PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

University Center El-wancharissi of Tissemsilt

Institute of Sciences and Technology

Department of Sciences and Technology

End of study thesis for graduation of

Academic Master in:

Faculty: Petrochemical Industries

Option: **Refining Engineering**

Presented by: **M'HAMMEDI Ali**

Industrial Wastewater Treatment using Filtration on Ceramic Membranes.

DATE:

Members of the jury:

Mr. CHELLALI Rachid	President	M.C.B.	CU-Tissemsilt
Mr. AISSAT Miloud	Supervisor	M.A.A.	CU-Tissemsilt
Mr. HAID Slimane	Examiner	M.C.B.	CU-Tissemsilt
Mr. LADEG Soufiane	Examiner	M.C.B.	CU-Tissemsilt

College year: 2019-2020

THANKS

First of all, praise and gratitude to Allah, most gracious and most merciful, for everything he has blessed me with;

Great thanks to my father and my mother, for their huge sacrifices, and for doing everything they can to make my dreams achievable;

A special thanks to my supervisor and my mentor Mr. AISSAT Miloud for being so helpful and understanding to the situations and difficulties I have been through.

Also I want to thanks all my teachers and professors for their unforgettable efforts.

Thanks to my family, brothers and sisters for their support, encouragement and motivation.

I want to thank the person who is always with me for all the bad times before the good once.

DEDICATE

To my Mother...

To my Father...

To my Brothers...

To my sisters...

To myself...

To my Friends...

To everyone who believed in me...

Abstract

Abstract:

Throughout human history, water was and still essential for life sustainability, and in the recent years, The decline in clean water supplies around the world create big problems that push human beings to the edge of their intellects to look for alternatives that fulfill the demands, one of the common used techniques is exploiting wastewater that comes along as a side effect (wastewater) of the industrial revolution. Environmentally speaking, wastewater represent a great danger to human lives and is hazardous to the planetary ecosystem, as a result, government regulations has imposed cleaning water facilities to most of the factories that use water in their chain of production. These cleaning facilities use big equipment and unoptimized methods to treat wastewater and eliminate chemical and physical impurities.

In our study, we will try another way or technic to treat and eliminate impurities form unclean water which appeared in the last few years using a cheap and available materials, with the hope that will achieve great results and optimize costs. This technic is called filtration on ceramic membranes

تلخيص:

على مدار تاريخ البشرية، كان الماء ولا يزال ضروريًا لاستدامة الحياة، وفي السنوات الأخيرة، أدى انخفاض إمدادات المياه النظيفة في جميع أنحاء العالم إلى خلق مشاكل كبيرة تدفع البشر إلى حافة عقولهم للبحث عن بدائل تلبي المتطلبات، إحدى التقنيات الشائعة المستخدمة هي استغلال المياه العادمة التي تأتي كأثر جانبي (مياه الصرف الصحي) للثورة الصناعية. من الناحية البيئية، تمثل مياه الصرف الصحي خطرًا كبيرًا على حياة الإنسان وهي خطرة على النظام البيئي الكوكبي، ونتيجة لذلك، فرضت اللوائح الحكومية مرافق مياه التنظيف على معظم المصانع التي تستخدم المياه في سلسلة إنتاجها. تستخدم مرافق التنظيف هذه معدات كبيرة وطرقًا غير محسنة لمعالجة مياه الصرف الصحي والقضاء على الشوائب الكيميائية والفيزيائية.

في دراستنا، سنحاول طريقة أو تقنية أخرى لمعالجة وإزالة الشوائب من المياه غير النظيفة التي ظهرت في السنوات القليلة الماضية باستخدام مواد رخيصة ومتوفرة، على أمل تحقيق نتائج رائعة وتحسين التكاليف. تسمى هذه التقنية بالترشيح على أغشية السيراميك.

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General Introduction

General introduction

The history of water supply and sanitation is one of a logistical challenge to provide clean water and sanitation systems since the dawn of civilization. Where water resources, infrastructure or sanitation systems were insufficient, diseases spread and people fell sick or died prematurely.

Major human settlements could initially develop only where fresh surface water was plentiful, such as near rivers or natural springs. Throughout history, people have devised systems to make getting water into their communities and households and disposing of (and later also treating) wastewater more convenient. **[01]**

Over the millennia, technology has dramatically increased the distances across which water can be relocated. Furthermore, treatment processes to purify drinking water and to treat wastewater have been improved where we can find many sewage plants in one country, and that is because of the decreasing of drinking water by pollution. The development of technology allows human beings to discover different methods to treat and to purify wastewater, each method has its advantages and disadvantages.

Among these different technologies, we will use ceramic membrane to purify polluted water, this separation by membrane method is used in many industries like: food industry, the pharmaceutical industry and the demineralization of seawater and brackish water. The main objective of these processes is the clarification, purification, and separation of molecules and inorganic salts into view of a possible enhancement of separate molecules or demineralized water in the various activities related to the daily life of citizens.

The objective of this work is the development of membrane supports from a local product (Kaolin KT2 from milia) known as Kaolin from Tamazert, these membrane supports are then improved by adding an inorganic layer prepared by the sol gel method. These membranes were produced in several stages, molding, drying and baking. The cooking temperature was tested for the preparation of the membrane supports is reached to 1100 ° C.

This thesis is divided into several parts, the first part present a bibliographic study about wastewater in general (its sources, components and treatment processes…). Secondly, talks about filtration process and its modes and different domains that each mode can be used in. Thirdly, general information on kaolin and membrane processes and ceramic membranes and their characteristics without forgetting the sol-gel method that is so important in our work.

The second part is devoted to operating parameters such as the production of kaolin-based membranes at the laboratory level, the characterization of these by different analysis methods, and finally the performance of filtration tests.

Finally, we are going to test the performance of synthesized membrane (membranes cooked at 1100 ° C without inorganic layer, 1100 C° improved with inorganic layer) which allowed us to conclude as to the possibility of producing, from kaolin, an effective membrane for the elimination of pollutants.

Chapter I

Generalities about wastewater

Chapter Ⅰ : Generalities about wastewater

Ⅰ. 1. Introduction:

Most of industries need water to use it in different ways, so they can complete their operations. After using water, this last one become a polluted water, which they cannot throw it directly into the environment. It must be treated from bacteria and chemical products that have a danger effect on environment. To treat and manage the industrial wastewater, the specialists must study its characters and parameters to know which method of treatment should be used, either physical, chemical or biological treatment.

Ⅰ. 2.Types of wastewater:
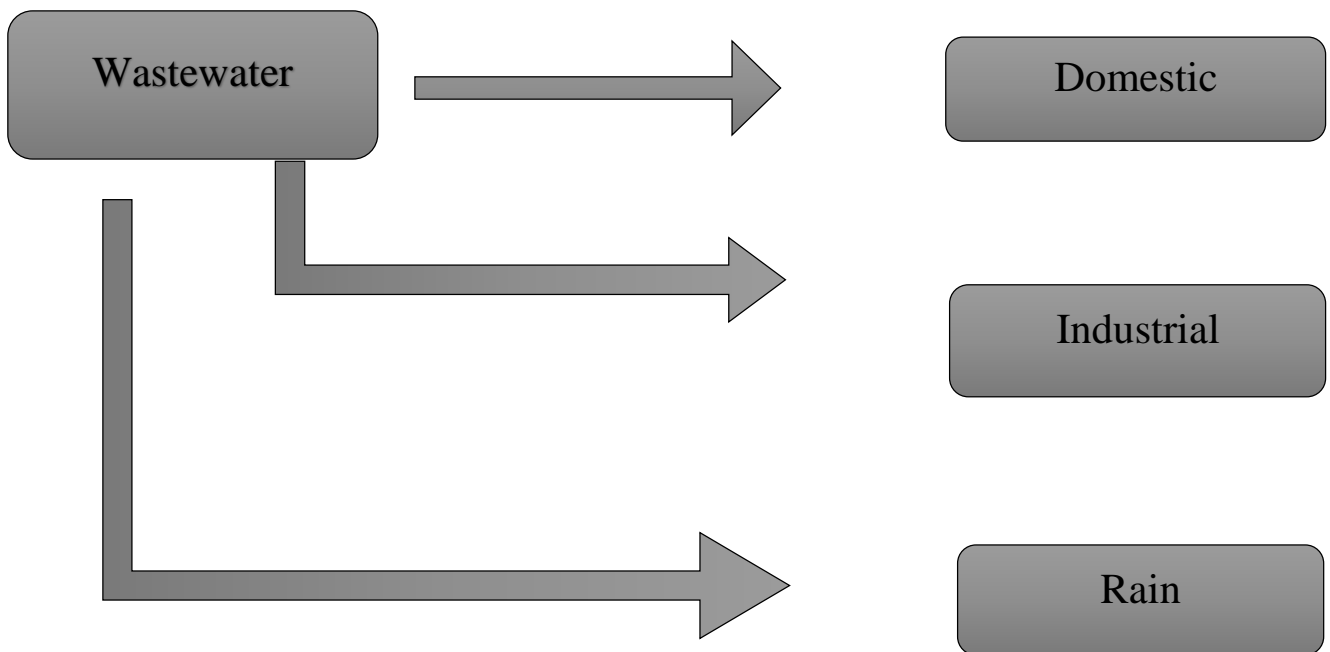
Fig.01. Wastewater Types.

Ⅰ. 2.1. Definition of domestic wastewater:

Domestic wastewater is the water that has been used by a community and which contains all the materials added to the water during its use. It is composed of human body wastes (faeces and urine) together with the water used for flushing toilets, which is the wastewater resulting from personal washing, laundry, food preparation and the cleaning of kitchen utensils. **[02]**

Ⅰ. 2.2. Definition of industrial wastewater:

Industrial wastewater is the aqueous discard that results from substances having been dissolved or suspended in water, typically during the use of water in an industrial manufacturing process or the cleaning activities that take place along with that process**. [03]**

Ⅰ. 3. Composition of industrial wastewater:

The composition of industrial wastewater depend on the nature or the type of industry, and into that type we can chose the method of treatment (physical, chemical or biological treatment), here are the main compositions of industrial wastewater.

Ⅰ. 3.1. Suspended matter:

The suspended matter is mainly biodegradable in nature. Most part of the pathogenic microorganisms contained in wastewater is transported by MES. They also give the water a cloudy appearance, a bad taste and a bad smell. **[04]**

Ⅰ. 3.2. Organic and non-organic micro-pollutants:

Micro-pollutants are elements present with unlimited quantities in wastewater, the main contamination way in the case of reuse purified wastewater is ingestion. It is the indirect contamination which is generally concern. **[03]**

Ⅰ. 3.3. Organic Matterm:

Organic materials are found everywhere in the environment. They are composed of the carbon-based chemicals that are the building blocks of most living things. Organic materials in wastewater originate from plants, animals, or synthetic organic compounds, and enter wastewater in human wastes, paper products, detergents, cosmetics, foods, and from agricultural, commercial, and industrial sources. Organic compounds normally are some combination of carbon, hydrogen, oxygen, nitrogen, and other elements. Many organics are proteins, carbohydrates, or fats and are biodegradable, which means they can be consumed and broken down by organisms. **[05]**

Ⅰ. 3.4. Inorganics Matter:

Inorganic minerals, metals, and compounds, such as sodium, potassium, calcium, magnesium, cadmium, copper, lead, nickel, and zinc are common in wastewater from both residential and nonresidential sources. They can originate from a variety of sources in the community including industrial and commercial sources, stormwater, and inflow and infiltration from cracked pipes and leaky

manhole covers. Most inorganic substances are relatively stable, and cannot be broken down easily by organisms in wastewater. **[03]**

Ⅰ. 3.5. Oil and Grease:

Fatty organic materials from animals, vegetables, and petroleum also are not quickly broken down by bacteria and can cause pollution in receiving environments. They can trap trash, plants, and other materials, causing foul odors, attracting flies and mosquitoes and other disease vectors. In some cases, too much oil and grease causes septic conditions in ponds and lakes by preventing oxygen from the atmosphere reaching the water. **[06]**

Ⅰ. 3.6. Nutrients

Wastewater often contains large amounts of the nutrients nitrogen and phosphorus in the form of nitrate and phosphate, which promote plant growth. Organisms only require small amounts of nutrients in biological treatment, so there normally is an excess available in treated wastewater. **[07]**

Ⅰ. 3.7. Solid matter:

Solid materials in wastewater can consist of organic and/or inorganic materials and organisms. The solids must be significantly reduced by treatment or they can increase BOD when discharged to receiving waters and provide places for microorganisms to escape disinfection. They also can clog soil absorption fields in onsite systems. **[08]**

Ⅰ. 3.7.1. *settleable solids*

Certain substances, such as sand, grit, and heavier organic and inorganic materials settle out from the rest of the wastewater stream during the preliminary stages of treatment. On the bottom of settling tanks and ponds, organic material makes up a biologically active layer of sludge that aids in treatment.

Ⅰ. 3.7.2. *Suspended solids:*

Materials that resist settling may remain suspended in waste-water. Suspended solids in wastewater must be treated, or they will clog soil absorption systems or reduce the effectiveness of disinfection systems.

Ⅰ. 3.7.3. *Dissolved solids:*

Small particles of certain wastewater materials can dissolve like salt in water. Microorganisms in wastewater consume some dissolved materials, but others, such as heavy metals, are difficult to remove by conventional treatment.

Ⅰ. 3.8. Gases:

Certain gases in wastewater can cause odors, affect treatment, or are potentially dangerous. Methane gas, for example, is a byproduct of anaerobic biological treatment and is highly combustible. The gases hydrogen sulfide and ammonia can be toxic and pose asphyxiation hazards. Ammonia as a dissolved gas in wastewater also is dangerous to fish. . **[06]**

Ⅰ. 4. Wastewater characteristics:

Table 1: wastewater characteristics.

Wastewater characteristics		
physical characteristics	**Chemical Characteristics**	**Biological Characteristics**
. Turbidity . Color . Odor . Total solids . Temperature	. Chemical Oxygen Demand (COD). . Total Organic Carbon (TOC). . Nitrogen, Phosphorus , Chlorides ,Sulfaes . Alkalinity, pH and Heavy Metals.	. Biochemical Oxygen Demand (BOD) . Oxygen required for nitrification . Microbial population

Ⅰ. 5. Physical Characteristics of Wastewater:

Ⅰ. 5.1. Color: Fresh sewage is normally brown and yellowish in color but over time becomes black in color.

Ⅰ. 5.2. Odor: Wastewater that includes sewage typically develops a strong odor.

Ⅰ. 5.3. Temperature: Due to more biological activity, wastewater will have a higher temperature.

Ⅰ. 5.4. Turbidity: Due to suspended solids in wastewater, wastewater will have a higher turbidity, or cloudiness.

Ⅰ. 6. Chemical Characteristics of Wastewater:

Wastewater contains different chemicals in various forms as mentioned below:

Ⅰ. 6.1. Chemical Oxygen Demand (COD):

COD is a measure of organic materials in wastewater in terms of the oxygen required to oxidize the organic materials. **[09]**

Ⅰ. 6.2. Total Organic Carbon (TOC):

Total organic carbon (TOC) is the amount of carbon found in any organic sample. It has a wide range of applications, including checking the water quality, analysing the cleanliness of pharmaceutical equipment, or even identifying the amount of carbon contained within a soil sample. It is important to note that TOC instrumentation does not help to identify non-organic compounds. **[10].**

Ⅰ. 6.3. Nitrogen: Organic nitrogen is the amount of nitrogen present in organic compounds.

Ⅰ. 6.4.Phosphorous: Organic phosphorous (in protein) and inorganic phosphorous (phosphates, PO_4^-).

Ⅰ. 6.5. Chlorides (Cl^-) and Sulfates (SO_4^{-2})

Ⅰ. 6.6. PH: is a parameter that measures the acidity, alkalinity or basicity of a water.

Ⅰ. 6.7. Heavy metals:

- Mercury (Hg)
- Arsenic (As)
- Lead (Pb)
- Zinc (Zn)
- Cadmium (Cd)
- Copper (Cu)
- Nickel (Ni)
- Chromium (Cr)
- Silver (Ag)

Ⅰ. 7. Biological Characteristics of Wastewater:

Ⅰ. 7.1. Biochemical oxygen demand (BOD):

Is the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific period. The BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20 °C and is often used as a surrogate of the degree of organic pollution of water. **[11]**

Ⅰ. 7.2. Nitrogenous Oxygen Demand (NOD):

NOD is the amount of oxygen needed to convert organic and ammonia nitrogen into nitrates by nitrifying bacteria.

Ⅰ. 7.3. Microbial life in wastewater: Wastewater contains the following microbes:

- Bacteria
- Protozoa
- Fungi
- Viruses
- Algae
- Rotifers

Ⅰ. 8. Modes of treatment wastewater:

Industrial wastewater has a lot of impact on the natural world and it is important to treat it effectively. By treating wastewater, we don't just save the creatures thriving on it, but also protect the environment of our whole planet. To treat wastewater, there are four main modes of treatment, which they are:

1. Physical treatment.
2. Chemical treatment.
3. Biological treatment.
4. Sludge treatment.
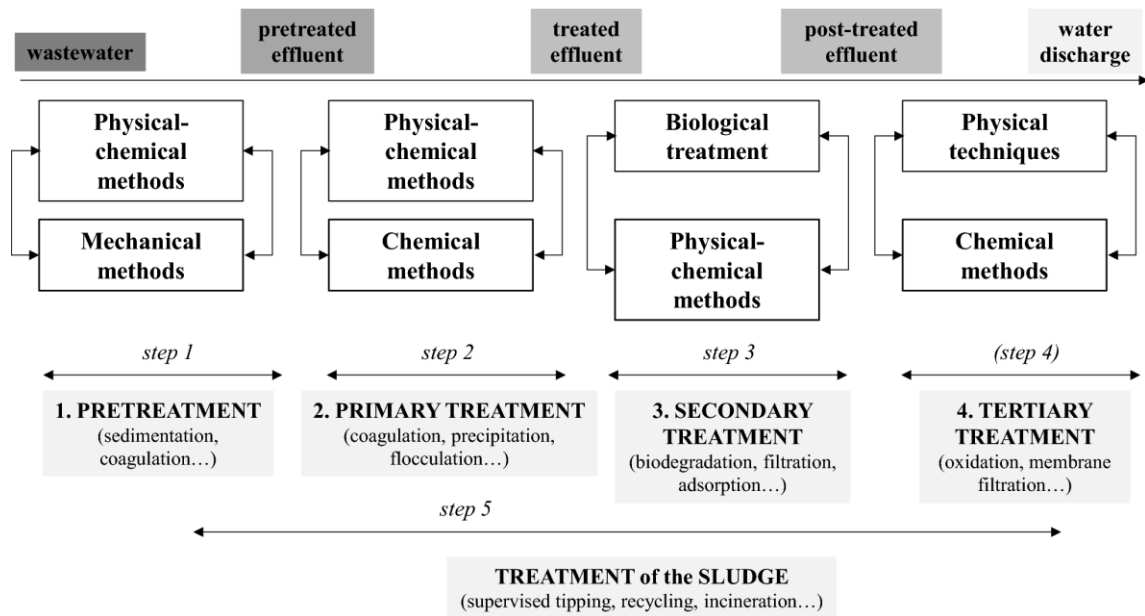
Fig.02. Different technics of treatment of wastewater.

I . 8.1. Physical treatment:

In this stage, physical methods are used for cleaning the wastewater. Processes like screening, sedimentation and skimming are used to remove the solids. No chemicals are involved in this process. One of the main techniques of physical wastewater treatment includes sedimentation, which is a process of suspending the insoluble/heavy particles from the wastewater. Once the insoluble material settles down at the bottom, you can separate the pure water.

Another effective physical water treatment technique includes aeration. This process consists of circulating air through the water to provide oxygen to it.

Filtration, the third method, is used for filtering out all the contaminants. You can use special kind of filters to pass the wastewater and separate the contaminants and insoluble particles present in it. The sand filter is the most commonly used filter. The grease found on the surface of some wastewater can also be removed easily through this method. **[12]**

I . 8.2. Biological Water Treatment:

This uses various biological processes to break down the organic matter present in wastewater, such as soap, human waste, oils and food. Microorganisms metabolize organic matter in the wastewater in biological treatment. It can be divided into three categories:

Ⅰ. **8.2.a. Aerobic processes:** Bacteria decomposes the organic matter and converts it into carbon dioxide that can be used by plants. Oxygen is used in this process.

Ⅰ. **8.2.b. Anaerobic processes:** Here, fermentation is used for fermenting the waste at a specific temperature. Oxygen is not used in anaerobic process.

Ⅰ. **8.2.c. Composting** A type of aerobic process where wastewater is treated by mixing it with sawdust or other carbon sources. **[12]**

Ⅰ. 8.3. Chemical Water Treatment:

As the name suggests, this treatment involves the use of chemicals in water. Chlorine, an oxidizing chemical, is commonly used to kill bacteria which decomposes water by adding contaminants to it. Another oxidizing agent used for purifying the wastewater is ozone. Neutralization is a technique where an acid or base is added to bring the water to its natural pH of 7. Chemicals prevent the bacteria from reproducing in water, this making the water pure. **[12]**

Ⅰ. 8.4. Sludge Treatment:

This is a solid-liquid separation process where the least possible residual moisture is required in the solid phase and the lowest possible solid particle residues are required in the separated liquid phase.

An example of this includes dewatering of sludge from industrial wastewater or sewage plant where the residual moisture in dewatered solids determines the disposal costs and the centrate quality determines the pollution load returned back to the treatment facility. You need to minimize both a solid-liquid separation device such as a centrifuge is used for removing the solids from the wastewater. **[12]**

Ⅰ. 9. Conclusion:

Demand on fresh water increase in the last few years because of the incredible growth of population and the big consummation of fresh water in different activities of human beings. These last ones produce a big amount of wastewater, but it is useless and danger on environment by causing pollution. In order to make this useless water useful, it must be treated by different processes and technics before thrown it into the nature or reuse it in a different ways.

Chapter Ⅱ

Filtration modes and Ceramic Membranes

Chapter Ⅱ : Filtration modes and Ceramic Membranes.

Ⅱ.1. Introduction:

As we see before, there are many technics to treat wastewater, from chemical to physical and biological technics. Filtration is a physical and chemical technic that we can use to treat wastewater and eliminate a big part of solids and matter that suspended in water, so in this chapter we will see about filtration and its different modes.

Ⅱ. 2. Definition of filtration:

Filtration is a process used to separate solids from liquids or gases using a filter medium that allows the fluid to pass through but not the solid. The term "filtration" applies whether the filter is mechanical, biological, or physical. The fluid that passes through the filter is called the filtrate. The filter medium may be a surface filter, which is a solid that traps solid particles, or a depth filter, which is a bed of material that traps the solid. **[13]**

Ⅱ. 3. Filtration modes:

Ⅱ. 3.1. Microfiltration (MF):

Microfiltration is a low-pressure means of separating large molecular weight suspended, it is also used to reduce the turbidity of feed water and remove suspended solids and bacteria. MF membranes generally have pore sizes between 0.1 to 0.2 microns (µm). **[13]**

Ⅱ. 3.2. Ultrafiltration (UF):

Ultrafiltration uses micro-porous membranes with pore diameters between 1 and 100 nm. Such membranes allow small molecules to pass through (water, salts) and stop molecules of high molar mass (polymers, proteins, colloids.

For this reason, this technique is used for the elimination of macro-solutes present in domestic, industrial use or medical wastewater. **[14]**

Ⅱ. 3.3. Nano-filtration (NF):

Nano-filtration is a unique filtration process in-between UF and RO designed to achieve highly specific separation of low molecular weight compounds such as minerals and salts from complex process streams. Typical applications include de-ashing of dairy products, recovery of hydrolyzed proteins, concentration of sugars and purification of soluble dyes and pigments. **[15]**

Ⅱ. 3.4. Reverse Osmosis (RO):

Reverse Osmosis is a high pressure, energy-efficient means of de-watering process streams, concentration of low molecular weight compounds or clean-up of waste effluents. Common applications include pre-concentration of dairy or food streams prior to evaporation, polishing of evaporator condensate, and purification of process water. **[15]**
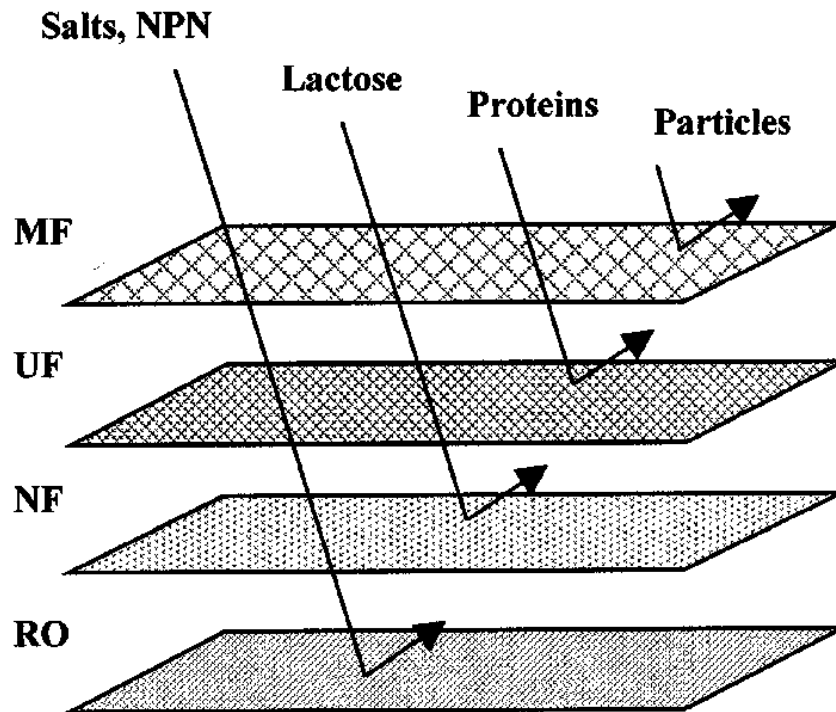
Fig.03. Illustration-of-filtration-membranes.

Ⅱ. 3.5. Examples of application of each membrane process:

Table2: Applications of different membrane processes.

Process	Applications	Alternative Processes
Microfiltration	Separation of bacteria and cells from solutions.	Sedimentation, Centrifugation
Ultrafiltration	Separation of proteins and virus, concentration of oil-in-water emulsions	Centrifugation

| Nano-filtration | Separation of dye and sugar, water softening | Distillation, Evaporation |
| Reverse Osmosis | Desalination of sea and brackish water, process water purification | Distillation, Evaporation, Dialysis |

Ⅱ. 4. Classification:

As we have seen, the suspension to be filtered is directed to a filtering medium which the liquid alone crosses under the influence of a pressure difference. One method for classifying filters is based on how to achieve this pressure gradient. We have:

Ⅱ. 4.1. Pressure filtration, when the pressure is applied to the upstream face of the filtering surface, the other side remaining at atmospheric pressure;

Ⅱ. 4.2. Vacuum filtration, if a vacuum is created on the downstream side of the porous medium, the other side remaining at atmospheric pressure;

Ⅱ. 4.3. Gravity filtration, when the suspension flows due to hydrostatic pressure; this method is generally used when it is a treatment of a large quantities of suspension containing few solid particles, for example for the filtration of water.

Other **filtration classification** are:

- **The operating mode:** continuous or discontinuous;
- **The filtration technique**: on a cake, with cross currents or on a membrane. **[16]**

Ⅱ. 5. Fundamental law of filtration:
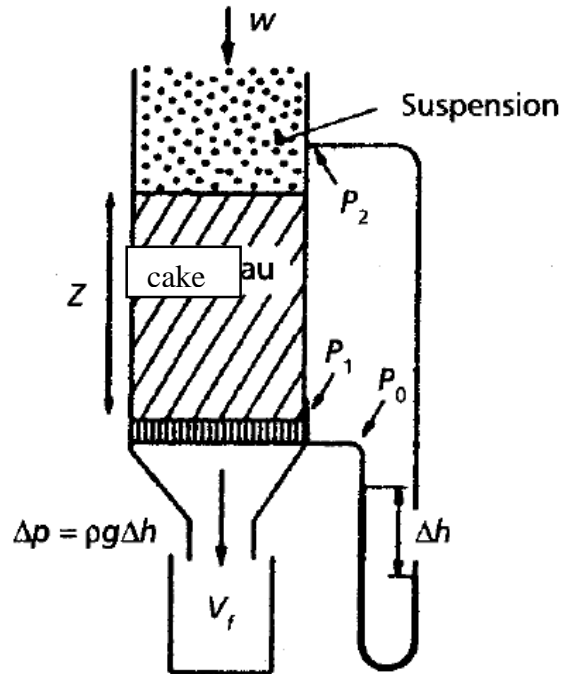
Fig.04. Filtration of liquids on support.

Using the simplified Koseny-Carman model (during filtration on support, without taking into account the hydraulic resistance of the support) which assimilates the porous mass to a bundle of straight cylindrical channels and identical, similarly inclined with respect to the direction of flow and independent of each other, the pressure difference o forces the suspension to pass through the filter mass at medium speed can be expressed by the relation: **[16]**

$$\Delta P = 180.Z.w.\mu\ (1-\varepsilon)^2 / d_p^2\ \varepsilon^3\ \dots\dots\dots\dots\dots\dots\dots(Eq.01)$$

Or, depending on the specific surface of the precipitate grains:

$$\Delta P = 5S_p^2 Z.w.\mu\ (1-\varepsilon)^2 / \varepsilon^3 \dots\dots\dots\dots\dots\dots\dots\dots..(Eq.02)$$

With:

• Z the thickness of the precipitate layer;

• d_p the equivalent diameter of the precipitate particles;

• ε the porosity of the cake;

• μ the viscosity of the filtrate at the filtration temperature;

• $S_p = a_p / v_p = 6 / d_p$ ………………… **(Eq.03)**

where a_p represents the area and v_p the volume of the considered particle of spherical shape. **[16]**

Ⅱ. 6. Ceramic Membrane:

Ⅱ. 6.1. Definition of Membrane:

A membrane is a semi-permeable thin layer of material capable of separating contaminants as a function of their physical/chemical characteristics. **[17]**

Ⅱ. 6.2. Membrane Filtration Design:

Membrane filtration is a mechanical barrier that uses a straining mechanism only to remove materials from the water, no particles larger than the membranes pore size can pass through the filter.
• This is illustrated in Figure05.
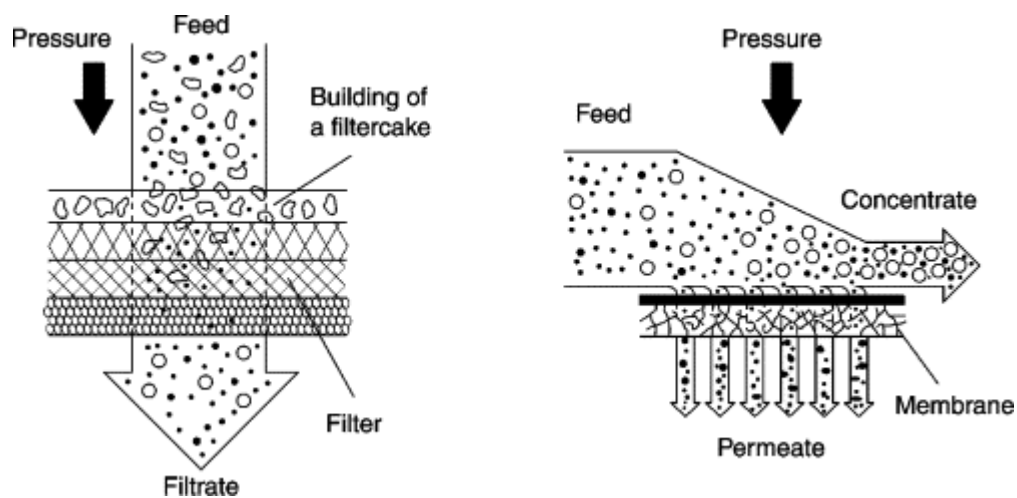
Fig.05. Membrane filtration mechanism.

Ⅱ. 6.3. Definition of ceramic:

Ⅱ. 6.3.1. Classical definition:

Ceramics is the art of making pottery based on the properties of clays to give with water a plastic dough easy to shape, becoming hard, solid and unalterable after firing. **[18]**

Ⅱ. 6.3.2. Modern definition:

Kingery (1960) proposed the following definition of a ceramic: "A ceramic is a solid product composed mainly of non-metallic and non-organic materials obtained by baking, sintering or calcining such as pottery, porcelain, refractories, abrasives, enamels, glasses, non-metallic magnetic materials, materials ferroelectric….."**[19].**

According to the definition of the United States Academy of Sciences, ceramics are inorganic, non-metallic materials formed or consolidated at high temperatures. **[18].**

Ⅱ. 7. MEMBRANE PERFORMANCE AND MAINTENANCE:

The performance of a membrane depends on:

- The characteristics of the membrane
- The feed solution being treated
- The operating conditions

The following parameters are used to measure membrane performance:

Ⅱ.7.1. Recovery Factor: measures how much of the feed is recovered as permeate.

$$\text{RECOVERY} = Q_{permeate} / Q_{feed} \ \text{……………..} \ (Eq.04)$$

Where $Q_{permeate}$ and Q_{feed} are the permeate flow rate and the feed flow rate respectively.

Ⅱ.7.2. Rejection or Retention: Measure of the fraction of solute that is retained for the membrane.

$$R = (C_{feed} - C_{permeate})*100 / C_{feed} \ \text{…………………}(Eq.05)$$

Where C_{Feed} is the concentration of a particular species in the feed and $C_{permeate}$ is the concentration of the same species in the purified stream.

Ⅱ. 7.3. Transmission: Percentage of solute that is not retained by the membrane.

$$T = (C_{permeate} / C_{feed})*100 \quad \text{or} \quad T = 100 - R \ \text{……………..}(Eq.06)$$

Ⅱ. 7.4. Decontamination Factor: Useful to evaluate the performance of waste treatment processes.

$$DF = C_{permeate} / C_{feed} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(Eq.07)$$

[20]

Ⅱ.8. Advantages and disadvantages of ceramic membrane:

Table3: Advantages and disadvantages of ceramic membrane.

Advantages	Disadvantages
• Able to resist high temperatures up to 280 °C. A special development onto modules and system could reach up to 700 °C. • Excellent corrosion resistance (towards organic solvents and a wide pH range). • Suitable for cleaning and steam sterilization • High mechanical strength. • Able to endure in harsh condition; e.g. high acid or alkaline solution. • Possess long life time. • High membrane flux for porous membrane.	• Brittle. Need a very careful handling. • Most ceramic membranes are in disc or tubular shape; possess low surface area/volume ratio. • The investment cost of ceramic membrane is very high.

Ⅱ.9. Conclusion:

Ceramic membranes have many desirable properties and are being used extensively in water purification, food and dairy applications as well as for industrial needs. These market uses of ceramics will continue to increase. As ceramic membrane production volume grows and product innovations reduce the capital cost, use of ceramic membranes will increase. They will be more prominent as they are better understood for use in potable water, wastewater recycling, reuse, and even produced water in the oil field.

Chapter Ⅲ

Generalities about Kaolin Clay

ChapterⅢ: Generalities about Kaolin Clay

Ⅲ. 1. INTRODUCTION:

The kaolin is considered as one of the most materials used in fabrication of ceramic membranes due to its excellent mechanical stability, chemical and thermal resistivity and most importantly, because it is most effective in some cases, compared to polymeric membrane. Unfortunately, ceramic membrane fabrication, even though commercially available, still remains highly expensive from a technical and economic point of view due to the use of expensive powders such as alumina, zirconia, titania and silica. Recently, the development of low cost ceramic membranes based on natural materials such as apatite powder, natural raw clay, graphite, phosphates, dolomite, kaolin and waste materials such as fly ash, appeared as an efficient solution to treat waste water at a low cost.

Ⅲ. 2. Overview of kaolin material:

Kaolin ($Al_2Si_2O_5$ $(OH)_4$) can be simply defined as a type of clays formed naturally in the earth. It is labelled as a soft clay, white in color, earthy and formed by the silicate mineral decomposition by chemical weathering, like feldspar. The historical name of kaolin is derived from the Chinese term 'kauling', named after a hill near the Jauchau Fu, China. The term kaolin is first used in 1867 by Johnson and Blake. In 1921, kaolin was first used in research to study its heating and cooling behavior. **[21]**

Kaolin and the clay mineral kaolinite are natural components of the soil and occur widely in ambient air as floating dust. Kaolinite is formed mainly by decomposition of feldspars (potassium feldspars), granite, and aluminium silicates. It is also not uncommon to find kaolin deposited together with other minerals (illite, bentonite). The process of kaolin formation is called kaolinization .

Kaolinite formation occurs in three ways:

• Crumbling and transformation of rocks due to the effects of climatic factors (Zettlitz type);

• Transformation of rocks due to hydrothermal effects (Cornwall type); and

• Formation by climatic and hydrothermal effects (mixed type). **[22]**

Ⅲ.3. Physical-chemical properties of kaolinite:

These properties have been extensively studied by **[23] [24].**

Kaolinite is considered to be:

- a non-inflating mineral.

- Low birefringent, the average refraction index is 1.56.

- Elemental crystals come in the form of hexagonal pads.

- Neutral or basic pH.

- Chemically inert in a relatively large area of pH (4 to 9).

- High whiteness.

- Good covering power (use as pigment).

- Soft and non-abrasive.

- Plastic, refractory.

- Low-conducting both heat and electricity.
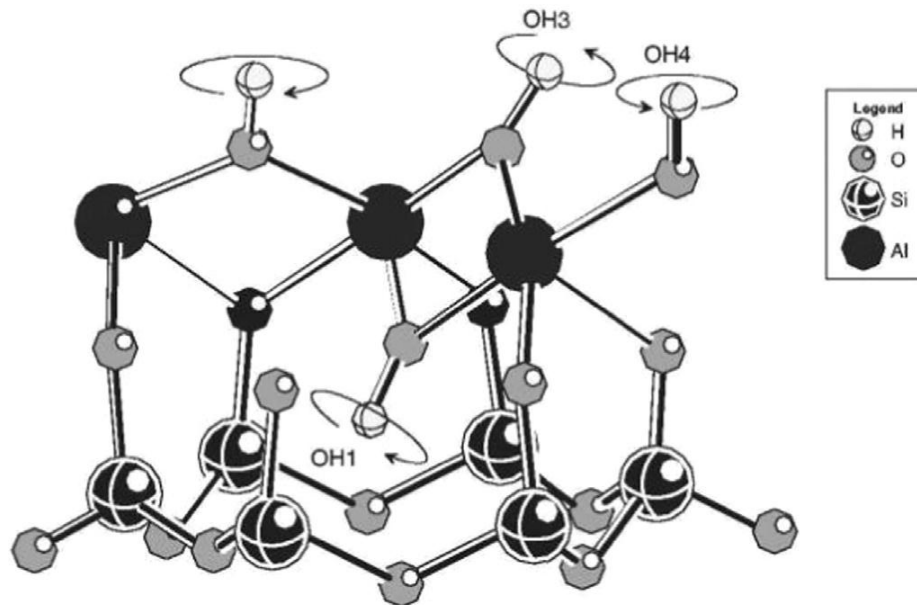
Fig.06. Chemical structure of kaolin.

Ⅲ. 4. X-ray Fluorescence (XRF):

The first kaolin found in the world has the main constituents of 46.54% SiO_2, 39.5% Al_2O_3 and 13.96% H_2O [23]. Furthermore, it is recommended that the total of Fe_2O_3 and TiO_2 is below 0.90%, as they are responsible for the dark color of final products after firing or sintering. Table2 lists the consolidated information of kaolin compositions obtained by various researchers by XRF analysis. Based on the table, the compositions of clays are not the same. This is because the properties of kaolin are different depending on the origin and source of the kaolin collected. Kaolin is abundantly available in many countries of different weather and temperature. **[21]**

Table 04: XRF analysis of kaolin powder.

No	Chemical compositions (wt%)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	LOI
1	48.40	37.00	0.25	0.002	0.05	0.31	0.13	0.46	13.4
2	54.5	29.4	1.4	2.8	0.2	0.2	0.2	0.2	11
3	51.52	36.9	0.96	–	0.08	0.58	–	–	13
4	60.28	30.38	0.70	0.25	0.17	0.22	0.11	6.02	–

Ⅲ. 5. Tamazert kaolin or kaolin (T):

Ⅲ. 5.1. Location:

The Tamazert deposit [4] is located in the North-East of Algeria in the daira of El Milia (wilaya of JIJEL). It is located 17 km north of El Milia and surrounded to the north-west by Jebel Adjar, to the West by Douar Ouled Boufaa, to the South by Douar Boubazine and to the east by the hills of Azrar. The deposit is between longitude 6 ° 5 'and latitude boreal 36 ° 5 '. The Douar M'chatt where the kaolin deposit is located is part of a massif mountainous in the heart of the mountains of the Collo and El Milia Kabylia. The highlight of the region is 701 meters (Ain Sra). The reliefs are relatively steep. Tamazert's kaolin is one of the worlds most formed mainly by a process of hydrothermal alteration of rich feldspars potassium element. **[25]**

Ⅲ.5.2. Chemical and mineralogical composition:

We are particularly interested in this mineralogical group because of its properties well suited to ceramic processes. Kaolin clays are made for the main part, kaolinite that is often associated with other minerals. The presence of quartz is almost systematic, originating from the geological processes of kaolin formation. For the same reasons, impurities in the form of oxides, micas and feldspar.

The classification of kaolinic clays is made according to the Al_2O_3 content of the material calcined. Clays with low alumina content (Al_2O_3 <30% by mass) are generally used in terracotta, while clays rich in alumina (Al_2O_3> 40% in mass) are used for refractory ceramics. Kaolins have a loss on ignition high (10% on average) which is due to the elimination of the water of constitution, to the decomposition of certain associated minerals such as carbonates and the combustion of organic materials.

The chemical composition of a kaolinite corresponding to the structural formula Theoretical $Si_2 Al_2O_5 (OH)_4$ is as follows:

SiO_2 = 46.5%; Al_2O_3 = 39.5%; H_2O = 14.0%.

Kaolinite is a refractory mineral (liquidus temperature of around 1800 ° C), but in combination with minerals such as micas, feldspar or carbonates, the temperature of appearance of a liquid phase

during sintering is lowered. Iron and titanium oxide contents influence the color of the shards ceramics. As for organic matter, it affects the rheology of the suspensions and the behavior of the material during shaping. It is therefore important to complete chemical analysis of kaolin by mineralogical analysis. The main minerals associated with kaolinite in clays used in ceramic technology are:

- illites, micas, muscovite ;

- smectites, chlorite, inter stratified;

- Quartz;

- Feldspar;

- Alkaline earth carbonates;

- Organic materials.

The associated minerals favor a very wide variety of properties of the kaolins. These the latter form with water, colloidal suspensions and plastic pastes, homogeneous, stable and suitable for molding and casting, which is why they are used in many ceramic processes. [26]

Chemical analysis of raw tamazert kaolin are classified in the table below:

Table 05: chemical compositions of raw tamazert kaolin (% by weight).

P.F	SiO_2	Al_2O_3	Fe_2O_3	$Ti O_2$	CaO	MgO	K_2O	Na_2O
5.32	71.57	18.48	0.58	0.15	0.22	0.26	3.15	0.10
5.09	70.72	18.66	0.86	0.32	0.27	0.19	3.83	0.21
4.45	71.5	18.19	1.03	0.34	0.29	0.36	0.36	0.23
4.00	70.22	19.10	1.5	-	0.4	0.33	3.10	-
4.90	70.90	18.70	0.88	0.32	0.01	0.34	3.44	0.12

P.F : perte au feu à 1000°

Ⅲ. 5.3. Application of kaolin:

The most common mineral by far in the kaolin group of minerals is kaolinite. Its physical and chemical properties and applications are discussed in this section. The physical and chemical properties of kaolin determine its use as an industrial mineral. These uses are governed by several factors including the geological conditions under which the kaolin formed the total mineralogical composition of the kaolin deposit, and the physical and chemical properties. Kaolin deposits can be sedimentary, residual, or hydrothermal and in almost every instance, the kaolin has different properties and thus must be fully tested and evaluated to determine its utilization. [27]

Table 06: Traditional applications of kaolin.

Paper coating	Plastic filler	Adhesives
Paper filling	Ink extender	Enamels
Paint extender	Cracking catalysts	Pharmaceuticals
Ceramic ingredient	Fiberglass	Crayons
Rubber filler	Cement	Molecular sieves

Ⅲ. 6. Conclusion:

Kaolin is one of the most used low cost ceramic materials in production of ceramic membrane. Kaolin based ceramic membrane has received much attention in many applications as filters as well as supports and substrates of composite membranes.

Chapter Ⅳ

Sol-Gel method

Chapter Ⅳ: Sol-Gel method

Ⅳ.1. Introduction:

Sol-gel chemistry is a versatile tool that can be used to produce organic and inorganic hybrid materials that have properties that can be difficukt to obtain from only inorganic or organic synthetic approaches. The synthetic approach involves the polycondensation of sol-gel active molecules to form a macromolecular network structure.

Ⅳ. 2. Definition:

The sol-gel synthetic technic is used to fabricate a porous structure composed of transition metal alkoxides. These structures most commonly use a siloxane (Si-O) to form the backbone structure. The the synthesis of sol-gels involves a hydrolysis of a silicon monomer followed by the condensation of the silica into a porous structure with a three dimensional networked structure. The physical structure of these sol-gels can be tailored to produce structures with a wide range of useful properties and the chemical surface chemistry can be modified to produce various surface interactions. **[28]**

Ⅳ. 3. Methode of Gel Production:

There are four methods for the production of gels-

- Flocculation of lyophilic- colloids by salts or precipitating liquids.
- Evaporation of certain colloidal solutions.
- Chemical reactions that lead to change in shape of lyophilic molecules (e.g. the denaturation of albumen on heating involves some uncoiling of the protein molecules and a gel structure results).
- Swelling of a dry colloid (xerogel) when placed in contact with a suitable liquid (e.g. starch granules added to water).**[29]**
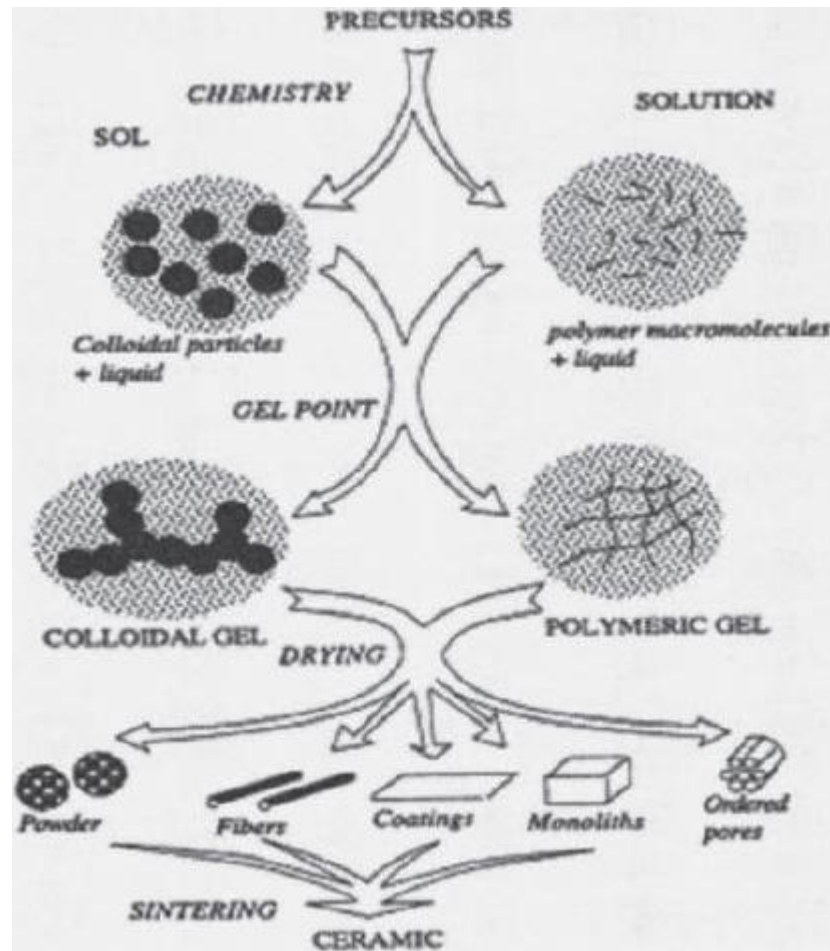
Fig.07. Schematic diagram of the sol-gel process.

Ⅳ. 4. Sol-gel applications:

The sol-gel process hasmany parameters to be controlled over the process. However, the process itself has a direct relation with its gelstate, as there are many shapes could be derived from this state such as fibers, powders and thin films. On the other side, the composition of the solution and curing temperature and time are vital in achieving a high quality coating layer. In the following sections, some of the current and potential applications of sol-gel coating are covered.

Ⅳ. 4.1. Thin films:

Thin films are types of layers ranging in thickness from fraction of nanometers to fraction of micrometers. These films could be used as light barriers, reflectors, storage means, corrosion resistant layers, adhesion improvement layers, conduction enhancement, etc. [30]

Ⅳ.4.2. Composites:

Composite sol-gel compounds are getting attention in cases that reinforced structure or matrix is needed. In the recent research reports, sol-gel composite layers such as SiC and alumina reinforced materials are of interest in applications such as turbine blades and ceramic tools.

Previously, these materials were fabricated by hot-pressing and composite layer assembly while the sol-gel process increases the easiness of the composite coating process. The sol part of the process has low viscosity and can easily penetrate to the complex geometry corners and create a reliable layer. **[30]**

Ⅳ.4.3. Nanoscale Powders:

In the process of precipitation, ultra-fine and uniform ceramic powders can be formed which are powders of single and multiple component compositions of nanoscale particle size for dental and biomedical applications. Composite powders have been patented for use as agrochemicals and herbicides. Powder abrasives, used in a variety of finishing operations, are made using a sol-gel type process. One of the more important applications of sol-gel processing is to carry out zeolite synthesis. Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicate sol formed by this method is very stable.

Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, pervaporation and reverse osmosis. When the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density material called aerogel is obtained. On drying the gel by means of low temperature treatments (25-100 °C), it is possible to obtain porous solid matrices called xerogels. In 1950s, a sol-gel process was developed for the production of radioactive powders of UO2 and ThO2 for nuclear fuels, without generation of large quantities of dust. **[31]**

Ⅳ.4.4. Opto-mechanical:

Sol gel route can be used to make macroscopic optical elements and active optical components as well as large area hot mirrors, cold mirrors, lenses and beam splitters all with optimal geometry at low cost. In the processing of high performance ceramic nanomaterials with superior opto-mechanical properties under adverse conditions, the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during the synthesis or formation of the object. Thus a reduction of the original particle size well below the wavelength of visible light (~ 0.5 μm or 500 nm) eliminates much of the light scattering, resulting in a translucent or even transparent material. **[31]**

Ⅳ.5. Advantages and drawbacks of sol-gel method:

Ⅳ.5.1. Advantages:

- VersatileVersatile: better control of the structure, including porosity and particlesize; possibility of incorporating nanoparticlesand organic materials into sol-gel-derived oxides;

- Extended composition ranges Extended ranges: it allows the fabrication of any oxide composition, but also some non-oxides, as well as the production of new hybrid organic-inorganic materials, which do not exist naturally;

- Better homogeneity Better homogeneity: due to mixing at the molecular level; high purity high purity;

- Less energy consumption: there is no need to reach the melting temperature, since the network structure can be achieved at relatively low temperatures near Tg;

- Coatings and thin films, monoliths, composites, porous membranes, powders and fibers;

- No need for special or expensive equipment.

Ⅳ. 5.2. Drawbacks:

- Cost of precursors;

- Shrink age of a wet gel upon drying, which often leads to fracture due to the generation of large capillary stresses and, consequently, makes difficult the attainment of large monolithic pieces;

- Preferential precipitation of a particular oxide during sol formation(in multi component glasses) due to the different reactivity of the alkoxide precursors;

- Difficult to avoid residual porosity and OH groups. **[32]**

Chapter V

Experimental part

ChapterⅤ: Experimental part

Part One : Characterization

Ⅴ.1. Strategy to follow:

During the experimental part, we will follow a certain methodology which consists in developing membranes based on kaolinite, followed by an improvement of these membranes by the deposition of an inorganic gel prepared by the sol gel methods. Before proceeding to the filtration tests we characterized these membranes by different techniques, DRX, XRF, FTIR, NAA, DSC and UV.

Ⅴ. 2. Synthesis of membranes:

First, we developed these membrane supports only with Kaolin KT2 from El-Milia, a series of membranes based on kaolin KT2 cooked at 1100°C. The membrane synthesis method is based on:

Ⅴ.3. Cooking membrane supports:

Kaolins, alone or mixed with other compounds, are transformed by cooking at high temperature, into ceramic products. Cooking allows agglomeration of the various compounds by sintering and vitrification.

Kaolins undergo significant and irreversible transformations at each temperature range during cooking, to give, in the end, totally different materials from the point of view of physical, mechanical, thermodynamic, or structural characteristics.

The cooking of kaolins therefore consists in a first step, for temperatures between 600 and 900°C, destruction of the kaolinite (or halloysite).

The second step, which corresponds to cooking temperatures above about 900 ° C, where we see the appearance and then the transformation of various crystalline phases, depending on the temperature range as well as the appearance and evolution also of one or more several vitreous phases which will play a large role in the mechanical, thermodynamic and thermal properties of refractory materials. **[33]**

The different stages of structural transformations as a function of temperature are as follows (Table 07).

Table07: Transformation of kaolin as a function of the calcination temperature

Temperature range	Kaolin transformation steps
Ambient→110° C	Mixing water
110°C →500 TO 600°C	Structural water shrinkage: 20% by volume, 7% linear

600 →700°C	Kaolinite→ meta-kaolinite: $Al_2O_3 2SiO_2$
700 →800°C	Weakening of the structure of meta-kaolinite
800 →900°C	Decomposition of meta-kaolinite →γ alumina, spinel
900 → 1000°C	mullite 3 $Al_2O_3 2SiO_2$ crystallization
1000 →1100°C	Crystallization of cristobalite SiO_2
1100 → 1500°C	Development of mullite crystals Development of cristobalite crystals Glass phase development
>1500°C	D↗ , porosity↘, shrinkage of 30% by volume and 10% linear Softening by vitrification

Ⅴ. 4. Gel Preparation:

Ⅴ. 4.1. Sol-Gel Method:

Sol-gel processes (or solution - gelation) allow the production of vitreous materials, possibly micro-porous to macro-porous by polymerization (and possibly thermal) without receiving melting.

The sol-gel application is a contraction of the terms "solution - gelation". Before the gel state is reached, the system is in the liquid state: it consists of a mixture of colloidal oligomers and small macromolecules as well as, depending on the degree of progress of the polymerization reaction, different partially hydrolyzed monomers.

Sol-gel techniques make it possible to control the size and the homogeneity of the particle distribution. They allow the production of solid parts, deposits of thin layers on plates, fibers or fibrous composites. **[34]**

Ⅴ. 4.2. Principle:

The sol-gel process makes it possible to manufacture an inorganic or hybrid polymer. The synthesis is carried out from alcoholates of formulas M (OR) n or M is a metal or silicon and R is an organic alkyl group CnH2n + 1. Solid particles (denser thanthe liquid) must be very small so that the gravitational forces do not exceed those which are responsible for the homogeneous dispersion of these particles in the liquid then in the gel (three-dimensional network of connection of van der Wales). The gelling reaction takes a certain time (known as freezing time or freezing point). **[35]**

Ⅴ. 4.3. Characteristics of sol gel:

The gel consists of an oxide network swollen by the solvent, with chemical bonds ensuring the mechanical cohesion of the material by giving it a rigid non-deformable character.

Ⅴ. 4.4. Chemical aspects of sol-gel polymerization:

It is possible to carry out sol-gel polymerization from precursors other than alkoxides (for example, from halides). Since these are the subject of 95% of the work described in the literature.It is possible to carry out sol-gel polymerization from precursors other than alkoxides (for example, from halides). Since these are the subject of 95% of the work described in the literature. [36]

Sol-gel polymerization can be "hydrolytic", that is to say require the addition of water and therefore include one or more hydrolysis steps or, on the contrary, be "non-hydrolytic" when it is performed without water. The case of hydrolytic gels is by far the most important and the most answered.

In our case we used a hydrolytic sol-gel, the method of preparation is as follows:

3.94 g of NiCl, 3.11 g of AlCl₃, 100 ml of methanol are mixed, the mixture is heated to 100 ° C. with stirring for a period of one hour (01 h), followed by adding drop by drop 4.34 g of acetic acid of 80% concentration, plus 30 ml of dimethyl glycol and 50 ml of distilled water. With heating with a hot plate at 80 ° C and stirring leaves the mixture until the gel forms.

Fig.08. Photo shows the preparation of the gel.

Ⅴ. 4.5. Application:

The applications of sol-gel materials are numerous. As sol-gel chemistry is a "soft" method of glass making, the main use is in the production of thin layers of glass of varying composition.

The sol-gel process has great potential for the development of thin films. These main advantages are simplicity, speed, simultaneous coating of the two faces and the possibility of forming multilayers. **[37]**

Ⅴ. 5. Elaboration of ceramic membranes:

Concerning the preparation of the membranes and the tests of the water treatment performances, the operations were carried out at the level of the National Institute of Soils, Irrigation and Drainage (INSID), Ksar Chellala station.

The cooking operations and characterization analyzes of the membrane supports and the UV-Visible spectrometer analysis of the permeate produced by the membrane were carried out at the CRNB Nuclear Center. The membrane supports in our case, are prepared based on kaolinite KT2 from El-Milia, they are obtained by the casting method, and the steps for preparing a membrane are summarized in the following diagram:

```
┌─────────────────────────────────────┐
│  Mineral Powder + Distilled Water    │
└─────────────────────────────────────┘
                  ↓
┌─────────────────────────────────────┐
│              Mixing                  │
└─────────────────────────────────────┘
                  ↓
┌─────────────────────────────────────┐
│               Slip                   │
└─────────────────────────────────────┘
                  ↓
┌─────────────────────────────────────┐
│             Casting                  │
└─────────────────────────────────────┘
                  ↓
┌─────────────────────────────────────┐
│             Cooking                  │
└─────────────────────────────────────┘
                  ↓
┌─────────────────────────────────────┐
│          Final Product               │
│        (Membrane Support)            │
└─────────────────────────────────────┘
```
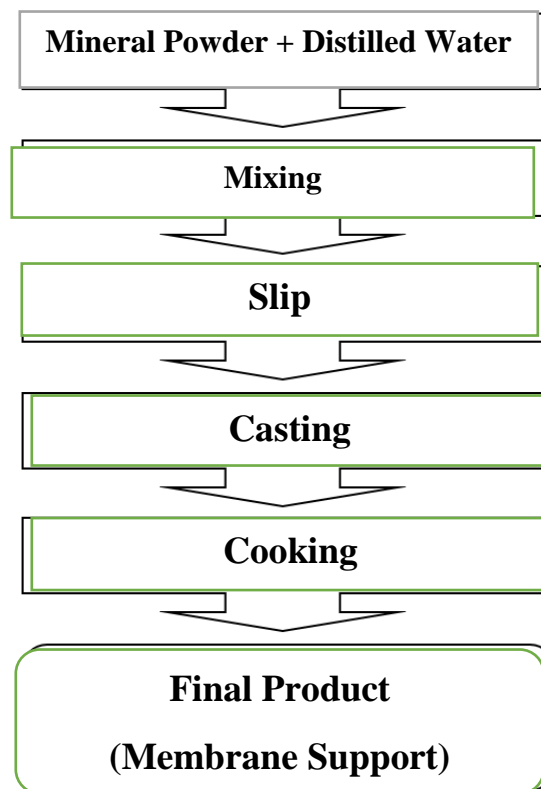
Fig.09. Flowchart showing the different stages in the production of a membrane support.

Chapter Ⅴ : Experimental part

Ⅴ. 5.1. List of materials and equipment:

Ⅴ. 5.1.1. Materials used in the operation of the synthesis of membranes:

- Balance
- Agitator
- Oven
- Mortar: for manual clay grinding,
- Sieve: After grinding, the montmorillonite was sieved through a 100 μm sieve,
- Water bath: used for the immersion of polymer solutions,
- Glassware: Beakers, flask, test tube pipettes,… etc.
- Oven for baking: Nabertherm brand Max temperature is 1300 ° C.

Ⅴ. 5.1.2. Equipment used during membrane characterizations:

- DRX: Diffractometer system = XPERT-PRO MPD (PHILIPS);
- XRF;
- FTIR;
- AAN: The spectrometry software *GENIE* 2000;
- DSC;
- UV-Visible.

Ⅴ. 5.2. Preparation of membranes based on raw kaolin:

The first step in our practical work is the preparation of kaolin-based membrane supports.

The process for developing membrane supports includes the following steps:

Ⅴ. 5.2.1. Mixing and molding:

- Kaolin is crushed in a grinder to reduce its particle size, then kaolin is added in an amount between 350 to 400 g of distilled water (300ml) little by little until a homogeneous mixture is obtained;
- Stirring until the mixture becomes sufficiently viscous;
- The membrane supports are obtained by the method of casting in plaster molds;
- Separation of the membrane supports from the plaster mold and then dry in the open air for 24 hours;
- The membrane support is then baked in an oven at high temperature.

Fig.10. Photos show the membrane molding tool.

Ⅴ. 5.2.2. Drying:

The membranes are placed on an absorbent paper to avoid their deformation and to allow homogeneous drying at room temperature, the drying is composed in two stages:

- Primary drying: the duration is approximately 24 hours and at room temperature;
- Secondary drying: it is carried out in an oven for 48 hours and at a temperature of 70 to 80C.

Fig.11. Photo shows the Oven used for drying of the membranes.

Ⅴ. 5.2.3. The cooking:

The firing is carried out in a muffle furnace at very high temperature, in our case the firing was carried out at the reactor chemistry laboratory level at the Birine nuclear research center, the firing program followed is as follows:

- A rise of 5 ° C / min in temperature up to 200 ° C with a two hour stage for the complete elimination of the water which was not eliminated during the drying as well as any water absorbed after drying.
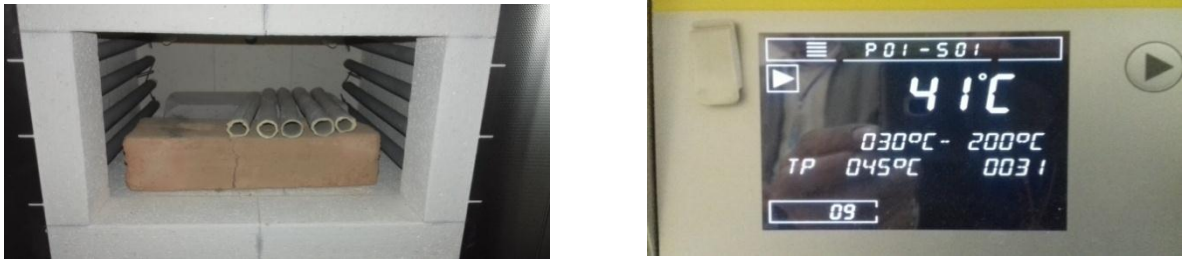
Fig.12. photos show membranes during cooking.

- Then increase the temperature to 573 ° C, for 2 hours, when will be the transformation of quartz from α form to β form.
- Then increase the temperature for 5 hours to 1100 ° C for the first series of membranes and to 1250 ° C for the second series.

.

Fig.13. Pictures of the baking oven.

Ⅴ. 6. Characteristics of the supports produced:

The second step in this work is to characterize by different methods and analyze our ceramic support, this characterization was carried out by the following analyzes:

Ⅴ. 6.1. Shrinkage study:

The length of a ceramic support is measured before and after firing to determine shrinkage. The shrinkage of the membrane support is represented with the following formula:

$$R_1 = (\% \text{ total shrinkage}) = [(L_i - L_c)/L_i].100 \dots\dots\dots\dots\dots\dots\dots\dots \text{(Eq.08)}$$

Where:

L_i: Initial length;

L_c: Length after cooking.

The following table shows the shrinkage of two spoon samples at 1100 ° C:

Table 08: Variation in the shrinkage rate as a function of the cooking temperature.

Membrane cooked at :	Length before cooking Li [cm]	Length after cooking Lc [cm]	R total shrinkage %
1100 °C	27	25.9	4.07

According to the results obtained, the shrinkage is low for the temperature 1100 ° C.

Ⅴ. 6.2. Loss on ignition:

The weight loss expressed in (%) is the weight loss of a sample after calcination at 1100 ° C, relative to the initial weight. It allows to know the quantity of products likely to decompose or volatilize during cooking. The loss on ignition was measured by placing a quantity of clay in a previously tared porcelain crucible, its weight P_1. The crucible is placed in an oven, with a gradual increase in temperature to 1000 ° C for 1 hour. The crucible was then removed and put in a desiccator to cool and weighed, its weight P_2. **[37]**

The value of the loss on ignition is given by the following relation:

$$\text{LOI} = \frac{(P_1 - P_2)}{P_1} \times 100; \qquad P_1 = 5,0010g; P_2 = 4.3813g;$$

LOI in our case is: LOI=12.39%.

Ⅴ. 7. Characterization of clay-based membranes:

Different analysis techniques were used in this work to characterize the structure of membranes such as X-ray diffractogram (XRD), Fourier transform infrared (FTIR), XRF, and analysis by neutron activation. (AAN).

Ⅴ. 7.1. X-ray diffractometry (XRD):

One of the most widely used techniques for identifying minerals is XRD. Any crystallized body can be analyzed by XRD; an X-ray beam is diffracted on a lattice of crystal planes according to Bragg's law: $2d_{hkl}\sin(\theta) = n\lambda$; **[39]**
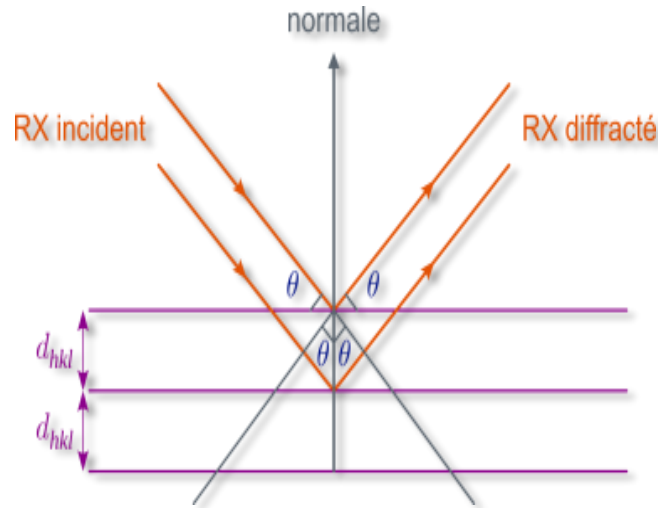
Fig.14. X-ray diffraction according to Bragg's law.

We carried out the XRD analyzes for our membranes at the laboratory level of the Nuclear Techniques Division (DTN) of the Nuclear Research Center of Birine, we carried out the analysis of crude kaolin KT2 from El-Milia and the membrane baked at 1100 ° C and the other 1250 ° C.

Fig.15. Photos of the DRX Equipment used.

The equipment used is a Philips type PW1710 diffractometer equipped with a copper anticathode ($\lambda = 1.5406$ Å) operating at a voltage of 45 kV and an intensity of 40 Ma. The spectra are recorded. in a 2θ angle range between 20 and 70°. The 2θ measurement step is 1° with an accumulation time of 1 second per step. The processing of the diffractograms was carried out using the X'PertHighScore Plus software version 2.1 (2004) edited by PAN analytical **[40]**

Ⅴ. 7.2. Fourier transform infrared spectroscopy analysis, FTIR:

Fourier Transform Infrared Spectroscopy (FTIR) - is an analytical technique for obtaining the absorption spectrum of a solid, liquid or gas sample. Non-destructive in nature, FTIR spectroscopy measures the amount of light absorbed by a sample as a function of the wavelength emitted by an infrared beam [41]

The measurements were carried out at the level of the rectors' chemistry laboratory at the Birine nuclear research center, with the instrument of the BRUKER Alpha brand.

Fig.16. Photo of FTIR BRUKER ALPHA equipment with ATR.

Ⅴ. 7.3. X-ray fluorescence analysis (XRF):

X-ray fluorescence (XRF) is a non-destructive technique that is used to quantify the elemental composition of samples, generally, this technique can be used for every varied materials: minerals, ceramics, cements, metals, oils, water, glasses ... in solid or liquid form [42]

X-rays are used to excite the atoms in the sample, causing them to emit X-rays with energy characteristic of each element present. The intensity and energy of these X-rays are then measured very varied materials: minerals, ceramics, cements, metals, oils, water, glasses ... in solid or liquid form [42].

X-rays are used to excite the atoms in the sample, causing them to emit X-rays with energy characteristic of each element present. The intensity and energy of these X-rays are then measured.

Fig.17. Operating principle of the XRF technique.

The basic measurements of the clay were carried out at the rectors' chemistry laboratory at the Birine nuclear research center, with the instrument of the brand: Thermo Scientific Niton XL2 XRF portable.
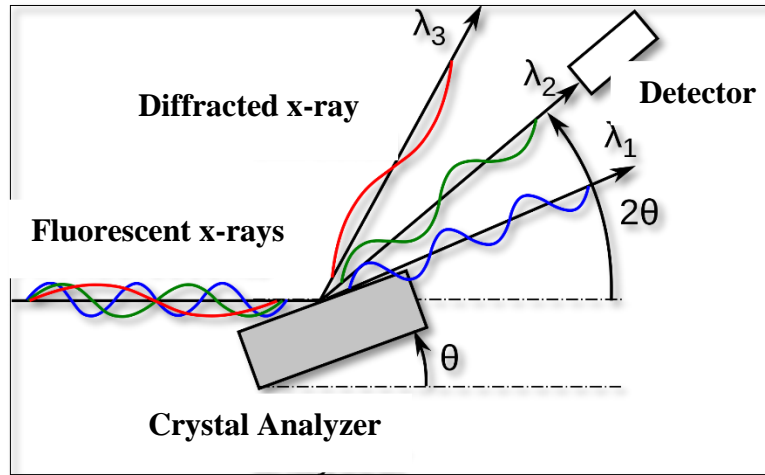
Ⅴ. 7.4. Neutron activation analysis:

Neutron activation is an analytical, sensitive and precise method, allowing the identification as well as the quantification of the elements present in a sample. Indeed, this technique allows an analysis of the characteristic gamma rays that were emitted during decay after they irradiated in a nuclear reactor. These energy signatures will allow the identification of the targeted compounds present while their count rate will be proportional to their concentration in the sample**. [43].**
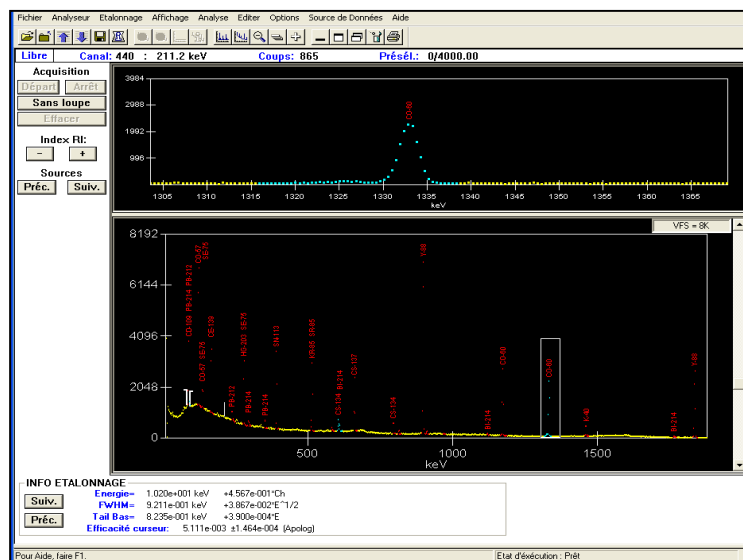
Figure.18. Example of a window showing the display of a spectrum.

Ⅴ. 7.5. Differential Scanning Calorimetry (DSC):

Differential scanning calorimetry is a thermal analysis technique used to measure the difference in heat emitted or absorbed by the material to be studied and a reference considered inert (Argon). Among the classic applications of DSC, we can mention:

(i) The determination of the glass transition temperature;

(ii) Measurements of crystallinity;

(iii) The study of phase transformations;

(iv) Measurement of heat capacities [44].

The CRNB has a Setsys-Evolution 1500 DSC device with SETSOFT2000 shown in Figure IV.15. We used this technique to reinforce in this study the identification of the existing phases during the heat treatments carried out.
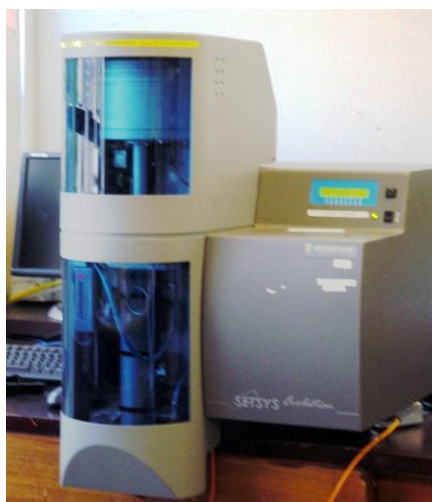
Fig.19.Photo of Setsys-Evolution 1500 DSC equipment.

Ⅴ. 7.6. Ultra-Violet-Visible Spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrometry is a spectroscopy technique involving photons whose wavelengths are in the ultraviolet (200 nm - 400 nm), visible (400 nm - 750 nm) range) or near infrared (750 nm -1 400 nm). When subjected to radiation in this range of wavelengths, molecules, ions or complexes are liable to undergo one or more electronic transitions. The substrates analyzed are most often in solution, but can also be in the gas phase and more rarely in the solid state. The electron spectrum is the function which relates the light intensity absorbed by the sample analyzed as a function of the wavelength [45]

Chapter Ⅴ : Experimental part

The analysis by this technique, which is very practical, in the field of water treatment was carried out at the CRNB Center in the chemistry laboratory. This assay is widely used for the characterization of dyes.
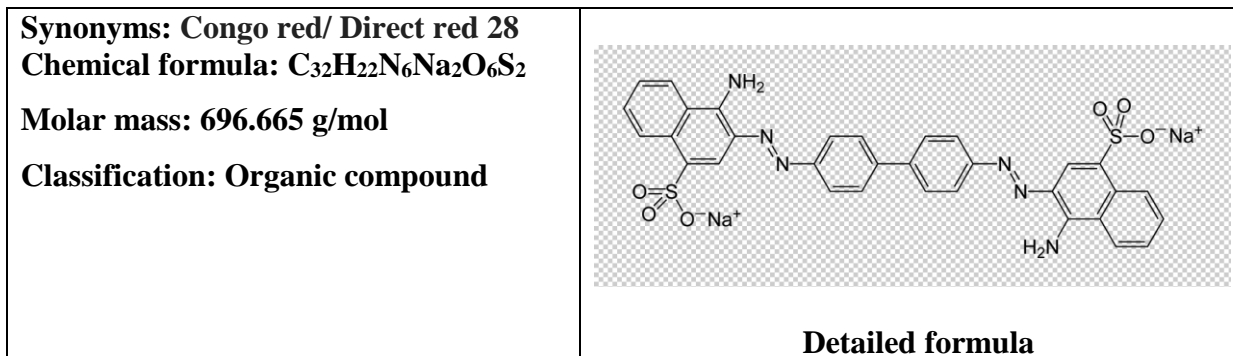
Ⅴ. 8. Preparation of water colored by Congo red:

Ⅴ. 8.1. Nature of the dye Congo red:

Congo red (CR) is a benzidine-based anionic diazo dye that can cause allergic reactions and can be metabolized to benzidine, a carcinogenic product. Depending on pH, various molecular structures of CR can be present in aqueous solution, which hinders its elimination.

Table09: Table show the form of each color.

Color	Form
Bleu	Below PH = 03
Red	Above PH = 5.2

This dye changes from blue to red at pH 3.0–5.2, Congo red can be used as a pH indicator. Since this color change is an approximate inverse of that of litmus, it can be used with litmus paper in a simple parlor trick: add a drop or two of Congo red to both an acid solution and a base solution. Dipping red litmus paper in the red solution will turn it blue, while dipping blue litmus paper in the blue solution will turn it red. This property gives Congo red a metachromatic property as a dye, both in strongly acidic solutions and with strongly acidophilic tissue.

Synonyms: Congo red/ Direct red 28 **Chemical formula: $C_{32}H_{22}N_6Na_2O_6S_2$** **Molar mass: 696.665 g/mol** **Classification: Organic compound**	 **Detailed formula**

Fig.20. Detailed formula of Congo red dye.

Part Two: Tests

Ⅴ. 9. Experimental setup:

After design, production and characterization of ceramic membranes, we will move on to their tests on the appropriate experimental set-up.
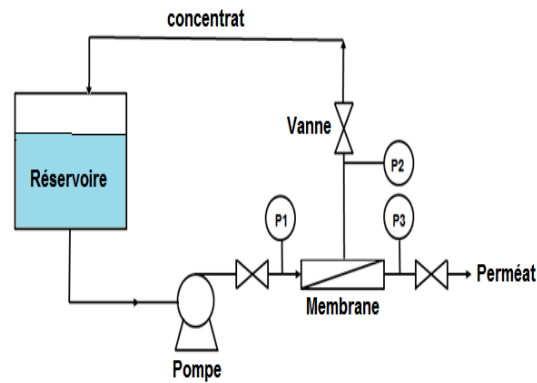
Fig.21. Synoptic diagram of the experimental setup.
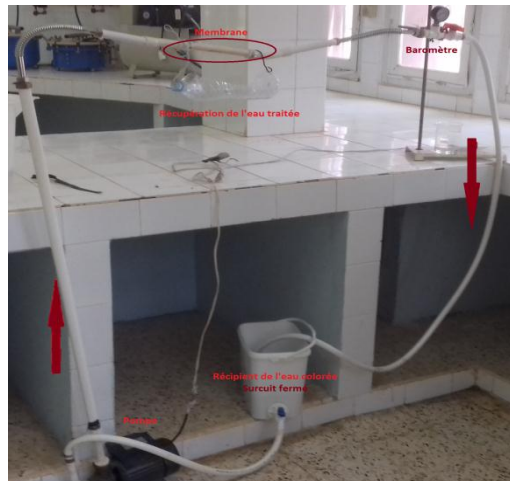
Fig.22. Photo of laboratory setup.

Fig.22 shows the various components of the test bench in order to qualify the ceramic membranes designed:

1. Pump Max 0.8 Bar;

2. A 20 liter capacity tank;

3. Shut-off valves;

4. The membrane.

5. Barometer

6. Treated water collection container

Ⅴ. 9.1. Results interpretation:

This chapter recapitulates all the results found in this study, we start with the results of the characterization of ceramic membranes, followed by the retention of these membranes under different operating conditions.

Ⅴ. 9.2. X-ray diffraction (XRD):

Diffractograms were obtained from disoriented samples (placed directly in powder form in a sample holder). The XRD diffractogram of the raw clay and that heat treated at 1100 is shown in Figure23 and Figure24. Spectral analysis indicates that it is composed of Quartz (SiO_2), Calcite Ca (CO_3), Kaolinite ($Al_2Si_2O_5$ $(OH)_4$), Illite [(K, H_3O) $Al_2Si_3AlO_{10}$ $(OH)_2$] and vermiculite [(Mg, Al)$_3$ (Si, Al) $4O_{10}$ $(OH)_2.4H_2O$]. It mainly reveals the presence of two intense peaks, one corresponds to Calcite and the other to a mixture of Quartz, Illite, Kaolinite and Vermiculite, which implies that our clay is heterogeneous.
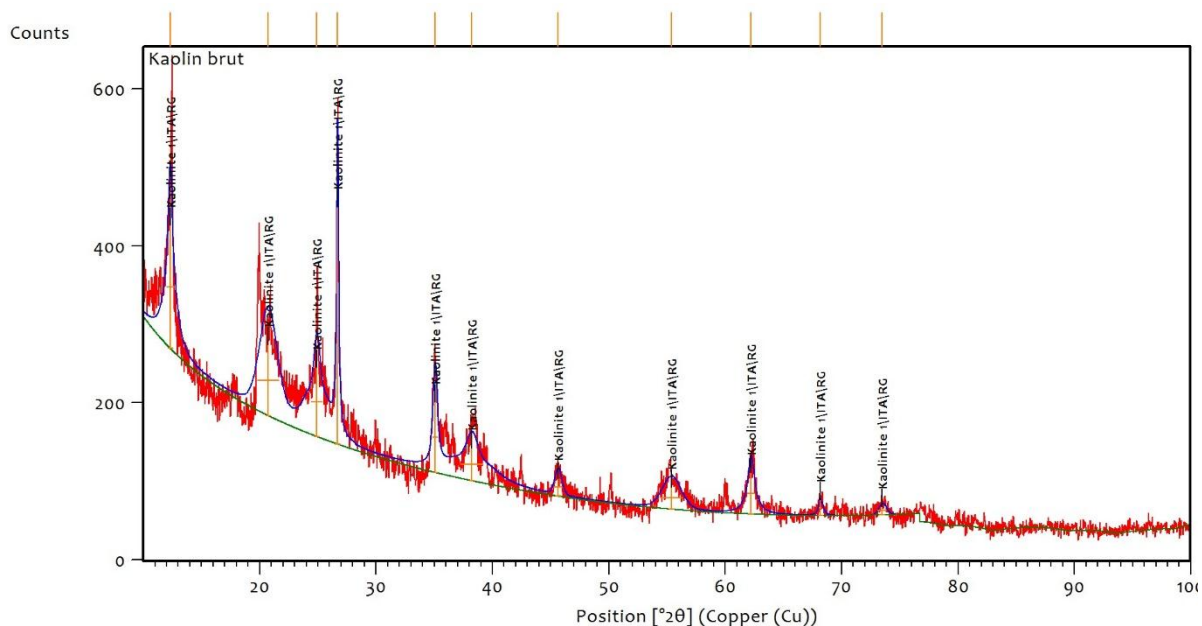
Fig.23. Diffractogram of raw kaolinite.

The clay fraction of our material consists of Quartz and Calcite as a major impurity in our sample, this confirms the results of the X-ray fluorescence which shows high proportions of SiO_2 (Quartz) and Calcite.
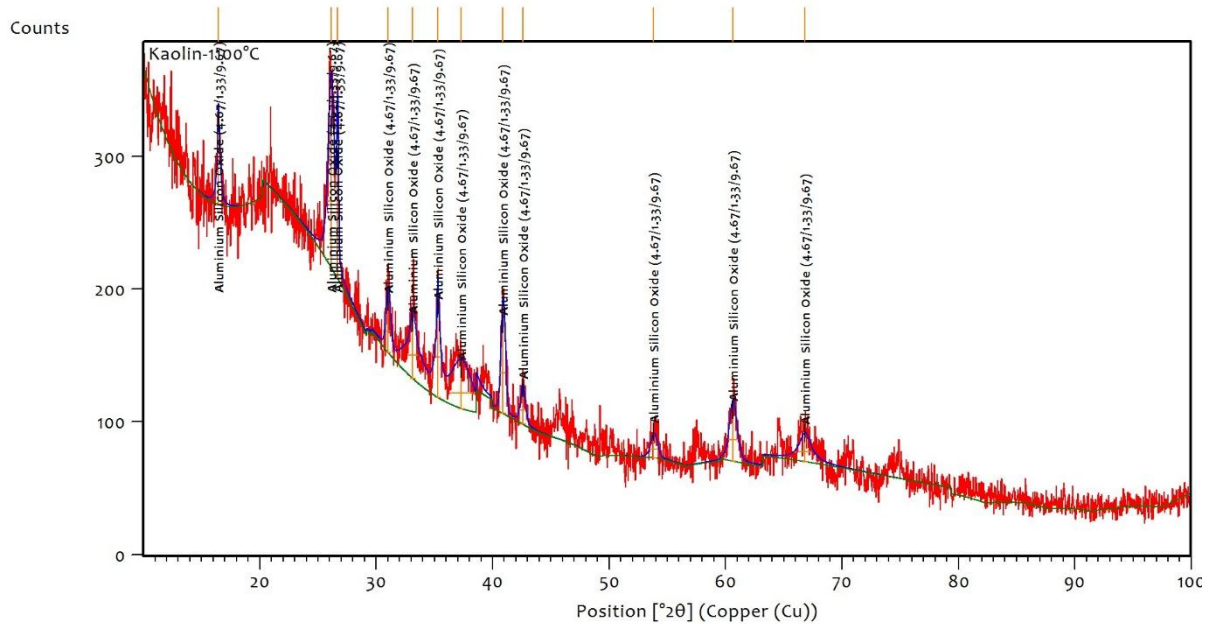
Fig.24. Diffractogram of kaolinite spoon at 1100 ° C.

Ⅴ. 9.3. Infrared (IR):

Infrared spectroscopy was used to complete the analysis of the clay sample. The spectra obtained are illustrated in Figure25. We aknowledge:

Two absorption bands located between 3200-3800 cm-1 and between 1600-1700 cm-1

- The band that extends between 1600-1700 cm-1 can be attributed to the valence vibrations of the OH group of the constituent water, in addition to the binding vibrations of the adsorbed water located at 1646.2.
- The band which extends between 3200-3800 cm-1, located at 3614.0 cm-1 corresponds to the vibrations of elongation of the internal –OH groups.

The Si-O bond is characterized by:

- The intense band located between900-1200 cm-1 and centered around 1008.9 cm-1 corresponds to the valence vibrations of the Si-O bond **[46].**
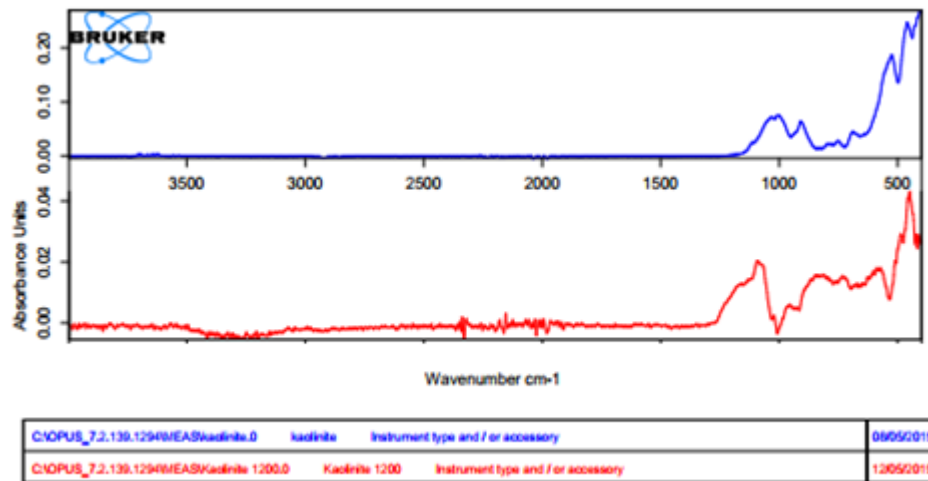
Fig.25. IR spectra of sample.
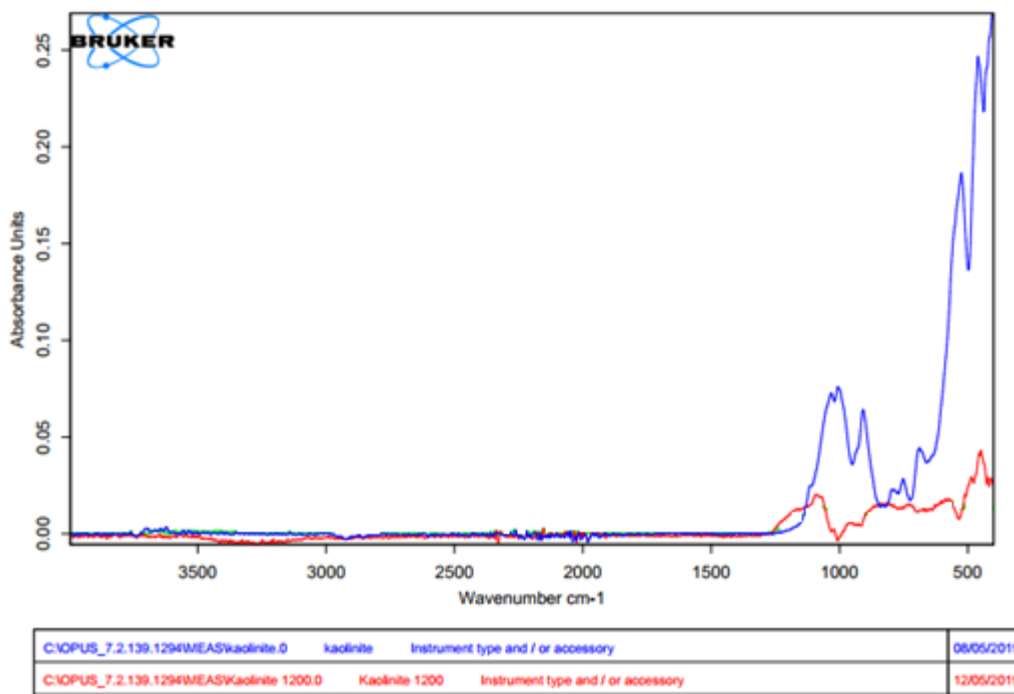
Fig.26. Merged IR spectra of the two samples.

The bands between 795 and 748 cm-1, originating from the Si-O-Al bond, also give way to a band around 778.4 cm-1 **[47].** The absorption bands located at 1008.9 cm-1 are consistent with the XRD indicating the presence of Kaolinite in the clay. The bands observed at 798 cm^{-1} are attributable to the vibrations of elongation of Si-O-Al bonds and to hydroxyls perpendicular to the surface (–OH translational) **[48].** The 663 cm-1 band is characteristic of the deformation vibrations of hydroxyls in tri-octahedral clay minerals in general.

Nevertheless, the absorption bands at 797 and 779 cm-1 may correspond to Quartz **[49].** The 872.6 cm^{-1} band corresponds to the presence of calcium carbonate $CaCO_3$. **[50]**

These results are in agreement with those found from DRX. They confirm the presence of Quartz, Kaolinite and Illite in the clay studied. Table10 groups together the vibration and strain bands from figure26.

Table10: Main infrared bands characteristic of the clay studied.

The bands cm^{-1}	Attributions
3500	3200-3800 O-H water
1100	900-1200 Si-O
1071	Characteristic connections of K_2O
900-1000	C-O bonds of calcium carbonate
800	Si-O-Al bonds
780	Quartz
630	Si-OH or Si-O (strain) and / or Al-O (elongation) bonds
558	Characteristic bonds of Fe_2O_3

V. 9.4. X-ray fluorescence spectrometry (XRF):

The XRF analysis showed the efficiency of the heat treatment, from this analysis, it appears that the clay fraction contains large amounts of silica (61.15% -55.63) and alumina (33.6% -25.7). The iron oxide has a titer equal to (2.8%), while the other oxides are present with low contents. The loss on ignition is (12.39%), a value not very far from that of kaolinite (13.9%).

It was found that the SiO_2 / Al_2O_3 ratio which characterizes the free quartz is around 2.0, which indicates a high kaolinite content, thus the majority elements silicon and aluminum and little iron as it is presented. In the table.

Table11: Elemental chemical composition of crude kaolinite; at 1100°C.

	Brute	1100 °C
	%	
SiO$_2$	61,155	56,155
MnO	0,000	0,000

CuO	0,024	0,024
ZnO	0,008	0,008
MgO	0,000	0,000
AL_2O_3	33,672	25,672
P_2O_5	0,771	0,271
Fe_2O_3	2,779	2,279
K_2O	3,091	2,591
LOI	12,390	

Ⅴ. 9.5. Neutron Activation Analyzes (NAA):

The analysis by AAN of crude kaolin, KT2 from El-Milia, is carried out exclusively at the Birine Nuclear Research Center, the results are presented in the table below:

Table12: Table represents the values found after the analysis of the irradiated sample.

| CHEMICAL ELEMENT	Concentration mg/Kg	CHEMICAL ELEMENT	Concentration mg/Kg	CHEMICAL ELEMENT	Concentration mg/Kg
K%	2,53	Ga	33,5	Yb	4,861
Fe%	1,43	Pr	26,73	Co	4,795
Na %	0,116	Sm	26,43	Eu	3,357
Ba	354,3	Th	25,76	Tb	2,413
Ce	153,4	As	16,76	W	2,004
Rb	131	Cs	15,45	Br	1,76
Sr	126,4	U	13,87	Tm	1,301
Nd	117,3	Cr	9,934	Ta	0,959
La	92,59	Sc	9,404	Hf	0,71
Zn	80,44	Sb	5,785		

We notice that the main compounds silicon and aluminum do not appear in the results presented in Table12, this is due to the measurement time of the sample is greater than the half-life of these elements (very short 3.60 sec for aluminum Al-30 and 4.16 sec for silica Se-27) which implies non detection. We also note that the actinide and lanthanide elements are presented.

Ⅴ. 9.6. Differential Scanning Calorimetry (DSC):

The availability of differential scanning calorimeter (DSC) equipment at the CRNB Center allowed us to analyze kaolin by this technique.

The measurements are made under an argon sweep at a pressure of 120 mm Hg at the heating rate of 10 ° C / min. The studied temperature range can go up to 1100 ° C. Figure27 represents a curve of the DSC where we have plotted the change in enthalpy as a function of temperature.
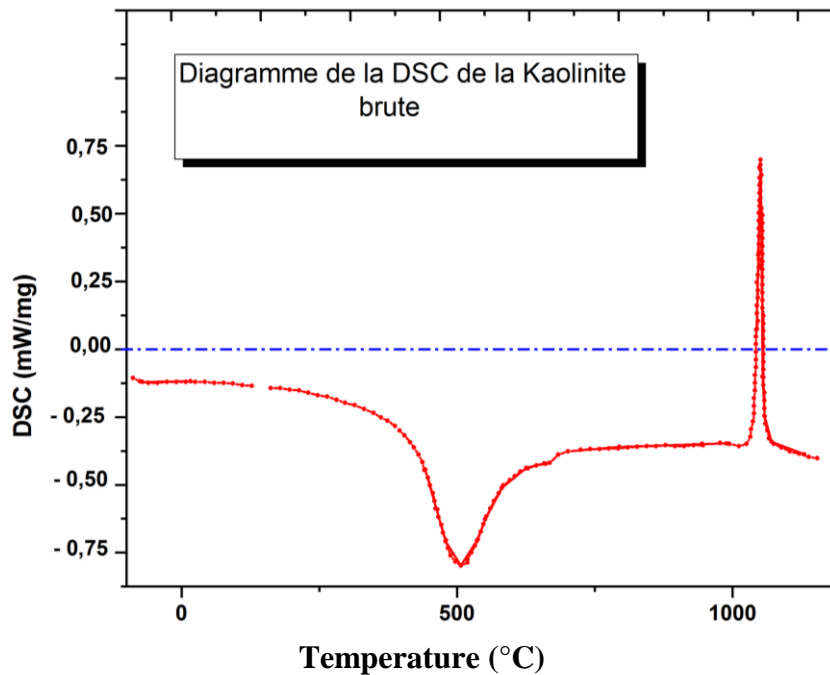
Fig.27. DSC spectrum for crude kaolin.

The figure above shows two endothermic peaks and one exothermic peak. The endothermic peaks are located at 535 ° C and at 672 ° C these two peaks correspond to the de- hydroxylation of its main component which is kaolinite (Al2Si2O5 (OH) 4). The exothermic peak which appears at the temperature 998 ° C (approximately 1000 ° C) comes from the formation of mullite.

Ⅴ. 10. Filtration tests:

After we have characterized the produced membranes, now we proceed to the filtration tests in order to qualify them.

In this part that includes the test of our produced ceramic membranes, experiments cannot be done as a result of the pandemic situation related to the spread of COVID-19, no corporation, public nor private, has granted any internships during the period of the pandemic;

Hence, we will take a look at what we were supposed to do in those tests:

Chapter Ⅴ : Experimental part

Ⅴ. 10.1. Membranes and Filtration pilots:

The membranes used for this study are the ones with a thickness of 2 to 5 µm, were deposited on the internal surface of tubular membrane supports, and developed in our laboratory. These tubes with an inside / outside diameter = 12 / 18mm, are available in 250mm to 300mm length. These membranes were used on a tangential filtration pilot.

The feed solution passes through the tubular membrane, a valve is placed downstream to allow control of the feed flow and the applied pressure. A manometer is installed in line to indicate the value of the applied pressure.

Ⅴ. 10.2. Filtration of dyes:

Filtration of the dyes is carried out on the different membranes synthesized using the same filtration pilot. The feed solutions are two dyes one cationic and one anionic. Filtration is of the tangential type at a pressure of 4 bar. The concentrations of the permeates of the dyes were measured by UV-visible spectrophotometry. The breakdown of such molecules by membranes does not only depend on molecular size, but also on the charge interactions between the membrane and the solution.

Ⅴ. 10.3. Results:

Theoretically, and according to previous studies on the same products, the technique has shown great filtrating efficiency and the dyes were removed from water in great amount.

GENERAL CONCLUSION

This study aims to develop a membrane separation process for treating liquid effluents. The application of this process in the treatment of effluents appears to be promising.

The membranes are extremely fine filters from a few hundred nanometers to a few millimeters thick, the membrane processes are classified into four families according to the size of the particles they retain, the families are: microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

The materials that make up the membranes are numerous (natural, synthetic, minerals or composites). Its geometry structure divides into three types: plates, tubes and multichannels. These membranes operate in different modes, either frontal or tangential mode, among the drawbacks of this technique is the clogging which is divided into two types of clogging on the outside or inside the membrane.

From a textural point of view, the results of characterization of the synthesized supports show that the latter have good porosity and suggest the use of this material as a filter element.
Due to the current sanitary conditions which prevent us from obtaining results, we were unable to try the developed supports. Previous studies show that these same supports have shown good results in the retention of dyes and industrial waste.

This work has allowed us to show that it is quite possible to use local materials as an alternative in the manufacture of membrane supports at a very reasonable cost and with promising use.

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