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Preparation and Characterization of Ceramic/Polymers Based Composite Membrane

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Dedication

"In the name of Allah, the most merciful the most passionate"

This work is wholeheartedly dedicated to those who have been there for me.

To my beloved parents

Whose unconditional love and endless encouragement gave me the strength and hope when mine faltered. whose sacrifices were etched in quiet moments and unspoken prayers, and their dreams for me were often bigger than my own.

This achievement is yours as much as it is mine.

To my friends and my loved ones, whom I encounter as my second family, who stood beside me and brought me support in the uncomfortable moment

***Ms.** KENDI Farah*
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LIST OF ABBREVIATIONS

GO: Graphene oxide

SGO: Sulfonated graphene oxide

rGO: Reduced graphene oxide

SGOAg: Sulfonated graphene oxide decorated with silver nanoparticles

SrGOAg: Reduces s sulfonated graphene oxide decorated with silver nanoparticles

MF: Microfiltration

UF: Ultrafiltarion

NF: Nanofiltration

SK: Sintered kaolin membranes

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CHAPTER II

RESULTS AND DISCUSSION

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Membrane technology is considered a powerful technique to face environmental challenges such as water sacristy and pollution, as they can meet multiple treatment objectives, where it encompasses a wide range of separation processes, with low energy consumption, high selectivity, and low carbon footprint [1].

Inorganic membranes (Ceramic) have been widely used due to their high thermal and chemical stability, high mechanical strength, ease of cleaning, and high durability, as they have been preferred for challenging water purification processes[2]. Ceramic membranes are fabricated using various techniques, such as powder pressing, colloidal processing, paste processing, and additive manufacturing (AM). Each of these methods offers unique advantages depending on the desired structural and functional properties of the membrane[3,4]. It can be noted however, ceramic membranes are commonly manufactured from a variety of inorganic materials, including Alumina (Al2O3), Zirconia (ZrO2), Titania (TiO2), Silica (SiO2), and other oxide mixtures [5]. These materials with different properties contribute to the overall membrane performance. In addition, ceramic membranes are well known for their high permeate flux, which is attributed to their hydrophilic surface properties that enhance water affinity as well as their high porosity enabling an efficient separation process by allowing greater permeability [6]. however, despite these advantageous properties, ceramic membranes remain susceptible to fouling, which can lead to a variation in selectivity and a significant decrease in permeate flux [7,8].

To overcome the challenges of conventional ceramic membranes, researchers have developed composite and hybrid membranes as a promising solutions. These advanced membranes integrate different materials to enhance the overall performance, where they get classified into ceramic-ceramic, polymer-ceramic, and ceramic-nanocomposite membranes. For instance, ceramic membranes combine different materials to enhance stability and separation efficiency, while ceramic polymer membranes integrate the flexibility of the polymers with ceramic's durability to enhance the composite membrane properties. On the other hand, ceramic nanocomposite membranes involve the incorporation of advanced nanomaterials, such as Graphene-based nanomaterials, to enhance their properties like chemical resistance and selective performance [6].

GENERAL INTRODUCTION

Ceramic Graphene Oxide (GO) composite membranes are being developed as a promising advancement in membrane technology, the incorporation of GO into the ceramic membrane has enhanced its performance due to the two-dimensional (2D) structure of GO, which contains various oxygenated functional groups on its basal planes and the edges [9]. These functional groups enhance membrane hydrophilicity, improving water permeability. It can also be noted that GO can form a defect-free ultra-thin layer with unique properties such as high resistance to fouling, high permeability, and enhanced durability [10]. this makes the ceramic-GO composite membranes suitable for different ranges of separation and filtration applications in the gas and liquid phases.

This work aim the preparation of different membrane, first of all, pristine and composite ceramic membranes are fabricated using the slip casting method made. As starting material the low-cost ceramic material (Algerian local kaolin) was selected for this work, and then the integration of Graphene oxide and its derivatives into the slurry matrix was also devoted on this study. These membranes were characterised using multiple characterization techniques, including DRX, FTIR, XRF, TGA, and antimicrobial test.

This manuscript is composed of three Chapters

- The first Chapter is a bibliographical research on ceramic composite membranes, where i will discussed the different type of ceramic materials with a general overview of the membrane technology. i will also discussed the different graphene-related nanomaterials, their hybridization, and their integration into the ceramic membranes.
- The second Chapter will discuss the ceramic membrane elaboration protocol with the incorporation of the different nanomaterials,
- The third chapter is the results and discussion, it is devoted to the experimental development, in which I will mainly describe the obtained results from the characterization.
- Finally, I will present a general conclusion summarizing the main results of this study.

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CHAPITRE I

CERAMIC-BASED COMPOSITES MEMBRANES

I.1. INTRODUCTION

Ceramic membranes have emerged as a promising material in different separation processes. This first chapter reviews the recent advancements in ceramic composite membranes and it was divided on three main part:

The first part is an overview of ceramics, where we discussed different types of ceramic materials for membrane fabrication. These materials were categorized into high-cost and low-cost ceramic materials.

The second part is an overview of membranes, where we discussed the membranes classification and the different elaboration techniques.

The third one is about the composite and hybrid membranes, as we have deeply discussed the different nanomaterials and the importance of incorporating these nanomaterials into the ceramic matrix to create a new generation of composite and hybrid ceramic membranes.

I.2. CERAMIC MATERIALS

I.2.1. Definition

Ceramics are one of the oldest and most versatile materials that existed on earth, the term ceramic which means “burnt stuff” is originated from the Greek word “ Keramiko”. It refers to any material derived from any clay rich raw material that has been treated with a firing process [1]. Ceramics are an inorganic material composed from metallic and non-metallic components combined with ionic and covalent bonds. The physical and chemical properties of these materials are mainly depending on the nature and arrangement of these bonds where they contribute to the ceramic high melting point , chemical inertness and strength [2]. Ceramics can exist in crystalline, non-crystalline or even a combination of both structures. The Ceramic materials play a crucial role in membrane fabrication due to their high thermal stability, mechanical strength and good resistance against harsh conditions. They can be categorized by their nature and overall performance into low-cost and high-cost materials. The high cost ceramics include metal oxide materials such as Aluminum Oxide (Al_2O_3), Zirconium dioxide (ZrO_2), Titanium dioxide (TiO_2), Silicon Carbide (SiC) where they are known also as the high-performance ceramic materials due to their high functional properties, and the low-cost ceramic materials, such as Kaolin, Fly ash, and Natural Zeolite which are more economically available alternatives [3,4].

I.2.2. High-Performance Ceramics For Membrane Fabrication

I.2.2.1. Aluminum Oxide (Al_2O_3)

Aluminum Oxide (Al_2O_3), commonly known as Alumina, is an amphoteric oxide of aluminum obtained by refining Bauxite. Alumina exists in two phases: a stable rhombohedral crystalline phase α-Al_2O_3 and unstable phases such as γ-Al_2O_3 [5,6]. Its great usefulness as a material rests on its great biological and physical properties, including chemical inertness and electrical insulation, corrosion, and oxidation resistance, high melting point, and high thermal conductivity [7]. In-addition~~,~~ Alumina are used as a reinforcement phase in various materials [8]. It is mostly used for membrane fabrication, where it has proved its efficiency, especially in the Microfiltration (MF) and Ultrafiltration (UF) membranes for the treatment of highly contaminated wastewater.

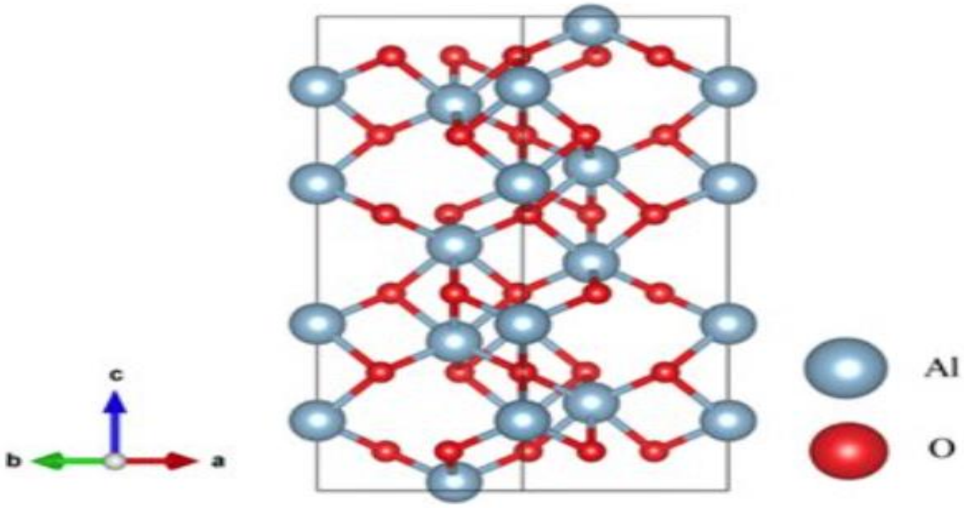

Figure I. 1. Alumina oxide structure [9].

I.2.2.2. Zirconium Oxide (ZrO_2)

Zirconium dioxide, is a white crystalline ceramic material, with a biphasic polycrystalline structure consisting of 3 phases: monoclinic phases at room temperature, tetragonal at a temperature of [1175°C-2370°C], and cubic phase at temperatures of [2370°C-2680°C][7].

Zirconium oxide play a crucial role in advanced filtration technology where it is commonly used for the development of microporous ceramic membranes due to its outstanding properties such as its super hydrophilicity where these membranes have high affinity for water that will allow for higher flux rate and lower fouling tendencies during water treatment as well as its high thermal resistance and mechanical strength that empower it to work under high temperatures and pressure [10], they also exhibit excellent chemical stability which allow them to function properly under harsh conditions and corrosive environments [11].

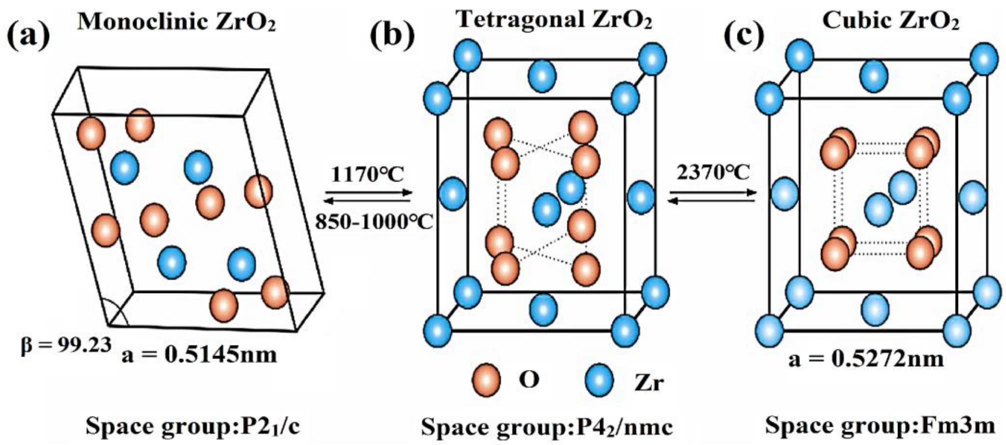

Figure I. 2. Zirconium oxide crystal structure [12].

I.2.2.3. Titanium dioxide (TiO_2)

Titania is a ceramic material that exists in three crystal phases: brookite, anatase, and rutile [13]. This material is widely used in membrane fabrication for different applications, especially in water and wastewater treatment, where the Titania can be applied as an active layer, intermediate barrier, and support substrate for the UF and NF membranes. These membranes have demonstrated high chemical and thermal stability, making them resistant to chemical degradation and stable under high temperatures. They also exhibit high mechanical strength and are resistant to fouling which contributes to their durability and long lifespan[14]. Moreover, its unique photocatalytic properties make it effective for the degradation of organic pollutants under UV lights [15].

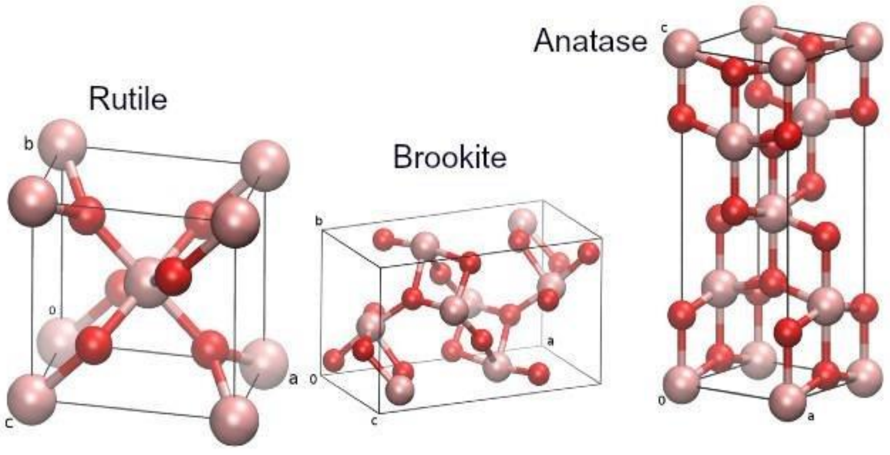

Figure I. 3. Titanium dioxide structure [16].

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I.2.2.4. Silicon Carbid (SiC)

Silicon Carbide (SiC) is a high-performance non-oxide ceramic material with a tetrahedral crystal structure **(Figure I.4)**. It exists in multiple forms, such as Cubic, Hexagonal, and Rhombohedral. SiC is extensively used for membrane fabrication, where its excellent thermal and hydrothermal stability, chemical resistance, and its mechanical properties make it highly suitable for high-temperature applications and harsh environments [17]. It is also known for it high porosity and low tortuosity, which enables it able to reach high permeate flux [18]. These membranes usually consist of multiple layers, an active layer made from SiC, an intermediate layer to control the porosity of the membrane, all deposited on a porous substrate. Generally, the substrate is made of the same material as the active layer to minimize the crack formation [19].

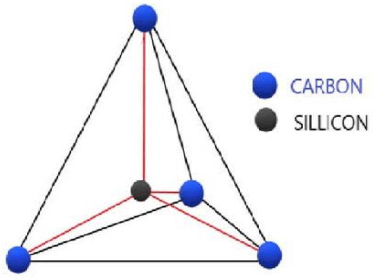

Figure I. 4. Schematic of the Silicon carbide structure [20].

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I.2.3. Low-Cost Ceramic Materials

I.2.3.1. Kaolin

Kaolin ($Al_2Si_2O_5(OH)_4$), the term kaolin is derived from the Chinese word ‘kauling’, which refers to a hill close to the Jauchau Fu in China. Kaolin is known as a soft white powder that is created through the chemical breaking of aluminum-rich silicate minerals by weathering [21]. Or through a hydrothermal alteration mechanism, due to the interactions between the sodium feldspar and water at elevated temperatures. At 200°C, the feldspar gets dissolved and releases sodium and silicate ions into the solution while leaving a reactive aluminum-rich layer. This layer interaction with water will form boehmite, which will later transform into kaolinite under specific pH conditions [22]. The reaction that resumes the hydrothermal process:

$2NaAlSi_3O_8+9H_2O^++2H\rightarrow Al_2Si_2O_5(OH)_4+4H_4SiO_4+2Na^+$……………………Eq1[23].

Kaolin ceramic possesses a crystal structure, known as non-swelling dioctahedral, due to it 1.1 layered silicate mineral. each structural unit consists of an alumina octahedral sheet (aluminum-oxygen/hydroxyl) deposited on the top of a tetrahedral silica sheet (silicon-oxygen). these layers are bonded with van der Waals forces and strong hydrogen bonds, resulting in non-expandable closed interlayer spacing, which will ensure structural stability. Its also known for its high refractoriness which allows it to withstand high temperatures. kaolin is valued for its diverse properties, which can vary depending on the region it is sourced from. as it occurs abundantly in nature, where it composition, particle morphology, and performance characteristics can vary depending on the environmental conditions and mineralogical process of its formation [24].

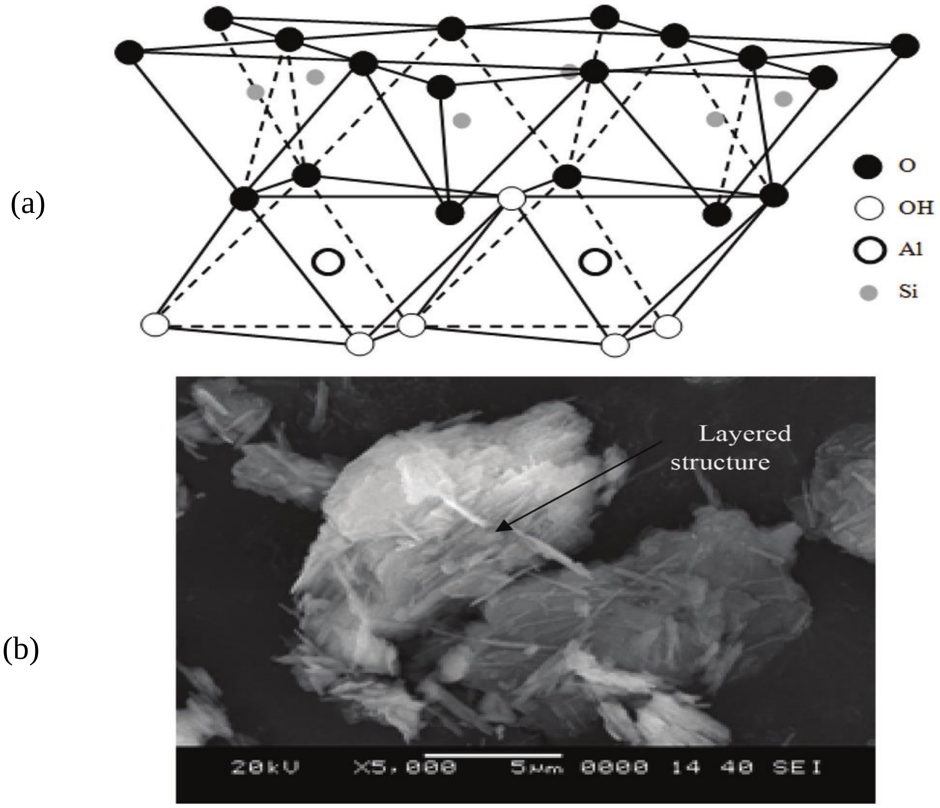


Figure I. 5. Schematic representation of kaolin, (a) represents the kaolin structure; (b) SEM image of kaolin layers [25].

I.2.3.2. Fly ash

Fly ash (FA) is a by-product of coal combustion, formed through sintering. It consists generally of inorganic minerals in both crystalline and amorphous phases, along with varying portions of partially or unburned carbon. the composition of FA includes a wide range of elements, with the majority of silicon dioxide (SiO_2), and others such as Aluminum, Calcium, and Iron, with trace amounts of Magnesium, Potassium, Sodium, and Titanium. Fly ash exhibits, a complex microstructure due to its interaction with other raw materials during the sintering process, where it possesses a crystalline phase which are Mullite ($3Al_2O_32SiO_2$), Quartz (SiO_2), and Anorthite ($CaAl_2Si_2O_8$) depending on the original composition and any added materials and amorphous (glassy) phases which originates from the rapid cooling of liquid Silicate that will cerate a glassy matrix that hold the crystalline components together. which will play a crucial role in the mechanical properties of the final product [26,27].

I.2.3.3. Natural Zeolite

Zeolite is a group of multiple aluminosilicate minerals with a crystalline structure bonded together through shared hydrogen atoms, resulting in a three-dimensional framework. It negatively charged framework allows it to easily exchange ions, which is beneficial for the catalytic performance and also to reversibly Adsorb and release not only water but also gases and vapor [28]. Zeolite can occur naturally, where it can form in volcanic lava flows, or it can be synthesized. This ceramic material is known for its high mechanical properties when it's sintered, moreover, it retains a good framework and chemical stability at high temperatures and an exceptional resistance against harsh environmental conditions [29].

I.3. OVERVIEW OF MEMBRANE TECHNOLOGY

I.3.1. Membrane Definition

A membrane is a semi-permeable barrier that separates two media and selectively allows the passage of certain molecules or ions, or particles, while rejecting others based on the difference in their properties, either in size or chemical affinity. The substances retained by the membrane are collected in the retentate while the ones that passed through form the permeate. Usually, the separation mechanism of the membrane is due to a difference in pressure, concentration gradient, or electrical potential. Membranes are broadly categorized into organic membranes, made of polymers, and inorganic ones, which are composed of inorganic materials such as ceramics [30].

I.3.2. Ceramic Membranes

Ceramic membranes are rapidly advanced materials that have been used for many years in various sectors including water treatment, the oil and gas industries, and biotechnology due to their excellent properties and unique asymmetric structure, these membranes consist of a support layer which is a thick and highly porous layer that provides mechanical strength and an active layer which is a thin layer with smaller porous positioned on the top of the support layer to ensure selectivity, This multilayer configuration allows for high permeate flux and effective separation performance [31]. Ceramic membranes are fabricated from inorganic materials such as metal oxide ceramics, Alumina, Zirconia, Titania, and Silicon Carbide, or low-cost ceramics such as kaolin, zeolite fly ash. Their unique structure and compositions give high mechanical strength, high chemical and thermal stress resistance, and a highly hydrophilic surface, making them suitable for harsh operating conditions and ideal for industry's demand [32].

I.3.3. Ceramic Membranes Classification

Membranes usually get classified according to their morphology, geometry, and separation mechanism.

I.3.3.1. Classification According To Morphology

The choice of the membrane morphology has a huge influence on the overall membrane performance, durability, and cost. ceramic membranes can be classified according to their morphology into:

I.3.3.1.1. Symmetric membranes

Symmetric membranes are generally composed of the same material, they can be porous or dense membranes. The term symmetric refers to membranes with uniform pore size and distribution throughout its whole cross-section [33].

I.3.3.1.2. Asymmetric membranes

Asymmetric membranes are known as a gradient pore membrane where the pore size gradually change from the top layer to the support layer. These membranes consist on a top layer deposited on a porous substrate where it can be composed from one material or a composite from different materials [34].

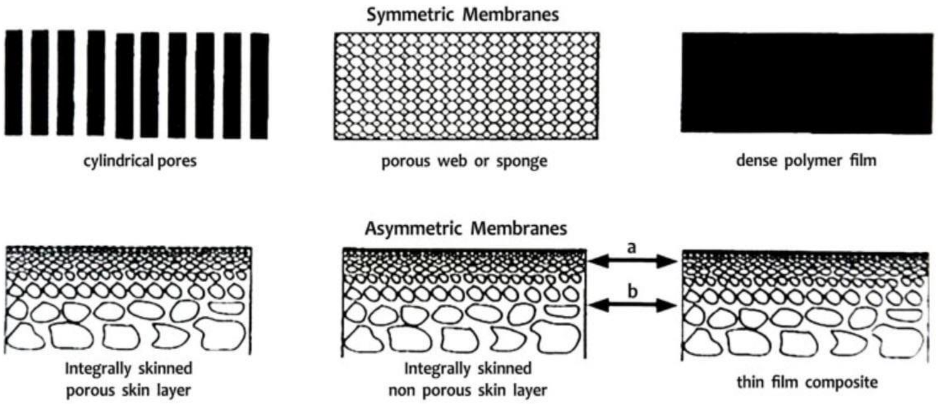


Figure I. 6. Schematic representation of symmetric and asymmetric membranes [35].

I.3.3.2. Classification According To The Geometry

The geometrical configuration is considered an essential aspect for ceramic membranes as it affects the surface area and the module design. They can be classified into tubular, flat sheet, and hollow fiber membranes.

I.3.3.2.1. Tubular membranes

Tubular membranes are composed of one or more membranes formed in the shape of cylindrical tubes with internal diameters usually between 4 and 25 mm. These tubes are housed in a structural casing or module. Multiple tubes can be arranged in parallel in one module, where it's known as a multichannel configuration, to enhance the uniform flow distribution and the industrial integration [36].

Figure I. 7. Tubular ceramic membrane [37].

I.3.3.2.2. Hollow fiber membranes

Hollow fiber module membranes typically consist of thousands of capillary-like fibers, each around 1 mm in diameter. These membranes are composed of two different layers, which can be made from the same materials or different ones. The first layer is the support layer that ensures mechanical properties, and the active layer, which provides selectivity in separation performance. To guarantee hydraulic sealing between the feed side and the permeate side, these fibers are bundled together and potted (glued) at both ends. The feed stream may flow from the outside to the inside (outside-in configuration) or from the inside to the outside (inside-out configuration) of the fibers, depending on where the active separation layer is located [38].

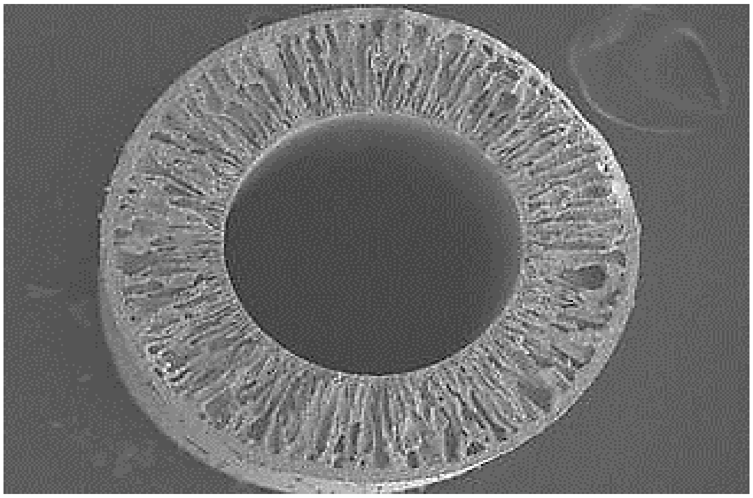


Figure I. 8. ceramic hollow fiber membrane [39].

I.3.3.2.3. Flat sheet membranes

Flat sheet membranes are large and usually shaped in rectangular or circular flat plates with a thickness of 100 µm. They can be either porous or dense membranes, and they are typically made so they can be mounted in plate and frame modules where multiple membrane sheets are arranged in parallel with a flow channel in between.

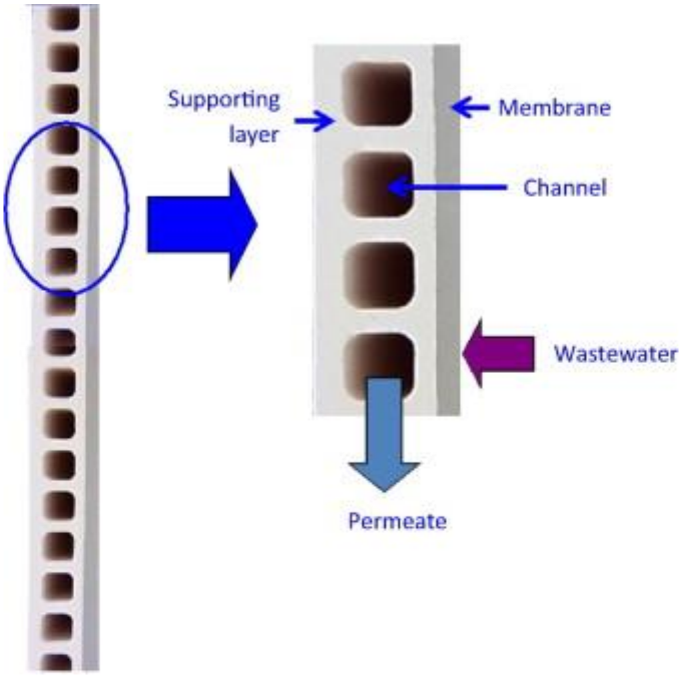


Figure I. 9. flat sheet ceramic membrane [40].

I.3.3.3. Classification According To Porosity

Membrane get classified according to porosity into two types of membrane: dense and porous.

I.3.3.3.1. Porous membranes

According to the International Union of Pure and Applied Chemistry (IUPAC), Porous Ceramic membranes have been classified into 3 categories:

Table I.1. Membrane classification according to the IUPAC [41].

Membrane category	Pore size (nanometer)
Micropores	Less than 2nm
mesopores	Between 2 and 50 nm
macrospores	More than 50 nm

I.3.3.3.2. Dense membranes

The term "dense ceramic membranes" refers to a class of ceramic membranes that are non-porous or have very low or negligible porosity, usually with pore sizes less than 1 nm. Dense membranes, as opposed to porous ceramic membranes, separate species through processes including solution-diffusion, ionic conduction, and molecular diffusion rather than size exclusion through pores [42].

I.3.4. Separation Mechanism in Ceramic Membranes

The separation performance of ceramic membranes is based on the combination of physical and chemical mechanisms that govern their selectivity, durability, and efficiency in different applications.

I.3.4.1. Size Exlusion

Size Exclusion, or as it is known as the mechanical sieving, is the most controlling separation mechanism in porous ceramic membranes for Microfiltration (MF), Ultrafiltration (UF), and Nanofiltration (NF). The rejection in this mechanism is based on the particles or molecules size; the ones that are larger than the membrane's pores are retained, while the smaller ones can pass through. The pore distribution is responsible for determining the cutoff separation limit of the membrane. This process is pressure-driven, and its efficiency depends on pore size, membrane porosity, and operating pressure.

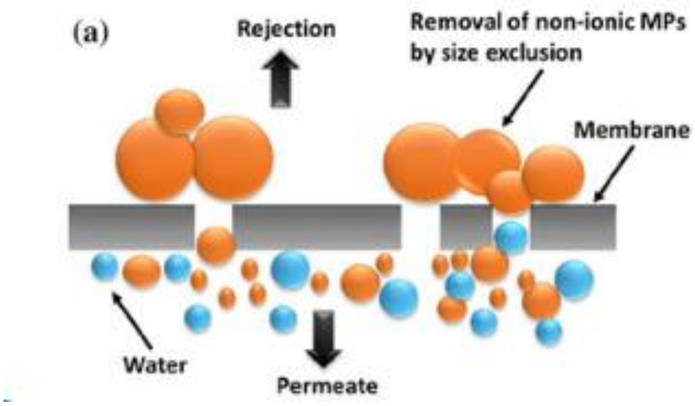


Figure I. 10. size exclusion separation mechanism [43].

I.3.4.2. Surface charge interaction (Electrostatic repulsion)

Ceramic membranes have surface charge-dependent separations because of their zeta potential. Under acidic and neutral pH conditions, the surface of the membrane possesses a positive charge and shows electrostatic exclusion of cations and attraction of anions at pH values below the isoelectric point of the membrane. Typically, multivalent ions are more strongly repelled than monovalent ions of the same size due to their higher charge. This enables selective ion rejection, even when ions are smaller than the membrane's nominal pore size.

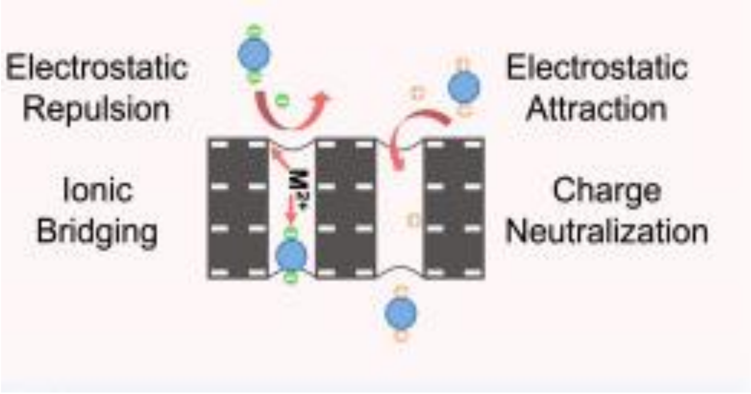


Figure I. 11. Electrostatic repulsion mechanism [44].

I.3.4.3. Solution diffusion mechanism

The solution diffusion model is the dominant driving force for the transport of permeating species when no open pores are present. In contrast to porous ceramic membranes which are size-selective, the process of permeation separation for dense ceramic membranes occurs in the following steps: (i) the selective molecules first dissolve (adsorb) on the membrane surface; (ii) they then diffuse from the surface through the dense ceramic matrix under a partial pressure or concentration gradient; and (iii) they desorb at the permeate side.

I.3.5. Ceramic Membranes Fabrication Techniques

Various fabrication techniques have been used for the elaboration of ceramic membranes; most of these techniques involve adding different additives to the ceramic material to make it more suitable for different applications.

I.3.5.1. Slip Casting Method

Slip casting is a widely employed method for the fabrication of flat ceramic membranes, especially when precise control over shape and thickness is needed. This process starts with the preparation of ceramic slurry by mixing the raw material with an appropriate solvent and other additives if needed. The resulting slurry is then poured into a mold to get the desired shape. The thickness and homogeneity of the flats are mainly influenced by the raw material nature and grain size, the slurry viscosity, and the temperature during casting it can be noted that these membranes go through a sintering process where they get heated at optimized temperatures and durations to facilitate particle bonding and enhance their mechanical stability [45].

I.3.5.2. Extrusion Method

Extrusion is a conventional ceramic membrane fabrication technique, where it is based on selecting an appropriate ceramic powder to mixed it with a solvent and different additives to form a slurry. the ceramic mixture is then poured into an extrusion die that has been created using the appropriate membrane geometry, such as tubular, monolithic, or multichannel designs. The material is extruded through the die under pressure, creating a continuous, formed ceramic body in a predefined direction. The mold design determines the membrane's dimensions and form, enabling customization according to application-specific needs. In order to get rid of the remaining moisture and solvents, the green ceramic membrane is carefully dried after extrusion.

Because inadequate drying might result in cracks, warping, or deformation, this phase is crucial. After drying, the membrane is sintered at high temperatures, which causes the ceramic particles to bind and densify [46].

I.3.5.3. Pressing method

The pressing method is a technique for creating ceramic membranes. This process is based on using an appropriate ceramic powder that is shaped and processed under pressure in molds, causing the ceramic particles to deform and bond together to form a dense precursor. The precursor is then sintered at high temperatures to further bond and crystallize the particles, resulting in a dense ceramic structure. Notwithstanding its effectiveness, the pressing method has several disadvantages, including the need for multiple steps, higher costs, limited shape complexity, and difficulties with precision and thickness control [47].

I.4. COMPOSITE AND HYBRID CERAMIC MEMBRANES

Composite and hybrid ceramic-based membranes are known as an advanced approach to improve the reliability and operational feasibility of the membrane separation process and achieve to a filtration process that is difficult for conventional filtration technologies to reach in different applications, especially in wastewater treatment, where the retention of small molecules and ions remains a challenge [48].This innovative approach involve the combination of the advantageous characteristics of different organic or inorganic materials to enhance the properties and enhance the membranes performance and characteristics such as the selectivity, permeability, thermal stability, and fouling resistance.

Ceramic-composite membranes consist of a ceramic substrate combined with other organic or inorganic substances such as polymers, metal-organic frameworks (MOFs), or nanomaterial-based additives to enhance the overall performance of the membrane, The ceramic substrate provides thermal stability and resistance to fouling while the polymers and the nanoparticles contribute in improving the selectivity and adsorption [49]. The ceramic composite membranes have shown a superior performance in gas separation and water purification. While Hybrid membranes involve chemical and covalent bonding of organic and inorganic substances to the ceramic matrix to create a unified structure with enhanced selectivity and help to optimize pore structure [50].

I.4.1. Ceramic Graphene-Based Membranes

In recent years, graphene-based materials have experienced significant expansion in membrane technology due to their unique properties including their thermal, chemical stability, and their high permeability [51]. The incorporation of the graphene nanomaterials and its derivatives into the ceramic membranes has shown superior performance in various separation processes. The perfect combination of the ceramic material properties and the graphene unique properties has shown great potential in creating highly selective and even electrically conductive ceramic membranes [52].

I.4.1.1. Graphene

Graphene is a two-dimensional carbon allotrope material composed of a single layer of carbon atoms[53]. Despite its thin structure, graphene has exceptional properties that make it a well-recognized nanomaterial utilized in various applications, especially in membrane technology, where the incorporation of Graphene into membranes has shown promising results to overcome multiple challenges facing the membranes, especially for water and wastewater treatment, such as fouling, scaling [54].

I.4.1.2. Graphene Oxide

GO is the most widely recognized carbon-based nanomaterial. It has a layer structure similar to Graphene but with the presence of various oxygen-containing functional groups such as hydroxyl(C-OH), carboxyl (C-OOH), and epoxy(C-O-C) groups as its shown in **Figure I.12.** With its inherent defects all of which contribute to its unique chemical and mechanical properties, these functional groups contribute in increasing the interlayer spacing of the GO nanosheets which will enable a highly precise molecular sieving and a higher selective separation [55]. Additionally, the GO oxygenated functional groups induce significant hydrophilicity and a negative surface charge that will enhance the water permeability and the retention of different contaminants [56]. The incorporation of GO with ceramic membranes will enhance its chemical stability and improve the mechanical integrity and electrical conductivity of the membrane making them suitable for various separation and filtration applications [57].

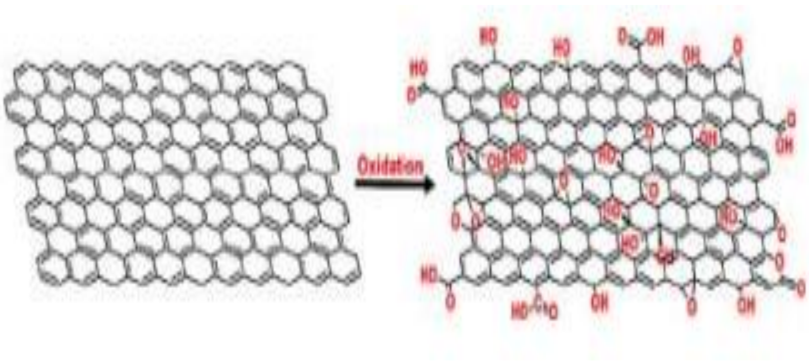


Figure I. 12. Structure of GO after the oxidation of a graphene sheet [58].

I.4.1.3. Reduced graphene oxide(rGO)

Reduced Graphene Oxide is a chemically modified derivative of GO, obtained through chemical, electrochemical, and thermal reduction of GO, this reduction will partially restore the SP^2 hybridized carbon network which will enhance the rGO mechanical robustness and also ensure the partial removal of the oxygen groups containing functional properties, which will significantly enhance its thermal and electrical conductivity compared to GO [59]. rGO exhibits a heterogeneous surface with high thermal and chemical stability, improving its performance in various applications [60]. In recent years developing ceramic membranes with the incorporation of rGO is gaining significant interest as the rGO has shown great results in the filtration and separation process due to its properties that help to enhance membrane performance, such as the rGO nanosheets that possess high surface area, which will enhance the density of the membrane structure. The incorporation of rGO on ceramic matrix helps in reducing the pore size and obtaining a membrane with optimized nanopore sizes, which is beneficial for the separation performance in different applications.

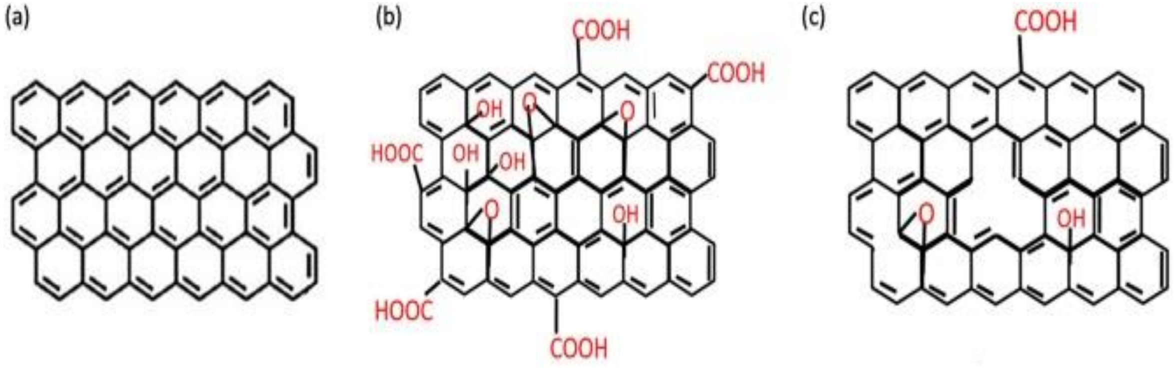


Figure I. 13. Structure of : (a): Graphene; (b): Graphene oxide (GO) and (c): rGO [61].

I.4.1.4. Sulfonated graphene oxide(sGO):

Sulfonated Graphene Oxide is a graphene oxide (GO) derivative modified with sulfonic acid groups. The sulfonication of the GO can be achieved using various sulfonating agents, including the chlorosulfonic acid [62], sulfonic acid, 2-chloroethane acid, and through other methods such as the diazonium salt technique. The sGO has a fine nanostructure with high thermal stability due to its multiple functional groups, such as hydroxyl and carboxyl groups, and also sulfonic groups($-SO_3H$) [63]. The incorporation of sGO into membranes has been an interesting approach to develop because of its multiple advantages. Notably, the incorporation of sGO has helped to enhance the catalytic performance of the membrane particularly when incorporated with Titanium Dioxide (TiO2), significantly improving the photocatalytic degradation of many dyes. Additionally, it has a high adsorption capacity, which makes the sGO effective for dye removal applications [64].

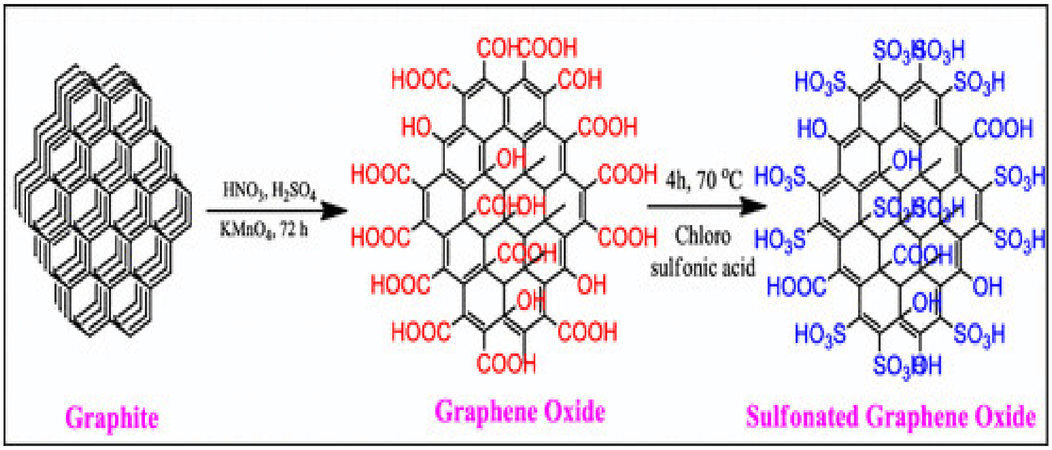
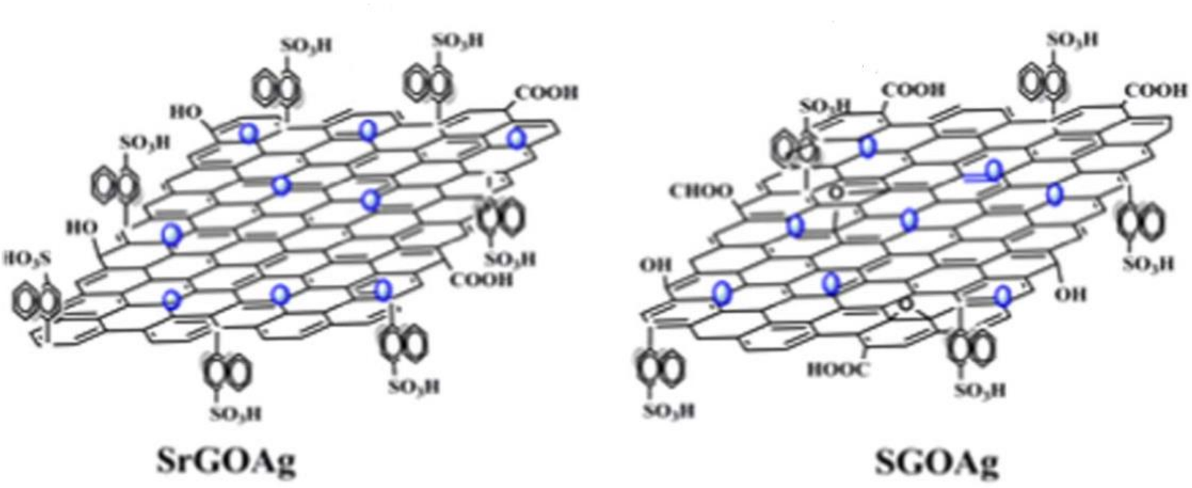


Figure I. 14. illustration of the synthesis mechanism and the final structure of sulfonated graphene oxide (sGO) [65].

I.4.1.5. Functionalization of graphene oxide hybrid

Graphene oxide has emerged as a transformative material in nanotechnology due to it unique structure and properties that make it widely used in various applications. However, GO still has limitations that alter its performance. Hence, the functionalization of GO-hybrid has emerged as a promising solution and unlocked various development opportunities, especially in membrane technology. There are various methods for the functionalization of the GO, including covalent and non-covalent approaches, composite materials integration, polymer grafting, and nanoparticle decoration such as metal oxide and gold nanoparticles. The functionalization of GO enables the development of superhydrophobic materials with enhanced thermal stability. it also provides high mechanical strength, chemical stability, and electrical conductivity, making them versatile materials for advanced membrane technologies [66,67].



SrGOAg SGOAg

Figure I. 15. Schematic illustration of chemically functionalized graphene oxide [68].

I.4.2 Synergistic Ceramic–GO Composite Membranes

Ceramic graphene oxide (GO) composite membranes have gained significant interest recently due to their exceptional performance in separation processes. The synergistic combination of the chemical stability and mechanical strength of ceramic materials with the unique two-dimensional structure and the tunable surface properties of the GO results in a membrane with superior selectivity, permeability, and antifouling properties [69,70]. The nanochannel structure of the GO allows the water molecules to pass primally through its hydrophilic oxidized region, then travel rapidly through the hydrophobic non-oxidized regions, where the low-friction pathway enables a fast and low-resistance transport [71]. meanwhile, the precise control over the interlayer spacing between the GO nanosheets allows the control over molecular sieving, enhancing membrane selectivity. Furthermore, the electrostatic interaction between the charged solutes and negatively charged GO nanosheets contributes in high rejection for ions and other charged compounds [72]. while the ceramic membrane provides mechanical strength and structural stability to prevent collapse under stress, the well-integrated structure of the ceramic

GO composite membrane, combined with its unique transport and separation properties, makes it highly suitable for a wide range of applications, including water and wastewater purification as well as gas separation [73].

I.5. CONCLUSIONS

An overview of ceramic materials, membrane technologies, and composite membranes development was presented in this chapter. Ceramic membranes have been demonstrated to have promising chemical, thermal, and mechanical stability, hence, they are also adapted for separation purposes in extreme environments. The insights gained from this review form the basis for the experimental work presented in the following chapters. The next section will focus on the preparation, modification, and characterization of ceramic and ceramic composite membranes.

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CHAPITRE II

MATERIALS AND METHODES

II.1. INTRODUCTION

Ceramic membranes utilization in different separation processes has been limited due to their high cost and limited properties. In this chapter we will present the different steps of elaboration of multiple flat and dense low-cost ceramic membranes which are made from local kaolin for the ceramic membrane and ceramic nanocomposite membrane with the incorporation of graphene oxide (GO) and its derivatives into the kaolin membranes structure.

II.2. MATERIALS AND METHODS

II.2.1. Materials for Preparation

Various materials have been used for the elaboration of the ceramic membranes, including the raw materials, some additives, and nanomaterials. The choice and the amounts of these materials are defined according to the required properties of the final product and the shape of the membranes, as there is no general rule to follow.

II.2.1.1. The binder

In our work, polyvinyl alcohol (PVA) with a molecular weight of 130.000 has been used as a binder as it helps to bind the slurry particles before the sintering process.

II.2.1.2. The deflocculant

Poly (sodium 4-styrenesulfonate) (PSS) with a molecular weight of 70.000 has been used as a deflocculant to limit the particles' agglomeration and to control the viscosity of the slurry both PVA and PSS were supplied by SigmaAldrich.

II.2.1.3. The solvent

Distilled water has been used as a solvent

III.2.1.4. Raw material

Ceramic membranes were fabricated using local kaolin, whose chemical composition is mentioned in Table 1. The results showed that the kaolin is mainly composed of Silica (SiO_2) (48.8%) and Alumina (Al_2O_3) (41.9%). The kaolin also contains a significant amount of (CO_2), CaO), and (SO_3) with trace amounts of other components

Table II.1. Chemical composition of local kaolin.

Mineral	SiO_2	Al_2O_3	CO_2	CaO	SO_3	ZnO	Fe_2O_3	MgO
%	48.8	41.9	8.61	0.2	0.13	<0.1	<0.1	<0.1

II.2.2. Raw Material Preparation

The raw material was pre-milled and sieved through a 250 µm sieve. Then the sieved powder was processed for 1h in a (Retsch PM 400 Planetary) ball mill, which operated at 350 rpm. The high-energy ball milling reduced the particle size to a finer size. The kaolin milling and size reduction will significantly enhance the slurry homogeneity, its surface properties and facilitate the membrane shaping.

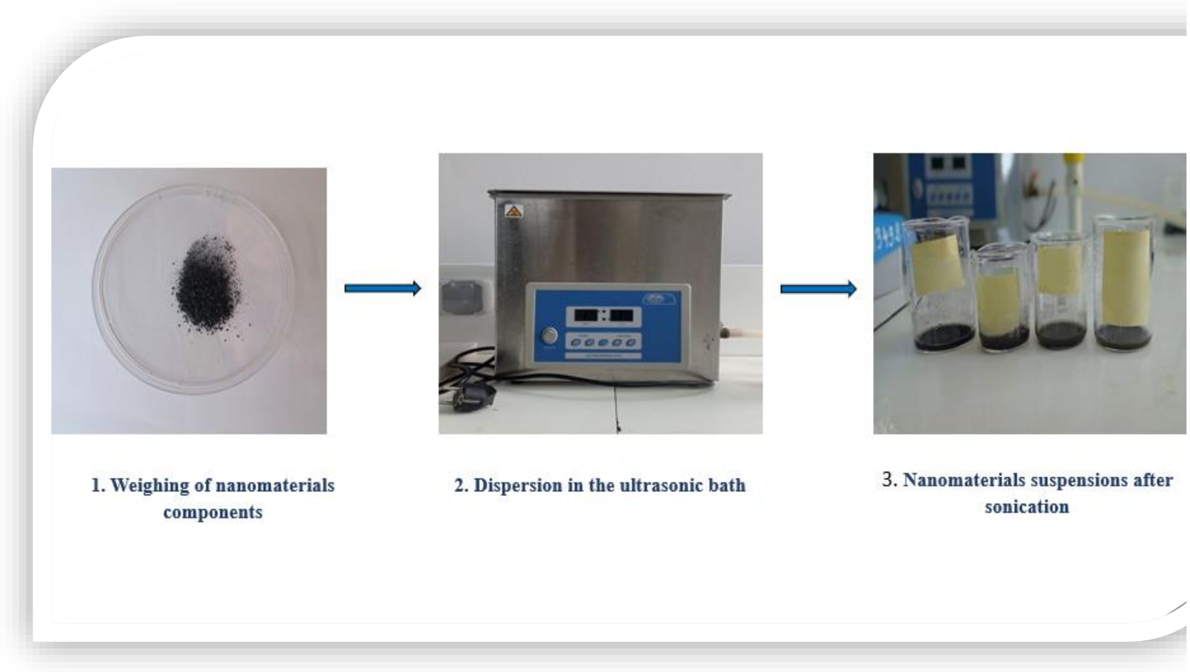
II.2.3. Modification With Nanomaterials

Graphene oxide (GO) and its derivatives are considered the most interesting graphene-related materials, where they have emerged in the field of membrane technologies as a promising approach to overcome multiple challenges [1,2] In our work, we have used GO and sulfonated graphene oxide (SGO), graphene oxide decorated with silver nanoparticles (SGOAg), and reduced sulfonated GO decorated with silver nanoparticles (SrGOAg) these nanomaterials were previously prepared .

Multiple ceramic membranes were modified with the incorporation of these nanomaterials.

First, appropriate amounts of each nanomaterial were dissolved in distilled water.

Then they were dispersed using an ultrasonic water bath (SELECTA, ULTRASON-HD) at Room temperature until they were fully dispersed, as shown in **Figure II.1.**



1. Weighing of nanomaterials components

2. Dispersion in the ultrasonic bath

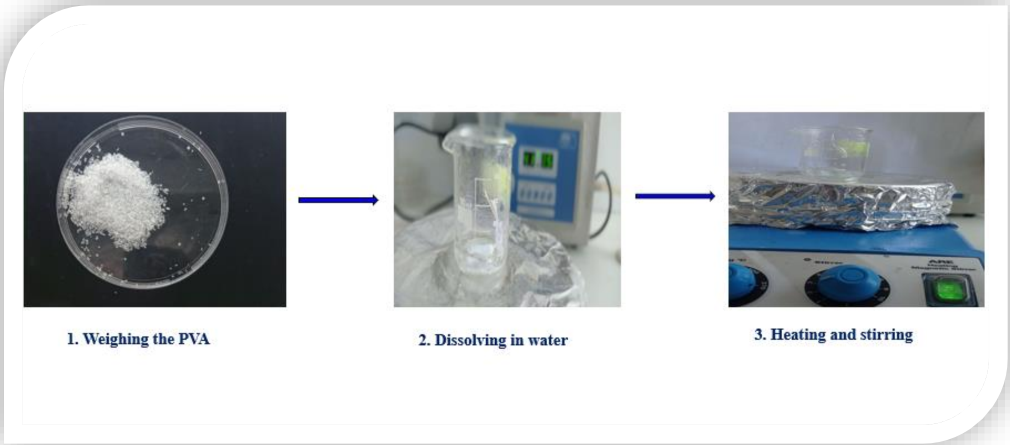
3. Nanomaterials suspensions after sonication

Figure II.1. Preparation steps of GO, SGO, SGOAg, SrGOAg suspensions.

II.2.4. Preparation of Binder and Deflocculant Solutions

III.2.4.1.The binder solution

A binder solution was prepared using polyvinyl alcohol; 10 mL of distilled water was initially heated till it reached 80°C, then a measured quantity of PVA was gradually added to the water under constant magnetic stirring to avoid agglomeration till it was fully dissolved in the water and resulted in a clear and homogeneous solution



1. Weighing the PVA

2. Dissolving in water

3. Heating and stirring

Figure II. 2. Preparation protocol of the Binder solution.

III.2.4.2. deflocculant solutions

The deflocculant solution was prepared using PSS, where a measured quantity of PSS was dissolved in distilled water under continuous magnetic stirring. Once the two solutions are perfectly dissolved, the PSS is added gradually to the PVA solution, then they are both mixed under continuous magnetic stirring till the final solution is homogenized.

II.2.5. Ceramic Membranes General Elaboration Protocol

Ceramic-based composite membranes were prepared using the slip casting method, multiple membranes were elaborated as shown in **Table II.2**, following these steps

II.2.5.1. Slurry preparation

II.2.5.1.1 Pristine membranes

First, pristine membranes were elaborated with different portions of kaolin and alumina as raw materials. After preparing the raw material and the binder-deflocculant solution, the latter was gradually added to the raw material under continuous stirring, with the addition of a specific amount of distilled water to achieve the required slurry viscosity. The prepared slurry was mixed until homogeneity is ensured.

II.2.5.1.2. Nanocomposite membranes

The nanocomposite membranes were prepared following almost the same steps as the pristine ones. The different nanomaterial suspensions were gradually added to the binder-deflocculant while keeping the magnetic stirring, the resulting suspension was mixed to ensure homogenization. Then the different solution of GO and its derivates were gradually added to the raw material, along with a specific amount of water, and mixed for an additional few minutes. The prepared slurries were poured into a premade flat mold made from plaster to ensure proper membrane solidification and achieve a well-defined shape.

II.2.5.2. Drying process

The drying process in membrane preparation is crucial to promote successful elaboration. The elimination of additional water will ensure the membrane solidification as a first step to increase the membrane's mechanical stability in the green state. Controlled drying conditions are essential to prevent cracks and internal stress due to the rapid and uneven moisture loss. Hence, it is important to control the atmospheric humidity and avoid the rapid drying of the membranes[3]. Therefore, the obtained membranes were left to dry at room temperature and then were dried in a precision incubator (Memmert INB).

II.2.6 Sintering Process

After the drying process the kaolin membranes entered a multi-step sintering process in a (Nabertherm) Oven, where the final temperature was set at 900°C, as shown in Figure 3, the membranes were firstly heated at 100°C for 1h with a heating rate of 3 C°/min to ensure the excess moisture elimination, then it was heated up to 300°C for 2h to ensure the complete elimination and decomposition of the organic additives. After that, the membranes were sintered at 700°C for 2h while keeping the same heating rate. Finally heated at 900°C for 3h with a heating rate of 5°C/ min, then they were left to cool down gradually.

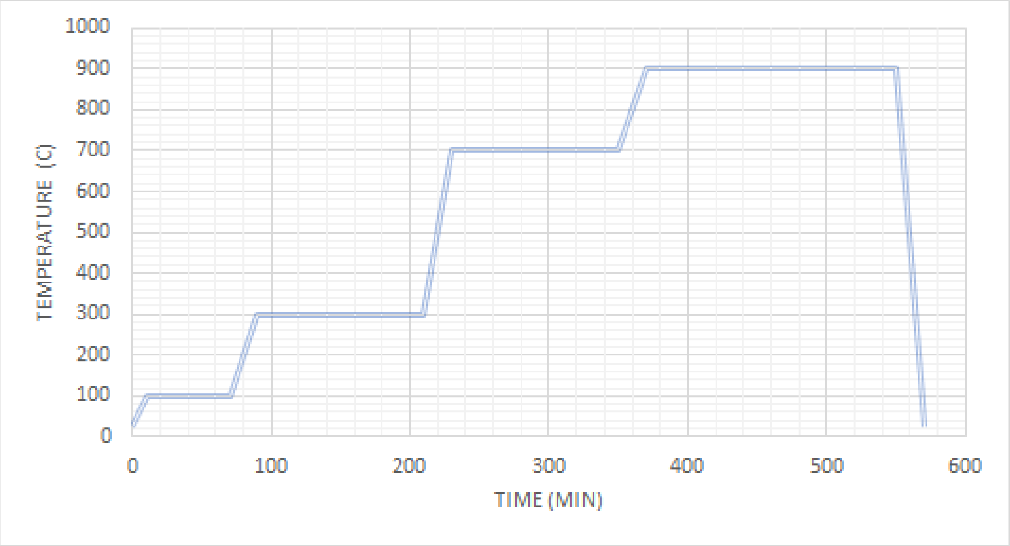


Figure II. 3. Heating temperature profile of kaolin membranes.

Table II.2. Composition of membrane samples**.**

Membranes	**Composition**	**Additives**
SK-100	100% Kaolin	-
SK90A10	90% Kaolin- 10% Alumina	-
SK-GO	100% Kaolin	1%GO
SK-SGO	100% Kaolin	1%SGO
SK-SGOAg	100% Kaolin	1%SGOAg
SK-SrGOAg	100% Kaolin	1%SrGOAg

II.3. MEMBRANES CHARACTERIZATION TECHNIQUES

Spectromic characterization techniques are essential tools in materials science, enabling a comprehensive analysis of the physical, chemical, and structural properties of various materials. Each technic uses a specific type of interaction to reveal unique information about the material.

II.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical method that involves infrared radiation-matter interaction. It works by passing a wide range of mid-infrared light (commonly 4000–400 cm^{-1}) through a sample. The sample absorbs unique wavelengths corresponding to vibrational molecular bond energies. The absorption creates a peak-containing spectrum, which can be interpreted to determine functional groups and analyze molecular constitution. The resultant infrared fingerprint is unique to a specific material, qualifying FTIR as a great tool for qualitative analysis. FTIR is particularly suited to materials with covalent bonds and can routinely be applied to polymers, ceramics, and composites in order to monitor chemical structures, as well as to verify the presence of functional groups [4]. In our case the FT-IR analysis was conducted at the Emerging Materials Research Unit of Sétif-URMES, at Ferhat ABBASS University, Sétif-1, the scan was realized on a JASCO-IR spectrometer, and the samples were analyzed by averaging the signals of 32 scans in the 4000–400 Cm^{-1} wavenumber range at a resolution of 4 cm^{-1}.

II.3.2. X-ray Diffraction (XRD)

The X-ray diffraction principle relies upon the interaction between an incoming beam of X-rays with atomic planes in a crystalline substance. When X-rays hit the organized lattice of a substance, they get deflected at predictable angles as per Bragg’s Law. The diffraction pattern obtained is captured and converted to peaks, which relate to atomic plane spacing. Peaks give information related to crystalline phases existing, crystallinity, or potential structural transformations in a substance. This method is very useful in defining solid materials like ceramics and powders [5]. The X-ray Diffraction (XRD) analysis was conducted at the physico-chemical laboratory at Chadli Bendjedid University of El-Tarf. the membranes were characterized using a Bruker-AXS D8 Davinci X-ray Powder Diffractometer, and the samples were analyzed in a 2θ range from (10° to 80°)

II.3.3. Thermogravimetric Analysis (TGA)

Thermogravimetry measures a substance's changing mass as it undergoes a controlled heating or cooling schedule, most often in an inert or oxygen-containing environment. The specimen sits in a very sensitive balance, with weight losses plotted as a function of either time or temperature. Such losses can relate to processes such as evaporation of water, breakdown of organic materials, or phase transitions. Thermogravimetry can provide information on the thermal stability, volatile content, or decomposition patterns of organic or polymeric phases [6]. The Thermogravimetric Analysis (TGA) was conducted at the Emerging Materials Research Unit–Sétif-URMES, Ferhat ABBASS University, Sétif-1, using a TA-SDTQ600 thermal analyzer. The samples were heated from 25 to 1500 °C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere with a flow rate of 20 mL min^{-1}.

II.3.4 X-ray Fluorescence (XRF)

X-ray fluorescence or XRF, as a non-destructive method, is employed to evaluate the elemental composition of a material. When exposed to a primary X-ray beam, atoms in the material get excited and give off secondary (fluorescent) X-rays corresponding to unique energies for each element. The intensity and energy of this emission can then be used to gain qualitative as well as quantitative information. This method is used extensively to evaluate raw materials as well as sintered products for determining the purity and homogeneity of the material [7]. X-ray Fluorescence (XRF) analysis was conducted at the Emerging Materials Research Unit–Sétif-URMES Ferhat ABBASS University, Sétif-1 using a ZSX Primus IV in vacuum atmosphere at 36 °C with spectrometer status of 4.0 W 30 kV in semi-qualitative mode.

II.3.5 Antibacterial Test

Antibacterial test is a test used in order to evaluate the antibacterial activity of the ceramic membrane and to quantify its ability to eliminate and reduce microbial contaminants[8]. An agar diffusion test or as known as the inhibition zone test, was performed in order to evaluate the ability of kaolin membranes to prevent bacterial attachment. A bacterial suspension of E-Coli was placed onto nutrient agar in a petri dish. Afterward, the Pristine and composite kaolin membranes were placed on the surface. The agar plates were then incubated at 31°C for 24h.

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CHAPITRE III

RESULTS AND DISCUSSION

III.1. RESULTS and DISCUSSION

The performance of ceramic membranes depends on their microstructure, composition and their physicochemical properties. In this chapter, multiple characterization techniques have been employed to understand these attributes comprehensively. It can be noted that kaolin-GO and its derivatives which are the composite membranes demonstrated good results through multiple characterization techniques, which confirms the role of nanomaterials to enhancing the ceramic membranes properties.

III.1.1. Structural Characterization

III.1.1.1. Fourier Transform Infrared Spectroscopy (FTIR) Characterization

FTIR analysis is used to identify the characteristic bands and functional groups that exist in pristine kaolin membranes and the composite ones. in our case we will start with FTIR of sintered kaolin (SK-100) and non-sintered kaolin (nSK), the table.III.1.presents the different peaks that existing on virgin membrane before sintering.

Table.III.1. Raw material Characterization peaks before sintering [1].

Peaks cm^{-1}	**Assignment**
3694	–OH Inner Surface Stretching
3659-3621	-OH Inner Stretching
1640	H-O-H Bending
1110-1030	-Si Stretching
750	Si-O Stretching
670-660	Al-O-Si

Figure III.1 illustrates the FTIR spectra of kaolin membranes before (nSK) and after sintering (SK-100) at 900 °C. The results reveal significant structural changes due to the thermal treatment. the unsintered sample (nSK), the OH-stretching vibration bands are observed at

3694 cm^{-1} and 3621 cm^{-1}, which are attributed to the hydroxyl groups present in the kaolinite structure. However, these peaks are no longer detected in the sintered sample (SK-100), indicating the dehydroxylation of kaolin and its transformation onto metakaolin.

Additionally, a prominent peak appears at 2973 cm^{-1} in the nSK spectrum, corresponding to the C–H stretching vibration**.** This peak is not observed in the SK-100 spectrum, suggesting the removal of organic components through decomposition and combustion during the sintering process at high temperature. These observations confirm the thermal decomposition of kaolin and the associated phase transformation, which are essential for the development of stable ceramic membranes [2]. A peak is observed at 1854 cm^{-1} in SK-100 while it was absent in the nSK, which is assigned to the stretching vibration of carbonyl groups(C=O), this phenomena is due decomposition of kaolin and the oxidation process CO_2. The peak at 1640 cm^{-1} is attributed to H-O-H functional groups in nSK, and it decreases in SK-100 due to the loss of adsorbed water [3]. Furthermore, a large band showed up in the SK-100 spectrum at 1267 cm^{-1}, which confirms the formation of Si–O–Al modes due to the transformation of kaolin to metakaolin [4]. nSK curves show intense peak at 1030 cm^{-1} , this peak is assigned to the presence of Si-O groups [5], while it became less prominent in the SK-100 after sintering. The peaks at 780 cm^{-1} and 754 cm^{-1} are also observed in both nSK and SK-100 and were assigned to Si-O-Al, while a peak at 659 cm^{-1} is observed, which presents the bending of Al-O [1].

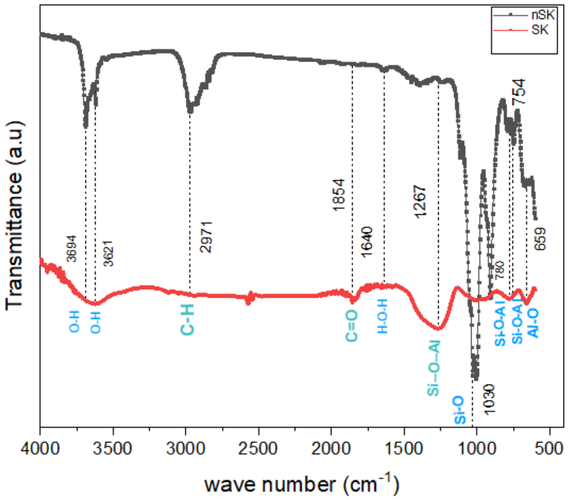

Figure III.1. FTIR results of SK-100, and nSK membranes.

The FTIR analyses present in Figure III.2 were recorded between (4000-400 cm^{-1}), multiple changes were observed on the kaolin membrane after the incorporation of GO. A new band appeared at 1375 cm^{-1}, which refers to the C-OH banding vibration of graphene oxide. The C=O bond presents on peak at 1720 cm^{-1} is associated to carboxyl groups [6], the C=C band was also observed in SK-GO at 1650 cm^{-1}, these peaks outline the oxide structure of GO and confirm the successful post-oxidation technique. A small Peaks are observed at 2849 cm^{-1} and 2921 cm^{-1}, corresponding to the asymmetric stretching vibration of C-H that is due to the presence of CH_2 groups which associated to 2D GO structure. The peaks observed at 1614 cm^{-1}, 3429 cm^{-1},3695 cm^{-1} are assigned respectively to O-H which mean, the hydroxyl groups exist on both kaolin and GO structure [7]. These results suggest the successful incorporation of graphene oxide (GO) into the ceramic membrane.

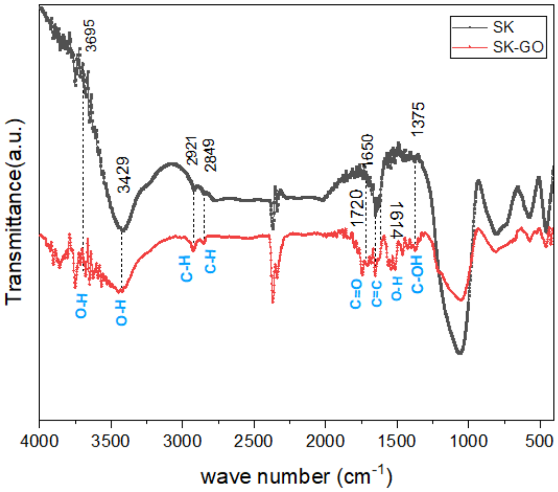

Figure III. 2. FTIR spectra of SK-100 membrane, and SK-GO composite membrane.

Figure III.3 presents the FTIR analyses of sintered kaolin (SK), kaolin-GO (SK-GO), and kaolin SGO (SK-SGO) composite membranes. It can be noted that SK-GO and SK-SGO curves present a large band at 3400 cm^{-1} compared to SK, these referring to O-H groups. However, the SGO spectrum, presents additional bands between [500-800 cm^{-1}] compared to the GO this confirm clearly the presence of additional hydrogen bonds attribute to sulfonic molecules. At 1720 cm^{-1},1620 cm^{-1}, tow peaks are detected and are assigned respectively to the C=O and C=C stretching vibrations assigned the SKGO and SKSGO composite membranes.

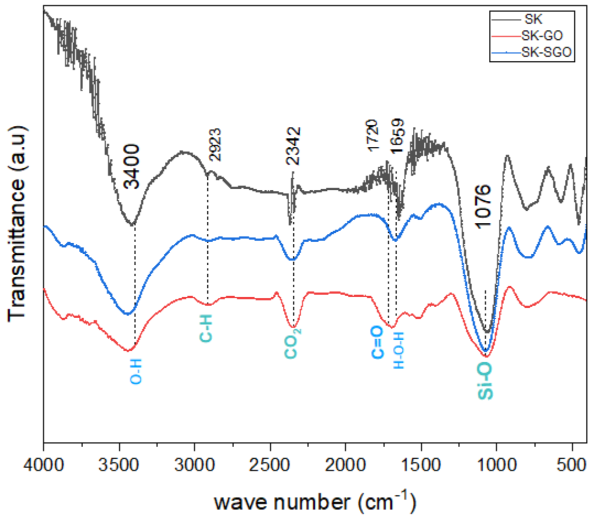

Figure III. 3. FTIR spectra of SK-100 membrane, SK-GO, and SK-SGO composite membranes.

Figure III.4, shows the spectra of the ceramic-composite membranes in which nanoparticles, GO, SGO, SGOAg and SrGOAg, were incorporated into the kaolin membrane. The curves show different peaks attributed to the O-H groups. Furthermore, two bands at 2900 cm^{-1}, 1686 cm^{-1}, qualified the presence of C-H and C=O groups, respectively. It can be noted however, A remarkable decrees on the peak's intensity of both SK-SGOAg and SK-SrGOAg compared to the SK-SGO and SK-GO due to the presence of Ag nanoparticles (NPTs)[9].

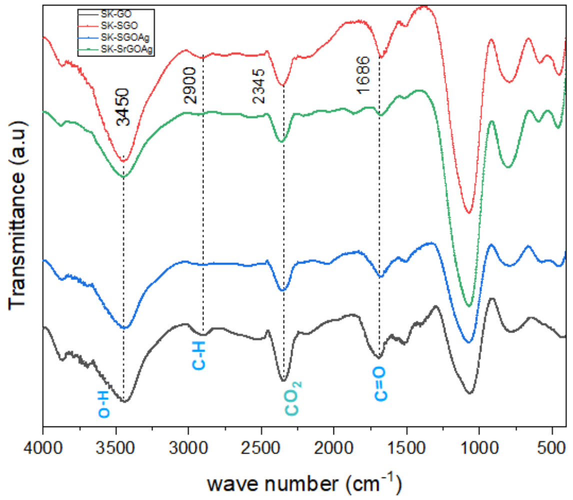

Figure III. 4. FTIR Spectra of SK-100 membrane, SK-GO, SK-SGO, SK-SGOAg, and SK-SrGOAg composite membranes.

III.1.1.2. X-ray Fluorescence (XRF)

The wavelengths of the X-ray fluorescence spectrometry enable the identification of the different elements constituting the samples. In our investigation a semi-quantitative mode analysis is proposed for the multielemental and ultra-trace determination of the analyzed samples. It should be mentioned that the intensities of the x-ray fluorescence lines are proportional to the concentration of each element, allowing to estimate quantitatively and qualitatively the content of the samples. In our study XRF analysis has been employed in order to qualitatively identify the chemical composition of the pristine and composite kaolin membranes. Table III.2 demonstrate the XRF results for the pristine kaolin membrane (SK-100) and the composite kaolin-GO (SK-GO) membrane. variation was detected in the SK-GO membrane compared with the pristine membrane, where a significant decrease was observed, especially in the (Al) and (Si) masses. Another significant observation was made, which is the appearance of carbon and oxygen in the SK-GO membrane, which confirms the presence of GO in the composite membrane.

Table.III.2. X-RF results for SK-100 membrane, and SK-GO composite membrane.

Component	**Na**	**Al**	**Si**	**P**	**Ca**	**C**	**O**	**S**	**Ag**
Sk-100 (%)	2.41	44.0	40.8	0.413	1.35	-	-	-	-
Sk-GO (%)	1.90	24.5	15.5	0.120	0.421	2.03	52.3	-	-

Table III.3 demonstrate the XRF results of kaolin-GO, and kaolin-SGO composite membranes. The results indicate a variation in the compositional mass of both membranes. An important appearance of Sulfone groups was detected in the SK-SGO composite membrane, which confirms the presence of the SGO and the successful integration into the kaolin membrane.

Table. III.3. XRF results for SK-GO, and SK-SGO composite membranes.

Component	**Na**	**Al**	**Si**	**P**	**Ca**	**C**	**O**	**S**	**Ag**
SK-GO (%)	1.90	24.5	15.5	0.120	0.421	2.03	52.3	-	-
SK-SGO(%)	2.24	23.8	15.7	0.117	0.357	1.88	52.8	0.634	-

The results of XRF characterization present on the Table III.4 shows the compositional variation between SK-SGO and SK-SGOAg composite membranes, the membranes hold nearly the same amount of sulfone (S) and oxygen (O). A notable presence of silver NPs (Ag NPs) in the SK-SGOAg membrane, which confirms the successful integration of SGOAg NPs into the kaolin membrane.

Table. III.4. XRF results for SK-SGO, and SK-SGOAg composite membranes.

Component	**Na**	**Al**	**Si**	**P**	**Ca**	**C**	**O**	**S**	**Ag**
SK-SGO(%)	2.24	23.8	15.7	0.117	0.357	1.88	52.8	0.634	-
SK-SGOAg(%)	1.75	24.4	15.5	0.151	0.427	2.09	52.5	0.668	0.0629

Table III.5 presents the component mass variation of SK-SGOAg and SK-SrGOAg composite membranes. The membranes are shown to contain the same components, though the mass of each varies. However, the decrees on C (%) of SK-SrGOAg membrane indicate the successful post-reduction step of SrGOAg in which was performed before SK-SrGOAg membrane preparation. The sulfone groups and Ag NPs exist on membranes structure, this also confirms the successful integration of both SGOAg and SrGOAg NPs into the kaolin membrane.

Table.III.5. XRF results for SK-SGOAg, and SK-SrGOAg composite membranes.

Component(%)	**Na**	**Al**	**Si**	**P**	**Ca**	**C**	**O**	**S**	**Ag**
SK-SGOAg	1.75	24.4	15.5	0.151	0.427	2.09	52.5	0.668	0.0629
SK-SrGOAg	2.11	24.7	16.1	0.113	0.360	1.43	52.0	0.699	0.0628

III.1.2. Thermal Characterization

III.1.2.1 Thermogravimetric analysis (TGA)

The thermogravimetric analysis has been applied due to its effectiveness in analyzing the structural evaluation of the local kaolin and after the sintering process of our membranes. The heating treatment of kaolin and kaolin-composite membranes leads to the elimination of any moisture or even organic matters, This elimination can be detected by weight loss or mass variation, which can inform about any decomposition, phase transformation or mass gain [10]. Figure III.5, presents the TGA analysis of raw material used in our study. notably the raw material was exposed to a heating temperature reached a final one of 1200°C. the local kaolin went through a total weight loss reached 18% , where it witnessed 2 stages of weight losses. the first loss was detected at the temperature of 65.55°C where the kaolin has witnessed a drop of about 3% of the total weight due to the evaporation of the free water in the kaolin. The second weight loss was detected at 500°C with a drop of about 15%. This loss is mainly attributed to the dihydroxylation of kaolinite [11].

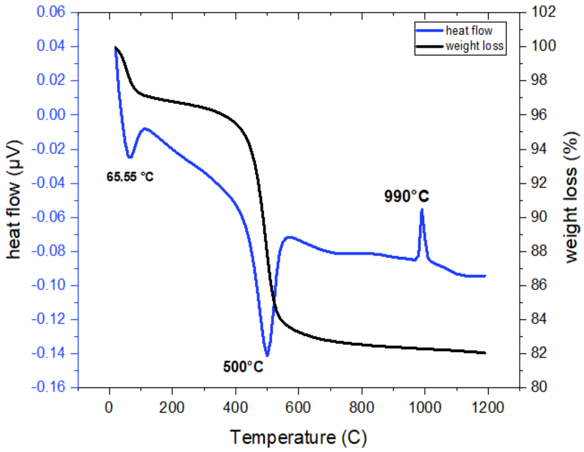

Figure III.5. TGA analysis of raw material

TGA determined the thermal stability of the prepared membranes. Figure III.6 presents the thermograms of pristine (SK-100), and kaolin-alumina (SK-90) membranes after sintering. The results show two weight losses in both curves, with a total weight loss of about 3.5% the first weight loss of SK-100 was about 70°C, which was attributed to the water loss that had been added to the starting slurry and the decomposition of the organic components was also appeared approximately at 350°C. While the second weight loss was between 800°C and 1000°C, which was related to the transformation of metakaolin to mullite[12,13]. For the SK-90, the first weight loss of about 1.5% was from 100°C to 300°C, assigned to the moisture loss, while the second was about 1.5% and from 1000°C to 1300°C. due to the slow formation of mullite, which is attributed to the presence of alumina [14]. As it's shown also in the Figure III.6 the SK-90 membrane present a lower weight loss compared to the SK-100 membrane which indicates that the incorporation of Alumina with the kaolin enhance the thermal stability of the pristine one.

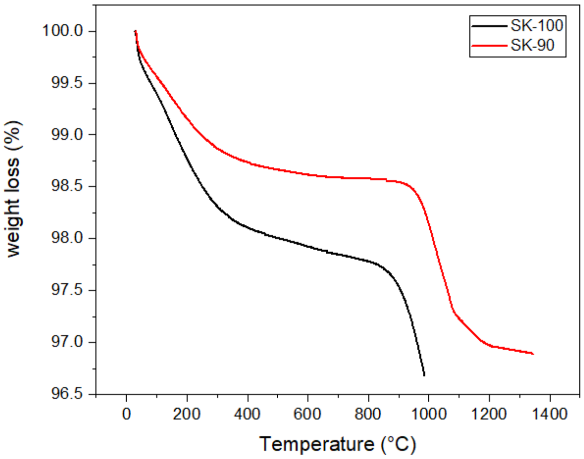

Figure III.6. TGA curves of SK-100, and SK-90 membranes after sintering.

Figure III.7(a), presents the TGA curves of the pristine membrane (SK-100) and the composite kaolin-GO membrane (SK-GO). The membranes exhibited a total weight loss between 3% and 3.5% with two stages of weight loss. The first one is from 100°C to 300°C confirm the loss of the adsorbed water that was used to prepare the slurry, then the degradation of the oxygen-containing OH groups was also observed on this stage. The second loss was between 900°C and 1300°C due to the transformation of metakaolin to mullite [15]. The weight loss of the SK-100 membrane was lower than the SK-GO membrane, this observation indicates that the addition of GO into the membrane is significantly enhance the membrane thermal stability. Figure III.7(b) presents the weight loss of the SK-100, SK-GO, and SK-SGO respectively it can be noted that the membranes show three main stage of degradation with a total weight loss of 3.5%. The first weight loss of is between 100°C and 400°C, which is assigned to the loss of moisture of the membrane and the burnout of organic additives, while the second weight loss is between 800°C and 1400°C due to the phase transformation from metakaolin to mullite. It can be noted. However, the SK-100 membrane show a less thermal stability compared to the SK-GO and SK-SGO. In contrast, the SK-SGO membrane showed lower thermal stability compared to the SK-GO membrane, which indicates that the kaolin-GO composite membrane exhibits the highest thermal stability among them all.

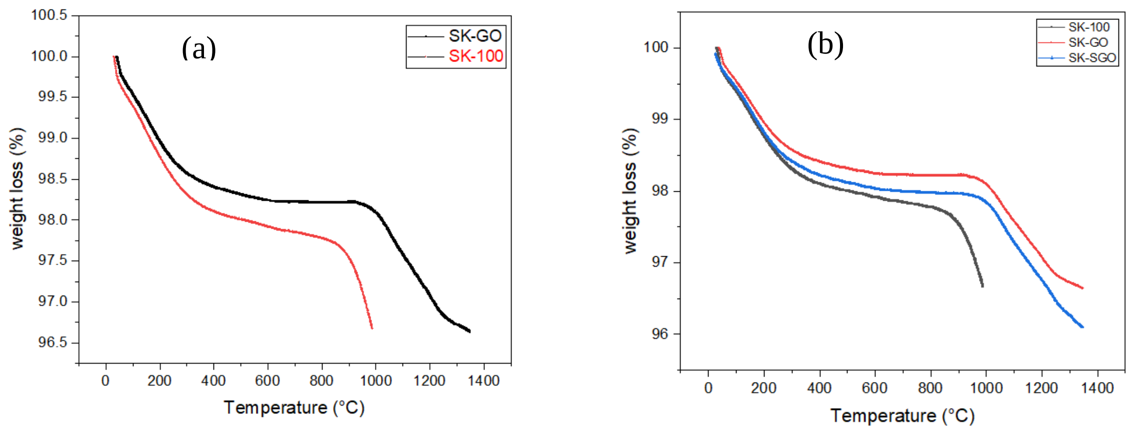

Figure III. 7. a) TGA curves of SK-100 membrane, and SK-GO composite membrane. b) SK-100 membrane, SK-GO, and SK-SGO composite membranes.

Figure III.9 presents the results of TGA analysis for SK-100 membrane, SK-GO, SK-SGOAg, and SK-SrGOAg composite membranes. It can be clearly seen that all membranes exhibited a total weight loss of approximately 3.5%, showing two distinct stages of weight loss, the first weight loss was about 1.5%, which is assigned to the loss of moisture that was added during the slurry preparation, while the second weight loss was about 2% due to the transformation of kaolin at high temperatures. These results revealed the thermal stability of each membrane, where the SK-SGOAg and SK-SrGOAg composite membranes exhibited higher thermal stability compared to the SK-100 and SK-GO membranes, implying that the deposition of silver NPs (Ag) on the graphene oxide surface enhance considerably the membranes thermal stability [15].

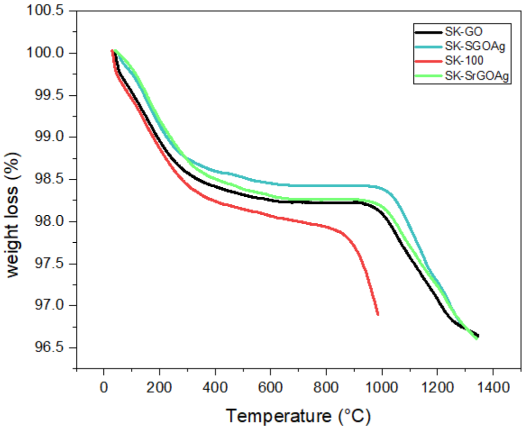

Figure III.8. TGA analysis of SK-100 membrane, SK-GO, SK-SGOAg, and SK-SrGOAg composite membranes.

III.1.3. Morphological Characterization

III.1.3.1. X-ray diffraction (XRD)

The XRD analysis were conducted in order to reveal the pristine and composite membranes crystalline phases and the and the morphological structure of the membranes. Figure III.9 shows the diffractogram pattern of the non-sintered kaolin (nSK), the analysis reveals the various crystalline phases present in kaolin, which is primarily composed of kaolinite and quartz. The peaks at 2θ of (12°, 17.9°, 25.5°, 38°) confirm the presence of kaolinite, while the peaks at 2θ of (20°, 55.7,62.3°, 68.4°) are attributed to the quartz elements. The pattern also shows the presence of some intense peaks at (30°, 48°), which confirms the presence of Illite [16].

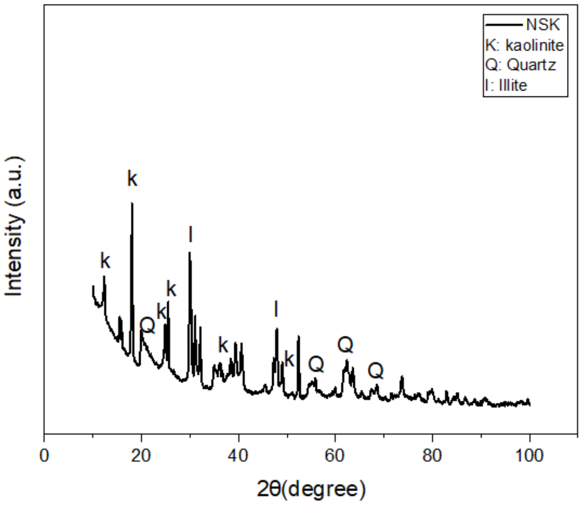

Figure III. 9. X-ray pattern of nSK

Figure III.10 presents the X-ray analysis of the composite membranes. The XRD pattern of SK-GO exhibits a diffraction peak at 2θ = 26°, corresponding to crystalline graphitic structures, this result provides clear evidence of the successful treatment of the composite membrane, which is also associated with a reduction in particle size. Subsequently, the shifting of the XRD peak from 11° in GO to 26° confirms the partial removal of oxygen groups and the restoration of the graphitic structure [17]. The SK-SGO spectrum display a peak at 2θ=27° which indicate the presence of sulfonic groups on the graphitic structure after the reduction of GO [18]. Furthermore, the SK-SGOAg and SK-SrGOAg samples exhibit the disappearance of the characteristic graphitic peaks, confirm the successful exfoliation of SGOAg and SrGOAg within the kaolin membrane [15].

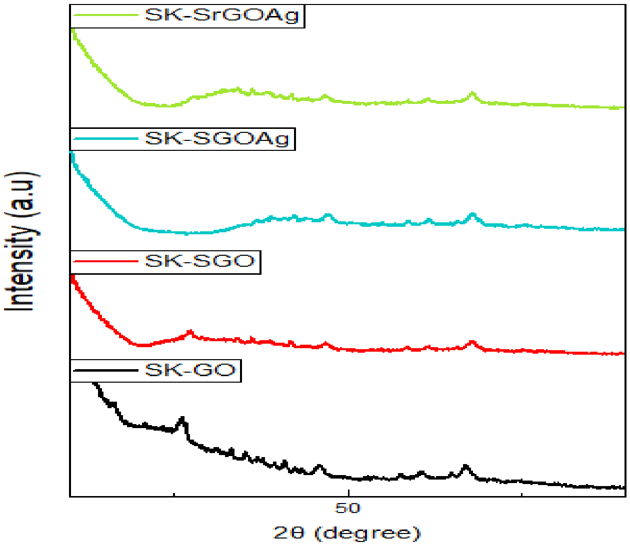

Figure III.10. X-ray analysis of SK-GO, SK-SGO, SK-SGOAg, and SK-SrGOAg composite membranes

III.1.4. Antibacterial Activity

To investigate the antibacterial performance of the pristine and composite membranes, the samples were tested using the agar diffusion test, the results are shown in Figure III. 11. In our case the antibacterial activity was tested against with a Gram-negative (*Escherichia coli*) bacterial strains using the standard disc diffusion method, unfortunately the samples of the membranes were not cute into uniform discs that way the obtained results are not sufficient clear however, the observed results of SK-GO, SK-SGOAg and SK-SrGOAg composite membranes show the formation of an inhibition zone around the samples. These results indicate clearly that the integration the functionalized GO with silver nanoparticles (Ag) enhance significantly the antibacterial performance of the composite membranes. It can be conclude that the composite membranes containing active component (Ag nanoparticles and or GO-NP) exhibited antibacterial activity compared to the control samples, indicating the successful integration of antibacterial agents and their effective release or contact-killing action. These findings suggest that the developed composite membranes could be promising candidates for applications in water purification, where antibacterial properties are essential.

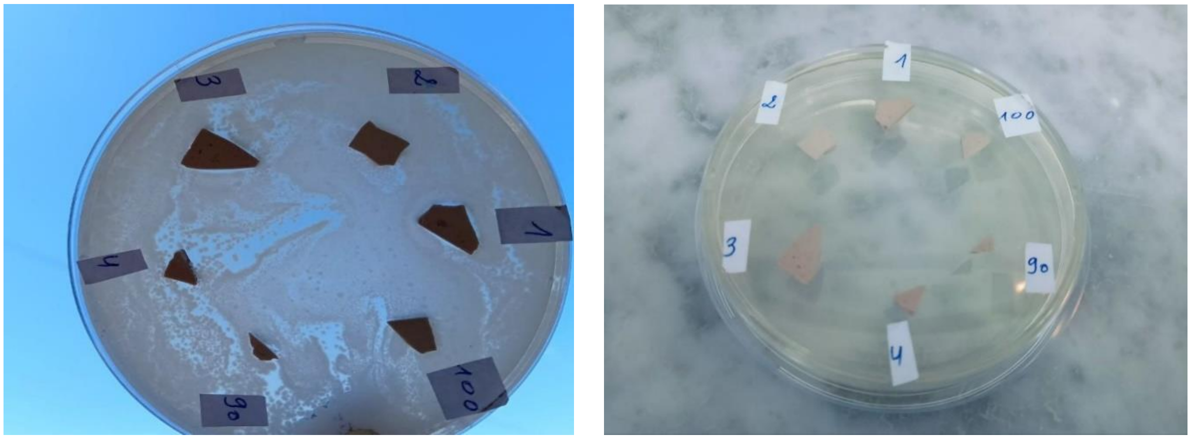

Figure III.11. Agar diffusion test for antibacterial performance of SK-100, SK-90, (1) SK-GO, (2) SK-SGO, (3) SK-SGOAg, and (4) SK-SrGOAg.

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GENERAL CONCLUSION

This thesis has explored a novel approach in order to create a new generation of ceramic composite membranes to be used in various applications. The elaboration process of pristine and composite ceramic membranes based on local kaolin, with the incorporation of graphene-related nanomaterials (GO, SGO, SGOAg, SrGOAg).

At the initial stages of our work, we have focused on the elaboration of the pristine and composite membranes where the different nanomaterials were incorporated into the kaolin membrane . The elaboration process went through multiple crucial steps, starting from slurry preparation to molding, then drying, and finally ending with a sintering process at temperature up to 900°C.

Multiple characterization techniques were employed to evaluate the properties of the prepared membranes, including FT-IR, XRD, TGA, XRF, and an antimicrobial test.

The results of FT-IR analyses revealed the presence of multiple bonding related to the kaolin structure in pristine membranes. While in composite membranes, the FTIR results revealed the presence of new distinct bands related to the presence of the graphene-related nanomaterials.

The XRF results demonstrated the mass variation of the various components that make up the kaolin membrane's structure, with the new components related to the presence of GO and its derivatives.

The TGA analysis results indicated two stages of weight loss for the pristine and composite membranes. The first one was due to the moisture release that has been added to the raw material during the preparation process, while the second is due to the structural transformations in the raw material during the sintering process. The results shown that the integration of Alumina and the GO and its derivatives enhance the membranes thermal stability.

The results of the XRD analysis showed the exist crystalline phases in the kaolin, which is composed mainly of kaolinite and quartz, and Illite. And also demonstrate the presence of GO in the membrane structure and the effect of the thermal treatment on the membrane crystalline structure.

The antimicrobial test that has been conducted on both the pristine and composite membranes revealed no antibacterial activity in the pristine membranes, whereas the composite ones showed a notable activity.

The prospects of ceramic composite membranes are very promising due to their superior performance in various separation and filtration processes. In our case the obtained results indicate that the developed composite membranes are promising candidates for water purification applications, particularly where strong antibacterial performance is crucial. Their ability to inhibit bacterial growth enhances membrane longevity and reduces fouling, making them suitable for sustainable filtration systems.

ABSTRACT

In our work, we have synthesized ceramic pristine and composite membranes made from local kaolin using the slip casting method. The composite membranes were elaborated with the incorporation of different graphene-based nanomaterials. And then they were subjected to high sintering temperatures.

The obtained membranes were characterized using multiple characterization techniques, including Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), and X-ray Fluorescence (XRF), and finally an antimicrobial test.

Key words: ceramic membranes, GO, SGO, composite membranes.

RESUME

Dans le cadre de nos travaux, nous avons synthétisé des membranes céramiques vierges et composites à base de kaolin local par coulée en barbotine. Ces membranes composites ont été élaborées en incorporant différents nanomatériaux à base de graphène. Elles ont ensuite été soumises à des températures de frittage élevées.

Les membranes obtenues ont été caractérisées par plusieurs techniques, dont la spectroscopie infrarouge à transformée de Fourier (FT-IR), la diffraction des rayons X (DRX), l'analyse thermogravimétrique (ATG), la fluorescence X (XRF), et enfin un test antimicrobien.

Mots clés : membranes céramiques, GO, SGO, membranes composites.

ملخص

في عملنا، قمنا بتصنيع أغشية سيراميكية نقية ومركبة من الكاولين المحلي باستخدام طريقة الصب الانزلاقي. صُممت هذه الأغشية المركبة باستخدام مواد نانوية مختلفة قائمة على الجرافين، ثم خضعت لدرجات حرارة تلبيد عالية. وُصفت الأغشية الناتجة باستخدام تقنيات توصيف متعددة، بما في ذلك مطيافية تحويل فورييه بالأشعة تحت الحمراء (FT-IR)، وحيود الأشعة السينية (XRD)، والتحليل الوزني الحراري (TGA)، وفلورة الأشعة السينية (XRF)، والمجهر الإلكتروني الماسح للميكروبات

الكلمات المفتاحية:. الأغشية الخزفية، GO, SGO الأغشية المركبة