Mohamed Khider University of Biskra
Faculty of Exact Sciences
Material Sciences Department

# MASTER MEMORY

Material Sciences
Physics
Physics of materials

Réf. : Entrez la référence du document

---

Presented by:
**Benbouzid Imane**

At : 2025-06-03

# Effect of Additives (Sunflower Oil) on Permeability of Filters Prepared from Local Clays

---

Jury:

| | | | | |
|---|---|---|---|---|
| **Mrs.** | **Majda Hamzaoui** | **MCA** | **University of Biskra** | **President** |
| **Mr.** | **Boukhemis Boudaira** | **MCA** | **University of Biskra** | **Supervisor** |
| **Mrs.** | **Nawel Benyahia** | **MCB** | **University of Biskra** | **Examiner** |

*Academic Year*: 2024-2025

# ***Dedication***

*To those who instilled values in my heart and watched over my comfort for years, I dedicate my success and gratitude to you, my generous parents.*

*To those whom God gave me the blessing of their presence, to my source of strength, my solid ground and the wall of my heart, my brothers and sisters.*

*To those who narrowed the world and sought their footsteps, and if I fell, they were the first to lift me up with their words, to the companions of the first step and the penultimate step. To those who, during the lean years, were rain clouds, Yousra Soukour and Aisha Barkat, I am grateful.*

*At the end of this journey, I dedicate this achievement to everyone who believed in me in my moments of weakness, and to everyone who was a light in my path... This graduation is not an end but the beginning of a big dream.*

# ***Acknowledgements***

*First and foremost, praise be to God, who has the credit first and last, outwardly and inwardly.*

*I praise and thank him for the success and help he gave me in completing this work despite the difficulties and challenges I encountered, and I ask him to make this effort purely for his face and to benefit me in my world and my afterlife.*

*I extend my deepest thanks and gratitude to my professor, Mr. Boudaira Boukhemis, for his supervision of this work, who did not spare me his knowledge and experience, and allocated me his valuable time and effort, whose guidance and valuable comments had a great impact in bringing this work to light in the best form.*

*I also extend my sincere gratitude to Dr. Melki Tarek for his valuable contribution to the success of the experimental aspect and for his eagerness and dedication in providing assistance with spirit and responsibility.*

*I cannot fail to express my great appreciation and thanks to the student Lehmaidi Assil for his continuous support and useful information that he never spared us, and he was truly a model of cooperation and commitment, so he has my utmost respect and appreciation.*

*I extend my sincere thanks and appreciation to Ms. Hamzaoui Majda and Ms. Benyahia Nawel for agreeing to discuss my note and devoting part of their valuable time to reviewing and evaluating this work. I am honored by your presence and your scientific contribution, and I wish you success in your academic career.*

*I extend my thanks and gratitude to all those who put their fingerprints on this work, asking God to make this effort purely for His face and a useful contribution to my scientific and professional field.*

# Table of Contents

# List of Tables

# List of Figures

# List of Graphs

## I. General Introduction

The need for water filtration capacity has increased significantly as a result of urbanization, industrialization, and ongoing population growth. One of the most urgent issues facing humanity is water shortage, as water use has grown more than twice as fast as the rise of the human population in the past century. The need for more water filtration and desalination capacity has been exacerbated by the fast industrialization in developing nations and the resulting contamination of freshwater sources.

Compared to other separation techniques like distillation and electrodialysis, partially permeable membranes require substantially less energy to apply, making them ideal for filtering and desalination applications. The majority of membranes that are sold commercially are composed of polymers. Although polymeric membranes are inexpensive to create, fouling causes these systems to have low stability and high lifetime costs. In contrast, inorganic membranes made of metals or ceramics demonstrate thermal and chemical stability, which lowers operating costs by enabling the use of heat or chemical solvents for defouling procedures. However, the high production costs of sintering-based fabrication processes and the high cost of the raw materials commonly used for ceramic membranes (alumina, zirconia, and titania) prevent conventional ceramic membranes from being used on a large scale and restrict their use to small-scale systems. The utilization of inexpensive raw materials as precursors for ceramic membranes has gained more attention in recent years. More than 2.5 billion people globally, primarily in areas with less economic development, lack adequate access to clean water, according to studies. Low-cost ceramic membranes have the potential to provide a high volume filtration capacity that would facilitate the provision of clean and reliable water in poorer regions of the world. Low-cost ceramic membranes made from naturally occurring raw materials and waste products are becoming more and more popular as a solution to large-scale water treatment problems. Finding structures with the right micro-scale pore structures to provide pollutant separation while preserving enough mass transfer and mechanical durability is a difficulty in the production of inexpensive membranes. To accomplish this goal, a variety of materials and processing techniques have been investigated utilizing inexpensive feedstocks, such as ash, clays, and unprocessed minerals. Pore formers, binders, fluxes, and other additives can drastically change the microstructures, durability, and filtration capabilities of membranes made from impure raw materials that are directly obtained from waste streams or mineral deposits. The creation of suitable processing methods[1].

This research aims to study the effect of additives, especially sunflower oil, on the permeability of the filters prepared from pure clay:

The first chapter deals with an overview of ceramic materials and membranes, addressing the methods of their preparation and study, including some of the additives used such as sunflower oil, and reviewing some of the different applications of ceramic materials and membranes.

As for the second chapter, it was devoted to the study of raw materials before processing, presenting the experimental methods adopted, and introducing the methods and devices used in the preparation of ceramic filters.

While the third chapter includes analyzing and discussing the results obtained during this study.

# *Chapter One:*

## *An Overview of Ceramic Materials And Membranes And Some Of Their Applications.*

## I.1. Introduction

Since it is essential to all living things and to many different economic sectors, water is regarded as a precious resource. Since there is a shortage of potable water, treating water and wastewater has become crucial to solving the water issue. Membrane separation plays a significant role in treating contaminated water through a number of purification techniques, such as reverse osmosis (RO), microfiltration (MF), nanofiltration (NF), and ultrafiltration (UF). Membranes can be classified into a number of groups based on their composition, such as ion-exchange, liquid, polymeric, and ceramic membranes. Ceramic membranes are particularly efficient for MF and NF water treatment procedures are made of silicon carbide (SiC) and oxides of Si, Al, Ti, or Zr. In the manufacturing process, a mixture of ceramic components, solvent, polymer binder, and water are used. This suspension undergoes a phase-reversal process induced by solvent/non-solvent exchange, leading to solidification. Depending on the desired configuration, spinning or casting are employed to immobilize the ceramic particles. Subsequently, a single-step thermal treatment is applied to remove organic components and enhance the mechanical properties[2].

## I.2.Ceramic Materials

### I.2.1. Definition of Ceramic Materials

Ceramic materials can be defined as inorganic materials composed of a combination of metallic and nonmetallic elements whose properties depend on the way in which these elements are linked. Ceramic materials are among the most versatile materials. The origin of this versatility lies in the chemical nature of their bonds, since they are mainly consist of a strong ionic and covalent bonds in different proportions. The bonds determine a series of particular properties of ceramic materials among which are relatively high melting temperatures, high elastic modulus, high wear strength, poor thermal properties, high hardness and brittleness combined with some toughness, and low ductility. In addition to the lack of free electrons due to their bonding forming chemical bonds, they are good electrical insulators[3].

### I.2.2. Classification of Ceramics

As illustrated in Figure I_1, a hierarchical approach is the most effective way to address inorganic and nonmetallic materials systematically. The three broad material categories metals, polymers, and ceramics—that are identified by their varying chemical bonding relationships are represented in the first triangle of level 1.

The inorganic-nonmetallic material classes—glasses, hydraulic binders, and ceramics—are depicted at the corners of the second-level of triangles. In the third hierarchical level, these classes can be further separated into silicate, oxidic, and nonoxidic materials. Finally, the specific qualities are determined by the chemical composition (fourth hierarchical triangle)[4].

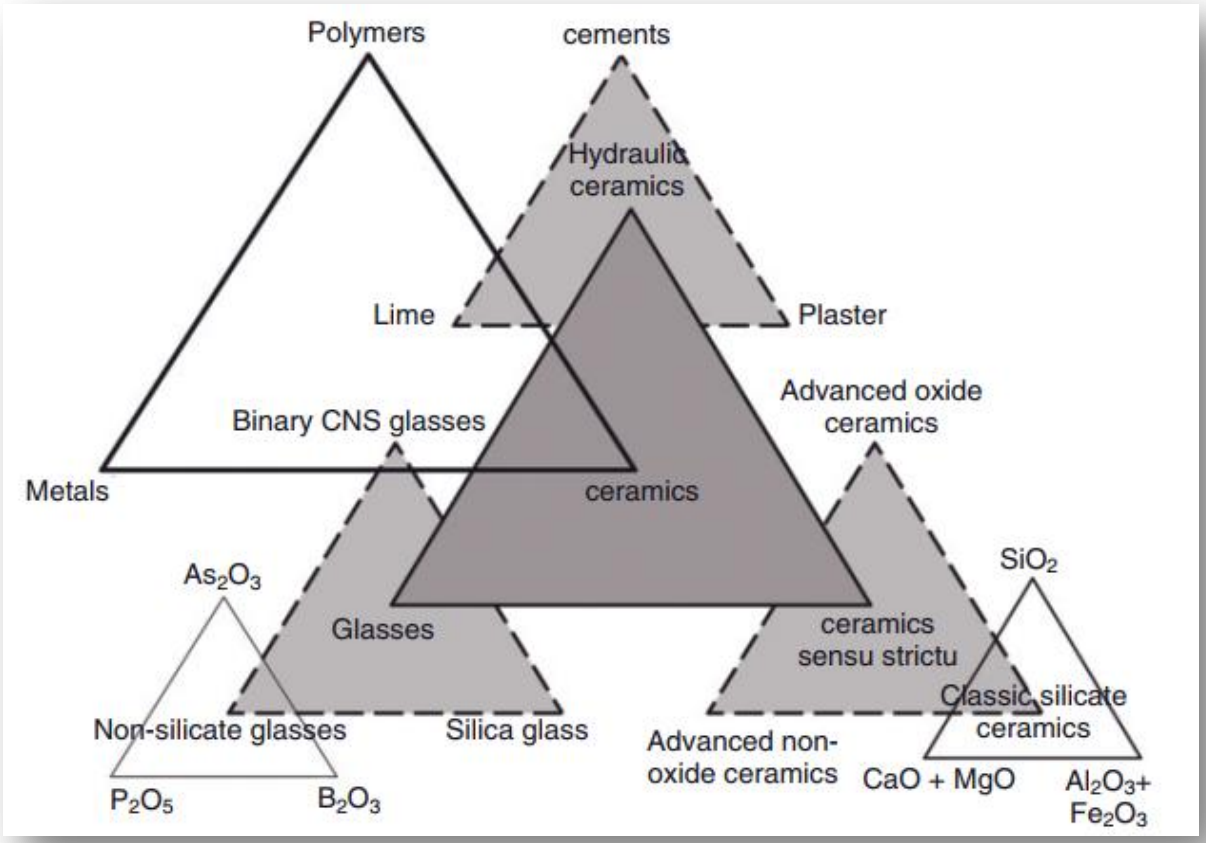



***Figure I.1 Four levels of hierarchical triangles relating different groups of materials* [4].**

***Table I.1 The three main groups of silicate ceramic materials* [4].**

| Material | Processing steps[a)] | | | $T_{max}$( ° C) | Time of invention |
|---|---|---|---|---|---|
| **Ceramics *sensu strictu*** | **P** | **F** | **H** | **<1450 <6000 B.C** | **<1450 <6000 B.C** |
| **Glasses** | **P** | **H** | **F** | **1500 <3000 B.C.** | **1500 <3000 B.C.** |
| **Cements (CBCs)[b)]** | **H F** | **P** | | **>1500 Around 1850** | **>1500 Around 1850** |

a) P = powder production; H = heating; F = forming.

b) CBC = chemically bonded ceramic.

This is intended to simply illustrate the basic concept in practice, a series of hierarchical triangles would be more intricate. For instance, silicate ceramics' enormous range of chemical compositions would need to be expanded or refined [4].

The three main groups of ceramics of level 2 are distinguished by their processing temperatures, the succession of processing steps (F = forming, H = heating, P = powder production), and the time of invention (Table I.1).

Historically, silicate - based ceramics have been classified in various ways. One of the most useful schemes divides various traditional ceramic types according to their starting powder sizes (coarse: >0.1-0.2 mm; fine: <0.1-0.2 mm), porosity of the fired product, water absorption capacity (2 <wt% > 6 ) mass, and color of the fired ceramic body (Figure I.2).
technical ceramics classification is illustrated in Figure (I.3).

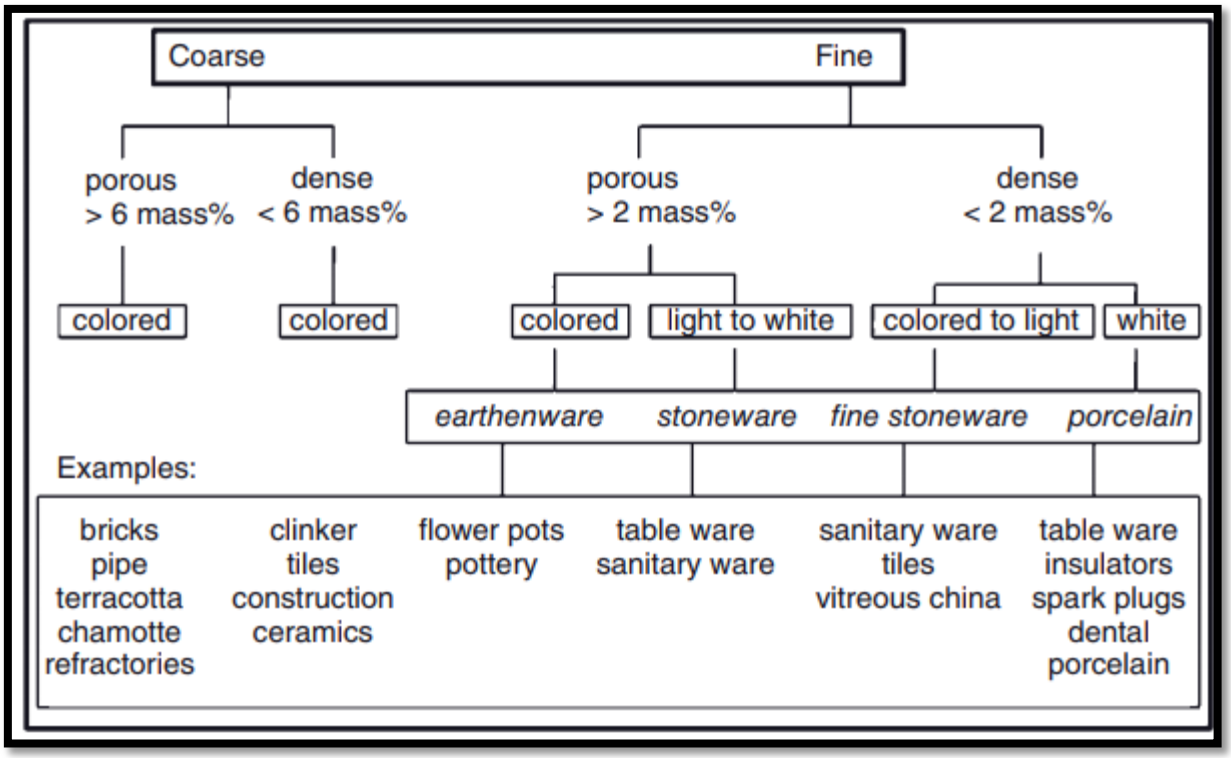



*Figure I.2 Classification of silicate-based ceramics*[4].

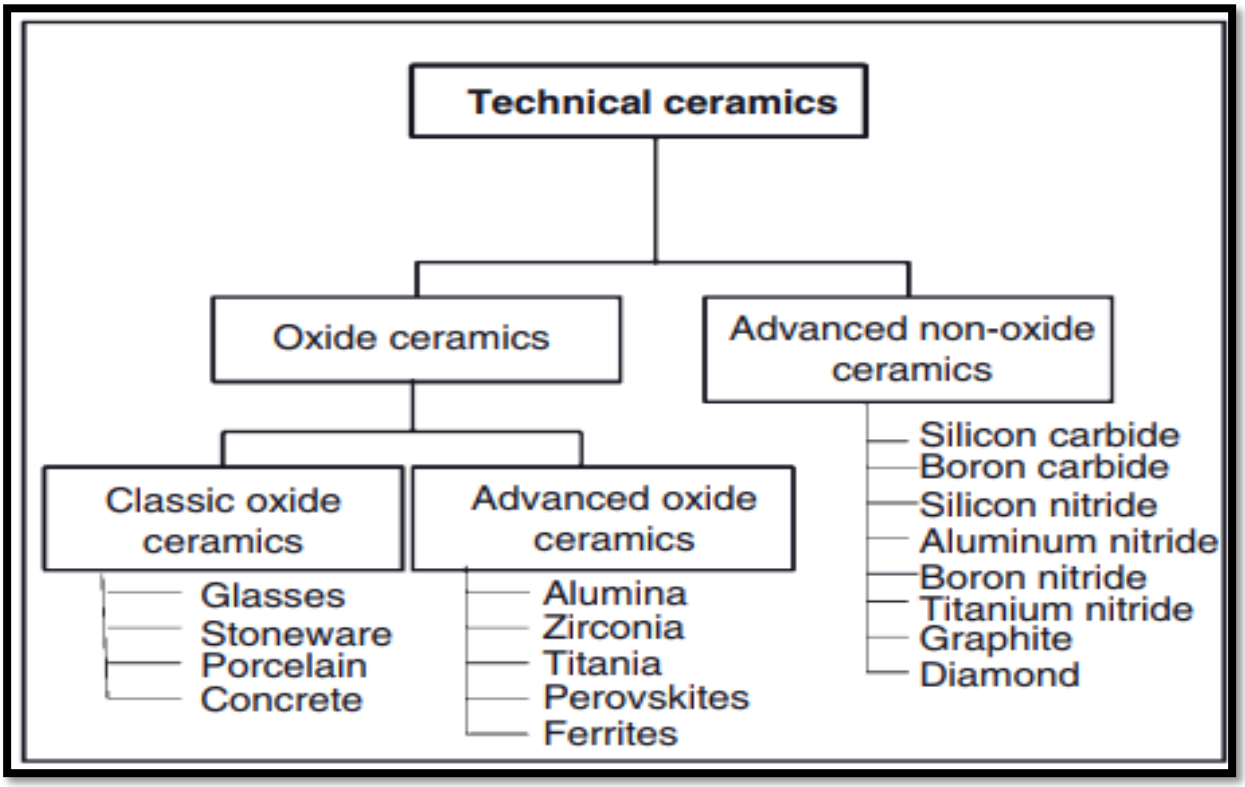



*Figure I.3 Classification of technical ceramics ( level 3 of figure (I_1))*[4].

### I.2.3. General Properties of ceramic materials

*Table I.2 Comparison of important properties of metals, engineering plastics, and advanced ceramics*[4].

| Property | Metals | Engineering plastics | Advanced ceramics |
|---|---|---|---|
| Maximum temperature for continuous use ( ° C) | | | |
| Typical | 1000 | 250 | 1200 |
| Maximum | 1500 | 350 | 2500 |
| Hardness | Medium – high | Low – medium | High |
| Toughness | | | |
| Flexibility | Medium – high | High | Low |
| Impact resistance | High | Medium – high | Low |
| Corrosion resistance | Low – medium | Medium | High |
| Coefficient of thermal expansion | High | Medium | Low |
| Electrical properties | Conductive | Insulative to conductive (with fillers) | Insulative to conductive |
| Density | High | Low | Medium |

### I.3. Raw Materials

The natural raw materials used to make silicate-based ceramics can be separated into three categories: (i) highly plastic materials, such as clays made of the minerals kaolinite, illite, or montmorillonite; (ii) minerals that are slightly plastic for specific electroceramic applications, like talc and pyrophyllite; and (iii) nonplastic materials, like feldspar, apatite, nepheline, calcite, dolomite, etc., that are added to clays to modify the chemical composition, improve, workability, and sintering behavior of the ceramic masses. For high- performance electroceramics, synthetic raw materials include hydrothermally produced wollastonite and diopside, synthetic kaolinite with a very narrow grain size distribution and high plasticity, and precursors of glazes (lead oxide, barium carbonate, and tin oxide) and special ceramic masses (alumina, zirconia, and magnesia)[4,18].

### I.3.1. Natural Clay Minerals

The processes involved in the oxidizing or reducing firing of clay minerals are influenced by the mineralogical composition of clays and their interactions with weathering and soil solutions. Clays are derived from the weathering of feldspars, micas, and other rock-forming minerals, creating a mechanical mixture with distinct components, each having its own particle size range. This mixture typically includes: (i) fine-grained weathering relics like **quartz**, **feldspar**, **sericite**, and **interlayer-deficient micas**; (ii) newly formed clay minerals such as **kaolinite**, **halloysite**, **illite**, and **montmorillonite**; (iii) remnants of organisms, including **calcite, aragonite**, **silica**, or **graphite** or other forms of **carbon**; and (iv) post-depositional neoformations such as pyrite, dolomite, or glauconite. Clay minerals generally have grain sizes smaller than 2 µm, whereas weathering relics can reach up to 20 µm[4,18].

- **Inheritance**: Clay minerals can form from processes that occurred in previous stages of the rock cycle.
- **Neoformation**: Clay minerals are formed through precipitation from dilute soil solutions or reactions involving amorphous materials.
- **Transformation**: This involves the alteration of inherited clay structures through chemical reactions, such as ion-exchange or layer transformation, which typically occurs during diagenesis.

While inheritance is predominant in sedimentary environments with slow reaction rates, transformation requires more energy and occurs in diagenetic or hydrothermal settings, where higher temperatures prevail. The weathering environment, where inheritance, neoformation, and transformation can all take place, exists between these two extremes. As a result, clay mineral formation in nature can follow nine distinct pathways, reflecting the remarkable complexity and variability of clay mineral chemistries.

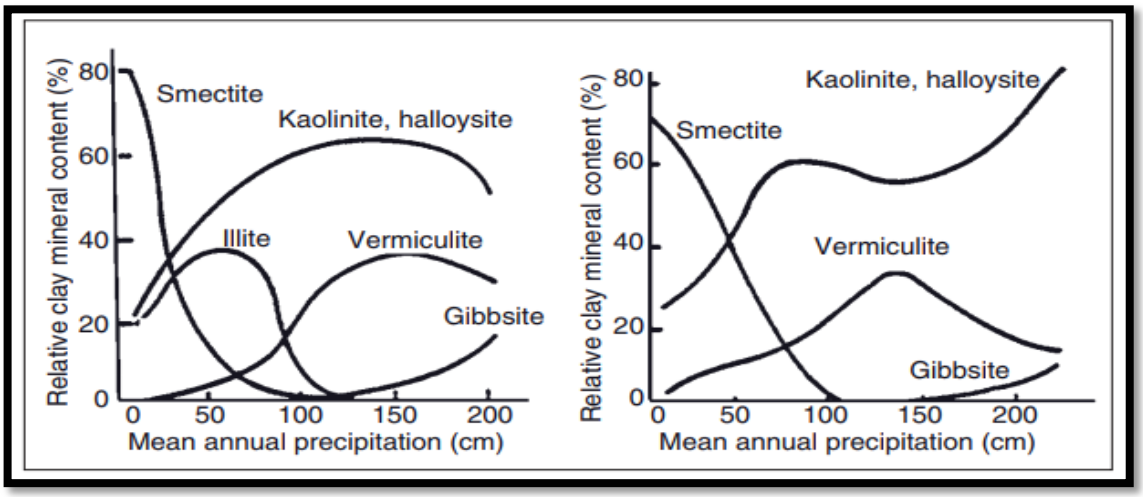



***Figure I.4 General scheme of the relationship between the frequency distribution of clay minerals and the amount of precipitation in residual soils of acid (left) and basic (right) igneous rocks*[4].**

### I.3.2. Structure of Important Clay Minerals

#### I.3.2.1. Kaolinite

Kaolinite ($Al_4$ $[(OH)_8/Si_4O_{10}]$) is a common weathering product of feldspar in temperate-humid climates with abundant slightly acidic water, which removes alkali and alkaline earth metal ions. It exists in four structural variants: triclinic kaolinite, monoclinic dickite, monoclinic nacrite, and a fireclay with a b-axis distortion. Studies by author and revealed a complex polytypic pattern with 36 transformations between kaolinite layers, including 20 energetically distinct transformations and 16 enantiomorphic transitions. Kaolinite and dickite are the most stable at ambient conditions, while nacrite has the lowest enthalpy under moderate pressure. Figure I.5 shows the structure of kaolinite, dickite, and nacrite[4,18].

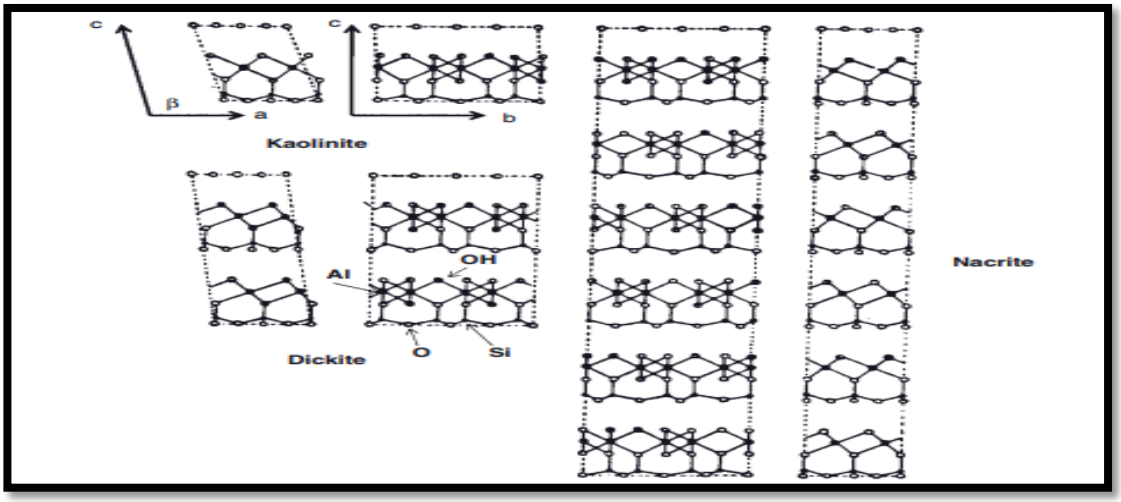



***Figure I.5 structure of kaolinite, dickite, and nacrite* [4].**

### I.3.2.2. Illite

Illite, one of the most abundant clay minerals after kaolinite, remains poorly inadequately defined by the AIPEA. Due to its complex formation and transformation processes, which are influenced by its variable chemical composition, small crystal size and degree of crystallinity. Illite primarily forms through inheritance by potassium loss from muscovite (dioctahedral) or biotite (trioctahedral), through the incorporation of potassium into montmorillonite, or potentially by neoformation from colloidal solutions resulting from weathering. However, potassium-argon dating suggests that originate from continental sources through inheritance rather than in-situ formation. The degradation of biotite and muscovite involves ion exchange, oxidation, and charge adjustments, leading to chemical shifts and water intercalation. Structurally, illite's chemical composition evolves towards that of kaolinite in composition but retains a montmorillonite-like structure, forming various interstratified variants. The two main polytypes, illite-1M and illite-2M1 differ in stacking order and tetrahedral layer geometry, with ilite-2M1 exhibiting a more ordered crystal stacking. Illite crystallinity (IC), measured by X-ray diffraction (XRD) sharpness, serves as an indicator of diagenetic and metamorphic grades, with increasing temperature enhancing crystal order. The Kübler Index (KI) and Crystallinity Index Standard (CSI) are key metrics for assessing illite structure, influenced by defect migration, stacking order, and polytypic transformation. With higher metamorphic grade, strain decreases, leading to a more ordered crystal lattice. Figure I.6 shows is Projection of the structure of muscovite-2M onto the a—c plane[4,18].

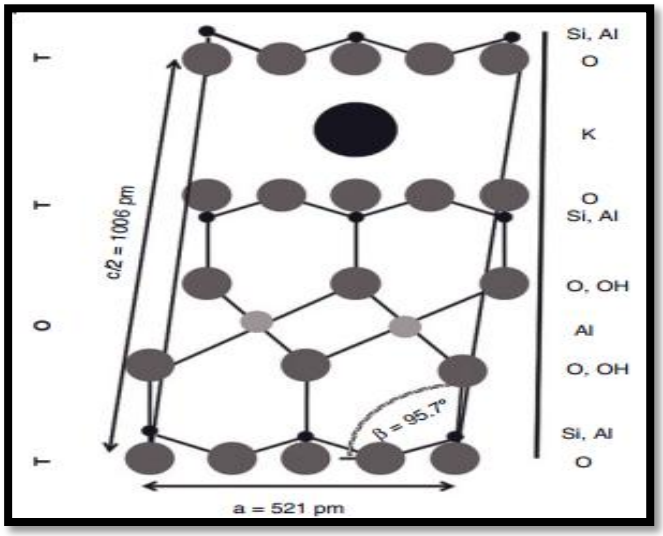



*Figure I.6 Projection of the structure muscovite-2M onto the a—c plane* **[4].**

### I.3.3. Montmorillonite

#### I.3.3.1. Structure and Application

The smectite–vermiculite group of clay minerals is formed by a number of rock cycle events, such as the weathering of feldspars in humid soils, the alteration of basaltic lavas by the sea, and the conversion of volcanic tuffs into bentonites. Structurally, smectites are formed by the partial substitution of aluminum with iron or magnesium in silicate layers. The ionic substitution in the layered structure of montmorillonite leads to a lack of charge, which is compensated for by positive cations such as $Ca^{2+}$ and $Na^{+}$ located between the layers. Temperature and humidity significantly influence these minerals' ability to absorb water and organic molecules. This results in expansion along the c-axis. In many industrial applications, the swelling capacity—particularly notable in montmorillonite—is essential. Rich in smectite, bentonites have long been used to absorb oils and are still essential for iron ore pelletizing, pet litter, drilling fluids, and foundry molds. They can also be used to remove pollutants, seal waste disposal sites, and used as a clarifying agent in the wine and beverage industry due to their adsorption qualities. Recent developments have produced polymer–clay nanocomposites (PCNs) with improved mechanical and swelling characteristics, which are utilized in energy, civil engineering, and environmental protection applications. In the automobile and aerospace industries, these materials act as structural reinforcements, enhance soil retention, and inhibit corrosion. Numerous rock cycle processes, including the weathering of feldspars in humid soils, the sea's alteration of basaltic lavas, and the transformation of volcanic tuffs into bentonites, result in the formation of the smectite–vermiculite group of clay minerals. When iron or magnesium partially replace aluminum in silicate layers, charge shortages occur. These shortages are balanced by interlayer cations like $Ca^{2+}$ or $Na^{+}$, forming smectites physically. The remarkable ability of these minerals to absorb water and organic molecules, which results in expansion along the c- axis, is influenced by temperature and humidity. This ability to swell, particularly in montmorillonite, is crucial in many industrial applications. Figure I.7 shows the structures of beidellite (top), montmorillonite (center), and nontronite (bottom)[4].

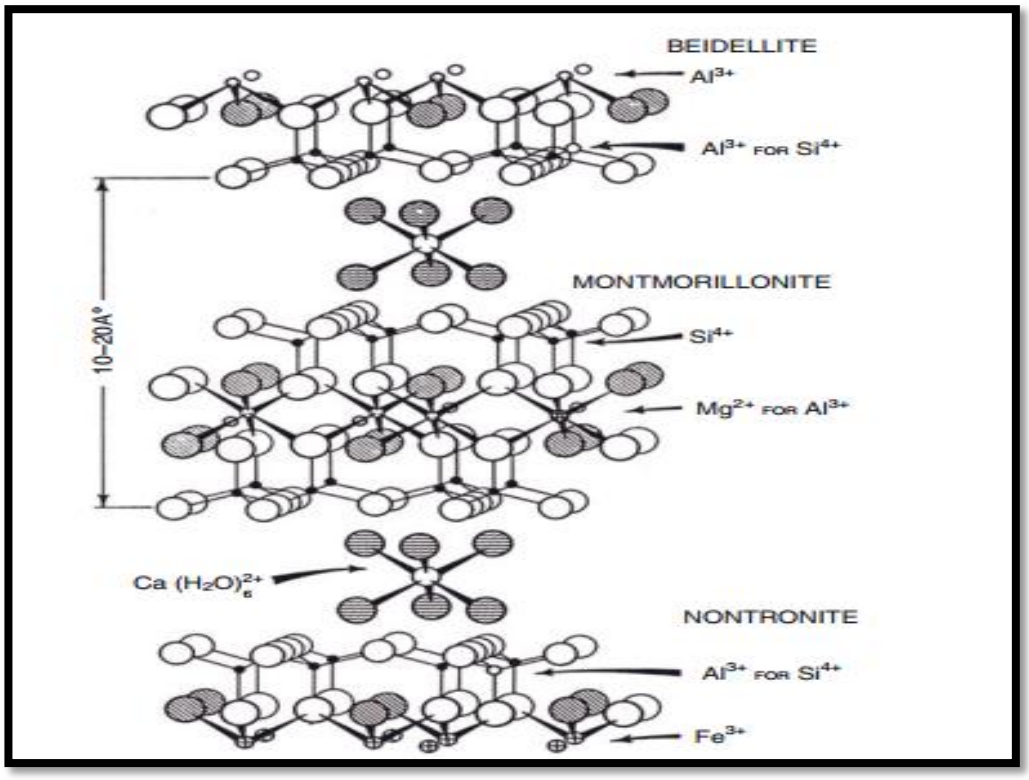



***Figure I.7 structures of beidellite (top), montmorillonite (center), and nontronite (bottom)*[4].**

### I.4. Sunflower Oil as a Ceramic Additive

Sunflower oil is considered an organic material and is a vegetable oil extracted from the seeds of the sunflower plant. containing high percentages of unsaturated fatty acids, which contain one or more double bonds between carbon atoms in the hydrocarbon chain, such as oleic and linoleic acid, used in cooking as well as in clay or ceramic mixtures during the manufacture of ceramic filters as it provides good control of pore distribution within the ceramic material and helps improve the properties of the filter from durability and filtration efficiency, as well as helping to improve the filter properties of durability and filtration efficiency. Sunflower oil has a pale yellow color and should have an acid value of 0.9-1.1% at most [19].

### I.5. Applications of Ceramic Materials

It is now well acknowledged that ceramic materials are used not only in industrial or scientific sectors, but also in home. Compared to metal and polymers, they have many significant advantages. Given their many excellent qualities, including brittleness, wear resistance, ceramic materials have a wide range of uses due to their refractoriness, thermal and electric insulation, non-magnetism, corrosion resistance (anti-corrosiveness), resistance to thermal

shock, and chemical stability. An outline of applications in the fields of biotechnology, electronics, magnetics, refractory materials, energy, and structure is provided below[20].

### I.5.1. Structural Applications

Advanced materials known as structural ceramics are made to endure mechanical stresses and strains while maintaining exceptional mechanical properties in harsh environments. Zirconium diboride ($ZrB_2$)-based ceramics, silicon nitride ($Si_3N_4$), silicon carbide (SiC), aluminum oxide ($Al_2O_3$), and yttrium-stabilized tetragonal zirconia polycrystals (5Y-TZP) are examples of common structural ceramics. These materials are frequently utilized in applications that require exceptional thermal stability, low density, and good wear resistance.

Structural ceramics are commonly used in armor, liners, nozzles, cutting tools, bearings, and seals. These ceramics offer advantages over traditional metals like steel, boron carbide and silicon nitride are essential components of gas turbines. For laser in components including pump chambers, feedthroughs, insulators, and waveguides, ceramics are especially favored because of their high dielectric strength, resistance to corrosion, and mechanical stability. Because of their hardness, resistance to corrosion, and low friction, silicon carbide and alumina are utilized in industrial settings for mechanical seals and fluid-handling systems or fittings. Alumina, boron nitride, and SiC are frequently used in high-performance valves that handle corrosive and erosive media, such as those found in coal slurries and drilling muds. Additionally, because of their resistance to wetting and corrosion, ceramics like carbon and graphite are used in the pulp and paper industry**.** Because silicon nitride is resistant to $CO_2$ and syrups, it is being employed in the food and beverage industry for emerging applications, such as soft drink valves and pistons. Additionally, the dairy, juice, beer, and biotechnology sectors are using ceramic membranes more and more for microfiltration, which successfully separates caustic and polluted materials. These developments demonstrate the increasing significance of structural ceramics across a range of industrial domains [20]**.**

## I.6. Membranes

### I.6.1. Definition of Membrane

A **membrane** is a barrier that separates two compartments and allows the selective passage of certain substances under the influence of a chemical (concentration difference) or physical (pressure difference) driving force. Smaller molecules can pass through the membrane's pores

when pressure is applied, while larger ones are retained. Membrane filtration technology is used for **fluid-fluid** or **particle-fluid** separation to recover valuable components such as water, lactose, and minerals. Membranes can have **porous** or **dense** structures, allowing selective passage based on pressure differences.

During the separation process, two fractions are obtained:

- **Retentate**: The portion retained by the membrane.
- **Permeate**: The portion that passes through the membrane.

Membrane performance is defined by two key factors:

- **Selectivity**: The ability to separate specific substances.
- **Permeability**: The ease with which substances pass through.

Membranes are characterized by their **cut-off threshold (SC)**, which is determined by pore size and other factors like molecule shape, charge, hydration, pH, ionic strength, applied pressure, and permeation flow. Molecules with a molecular weight above the **SC** are retained by more than 90%, while those below it are retained by less than 90%. These factors influence membrane efficiency and separation effectiveness [21].

### I.6.2. Types of Ceramic Membranes

#### I.6.2.1. Tubular-shaped membranes (Tubular / straw membranes)

Generally used for viscous or bad quality fluids. These modules do not need a preliminary pre-treatment of the water. As the feed solution flows through the membrane core, the permeate passes through the membrane and is collected in the tubular housing. Tubular membranes are the most used membranes seen the costs and effect, shall not easily be polluted. Tubular membranes are not self-supporting membranes. They are located on the inside of a tube, made of a special kind of material. This material is the supporting layer for the membrane. Because the locations of tubular membranes are inside a tube, the flow in a tubular membrane is usually inside out. The main cause for this is that the attachment of the membrane to the supporting layer is very weak. Tubular membranes have a diameter of about 5 to 15 mm. Because of the size of the membrane surface, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low,

which results in high prices per module. The following figure I.8 shows the shape of tubular / straw membranes [22].

*Figure I.8 Tubular / straw membranes (diameter ≥ 5 mm)* **[22].**

### I.6.2.2. Hollow Fiber Membranes

The figure below I.9 shows Hollow fiber membranes are membranes to be membranes with a diameter of below 0.5 mm. Consequentially, the possible membrane blockage of a hollow fiber membrane are very high. The membranes **c**an only be used for the treatment of water with low percentage of suspended solids. The packing density of a hollow fiber membrane is very high. Hollow fiber membranes are nearly always used merely for nano-filtration and reverse osmosis (RO). As the feed solution flows through the open cores of the fibers, permeate is collected in the cartridge area surrounding the fibers. It can carry out the filtration in two ways, either "inside-out" or "outside-in". The following figure shows the shape of hollow fiber membranes[22].

*Figure I .9 Hollow fiber membrane (diameter < 0.5 mm)* **[22].**

### I.6.2.3. Porous Membranes

A porous membrane is generally characterized by pore size, surface porosity and thickness. The pore size of these membranes is the only factor which controls the application in which the porous membranes can be used. Table I.3 summarizes the different types of ceramic membranes used for separation according to their pore size**.**

Porous membranes are typically used for solid-liquid and solid-gas separation. The structure of a porous ceramic membrane can be symmetric if its pores are more or less equally sized throughout its structure or asymmetric when pore size gradually decreases towards the surface where separation occurs. Separation mechanism in porous membranes takes place by molecular filtration.

Micro-filtration membranes are an excellent choice to remove suspended matter and bacteria. However, they fail to remove dissolved substances and some microorganisms. Thus, removing viruses and dissolved substances such as salt in seawater will required smaller pore size characteristic of nano-filtration[22].

***Table I.3 Types of ceramic Membrane*** [22].

| Types | Pore size (nm) | Application |
|---|---|---|
| **Macro-porous** | >50 | UF, NF |
| **Meso-porous** | 2-50 | UF, NF, GS |
| **Micro-porous** | <2 | GS |
| **Dense** | - | GS, reaction |

**UF : ultra filtration**

**NF: nano filtration**

**MF: micro filtration**

**GS: gaz separation**

### I.7. Ceramic Materials

Among the array of ceramic materials, a noteworthy category is oxide ceramics, encompassing materials such as alumina ($Al_2O_3$), silica ($SiO_2$), zirconia ($ZrO_2$), and titania ($TiO_2$). The membranes prepared from these ceramic materials exhibit outstanding physical and chemical stabilities. In addition, the membranes can be tailored to exhibit precise pore

sizes and surface characteristics, thus enabling meticulous control over separation procedures**.** The widespread utilization of $Al_2O_3$ arises from its versatility and high strength, whereas $ZrB_2$ is preferred for its exceptional toughness another group is non-oxide ceramics, which majorly include silicon carbide (SiC). In addition, silicon nitride ($Si_3N_4$), tungsten carbide (WC), boron carbide ($B_4C$), and zirconium diboride ($ZrB_2$) are also gaining more prominence. These materials exhibit exceptional mechanical traits, thermal stability, and a formidable resistance to chemical attacks. They are especially well-suited for applications involving aggressive chemicals and high temperatures. Processing of these ceramics is challenging when compared to oxide ceramics. These materials are characterized by higher hardness and typically require more than 1700℃ sintering temperatures. Moreover, their fabrication often necessitates pressure-assisted firing within a controlled inert atmosphere[ 23].

### I.7.1. Microfiltration

Microfiltration is loosely defined as a membrane separation process using membranes with a pore size of approximately 0.03 to 10 microns (1 micron = 0.0001 millimeter), a molecular weight cut-off (MWCO) of greater than 1000,000 daltons and a relatively low feed water operating pressure of approximately 100 to 400 kPa (15 to 60psi) Materials removed by MF include sand, silt, clays, Giardia lamblia and Cryptosporidium cysts, algae, and some bacterial species. MF is not an absolute barrier to viruses. However, when used in combination with disinfection, MF appears to control these microorganisms in water. There is a growing emphasis on limiting the concentrations and number of chemicals that are applied during water treatment. By physically removing the pathogens, membrane filtration can significantly reduce chemical addition, such as chlorination. Another application for the technology is for removal of natural synthetic organic matter to reduce fouling potential. In its normal operation, MF removes little or no organic matter; however, when pretreatment is applied, increased removal of organic material can occur. MF can be used as a pretreatment to RO or NF to reduce fouling potential. Both RO and NF have been traditionally employed to desalt or remove hardness from groundwater. Figure I.10 shows a scanning electron microscope image of: (a) unmodified microfiltration membrane (MFFK-1), (b) poly (1-trimethylsilyl-1-propene) (PTMSPM) composite with MFFK-1 support[24].

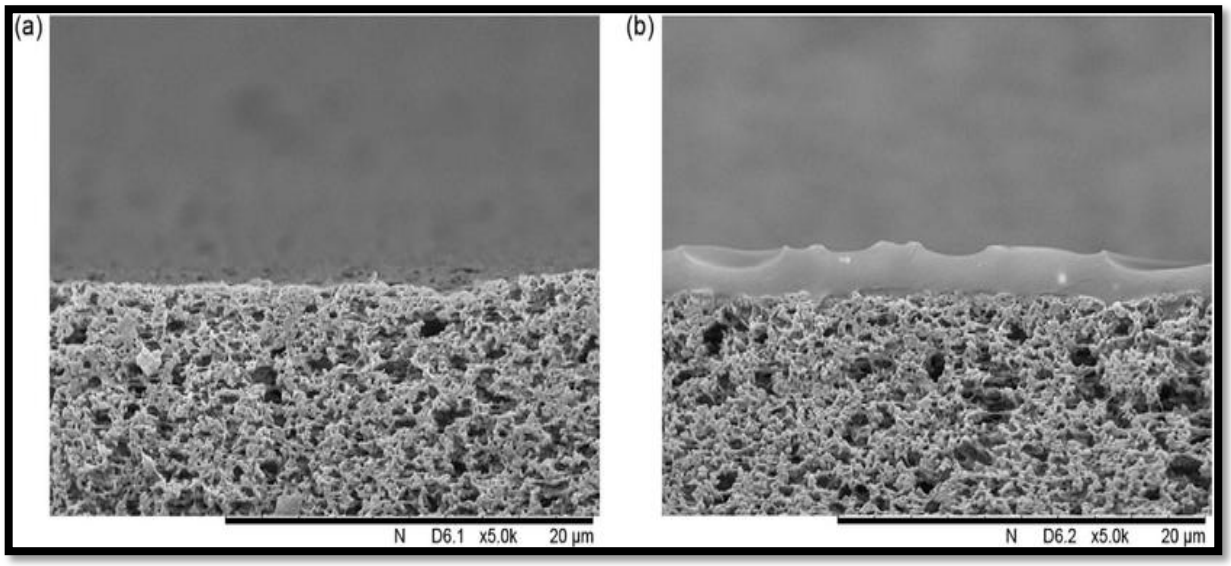



***Figure I.10 SEM image of: (a) Non-modified microfiltration membrane (MFFK-1), (b) composite poly (1-trimethylsilyl-1-propyne) (PTMSPM) with MFFK-1 support* [25].**

### I.7.2. Ultrafiltration

Figure I.11 A diagram that shows microfiltration thin layer and setup. Ultrafiltration has a pore size of approximately 0.002 to 0.1 $\mu m$, an MWCO of approximately 10,000 to 100,000 daltons, and an operating pressure of approximately 200 to 700 kPa (30 to 100 psi). UF will remove all microbiological species removed by MF (partial removal of bacteria), as well as some viruses (but not an absolute barrier to viruses) and humic materials. Disinfection can provide a second barrier to contamination and is therefore recommended.

The primary advantages of low-pressure UF membrane processes are compared with conventional clarification and disinfection (post-chlorination) processes are:

- No need for chemicals (coagulants, flocculants, disinfectants, pH adjustment)
- Size-exclusion filtration as opposed to media depth filtration
- Constant quality of the treated water in terms of particle and microbial removal
- Process and plant compactness
- Simple automation

However, fouling can cause difficulties in membrane technology for water treatment [24].

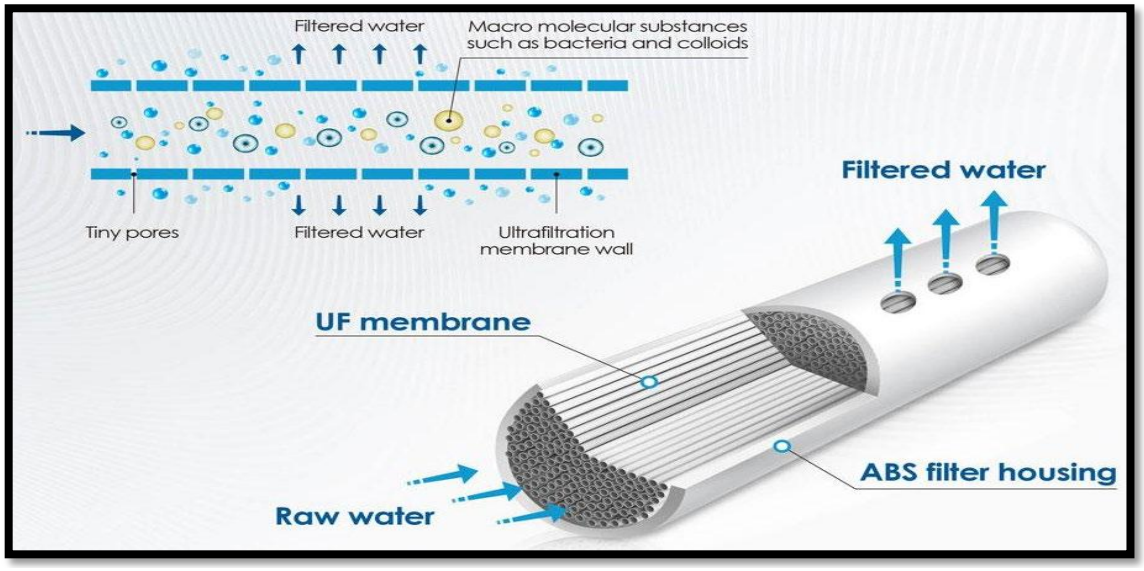



*Figure I.11 a diagram that shows microfiltration thin layer and setup* **[25].**

### I.7.3. Nanofiltration

Nanofiltration membranes have a nominal pore size of approximately 0.001 microns and an MWCO of 1,000 to 100,000 daltons. Pushing water through these smaller membrane pores requires a higher operation pressure than either MF or UF. Operating pressures are usually near 600 kPa (90psi) and can be as high as 1,000 kPa (150psi). These systems can remove virtually all cysts, bacteria, viruses, and humic materials. They provide excellent protection from DBP formation if the disinfectant residual is added after the membrane filtration step. Because NF membranes also remove alkalinity, the product water can be corrosive, and measures, such as blending raw water and product water or adding alkalinity, may be needed to reduce corrosivity. NF also removes hardness from water, which accounts for NF membranes sometimes being called “softening membranes.” Hard water treated by NF will need pretreatment to avoid precipitation of hardness ions on the membrane. However, more energy is required for NF than MF or UF [24].

Nanofiltration techniques concentrate on the membrane's pore size, charge (repulsion), and shape properties. For nanofilters to function well, a moderate pressure is needed [26].

### I.7.4. Reverse Osmosis

Reverse osmosis can effectively remove nearly all inorganic contaminants from water. RO can also effectively remove radium, natural organic substances, pesticides, cysts, bacteria and viruses. RO is particularly effective when used in series with multiple units. Disinfection is also recommended to ensure the safety of water. Some of the advantages of RO are:

• Removes nearly all contaminant ions and most dissolved non-ions,

• Relatively insensitive to flow and total dissolved solids (TDS) level and suitable for small systems with a high degree of seasonal fluctuation in water demand.

• RO operates immediately, without any minimum break-in period,

• Low effluent concentration possible,

• Bacteria and particles are also removed, and

• Operational simplicity and automation allow for less operator attention and make RO suitable for small system applications.

• Some of the limitations of RO are:

• High capital and operating costs.

• Managing the wastewater (brine solution) is a potential problem.

• High level of pretreatment is required in some cases.

• Membranes are prone to fouling and

• Produces the most wastewater at between 25-50 percent of the feed. Figure I.12 shows the total filtration spectrum[24].

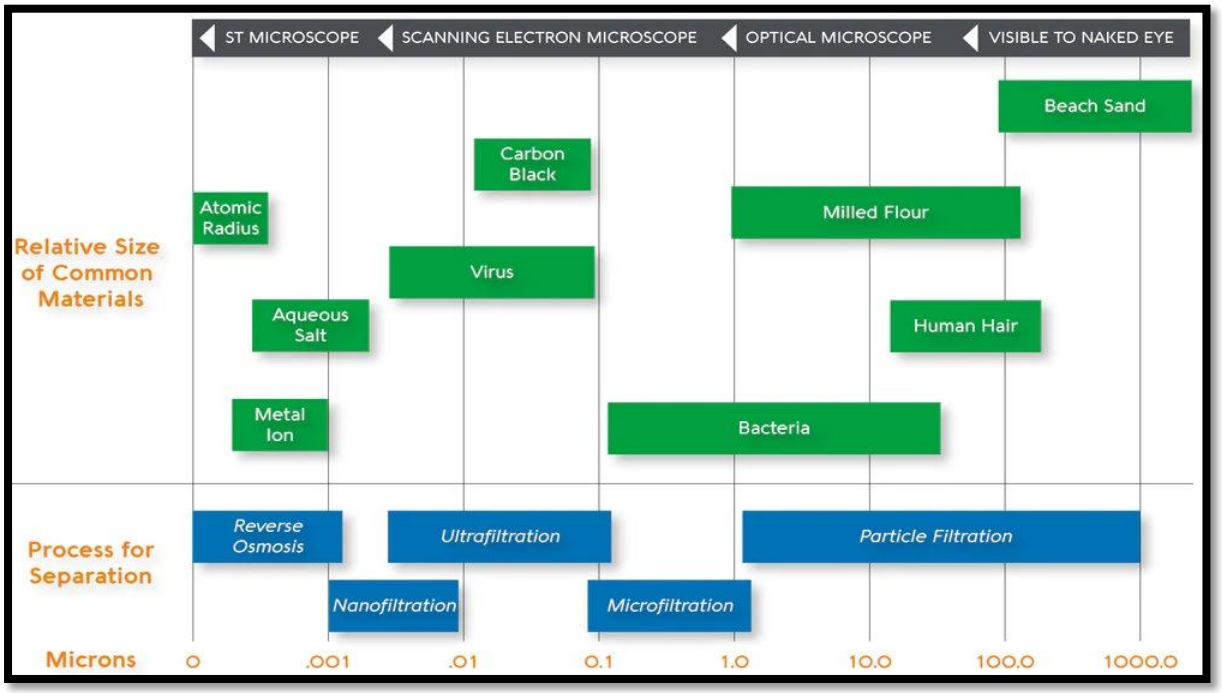



***Figure I.12 Overall Filtration Spectrum* [25].**

## I.8. Manufacture Of Ceramic Membranes

Ceramic membranes can be prepared using a variety of techniques, including pressing, extrusion, and slip casting. The steps that follow provide a broad summary of the preparation process:

- Suspension preparation: This involves combining the initial particles with an appropriate binding liquid.
- The process of forming involves forming the prepared suspension using a predetermined technique.
- Heat treatment is the process of binding the membrane particles by sintering them at high temperatures.

Regardless of subsequent preparation stages, this firing step is the most crucial one in the creation of ceramic membranes. Multi-layer membranes can be created by applying the necessary layers (sol-gel, CVD, etc.) to a membrane support prior to the firing stage.

As shown in Fig I.13, composite membranes are created by covering the membrane support and then firing. The subsequent section examines the various techniques utilized in the production of ceramic membranes [22].

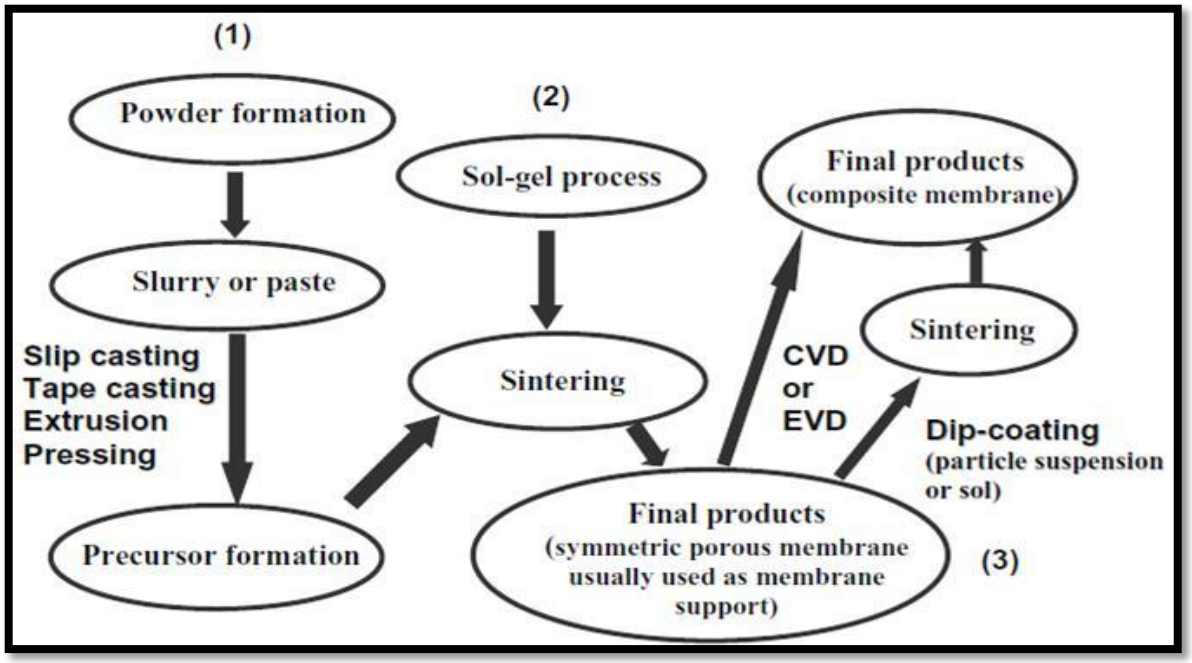



*Figure I.13 General ceramic membrane preparation procedures* **[22].**

### I.8.1. Solid State Method

One of the earliest and most traditional techniques for creating ceramic compounds is this one. In this sense, the initial materials powders, such as oxides, carbonates, or salts, are mechanically combined, then heat-treated for up to 24 hours at temperatures above 1000 °C. The final ceramic product forms as a result of the prolonged heat treatment, which permits the diffusion of cations and anions in the solid state across the grain boundaries. Dense ceramic membranes are always assumed in accordance with the solid state reaction concept. Additionally, by employing pore generators or pore formers, sometimes referred to as porogens, porous Ceramic powders can be processed in a solid state to create ceramic membranes. Examples of dense and porous ceramic membranes prepared by this method include alumina**,** mullite**,** silica**,** titania**,** and zirconia**,** as well as their combinations [22].

The simplest approach is the solid-state approach. Although there aren't many acting parameters, they are challenging to regulate. This process is frequently employed to create monovalent cations, phosphates, and arsenates of transition metals in single crystals and polycrystalline powders[27].

### I.8.2. Slip Casting Method

It is the most often used technique for creating membranes. It normally takes a long time to cast using this method. It's challenging to regulate the wall thickness during casting, and typically, thick walls are formed.

After thoroughly mixing the powder suspension, it is put into a porous mold to allow the solvents to permeate the pores and form a gel layer by precipitating particles on the mold's interior surface. A consolidation step must then be completed quickly to prevent any particles from entering the pores. The following figure provides an example of the method.

Examples of porous ceramic membranes prepared by slip casting method include $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$, alumina, zirconia, Ceramic membranes prepared by slip casting are known for their high permeability, which is attributed to the presence of smaller pore size over a thinner region, thereby giving superior permeation properties. Figure I.14shows the slip casting method[ 22].

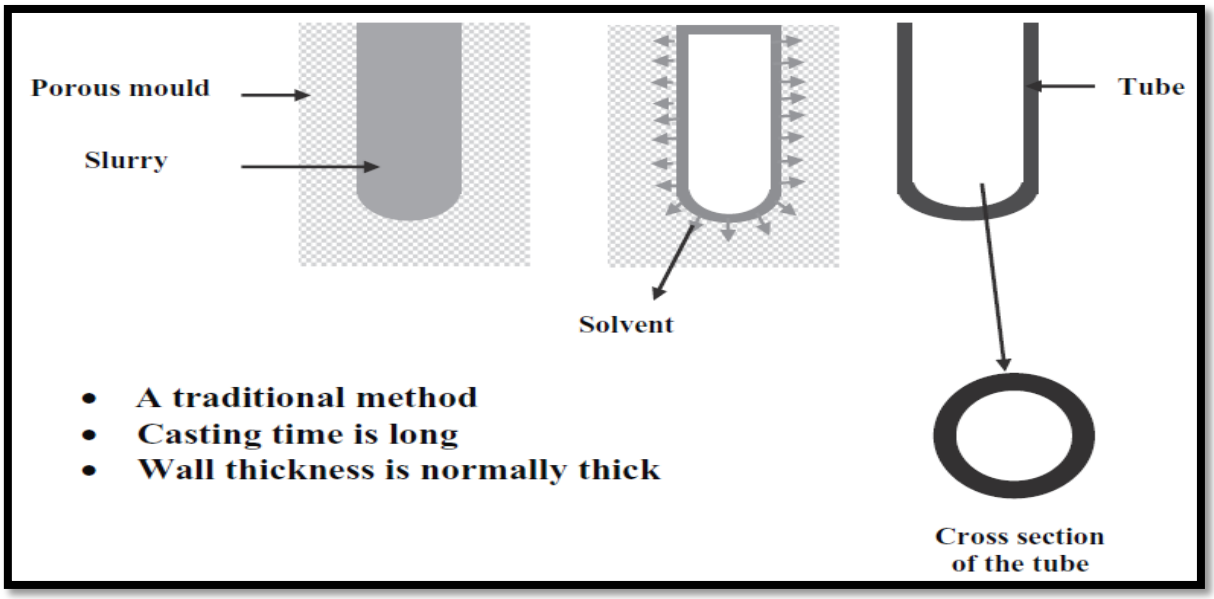



*Figure I .14 Slip casting method* **[22].**

### I.8.3. Extrusion Method

This is a straightforward, significant, and very efficient technique for creating ceramic membranes. It has been widely employed in the production of ceramic tubes with pores. With this approach, the final green membrane is created by forcing a homogenous stiff paste through a nozzle to be compressed or molded, as seen in Fig I.15 In order to maintain the

membrane's final shape, any leftover plasticizer, solvent, and binder should be vaporized. The final product's form, porosity, and pore size distribution are determined by the die [22].

Extrusion processing combines a number of transport activities, including as mass transfer to and within the material during extrusion, thermal energy transfer to and within the material, and material movement within the system of a practically controlled environment[28].

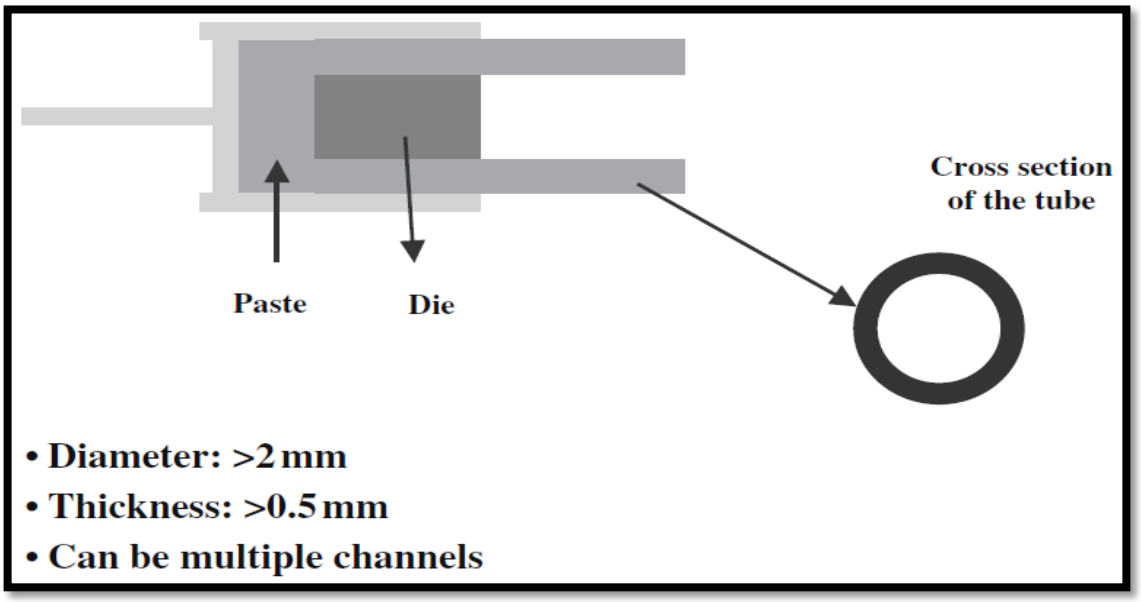



*Figure 1.15 Extrusion methods* **[22].**

**I.9. Uses of Ceramic Membranes**

There are numerous applications of membranes in the field of water treatment, water desalination, micro-filtration, and ultrafiltration in which ceramic membranes have proved to be economically suitable due to their availability, high flux, and relatively low operating cost. Various ongoing research efforts aim to implement the use of ceramic membranes in various separation fields. Refineries and metallurgical plants produce a huge amount of oily wastewater that should be treated before being discharged to the municipal sewage system. Ceramic membranes offer an efficient separation, low operational cost, and a compact design**.**

Dense ceramic membranes are highly efficient in gas separation. Used a ceramic carbonate membrane to directly separate CO2 from flue gas in the temperature range 550-650°C. Some ceramic membranes are promising for application in high-temperature processes such as steam methane reforming due to their chemical stability. The application of hydrogen as

energy source promoted the development of ceramic membranes that are used for gas separation**.** Specifically, ceramic membranes have become more significant in the water treatment industry over the past 20 years. Utilizing inexpensive raw materials is a compelling feature for more Ceramic membrane research in the field of water treatment Seawater desalination is one of the promising channels for ceramic membrane usage There are three membrane mechanisms that are made use of in:

- **Pervaporation**: the membrane depends on water vapor pressure difference to allow the passage of water molecules through molecular sieves.
- **Membrane distillation (MD)**: The porous membrane allows the passage of water vapor molecules after thermal treatment.
- **Reverse osmosis (RO)**: The membrane repels the salt ions and allows the passage of water molecule.

Water desalination can currently be accomplished using ceramic or polymeric membranes. Despite being widely employed in this industry, polymeric membranes have swelling issues. phenomenon, inadequate chemical and thermal stability, and biofouling. Conversely, ceramic membranes have superior chemical and thermal stability, which makes them a viable substitute for use in the desalination process of water [22].

# *Chapter Two:*

# *Study of Raw Materials And Experimental Methods Used.*

## II.1. Introduction

In this chapter, we will address the study of local raw materials, mainly montmorillonite (MMT), which is used in the preparation and development of innovative ceramic membranes. The work is based on a set of analyses and accurate measurements using advanced equipment, with the aim of studying and improving the properties of these membranes. It will also review the various experimental methods used in the analysis and evaluation of ceramics, with a focus on performance and conductivity measurement techniques that contribute to improving the effectiveness of this material in various applications.

## II.2. Empirical methods used to conduct the study

### II.2.1. Fourier transform infrared spectroscopy (FTIR)

The ideal technique for infrared spectroscopy is called Fourier Transform Infrared, or FT-IR. Infrared spectroscopy involves passing IR light through a material. The sample absorbs a portion of the infrared energy and a portion of it is transferred, or passed through. The resulting spectrum creates a molecular fingerprint of the material by representing the molecule absorption and transmission. Similar to fingerprints, no two distinct chemical structures emit the same spectrum of infrared light. Because of this, infrared spectroscopy can be applied to a variety of analysis kinds [29].

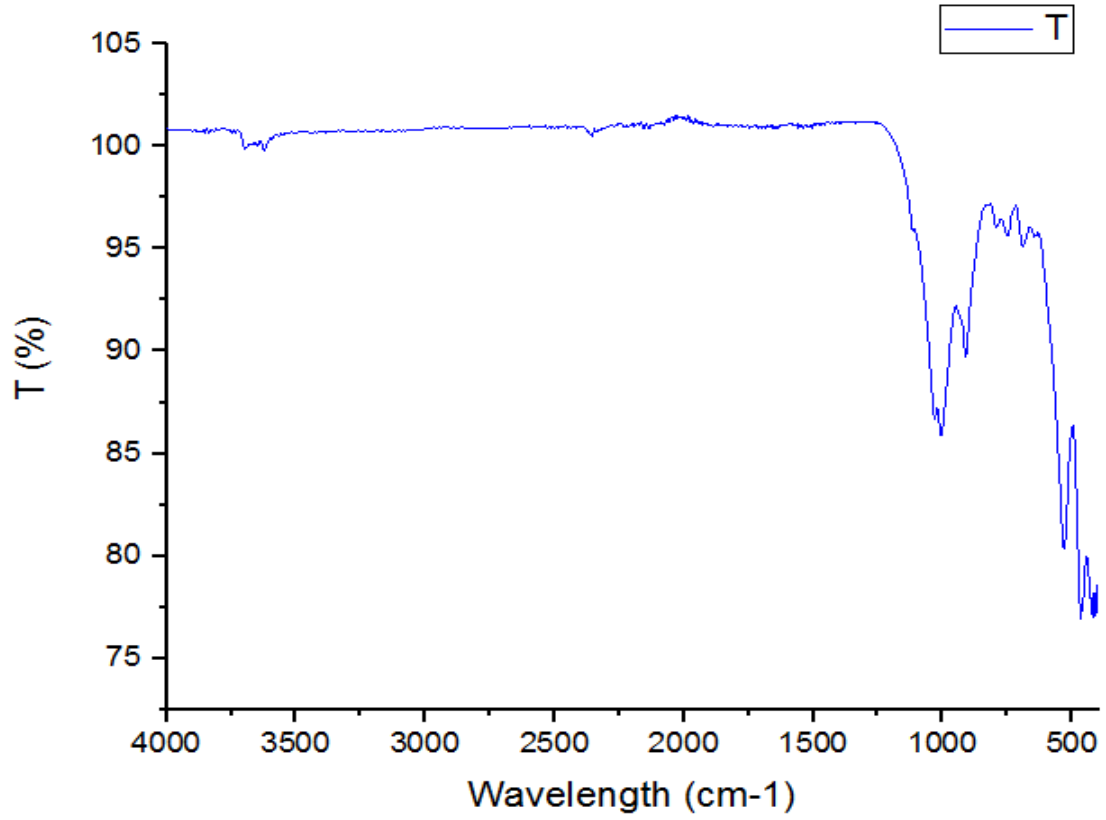
*Figure II.1 PerkinElmer Spectrum Two™ IR Spectrometer.*

### II.2.2. MMT Analysis using infrared rays

Graph II_1 represents the Fourier transform infrared spectroscopy of a sample of montmorillonite, a clay of the smectite group characterized by a layered structure and high absorption and ion exchange capacity. The spectrum shows the relationship between

transmittance T (%) on the vertical axis and oscillation number ($cm^{-1}$) on the horizontal axis, revealing the chemical and functional bonds present in the sample.

The Fourier transform infrared spectrum of the montmorillonite sample shows several distinctive absorption peaks that reflect its chemical composition and characteristic properties.




***Graph II.1 shows MMT analysis by infrared rays.***

- In the high wave number region (3700-3400) $cm^{-1}$

An absorption peak can be observed due to the bending vibrations of the O-H groups in the adsorbed water between the layers, which is a clear indication of the presence of interfacial water that can change with environmental conditions such as drying or heating.

- In the range (1200-900) $cm^{-1}$

Refers to the vibrations of the Si-O-Al and Si-O-Mg, and Al-OH bonds bonds that bind to the octahedral layer containing metal ions, such as aluminum and magnesium, which are included in the crystalline structure of clay.

- At low frequencies (600-400) $cm^{-1}$

Peaks can be observed due to the vibrations of Si-O-Fe and Si-O-Al bonds, which reflect the presence of partially substituted iron and aluminum ions in the crystal lattice. These low-energy vibrations are indicative of the nature of the strong bonds between silicon, aluminum and oxygen atoms, which enhances the stability of the layered structure of montmorillonite.

***Table II.1 represents the values of the spectral peaks of montmorillonite with their mappings.***

| ***Wavelength ($cm^{-1}$)*** | ***Bond type and vibration*** |
|---|---|
| **3695-3620** | stretching vibration of the O-H bond (hydroxyl group) |
| **3450-3400** | stretching vibration of the O-H bond (absorbed water) |
| **1100-1000** | stretching vibration of a Si-O-Si bond (silicate structure) |
| **900-800** | Al-OH and Mg-OH vibrations |
| **600-500** | Si-O-Al and Si-O-Fe vibrations |
| **450-400** | Si-O Bending vibrations in the crystal structure |

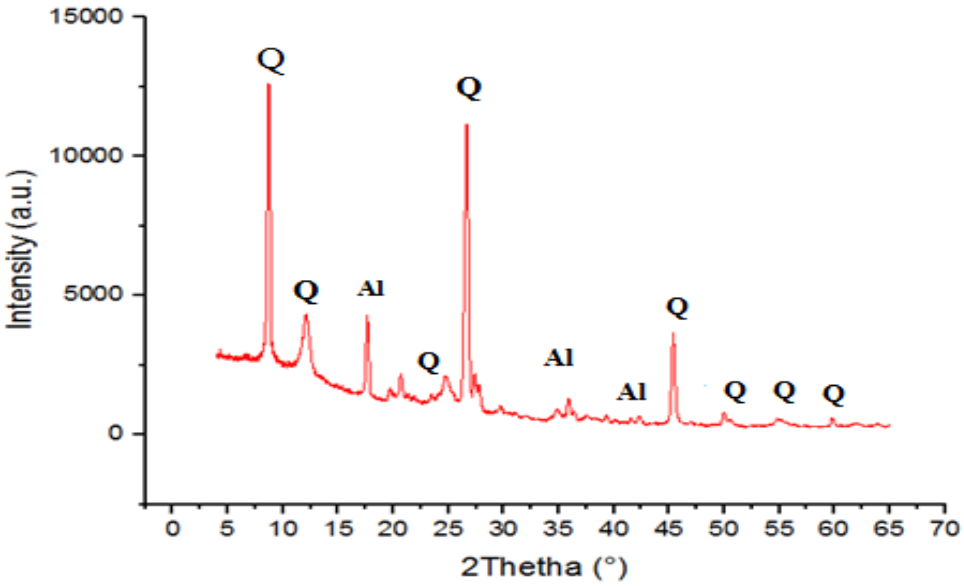
**II.3. X -ray diffraction**

An analysis method based on X-ray diffraction by matter is called diffractometry. The standard procedure is to bombard ecanthelone with X-rays and then measure the intensity of the scattered X-rays according to the direction in space. The phenomenon known as "diffraction" occurs when the scattered X-rays interfere with each other, causing the intensity to be higher in some directions. The detected intensity is recorded based on the 2θ deviation angle of the paizo's deviation angle[30]**.**


*Figure II.2 CubiXX3 X-ray Diffractometers.*

### II.3.1. MMT Analysis by X-ray Diffraction

Graph II.2 shows the X-ray diffraction diagram for montmorillonite. Using HighScore plus software to analyze the plot revealed that most of the diffraction lines belong to quartz. The chemical formula is $SiO_2$ and its reference code is 00-046-1045. Most of the remaining peaks likely correspond to $Al_2O_3$.




*Graph II.2 shows the analysis of MMT by X-ray diffraction.*

## II.4. Fluorescent x –ray (XRF)

X-ray fluorescence spectrometry is a quantitative analysis method that estimates the concentration of each element and determines the elemental chemical makeup of a sample.

An X-ray beam is directed at the sample to be examined. The atoms that make up the sample transition from their ground state to an excited state as a result of these X-rays. Since the excited state is unstable, the atoms tend to release energy—specifically X-ray photons—in order to return to the ground state. Every atom will release photons with a unique energy and wavelength due to its unique electrical structure. Every atom will release photons with a unique energy and wavelength due to its unique electrical structure. This is the X-ray fluorescence phenomenon, a secondary X-ray emission that is specific to the atoms that make up the sample. Both the type of chemical elements contained in a sample and their mass concentration can be determined by analyzing this secondary X-ray emission [30].

XRF happens when a sample energized by a primary X-ray source emits a fluorescence (or secondary) X-ray. Since this fluorescence is specific to the sample's elemental makeup, XRF is an outstanding technology for both quantitative and qualitative material composition analysis [31].


***Figure II.3 The Zetium XRF Spectrometer.***

### II.4.1. Chemical composition of MMT

We used X-ray fluorescence (XRF) to analyze the chemical composition and determine the weight ratios of the constituent elements. This analysis allowed us to accurately detect the chemical constituents, with the results yielding the values shown in the table below.

*Table II.2 Chemical composition of MMT.*

| Elements | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $CaO$ | $MgO$ | $SO_3$ | $K_2O$ | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|
| Weight ratios | 66.75 | 24.77 | 1.37 | 0.40 | 0.05 | 0.03 | 4.62 | 0.00 |

The results in Table II.3 showed that the MMT is mainly composed of 66.45% silica, along with 24.77 wt% alumina, as well as a trace amounts of impurities about 4.62 wt% of potassium oxide and of 1.37 wt% of iron oxide .

## II.5. Thermal Analysis

### II.5.1. Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) is one of the most frequently used techniques in the field of thermal characterization of solids and liquids**.**

- A **calorimeter** measures the heat into or out of a sample.
- A **differential calorimete**r measures the heat of a sample relative to a reference.
- A **differential scanning calorimeter** does all of the above and heats the sample with a linear temperature ramp.
- **Endothermic** heat flows into the sample.
- **Exothermic** heat flows out of the sample [32]**.**

#### II.5.1.1. Principle of Operation

- A reference pan, which is typically empty (inert gas may be used), and a sample are placed within a crucible, which is then placed into the DSC system's measurement cell (furnace).
- Phase shifts and/or a material's specific heat can be identified by implementing a controlled temperature program (isothermal, heating or cooling at constant rates).
- The cell's calibrated heat flow characteristics are used to determine heat flow quantities [32]**.**

### II.5.2. Thermal gravimetric analysis (TGA)

Thermogravimetry (TG) determines the mass change of a sample as a function of temperature or time.

It examines how a specimen's weight varies with temperature; this method works well for transformations involving absorption.

or the development of gasses from a solid-phase object.

• **Gas + Reactant(s) + Product(s)**

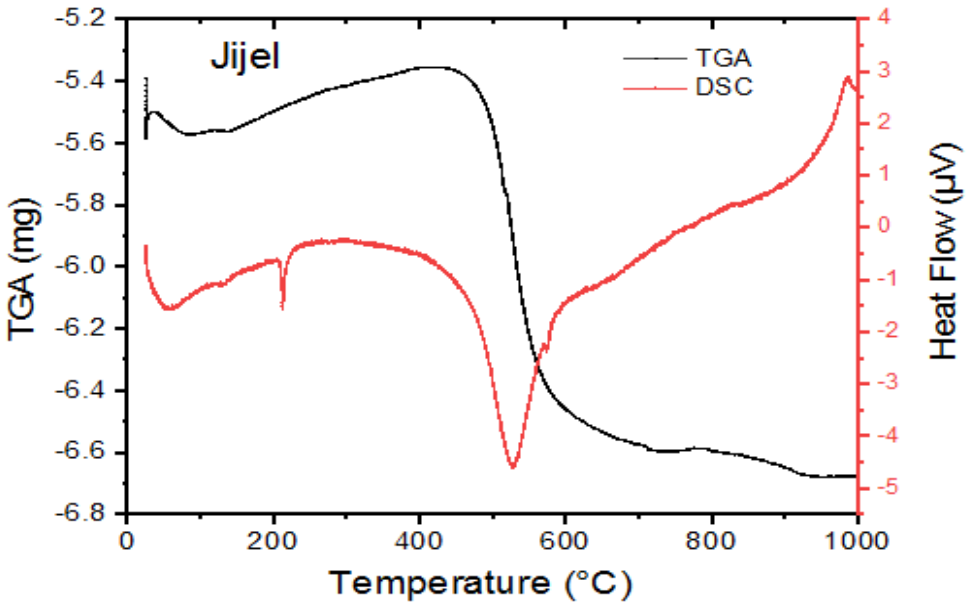
The product of gas and reactant(s) is either a mass gain or a mass loss.

• Thermal stability, reaction rate, reaction mechanisms, and sample composition can all be assessed using a mass vs temperature plot.

• Thermo balance is used to measure how the mass of the sample changes with temperature. To control the atmosphere, the balance needs to be in a system that is appropriately enclosed [32]**.** Using the TGA approach, a material's weight can change when it is heated. A Basic TGA Idea to Keep in Mind: As a sample is heated or cooled in a furnace, TGA weighs it[ 33]**.**


*Figure II.4 LABSYS evo Device by Setaram.*

### II.5.3. DSC/TGA Analysis Results




*Graph II.3 TGA/DSC Analysis.*

Graph II.3 the thermal analysis of the montmorillonite sample was performed using TGA and DSC techniques to determine the physical and chemical changes in the material during heating. The TGA curve shows a gradual decrease in mass at first, then a sharp and sudden loss of mass between about 500 and 700 °C, which is a clear indication of dehydroxylation, where the OH groups attached to the silicate sheets are dissociated within the layered structure of the mineral. This phenomenon leads to a partial breakdown of the crystal structure of montmorillonite and is considered a critical stage because it is accompanied by significant microstructural changes. The DSC curve shows the changes in heat flow associated with these reactions. Initially, we observe small fluctuations between 100 and 300 °C, which do not reflect water evaporation as is commonly believed, since there are no water bonds in the sample, but may be due to small surface changes or interactions between impurities or interlayer cations. A prominent endothermic peak appears around 600 °C, coinciding with the loss of mass in the TGA, confirming that the internal endothermic reaction is related to the breakdown of crystal structures or the breaking of strong chemical bonds. After this peak, the DSC curve starts to rise gradually, indicating exothermic reactions starting around 700°C, which could be the result of recrystallization or the formation of new, more thermally stable crystalline phases. During this phase, the TGA curve is nearly stable, indicating that the material is no longer losing significant weight and is only undergoing internal changes at the crystalline level.

### II.6. Scanning Electron Microscopy (SEM)

The ability to identify the crystal structure and grain orientation of crystals on the surface of prepared specimens is one of the most exciting developments in the development of the SEM. Electron Backscatter Diffraction (EBSD) is based on the diffraction of electrons bouncing off the surface of the sample, where the sample is tilted at an angle of approximately 70° to obtain the highest intensity diffraction pattern. Due to the low intensity of these Kikuchi patterns and poor signal contrast, this technique requires high-sensitivity cameras and contrast-enhancing devices. The creation of a system for recording backscatter Kikuchi patterns represents a recent advancement in the use of Kikuchi patterns in bulk materials A very sensitive charge-coupled-device (CCD) camera, or more recently, a very sensitive video camera. A computer-assisted indexing technique is then used to examine these patterns. This method demonstrates misorientation across grain boundaries and identifies phases by computer-automated crystal lattice orientation mapping and automated pattern indexing, respectively [34]**.**

### II.6.1. Microstructure of MMT

Figure II.5 shows a scanning electron microscope image shows the layered structure of the mineral montmorillonite, made up of thin silicate sheets that expand when water is absorbed. It achieves high resolution to visualize fine details.

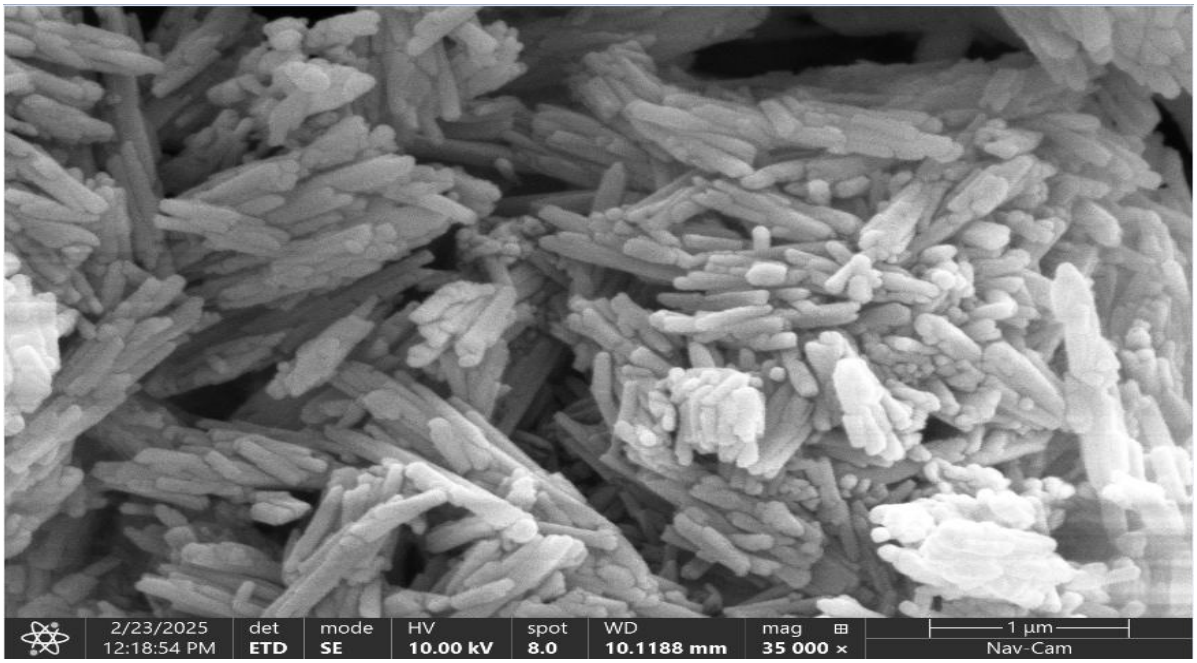



*Figure II.5 Scanning electron microscope image of MMT.*

### II.6.2. MMT Microstructure analysis

The image shows the microstructure of a sample of montmorillonite, where the particles appear as fine plates or needles that are randomly and densely packed. This accumulation indicates a layered structure with high porosity, which enhances the material's ability to absorb and retain liquids within the interstitial spaces. This is important for optimizing performance in practical applications such as filtration or adsorption.

### II.7. Organic additives

We have added oil as an organic material to fulfill several purposes, The first improves the cohesion of the molecules before the sintering (firing) process. It makes the dough more elastic and facilitates the molding process and is also used to adjust the ceramic, which reduces surface tension during drying, which prevents cracks. It decomposes during the firing process, leaving fine voids that improve porosity and reduce weight.

*Figure II.6 Sunflower oil.*

### II.8. Creating innovative ceramic filters from montmorillonite

The ceramic filters were prepared according to a precise scientific methodology that included the following stages:

### II.8.1. Preparation of the raw material

The montmorillonite material underwent a precise mechanical crushing process, with the aim of obtaining a homogeneous granular powder, which ensures consistent physical and chemical properties in the subsequent stage.

*Figure II .7 Apparatus for the grinding process (RRH-3000A).*

We then sifted the montmorillonite material using a sieve with an aperture size of 160 micrometers to obtain fine, uniformly sized particles.

*Figure II.8 A picture of the sieving process when 160 µm.*

### II.8.2. Preparation of the mixture

Three different compositions containing different percentages of montmorillonite were prepared, according to the following compositions:

- **22.07 wt% of oil and 0 wt% of water:** 180 grams of oil was mixed with 18 grams of amijel and 617.26 grams of montmorillonite.
- **12.41 wt% of oil and 17.24 wt% of water:** 90 grams of oil was mixed with 18 grams of amijel, 492 grams of montmorillonite, and 125 ml of water was added to adjust the viscosity of the paste.
- **0 wt% of oil and 29.41 wt% of water:** 582 grams of montmorillonite was mixed with 250 ml of water, as well as 18 grams of amijel, without adding any percentage of oil, to study the effect of these substances on the properties of the formed material.

All ingredients were mixed using a high-efficiency electric mixer to ensure the formation of a homogeneous and moldable paste, and then the paste was kept inside a plastic bags for 24h time period, which allows the homogeneous distribution of water and oil within the mixture, which enhances the quality of subsequent molding.


*Figure II.9 Image of the sensitive electronic scale(KERN ALS).*

*Figure II.10 KENWOOD 1100W Mixer.*

### II.8.3. Forming by Extrusion

The prepared dough underwent the extrusion process using a specialized machine, where it was molded into ceramic tubes that act as filters.

*Figure II.11 Shop Press 40 Tons.*

### II.8.4. Drying and heat treatment

#### II.8.4.1. Drying

Due to the high water content of the tubes, prior experiments have shown that an initial air-drying procedure must take place before beginning heat treatment. At this point, heat treatment may result in the formation of cracks. Furthermore, it was discovered that letting the tubes dry on a level surface caused surface fractures and twisted tubes. In order to solve this problem, as shown in Figure II.12 the device was employed for air drying, while the cylinders simultaneously maintained the alignment of the tubes.

*Figure II.12 Custom-Built Roller Dryer Table.*

The roller dryer can accommodate four tubes, each 40 centimeters in length, at a time. It is sprayed with clay dust to prevent the fresh tubes from sticking to the surface and breaking. The dryer is then operated in cycles: it rolls the tubes for 45 minutes, stops for 15 minutes, and then restarts. This cycle continues for around 24 hours.

#### II.8.4.2. Heat treatment

There were two main objectives that we sought to achieve through the heat treatment process. The first was to remove moisture from the tubes, allowing them to harden and significantly increase their rigidity, thereby enhancing their ability to withstand high mechanical stresses. The second objective was to remove the added oil, which was used as a porosity-forming agent to improve the porosity of the ceramic structure.

In this batch, the heat treatment was carried out by gradually heating the samples from room temperature to 1100°C. During this process, the residual oil within the formulation burned off, forming micropores within the material, while the high temperature promoted sintering and achieved the desired structural cohesion of the tubes.

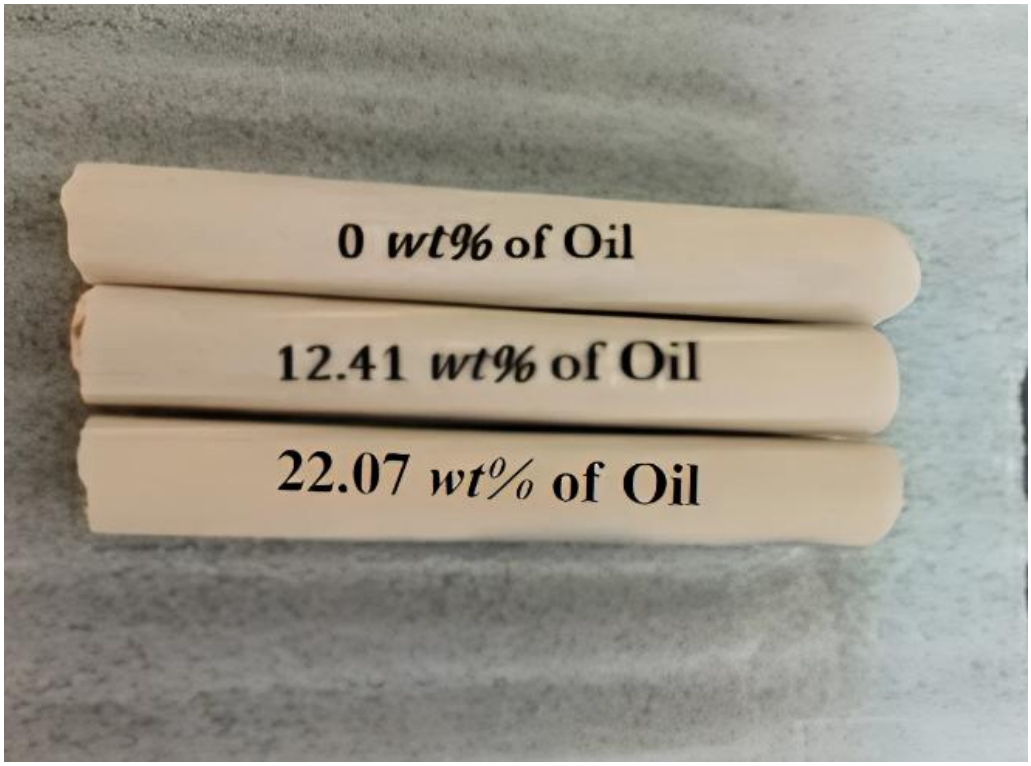



*Figure II.13 Image of sample filters after 1100 ℃.*

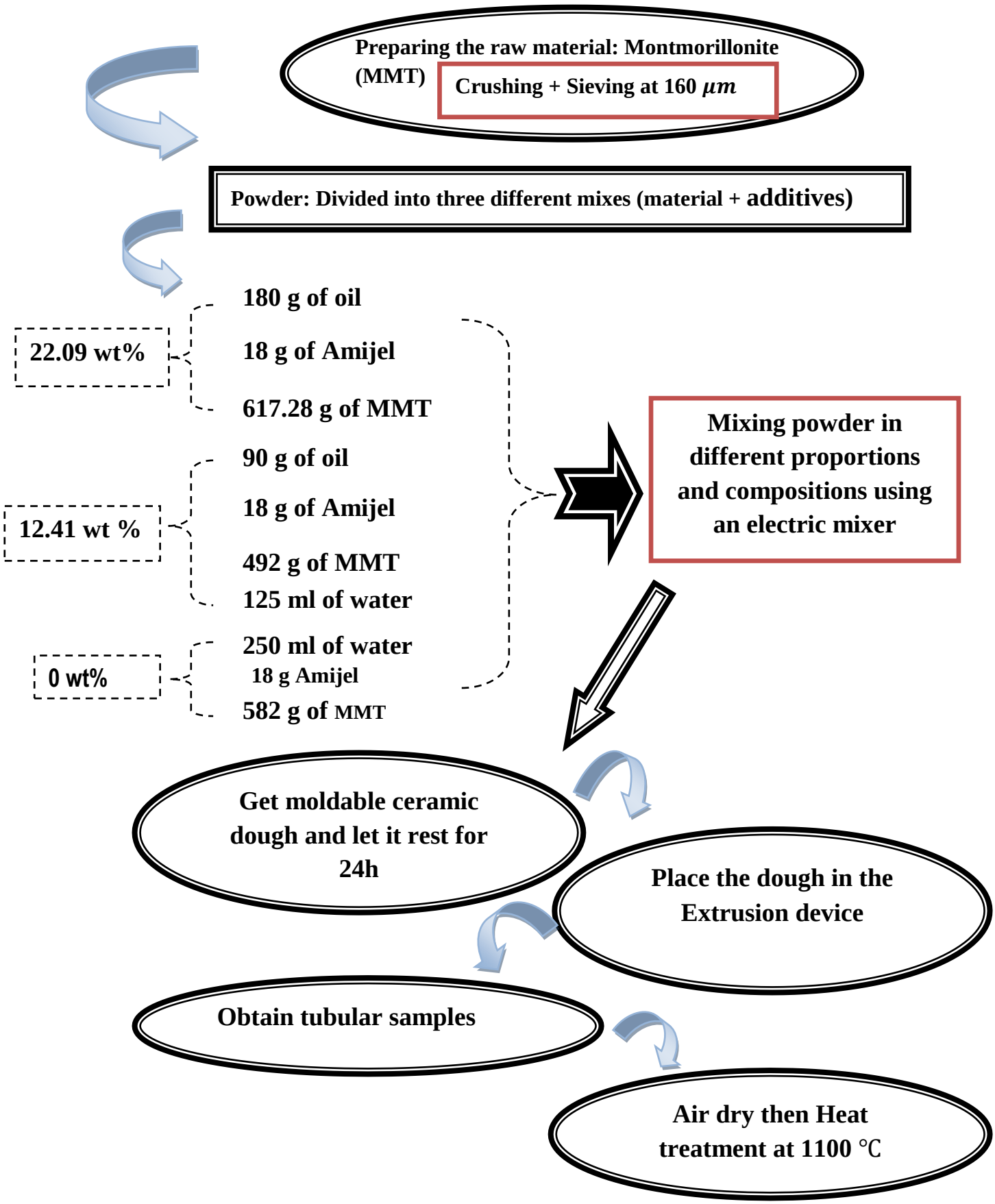



*Figure II.14 The most important stages followed in preparing and developing montmorillonite ceramic filters.*

# *Chapter Three:*

# *Discussion and Analysis of Results*

### III.1. Introduction

In this chapter, I will focus on the preparation of ceramic filters using montmorillonite (MMT) and discuss the most important results obtained in the study to prepare ceramic filters using montmorillonite.

### III.2. Analysis of the absorption and permeability properties of ceramic filters developed from montmorillonite

The ceramic filters were prepared using montmorillonite, as this mixture resulted in filters with a light sandy color. These filters were then subjected to a permeability test, which yielded satisfactory results, indicating that the raw material used is of high quality and efficiency and is suitable for use.

### III.3. X-ray Diffraction analysis

Figure III_1 shows the X-ray diffraction plot of a sample of montmorillonite material heat treated at 1100 ° C, Analysis using HighScore plus software to analyze this drawing revealed the presence of several crystalline phases, including anorthite, mullite and gehlenite, in addition to other phases such as dickite, melilite and albite, and it is noted that anorthite and albite are the dominant phases in the sample.

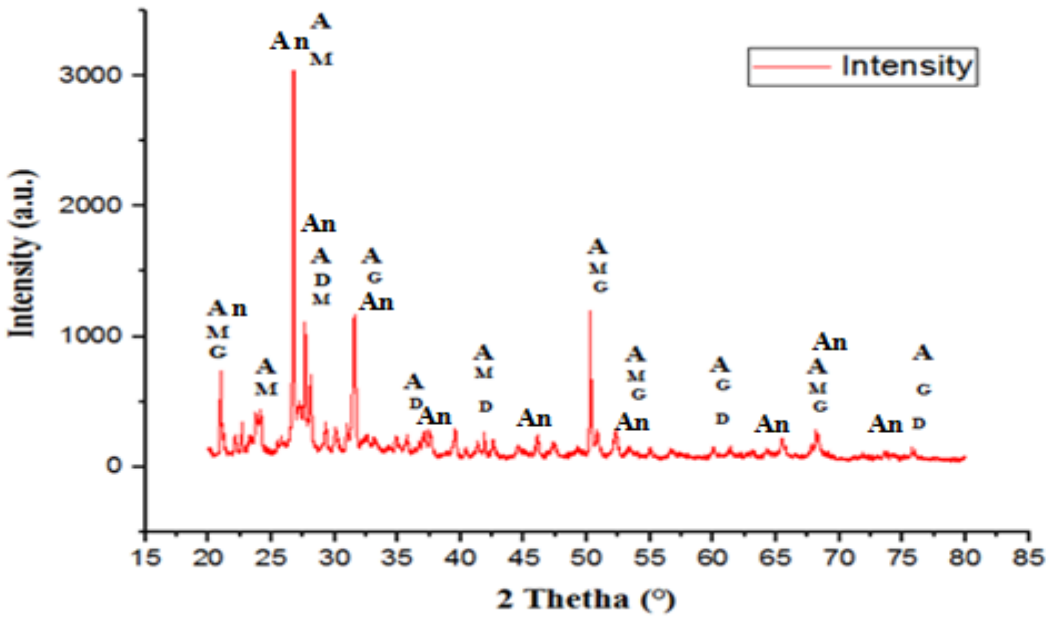



*Figure III.1 shows the X-ray diffraction pattern of an MMT sample after heat treatment at 1100°C.*

***Table III.1 shows the crystalline phases formed along with the ASTM label number of each phase.***

| The name of the phase | Chemical formula | Card Number (ASTM) |
|---|---|---|
| **Anorthite** | $Al_4Si_4Ca_2O_{16}$ | **96-901-6973** |
| **Albite** | $Na_2Al_2Si_6O_{16}$ | **96-900-0587**<br>**96-900-0531**<br>**96-900-2198** |
| **Gehlenite** | $Ca_4Al_4Si_2O_{14}$ | **96-100-0049** |
| **Mullite** | $Al_{5.65}Si_{0.35}O_{9.18}$ | **96-900-1622** |
| **Dickite** | $Si_8Al_8O_{36}H_{16}$ | **96-900-3083** |
| **Melilite** | $Ca_2Na_2Al_2Si_4O_{14}$ | **96-900-8196** |

### III.4. Permeability test

This test determines the ability and efficiency of the prepared filters and calculates their permeability. Before starting the test, the samples were immersed in distilled water for 24 hours in order to ensure stabilization of the flow during the initial phase of the experiment.

### III.5. Flow Rate Data for Different Sunflower Oil Percentages

#### III.5.1. Change of flow in terms of time

- **At 22.07 wt%**

Figure III_2 shows the change of flow with time for different pressures of 0.3 bar, 0.6 bar and 1 bar for the sample treated at a temperature of 1100. We observe initially for all three curves a strong decrease in flow followed by a relative stabilization phase in all cases.

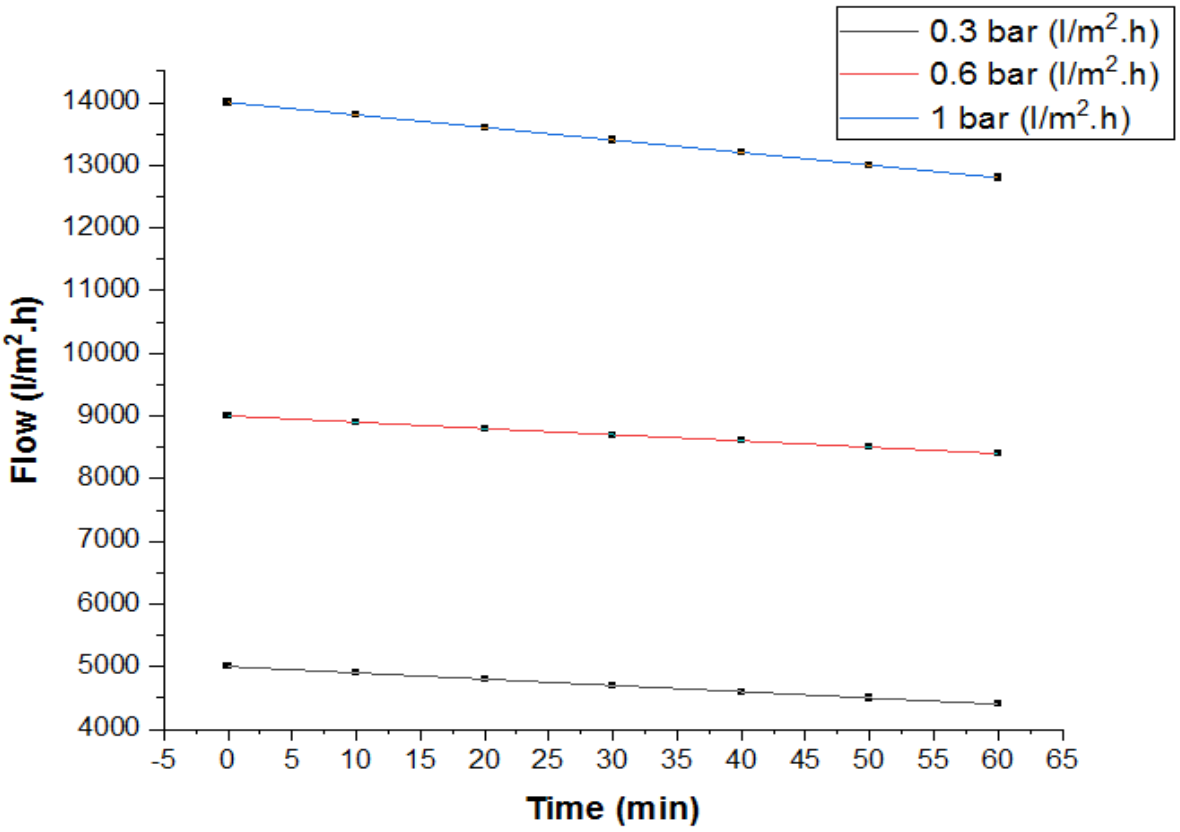



*Figure III.2 shows the change in flux with respect to time at 1100 °C at 22.07 wt %.*

- **At 12.41 wt%**

Figure III.3 shows the change of flow over time for a sample treated at 1100 °C under the influence of three different pressure values 0.3 bar, 0.6 bar and 1 bar, where we observe for the three curves with increasing pressure a sharp decrease in flow followed by a relative stabilization phase in all cases.

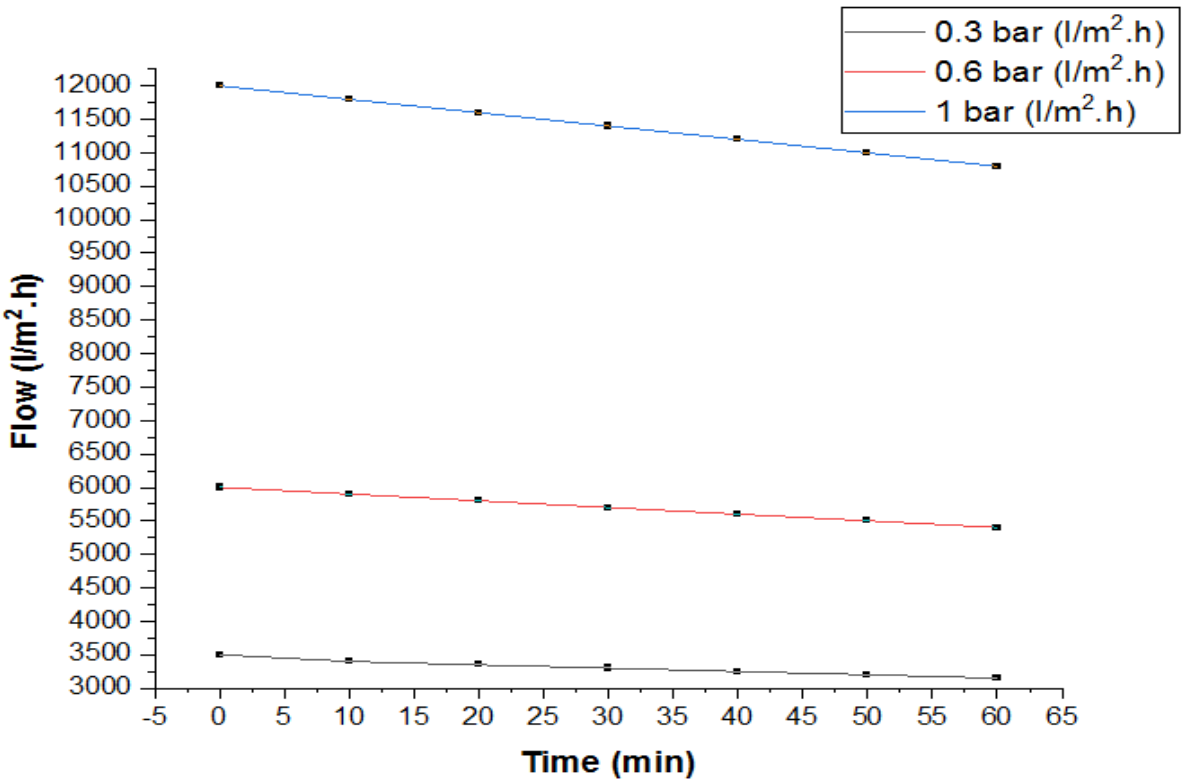



*Figure III.3 shows the change in flow with respect to time at 1100 °C at 12.41 wt%.*

❖ **At 0%**

Figure III.4 shows the change of flow rate with time under different pressures (0.3 bar, 0.6 bar, 1 bar). We observe for all three curves with an increase in pressure there is a slight decrease in flow followed by a relative stabilization phase in all cases.

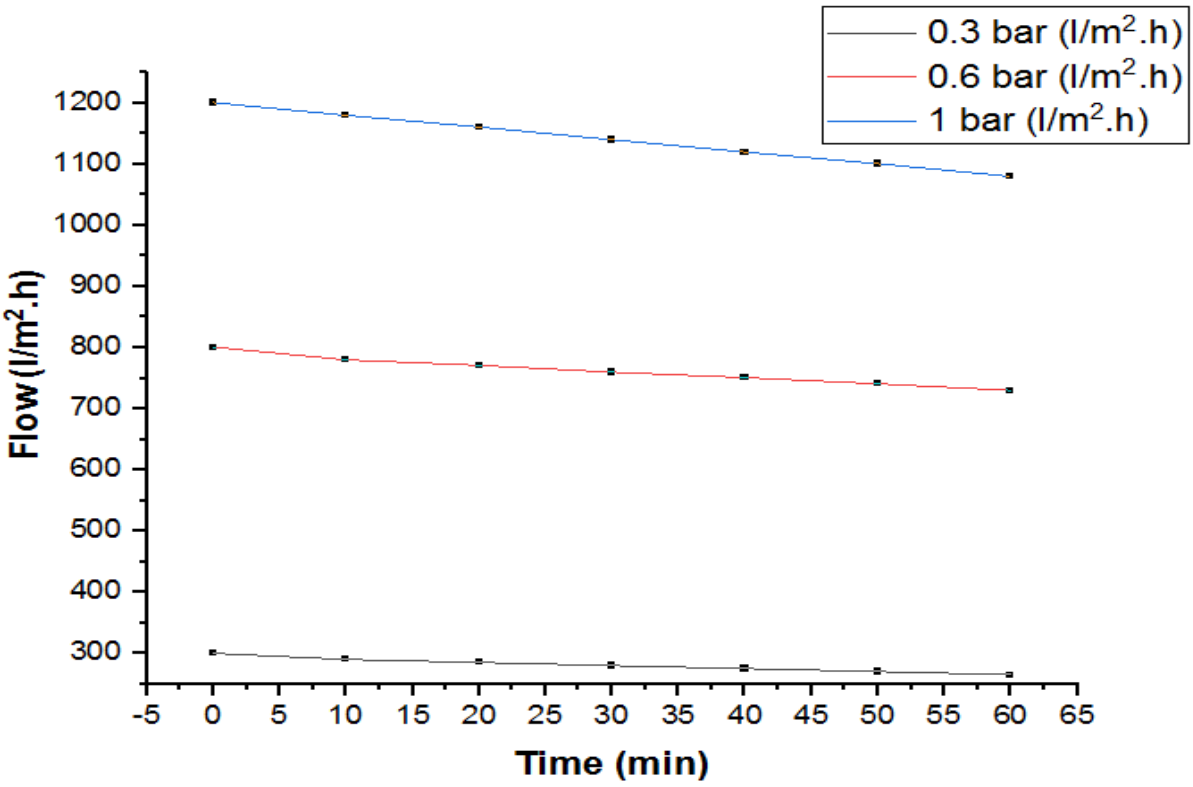



*Figure III.4 shows the change in flow in terms of time at 1100°C from 0 wt%.*

This behavior is explained by the fact that increasing pressure negatively affects the flow through the material, due to the contraction and shrinkage of the pore channels, while at lower pressures the effect of pressure is less severe, allowing to maintain relative stability in the pore structure during the first time period.

### III.5.2. Calculating the Permeability Coefficient

The effect of pressure on the flow value was studied in order to calculate the permeability coefficient K. For this purpose, we performed a series of experimental measurements to see how pressure affects the flow and we obtained the results represented and we obtained the results represented in Figures III.2, III.3, and III.4. The resulting curves show that they pass through the point of principle, while the slope of each represents the value of the permeability coefficient K.

❖ **At 22.07 wt%**

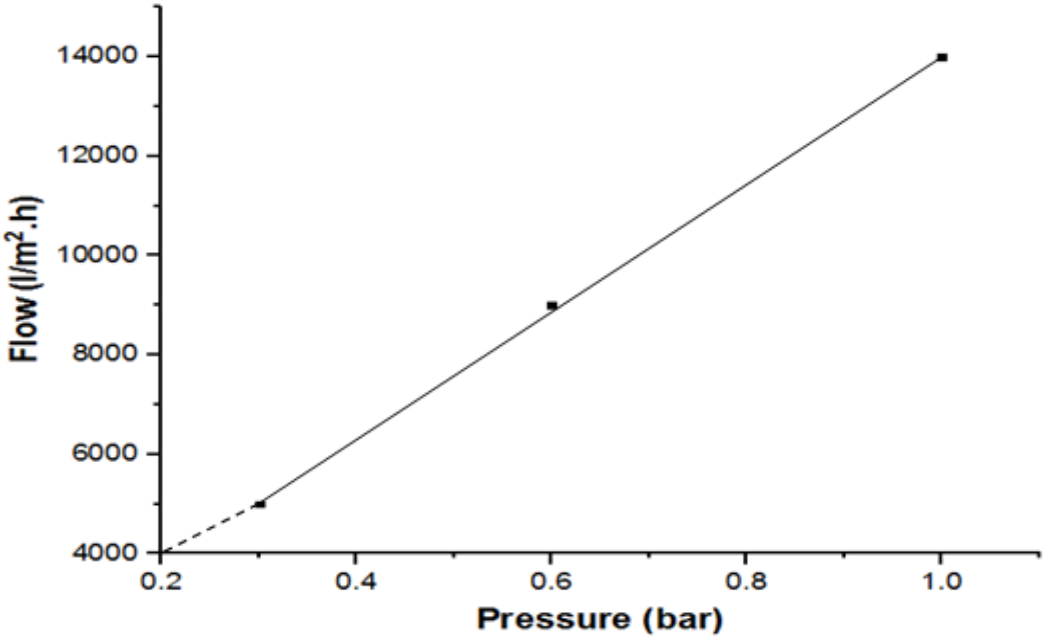



*Figure III.5 shows the change of flow in terms of pressure at 1100°C at 22.07 wt%.*

❖ **At 12.41 wt%**

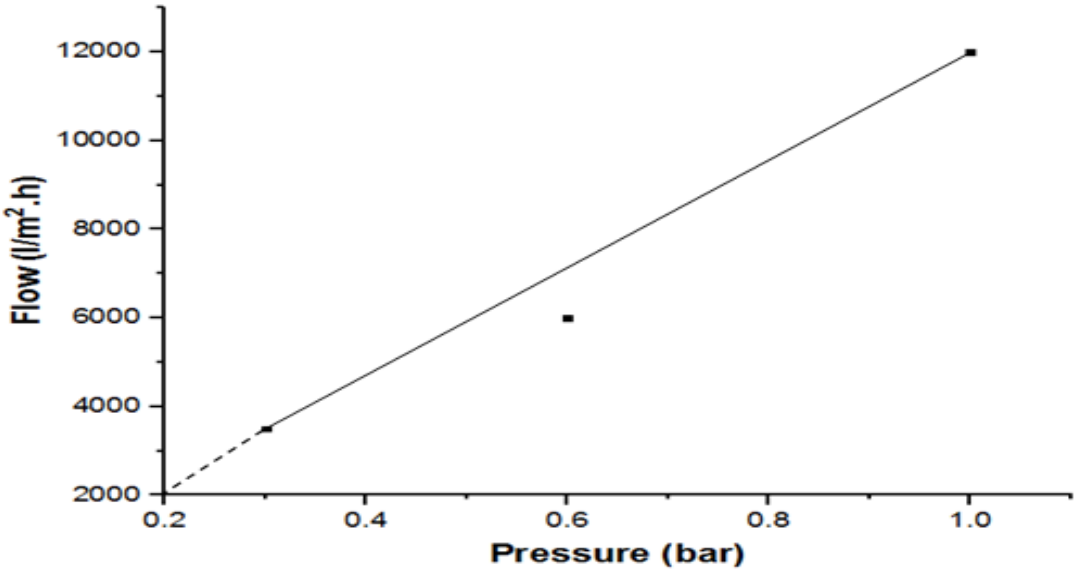



*Figure III.6 shows the change of flow in terms of pressure at 1100°C at 12.41 wt%.*

❖ **At 0 wt%**

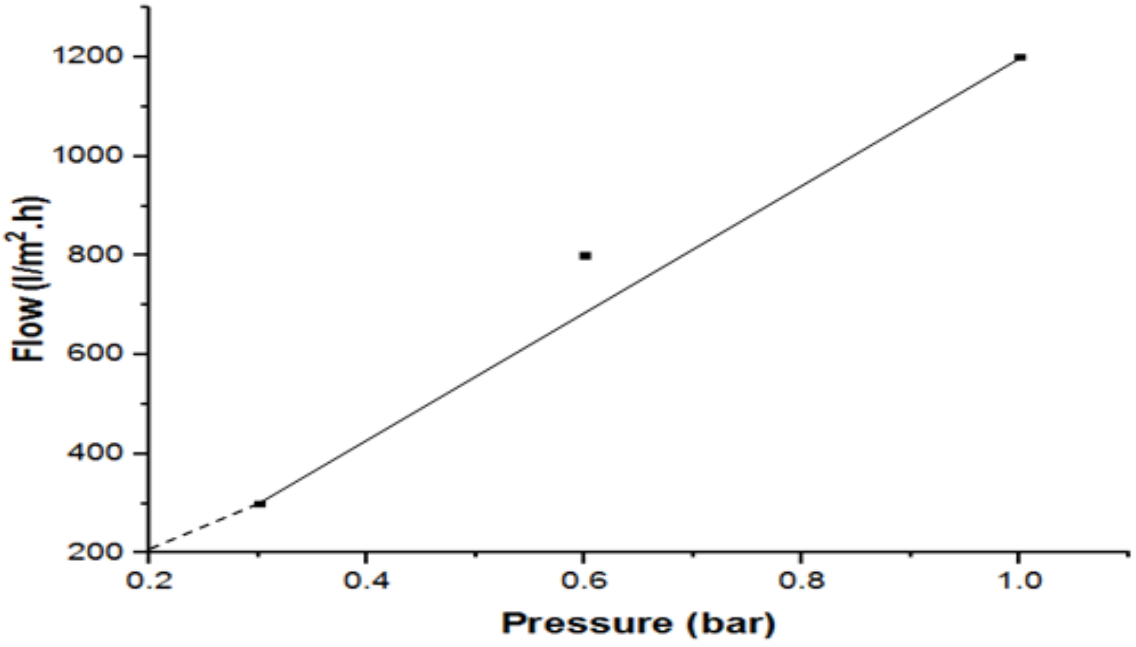



*Figure III.7 shows the change of flow in terms of pressure at 1100°C at 0 wt%.*

*Table III.2 Permeability coefficient values under different pressures at 1100°C.*

| Ratio | 22.07 % | 12.41% | 0 % |
|---|---|---|---|
| Temperature (℃) | 1100 | 1100 | 1100 |
| Permeability coefficient ($l/m^2.h.bar$) | 12857.14 | 12144.28 | 1287.14 |

From the figures, we notice that the value of the permeability coefficient at 0 wt% was small and reasonable (small pores), while the value of the permeability coefficient at 12.41 and 22.07 wt% was very high compared to some references, and this is explained by the increase in the size or number of effective pores in addition to the possibility of partial expulsion of the absorbed water inside the micropores [35,36].

## Conclusion

With the growth and development in the industrial sector, there are serious environmental issues due to increasing pollution of natural resources, especially water. This situation has led to the need to develop effective techniques to treat contaminated water. Among the strategies adopted is the use of ceramic filters manufactured from natural resources due to their high efficiency in the separation and purification processes. This work deals with the study of the effect of adding sunflower oil on the permeability of filters prepared from pure clay with the aim of improving their performance in filtration processes and ceramic samples were prepared under controlled conditions and their performance was evaluated to monitor the changes in the permeability characteristic as a result of this addition, which opens new horizons towards the development of more efficient and sustainable filtration materials.

At the beginning of the chapter, an overview of ceramics was presented with a review of its most prominent basic characteristics, as well as a study of the primary materials adopted in this work, mainly montmorillonite, with the definition of organic additives (sunflower oil). After that, we addressed the study of ceramic membranes, where we recognized their different types and reviewed the methods used in their preparation.

In the last part of this work, we prepared ceramic filters using extrusion technique to obtain tubular shaped membranes for three different percentages (0%_12.41%_22.07%). Montmorillonite was used as a starting point in the preparation, followed by heat treatment at 1100 °C. After that, the permeability coefficient was calculated for the prepared samples. The results showed a rather high permeability coefficient value of 12857.14 compared to some references. Despite this high value, this filters acceptable in terms of their effectiveness and can be adopted in filtration applications.

Through this work, these ceramic filters can be used as a ceramic membrane with the aim of reducing flux and obtaining high purity filtration using different types of membranes such as micron and nanometer membranes.

**References**


**[**1]. Abdullayev A, Bekheet MF, Hanaor DAH, Gurlo A. Materials and applications for low-cost ceramic membranes. Membranes (Basel). 2019;9(9).

[2]. Akash FA, Shovon SM, Rahman W, Rahman MA, Chakraborty P, Prasetya TAE, et al. Advancements in ceramic membrane technology for water and wastewater treatment: A comprehensive exploration of current utilizations and prospective horizons. Desalination and Water Treat [Internet]. 2024;319(April):100569. Available from: https://doi.org/10.1016/j.dwt.2024.100569

[3]. Eliche-quesada D, Pérez-villarejo L. Ceramic Materials - Synthesis, Characterization, Applications and Recycling. Ceram Mater - Synth Charact Appl Recycl. 2019;0–5.

[4]. Heimann RB. Classic and advanced ceramics: From fundamentals to applications. Weinheim: Wiley-VCH; 2010

[5]. B. Boudaira, A. Harabi, F. Bouzerara, S. Condom, ‘‘Preparation and characterization of microfiltration membranes and their supports using kaolin (DD2) and CaCO3’’, Desalination and Water Treatment, 9, 142-148 (2009).

[6]. F. Bouzerara, S. boulanacer, A. Harabi, B. Boudaira, S. Achour and S. Condom ‘‘Preparation and characterization of macroporousceramic supports for membranes’’, Journal of Physics Proc, 2, 1449–1453, (2009).

[7]. Ferhat Bouzerara, Abdelhamid Harabi, BoudjemaGhouil, Nabila Medjemem, BoukhemisBoudaira& Sylvie Condom, ‘‘Elaboration and Properties of Zirconia Microfiltration Membranes’’, Procedia Engineering, 33, 278–284, (2012).

[8]. A. Harabi, F. Zenikheri, B. Boudaira, F, A. Guechi, L. Foughali, ‘‘A new and economicapproach to fabricateresistantporousmembranesupportsusing kaolin and CaCO3’’, Journal of the EuropeanCeramic Society 34 1329–1340 (2014).

[9]. L. Foughali, A. Harabi, J. P. Bonnet, D. Smith, B. Boudaira, ‘‘Effect of calcium phosphate addition on sintering of El-Oued sand quartz rawmaterials ‘‘, Cerâmica 60 546-551 (2014).

[10]. B. Boudaira, A. Harabi, F. Bouzerara, F. Zenikheri, L. Foughali&A. Guechi: ‘‘Preparation and characterization of membrane supports for microfiltration and ultrafiltrationusing kaolin (DD2) and CaCO3’’, Desalination and Water Treatment, 57 (2016) 5258–5265.

[11]. A. Guechi, A. Harabi, S. Condoum, F. Zenikheri, B. Boudaira, F. Bouzerara& L. Foughali: ‘‘Elaboration and characterization of tubular supports for membranes filtration’’, Desalination and Water Treatment, 57 (2016) 5246–5252.

[12]. L. Foughali, S.E. Barama, A. Harabi, F. Bouzerara, A. Guechi& B. Boudaira: Effect of sodium phosphate addition on mechanicalproperties of porous Sigue quartz sand’’,Desalination and Water Treatment, 57 (2016) 5286–5291.6

[13]. B. Ghouil,A. Harabi, F. Bouzeraraa, B. Boudaira, A. Guechi, M. M. D.A. Figoli,‘‘ Development and characterization of tubular composite ceramic membranes usingnatural alumino-silicates for microfiltration applications’’Mterchract, 103 (2015) 18–27,

[14]. A. Harabi, B. Boudaira, F. Bouzerara, L. Foughali, F. Zenikheri, A. Guechi, B. Ghouil, S. Condom' PorousCeramic Supports for Membranes Prepared from Kaolin (DD3) and Calcite Mixtures' ACTA PHYSICA POLONICA A, 127 1164-1166 (2015).

[15]. N. Mdjemem, A. Harabi, F. Bouzerara, L. Foughali, B. Boudaira, A. Guechi, N. Brihi ' Elaboration and characterization of lowcostceramics microfiltration membranes applied to the sterilization of plant tissue culture media' , J. Taiwan. Inst. Chem. Eng., 59 (2016) 79–85.

[16]. B. Boudaira, A. Harabi, F. Bouzerara, S. Condom, F. Zenikheri, A. Guechi1, L. Foughali, N. Karboua, ' Preparation and characterization of ZnO microfiltration membrane and its support using kaolin (DD3) and CaCO3'; Cerâmica 62 (2016) 186-190.

[17]. F. Zenikheri, A. Harabi, B. Boudaira, F. Bouzerara, A. Guechi, S.-E. Barama, L. Foughali, N. Karboua, 'Elaboration of porousgehlenite and anorthite basedceramicsusinglow pricerawmaterials'; Cerâmica 62 (2016) 242-248.

[18]. Cheikh Kadiri, Abdelhamid Harabi, Ferhat Bouzerara, LazharFoughali, Noureddine Brihi, Sarah Hallour, Abdelkrim Guechi, BoukhemisBoudaira; "Preparation and properties oftubularmacroporousceramic membrane supports based on natural quartz sand and dolomite"; Journal of the AustralianCeramic Society 56 (2), (2020) 379-387.

[19]. C argoHandbook.com. Sunflower Oil [Internet]. Cargo Handbook - the world's largest cargo transport guidelines website. [cited 2025 May 24]. Available from: https://www.cargohandbook.com/Sunflower_Oil

[20]. Misra RDK, Misra KP. Fundamentals of ceramics: introduction, classification, and applications. Ceram Sci Eng Basics to Recent Adv. 2022;5–20. Available from: https://doi.org/10.1016/B978-0-323-89956-7.00020-6.

[21]. http://thesis.univ-biskra.dz/1283/4/Chapitre1.pdf

[22]. Amin SK, Abdallah HAM, Roushdy MH, El-Sherbiny SA. An overview of production and development of ceramic membranes. Int J Appl Eng Res. 2016;11(12):7708–21.

[23]. Kanth MS, Sandhya Rani SL, Raja VK. Advancing ceramic membrane technology in chemical industries applications by evaluating cost-effective materials, fabrication and surface modification methods. Hybrid Adv [Internet]. 2025;8(November 2024):100380. Available from: https://doi.org/10.1016/j.hybadv.2025.100380s

[24]. Minnesota Rural Water Association. Chapter19: Membrane Filtration. Minnesota Water Work Oper Man [Internet]. 2001;1–12. Available from: http://www.mrwa.com/WaterWorksMnl/Chapter 19 Membrane Filtration.pdf

[25]. Lehmaidi A. Elaboration And Characterization of Local Ceramic Materials For Agricultural Microfiltration Applications [Master's thesis]. Mohamed Khider University of Biskra; 2023-2024.

[26]. Instructions T. Lesson 3 : Nanofiltration Teacher Materials. Teacher.

[27]. Ben Smida Y, Marzouki R, Kaya S, Erkan S, Faouzi Zid M, Hichem Hamzaoui A. Synthesis Methods in Solid-State Chemistry. Synth Methods Cryst. 2020;(October).

[28]. Singh B, Sharma C, Sharma S. Fundamentals of extrusion processing. In: Novel Food Processing Technologies. Nov Food Process Technol. 2017;(May 2020):1–45.

[29]. Ganzoury MA, Allam NK, Nicolet T, All C. Introduction to Fourier Transform Infrared Spectrometry. Renew Sustain Energy Rev [Internet]. 2015;50:1–8. Available from: http://mmrc.caltech.edu/FTIR/FTIRintro.pdf%5Cnhttp://dx.doi.org/10.1016/j.rser.2015.05.073

[23]. I zemmouren O. Analyses par spectrométrie de fluorescence X (XRF) et/ou par diffraction des rayons X (DRX). Université Mohamed Khider.

[31]. ThermoFisher Scientific. XRF Technology in The Field. ThermoFisher Sci [Internet]. 2021;31. Available from: http://assets.thermofisher.com/TFS-Assets/CAD/brochures/TS-eBook-XRF-Technology-in-the-Field.pdf

[32]. Pani R. Thermal Analysis techniques.UNIT-2.Indus University.

[33]. Perkin Elmer. A Beginner's Guide Introduction. Perkin Elmer [Internet]. 2004;3–19. Available from: https://www.perkinelmer.com/lab-solutions/resources/docs/FAQ_Beginners-Guide-to-Thermogravimetric-Analysis_009380C_01.pdf

[34]. G oldstein JI, Newbury DE, Echlin P, Joy DC, Lyman CE, Lifshin E, Sawyer L. Scanning Electron Microscopy and X-Ray Microanalysis. 3rd ed. New York: Springer Science+Business Media; 2003

[35] رغيس سلمى .دراسة وتحضير مساند لشرائح من صلصال محلي لتصفية المياه المستعملة [مذكرة ماستر]. بسكرة: جامعة محمد خيضر بسكرة؛ 2024.

[36] بن بريكة يوسف ، بوزكوط محمد .تحضير ودراسة حوامل لأغشية خزفية انطلاقًا من مواد أولية محلية [مذكرة ماستر]. بسكرة: جامعة محمد خيضر بسكرة؛ 2018-2019.

**Summary**

In this work, we were able to prepare and develop ceramic filters from a local natural material, montmorillonite, in three different proportions (0%, 12.41% and 22.07%). The extraction technique was used to form these filters, and finally single-channel ceramic tubes were obtained, which were subjected to a heat treatment process at 1100 °C.

Through X-ray diffraction analysis, several crystalline phases were formed in the prepared samples, but the anorthite phase was the dominant phase, which is attributed to the ability of this phase to crystallize at high temperatures, in addition to its high hardness and good crystalline stability, which are properties that enhance the efficiency of the materials in filtration applications.

After that, the permeability test was performed on the samples, while we studied the time dependent flow changes under different pressures. The results showed that high pressure leads to a decrease in flow, while at low pressures it contributed to the stabilization of the porous structure and improved filter performance.

The permeability coefficient was then calculated for each formulation and the following values were recorded:

For (0 %): 1287.14 ($l/h.m^2.bar$).
For (12.41%): 12144.28 ($l/h.m^2.bar$).
For (22.07%): 12857.14 ($l/h.m^2.bar$).

The achieved results contribute to the understanding of the effect of the composition of local materials such as montmorillonite on the properties of ceramic filters and open promising prospects for the development of low-cost, high-efficiency filtration membranes for water treatment and industrial environments.

Keywords: MMT, oil, ceramic filters, extrusion, microfiltration.

**ملخص**

في إطار هذا العمل .تمكنا من تحضير وتطوير مرشحات خزفية انطلاقا من مادة طبيعية محلية ، وهي المونتموريلونيت ، وذلك بثلاث نسب مختلفة (0 بالمئة ،12.41 بالمئة، 22.07بالمئة) .تم استخدام تقنية الاستخراج لتشكيل هذه المرشحات ،حيث تم الحصول في النهاية على أنابيب خزفية أحادية القناة .خضعت لعملية معالجة حرارية عند درجة حرارة 1100 . من خلال تحليل انعراج الناشعة السينية ، تبين تشكل عدة أطوار بلورية في العينات المحضرة ،إلا ان طور الانورثيت هو الطور الغالب مما يعزي ذلك إلى قدرة هذا الطور على التبلور في درجات حرارة مرتفعة. بالإضافة إلى ما يتميز به من صلادة عالية واستقرار بلوري جيد وهي خصائص تعزز من كفاءة المواد في تطبيقات الترشيح.

بعد ذلك تم إجراء اختبار النفاية على العينات في حين درسنا تغيرات التدفق بدلالة الزمن تحت تأثير ضغوط مختلفة.وقد أظهرت النتائج ان ارتفاع الضغط يؤدي إلى انخفاض التدفق أما في حالات الضغوط المنخفضة فقد ساهم في استقرار البنية المسامية وتحسين أداء المرشح .

اجري بعد ذلك حساب معامل النفاذية لكل تركيبة ،بحيث تم تسجيل القيم التالية :

بالنسبة ل ( 0بالمئة) : 1287.14 ($l/h.m^2.bar$).

بالنسبة ل(12.41بالمئة):12144.28 ($l/h.m^2.bar$).

بالنسبة ل(22.07بالمئة):12857.14 ($l/h.m^2.bar$).

تساهم النتائج المحققة في تعزيز فهم تأثير تركيب المواد المحلية مثل المونتموريلونيت على خصائص المرشحات الخزفية ما تفتح آفاقا واعدة لتطوير أغشية ترشيح منخفضة التكلفة وعالية الكفاءة تستخدم في معالجة المياه والبيئة الصناعية.

الكلمات المفتاحية : مادة ال MMT ، الزيت ، المرشحات الخزفية ، البثق ، التنقية الميكرونية .

REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE
MINISTERE DE L'ENSEIGNEMENT SUPERIEUR
ET DE LA RECHERCHE SCIENTIFIQUE
UNIVERSITE MOHAMED KHIDER BISKRA
Faculte des SE

الجمهورية الجزائرية الديمقراطية الشعبية
وزارة التعليم العالي والبحث العلمي
جامعة محمد خيضر بسكرة
كلية العلوم الدقيقة

Département des Sciences de la matière
Filière: Physique

قسم :علوم المادة
شعبة :الفيزياء

جامعة محمد خيضر بسكرة
قسم علوم المادة
كلية العلوم الدقيقة

# تصريـــح شرفـــي

## خاص بالالتزام بقواعد النزاهة العلمية لإنجاز بحث

(ملحق القرار 1082 المؤرخ في 2021/12/27)

أنا الممضي أسفله،

السيد(ة):.....

تخصص:.....الصفة: طالب(ة) سنة ثانية ماستر فيزياء

الحامل(ة) لبطاقة التعريف الوطنية رقم: .....الصادرة بتاريخ:.....

المسجل بكلية: .....قسم: .....

والمكلف بانجاز أعمال بحث : مذكرة ماستر في الفيزياء

عنوانها: .....

.....

**أصرح بشرفي أني ألتزم بمراعاة المعايير العلمية والمنهجية ومعايير الأخلاقيات المهنية والنزاهة الأكاديمية المطلوبة في انجاز البحث المذكور أعلاه وفق ما ينص عليه القرار رقم 1082 المؤرخ في 2021/12/27المحدد للقواعد المتعلقة بالوقاية من السرقة العلمية ومكافحتها.**

التاريخ: .....

**إمضاء المعني بالأمر**