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FINAL DISSERTATION FOR AN ACADEMIC MASTER'S DEGREE

Major: Process Engineering

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THESIS TITLE

Fabrication and application of natural clay ceramic membrane

Presented by: Miss OUANID Manal

Thesis defended on June 23, 2025, before a jury composed of:

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Acknowledgment

By the grace and guidance of Allah, I have reached this stage.

I sincerely pray that this work is solely for His noble sake and that it brings benefit to others.

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May Allah accept this work sincerely for His sake and make it beneficial to others.

Dedication

To the soul of my beloved mother
you were present in every moment of my struggle and effort, watching over me with your prayers, kindness, and patience.

You waited for this day the day you dreamed of seeing
but death took you before you could witness my joy.
I pray that Allah makes your grave a garden from the gardens of Paradise.

To my dear father
Thank you for everything you have given me your patience, your sacrifices.

I ask Allah to reward you generously on my behalf.

To my brother Mourad
The support I leaned on more than a brother, you were my friend, my motivator.

This achievement may bear my name, but it carries your mark and steadfast support.

I thank Allah for blessing me with a brother like you.

To my beloved siblings: Hamid, Hocine, Maimouna, Fatima, and Bouchra.

Thank you for your love, encouragement, and constant presence in my life.

To my brother Hamid's wife
thank you for standing by me throughout my academic journey.

And to the wives of Mourad and Hocine
Thank you for your sincere love and kind hearts, which were more tender than I ever expected.

To all the sons and daughters of my brothers and sisters
I pray that Allah grants you happiness and success in every step of your lives.

And to my dear friends,
your love and presence are a precious blessing beyond measure.

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Abstract:

With increasing water scarcity and pollution of natural sources, water treatment technologies have become essential to ensure access to clean and safe water. Membrane technology represents an effective and innovative solution for water purification and wastewater treatment, enabling efficient removal of contaminants. Although polymeric membranes are widely used, their limitations in corrosion and thermal resistance and short lifespan have driven researchers to explore ceramic membranes based on natural materials like clay.

This research focuses on the preparation of ceramic membranes using locally sourced natural clay, investigating the impact of raw material composition, pore-forming agents, drying, and sintering temperatures on the physical and mechanical properties of the membranes. A mixture of clay, kaolin, starch, and sodium carbonate was used to produce membranes with high mechanical strength and appropriate porosity, ensuring effective filtration and sustainable performance.

The study includes the steps of collecting and preparing raw materials, membrane shaping, drying, and sintering at various temperatures, while monitoring their influence on microstructure, mechanical strength, and permeability. This work contributes to the development of cost-effective and high-performance ceramic membranes from abundant natural resources, paving the way for their application in efficient and sustainable water and wastewater treatment.

Keywords: ceramic membranes, natural clay, water treatment, wastewater treatment, membrane technology.

ملخص:

في ظل تزايد ندرة المياه وتلوث مصادرها، أصبحت تقنيات معالجة المياه من الضروريات الأساسية لضمان توفير مياه نقية وصالحة للاستخدام. تُعتبر تقنية الأغشية من الحلول الفعالة والمبتكرة في مجال تنقية المياه ومعالجة مياه الصرف الصحي، حيث تتيح فصل الملوثات بكفاءة عالية. وعلى الرغم من الانتشار الواسع للأغشية البوليميرية، إلا أن محدوديتها في مقاومة التآكل والحرارة وقصر عمرها التشغيلي دفعت الباحثين إلى تطوير أغشية خزفية تعتمد على مواد طبيعية مثل الطين.

يركز هذا البحث على تحضير أغشية خزفية من الطين الطبيعي المستخرج من مصادر محلية، ودراسة تأثير تركيبة المواد الخام وعوامل تشكيل المسام ودرجات حرارة التجفيف والتلبيد على الخصائص الفيزيائية والميكانيكية للأغشية. تم استخدام خليط من الطين، الكولين، النشاء، وكربونات الصوديوم لتحضير أغشية ذات قوة ميكانيكية عالية ومسامية مناسبة تضمن كفاءة في الترشيح واستدامة في الأداء.

تشمل الدراسة مراحل جمع وتحضير المواد الخام، تشكيل الأغشية، التجفيف، والتلبيد بدرجات حرارة مختلفة مع مراقبة تأثيرها على البنية المجهرية، القوة الميكانيكية، ونفاذية الأغشية. هذا البحث يساهم في تطوير أغشية خزفية منخفضة التكلفة وعالية الأداء تعتمد على موارد طبيعية متوفرة، مما يفتح آفاقًا جديدة لاستخدامها في معالجة المياه ومياه الصرف البيئي بكفاءة واستدامة.

الكلمات المفتاحية : الأغشية الخزفية، الطين الطبيعي، معالجة المياه، معالجة مياه الصرف، تقنية الأغشية.

Résumé :

Face à la raréfaction croissante des ressources en eau et à la pollution des sources naturelles, les technologies de traitement de l’eau sont devenues indispensables pour garantir l’accès à une eau propre et potable. La technologie membranaire constitue une solution efficace et innovante pour la purification de l’eau et le traitement des eaux usées, permettant une séparation efficiente des polluants. Bien que les membranes polymères soient largement utilisées, leurs limites en termes de résistance à la corrosion, à la chaleur et leur courte durée de vie ont poussé les chercheurs à développer des membranes céramiques à base de matériaux naturels tels que l’argile.

Ce travail de recherche porte sur la fabrication de membranes céramiques à partir d’argile naturelle locale, en étudiant l’influence de la composition des matières premières, des agents formateurs de pores, ainsi que des températures de séchage et de frittage sur les propriétés physiques et mécaniques des membranes. Un mélange composé d’argile, de kaolin, d’amidon et de carbonate de sodium a été utilisé pour produire des membranes présentant une résistance mécanique élevée et une porosité adaptée garantissant une filtration efficace et durable.

L’étude couvre les étapes de collecte et de préparation des matières premières, de mise en forme des membranes, de séchage et de frittage à différentes températures, avec une analyse de leur effet sur la microstructure, la résistance mécanique et la perméabilité. Ce travail contribue au développement de membranes céramiques performantes et à faible coût, à partir de ressources naturelles abondantes, ouvrant de nouvelles perspectives pour leur application dans le traitement durable et efficace de l’eau et des eaux usées.

Mots-clés : membranes céramiques, argile naturelle, traitement de l’eau, traitement des eaux usées, technologie membranaire.

General Introduction

Water is one of the essential elements of life on Earth. In many regions worldwide, water is not only a fundamental necessity but is also regarded as a crucial economic and social asset. Approximately 71% of the Earth's surface is covered by water, yet only about 2.5% of it is fresh water. Fresh water is indispensable for sustaining life and maintaining ecological balance. Key sources of fresh water include rivers, lakes, ponds, groundwater, and streams. However, only about 1% of this water is accessible for human and industrial use, while the remaining portion exists in deep groundwater reservoirs and glaciers, making it largely unavailable for direct use.

These vital resources are undergoing depletion due to continuous population growth and rapid industrialization. Additional factors contributing to freshwater scarcity and depletion include climate change, inter-annual climate variability, and extensive water usage in energy generation. The increasing shortage of fresh water has become a significant environmental issue. According to a report by the United Nations FAO, approximately 1.8 billion people will face absolute water scarcity, while two-thirds of the global population may experience water stress.

Freshwater resources are increasingly threatened by various pollutants resulting from industrial, agricultural, and domestic activities. Industrial wastewater, agricultural runoff containing fertilizers and pesticides, and household waste discharge are among the major sources of water pollution. These contaminants degrade water quality, making it unsafe for human consumption and harmful to aquatic life. Pollutants such as heavy metals, organic compounds, and microbial pathogens pose serious health risks, leading to diseases and long-term environmental damage.

To mitigate water scarcity issues, it is essential to recover water from existing wastewater or explore alternative water resources for human consumption. Wastewater remediation presents a viable solution, enabling the recovery of water from industrial wastewater. Typically, industrial manufacturing and other processes generate wastewater containing dissolved substances, which are discharged as industrial effluents. Industrial wastewater is recognized as one of the leading causes of environmental pollution. Given the vast quantities of effluents, their complex composition, and the growing number of industries, wastewater treatment has become a crucial concern for environmental protection.

Industrial wastewater contains various contaminants, including heavy metals, dyes, pesticides, herbicides, pharmaceuticals, and other aromatic compounds. Upon entering the environment, these substances pose serious ecological and health risks. While low concentrations of these pollutants may not cause immediate harm, their persistent accumulation can lead to hazardous consequences over time. Wastewater discharged from mining, petrochemical, textile, and dye industries contains toxic chemicals that present severe health hazards to humans.

Water is regarded as an invaluable resource, essential for the survival of all living organisms and critical to various economic sectors. Given the limited availability of usable fresh water, both water treatment and wastewater purification have become indispensable strategies to address the global water crisis.

Membrane separation technologies offer several purification techniques, including nanofiltration (NF), reverse osmosis (RO), microfiltration (MF), and ultrafiltration (UF), all of which play a crucial role in treating contaminated water. These technologies rely on selective permeation, where membranes allow certain molecules to pass through while retaining unwanted contaminants. Membranes can be classified based on their composition into various categories, including polymeric, liquid, ceramic, and ion-exchange membranes.

Ceramic membranes, in particular, have gained significant attention due to their superior properties compared to polymeric membranes. These membranes are primarily manufactured from metal oxides such as Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 , each contributing unique properties that enhance the filtration process. These membranes are distinguished by their excellent chemical and mechanical resistance, high selectivity, and ability to function under extreme temperature and pH conditions. Advanced manufacturing techniques, such as thermal sintering, enable the production of membranes with precisely controlled porous structures, which are crucial for optimizing filtration performance.

Given these advantages, ceramic membranes are increasingly being utilized in water and wastewater treatment for the removal of suspended solids, heavy metals, organic pollutants, and microorganisms. Their durability and efficiency make them a promising alternative to conventional treatment methods.

This research aims to investigate the feasibility of fabricating ceramic membranes from natural clay and evaluating their efficiency in water treatment. The study seeks to address the following key questions:

A. To what extent can ceramic membranes made from natural clay effectively remove contaminants from water?

B. What factors influence the performance of these membranes, such as porosity, permeability, and mechanical strength?

C. How do naturally derived ceramic membranes compare with commercially available membranes in terms of efficiency and cost-effectiveness?

By answering these questions, the study aspires to contribute to the development of sustainable and cost-effective water treatment solutions using locally available materials.

The research follows an experimental approach to develop and evaluate ceramic membranes made from natural clay. The methodology consists of the following steps:

1. **Raw Material Preparation**: Collection, grinding, sieving, and weighing of natural clay samples.
2. **Membrane Fabrication**: Mixing clay with water, shaping membranes, and subjecting them to thermal sintering at varying temperatures.
3. **Characterization of Membranes**: Assessing physical and chemical properties such as porosity, permeability, mechanical strength, and structural integrity.

4. **Performance Evaluation**: Testing the filtration efficiency of the fabricated membranes using synthetic and real wastewater samples.
5. **Comparison with Commercial Membranes:** Benchmarking the results against standard ceramic membranes used in water treatment application.

This methodology ensures a comprehensive assessment of the potential of natural clay-based ceramic membranes in water purification and their practical applicability in real-world scenarios.

CHAPTER I :

Membrane Technology Concepts & Applications

I. CHAPTER I: MEMBRANE TECHNOLOGY CONCEPTS & APPLICATIONS

I.1. Overview of Membrane Technology:

Membrane technology is a general term used for a range of different separation processes. Membrane separation processes have been proven to be well-established technologies in a wide range of water, energy, food, and environmental applications throughout the production, purification, and formulation of useful products. Thus, the membrane separation processes have become the leading separation technology over the past two decades.

The membrane is defined as a selective thin layer of a semipermeable material that acts as a selective barrier and separates undesired species from a feed solution based on their sizes or affinity by exerting a potential gradient, such as pressure, temperature, electrical, or concentration difference. Separation is accomplished if one species of a mixture moves through the membrane faster than another species in the mixture.

The main advantage of membrane technology, which differentiates it from traditional separation, purification, and formulation processes, is that it produces stable products without adding chemicals with a relatively low energy consumption with a remarkable potential for an environmental impact. Other benefits include modular and easy to scale-up, well-arranged, compact, and straightforward process in concept and operation, decreased capital and operational cost of technology applications using membrane, and environment friendly.

In general, membranes are classified based on their average pore size, driving force, morphology, and materials. The pore size of the membrane material or surface is a paramount factor in its first differentiation. Nevertheless, membrane materials can be organic and inorganic. All of the membrane separation processes are effective methods of treating the feed mixture, e.g., water, gas, and food that hardly is treated using conventional separation methods [1].

I.2. Classification and Types of Membranes:

I.2.1. Classification by Structural Composition:

A. Homogeneous Membrane:

A homogeneous membrane is essentially a thin film or a homogeneous interphase through which a mixture of chemical species is transported by molecular diffusion.

The separation of various components in the mixture is directly related to their transport rates within the interphase, which are in turn determined by the diffusivities and concentrations of the individual components in the film. With homogeneous diffusive membranes, particles or molecules of the same size can also be separated when their concentrations differ significantly [2].

B. Heterogeneous Membranes:

Heterogeneous membranes are membranes composed of multiple layers or different materials, where each layer has distinct properties. They often consist of a porous mechanical support layer and a thin active layer responsible for separation or filtration.

In these membranes, the separation of components is primarily achieved due to differences in permeability and selectivity between the layers. They are widely used in industrial applications such as water desalination, ultrafiltration, and reverse osmosis, where the support layer provides mechanical strength while the active layer ensures the desired separation.

I.2.2. Classification by Separation Mechanism:

1. Porous Membranes:

Rely on pore size for separation and include:

a) Microfiltration (MF):

Microfiltration (MF) is the first classification of membrane separation techniques based on pore size. The MF membrane was first developed to analyze the bacteria in the water. In the 1960s, the first commercial MF membrane was also developed in biological and pharmaceutical applications. Since then, MF membranes have been widely applied in wastewater treatment and juice technology to remove microorganisms, clarify cider and other juices, and sterilize beer and wine. The separation mechanism in MF membranes is governed by the sieving effect or size exclusion technique. Thus, the species are separated according to their size. Large pores of MF remove suspended solids, while even proteins can pass through the MF membrane easily. The MF membranes can also be used to separate sand, clays, algae, and some bacteria from aqueous feed streams. They are recommended to separate species with a diameter larger than 0.1 µm. The applied pressure in MF is low (usually <2 bar), while this is the lowest applied pressure in other pressure-driven membrane separation processes [1].

b) Ultrafiltration (UF):

Ultrafiltration (UF) is also included in size exclusion-based pressure-driven membrane separation processes. The pore size of UF membranes is around 0.01 µm. These membranes can prevent species in the molecular weight range of 300–500 000 Da to pass through. UF rejects protein and suspended solids. However, dissolved substances could not be removed by UF unless they are first pretreated in an adsorption column like with activated carbon or coagulated with alum or iron salts. Similarly, UF membranes cannot retain the mono- and disaccharides, salts, amino acids, organics, inorganic acids, or sodium hydroxide. They exhibit small osmotic pressure differentials due to their inability to reject salts, as compared with reverse osmosis (RO). UF processes operate at 2–10 bars. Separation efficiency will further be augmented if the difference in the sizes of the species is high enough. UF is considered nowadays to be the dominant part of membrane

separation processes due to its diverse applications in water, energy, food, and the environment. UF processes are considered the most used membrane separation process next to dialysis and MF [1].

c) Nanofiltration (NF):

Nanofiltration (NF) is another pressure-driven membrane process between RO and UF pore size of around 0.001 μm. NF membranes remove most organic molecules, viruses, and a range of salts. These membranes are often applied to soften the hard water by removing divalent ions.

NF membranes possess a negative charge on the surface. It demonstrates the anion repulsion, which mainly causes the species rejection. Low rejection is witnessed for salts with monovalent anion and nonionized organics with a molecular weight below 150. However, high rejection can be observed for salts with di- and multivalent anions and organics with a molecular weight above 300. NF is advantageous over RO in different aspects, such as being operated at low pressure, giving high permeate flux, retention of multivalent salt and organic solutes, and having low investment and operation and maintenance costs.

NF membrane is more suitable for ions with more than one negative charge in single charged ions pass, such as sulfate or phosphate. However, NF membranes also reject uncharged and positively charged ions according to the molecule’s size and shape. For example, the same rejection of calcium chloride and sodium chloride can be observed while the rejection of sodium sulfate is the same for magnesium sulfate. Instead, the rejection of di- and multivalent anions is high compared with that for monovalent ions. The species rejection decreases with increasing concentration.

The Donnan exclusion model can explain this phenomenon. The higher the species concentration, the more cations available to shield the negative charges on the membrane surface, making it easier for the anions to pass through the membrane pores. On the other hand, the charge density of ions also plays an important role in its rejection. For example, the sulfate ion has a higher charge density than the chloride ion and is almost completely repelled by the NF membrane even in a high ionic strength solution such as seawater [1].

d) Reverse Osmosis (RO):

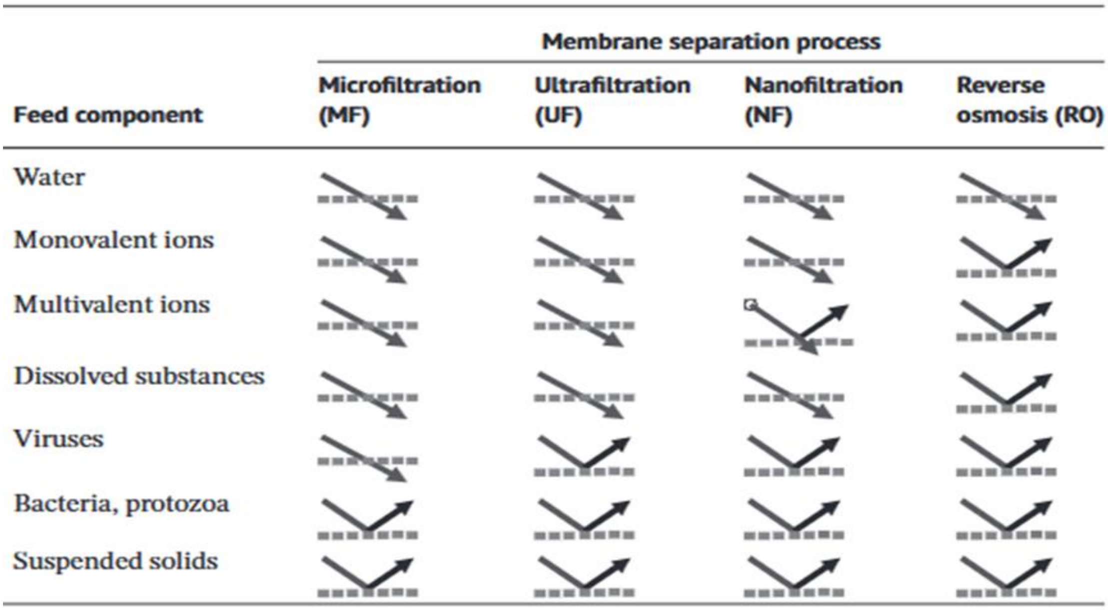
RO demonstrates, in principle, the least possible pore structure among the membranes. Water is the only species that can pass through the RO membrane; essentially, all dissolved and suspended species are rejected. RO membranes have a pore size of around 0.0001 µm. The permeate is essentially the pure water because RO also removes most healthy minerals such as calcium, zinc, magnesium, etc. that are present in the water and are useful in a certain quantity for drinking water especially for people with inadequate diets and people living in hot climates. The water can be made healthy bypassing the RO water through calcium and magnesium beds. RO removes monovalent ions to desalinate the saline water. Both NF and RO are also termed as dense membrane separation processes because separation relies to some extent on physicochemical interactions between the permeate (species) and the membrane material.

In wastewater treatment and reclamation, RO systems are typically used as the last step for removing total organic carbon (TOC). RO has been proven to remove dissolved species effectively, microbes, and neutral base compounds. To understand the working principle of RO, it is helpful to understand first osmosis.

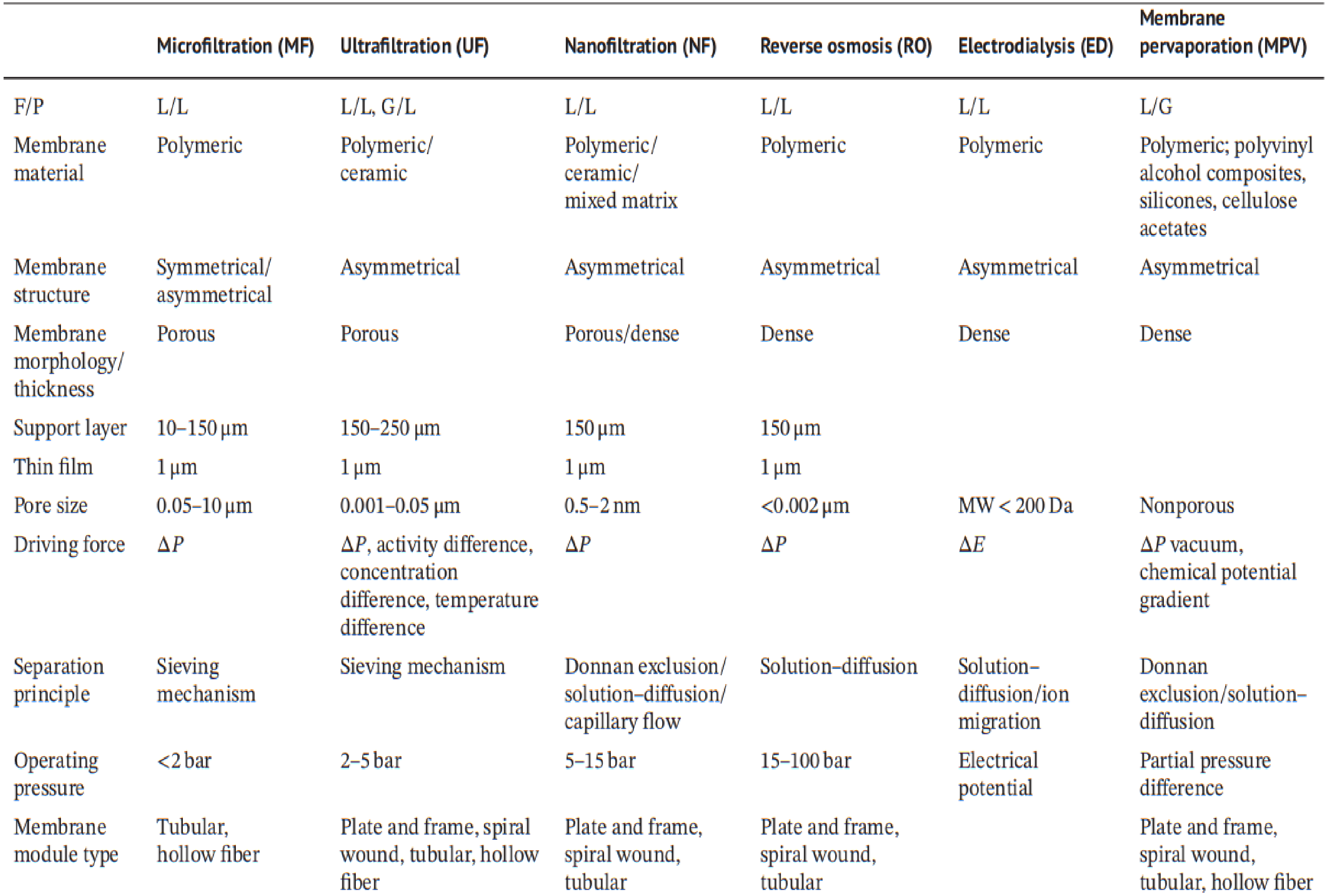
Osmosis refers to the migration of water from a weaker solution to the stronger solution when a semipermeable membrane separates two salt solutions of different concentrations. The migration of salts continues until the two solutions reach the same concentrations, achieving the osmotic equilibrium. The semipermeable membrane allows the water species to pass through naturally, but not the salt. In RO, the two solutions are still separated by a semipermeable membrane, but the pressure is applied to reverse the water's natural flow. This forces the water species to move from the more concentrated solution to the weaker. Thus, the solute aggregate on one side of the semipermeable membrane and the pure water pass through the membrane on the other side.

The concept of osmosis and RO is described schematically where (a) and (b) illustrate the process of osmosis and (c) represents the RO. If a certain pressure (ΔP) applied to the concentrated solution equals the osmotic pressure difference between the two solutions ($\Delta\pi$), the system reaches the osmotic equilibrium, and water flow stops. If the applied pressure exceeds osmotic pressure ($\Delta P > \Delta\pi$), water flows from the concentrated solution to the dilute solution [1]. A summary of pressure-driven processes is outlined in tab Ι.1 and Ι.2 [1].

Table I-1 :Pressure-driven size-based membrane processes for the removal of typical pollutants.



	Membrane separation process			
Feed component	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)
Water	↘	↘	↘	↘
Monovalent ions	↘	↘	↘	↗
Multivalent ions	↘	↘	↗ ↘	↗
Dissolved substances	↘	↘	↘	↗
Viruses	↘	↗	↗	↗
Bacteria, protozoa	↗	↗	↗	↗
Suspended solids	↗	↗	↗	↗



	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)	Electrodialysis (ED)	Membrane pervaporation (MPV)
F/P	L/L	L/L, G/L	L/L	L/L	L/L	L/G
Membrane material	Polymeric	Polymeric/ ceramic	Polymeric/ ceramic/ mixed matrix	Polymeric	Polymeric	Polymeric; polyvinyl alcohol composites, silicones, cellulose acetates
Membrane structure	Symmetrical/ asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical
Membrane morphology/ thickness	Porous	Porous	Porous/dense	Dense	Dense	Dense
Support layer	10–150 µm	150–250 µm	150 µm	150 µm		
Thin film	1 µm	1 µm	1 µm	1 µm		
Pore size	0.05–10 µm	0.001–0.05 µm	0.5–2 nm	<0.002 µm	MW < 200 Da	Nonporous
Driving force	ΔP	ΔP, activity difference, concentration difference, temperature difference	ΔP	ΔP	ΔE	ΔP vacuum, chemical potential gradient
Separation principle	Sieving mechanism	Sieving mechanism	Donnan exclusion/ solution–diffusion/ capillary flow	Solution–diffusion	Solution–diffusion/ion migration	Donnan exclusion/solution–diffusion
Operating pressure	<2 bar	2–5 bar	5–15 bar	15–100 bar	Electrical potential	Partial pressure difference
Membrane module type	Tubular, hollow fiber	Plate and frame, spiral wound, tubular, hollow fiber	Plate and frame, spiral wound, tubular	Plate and frame, spiral wound, tubular		Plate and frame, spiral wound, tubular, hollow fiber

Table I-2: Comparative Analysis of Conventional Membrane Processes.

2. **Non-Porous Membranes:**

   - Rely on diffusion or absorption mechanisms rather than pore size.
   - Used in gas separation and petrochemical applications.

3. **Charged Membranes:**

   - Possess electrical charges that influence ion transport.
   - Include Ion-Exchange Membranes, used for desalination and industrial wastewater treatment.

I.2.3. Classification of Membranes by Material:

1. **Organic Membranes:**

Organic membranes are membranes made from synthetic or natural polymers, used in ultrafiltration (UF) and microfiltration (MF) applications. Common polymer materials include polyethersulfone (PES), polyvinylidene fluoride (PVDF), and polyacrylonitrile (PAN). The selection of a suitable membrane depends on factors such as feed solution composition, operating conditions, application type, and separation objectives.

These membranes can be made from either natural or synthetic polymers, or a combination of both. Examples of synthetic polymers used in membrane fabrication include polytetrafluoroethylene (PTFE or Teflon), polyamide-imide (PAI), and polyvinylidene fluoride (PVDF), whereas natural polymers include rubber, wool, and cellulose.

Polymers used in organic membranes are synthesized through polymerization, which can result in different structural configurations:

- Linear chains (e.g., polyethylene) soluble in organic solvents and thermoplastic.
- Branched chains (e.g., polysulfone) influence flexibility and mechanical strength.
- Cross-linked structures (e.g., phenol-formaldehyde) – highly resistant to solvents and thermosetting, meaning they do not soften with heat.

The selection of a polymer for membrane fabrication depends on compatibility with membrane processing technology and intended application. Some membranes require low affinity toward the permeate, while others need high resistance to harsh cleaning conditions due to fouling. Factors such as polymer chain interactions, rigidity, functional group polarity, and stereoisomerism influence membrane performance and durability. A representative membrane classification is shown in Fig. I.3 [3].

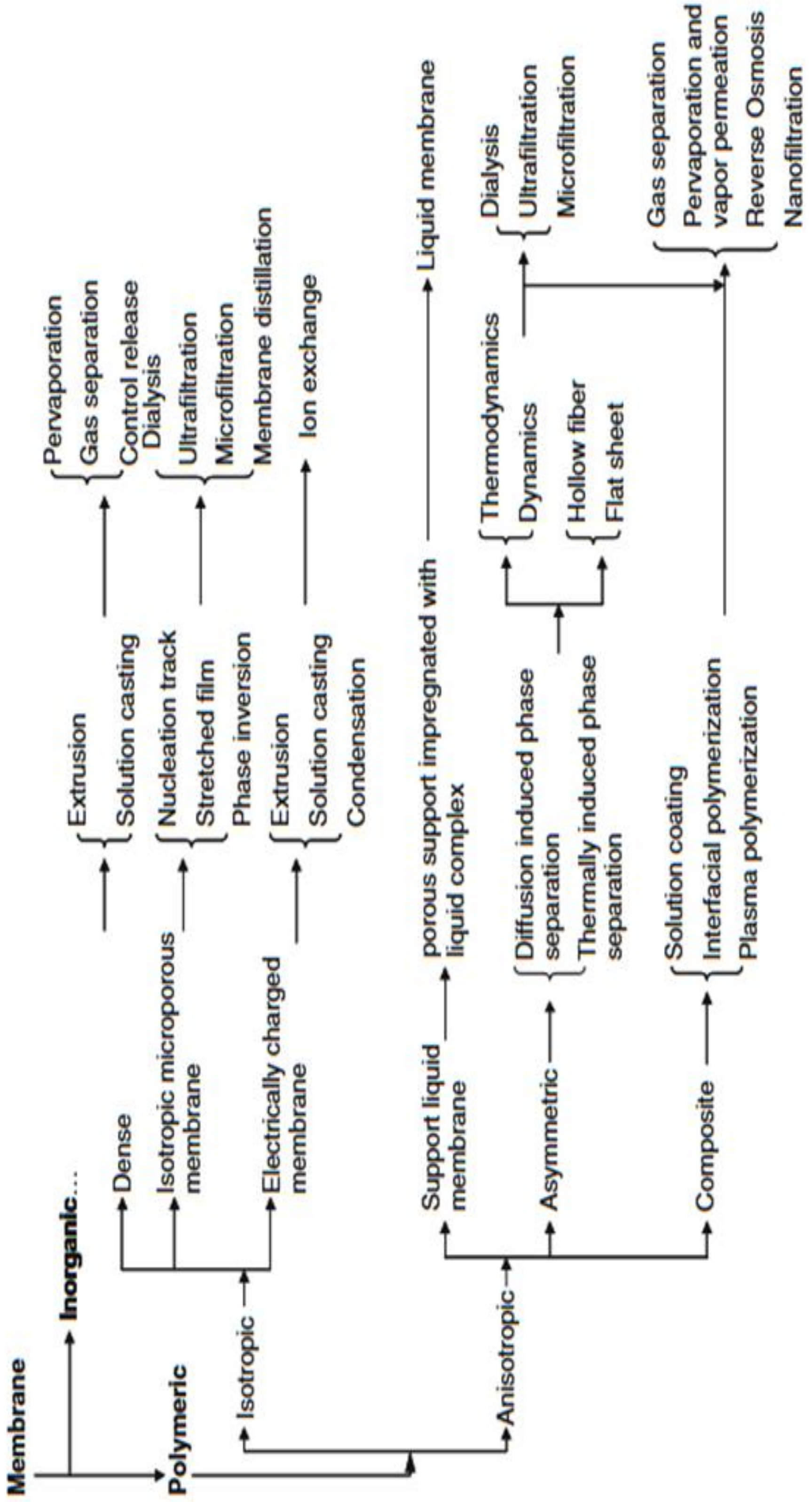


Figure I-1: Schematic Diagram of Membrane Classification and Manufacturing Processes

2. Inorganic Membranes:

Inorganic membranes are membranes made from non-polymeric materials, such as metals, ceramics, and zeolites, offering high resistance to heat and chemicals for extreme industrial applications [3].

3. Metallic Membranes:

These membranes are produced by sintering metal powders (e.g., tungsten, palladium, stainless steel) and depositing them onto a porous substrate. Their primary application is hydrogen separation, with palladium and its alloys being the preferred materials. However, surface poisoning is a major disadvantage of metallic membranes, affecting their efficiency over time [3].

4. Ceramic Membranes:

Ceramic membranes are composed of metallic elements (e.g., aluminum, titanium) and non-metallic compounds (e.g., oxides, nitrides, carbides). These membranes are widely used in harsh acidic and basic environments due to their strong chemical inertness. However, they are highly sensitive to thermal stress, which can lead to membrane cracking when exposed to sudden temperature variations [3].

5. Zeolite Membranes:

Zeolite membranes are known for their highly uniform pore size, making them ideal for selective gas separation. They also exhibit catalytic properties, making them useful in catalytic membrane reactors. However, their low gas flux and the need for thicker layers to prevent cracks and pinholes are key limitations [3].

I.3. Comparison between Organic and Inorganic Membranes:

Understanding the differences between these two classes of membranes is essential for selecting the appropriate material for specific applications. The following table, see (Tab I-3) presents a detailed comparison between organic and inorganic membranes based on key performance and structural characteristics.

Table I-3 : Comparison between Organic and Inorganic Membranes.

Aspect	Organic (Polymeric) Membranes	Inorganic Membranes
Material Composition	Made from natural or synthetic polymers such as PES, PVDF, PAN, PTFE, Cellulose	Made from metals, ceramics, or zeolites such as aluminum, titanium, stainless steel, metal oxides
Structure & Morphology	Flexible, can be homogeneous or heterogeneous, available in porous or non-porous forms	Rigid and brittle, mostly porous or with dense layers for separation
Manufacturing Methods	- Solution casting - Electrospinning - Interfacial polymerization - 3D printing	- Sintering - Chemical vapor deposition - Dip coating - Thermal reaction synthesis
Mechanical Properties	High flexibility but lower mechanical strength, moldable	High mechanical strength but brittle
Chemical Resistance	Resistant to some chemicals but may degrade in strong solvents	Highly resistant to acids, alkalis, and extreme chemical environments
Thermal Resistance	Can withstand low to moderate temperatures (<150°C)	Can tolerate very high temperatures (>600°C)
Cleaning & Maintenance	Cleanable but prone to damage from frequent cleaning	Easy to clean and sterilize using steam or strong chemicals
Lifespan	Moderate lifespan, degrades over time due to chemical exposure or high pressure	Long lifespan due to high resistance to environmental factors
Cost	Relatively low cost and easy to manufacture	High cost due to complex manufacturing and specialized materials
Applications	Water filtration, food industry, biomedical uses.	Gas separation, harsh chemical environments, high-temperature applications
Advantages	- Lightweight and easy to install - Lower production cost - Can be tailored into different structures and forms	- High chemical and thermal resistance - Longer lifespan - Stable performance in extreme conditions
Disadvantages	- Sensitive to harsh chemicals - Shorter lifespan	- Expensive - Complex manufacturing processes

I.4. The Membrane Market and Its Future Development:

Membrane-based market industry covers the membrane itself and its module, including additional equipment and the systems. Commercial success is one of indicator showing the important role played by membrane technology in various applications. The benefits in membrane process applications include reduced operating costs relative to competitive technology, saving of product, recovery of by-products, savings of water, energy, chemical, etc. In effluent reduction applications, savings in transport and disposal cost become important.

Membranes and membrane processes are used in four main areas, which are, in the separation of molecular and particulate mixtures, in the controlled release of active agents, in membrane reactors and artificial organs, and in energy storage and conversion systems. Membrane has become a multi-billion-dollar business and still growing fast. The worldwide membrane market in 1998 particularly in sales of membrane and modules reached more than 4 billion USD. While sales of membrane system reached more than 15 billion USD [4]. The annual sales of membrane and modules for various membrane processes were increased over the years and reached a value of approximately 4500 million USD in 1998 [4, 5].

From the applications view, approximately 40% of membrane sales are destined for water and wastewater applications, while food and beverage processing combined with pharmaceuticals and medical applications account for another 40% of sales and the use of membranes in chemical and industrial gas production is growing [6]. The total membrane market is unevenly distributed, 75% of the market share belongs to USA, Japan and Western Europe [7]. The development of membrane market is determined by energy costs, required product quality, environmental protection needs, new medical therapies, and the availability of new and better membranes and membrane processes [4].

Some applications of membrane processes, such as water desalination or wastewater treatment, have high industrial relevance. However, in these applications the membrane processes compete with conventional water desalination or water treatment techniques, such as multistage flash evaporation or biological sewage treatment plants. In other applications of high commercial relevance, such as in hemodialysis or in fuel cells, membranes are key components and no economic alternative technique that could compete with membrane is currently available.

There are other applications, such as the production of ultrapure water, where membrane processes compete with conventional techniques, but have a clear advantage. There are also a large number of membrane applications of lower industrial relevance, such as the dehydration of organic solvents by pervaporation or the recovery of organic vapors from waste air streams by gas and vapor permeation membranes. In certain biosensors and diagnostic devices, membranes are key components, but in terms of the total costs of the final device, the cost of the membranes in these devices is negligibly low. Therefore, this application is often of lesser interest to the membrane producing industry [4].

As the membrane market has grown, the scale of membrane facilities has become more ambitious. The first UF facility for potable water treatment, inaugurated in 1988 at Aubergenville, France, had a design capacity of 160 m^3/day, today; facilities' exceeding 100,000 m^3/day is being planned [6].

In spite of impressive sales and growth rate of the industry, the use of membranes in industrial-scale separation process is not without technical and economic problems. Technical problems are related to insufficient membrane selectivities, relatively poor transmembrane fluxes, general process operating problems, and lack application know-how. Economic problems originate from the multitude of different membrane products and processes with very different price structure in a wide range of applications, which are distributed by a great number of sales companies, very often as individual products [8].

In future, the largest market for membrane will continue to be water treatment, with sales to manufacturers of consumer water purification equipment becoming more important. The primary group of customers (electric utilities, industrial water users and municipal water works) will continue to dominate demand in this sector, but this segment is rapidly maturing and sales are increasingly dependent upon replacements for existing systems. In addition, as both the physical and chemical means of cleaning membranes continue to improve, the average life span of the membranes is lengthening, thus reducing replacement sales [9].

I.5. The Future of Membrane Science and Technology:

Though the application of membrane for treating of urban and industry wastewater is new, its high rate of efficiency contrast to conventional method has facilitated its global utilization and acceptance. Despite the remarkable improvement in the recent times on membranes development and processing, its technology's intensive approach within sustainable water resource administration and wastewater purification for re-use is still encountering many difficulties. Investments, operating as well as maintenance costs are still high [10]. Here, reduction of energy requirement during treatment stage is of concern for sustainable application of the technologies.

Also, quality of water variation with respect to suspended solid, dissolved salt, in addition to organic matter could activate increased fouling and loss of membrane efficiency at long run [11]. Besides, fouling can be present and remarkably impacts the membrane efficiency. Aside fouling, the utilizing membrane for water resources recovery is also being affected by other issues like low permeability in addition to short lifespan, development of separation between solute, insufficient selection of contaminated and desire for an enhanced model in addition to simulations [12]. This issue increases operating as well as energy costs and frequent membrane chemical cleaning and shutdown. The environmental challenge comprises of seeking the better solution in administration of highly salty concentrates that is accumulated at the time of the water recovery.

Membrane technology indicates great potentials in various means of water recovery like water desalination, municipal wastewater treatment, industrial wastewater treatment and wastewater treatment for reclamation and reuse. Notwithstanding, for any type of usage, a high performing membrane's material is needed at the same time considering some key factors like transportation properties, durability as well as mechanical strength. Membrane qualities (permeability and rejection), mechanical strength, chemical and thermal stability under a specific operation condition, membrane design module, membrane durability over long period of being exposed to real process conditions can be further studied to achieve a high efficiency membrane operation.

Three specific factors, environmental, economic in addition to social indices are normally used for comparing membrane technology with rest conventional unit operation towards sustainability and determining technology suitable for a given application. Furthermore, for any required usage, condition of the process needs to be considered critically prior to decision taking. The expectation however is that membrane technology needs very little chemicals when compared to standard unit operations. Besides, it is easy to scale up, low energy requirements, will be eco-friendly technology for water recovery application in future.

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CHAPTER II :

The Ceramic Membranes

II. CHAPTER II: THE CERAMIC MEMBRANES

II.1. Introduction:

A membrane is a selective barrier that allows certain components to pass while retaining others in the liquid phase. The feed stream is referred to as the influent to the membrane, while the liquid that passes through the membrane is called the permeate, and the liquid containing the retained components is known as the retentate.

Membrane separation technologies are gaining increasing attention due to rising environmental regulations and the growing demand for desalinated water. Membranes contribute to reducing waste disposal costs and enable material recovery and recycling, providing an economic advantage. Over the past two decades, membranes have become a standard procedure for these reasons. They are widely used in microfiltration, ultrafiltration, and nanofiltration processes, particularly in water and wastewater treatment.

Based on manufacturing materials, membranes are classified into two main types: polymeric membranes and ceramic membranes. Ceramic membranes are made from inorganic materials such as alumina oxides, zirconia, and titania. Although ceramic membranes are more expensive than polymeric membranes due to the high cost of raw materials and the complexity of their manufacturing process, they offer long-term durability, high mechanical strength, resistance to chemicals and solvents, and thermal stability. In fact, it has been proven that using ceramic membranes instead of traditional water treatment steps (such as coagulation, sedimentation, and filtration) is more efficient and effective.

Ceramic membranes typically consist of three layers: the inner layer is a porous support layer, which provides high mechanical strength to the manufactured membrane. This is followed by an intermediate layer, which is coated over the support layer and has a smaller pore size. Due to the difference in pore size between the support layer and the upper layer, the intermediate layer acts as a bridge between the two. The final layer is the top layer, where the actual separation process takes place.

There are various methods for fabricating ceramic membranes from raw materials, including slip casting, tape casting, pressing, extrusion, sol-gel processing, dip coating, chemical vapor deposition, and anodic oxidation. The choice of method depends on the intended application and the target membrane structure [1].

This chapter aims to study ceramic membranes in terms of their definition, differences from polymeric membranes, and their physical and chemical properties. Additionally, it explores their various applications, with a focus on their role in water treatment technologies such as ultrafiltration and microfiltration. Furthermore, challenges associated with ceramic membranes and potential solutions for improving their efficiency and reducing manufacturing costs will be discussed.

II.2. Definition of Ceramic Membranes:

A ceramic membrane is an artificial membrane made from non-metallic inorganic materials. Like all membranes, it allows for the selective passage or retention of certain substances between the two separated media. Most ceramic membranes are composed of metallic oxides such as alumina (Al_2O_3), titanium dioxide (TiO_2), or zirconium dioxide (ZrO_2). Some ceramic membranes are also made from silicon carbide (SiC), which requires a higher sintering temperature compared to oxide-based membranes. These materials provide ceramic membranes with exceptional chemical, thermal, and mechanical stability, making them highly durable and suitable for use in extreme conditions such as high temperatures, aggressive chemical environments, and high-pressure applications [2].

II.3. General Properties of Ceramic Membranes:

1. Physical and Structural Properties:

- High **porosity**, which enhances filtration efficiency.
- Low **bulk density**, facilitating fluid permeability.
- **Homogeneous microstructure** with well-distributed pores, improving functional performance.

2. Mechanical Properties:

- Good **mechanical strength** and **abrasion resistance**, increasing durability.
- Balanced **rigidity and flexibility**, making them adaptable to various operating conditions.

3. Chemical Properties:

- High **chemical stability** under different operational environments.
- Resistant to **chemical variations** in water composition without losing efficiency.

4. Filtration Properties:

- Effective in removing **impurities and fine particles** from water.
- Improves **water quality** by reducing **turbidity and organic contaminants.**

- Exhibits **high permeability** with **low fouling resistance**, ensuring long-term performance. [3], [8].

II.4. Comparison between Ceramic and Polymeric Membranes:

Among the various membrane materials, ceramic membranes (inorganic) and polymeric membranes (organic) are the two most commonly used types. Each type offers distinct advantages and limitations in terms of performance, stability, cost, and applicability. The following table present the comparison highlighting the key differences between ceramic and polymeric membranes.

Table II-1: Comparison between Ceramic and Polymeric Membranes.

Property	Ceramic Membranes	Polymeric Membranes
Pore Size Distribution	Can be narrow, but there is no conclusive evidence that it is narrower than polymeric membranes.	Can also be narrow, depending on the type of polymer material.
Porosity and Flux	Has higher porosity, leading to higher flux.	Lower porosity, which may reduce flux rate.
Mechanical Stability	Higher, allowing operation under high pressures, but more prone to breakage.	Lower than ceramic membranes but more flexible and less prone to breakage.
Chemical Stability	Higher than polymeric membranes, decreasing in the order: $TiO_2 > ZrO_2 > Al_2O_3 > SiO_2$.	Lower stability, making them more sensitive to harsh chemicals.
Hydrothermal Stability	Varies by material, with the order: $ZrO_2 > Al_2O_3 > TiO_2 > SiO_2$.	Less stable at high temperatures.
Hydrophilicity	Varies by material, making comparison difficult.	Depends on the type of polymer used, with some having low contact angles as low as 10°.
Fouling Behavior	Less prone to organic fouling, especially from polysaccharides.	More susceptible, particularly to proteins and polysaccharides.
Operational Procedures	Works at higher flux, often without pretreatment.	Operates at lower flux; pretreatment is often required.
Non-Purgeable Organic Carbon (NPOC) Removal	Approximately 30%.	Between 13-25%.
Reversible Fouling Rate	Decreases in the order: Polymeric $\approx Al_2O_3 \approx ZrO_2 > TiO_2 > SiC$.	Similar to ceramic membranes, except SiC shows the lowest reversible fouling.
Irreversible Fouling Rate	Decreases in the order: Polymeric $> ZrO_2 > Al_2O_3 > TiO_2 > SiC$.	More prone to irreversible fouling compared to ceramic membranes.
Need for Pretreatment	Often operates without pretreatment, but in some cases, chemical coagulation is used.	Depends on the application, but 30-40% operate without pretreatment, with coagulation and activated carbon being commonly used.

Ceramic membranes are distinguished by their high mechanical and chemical stability and their ability to operate under higher pressures, making them suitable for harsh conditions. On the other hand, polymeric membranes offer greater flexibility and are less prone to breakage, but they are more susceptible to fouling and have a shorter lifespan when exposed to harsh chemicals [5].

II.5. Microstructure and porosity of ceramic membrane:

II.5.1. Microstructure of Ceramic Membranes:

Ceramic membranes exhibit a multi-layered microstructure, composed of densely packed crystalline grains with pores and grain boundaries between them. This structure forms during various fabrication processes, such as the sol-gel method and thermal sintering, which influence grain size and connectivity.

- **Support Layer:** Contains large pores and is responsible for providing mechanical support to the membrane.
- **Intermediate Layers:** Used to gradually reduce pore size, enhancing selectivity and hydraulic properties.
- **Top Layer:** Possesses the smallest pore size and determines membrane performance in terms of selectivity and separation capability.

The microstructure largely depends on sintering temperature; higher temperatures lead to grain growth and a reduction in porosity, which enhances membrane stability but may reduce permeability. Additionally, grain boundaries play a crucial role in the membrane's mechanical and chemical properties, as they may contain impurities and glassy phases that affect its resistance to corrosion and heat.

1. **Effect of Materials on Microstructure:**

- Al_2O_3 (Alumina): Forms crystalline grains with high hardness, commonly used in the support and intermediate layers.

- ZrO_2 (Zirconia): Provides high chemical and thermal stability, often used in the surface layer.

- TiO_2 (Titania): Can be crystalline or amorphous depending on the temperature, contributing to improved chemical performance.

- SiO_2 (Silica): Typically amorphous, making it more susceptible to chemical corrosion in alkaline environments.

The microstructure of ceramic membranes depends on fabrication techniques, material composition, and thermal treatment processes. These factors influence grain size, porosity, and grain boundary connectivity, which ultimately define membrane performance in various applications. Thanks to their multi-layered structure, ceramic membranes achieve a balance between permeability, durability, and chemical and thermal stability, making them an ideal choice for water treatment, filtration, and gas separation applications.[6][7].

II.5.2. Porosity in Ceramic Membranes:

1. **Effect of Raw Materials on Porosity:**

   - The open porosity of ceramic membranes depends on the packing of initial particles, which is significantly influenced by particle morphology and size distribution.
   - Ceramic membranes are typically fabricated from materials such as coal fly ash, bauxite, kaolin, and sepiolite, with varying porosity levels depending on these raw materials.

2. **Effect of Sintering on Porosity:**

   - Porosity is controlled by sintering temperature and dwelling time.
   - High-temperature sintering promotes strong bonding between particles, leading to a reduction in open porosity and an increase in mechanical strength.

3. **Enhancing Porosity Using Pore-Forming Agents:**

   - Porosity can be increased by adding pore-forming agents such as graphite powder and organic compounds, which burn out during heating, leaving additional pores.
   - Although this method enhances porosity, it may reduce the mechanical strength of the membranes.

4. **Improving Porosity without Mechanical Strength Degradation:**

   - To achieve a balance between porosity and strength, a highly porous structure based on interlocked mullite whiskers is developed.
   - The addition of MoO_3 and AlF_3 enhances mullite whisker growth, leading to the formation of a high-porosity structure without significantly compromising mechanical resistance.

5. **Importance of Porosity in Practical Applications:**

   - High porosity is essential for reducing fluid flow resistance and improving

- performance in water treatment and industrial separation applications.
- Ceramic membranes must maintain a balance between porosity and mechanical strength to withstand high-pressure gradients during practical operations.[8]

II.6. Application of ceramic membrane in water and wastewater treatment:

The success of ceramic membranes in many industrial applications, such as microfiltration for bacteria removal from food and dairy products, juice clarification, hot gas filtration, and the filtration of fermentation broths in biotechnology and pharmaceutical applications, has attracted much attention in membrane technology development. Ceramic membranes have also become a significant interest for wastewater treatment, including pollution treatment in industrial areas, oily wastewater separation, heavy metal removal from industrial effluents, and textile mill treatment.

Several studies investigating ceramic membranes have been carried out on the application of industrial wastewater. A recent study elaborated on ceramic membrane filtration based on Sayong ball clay, obtained from Sayong District in Perak State, Malaysia, for nickel removal from industrial wastewater. About 82% to 89% of nickel was efficiently rejected. Another study focused on potential applications of ceramic membranes in the pulp and paper industry for the treatment of bleach plant effluent. Semi and series batch membrane processes consisting of microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) ceramic membranes were designed to remove residual lignin and reduce the chemical oxygen demand (COD) during sulfite pulp production.

The two-stage process of MF followed by UF gave good performance in separation and efficient alkaline bleaching effluent treatment, reducing residual lignins by more than 70% and COD concentration by over 35%.

A study by Almandoz investigated the use of ceramic membranes made from natural alumino-silicates (clay, feldspar, quartz, bentonite, and alumina) due to their low price and local availability. The performance of these membranes was tested with various substances from the food industry, such as goat milk pasteurization and slaughterhouse wastewater treatment, achieving excellent results with bacterial removal rates of 87% to 99% and 100% rejection of insoluble residues, making them suitable for microfiltration applications. This shows that natural clay has significant potential as a low-cost and efficient ceramic membrane material.

In household water treatment, a study described the development and characterization of a TiO2-modified kaolinite ceramic membrane, prepared using natural kaolinite with a tubular support configuration. The membrane was tested for bacteria content, iron (Fe), manganese (Mn), nitrate (NO-), total dissolved solids (TDS), and total suspended solids

(TSS) before and after filtration. The results showed significant reduction in Fe, Mn, NO-, and bacteria levels, while COD, TSS, and TDS were not significantly affected. Similarly, another study on heavy metals (zinc, nickel, manganese, lead, chromium, copper) and physicochemical parameters in home-use water using ball clay as the main precursor for ceramic water filters demonstrated excellent reduction in all studied parameters.

In oily wastewater treatment, a study fabricated a tubular mullite ceramic microfiltration membrane from kaolin clay, achieving more than 94% rejection of total organic carbon for synthetic feeds. Similarly, oily wastewater treatment with a low-cost ceramic membrane made from inorganic precursors such as quartz, kaolin, feldspar, sodium carbonate, sodium metasilicate, and boric acid achieved 98.51% rejection efficiency.[9]

II.7. Future perspective:

The development of membrane technology in the industry depends on its performance as well as its cost. The ceramic membrane is more focused on nowadays in the scientific research world compared to the polymeric membrane due to its benefits. However, the major issue with ceramic membranes is their high fabrication cost. Therefore, comprehensive studies leading to the benefits of ceramic membranes in terms of long service lifespan and better performance will definitely be more focused on in the future to compensate for the high cost.

On the other hand, other alternatives should also be focused on, such as the fabrication cost of ceramic membranes. This can be realized by selecting raw materials and methods used. For example, natural clay, solid waste, or any cheap materials can be used as the main material in the fabrication of ceramic membranes, as well as in terms of the method. Most researchers use the pressing method, which is ex pensive compared to other methods. The slip casting method offers an excellent method that is cheap, involves no complicated technique, and requires no high-technology machinery. However, the thickness of the ceramic membrane using the slip casting method depends on the casting time and slurry condition, which makes it challenging to control. Thus, a modified slip casting technique should be introduced to overcome this problem.

In addition, the performance of ceramic membranes should be focused on, and this is strongly connected to the factors contributing to the production of effective, low-cost ceramic membranes. Further investigation, such as the optimization of composition and size of precursor materials and pore formers through the design of experiments (DOE), is necessary to improve the development and properties of the ceramic membrane [9].

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CHAPTER III :

Materials, Experimental Methods, and Analytical Techniques

III. CHAPTER II: THE CERAMIC MEMBRANES

III.1. Introduction:

This chapter provides a comprehensive and detailed overview of the raw materials used in the preparation of ceramic membranes, the experimental procedures followed in their fabrication, and the analytical techniques applied to evaluate their physical and structural properties. These steps aim to ensure the quality of the membranes and their suitability for water treatment.

III.2. Preparation of Ceramic Membranes:

The use of membrane technologies for pollution control remains limited in developing countries due to their relatively high cost. However, the abundance of natural materials such as various types of clay, including kaolin and natural clay offers the potential for producing low-cost ceramic supports. These materials have been shown to enable the fabrication of supports in various shapes (such as cylinders and discs) with good porosity and satisfactory mechanical strength.

III.2.1. Raw Clay Materials:

The primary materials used in the fabrication of ceramic supports consist of inorganic powders, organic additives, and solvents. The properties of the inorganic powders such as particle size, particle size distribution, and particle shape play a critical role in determining pore distribution, pore size, and the shape stability of the final product [1].

To enhance porosity and facilitate shaping, organic additives such as plasticizers, lubricants, dispersants (anti-flocculants), and water-retaining agents are used. The selection of these materials and their respective quantities is crucial, as they significantly influence the shaping method (e.g., extrusion or casting) and the final properties of the ceramic support [2][3].

III.2.2. Raw Materials Used in This Study:

In this study, a mixture of natural clay and kaolin was used as the base material for the preparation of ceramic disc-shaped supports for filtration. This mixture was enhanced with starch and sodium carbonate to improve porosity and shaping properties

1. Kaolin:

Supplied by the Ghazaouet Ceramics Company (Tlemcen), it is provided as a fine white powder with low impurity content (see Fig. III.1). The mineralogical and chemical compositions are presented in the corresponding tables, Tab III-1 and III-2.

Figure III-1: Natural kaolin powder

Table III-1:Mineralogical composition of kaolin.

Mineral Material	**Kaolinite**	**Halloysite**	**Quartz**	**Illite**
Percentage (%)	**83%**	**8%**	**5%**	**4%**

Table III-2: Chemical composition of kaolin.

Mineral	SiO2	Al2O3	Fe2O3	TiO2	K2O	Na2O	CaO	MgO	PF
%	49.4	35.5	0.9	‹0.3	1.55	‹0.1 ‹	‹0.1	‹0.4	11.8

2. Natural clay:

Two types of clay were collected from the Relizane region:

- One from a seasonal wadi (wadi clay), (see Fig. III.2).
- The other from reservoir sediments (dam clay), (see Fig. III.3).

Figure III-2: Wadi Clay.

Figure III-3: Dam clay.

Both were dried, ground, and sieved in the laboratory.

III.2.3. Methodology for Clay Mixture Preparation:

Two types of clay were used in this study: one from a river (wadi clay), and the other from dam sediment (dam clay). The preparation steps included:

1. **Initial Washing (Water Pre-treatment):**

   - **Method:** Each type of clay was immersed in distilled water and stirred continuously for two hours using a magnetic stirrer.

- **Objective:** To remove dissolved impurities and surface organic matter that might affect the chemical composition of the clay or interfere with the sintering process.

2. **Sedimentation and Separation:**

- **Method:** After stirring, the mixture was left to settle. The supernatant water was then separated from the precipitated solids.

- **Results:**
  - **Wadi clay:** pH = 7, indicating a neutral pH and a relatively stable chemical composition.
  - **Dam clay:** pH = 8.5, indicating high alkalinity likely due to the presence of carbonate or alkaline minerals.

3. **Second Washing (for Dam Clay Only):**

- **Method:** Dam clay underwent a second washing with distilled water.
- **Result:** The pH remained stable at 8.5, confirming that the alkalinity was due to internal mineralogical components rather than removable surface impurities.

III.2.4. Layer Separation:

- Observation: After sedimentation, two distinct layers were observed in the dam clay:
  - A fine-grained upper layer,
  - A coarse-grained lower layer.
- **Method:** The coarse layer was selected for use in the final mixture due to its superior shaping and mechanical properties.

III.2.5. Drying and Grinding:

- **Method:** Both clays were dried separately, then ground and sieved to obtain a fine and homogeneous powder with particle sizes suitable for membrane fabrication.

Figure III-4: Fine wadi clay powder.

Figure III-5: Coarse dam clay powder.

III.3. Clay Mixture Preparation:

1. Components and Their Roles:

A. **Wadi clay (fine):** Serves as the primary base of the mixture, providing good cohesion and sintering strength.

B. **Dam clay (coarse):** Enhances mechanical strength and reduces shrinkage during sintering.

C. **Kaolin:** Improves cohesion and the physical properties of the mixture.

D. **Starch:** Increases flexibility and facilitates shaping.

E. **Sodium carbonate:** Raises alkalinity, improves chemical stability, and promotes better component distribution.

III.4. Successful Experiment on a Ceramic Disc:

After determining the appropriate proportions for each component and applying a systematic mixing method, several experiments were conducted to prepare ceramic discs. However, most of the initial attempts failed due to the appearance of cracks during the drying or sintering stages.

Through gradual adjustments to the composition and processing conditions, a successful mixture was developed, exhibiting excellent mechanical and structural stability when shaped into a ceramic disc.
This composition was adopted as a reference point for scaling up the process to fabricate a cylindrical ceramic membrane, with necessary adjustments made to suit its geometric dimensions.

Figure III-6: Ceramic discs prepared from the successful mixture.

III.4.1. Preparation of the Clay Mixture for a Cylindrical Ceramic Membrane:

1. **Successful Experiment on a Ceramic Disc:**

After several unsuccessful attempts due to cracks appearing during drying or sintering, we were able to develop a clay mixture that showed mechanical and structural stability when shaped into a disc.

- **Disc dimensions:**
  - **Diameter:** D=3.3 cm
  - **Thickness:** e=2 mm=0.2 cm
- **Surface area:**

$S=\pi\cdot r^2=\pi\times(23.3)^2\approx 8.55cm^2$

Table III-3: The mass and the Role of each materials

Material	Mass (g)	Scientific Role
Wadi Clay (fine)	1.5	Provides plasticity and cohesion during shaping due to its fine particle size, facilitating the formation of a homogeneous mixture. Enhances adhesion between clay particles during sintering.
Dam Clay (coarse)	0.7	Increases porosity and enhances membrane permeability. The larger particles create voids within the membrane structure, improving filtration capacity, especially for water treatment.
Kaolin	0.7	Offers thermal stability and a stable crystalline structure during sintering. Kaolin withstands high temperatures, improving crack and fracture resistance.
Starch	0.3	Acts as a pore-forming agent. It burns off during sintering, leaving voids that improve water permeability, making the membrane suitable for filtration systems.
Sodium carbonate	0.025	Enhances dispersion and homogeneity. It acts as a deflocculant, evenly distributing particles, and can lower sintering temperature by reducing agglomeration.
Distilled water	5	Facilitates mixing and provides plasticity for shaping. Promotes interaction between components and improves moldability.

- **Total solid mass:**

M_{disk}=1.5+0.7+0.7+0.3+0.025=3.225 g

III.4.2. Scaling the mixture for a cylindrical ceramic membrane:

To fabricate a ceramic membrane in cylindrical form, the following dimensions were selected:

- **Cylinder dimensions:**
  - Diameter: D =2.6 cm
  - Height: h =14.5 cm
  - Thickness: e =2 mm=0.2 cm

- **Total surface area of the cylinder:**
  - Lateral surface area:

$$S_1 = 2\pi rh = 2\pi(\frac{2.6}{2})\times 14.5 \approx 118.44\text{cm}^2$$

  - Top and bottom base area:

$$S_2 = 2\pi r^2 = 2\pi \times (\frac{2.6}{2})^2 \approx 10.62\text{cm}^2$$

  - Total surface area:

$$S_{tot} = S_1 + S_2 = 118.44 + 10.62 \approx 129.06\text{cm}^2$$

- **Expansion factor:**

$$K = (S_{tot,\ cylinder}/S_{disk}) = (129.06/8.55) \approx 15.1$$

- **Total solid mass for the cylinder:**

$$M_{cylinder} = K\cdot M_{disk} = 15.1\times 3.225 \approx 48.73\text{ g}$$

III.4.3. Calculation of Each Component's Mass for the Cylinder (Using Proportion Method):

Material	**Mass in Disk (g)**	**Mass in Cylinder (g)**
Wadi clay	1.5	1.5×15.1=22.65
Dam clay	0.7	0.7×15.1=10.57
Kaolin	0.7	0.7×15.1=10.57
Starch	0.3	0.3×15.1=4.53
Sodium carbonate	0.025	0.025×15.1=0.38
Total	3.225	48.73

Calculation of Required Volume of Distilled Water for the Cylinder:

$$V_{water,\ cylinder} = K\times V_{water,\ disk} = 15.1\times 5 = 75.5\text{ ml}$$

III.5. Preparation Method of the Cylindrical Membrane Mixture:

The cylindrical membrane mixture was prepared following a precise and systematic procedure aimed at ensuring complete homogeneity among the components and obtaining a structure suitable for the intended applications. The process began with the preparation of a basic solution by dissolving 0.38 grams of sodium carbonate (Na_2CO_3) in 75.5 mL of distilled water. The solution was stirred using a magnetic stirrer until complete dissolution was achieved. Sodium carbonate plays a key role in adjusting the pH and increasing the alkalinity of the medium, which enhances the dispersion of clay particles and improves the overall mixability.

Subsequently, 4.53 grams of starch were gradually added to the solution while continuing the stirring until a homogeneous mixture was obtained. Starch serves as an organic binder that improves temporary cohesion between particles during shaping and drying. Additionally, it contributes to the development of extra porosity after it burns off during the sintering process.

Next, 10.57 grams of kaolin were added and thoroughly mixed until a uniform blend was achieved. This was followed by the addition of an equal amount (10.57 grams) of dam clay, characterized by its coarse particles, which promote internal aeration of the mixture and aid in forming larger pores after firing. In the final step, 22.65 grams of fine-grained river clay were added, which helps fill the gaps between larger particles and improves the density and structure of the overall mixture.

Manual mixing of the components continued for approximately one hour to ensure a uniform distribution of the solid particles within the solution. The homogeneous mixture was then poured into a cylindrical mold made of plaster (gypsum), previously prepared according to the desired dimensions.

Figure III-7: Cylindrical mold made of gypsum for shaping ceramic membranes.

After pouring, the mold was sealed and manually rotated from all sides for 45 minutes to eliminate air bubbles and ensure even distribution of the mixture within the mold. The mixture was left inside the mold for four 4 hours to take its final shape, after which the mold was carefully dismantled to avoid breaking the newly formed membrane. A small hole was made on the side of the membrane to enhance ventilation and improve the drying process. Finally, the membrane was left to dry in open air for two days until it was completely dry.

III.6. Thermal Treatment:

After demolding the support and drying it for two days, the sample undergoes thermal treatment at a temperature reaching 1100°C, with a heating rate of 10°C per minute. This thermal treatment gives the ceramic product its final shape, dimensions, and the required mechanical properties.

In this study, a controlled thermal treatment was applied to determine the temperature ranges for the evaporation of temporary additives and the solidification of the structure. The graph in Figure (8) shows a gradual temperature increase up to 200°C, followed by a stabilization phase representing the complete removal of organic materials and water that was not removed during the drying stage, in addition to moisture absorbed after drying, occurring in the thermal range between 100 and 170°C.

The thermal decomposition of starch begins at approximately 280–300°C, where starch loses its bound water and the hydroxyl bonds begin to break, accompanied by an endothermic reaction [4,5]. The degradation continues with the formation of carbonaceous residues above 600°C, which influences the properties of the final product [4,5].

The temperature then continues to rise gradually up to 570°C, where quartz undergoes a phase transformation from α-quartz to β-quartz, resulting in volume changes that may cause shrinkage or cracking.

Between 400 and 700°C, dehydroxylation occurs in the clay minerals, especially kaolinite, as it loses structural hydroxyl groups and transforms into metakaolinite [6, 7, 8]. This water loss is irreversible and is accompanied by shrinkage and a heat absorption phenomenon.

The decomposition of metakaolinite begins between 900 and 950°C, with the formation of mullite starting around 950°C, and the formation of γ-alumina starting at approximately 970°C. These transformations contribute to the strengthening of the ceramic structure.

Finally, the temperature is raised to 1100°C and maintained for 9 hours, followed by a slow cooling process to prevent the formation of cracks in the support due to thermal stress.

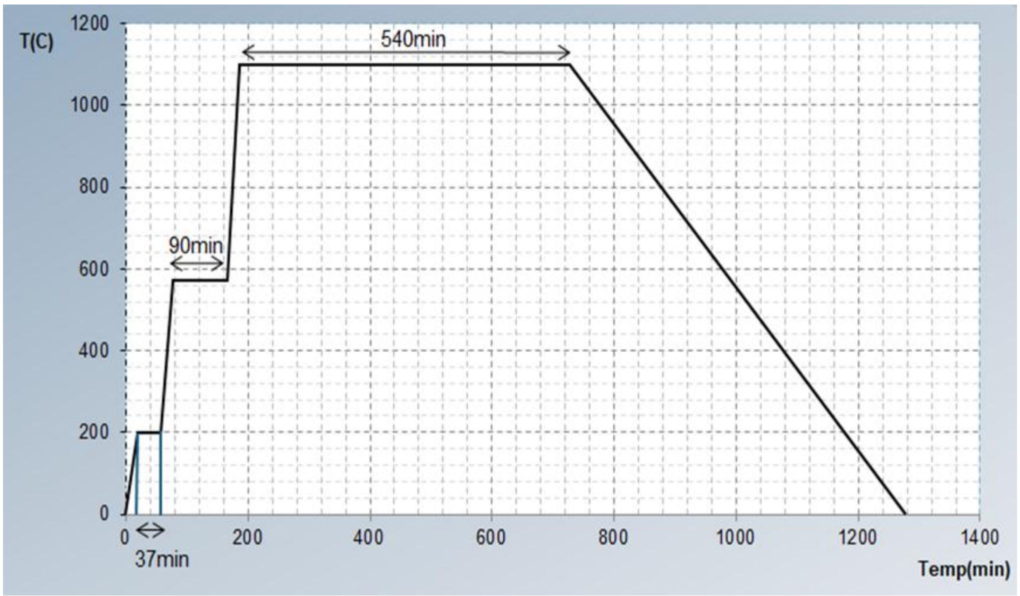

Figure III-8: Thermal treatment diagram of membrane supports.

The sintering curve was plotted based on the time temperature data recorded during the thermal treatment of the ceramic sample.

The curve reveals three main distinct stages ,The first stage involves a gradual increase in temperature from 0°C to 200° C over the first 20 minutes, followed by a thermal holding period at 200°C from minute 20 to 57, This step allows for the evaporation of residual moisture and helps prevent cracking. In the second stage, the temperature rises to 570°C between minutes 57 and 77, with a prolonged plateau from minute 77 to 167. During this phase, physical and chemical changes occur, such as the decomposition of organic matter and the onset of phase transformations. The third stage consists of heating up to the maximum sintering temperature (1100°C) between minutes 167 and 187, with a sustained holding period at this temperature from minute 187 to 727, which promotes densification and microstructural cohesion. The process concludes with a gradual cooling phase, reaching room temperature at minute 1277. This carefully designed thermal program ensures the formation of a defect-free ceramic structure with optimal mechanical and structural properties.

Figure III-9: The prepared ceramic membrane.

III.6.1. Shrinkage Study:

Shrinkage, expressed as a percentage, can refer to linear shrinkage, surface shrinkage, or volume shrinkage. The choice of measurement depends on practical considerations. For tubular supports, linear shrinkage is measured by recording the lengths before and after firing. Shrinkage, however, allows estimating the compactness of the material obtained.

The calculation of the shrinkage rate Rc is given by the following formula:

$$\mathbf{R_c\ (\%)} = \frac{L_0 - L_c}{L_0} \times 100$$

Where:

- L_0: the length of the sample before firing.
- L_C : the length of the sample after firing.

The result of the shrinkage rate:

L_0= 13.6 cm
L_c= 12.9 cm
R_c (%) = 5.14705%

The linear shrinkage rate of the prepared ceramic membrane was found to be 5.15%, which falls within the acceptable and commonly reported range for ceramic materials (typically between 5% and 10%). This result indicates that the sample underwent effective sintering, leading to particle densification and compaction without significant cracks or deformation. The shrinkage rate also reflects the homogeneity of the ceramic mixture and the dimensional stability of the membrane after firing. Such a compact structure is expected to enhance the mechanical and functional properties of the membrane, especially for filtration applications.

III.6.2. Study of the Absorption Rate:

The absorption rate represents the amount of water that a ceramic support can absorb until saturation. The absorption capacity is a measure of the open porosity. The supports were immersed in boiling water at 100°C for two hours, and their weights were measured before and after immersion.

The absorption rate A(%) is calculated using the following formula:

$$A(\%) = \frac{w_b - w_a}{w_a} \times 100$$

Where:

- W_a : Wet weight of the samples (after immersion).
- W_b : Dry weight of the samples (before immersion).

The result of the absorption rate:

w_H= 33.87 g
w_s= 44 g
A(%) = 29.908

The measured absorption rate of the prepared ceramic support was 29.904%, which indicates a relatively high level of open porosity. This is a favorable characteristic for water filtration applications, as it facilitates fluid permeability through the membrane. This result reflects the effectiveness of the selected formulation, particularly the use of natural clays (from the river and dam), which contain inherent impurities that contribute to pore formation, as well as starch, which decomposes during sintering and leaves behind fine voids that enhance porosity.

Therefore, the obtained value demonstrates that the adopted preparation conditions were suitable for producing a ceramic support with desirable porous properties.

III.7. Characterization of Membrane Supports:

III.7.1. Phase Identification (X-ray Diffraction):

X-ray Diffraction (XRD) is a commonly used technique for the identification of crystalline phases, providing information about the mineral species present in the material. Powder X-ray Diffraction (commonly referred to as "XRD on powder samples") is widely used for the characterization of solid materials [9].

The method involves exposing the powdered sample to a monochromatic X-ray beam and collecting the resulting diffraction pattern. The diffraction conditions of X-rays by a family of crystal planes are defined by Bragg's Law:

$$n\lambda = 2d_{hkl}\sin\theta$$

Where:

n: an integer representing the order of reflection,
λ: the wavelength of the X-ray radiation,
d□□□: the distance between crystal planes within a family, conventionally denoted by Miller indices (h, k, l),
θ: the angle between the incident beam and the crystal planes.

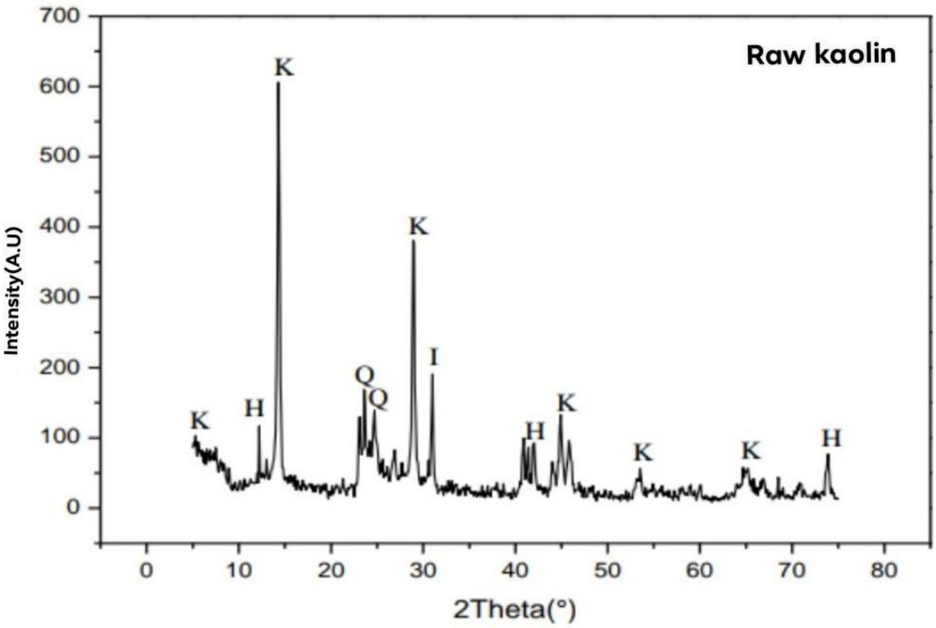

Figure III-10: X-ray diffractogram of raw kaolin.

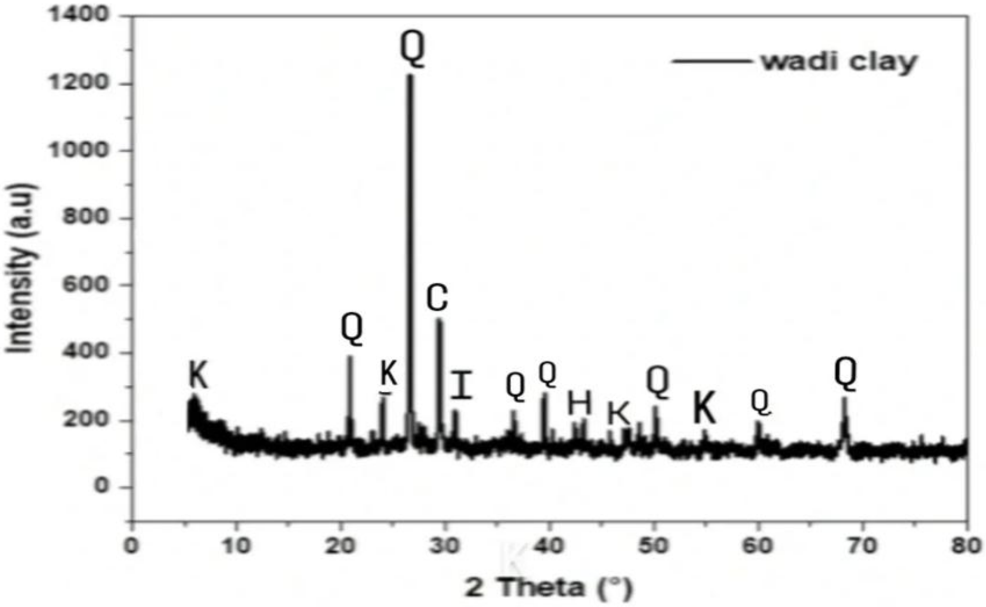

Figure III-11: X-ray diffractogram of raw wadi clay.

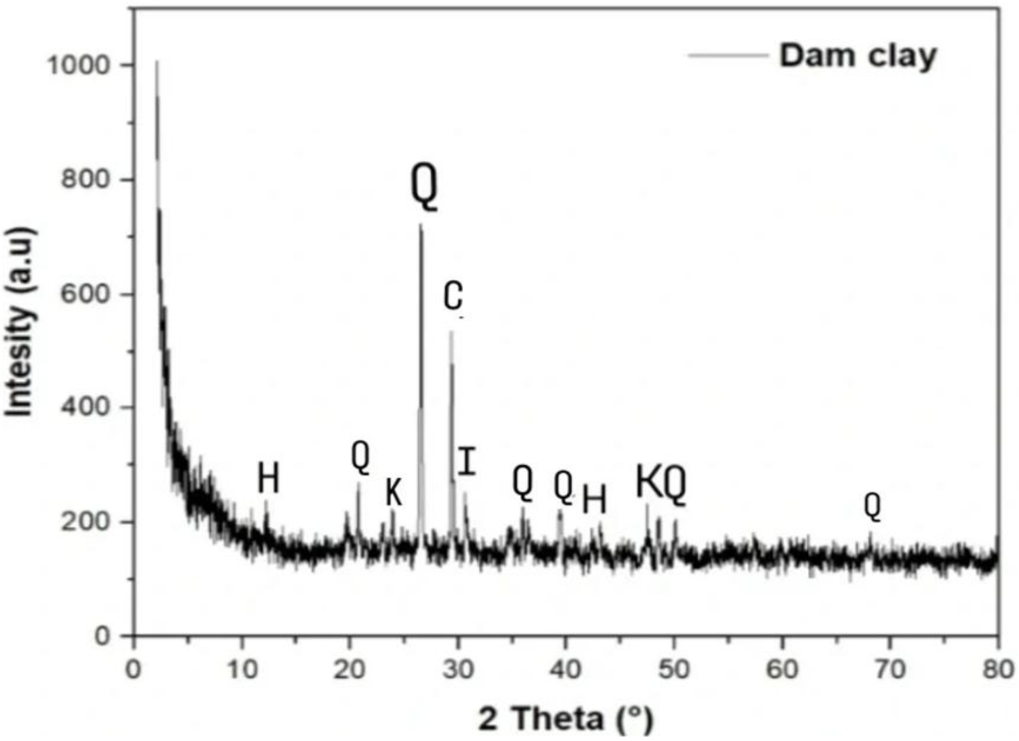

Figure III-12: X-ray diffractogram of raw dam clay

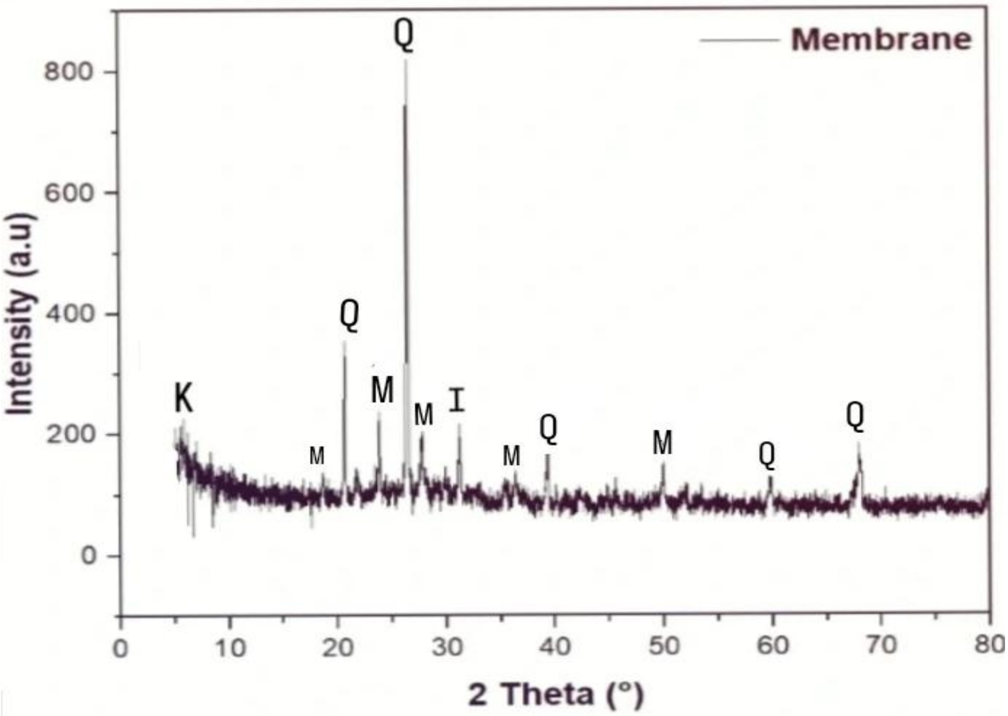

Figure III-13: X-ray diffractogram of membrane.

III.7.2. Spectrum Processing and Identification of Clay Minerals:

After performing X-ray diffraction, an energy spectrum of the diffracted beam is obtained as a function of the diffraction angle 2θ.

The angular values in this spectrum can be converted into basal spacings d (in angstroms) by applying Bragg's Law and using the Kα wavelength of the anode used to produce the incident X-ray radiation (source: cobalt).

The ASTM standards enabled us to identify the clay phases and impurities present in raw wadi and dam clays, raw kaolin, and the wadi/dam clay kaolin mixture.

1. **Preliminary analysis of the raw kaolin XRD pattern (Figure 10):**

This pattern reveals the presence of the following minerals:

Kaolinite (K): 5.13°, 14.41°, 28.99°, 44.89°, 53.65°, 65.2°
Illite (I): 30.94°
Quartz (Q): 23.65°, 24.93°
Halloysite (H): 12.14°, 41.98°, 73.96°

2. **Preliminary analysis of the raw wadi clay XRD pattern (Figure11):**

This pattern reveals the presence of the following minerals:

Kaolinite: 5.6°, 24.9°, 48°, 54.8°
Illite: 30.94°
Quartz: 21°, 26.6°, 36.5°, 39.4°, 60°, 68.6°
Halloysite: 44°
Calcite: 29.9°

3. **Preliminary analysis of the raw Dam clay XRD pattern (Figure 12):**

This pattern reveals the presence of the following minerals:

Kaolinite: 20°, 24°, 35°, 47.5°, 48.5°
Illite: 30.94°
Quartz: 21°, 23°, 36.5°, 39.4°, 50°, 60°
Halloysite: 12.1°, 43.5°
Calcite: 29.9°

4. XRD Pattern Analysis of the Membrane After Calcination (Figure 13):

Kaolinite: 5.6°
Illite: 30.94°
Quartz: 21°, 26°, 39.4°, 60°, 68°
New phases (Mullite, Metakaolinite.): 18.5°, 24°, 28°, 36°, 50°

III.7.3. Comparison of Mineral Phase Evolution (Before and After Calcination) (Tab III-5):

Table III-4: Comparison of Mineral Phase Evolution Before and After calcination

Mineral Phase	Raw Kaolin (Kaolin brut)	Wadi Clay	Dam Clay	After Calcination (Membrane)
Kaolinite	High	Moderate	Moderate	Very low / Decomposed
Quartz	Moderate	Very high	High	High
Illite	Low	Low	Low	Low
Halloysite	Present	Weak	Weak	Absent
Calcite	Absent	Moderate	Moderate	Absent / Decomposed
New thermal phases (M)	Absent	Absent	Absent	Clearly present

The XRD analysis results show that the calcination process significantly affected the mineralogical structure of the clay mixture. Halloysite completely disappeared, and kaolinite decomposed due to thermal transformation, leading to the formation of new mineral phases such as metakaolinite and possibly mullite, which are desirable ceramic phases for filtration applications. Quartz remained stable, contributing to the structural integrity of the membrane.

Illite persisted in low amounts, indicating partial thermal resistance. These changes confirm the successful transformation of the clay mixture into a ceramic material with enhanced mineral composition, favoring stronger and more thermally stable phases suitable for water treatment applications.

III.8. Permeability of Membrane Supports:

Permeability is a property that determines the amount of water that passes through the tubular support per unit area and time, under specified pressure and temperature conditions. It is considered a very important property of the support we have prepared and improved, as it determines the effectiveness of using this support in the treatment of industrial wastewater.

The permeate flux is given by the following equation:

$$J_p = \frac{Qp}{S}$$

Where:

J_p: Permeate flux (L/hm²)
Q_p: Permeate flow rate (L/h)
S: Surface area (m²)

In order to evaluate the performance of the prepared ceramic membrane in removing pollutants from water, a filtration experiment was conducted using a solution dyed with methylene blue as a model organic contaminant. A simple filtration system was set up, consisting of a pressure-generating pump, connecting tubes for transporting the solution, and a ceramic membrane installed inside a dedicated filtration chamber. The objective of this test is to study the membrane's ability to separate dye molecules from water under constant pressure and to determine its efficiency by analyzing the solution samples before and after passing through the membrane.

Figure III-14: Filtration system used to evaluate the performance of the ceramic membrane

The pump was activated to generate a constant pressure of 5 bar, which caused the methylene blue solution to flow through the pipes toward the ceramic membrane installed in the filtration system. At the start of the operation, a manual timer was started to measure the filtration time, and the filtrate was collected in a designated container. After 7 minutes of continuous operation, 75 mL of filtered water was collected. Based on visual observation, the resulting water was completely clear and colorless, indicating the membrane's preliminary ability to remove methylene blue dye from the solution.

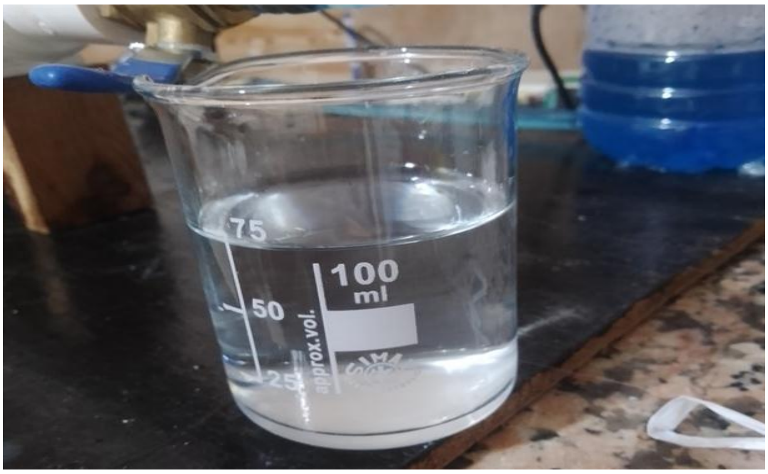

Figure III-15: Filtered water sample after passing through the ceramic membrane.

The image shows the clarity of the filtered water, which appears colorless, indicating the preliminary efficiency of the membrane in removing methylene blue dye.

III.8.1. Flux Calculation:

Flux is calculated to express the volume of water permeated through the ceramic membrane per unit area and time, using the following formula:

Given data:

- Membrane diameter: $D=2.2\ \text{cm}=0.022\ \text{m}$
- Membrane height: $h=12.9\ \text{cm}=0.129\ \text{m}$
- Filtrate volume: $V=0.075\ \text{L}$
- Time: $t=7\ \text{min}=0.1167\ \text{h}$

The flux rate measured during this experiment was approximately 72.1 $L/m^2{\cdot}h$, which is considered acceptable under the applied operating conditions, particularly with an applied pressure of 5 bar. This result demonstrates the ceramic membrane's ability to allow a substantial amount of water to pass through in a relatively short period, without any signs of clogging or a noticeable decline in permeability. This highlights the efficiency of the membrane's porous structure in filtering the colored water containing methylene blue dye after treatment.

Such performance can be attributed to the structural properties of the membrane, including its mineral composition, particle size distribution, and sintering temperature. These factors collectively contribute to the development of effective pores capable of removing contaminants while maintaining an adequate filtration rate.

1. Measurement of Concentration and pH After Filtration

As part of the evaluation of the ceramic support's performance in removing organic substances from water, a chemical analysis was carried out on a colored solution before and after passing through the support.

The initial concentration of the solution was measured at 10-4mol/L, a standard value used to assess separation efficiency. After filtration, the concentration significantly dropped to approximately 10-9mol/L.

This considerable reduction reflects the high retention capacity of the support, with a calculated removal efficiency of:

R_e (%) $=\frac{C0-Cf}{C0}\times 100$
R_e: Removal efficiency
$\mathbf{C_0}$: Initial concentration of the pollutant before filtration (mol/L)
$\mathbf{C}_f$: Final concentration after filtration (mol/L)
R_e (%) $=\frac{C0-Cf}{C0}\times 100=99.999\%$

This result demonstrates the excellent separation performance of the support. It indicates that the porous structure and surface behavior of the ceramic matrix provide ideal conditions for retaining dye molecules, whether through physical adsorption or size-based filtration.

Additionally, the variation in pH before and after filtration was monitored. The initial pH of the solution was 6.7, which increased to 7.8 after filtration. This shift suggests a chemical interaction between the solution components and the surface of the ceramic support. It is likely that the support adsorbed acidic ions or released basic species through ion exchange or surface charge effects, thereby increasing the pH value.

This change in pH indicates that the support not only removes organic pollutants efficiently, but also alters the chemical nature of the treated water, enhancing its suitability for applications requiring controlled chemical environments.

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General Conclusion

IV. General Conclusion

This research successfully demonstrated the potential of natural clay-based ceramic membranes in water treatment applications.

- Theoretical analysis clarified membrane types, classifications, and future directions of membrane technology.
- Ceramic membranes showed favorable characteristics such as high porosity, thermal stability, and chemical resistance.
- Experimental work confirmed that a mixture of wadi clay, dam clay, kaolin, starch, and sodium carbonate could be effectively shaped into a functional membrane.
- The sintering process at 1100°C for 13 hours proved sufficient for phase transformation, resulting in a stable ceramic structure.
- The membrane exhibited 5.15% shrinkage, 29.91% absorption, and high permeability (72.1 $L/m^2 \cdot h$), all within optimal ranges reported in literature.
- Structural analysis revealed the formation of beneficial mineral phases (metakaolinite, mullite), indicating a successful calcination process.
- Filtration tests showed no fouling and ensured continuous water flow with effective pollutant removal (up to 99.999%).
- The membrane slightly increased the pH of the treated solution, indicating interaction with the medium and possible neutralizing effects.
- Overall, the results confirm that ceramic membranes from local natural clay offer a cost-effective, efficient, and eco-friendly solution for water filtration.