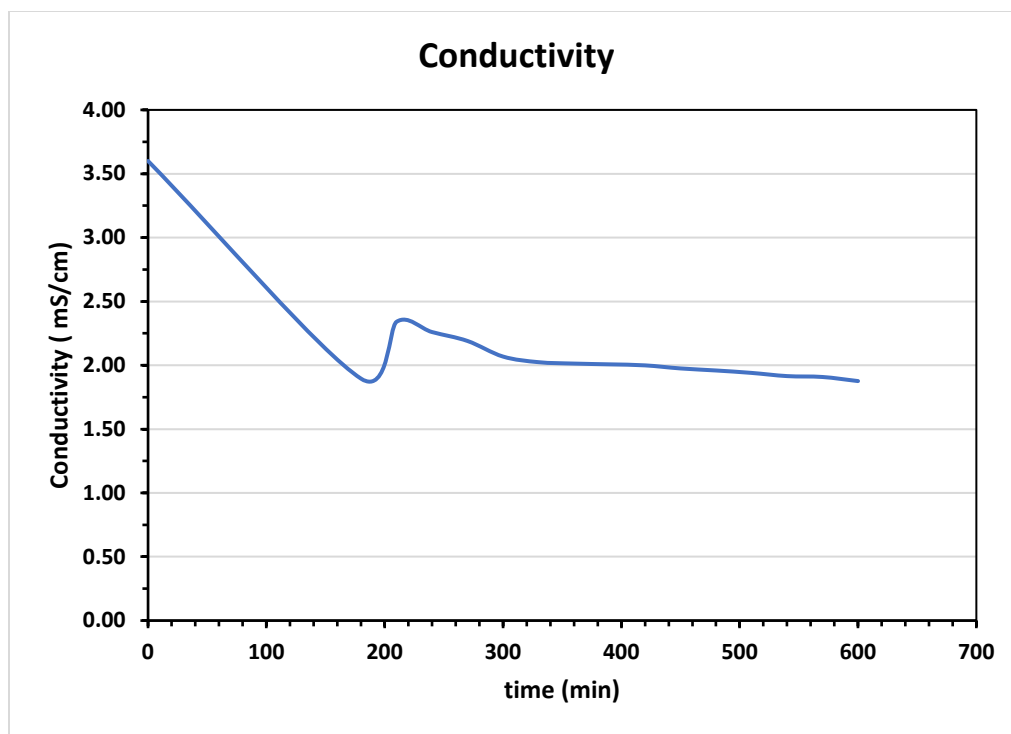


Figure 32. Performance of membrane C

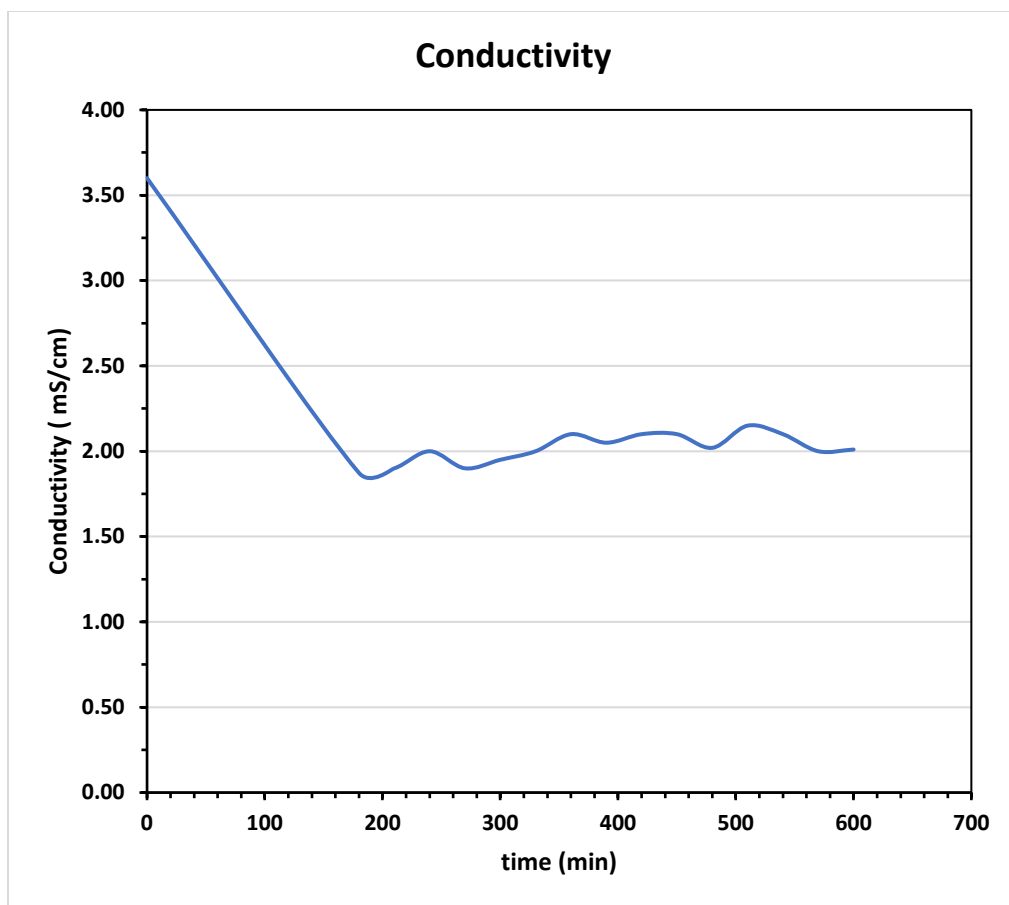


Figure 33. Performance of membrane D

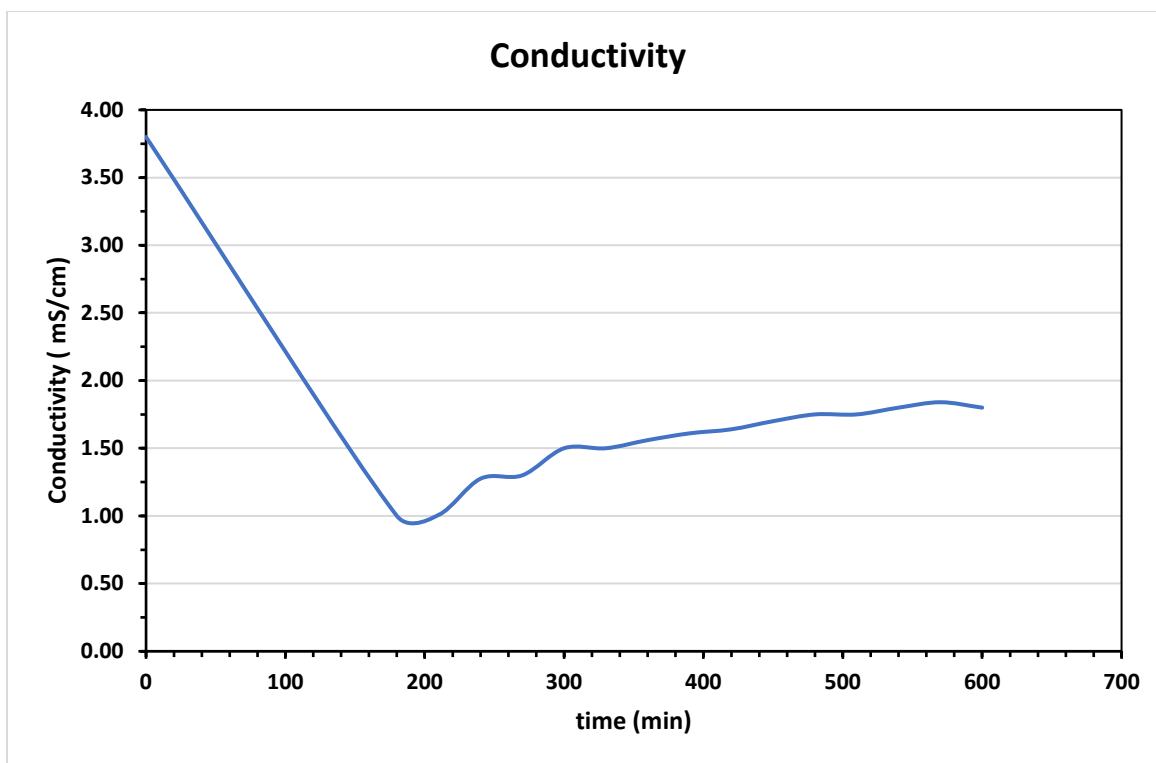


Figure 34. Performance of membrane E at constant pressure, 1000kPa

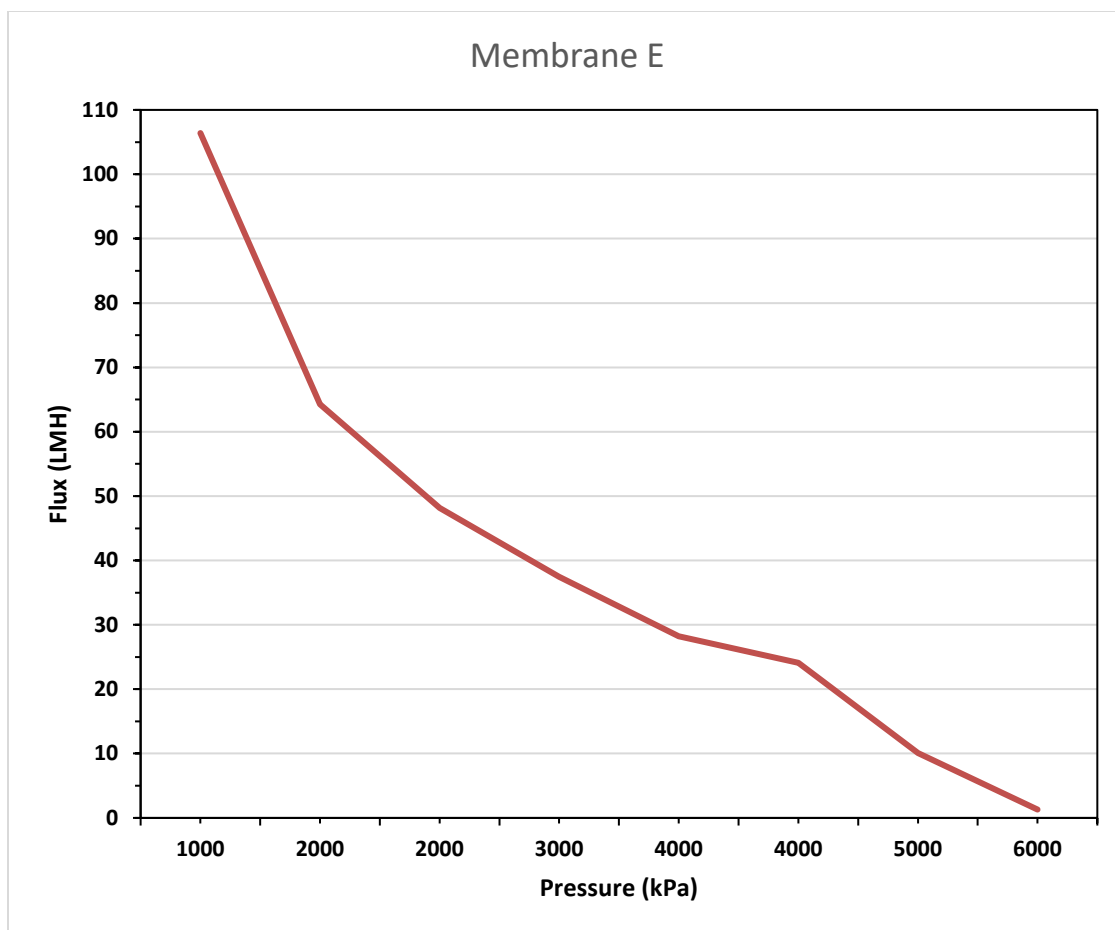


Figure 35. Performance of membrane E at different pressure values

4.3. Filtration performance

Filtration parameters including flux, monovalent and divalent salts rejection (NaCl , MgSO_4 , and CaCl_2), and hydrocarbons rejection (toluene, decane, hexadecane) and heavy metals (Ni , Pb , Cr) were investigated. Permeability of the bare and modified membranes at pure water, salt solution, and oil solution. Overall, the permeability is enhanced by embedding GO-amines into the membrane surface. The properties of the membrane filtration need to be tested after treatment of the surface due to the presence of some pollutants on the membrane surface which adds an extra barriers layer to the permeate flux. To evaluate the separation properties, the main output variables attribute to the effectiveness and efficiency of the rejection of metals and hydrocarbons. Figure 36 illustrates the percentage of the rejection of the MPD with graphene for Hydrocarbons (Toluene, decane, and Hexadecane). It was observed that almost 99.9% of hydrocarbon has been rejected with different pressures [41-44]. On the other hand, Figure 37, at pressure 1000kpa 96% of the metal rejection rate was achieved. However, the reduction was decreased with an increase in the pressure. Almost 75% metal removal was obtained at 2000kPa and 58 % was achieved at 6000 kPa. This indicates that when the pressure increased the flux increase which allows for metals to permeate fast through the membrane [45-55]. The flux becomes faster with an increase in pressure. While the removal of the chloride Figure 38 started with the percentage of removal of almost 70% at 1000kPa and decreased with increased the pressure to reach 20% with 6000kPa. As shown in Figure 39, the rejection rate of sodium and magnesium

starts with 30% at 1000 kPa and less than 10 % at higher pressure. While the percentage rejection of sulfate ions was more than 80% at 1000kPa and 33% at 6000kPa, Figure 40. The rejection of calcium was about 60 % at low pressure and about 20% at high pressure, Figure 41. Compare the performance between MPD & amine-modified graphene membrane with a membrane made of graphene nanosheets only without amines indicates the high performance of the membrane in presence of amine, Figure 42. A comparison between graphene oxide membrane and amine-modified graphene This indicates that the amines play some role in the rejection and removal of the tested pollutants (salts, metal ions, and hydrocarbons) [56-62].

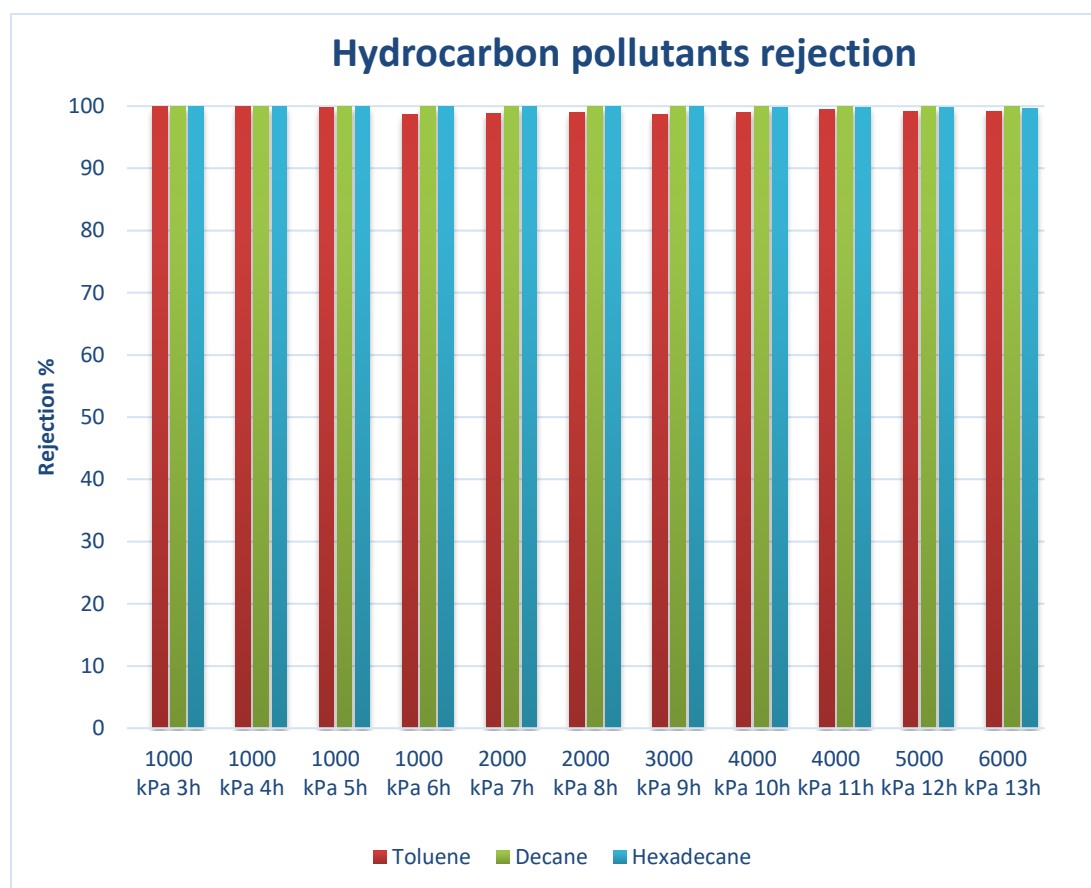


Figure 36. The hydrocarbon rejection rate using the prepared membrane E

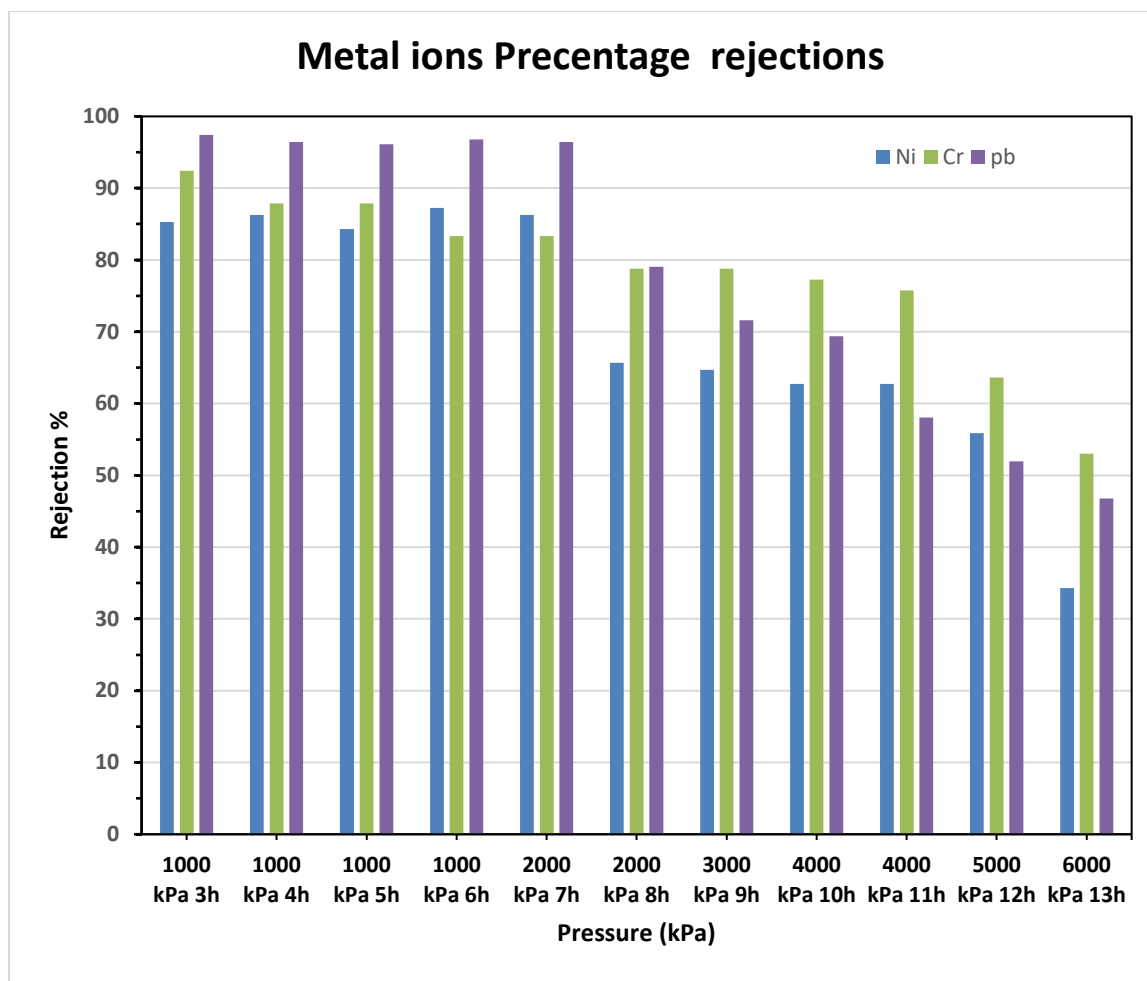


Figure 37. The metal ions rejections using the prepared membrane E

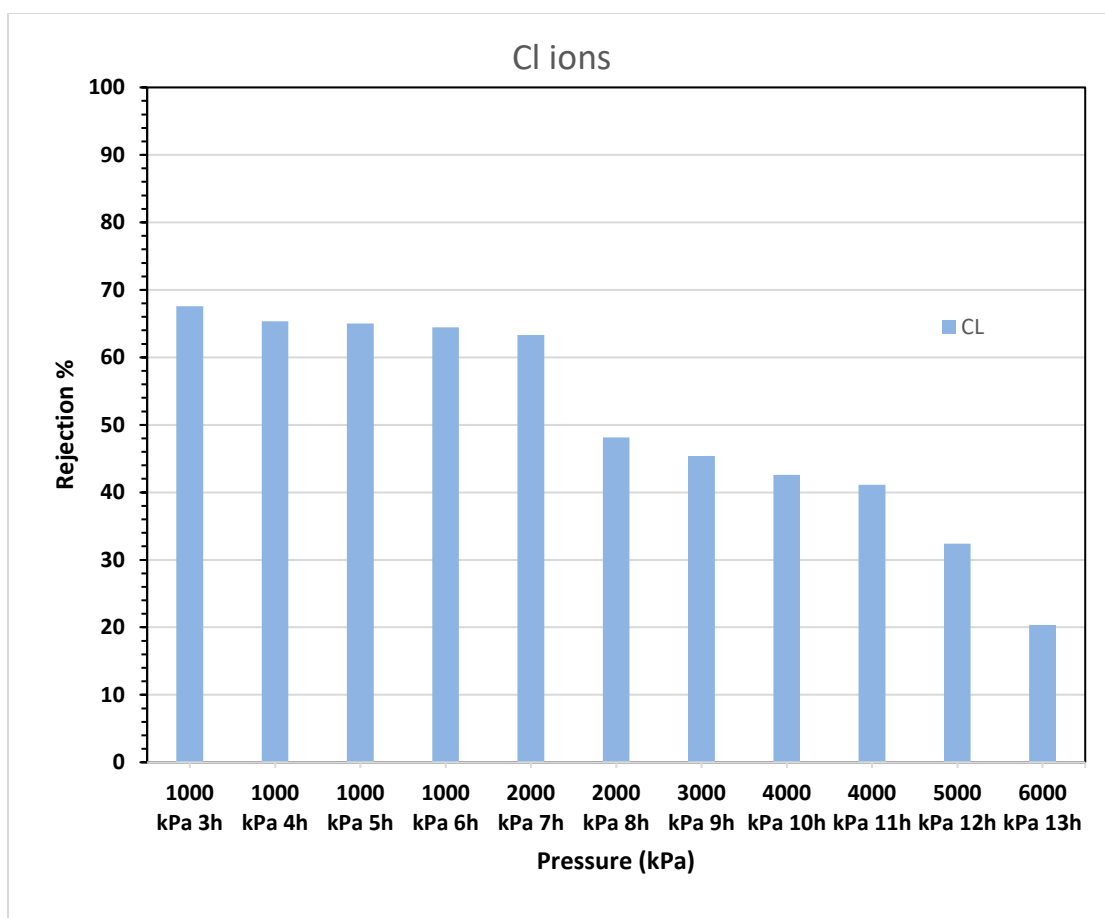
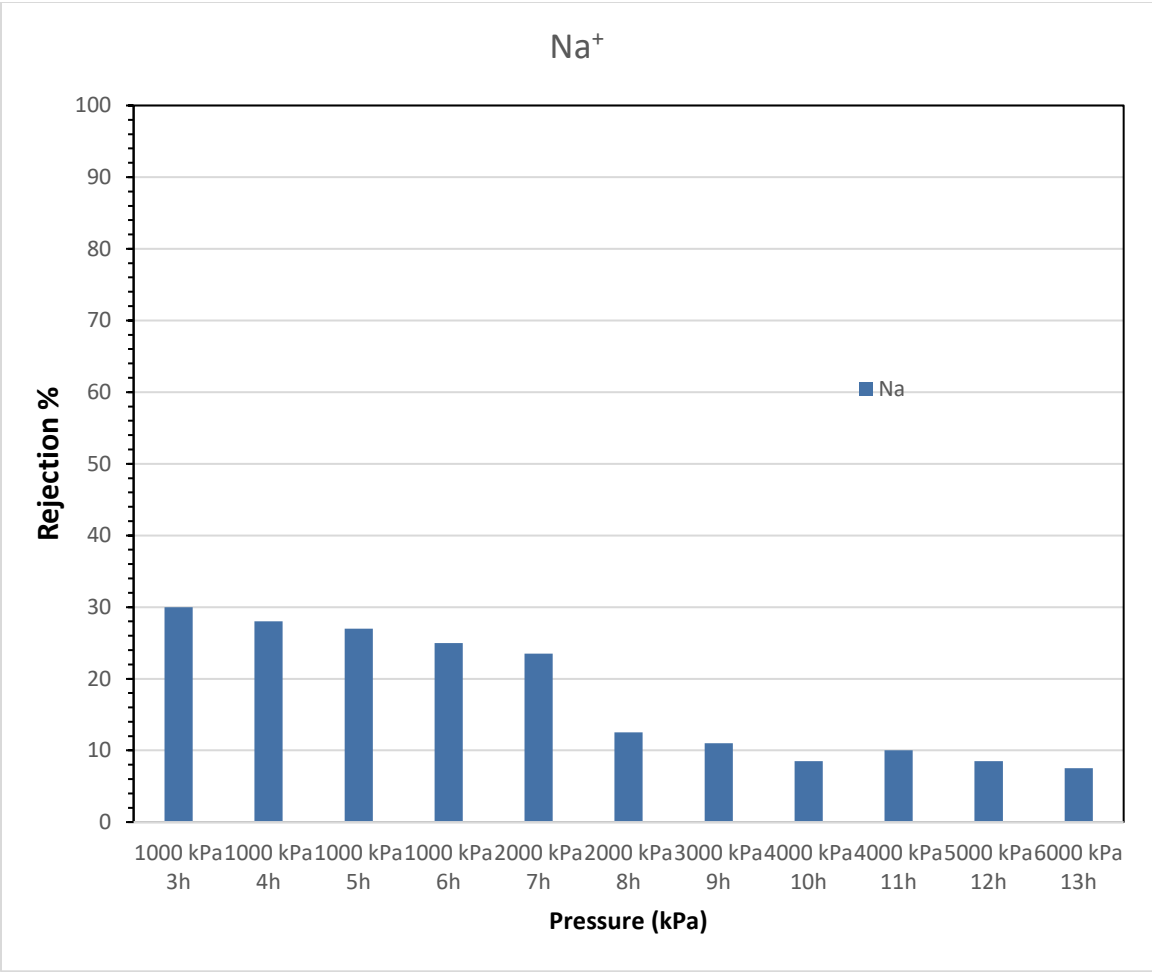


Figure 38. The rejection rate of chloride ions using the prepared membrane E



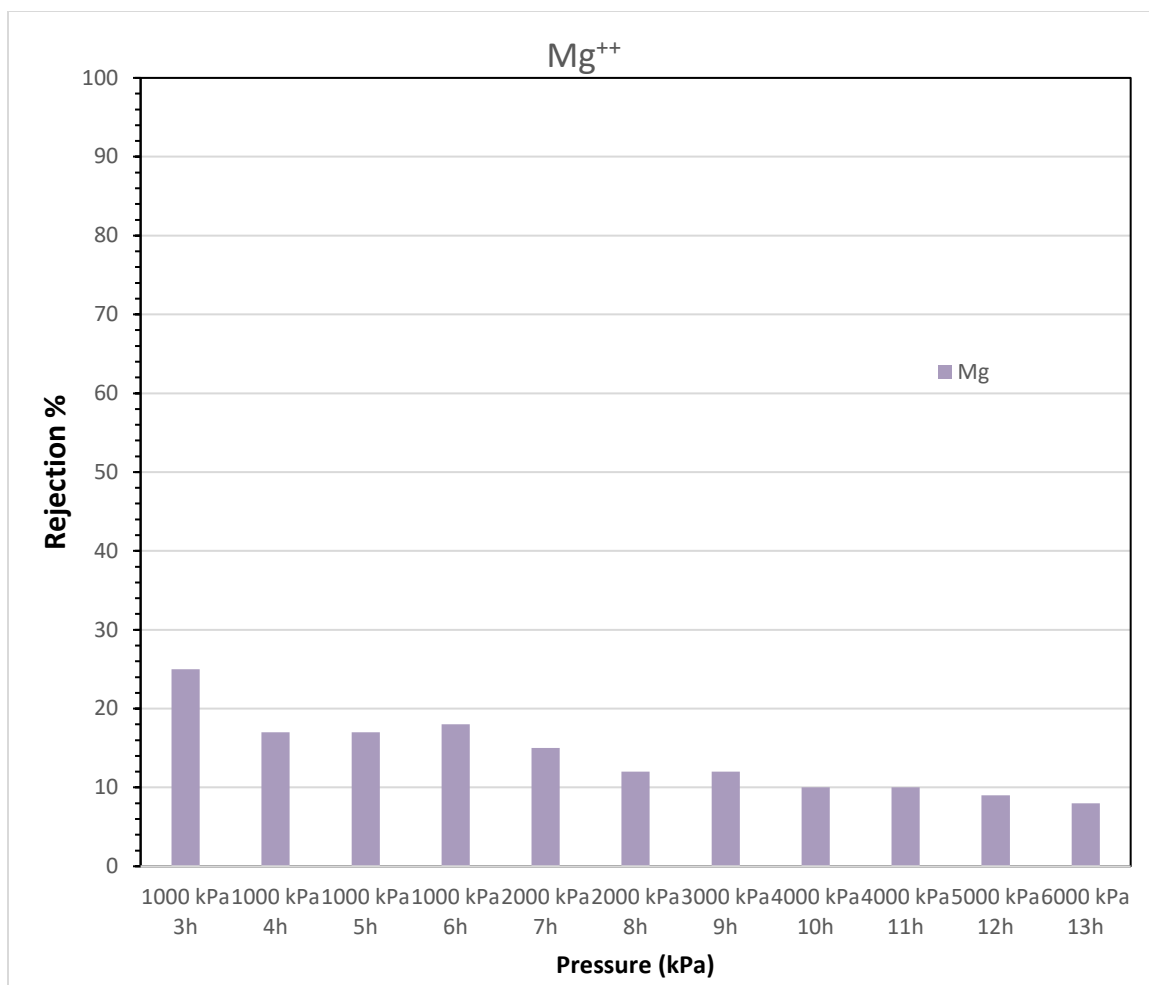


Figure 39. The sodium and magnesium ions percentage using the prepared membrane E

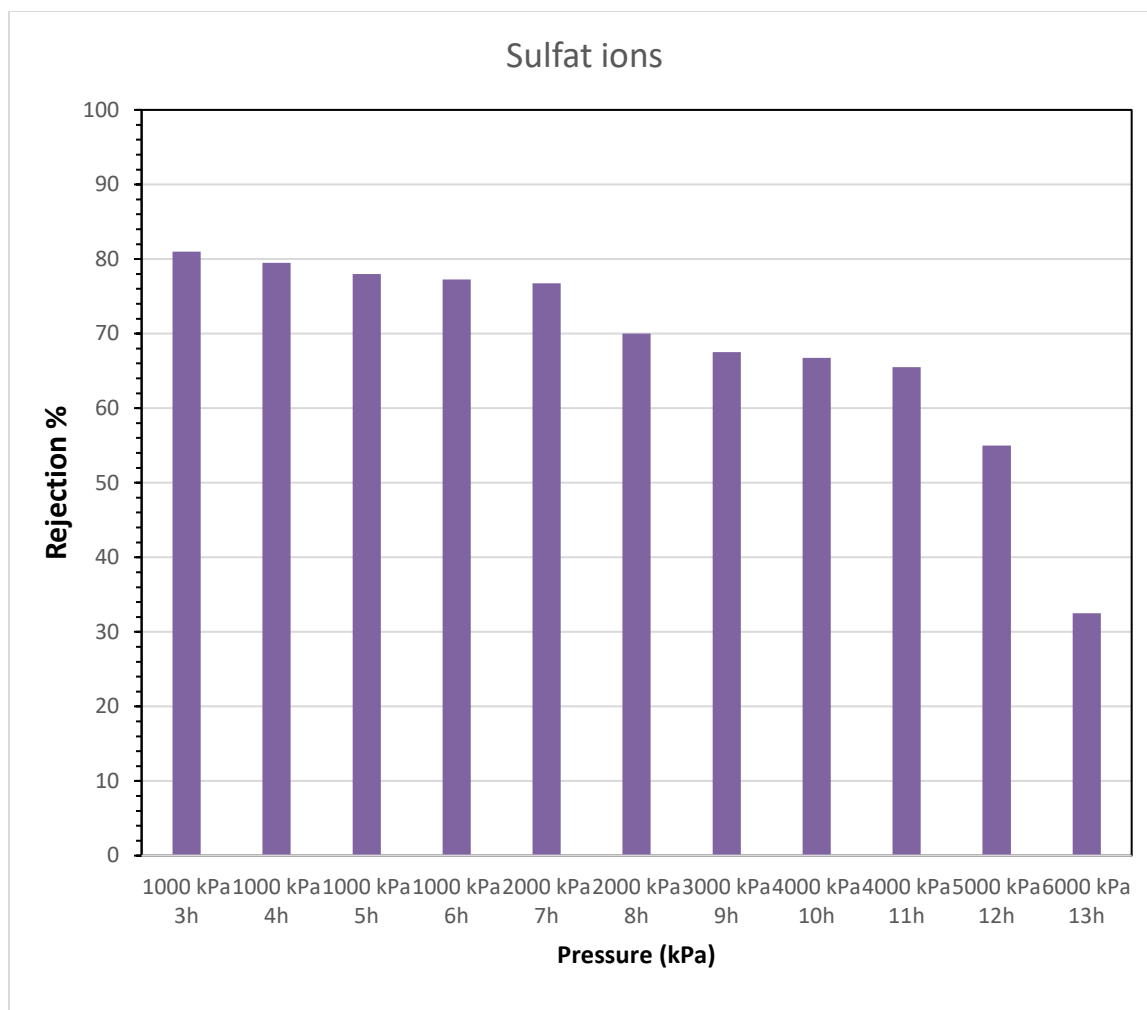


Figure 40. The sulfate ions rejection rate using the prepared membrane E

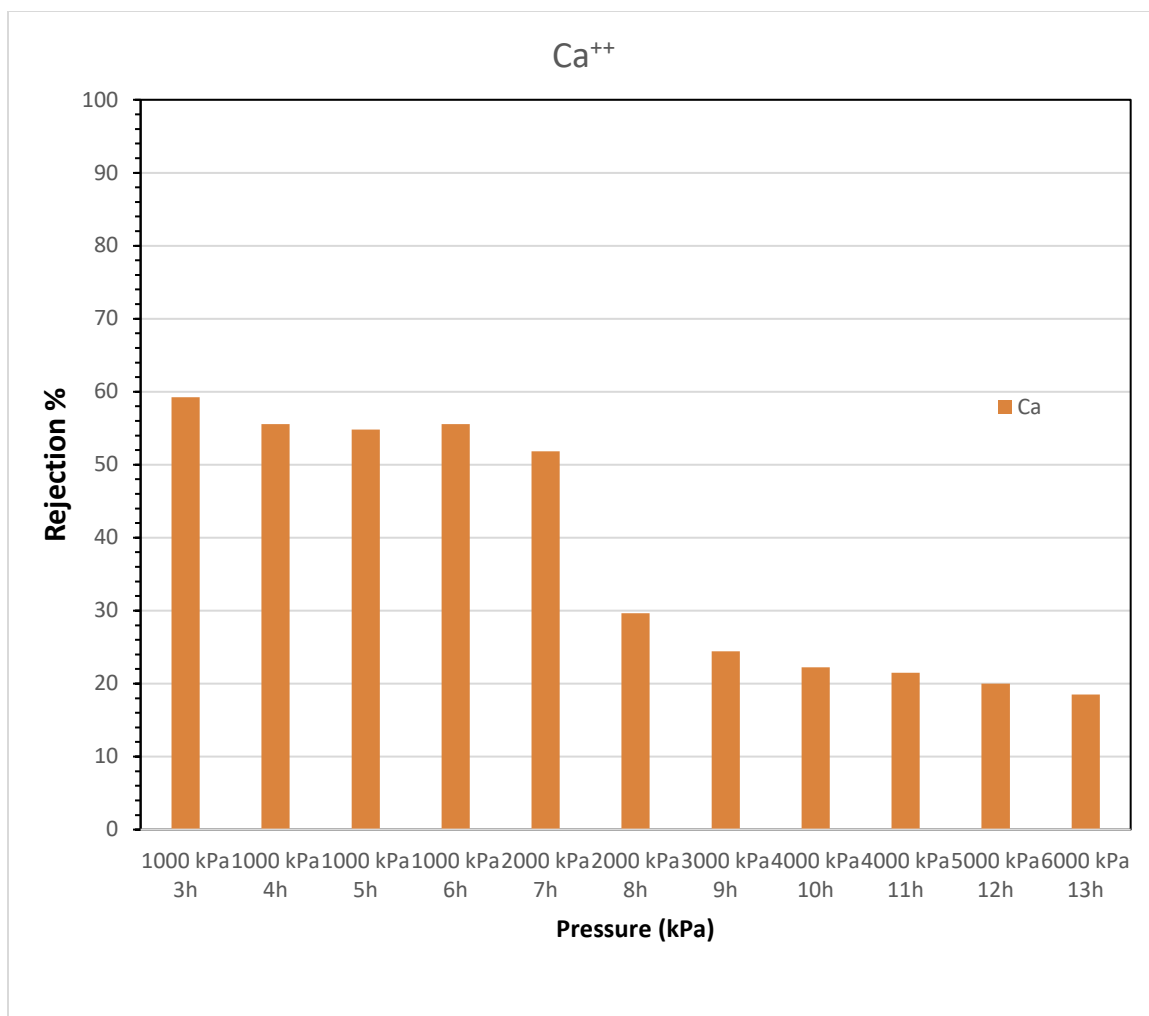


Figure 41. The calcium ions rejection rate using the prepared membrane E

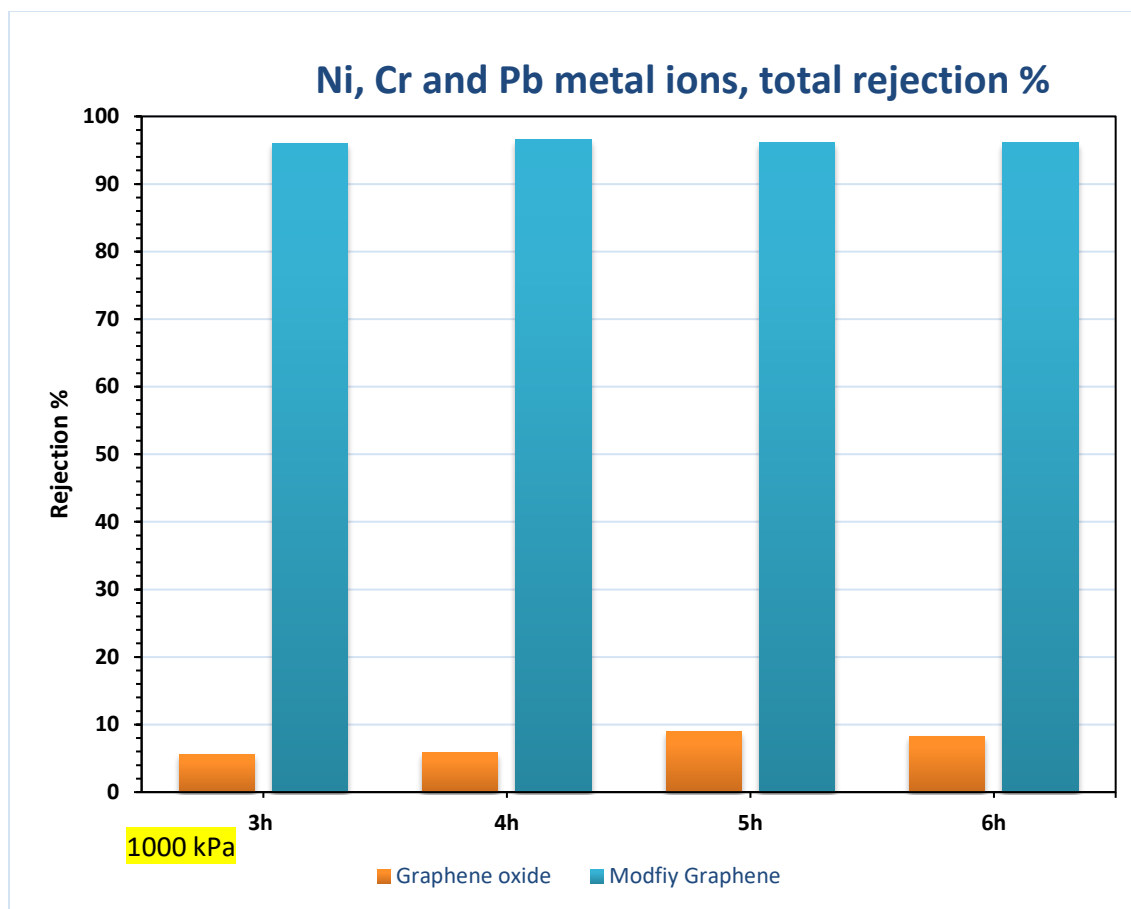


Figure 42. A comparison between graphene oxide membrane and amine-modified graphene membrane

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

Several membranes consisting of TMC and MPD with amine-modified graphene oxide were successfully synthesized by interfacial polymerization. Different characterization techniques such as XRD, SEM, and FTIR were utilized to characterize the prepared membranes. FTIR and XRD indicated the presence of amine-functionalized graphene embedded within the polymeric membranes. SEM images confirmed the uniform morphology of the prepared membranes. Filtration testing of the modified membranes showed that the polymeric membrane revealed high performance for the rejection of several pollutants. The prepared membranes showed good salt rejection, hydrocarbons rejection, and water permeability. These improvements were obtained due to the increase in negative surface charge and hydrophilicity.

5.2. Recommendations

Based on the results observed in this study, it is recommended that the prepared modified membranes are to be tested under real conditions such as real seawater. This will allow getting clear information on the reliability of the membranes to be used in the real application. Furthermore, the membrane can be tested under long-

term experiments to make sure that the membrane can stand the higher temperature produced by the continuous higher pressure and check the fouling resistance at the same time.

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