The People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research
University of Tissemsilt

Faculty of Science and Technology
Department of Science and Technology

Final thesis for the obtaining of the degree of Academic Master in

Field:**Petrochemical Industries**

Major:**Refining Engineering**

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Theme

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Ceramic membrane supports modified by metallic nanoparticles and application in the treatment of water and oil discharges.

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Defended on June 14th, 2023.

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Academic Year: 2022-2023

Acknowledgement

First and foremost, allow me to thank Allah the Almighty, who has illuminated my path, and by His grace alone, we have been able to accomplish this work.

We would like to express our gratitude to our supervisor, Mr. AissatMiloud, for his guidance, availability, valuable advice, and attentive support. My deepest thanks go to the entire laboratory team for their assistance and understanding.

And we would like to thank everyone who has helped us, directly or indirectly, in the completion of this work.

dedication

Here comes the date of our graduation and the end of university years, and on this occasion, I dedicate this work to My family and friends.

Radouane

dedication

Here comes the date of our graduation and the end of university years, and on this occasion, I dedicate this work to My family and friends.

Abdelah

ملخص

من أجل معالجة النفايات الملوثة بالزيوت في المصافي أو النفايات الملوثة بالأصباغ في مصانع النسيج، قمنا بتطوير تقنية ترشيح تعتمدعلى استخدام أغشية داعمة مصنوعة من الكاولين المحلي،   والتيتم تحسينها بواسطة ترسيب طبقة رقيقة من الجسيمات النانوية. تم تشكيل الأغشية الداعمة، التي تعرضت في البداية للطهي بدرجات حرارة عالية، وتم توصيفها باستخدام تقنيات مثل الطيف الأشعة تحت الحمراء وتفاوت الأشعة السينية (DRX) ، وما إلى ذلك. في النهاية، قمنا باختبار فعالية هذه التقنية على التصريفات البتروليةوالصناعية.

Résumé

Dans le but de traiter les rejets contaminés par des huiles dans les raffineries ou par des colorants dans les usines textiles, nous avons développé une technologie de filtration qui repose sur l'utilisation de supports membranaires à base de kaolin local et amélioré par le dépôt d'une couche mince de nanoparticules. Les supports membranaires après avoir été initialement cuit sous haute température ont étécaractérisépar (infrarouge, DRX, etc.). Enfin, nous avons testé l'efficacité de cette technologie sur des rejets pétroliers et industriels.

Abstract

In order to treat oil-contaminated effluents in refineries or effluents contaminated with dyes in textile factories, we have developed a filtration technology based on the use of membranous supports made from local kaolin, enhanced by the deposition of a thin layer of nanoparticles. The membranous supports, initially subjected to high-temperature baking, were characterized using techniques such as infrared spectroscopy, X-ray diffraction (DRX), etc. Finally, we tested the effectiveness of this technology on oil and industrial effluents.

List of abbreviations

CVD	**Chemical vaper desposition**
ALD	**Atomic layer desposition**
PVD	**Physical vapeur disposition**
MBE	**Molecularbeamepitaxy**
CNT	**Carbon nano-tube**
LASIS	**Laser ablation synthesis in solution**
DLS	**Dynamic light scatting**
SEM	**Scanning electron microscope**
XRD	**X-ray diffraction**
PVdF–HFP	**Poly (vinylidene fluoride-hexafluoropropylene)**

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GENERAL

INTRODUCTION

General Introduction

GENERAL INTRODUCTION

The global community has been paying increasing attention to environmental pollution and ecological issues, particularly in recent years, as mankind witnesses the advancement of its knowledge and technology. Pollution problems have become an undeniable reality that poses a significant threat to both present and future human life. Human activities contribute to various forms of pollution, with potential detrimental effects on wildlife, plant life, and human beings themselves. All components of the environment, including air, soil, and water, are affected by these pollution impacts. Among these concerns, water pollution stands out as one of the most concerning aspects of the degradation of the natural environment caused by modern civilization. **[1]**

Petroleum waste waters are generated from various industries such as petrochemical, biomedical, and mechanical processing. These wastewaters need to be treated properly before being discharged to the environment. Compared with conventional methods, such as air flotation and coagulation, membrane-based separation has received increasing attention especially for treating highly emulsified oily wastewater because of its unique advantages such as high separation efficiency, low energy/chemicals consumption, small footprint, and continuous operation. In the majority of studies employing membranes for oil-water separation, the membranes were tested using synthetic oil-in-water emulsions under moderate conditions. However, it is more challenging to treat real emulsified wastewaters from certain industries as they exhibit harsh chemical conditions. For such separation applications, robust ceramic membranes with longer life span are generally preferred over their organic counterparts due to their better mechanical, thermal, chemical and fouling resistances. [2]

And many industries (textiles, stationery, plastics, food, etc.) are big consumers of water and use organic dyes (soluble or pigmentary) to color their products. These synthetic dyes are both toxic and responsible for coloring water [3,4]. Indeed, it is known that certain dyes are fixed more or less effectively despite the use of fixing agents. This then results in colored waste water which must be treated before being discharged. Wastewater discharge regulations are also increasingly stringent and require manufacturers to treat their effluents. [5]

Membrane operations are increasingly important in desalination, water treatment, gas separation, and the agri-food sector, directly addressing major societal needs. Furthermore, they now extend to gas treatment, energy production, medicine (artificial organs), and various industrial sectors (pulp and paper, petrochemicals, textiles, chemistry, and biotechnology). There is, therefore, a growing demand for increasingly high-performance membranes in terms of selectivity, even up to molecular recognition. [6]

General Introduction

The objective of this work is the development of membrane supports from a local product (Kaolin KT2 of El-Milia) known under the name of Kaolin of Tamazert, these membrane supports are then improved by the addition of a inorganic layer prepared by the sol gel method. These membranes are then used in the clarification of petroleum and industrial waste. These membranes were manufactured in several stages, molding, drying and firing at 1150°C. This thesis is divided into two parts. The first part aims to present a bibliographical study which consists of two chapters:

For the first chapter it contains two part for the first part we present the information concerning the filtration by membranes their major processes, the properties and the use of each process then the advantage and disadvantage of this method. The second part we talking about sol gel method and its use for the production of gels and thin layers.

About the second This chapter focuses on nanoparticles and their properties, with a specific emphasis on the description of metallic nanoparticles, their characterization, and applications.

The last part of the study focuses on an experimental protocol, where we have employed a specific experimental protocol to achieve the assigned objective. This part is divided to three part the first one is the method how make a membrane, the second one is how to produce the gels what we need, for the last one It talks about applying the filtration process.

CHAPTER I
THE MEMBRANES

I.1. Introduction

Ceramic membranes are porous filters made from inorganic materials such as alumina, zirconia, or Titania. They are commonly used in various industries for separation, purification, and filtration processes. Compared to other types of membranes, ceramic membranes have excellent thermal and chemical stability, high mechanical strength, and can withstand harsh environments. They also have a longer lifespan and require less maintenance. However, they are generally more expensive and may have lower permeability than polymeric membranes

I.2. Definition

A membrane can be defined as being a thin layer of material, allowing the stopping or the selective passage of substances dissolved or not, under the action of a driving force of transfer (FigureI.1). The separation criteria for particles, molecules and/or ions can be **[7]**:

- Size and shape ;
- The chemical ature ;
- physical condition;
- Electric charge, etc.
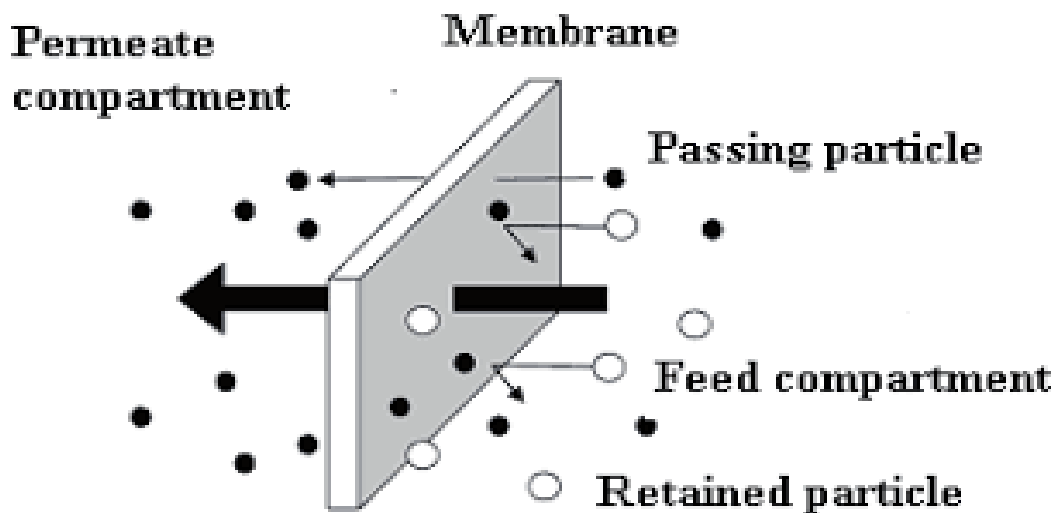
Figure I.1. Diagram of the operating principle of a permselective membrane

I.3.The different membrane process

There are 4 types of baromembrane processes. The main difference between them is the pore size of the membranes and their ability to retain different compounds. The retention capacity of a membrane is generally indicated by membrane manufacturers using its cutoff threshold, which is usually expressed in Daltons (1 Da = 1 g.mol-1).

Table I.1. Specificity of the 4 membrane processes.

process	pores size	applied pressure	Type of membrane
Microfiltration	0.1- 10 μm	0.01 – 2 bar	Poreuse
Ultrafiltration	2 – 100 nm	1 – 10 bar	Poreuse
Nanofiltration	0.5 – 2 nm	4 – 20 bar	Poreuse
Osmose inverse	Dense	20 – 80 bar	Dense

I.3.1. Reverse osmosis

Reverse osmosis is a process for desalting water using membranes that are permeable to water but essentially impermeable to salt. Pressurized water containing dissolved salts contacts the feed side of the membrane; water depleted of salt is withdrawn as a low-pressure permeate. The ability of membranes to separate small solutes from water has been known for a very long time. Pfeffer, Traube and others studied osmotic phenomena with ceramic membranes as early as the 1850s. In 1931 the process was patented as a method of desalting water, and the term reverse osmosis was coined. **[8]**
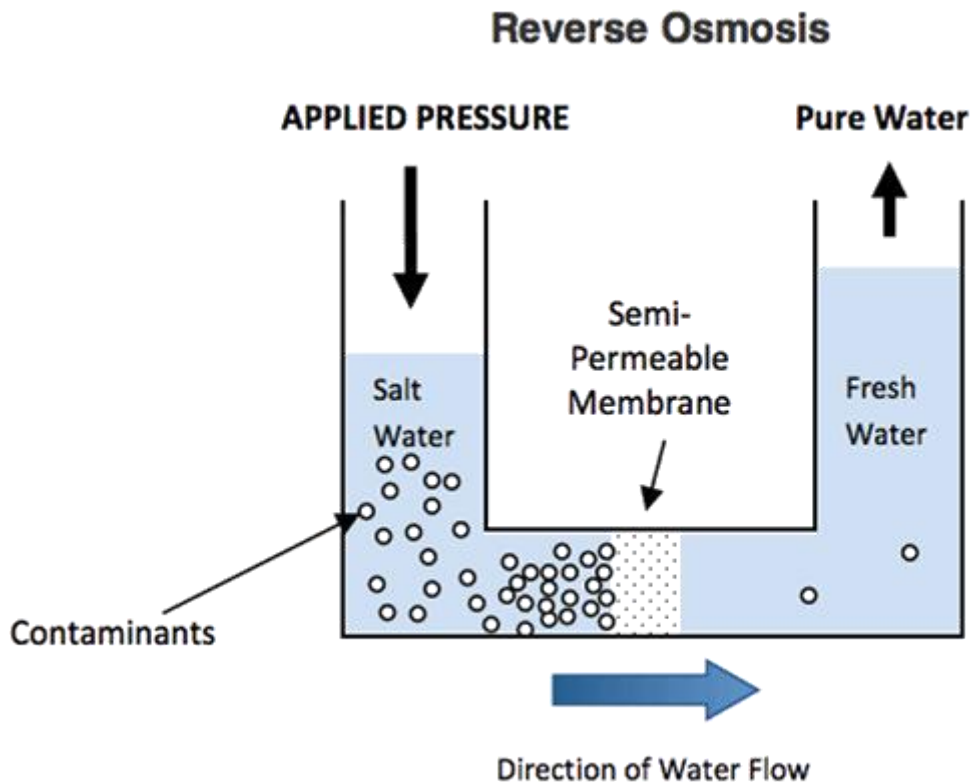
Figure I.2. Reverse osmosis. [9]

I.3.2.Ultrafiltration

Is a porous artificial membrane, organic or inorganic, of anisotropic (asymmetric) or composite type. The thin layer, or active layer, or skin, with a low thickness (around 10 mm) and containing meso-pores, is supported by one or more layers that are more porous and mechanically stronger, with a total thickness of approximately 15 mm in the case of organic membranes. In the case of an anisotropic membrane, the skin is supported by a medium of the same nature but with larger pores, ensuring easy drainage and good mechanical strength. **[10]**
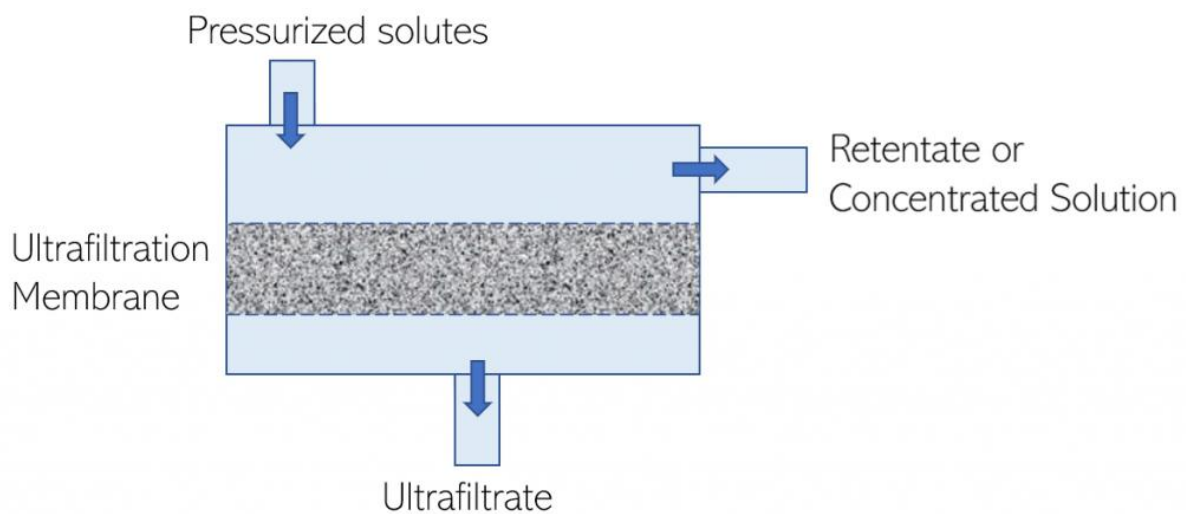
Figure I.3. Ultrafiltration [11]

I.3.3. Nanofiltration

Is currently an important branch of membrane technology as it allows the separation of small organic solutes and divalent ions from water. The most commonly applied NF membranes are synthesized either through a process called phase inversion, giving rise to a rather thick (μm-range) membrane, or through interfacial polymerization, creating a thin, selective layer (nm-range). Both synthesis procedures with their respective tuning parameters are extensively discussed in this chapter. The different methods to apply coatings or to modify surfaces are also included. **[12]**

I.3.4.Microfiltration

Is a separation technique for removing micron-sized particles, like bacteria, yeast cells, colloids, and smoke particles, from suspensions or gases? The process uses membrane filters with pores in the approximate size range 0.1 to 10 m, which are permeable to the fluid, but retain the particles, thus causing separation. **[13]**

I.4.Classification of membranes

I.4.1. Organic membrane

Organic membranes are membranes made from polymers. Polyamide membranes are the most used for nanofiltration and reverse osmosis. Polyvinylidene fluoride (PVDF) is widely used in microfiltration (MF) and ultrafiltration (UF). Polyacrylonitriles (PAN), polyether sulfone (PES), polysulfone (PS) or even cellulose acetate are also used to manufacture NF, UF, MF (and OI in the case of cellulose) membranes.

I.4.2. Inorganic membranes

Inorganic membranes consist of oxides, or metals, and can be present in multi-layer supporting structures, or as self-supporting structures. Dense membrane materials are ideally selective for O_2 or H_2 molecules. Micro-porous membranes (0.5–2 nm) can be highly selective for CO_2, H_2O and hydrocarbon. Meso-porous membranes (2–50 nm) are used as supporting structures, or in water purification. Macro-porous layers (>50 nm) are used as supporting structures and particulate filtration applications. Compared to polymeric membranes, inorganic membranes can be more selective and permeable, and can withstand more extreme conditions. To make them fully competitive their cost price must be reduced by improvements in processing, introduction of rapid fabrication methods, and possibly incorporation in hybrid, polymeric structures. [14]

I.4.3. Ceramic membranes

In industry, ceramic membranes are commonly used in areas where they can compete with polymer membranes in performance, as wellasin specific cases that require their unique features. But recently in the literature more and more attention is paid to ceramic membranes due to the possibility of their reuse, greater resistance to contamination compared to polymer membranes, and the presence of functional properties, such as photo-catalytic.[15]

I.4.3.1. Generality

The ceramic materials used for membrane fabrication are essential in determining the function and performance of the membrane. The selection of ceramic materials for membranes in water and wastewater treatment is not random, but based on their physical and chemical properties, such as microstructure (porosity and pore size), hydrophilicity, chemical and thermal stability, mechanical strength, and other characteristics necessary for water treatment. In addition, cost-effectiveness is also a factor to consider. [16]

I.4.3.2.Types

Alumina, zirconia, titania, silica, and zeolite are five common candidates employed in the production of commercial ceramic membranes for water treatment and Wastewater. **[17]**

a) Alumina (Al2O3) membranes

Alumina (Al2O3) is the most applied material due to economical consideration along with its ability to resist in high transmembrane pressures (TMP).**[18]**

b) Zirconia (ZrO2) membranes

Zirconium oxide (ZrO2) was used to prepare a flexible and thermally stable porous ceramic membrane, using PVdF–HFP as a binder.Ceramic zirconium membranes were used in the separation of oil-in-water emulsion.**[19]**

c) Titania (TiO2) membranes

Titanium (TiO2) has three well-known minerals: rutile, anatase and brookite. Among the ceramic materials for membranes, titanium oxide has the better chemical resistance. **[17]**

d) Silica membranes

Silica membranes have been formed by floating a solution of tetraethyl orthosilicate (TEOS)-water-ethanol on a dense, non-polar organic liquid. The solution reacts with atmospheric moisture and gels to a flexible skin. **[20]**

e) Zeolites membranes

Zeolite membranes are used in highly-selective gas separation due to highly uniform pore size. This material also has a catalytic characteristic, which is beneficial for catalytic membrane reactor applications. Few downsides of zeolite membranes include relatively low gas flux and thicker layer requirements to prevent cracks and pinholes. **[21]**

I.4.3.3. Application

Ceramic membranes are widely used in harsh conditions, such as cleaning/separation of water bodies at high temperatures and in aggressive chemical environments (various solvents, strongly acidic or alkaline solutions) and in the oily effluents treatment (Goh 2018). But recently, more often ceramic membranes began to be used in the production of drinking water. In this case, ceramic membranes can be used to provide high capacity and to create mobile membrane systems for local use (Staff 2011), among which are popular autonomous and hybrid systems in the water purification process. Such systems are able to remove completely suspended solids, microorganisms, and harmful chemicals.**[22]**

I.5. Definition

The sol-gel method, or S-G method for short, is to use a compound containing a high chemically active component as a precursor, uniformly mix these raw materials in the liquid phase, and perform hydrolysis and condensation chemical reactions to form a stable transparent sol system in solution. The sol slowly polymerizes between the aged colloidal particles to form a gel with a three-dimensional network structure. The gel network is filled with a solvent that loses fluidity to forma gel. The gel is dried, sintered and solidified to prepare molecular and even nano substructure materials. **[23]**

I.6. Sol

Sol The colloidal suspension of very tiny solid particles within a continuous liquid medium where only Brownian motion keeps the particles suspended is termed as 'sol'. Sols are highly stable and demonstrate Tyndall effect, e.g., blood, paint, etc. Sol-gel processing involves producing inorganic polymers and ceramics from solution, where the liquid precursors are transformed into a sol and then eventually into a networked structure termed as 'gel'. Conventionally, the sol is prepared via hydrolysis and condensation of metal alkoxide precursors. **[24]**

I.7.Gel

The colloidal particles or polymers in the sol or solution are connected to each other under certain conditions to form a spatial network structure, and the structural voids are filled with liquid as a dispersion medium (in xerogel, it can also be gas, xerogel is also called aerogel), such a special dispersion system is called a gel. The gel has no fluidity and often contains a large amount of liquid. The content of the dispersed phase is very low, generally between 1% and 3%. Even the water content of blood gel and agar can reach more than 99%. The process of forming a gel from a solution or sol is often called gelation.**[23]**
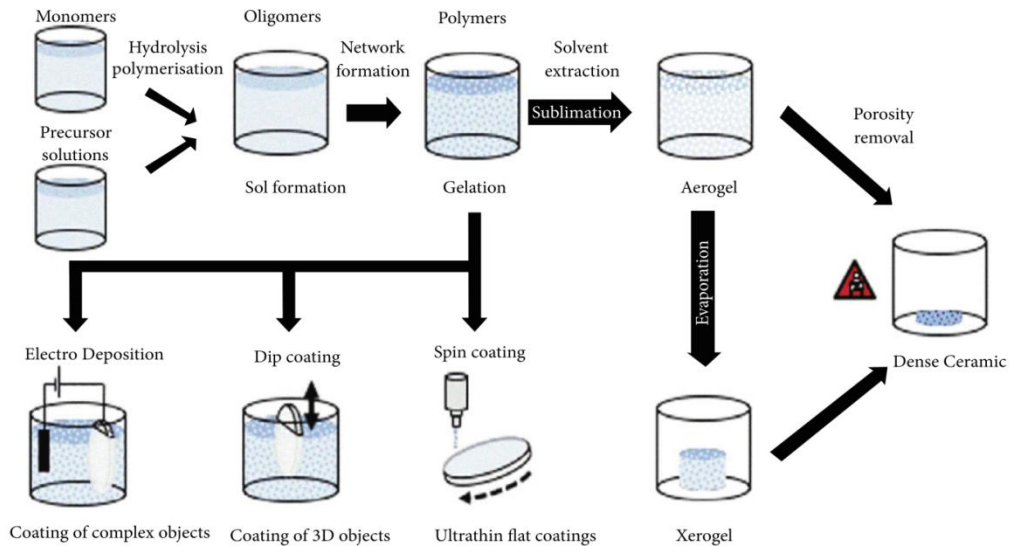
FigureI.4.Different methods of gel processing in the sol-gel process [25]

I.7.1.Physical gel

Physical gels are characterized by dynamic cross-links that are constantly created and broken, changing its state between solid and liquid under influence of environmental factors.**[26]**

I.7.2.Chemical gel

Chemical gels are covalently cross linked network polymers swollen in a large amount of solvent and are generally thermally irreversible.**[27]**

I.8.Sol-gel

The sol-gel process is a wet chemical technique that uses traditional methods such as observation to analyze materials (Azam, Zulkapli, Nawi, &Azren, 2015). It is called a wet chemical technique because most of the analysis is done in the liquid phase. This method allows the production of nanomaterials from metal oxide or colloidal-based solutions or tune the chemical compound in the solution in the form of pore volume, surface area and size of grain.**[28]**
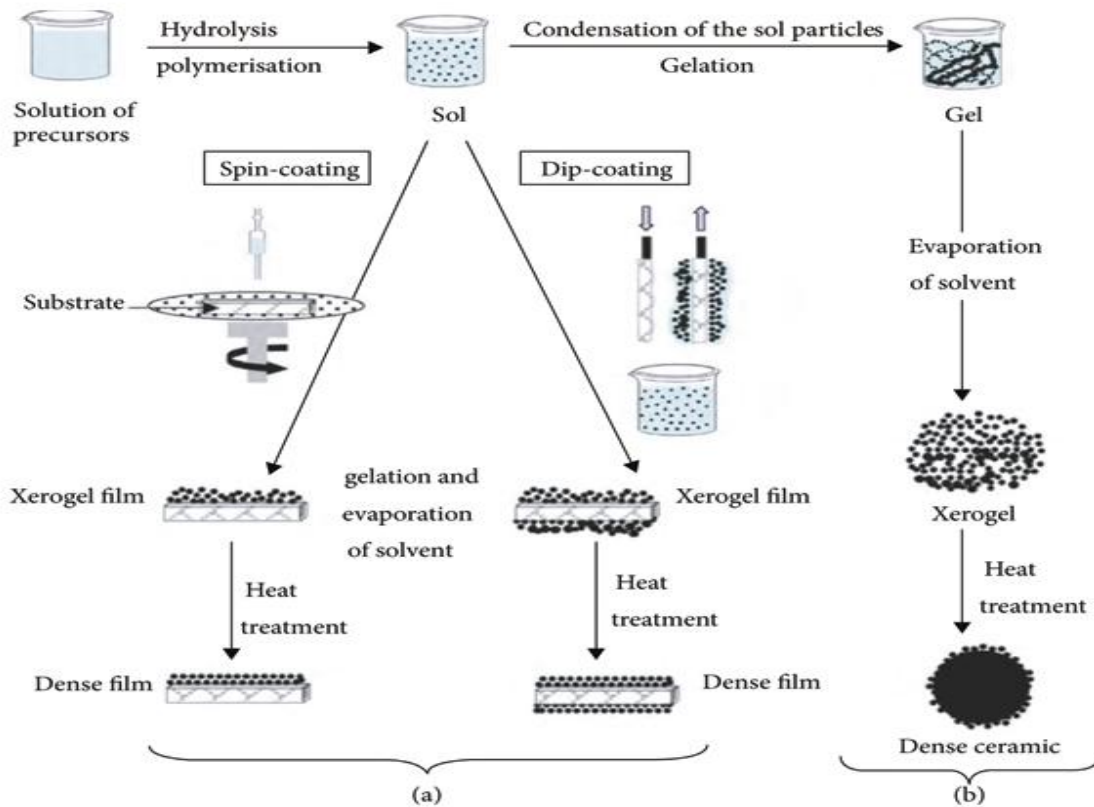
Fug I.5. Scheme of synthesis of samples by sol-gel method: (a) films synthesized from colloidal sol and (b) powder synthesized from gel[29].

The sol-gel process involves the conversion of a sol (a colloidal suspension of nanoparticles in a liquid) to a gel (a three-dimensional network of nanoparticles interconnected by chemical bonds).

The sol-gel process can be divided into four main stages:

(1) Hydrolysis,

(2) Condensation,

(3) Gelation,

(4) Aging and drying

There are two sol-gel synthesis pathways which are

- ❖ Inorganic : obtained from metallic salts(chlorides, nitrates, oxychlorides <) in aqueous solution. This way isinexpensive but difficult to control, which is why it is still very little used. However, it is the preferred way to obtain materials ceramics.

- ❖ Metallo-organic: This pathway uses precursors such as the alkoxides $M(OR)_n$ where M is a metal, R an organic radical (of the methyl CH_3, ethyl C_2H_5 type, etc.) and n the degree of valence of the metal.**[29]**

I.8.1. The advantages of the sol-gel process

- Ability of designing and controlling chemical composition and obtaining a homogeneous composition

- Ability of using the product with special shapes such as fibers and aerogels

- Surface coverage

- Ability of using this process to synthesize amorphous materials in thin layers

- Production of materials with modified physical properties, such as low thermal expansion coefficient, low UV absorption, and high optical transparency

- Production of porous and rich materials with organic and polymeric compounds

- High chemical reactivity of precursors due to process in solution phase

I.8.2. The disadvantages of the sol-gel process [30]

- Long process time

- High cost of raw materials.

I.9.Thin film

Thin film is a layer that extends infinitely along any two directions but restricted along the third direction. [31]

I.9.1.The different methods of deposition of thin films by sol-gel

Two common deposition techniques:

I.9.1.1. Chemical deposition

A fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer.

   a) Chemical deposition

CVD is a technique where a solid material is deposited from a vapor by some chemical reaction occurring on or in the vicinity of a normally heated substrate surface (Fig. 4). CVD is an example of vapor-solid reaction. The process is often used in the semiconductor industry to produce thin films. Micro-fabrication processes widely use CVD to deposit materials in various forms.**[32]**

   b) Atomic Layer Deposition

(ALD) is a thin film deposition technique enabling the fabrication of next-generation devices across the globe's most innovative industries. Used to manufacture high-quality coatings with Angstrom-level precision and conformality unrivaled by other deposition technologies, ALD has become a necessary coating tool for the advancement of nanotechnology.**[33]**

c) Electrochemical deposition

Electrochemical deposition is a process that uses oxidation and reduction to accumulate one material onto the surface of another material. During the electrochemical deposition process, electricity is introduced to an electrolyte through the use of electrodes. After a while, the ions of the deposition material in the electrolyte adhere to one of the electrodes.[34]

d) The sol–gel deposition

process includes synthesis techniques to produce a large quantity of nano-sized material with modeled and controlled particle size, morphology, orientation, and crystal structure as well as optimized physical and chemical properties. It applies to the fabrication of metal oxide thin-films including chemical reaction, nucleation, growth, and aging, as an aqueous thin-film processing method (aqueous chemical growth).[35]

I.9.1.2. Physical deposition

Uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid.

a) Physical vapor deposition

(PVD) is a vaporization coating technique, involving the transfer of material on an atomic level under vacuum conditions. The process is in some respects similar to CVD, except that in PVD the precursors, i.e. the material to be deposited, start out in solid form, whereas in CVD, the precursors are introduced to the reaction chamber in gaseous form.[36]

b) MBE

Is an evaporation process performed in an ultra-high vacuum for the deposition of compounds of extreme regularity of layer thickness.[37]

c) Electroplating

Electroplating is a process in which a metal is deposited onto a substrate by passing an electric current through a solution containing the metal ions. The metal ions are reduced at the substrate, resulting in the deposition of a thin film.

Conclusion

In conclusion, membranes produced using sol-gel methods have shown great potential for various applications due to their unique properties, including high surface area, tunable pore size, and uniform pore distribution. Sol-gel membranes have been extensively studied in recent years and have shown promising results in areas such as water treatment, gas separation, and biomedical applications.

CHAPTER II :

THE

NANOPARTICLES

II.1. Introduction

Nanotechnology has gained huge attention over time. The fundamental component of nanotechnology is the nanoparticles. Nanoparticles are particles between 1 and 100 nanometers in size and are made up of carbon, metal, metal oxides or organic matter **[38]**. The nanoparticles exhibit a unique physical, chemical and biological properties at nanoscale compared to their respective particles at higher scales. This phenomenon is due to a relatively larger surface area to the volume, increased reactivity or stability in a chemical process, enhanced mechanical strength, etc. **[39]**. These properties of nanoparticles has led to its use various applications. The nanoparticles differ from various dimensions, to shapes and sizes apart from their material **[40]**. A nanoparticle can be either a zero dimensional where the length, breadth and height is fixed at a single point for example nano dots, one dimensional where it can possess only one parameter for example graphene, two dimensional where it has length and breadth for example carbon nanotubes or three dimensional where it has all the parameters such as length, breadth and height for example gold nanoparticles. The nanoparticles are of different shape, size and structure. It be spherical, cylindrical, tubular, conical, hollow core, spiral, flat, etc. or irregular and differ from 1 nm to 100 nm in size. The surface can be a uniform or irregular with surface variations. Some nanoparticles are crystalline or amorphous with single or multi crystal solids either loose or agglomerated **[41]**. Numerous synthesis methods are either being developed or improved to enhance the properties and reduce the production costs. Some methods are modified to achieve process specific nanoparticles to increase their optical, mechanical, physical and chemical properties **[40]**. A vast development in the instrumentation has led to an improved nanoparticle characterization and subsequent application. The nanoparticles are now used in every objects like from cooking vessel, electronics to renewable energy and aerospace industry. Nanotechnology is the key for a clean and sustainable future.

II.2. Classification of nanoparticles

The classification of nanoparticles is based on their morphology, size, and shape. This review highlights some of the important categories of nanoparticles.

II.2.1. Organic nanoparticles

The organic nanoparticles include ferritin, micelles, dendrimers and liposomes show in FigureII.1. The organic nanoparticles are not toxic, biodegradable and some organic nanoparticles have a hallow sphere i.e. micelles and Liposomes. It is also familiar with name of nanocapsules which are heat and light sensitive **[42].** Organic nanoparticles are an ideal

choice for drugs delivery due to these characteristics. Then nanoparticles are also widely used in target drug delivery. The organic nanoparticles are also known as polymeric nanoparticles. The most known shape of organic or polymeric nanoparticles is nanosphere or nanocapsule[43]. The matrix particles are former overall mass of which is solid and outer boundary of spherical surface adsorb other molecules. In the later case, particles encapsulated the solid mass.[44]
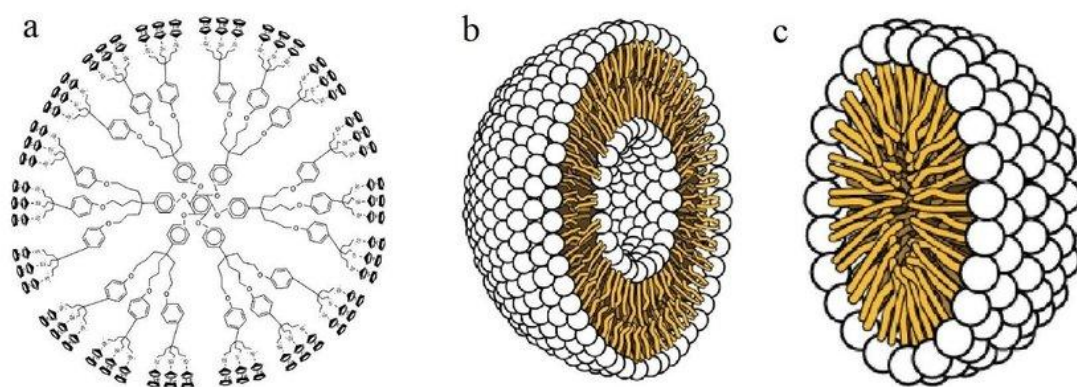
a – Dendrimers, b – Liposomes and c – micelles

Figure II.1. Organic nanoparticles

II.2.2. Inorganic nanoparticles

Inorganic nanoparticles are particles that are not made up of carbon. Metal and metal oxide based nanoparticles are generally categorized as inorganic nanoparticles

II.2.2.1. Metal based

Nanoparticles that are synthesized from metals to nanometric sizes either by destructive or constructive methods are metal based nanoparticles. Almost all the metals can be synthesized into their nanoparticles [45]. The commonly used metals for nanoparticle synthesis are aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn). The nanoparticles have distinctive properties such sizes as low as 10 to 100nm, surface characteristics like high surface area to volume ratio, pore size, surface charge and surface charge density, crystalline and amorphous structures, shapes like spherical and cylindrical and color, reactivity and sensitivity to environmental factors such as air, moisture, heat and sunlight etc.

II.2.2.2. Metal oxide nanoparticles

The purpose of the synthesis of metal oxide nanoparticles is to modify the property of their respective metals nanoparticles such as iron nanoparticles are oxidized to iron oxide nanoparticles. The reactivity of iron oxides nanoparticles is increased as compared to the iron

nanoparticles. Due to an increase in reactivity and efficiency of metal oxide, the nanoparticles of metal oxides are synthesized [46]. The example of metal oxide nanoparticles are zinc oxide, silicon dioxide, iron oxide, aluminum oxide, cerium oxide, titanium oxide and magnetite.

II.2.3. Ceramics NPs

Ceramic nanoparticles are also known as nonmetallic solid. The ceramics nanoparticles are synthesized via heating or successive cooling. The ceramic nanoparticles may polycrystalline, amorphous, porous, dens or hollow form [47]. The researcher focuses on these nanoparticles due to their wide application such as photodegradation of dye, photocatalysis, catalysis and imaging applications [48].

II.2.4. Carbon based

The nanoparticles made completely of carbon are knows as carbon based [49]. They can be classified into fullerenes, graphene, carbon nano tubes (CNT), carbon nanofibers and carbon black and sometimes activated carbon in nano size and are presented in FigureII.2
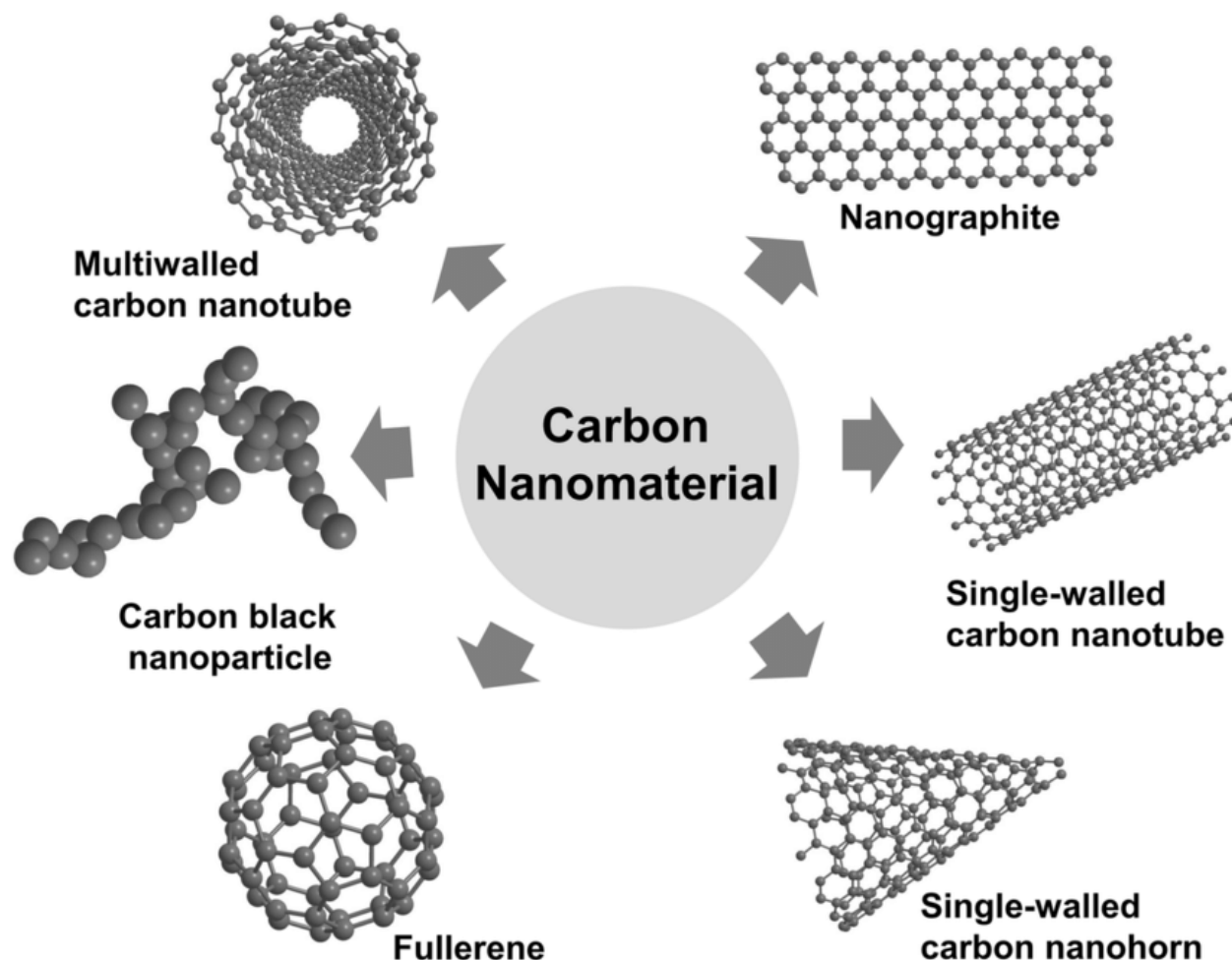
FigureII.2. Various-carbon-based-nanomaterials-were-reported-to-induce-cytotoxicity-Carbon-nanotubes

II.2.4.1. Fullerenes

Fullerenes are spherical shaped carbon molecules consisting of carbon atoms bonded through sp2 hybridization. They can contain 28 to 1500 carbon atoms and range in size from 8.2 nm for a single layer to 4 to 36 nm for multi-layered fullerenes.

II.2.4.2. Graphene

Graphene is an allotrope of carbon that is comprised of a hexagonal honeycomb lattice made up of carbon atoms arranged in a two-dimensional plane. Its thickness is typically around 1 nm.

II.2.4.3. Carbon Nano Tubes (CNT)

Carbon Nano Tubes (CNT) are formed by winding a graphene nanofoil, which is made up of a honeycomb lattice of carbon atoms, into hollow cylinders. Their diameters can range from as low as 0.7 nm for single-layered tubes to 100 nm for multi-layered tubes, and their lengths can vary from a few micrometers to several millimeters. The ends of CNTs can either be open or closed by a half fullerene molecule.

II.2.4.4. Carbon Nanofiber

Carbon Nanofiber is produced from the same graphene nanofoils as Carbon Nano Tubes (CNT), but they are wound into a cone or cup shape instead of a cylindrical tube.

II.2.4.5. Carbon black

Carbon black is an amorphous material composed of carbon, typically in a spherical shape with diameters ranging from 20 to 70 nm. The high inter-particle interactions result in the particles being bound together in aggregates, resulting in the formation of agglomerates with diameters of around 500 nm.

These are normally organic based NPs and in the literatureaspecial term polymer nanoparticle (PNP) collective used forit. They are mostly nanospheres or nanocapsularshaped[50]. The former are matrix particles whoseoverall mass is generally solid and the other molecules areadsorbed at the outer boundary of the spherical surface.Inthe latter case the solid mass is encapsulated within the particlecompletely[51]. The PNPs are readilyfunctionalize and thus find bundles of applications in the liter-ature[52].

II.3. Synthesis of Nanoparticles

The nanoparticles are synthesized by various methods that are categorized into bottom-up or top-down method

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                    ┌──────────────────┐
                    │   Synthesis of   │
                    │  nanoparticales  │
                    └──────────────────┘
              ┌──────────────┴───────────────┐
     ┌──────────────────┐          ┌──────────────────┐
     │ Top-down synthesis│          │ Bottom-up synthesis│
     └──────────────────┘          └──────────────────┘
     ┌──────────────────┐          ┌──────────────────┐
     │Thermal decomposition│        │ Chemical vapoure │
     │                  │          │    deposition    │
     └──────────────────┘          └──────────────────┘
     ┌──────────────────┐          ┌──────────────────┐
     │ Mechanical miling │          │   Sol-gel method │
     └──────────────────┘          └──────────────────┘
     ┌──────────────────┐          ┌──────────────────┐
     │   Lithographic   │          │     Spinning     │
     └──────────────────┘          └──────────────────┘
     ┌──────────────────┐          ┌──────────────────┐
     │   Laser ablation │          │     Pyrolysis    │
     └──────────────────┘          └──────────────────┘
     ┌──────────────────┐          ┌──────────────────┐
     │     Sputtering   │          │    Biosynthesis  │
     └──────────────────┘          └──────────────────┘
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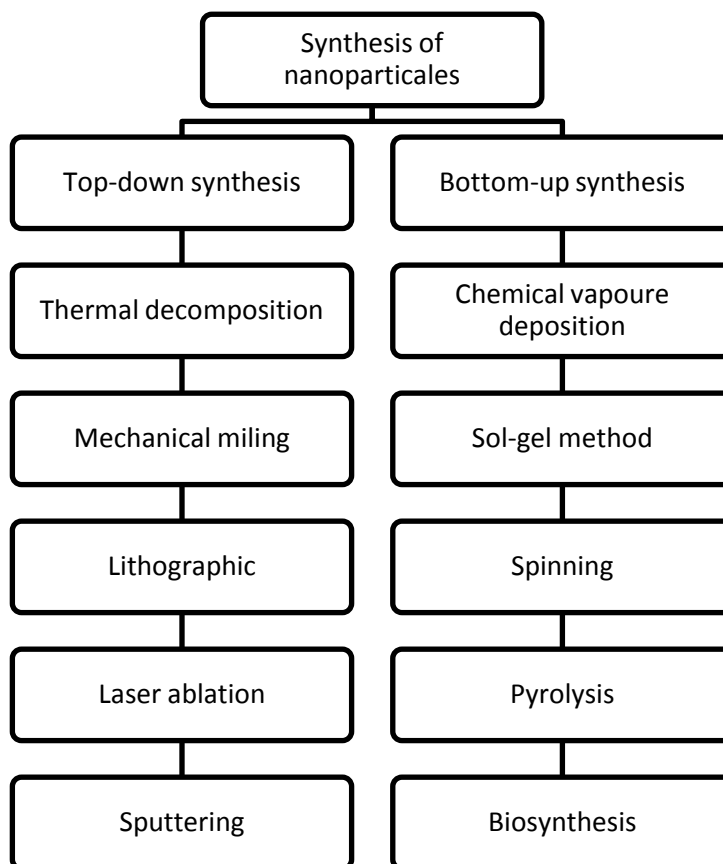
Figure II.3. Top down and bottom up synthetic methods of nanoparticles

II.3.1. Bottom-up method

Bottom-up or constructive method is the build-up of material from atom to clusters to nanoparticles. Sol-gel, spinning, chemical vapor deposition (CVD), pyrolysis and biosynthesis are the most commonly used bottom-up methods for nanoparticle production

II.3.1.1. Chemical Vapor Deposition (CVD)

Chemical vapor deposition is the deposition of a thin film of gaseous reactants onto a substrate. The deposition is carried out in a reaction chamber at ambient temperature by combining gas molecules. A chemical reaction occurs when a heated substrate comes in contact with the combined gas **[49].** This reaction produces a thin film of product on the substrate surface that is recovered and used. Substrate temperature is the influencing factor in CVD. The advantages of CVD are highly pure, uniform, hard and strong nanoparticles. The disadvantages of CVD are the requirement of special equipment and the gaseous by-products are highly toxic **[53].**

II.3.1.2. Sol–gel method

Sol–gel method is a combination of two words sol and gel. Sol is a colloid formed from solid particles suspended particles in continuous liquid. Gel is a solid macro-molecule which is dissolved in solvent. Due to simplicity, sol–gel method is the most preferred bottom-up method for the synthesis of nanoparticles. It is the method in which suitable chemical solution act as precursor. The typical precursors are metal oxide and chloride used in sol–gel method [54]. By using different methods such as stirring, sonication and shaking, the precursor is dispersed in host liquid. The resultant solution consists of solid phase and liquid which is separated by using different techniques such as filtration, sedimentation and centrifugation to recover the nanoparticles. It is the transformation process of sol into gel. Its involve condensation and hydrolysis reaction shown in fig. The nanoparticles of TiO 2 is synthesized using different precursor such asTiCl3 [55],Ti[OCH(CH$_3$)$_2$]4 (TTIP) [56], TiCl4 [57] and Ti(OBu)4 [58].

II.3.1.3. Spinning

Nanoparticles are synthesized by spinning. The nanoparticles are synthesized by using spinning disc (SDR) which consist of rotating disc where physical parameter can be controlled such temperature. In order to avoid chemical reaction and remove oxygen, the reactor is filled with nitrogen or inert gases. The liquid such as water and precursor is pumped inside the chamber or reactor. The characteristics of nanoparticles synthesize from SDR is determined by various factors such as disc surface, liquid/precursor ration, disc rotation speed, liquid flow rate and location of feed. The particles size ranged from size range 3 to 12nm.

II.3.1.4. Pyrolysis

Pyrolysis is the most commonly used process in industries for largescale production of nanoparticle. It involves burning a precursor with flame. The precursor is either liquid or vapor that is fed into the furnace at high pressure through a small hole where it burn[59]. The combustion or by-product gases is then air classified to recover the nanoparticles. Some of the furnaces use laser and plasma instead of flame to produce high temperature for easy evaporation [60]. The advantages of pyrolysis are simple, efficient, cost effective and continuous process with high yield.

II.3.1.5. Biosynthesis

Biosynthesis is a green and environmental friendly approach for the synthesis of nanoparticles that are nontoxic and biodegradable [61]. Biosynthesis uses bacteria, plant extracts, fungi, etc. along with the precursors to produce nanoparticle instead of convention chemicals for bioreduction and capping purposes. The biosynthesized nanoparticles has unique and enhanced properties that finds its way in biomedical applications [38].

II.3.2. Top-down synthesis

In this synthesis, destructive method is used. The larger molecule (bulk material) decomposed into a smaller molecule and then these smaller molecules transform into the nanoparticles. Grinding or milling, physical vapor deposition and other destructive approaches are the example of Top-down synthesis **[62]**.

One study showed the synthesis of magnetite having spherical shape from iron oxide by using top-down method **[63]**. The top-down approach was used to synthesize colloidal carbon spherical particles having size range from 20 to 50 nm. The synthesis method was depended on chemical adsorption of polyoxometalates on the surface of interfacial carbon. The micrograph showed that carbon particle size becomes smaller with sonication time. By the combination of grinding a sonication techniques, a series of transitional metal dichalcoenidenano dot (TMD-ND,s) from their bulk material. It showed that all the size of transitional metal dichalcoenidenano dot (TMD-ND,s) was smaller than 10 nm. The transitional metal dichalcoenidenano dot (TMD-ND,s) represent excellent dispersion due to narrow distribution of size **[64]**.

II.3.2.1. Thermal decomposition method

It is an endothermic process in which chemical decomposition is produced by heat. The chemical bond in compound is broken by this heat **[65]**. The decomposition temperature may be defined as specific temperature at which element is chemically decomposed. The nanoparticles are consequences of decomposition of meta at specific temperature. Ahab, Atika, et al. Synthesized gadolinium oxide nanoparticles functionalized by paramagnetic polyethylene glycol by using thermal decomposition method shown in Figure II.4
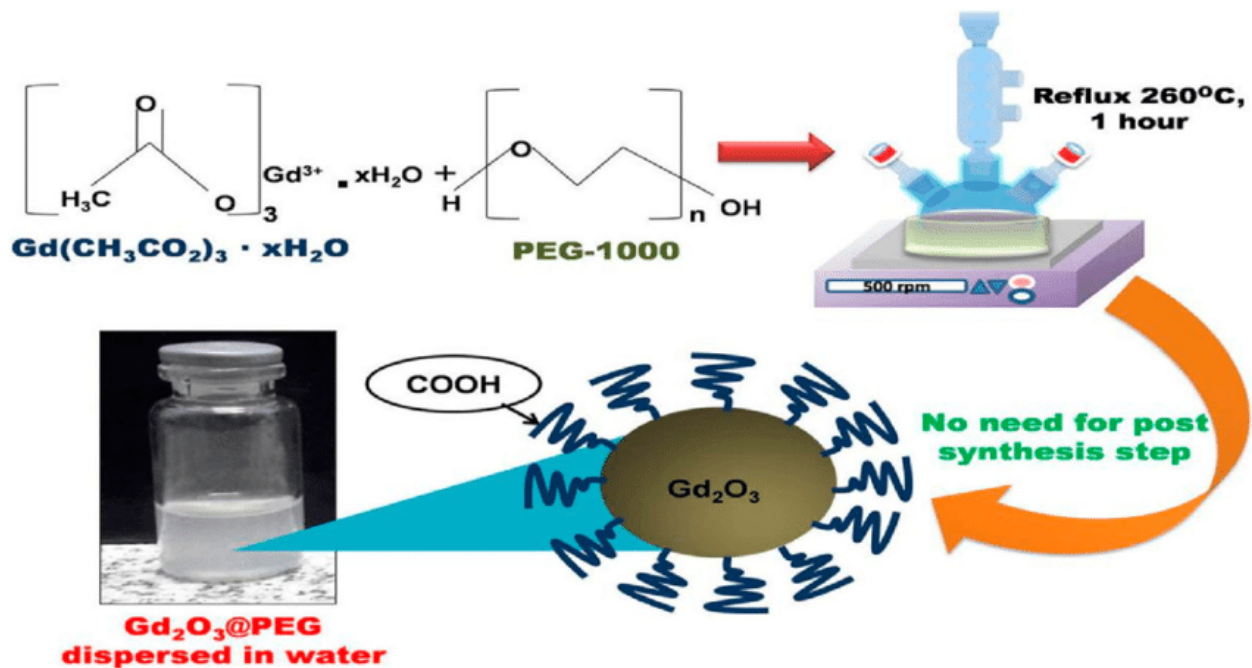
FigureII.4. A simple straightforward thermal decomposition synthesis of PEG-covered Gd2O3 (Gd2O3@ PEG) nanoparticles [66]

II.3.2.2. Mechanical milling

Among the various top-down methods, mechanical milling is the most extensively used to produce various nanoparticles. The mechanical milling is used for milling and post annealing of nanoparticles during synthesis where different elements are milled in an inert atmosphere **[67]**. The influencing factors in mechanical milling is plastic deformation that leads to particle shape, fracture leads to decrease in particle size and cold-welding leads to increase in particle size .

II.3.2.3. Lithographic methods

Lithographic methods are top-down methods which are capable of making for most part micron size feature but are energy intensive and requiring costly equipment. Lithography is used to make printed circuit and computer for several decade now. Nanoimprint lithography is type of lithography which is different from typical lithography. It is similar to the template synthesis. Firstly a template material is made and then soft polymeric material is stamped to form pattern. Top down method is used to make stamped material. Latex sphere is utilized by nanosphere lithography to form templated matric. There are different type of lithography techniques, for instance, photo-lithography, electron beam lithography, soft lithography, focused ion lithography, nano-imprint lithography and dip pin lithographyphoto-lithography involved contact an proximity printing and projection printing

II.3.2.4. Laser ablation

Laser Ablation Synthesis in Solution (LASiS) is a common method for nanoparticle production from various solvents. The irradiation of a metal submerged in a liquid solution by a laser beam condenses a plasma plume that produces nanoparticles [68]. It is a reliable top-down method that provides an alternative solution to conventional chemical reduction of metals to synthesis metal based nanoparticles. As LASiS provides a stable synthesis of nanoparticles in organic solvents and water that does not require any stabilizing agent or chemicals it is a 'green' process.

II.3.2.5. Sputtering

Sputtering is the deposition of nanoparticles on a surface by ejecting particles from it by colliding with ions [69]. Sputtering is usually a deposition of thin layer of nanoparticles followed by annealing. The thickness of the layer, temperature and duration of annealing, substrate type, etc. determines the shape and size of the nanoparticles [70].

II.4. Characterization of nanoparticles

The nanoparticles can be categorized into quantitative and qualitative. These methods include dynamic light scattering (DLS), scanning electron microscope (SEM),

Table II.1. Synthesis of different nanoparticles using different fungi

Sr no	Type of NPs	Fungal strain	Size	Shape	Ref
1	ZnO	Aspergillus strain	50–120 nm	Spherical	[71]
2	ZnO	Candida albicans	15–25 nm	Hexagonal	[72]
3	ZnO	Aspergillus terreus	29 nm	Hexagonal	[73]
4	Ag	Trichoderma viride	2–4 nm	Spherical	[74]
5	Ag	Fusarium oxysporum	5–13 nm	Spherical	[75]
6	Ag	Arthrodermafulvum	20.56 nm	Spherical	[76]
7	Au	Collectotrichum.sp	8–40 nm	Spherical	[77]
8	Au	Candida albicans	60–80 nm	Non spherical	[78]
9	TiO2	Aspergillus flavus	62–74 nm	Spherical	[79]
10	TiO2	Aspergillus flavus TFR7	12–15 nm	–	[80]
11	Pt	Fusarium oxyporum	70–180 nm	Rectangular, riangular and spherical	[81]

energy dispersive spectroscopy (EDS), UV-Vis spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), surface-enhanced remain spectroscopy (SERS), Atomic force microscopy (AFM), high angle annular dark field (HAADF), atomic absorption spectroscopy (AAS) and ray photoelectron spectroscopy (XPS) [82,83]

II.4.1. Qualitative analysis

II.4.1.1. Fourier transform infrared spectroscopy (FTIR)

Biomolecules those are responsible for capping, reduction and stabilizer, are identify by using FT-IR.

II.4.1.2. UV–Vis spectrophotometry

The UV-Vis technique is utilized to characterize the nanoparticles of diverse metals, which exhibit sizes ranging from 2 to 100 nm, typically employing a wavelength range of 300 to 800 nm. This method is used to ascertain the formation and durability of nanoparticles in aqueous solutions. On the other hand, the scanning electron microscope (SEM) produces an output image using electrons instead of light, and is employed to assess the shape, size, morphology, and distribution of the synthesized nanoparticles.

II.4.2.3. Scanning electron microscope (SEM)

The image produced through SEM employs electrons instead of light, and this method is utilized to examine the shape, size, morphology, and distribution of the synthesized nanoparticles.

II.4.1.4, X-ray diffraction (XRD)

XRD is a technique utilized for determining the atomic structure of materials, which serves both qualitative and quantitative purposes. This method is employed to determine the crystal structure, calculate the size of crystalline nanoparticles, and confirm the presence of nanoparticles.

II.4.1.5. Atomic force microscopy (AFM)

The study of the shape, size, and surface area of synthesized nanoparticles is achieved through the utilization of AFM.

II.4.2. Quantitative analysis

II.4.2.1. Transmission electron microscopy (TEM)

It is used for the study of particle size of material in nanoscale and crystal structure.

II.4.2.2. Annular dark-field imaging (HAADF)

Using HAADF, it is possible to investigate the mechanism by which nanoparticles interact with bacteria. The HAADF image provides information regarding the size distribution of nanoparticles as they interact with different types of bacteria.

II.4.2.3. Intracranial pressure (ICP)

To determine the metal concentration in both the deionized and original nanoparticle solutions, ICP spectrometry is utilized. The resulting metal concentration is then measured

using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled emission spectroscopy (ICP-ES).

II.5. Applications

Below are some of the significant applications of nanoparticles.

II.5.1. Cosmetics and Sunscreens

The conventional ultraviolet (UV) protection sunscreen lacks long-term stability during usage. The sunscreen including nanoparticles such as titanium dioxide provides numerous advantages. The UV protection property of titanium oxide and zinc oxide nanoparticles as they are transparent to visible light as well as absorb and reflect UV rays found their way to be used in some sunscreens. Some lipsticks use iron oxide nanoparticles as a pigment [84].

II.5.2. Electronics

The higher necessity for large size and high brightness displays in recent days that are used in the computer monitors and television is encouraging the use of nanoparticles in the display technology. For example, nanocrystalline lead telluride, cadmium sulphide, zinc selenide and sulphide, are used in the light emitting diodes (LED) of modern displays **[85]**. The increase in electrical conductivity of nanoparticles are used to detect gases like NO2 and NH3 **[86]**. This is due to increase in the pores of nanoparticles due to charge transfer from nanoparticles to NO2 as the gas molecules bind them together making them a better gas sensors.

II.5.3. Catalysis

Nanoparticles contain high surface area that offers higher catalytic activity. Due to their extremely large surface to volume ratio the nanoparticles function as efficient catalyst in the production of chemicals **[87]**. One of the important application is the use of platinum nanoparticles in the automotive catalytic converters as they reduce the amount of platinum required due to very high surface area of the nanoparticles thus reducing the cost significantly and improving performance. Some chemical reactions for example, reduction of nickel oxide to metal nickel (Ni) is performed using nanoparticles.

II.5.4. Medicine

Nanotechnology has improved the medical field by use of nanoparticles in drug delivery. The drug can be delivered to specific cells using nanoparticles **[88]**. The total drug consumption and side effects are significantly lowered by placing the drug in the required area in required dosage. This method reduces the cost and side effects. The reproduction and repair of damaged tissue (Tissue engineering) can be carried out with the help nanotechnology. The traditional treatments such as artificial implants and organ transplants can be replaced by tissue engineering. One such example is the growth of bones carbon nanotube scaffolds **[89]**.

The use of gold in medicine is not new. In Ayurveda an Indian medical system, gold is used in several practices. One common prescription is the use of gold for memory enhancement. To enhance the mental fitness of a baby gold is included in certain medical preparations **[90].**

II.5.5. Food

The improvement in production, processing, protection and packaging of food is achieved by incorporating nanotechnology. For example a nanocomposite coating in a food packaging process can directly introduce the anti-microbial substances on the coated film surface **[91]**. One of the example is and minerals in the food.

II.5.6. Construction

Nanotechnology has improved the construction processes by making them quicker, inexpensive and safer. For example, when nanosilica (SiO2) is mixed with the normal concrete, the nanoparticles can improve its mechanical properties, and also improvements in durability **[81]**. The use of nanotechnology provides a better blocking of light and heat penetrating through the windows. The paints with self-healing abilities and corrosion resistance and insulation are obtained by adding nanoparticles to the paints. The hydrophobic property of these paints repels water and hence can be used to coat metal pipes to offer protection from salt water attack. The addition of nanoparticles in paints also improves its performance by making them lighter with enhanced properties **[92]** so when used for example on aircraft, it might reduce their overall weight and the amount of paint required, which is favorable to the environment as well the company to improve cost savings.

II.5.7. Renewable energy and environmental remediation:

The unique physical and chemical properties of nanoparticles has made them an ideal choice to be used nowadays in environmental remediation to enhancing the performance in renewable energy sector **[93]**. Nanoparticles occur in nature themselves and some of them are found to cure the environment. Environmental remediation using nanoparticles or nanoremediation is successfully being used to treat or decontaminate the air, water and soil for over a decade **[39]**. Nanoremediation presents a highly effective solution for environmental contamination, as it allows for in situ treatment without the need for excavation or pumping of groundwater. Instead, nanoparticles are injected into the targeted location and carried along the groundwater flow to immobilize and decontaminate harmful pollutants, such as heavy metals, pathogens, and organic contaminants, through redox reactions. This approach has proven to be more efficient and cost-effective than traditional chemical treatments, which may produce secondary reaction products. Moreover, nanoparticles can be utilized to disinfect, purify, and desalinate surface water, as well as to

clean up oil spills. The use of nanoparticles for municipal and industrial wastewater treatment, including sludge.

Conclusion

The enhancement of everyday objects' performance and efficiency is made possible by nanotechnology, which is gradually improving our daily lives. Nanotechnology contributes to a cleaner environment by providing safer air and water, as well as clean, renewable energy, thereby promoting a sustainable future. The field of nanotechnology has gained significant attention, leading to increased research and development investment by top institutions, industries, and organizations. Considerable research efforts are conducted to implement nanotechnology, making it a cutting-edge scientific field. Nanotechnology is being tested for various applications to enhance object or process efficiency and performance, subsequently reducing costs to make it accessible to everyone. Its environmentally friendly nature and efficiency make nanotechnology an extremely promising field with a bright future.

CHAPTER III

EXPERIMENTAL PART

III.1.Strategy to follow

During the experimental part, we will follow a certain methodology that consists in developing membranes based on kaolinite, followed by an improvement of these membranes by depositing an inorganic gel prepared by the sol gel and nanoparticle gel methods. Before carrying out the discharge filtration tests

III.2. Synthesis of membranes

In the first link, we developed these membrane supports only with Kaolin KT2 from El-Milia, we produced a series of membranes based on kaolin KT2 cooked at 1150 ° C:

III.3.Physico-chemical characterization of the material

In this study, the clay used for the production of the membrane supports is Kaolin KT2 from Milia (Kaolin from Tamazert); it is intended for the manufacture of ceramics, the composition of which is given in Table III.1. The results show that the clay is essentially made up of silica (67.4%) and alumina (18.6%).

This clay contains significant Fe2O3, TiO2, K2O and Na2O contents. In addition, the other constituents are present in trace amounts. A percentage of 5.68 was recorded for fire losses.

Table III.1. Chemical composition of Kaolin KT2

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	Others	PF
%	67.4	18.6	0.88	0.31	2.03	0.39	0.07	0.22	3.92	5.68

III.4. Elaboration of membrane supports

The membrane supports are prepared from natural KT2 kaolin according to the following steps:

The preparation of the suspension from well ground kaolin and mixed with a suspensive liquid, in our case it is water. The optimal value obtained was 1.66 cp. This viscosity value corresponds to the proportions of 300 ml of distilled water for 200 grams of kaolin.

The addition of 2 to 3 drops of a deflocculant (sodium silicate) 〚Na〛_2 〚SiO〛_3 for the homogenization of the suspension in order to avoid the presence of undesirable agglomerates within the suspension, this allows obtaining a membrane of good quality before and after sintering **[94]**. This type of compound forms a double Helmotz layer, thus promoting electrostatic repulsion between the grains by eliminating the risk of surface charge anisometry

which allows a reduction in the viscosity of the slip to an adequate value to obtain good casting.

The mixture is subjected to vigorous stirring for a few minutes until a homogeneous suspension is obtained. The latter is poured into the support where a controlled diffusion process occurs **[95]** which amounts to a simple loss of water from the suspension in the mass of the support **[96]**. This causes the accumulation of particles on the surface of the support. The driving force of this process is the suction force of the support (capillary suction). The absorption of water by porous media under the action of capillary forces has been the subject of numerous modeling by type laws **[97]**:

$$m = K\_s.t^{(1/2)} \text{ ---------------------------Eq.III.1}$$

m: mass of water absorbed

t: contact time between the porous medium and the water

Several models of the formation of a deposit have been proposed; they all indicate that the thickness of the layer formed is proportional to $t^{(1/2)}$ **[98]**. When the desired thickness is reached, the suspension is discharged and the remaining layer is dried and sintered. The drying of the deposit is carried out at ambient temperature for 48 hours and constitutes the first stage of solidification of the deposit by evaporation of the solvent. Drying is followed by sintering and figures III.1, III.2, III.3 and III.4 show the different stages for the preparation of the membrane supports.

The main parameters influencing homogeneous casting of the suspension as well as obtaining an adequate thickness are the shape, grain size, viscosity and bulk density of the prepared suspension **[99]**. The choice and quantity of organic additives are very important. It has an effect on the properties of the support, which affect the choice of manufacturing method (extrusion, casting, etc.) and the properties of the finished product **[100, 101].**

Figure III.1. Raw KT2 Kaolin Powder

Figure III.2. Mechanical grinding of kaolin

Figure III.3. Preparation of slip for casting

FigureIII.4 Casting of membrane supports

III.4.1. Characteristics of slip

A well-dispersed suspension will lead to the deposition of a membrane with low porosity and the microstructure is very homogeneous; on the other hand, the deposition of a suspension containing clusters of particles will lead to a very porous deposit but presenting a distribution of the diameter of the pores much wider if the compressibility induced by the capillary suction of the support is low **[102].**

A membrane has characteristics strongly linked to the quality of the slip and in general, the membranes are not characterized by their pore diameter, but by the size of the particles or molecules likely to be retained.

III.4.2. Powder particle size

When the particle size of a suspension decreases, the density of the compacted product increases, the quantity of addition and water to be introduced into the mixture to regain the same viscosity decreases [103]. The shape of the grains is particularly important. The round particles promote compaction and homogenize shrinkage forces during drying and firing. On the other hand, the flattened grains are aligned on the surface, which significantly improves the surface condition of the shard [104].

III.5. Drying

The drying of the membrane supports leads to the consolidation of the raw part by elimination of the water introduced during the mixing; it is accompanied by a first withdrawal [105]. Drying too quickly dries out the outside of the substrates while the inside remains damp because the water does not have time to migrate to the surface. The stresses due to drying shrinkage are then inhomogeneous and cause cracks in the structure of the material [106].

The drying rate must not exceed the rate of water migration in the material; for this reason, it is essential to control the humidity of the atmosphere during drying. It should be noted that the drying steps are important because it is generally during drying that micro-cracks occur which reduce the solidity of a ceramic [104]. A reduction in the drying time leads to a significant proportion of micro-cracks in the structure of the material or cracks in the walls.

III.5.1. Cooking

The heat treatment of the supports allows the final consolidation of the shaped part after elimination by evaporation or carbonization of the temporary additions. Firing gives the ceramic supports their final dimensions. We speak of ceramic firing when the heat treatment leads to the formation of a vitreous phase which coats and binds the dispersed crystals [105]. The maximum temperature of the heat treatment influences the porosity of the supports; indeed, from the moment the enamel begins to melt, consolidation occurs and increases with temperature [106].

III.5.1.1. Thermal program

The transformations during the heat treatment have a direct influence on the development of the phases formed [107-108] as well as on the liquid phases [107, 109, 110] likely to form at the high temperatures which are at the origin of the recrystallization and secondary formation of mullite. These sintered supports take the final consolidation after removal by evaporation

or carbonization of the temporary additions. Sintering gives the ceramic supports their final dimensions. The results obtained show that there is a good porosity formed with the sintering temperature [111]. The onset of material densification occurs when the temperature has increased [112-113].

The maximum temperature of the heat treatment influences the porosity of the supports; in fact, from the moment the enamel begins to melt, consolidation occurs and increases with temperature. An increase of 5°C/min is carried out 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. Complete removal of organic additives is between 400 and 700°C.

Arrived at the temperature of 573°C, it can be seen that this value corresponds to the transformation of the quartz from its α form to its β form. We reach the temperature of 1150°C, with a plateau of 5 hours, where the formation of alumina-ɣ and mullite occurs. Finally, slow cooling of the furnace avoids any risk of cracking of the supports [114].

It is thanks to the gravimetric thermal analysis (A.T.G) that we were able to determine the temperatures of elimination of the additions as well as the temperatures of consolidation by developing the program of heat treatment quoted.

III.6. Study of withdrawal:

The shrinkage expressed by the Bigot curve only appears after a certain drying time which corresponds to the loss of free water in contact with the exterior. The measurement of the evaporated water volume gives approximately the open porosity of the green sample. The apparent volume of the sample makes it possible to estimate the open porosity of the raw sample [115, 116]. The shrinkage expressed in percentage can concern the linear shrinkage of surface or volume. This value will allow us to estimate the compactness of the supports obtained.

For the calculation of the shrinkage of the supports, the following formula was used:

$$R_t = (\% \text{ total shrinkage}) = [(L_i - L_c)/L_i].100 \text{ ------------------Eq. III.3}$$

With: Li: initial length and Lc: length after cooking

The length of each ceramic carrier is measured before and after firing to determine the shrinkage of each carrier.

III.7. Absorption rate

Porosity is measured by the ratio of pore volume to total apparent volume. It is the property of a body, of a medium, of having interconnected voids or not, expressed quantitatively by the

ratio of the volume of these voids to the total volume of the medium. It is equivalent to the water content by volume of the saturated medium.

The cooked supports are weighed before and after immersion in boiling water for two hours, the absorption rate (A%) is determined using the following formula:

$$A(\%) = [(P\_h - P\_s) / P\_h].100 \text{ -----------------------------Eq.III.4}$$

Where Ph: Weight of the wet support (after boiling)

Ps: weight of the dry support

The results of the absorption rates are graphically represented in Figure III.5. :
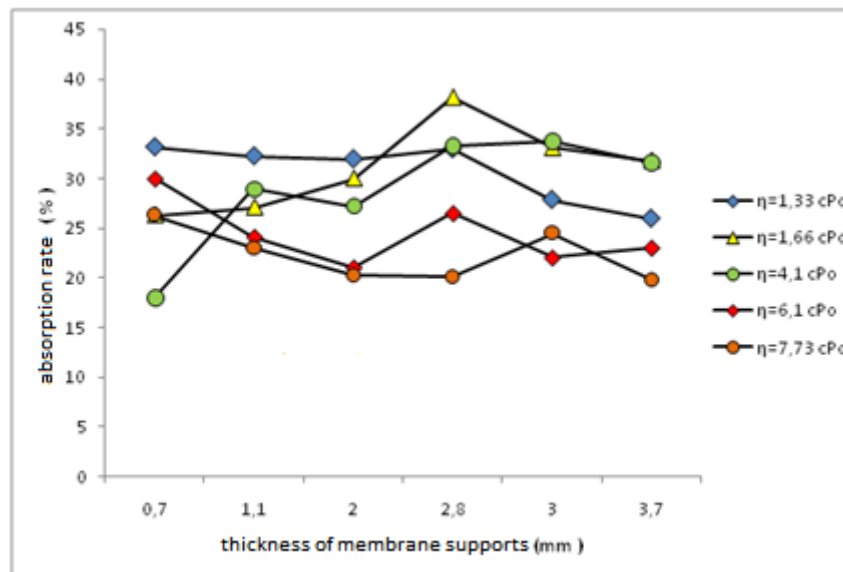
Figure III.5. Variation of the absorption rate according to the thickness of the support for each viscosity

It can be deduced that the highest absorption rate is obtained by using a slip with a viscosity of 1.66 cPo and for a casting time equal to 2.8 min; this rate is around 38.2%.

III.8. Characterization of ceramic shards

III.8.1. Study by X-ray diffraction

XRD is one of the most widely used techniques in the identification of minerals. The analyzes were carried out using an expert SW PRO diffractometer with copper anticathode ($\lambda = 1.5418$ Å) equipped with a nickel filter, an operating voltage of 45 kV and a working current of 40 mA. The sweep is between $2\Theta = 1°$ and $2\Theta = 70°$ with a step of 0.02°. The integration time is one second for each step
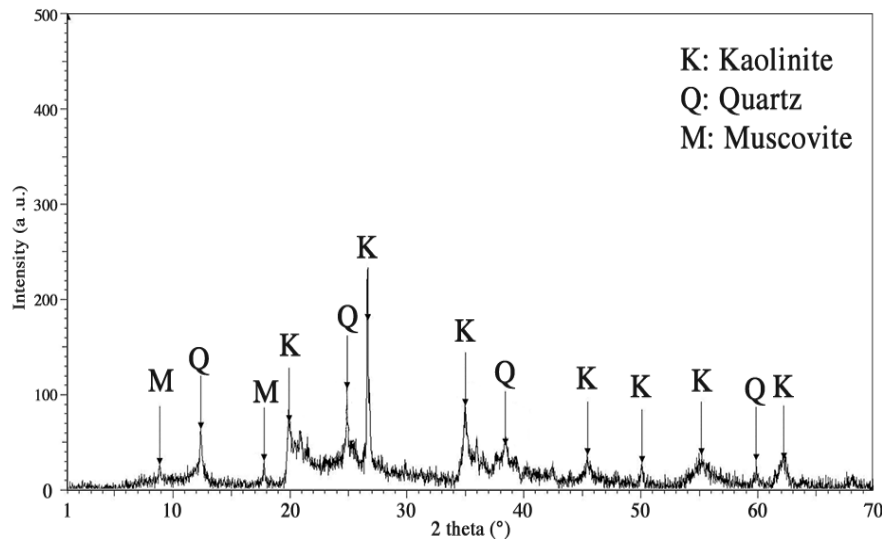
Figure III.6. Diffractogram of Kaolin KT2 Raw

Figure III.6. shows the Kaolin KT2 diffractogram. Analysis of the powder shows the main crystalline phases present in kaolin and confirms that its structure is essentially formed by a mixture of two crystalline phases identified as kaolinite and quatz. The characteristic peaks of kaolinite (20°, 26.8°, 35°, 45.5°, 50°) are observed. In addition to these main peaks attributed to kaolinite, the characteristic peaks of muscovite (8.9°, 17.8°) and quartz (12.3°, 25°, 38.5°, 60°) are also present. These are crystalline phases expected in such a type of kaolin [117, 118]. Other traces of phases are detected as in the case of free muscovite, which was also detected [118].
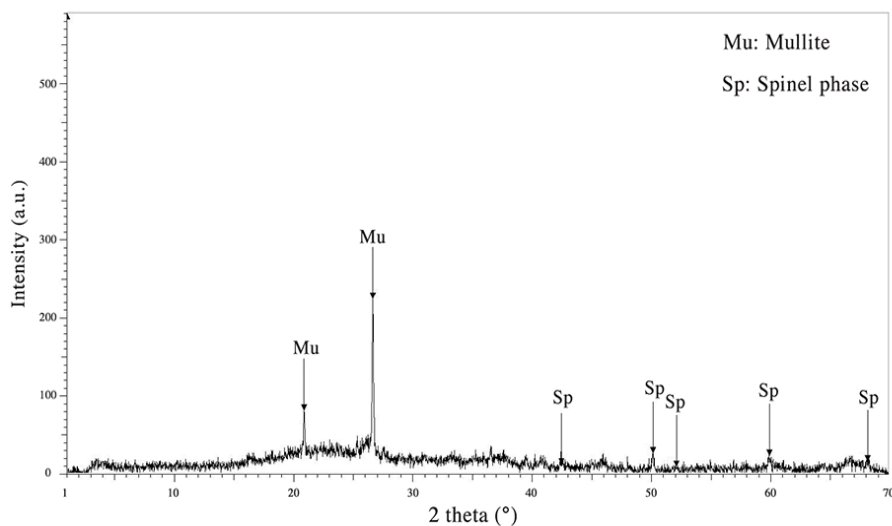
Figure III.7. Diffractogram of Cooked Kaolin KT2

The identification of the phases is of great importance before any membrane fabrication. Prior to heat treatment, it can be seen that kaolinite (K) was the major mineral component. At a

temperature of 1150°C, mullite (Mu) peaks appeared due to the transformation of metakaolinite. The main phases detected in the sintered membrane support at 1150°C were mullite phases and spinel phases **[119]** as shown in Fig. III.7.

III.8.2. Thermal analyzes

III.8.2.1. Thermal analysis (ATG-ATD)

ATG thermal analysis is a technique that consists of measuring the variation in mass of a sample as a function of temperature or as a function of time during isothermal experiments. This technique detects phenomena such as dehydration, and others. The ATD makes it possible to follow in real time the thermodynamic state of the samples during a heat treatment by comparing the flow of heat in the sample to be analyzed with that of a reference sample. The latter is used to show the energy released or absorbed through chemical reactions during the heating or cooling process.

The heating of the clay material leads to the elimination of organic matter, the departure from the water of constitution of certain mineral species such as kaolinite, the decomposition of carbonates, etc. It is therefore possible to follow the influence of temperature on the mass losses of the material studied, followed by thermo-gravimetric analysis (TG). The continuous weighing of substances can be done during a linear variation of temperature as a function of time. When the temperature of the reacting substances is kept constant, we pass to the limiting case of isothermal thermo-gravimetry. Figure III.8 represents the analyzes by ATG and ATD of our simple.
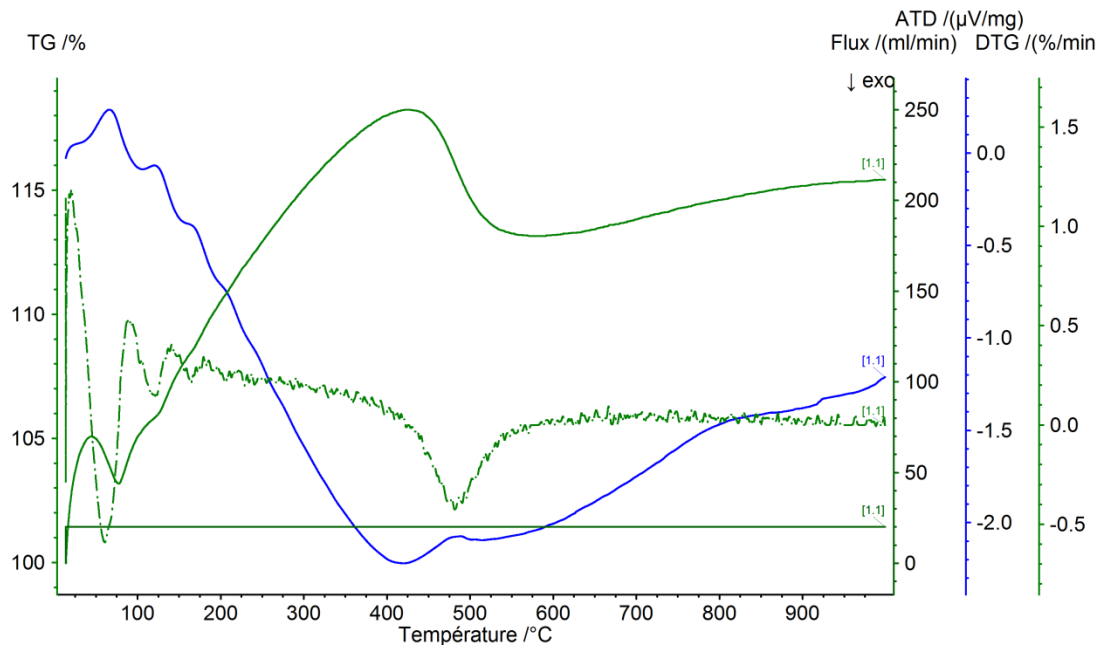
Figure III.8. Thermal analyses of Kaolin (ATG-ATD)

The raw material used, kaolin KT2, underwent a structural evolution and a loss of weight during its heating; therefore, thermogravimetric analysis has proven useful. This mass variation informs us about the possible transformations undergone by the material; for example, mass loss due to decomposition, phase transformation or mass gain **[120].** TG analysis of KT2 carrier showed total weight loss to be approximately 18%. In fact, this rate of weight loss includes two distinct stages. The first is attributed to the loss of the water added in the starting mixtures, while the second is linked to the loss of the water of composition of the kaolin (by vaporization) and from 573 °C, we witness a a densification of the material resulting from the allotropic transformation of the α-phase silica quartz into the β-phase. These observations are also confirmed by ATD**[121]**. Figure III.8.

III.8.3. Study by scanning electron microscopy (SEM)

Microscopy (SEM) allows the observation of the material, under vacuum, using an electron beam. The micrographs obtained from this technique show the microstructure of the material obtained after its heat treatment.
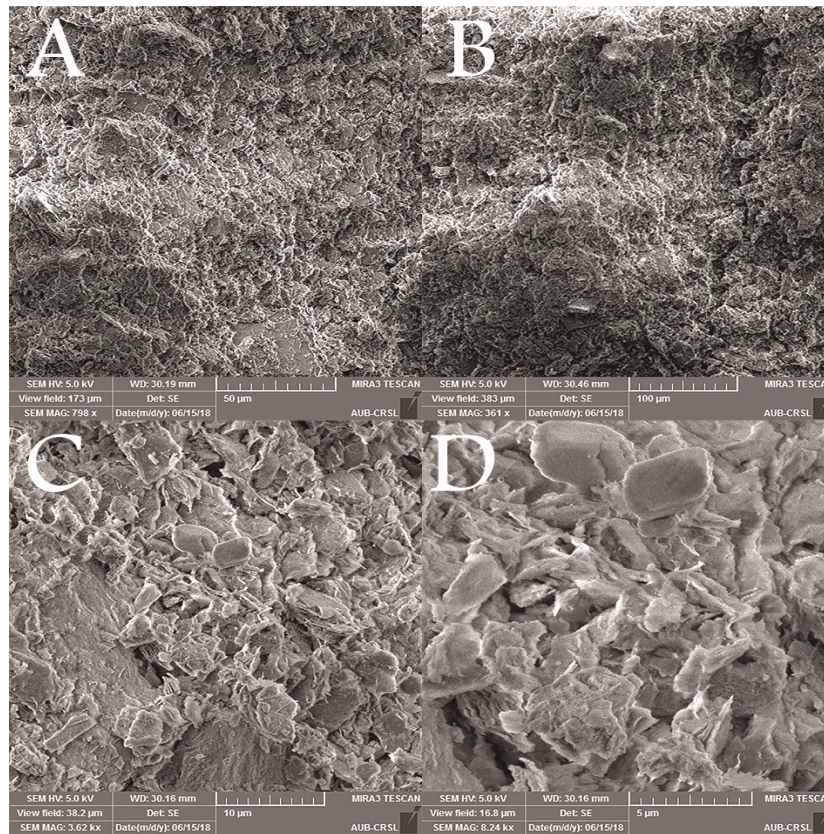
Figure III.9. SEM micrographs of the calcined support at different scales: surface section

To follow the micro-structural modifications of the ceramic supports obtained after calcination, a morphological study was carried out and the micrographs are illustrated in figures III.9. and III.10. It can be observed that the morphology of the calcined samples on the surface and in the section is very similar and that both have pores of various shapes. The presence of macropores is highlighted in the images of the calcined support in profile and in section showing a similar morphology already observed in the membranes made from kaolin alone **[122]**.
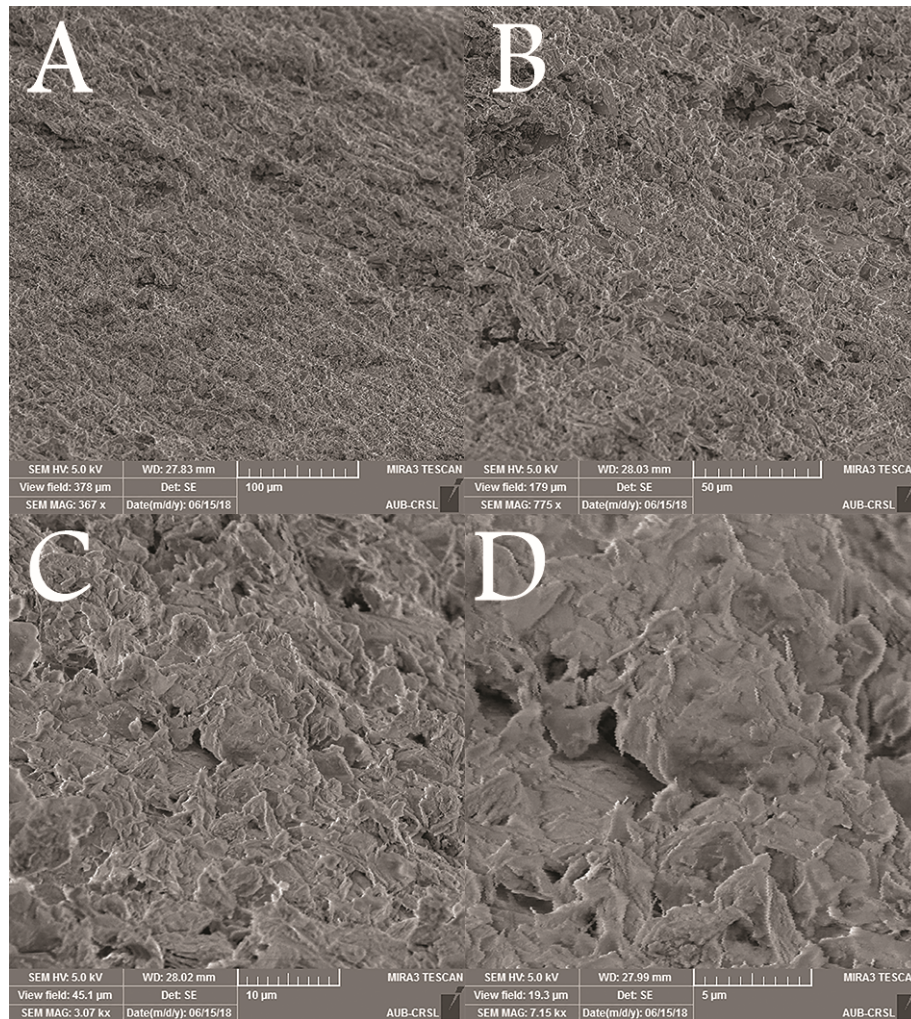
Figure III.10. SEM micrographs of the calcined support at different scales: profile section

The surface and profile micrographs show the absence of macro-defects such as cracks; densification corresponding to an increase in resistance and a decrease in porosity. This phenomenon is mainly due to the formation of a vitreous mass formed by the free silica and the molten impurities contained in the clay **[123]**. During the sintering of the ceramic supports, all the constituents remain in the solid state and the densification then results from the welding and the change in the shape of the grains. When this happens during solid phase sintering, densification occurs in three steps: formation of bridges between grains, elimination of open porosity and elimination of closed porosity until the end of sintering, this last step is the more difficult **[124].** The establishment of the heating program leading to the manufacture of a flawless material was necessary. From the structural point of view, the results obtained by the different modes of analysis helped us to use the material as a support and which will be used as a filtration membrane.

III.9.Gel Preparation

III.9.1 Sol-Gel Process

The name sol-gel is a contraction of the terms "solution-gelling". Before the gel state is reached, the system is in the liquid state: it consists of a mixture colloidal oligomers and small macromolecules. This stable dispersion of particles colloids within a liquid is called "sol". The gel consists of an oxide network swollen by the solvent, with chemical bonds ensuring the mechanical cohesion of the material giving it a rigid, non-deformable character. The time required for the "ground" to turn into a "gel" is called the gelation (or freezing point).**[125]**

The Sol-gel process is based on the use of a series of hydrolysis-condensation reactions carried out at room temperature, in order to produce networks of oxides which can then be thermally treated. This process is based on the principle of low-temperature synthesis, which makes it possible to produce materials efficiently and economically while controlling their structure and properties. By combining different chemical precursors.

III.9.2.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 (a gel can have an elastic character, but no macroscopic viscosity) **.[126]**

III.9.3.Nanopartules gel by sol gel method:

The sol-gel method is a conventional and industrial method for the synthesis of nanoparticles with different chemical composition. The basis of the sol-gel method is the production of a homogeneous sol from the precursors and its conversion into a gel.

In our case we made the synthesis of 5 gel one by sol gel method and four Nanoparticles gel by the same method .

For the first gel the operatin gprocedure is like that

We mix 3.94g of $NiCl_2$,3.11g of $AlCl_3$,100ml Methanol , we heat the solution to 80℃ with stirring for a period on one hour and half (1.30h) then we add drop by drop 4.34g of acetic acid ,plus 30ml of Ethylene glycol and 30ml distilled water. Continuous heating and stirring

Figure III.11. Photo shows the preparation of Nickel gel

For the second gel is zinc Nanoparticles gel by sol gel

For this purpose, 2 g of zinc acetate dihydrate was dissolved with a 15 ml of distilled water and 8 g of sodium hydroxide was dissolved in a 10 ml of distilled water. The solutions were stirred. Then the sodium hydroxide solution was added to the solution of zinc acetate with a constant stirring. Then 100 ml of ethanol was added the solution containing both sodium hydroxide solution and zinc acetate. After the reaction, ZnO nano gel was formed.
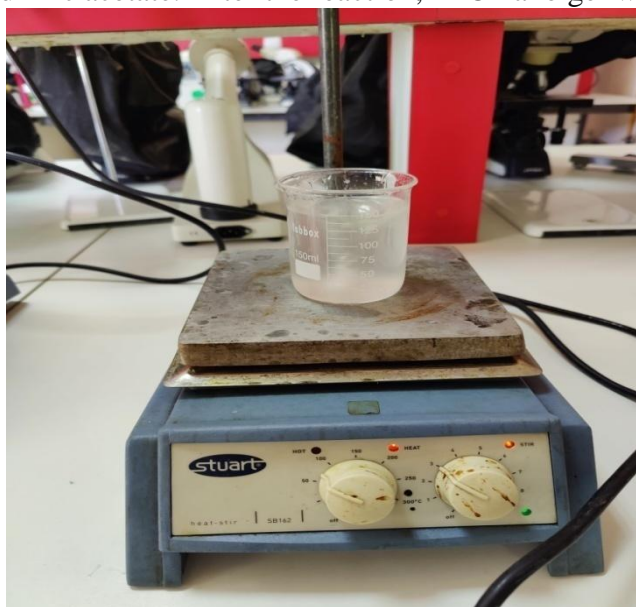
Figure III.12. Photo shows the preparation of zinc Nanoparticles gel

For the third gel is ferric Nanoparticles gel by sol gel

Put 15g ferric sulphat with 200 ml on heater and stirring and make another solution put in Becher 5g of ferrous sulphat with 50ml distilled water after that we mix the two solution and add ammonia solution until the gel forms
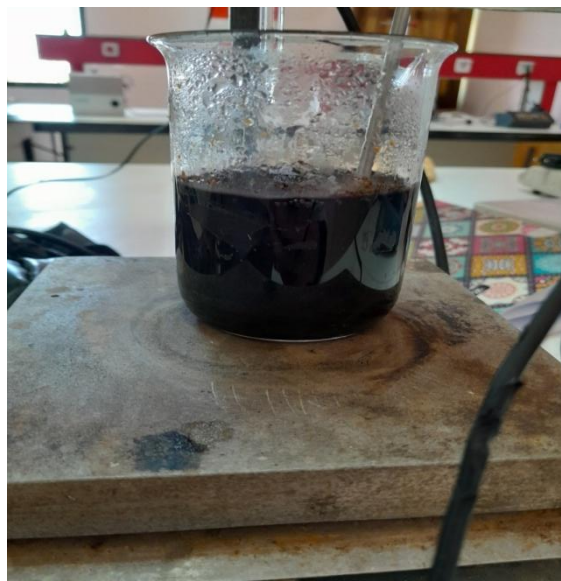
Figure III.13. Photo shows the preparation of ferric Nanoparticles gel

For the fourth gel is nickel Nanoparticles gel by sol gel

We mix 3.94g of $Ni(NO_3)_2$,3.11g of $CU(NO_3)_2$,100ml Methanol, we heat the solution to $80°C$ with stirring for a period on one hour and half (1.30h) then we add drop by drop 4.34g of acetic acid ,plus 30ml of Ethylene glycol and 30ml distilled water. Continuous heating and stirring until the gel forms.

Figure III.14. Photo shows the preparation of nickelNanoparticles gel

For the fifth gel is copper Nanoparticles gel by sol gel method

Aqueous solution of $CuCl_2.2H2O$ (0.2 M) was prepared in cleaned round bottom flask. 1 ml of glacial acetic acid was added to above aqueous solution and heated to 100 °C with constant stirring. 8 M NaOH was added to above heated solution till pH reaches to 7. The color of the solution turned from green to black immediately and the large amount of black precipitate was formed immediately While the black precipitate was formed about 10 g of neutral alumina was added with constant stirring for one hour.

Figure III.15. Photo shows the preparation of copper Nanoparticles gel

III.10.Application

We put gel in membrane(we closed a membrane side and put gel and closed the another side and keep moving until the gel speards to all the space) an heat it on 350 ^{0}C for a 2h and we reapeated the operation for each gel this operation allow to create a thin film inside the membrane

III.10.1.Experimental setup

After making membrane supports now we gone a start the
filtering process
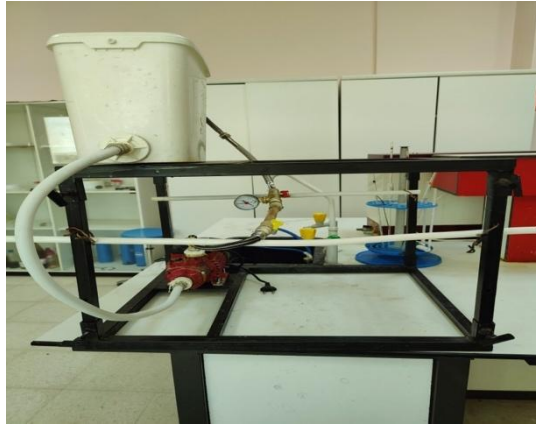
Figure III.16. shows the various components of the test bench in order to qualify the ceramic membranes designed

1. Pump;
2. A 20 liter capacity tank;
3. Shut-off valves;
4. The membrane.
5. Barometer
6. Treated water collection container

III.11. Filtration tests

After having characterized the developed membranes and finished the nanoparticle gels,We tested the effectiveness of membrane supports withtwo rejection:

III.11.1.The first one is oil discharge (ARZEW)

We try five different types of gelsin the same type of membrane baked at 1150°C and this is the result

a) Nickel sol-gel
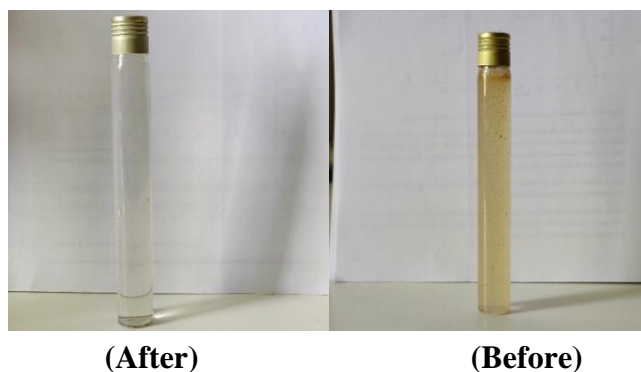
(After)   (Before)

Figure III.17. The oil discharge before and after the treatment with Nickel sol-gel thin film

as we see there are a difference between before and after filtering and this due to Membranes with thin layers it's have small pores, which effectively trap particles or molecules of larger sizes.

b) Nickel nanoparticle gel
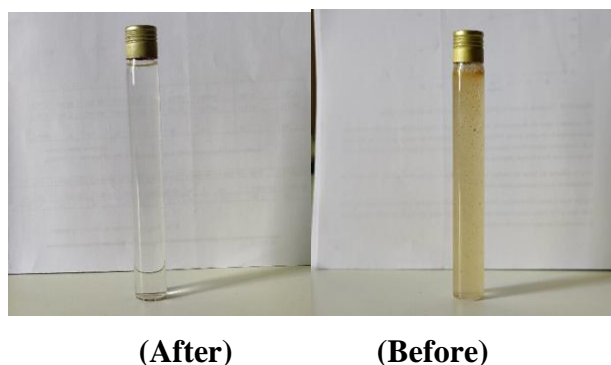
(After)   (Before)

Figure III.18.The oil discharge before and after the treatment with Nickel nanoparticle gelthin film

The observed difference before and after filtering can be attributed to the unique characteristics of the thin-layered membranes used in the experiment. These membranes possess small pores that play a crucial role in capturing particles or molecules of larger sizes. This capability is achieved through the membranes' selective permeability, allowing them to selectively permit the passage of desired components while blocking unwanted substances.

c) Zincnanoparticle gel
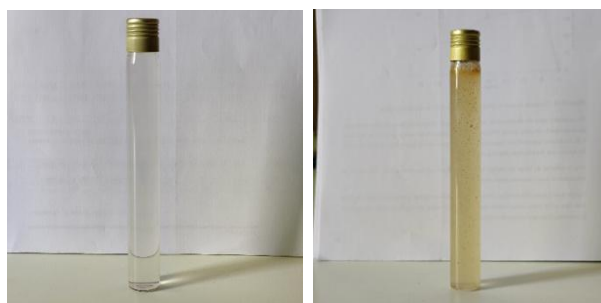
(After)   (Before)

Figure III.19.The oil discharge before and after the treatment with Zincnanoparticle gelthin film

The noticeable difference before and after filtering is attributed the membranes' ability to effectively trap particles or molecules of larger sizes through their small pores, combined with their selective permeability, leads to the observed difference between the initial and filtered samples.

d) Copper nanoparticle gel

(After)   (Before)

Figure III.20. The oil discharge before and after the treatment with copper nanoparticle gel thin film

The membranes' small pores, selective permeability, and the influence of pressure or flow rate collectively contributed to the observed difference before and after filtration. These characteristics enabled the membranes to effectively capture larger particles or molecules and selectively separate the substances based on their permeability, resulting in a successful filtration outcome.

e) Iron nanoparticle gel

| (After) | (Before) |

Figure III.21.The oil discharge before and after the treatment with Iron nanoparticle gelthin film

The noticeable difference observed between the pre-filtered and post-filtered samples can be attributed to a combination of factors, including selective permeability, pressure or flow rate, and surface properties of the membranes.

III.11.2. The second one is Textiledischarge (SOFACT)

Alsowe try five different types of gelsin the same type of membrane baked at 1150°C

a. Nickel sol-gel
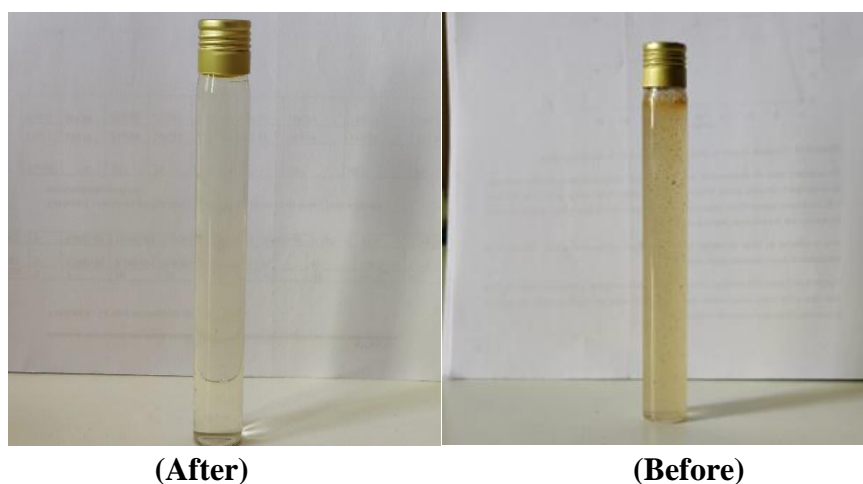
| (After) | (Before) |

**Figure III.22. The Textile discharge before and after the treatment
with Nickel sol-gel thin film**

The applied pressure or flow rate during the filtration process plays an important role. By optimizing the pressure or flow rate, the membranes can effectively enhance the filtration efficiency. This improved condition allows for more efficient removal of unwanted particles or particles from the solution, which contributes to the observed difference between the raw and filtered samples.

b. Nickel nanoparticle gel
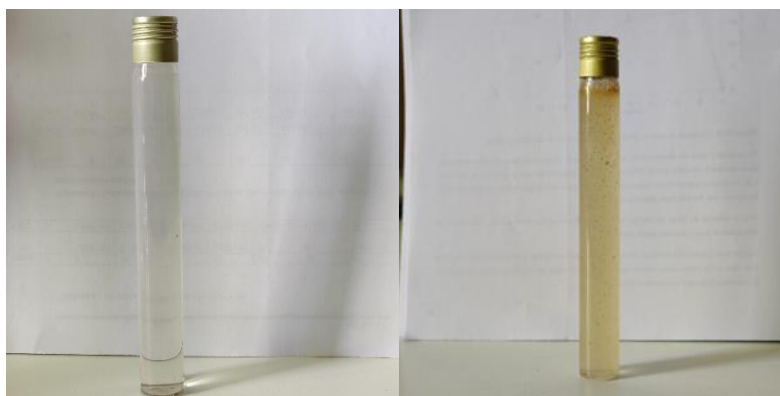

(After)   (Before)

Figure III.23. The Textile discharge before and after the treatment with Nickel nanoparticles gel thin film

The difference observed before and after filtering can be attributed to several factors. First, the membranes used in the filtration process exhibit selective permeability, allowing only some materials to pass through while blocking others. This property enables the membranes to specifically target and remove impurities present in oil discharges and industrial discharges, resulting in a clean, filtered solution.

c. Zincnanoparticle gel
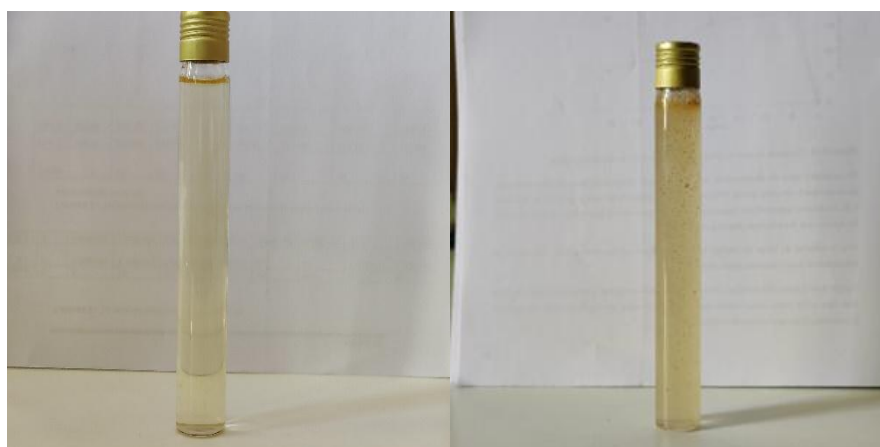
(After) (Before)

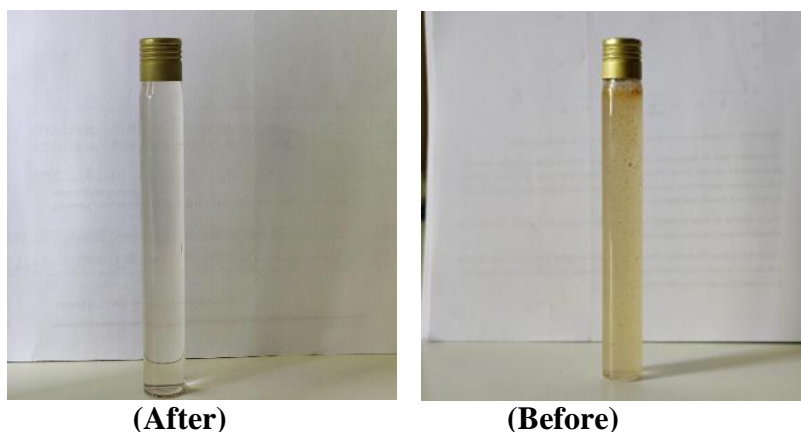**Figure III.24. The Textile discharge before and after the treatment with Zinc nanoparticles gel thin film**

The observed difference between the initial and filter states can be attributed to several factors, namely the selective permeability, pressure or flow rate, and surface properties of the membranes.

d. **copper nanoparticle gel**
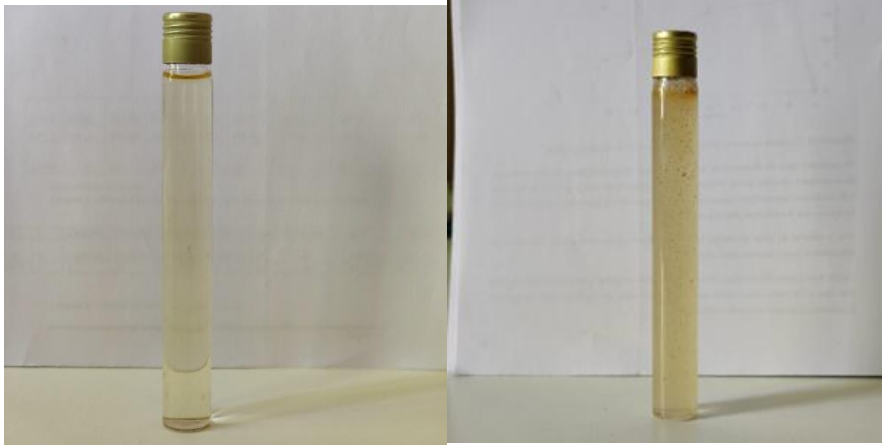
Figure III.25.TheTextile discharge before and after the treatment with copper nanoparticles gel thin film

The membranes used in the filtration process may possess adsorptive properties, allowing them to attract and retain certain substances on their surfaces. In the case of oil discharge and industrial discharge, the membranes could have adsorbed the oil or other contaminants, effectively removing them from the solution.

e. **Iron nanoparticles gel**
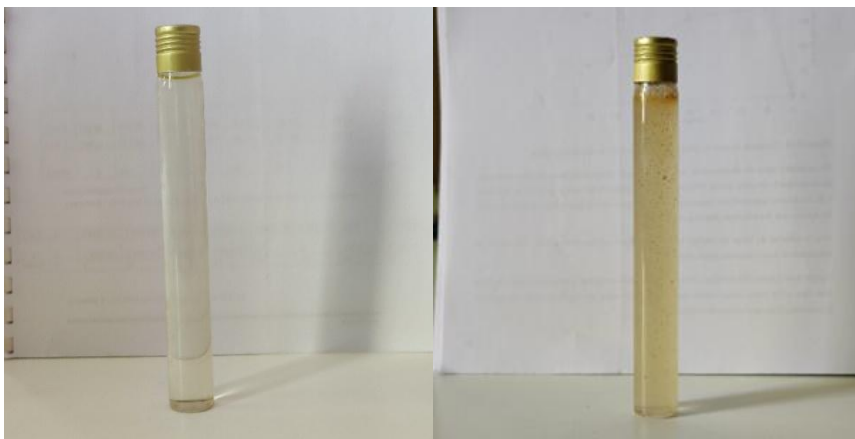
(After)   (Before)
Figure III.26. The Textiledischarge before and after the treatment with

Iron nanoparticles gel thin film

Adsorption played an important role in the filtration process, moreover, the pore size of the membranes played a vital role in the filtration efficiency. The membranes contain micro-sized pores that effectively trap particles and particles larger than the pore size.

Table III.2.Table represents the pH values

	Textile discharge		Oil discharge	
	Before	After	Before	After
Nickel	6.41	6.93	7.45	7.49
Nickel NPs		7.32		7.29
Zinc		8.00		12.29
Iron		6.00		10.33
Copper		8.30		9.78

Table III.3.Table represents the (COD)and (BOD) values before and afterthe treatment with Nickel nanoparticles gel thin film

Textile discharge				Oil discharge			
(COD)		(BOD)		(COD)		(BOD)	
Before	After	Before	After	Before	After	Before	After
221 mg/l	87 mg/l	12.43 mg/l	7.81 mg/l	235 mg/l	96 mg/l	13.59 mg/l	9.75 mg/l

After visual inspection, we did the(COD)and (BOD)before and after the treatment with Nickel nanoparticles gel thin film for each discharge because he gave us a best result and we get a decrease in valuesof (COD)and (BOD) , This means there is a good treatment

GENERAL CONCLUSION

General Conclusion

The aim of this work was the treatment of oil and industrial discharge using ceramic membranes modified by metallic nanoparticles prepared from Algerian kaolin (Kaolin KT2 from Tamazert).

In this study, the characterization of the prepared ceramic membranes was one of the main objectives.

At the initial stages of the research, our focus was directed towards the preparation of membrane supports using kaolin, involving several sequential steps including molding, drying, and firing up to a temperature of 1150°C. Subsequently, a thin layer was meticulously deposited onto the membrane support to enhance its filtration capabilities. Following the gel deposition via the

Engbing method, the membrane supports were subjected to firing at a temperature around 300°C for a duration of two hour.

In a subsequent step, the ceramic membranes underwent the following characterizations: X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and differential thermal analysis (DTA).

The TGA/DTA analysis results indicated two stages of weight loss. The first stage was attributed to the release of moisture, which included both added water and chemically bound water within the kaolin mixture. The second stage corresponded to the release of chemically bonded water and water originating from the chemical composition of the kaolin. This stage predominantly exhibited the formation of mullite and spinel phases, along with the densification of the material resulting from the allotropic transformation of silica quartz. The X-ray diffractogram of the samples sintered at 1100°C and 1250°C for five hours reveals the appearance of a low-intensity first peak corresponding to mullite grains. The low intensity suggests weak grain development in this direction. Additionally, there is an overlapping, more intense quartz peak at the base with two mullite peaks.

The application of these membranes in the elimination of pollution has shown promise a reduction in the COD and BOD of industrial effluents shows that the application of these membranes improved by a deposit of thin membranes based on nanoparticles is very encouraging and that studies in the future can improve this process of treatment

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ANNEX

Annex

Introduction

The Dissolved Chemical Oxygen Demand (DCO) and Biochemical Oxygen Demand (BOD) are parameters used in environmental and water quality analysis to assess the organic pollution levels in water and wastewater. Both DCO and BOD are essential indicators in monitoring and managing water quality, assessing the efficiency of wastewater treatment processes, and evaluating the environmental impact of discharged effluents. These parameters help in understanding and safeguarding the health and integrity of aquatic ecosystems.

Products and materials

- ❖ **Products**
    - Concentrated sulfuric acid d = 1.83 g/l (hazardous);
    - 4 M dilute sulfuric acid;
    - Solution of silver sulphate in concentrated sulfuric acid, (dangerous);
    - Ammonium iron sulfate solution approximately 0.12 M;
    - Mercury sulphate in crystals;
    - 0.04 M potassium dichromate solution;
    - Ferroin solution.

- ❖ **Material**
    - Reflux device;
    - 250ml balloons;
    - 5 ml volumetric pipette;
    - 25 ml burette;
    - Test tube of 10 ml and 20 ml;
    - Heating ramp;
    - Magnetic agitator.

Operating mode

It is necessary, before carrying out the determination of the COD itself, to check the titer of the ferrous solution and to carry out a blank test.

Verification of the titer of the ferrous solution

Given the extreme oxidizability of Fe++, this verification must be done every day.
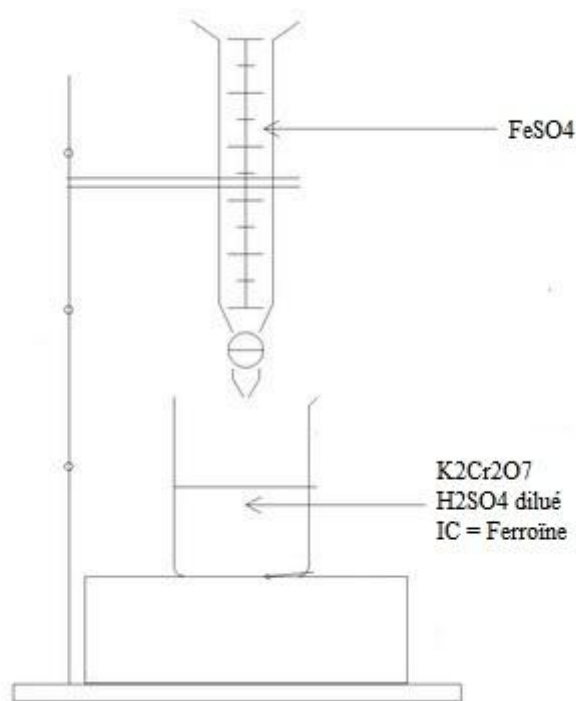
Annex

❖ **Schema**

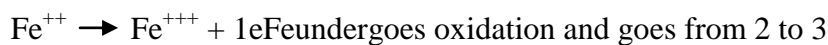**Figure 2 :Dispositif de dosage de la solution fer reuse**

❖ **Protocol**

- Introduce 10 ml of dichromate solution into a beaker using a pipette;
- Make up to approximately 100 ml with the dilute sulfuric acid solution;
- Add with the ferrous solution until the mixture turns purplish red.

    Let V1 be the volume of ferrous solution used.

❖ **Expression of results**

During the redox reaction, the following changes in the oxidation states are observed:

$Cr_2O_7^{-} + 6e \rightarrow 2\,Cr^{+++}$Cr Undergoes reduction and transforms 6 to 3

$Fe^{++} \rightarrow Fe^{+++} + 1e$Feundergoes oxidation and goes from 2 to 3

So: A molar solution of $Cr_2O_7^{-}$ corresponds to 6 N and a molar solution of Fe^{++} corresponds to 1N.

Let: N_1 = normality of Fe^{++},

V_1 = volume of ferrous solution used

N_2 = normality of the dichromate solution, i.e. 0.04 X 6 = 0.24 N

V_2 = volume of dichromate

we have: $N_1 . V_1 = N_2 . V_2$(Eq. 01)

$N_1 = (N_2 . V_2)/V_1$(Eq. 02)

From where$N_1 = (0.24 \times 10)/V_1 = 2.4/V_1$(Eq. 03)

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Blank test

Its purpose is to evaluate the consumption of dichromate by the reducing agents which could be found in the mixture and which originate from a lack of purity of the reagents and the use of questionable glassware. Carry out this test in parallel with the COD determination, see below (B − 3 − 3), but replacing the test portion with 10 ml of distilled water. We will call VB the volume of ferrous solution used to obtain the color change

COD determination

Sample preparation

Homogenize the sample if necessary and introduce the following in the order given, into a 250 ml flask:

- Add 10 ml of the sample using a graduated cylinder; rinse the cylinder with a stream of distilled water, transfer the washings into the flask.
- Add a few glass beads or equivalent.
- Add a pinch of mercuric sulfate, approximately 0.4 g.
- Add 5 ml of dichromate using a pipette.
- Add 15 ml of concentrated sulfuric acid (dangerous) using a graduated cylinder; perform this operation carefully while gently swirling the flask in a circular motion.
- It is desirable to place the flask on a bed of ice throughout the procedure to prevent the release of heat from causing the volatilization of substances. (The flask can optionally be cooled under tap water).
- Connect the condenser to the flask and supply it with tap water.
- Bring to a reflux boil for 2 hours; the boiling should be steady without any surges or excessive boiling.
- Allow the flask to cool.
- Dislodge any deposits that have formed on the inner wall by using a stream of water from a wash bottle directed towards the bottom of the flask.
- Remove the flask from the heating apparatus and condenser.
- Bring the volume up to approximately 75 ml with distilled water and allow it to cool to room temperature.
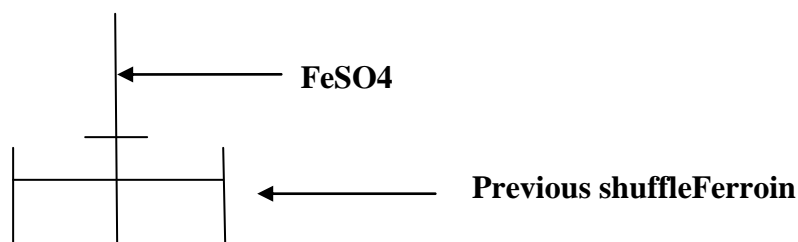
Annex

Dosage

Figure 3: COD dosing device

❖ Protocol:

- Transfer the contents of the flask into a 250 ml Erlenmeyer flask.
- Rinse the flask with a minimal amount of distilled water and add the rinsing water to the mixture.
- Add a few drops of ferroin into the Erlenmeyer flask.
- Titrate with the ferrous solution until the blue-green color changes to reddish-brown.
- Let Ve be the volume of ferrous solution used.

❖ Expression of results

The COD expressed in mg/l is given by the formula

DCO mg/l $= (800.N_1.(V_b-V_e))/V_0$

With : V_B = volume of ferrous solution used for the blank test

V_e = volume of ferrous solution used for the sample

V_0 = volume of the test aliquot

N_1 = normality of the ferrous solution

❖ **Application domain**

The method is applicable to water whose COD is between 30 and 700 mg/l. The chloride concentration must not exceed 2000 mg/l. A dilution of the sample is necessary if these maximum limits are reached.

Biochemical Oxygen Demand

❖ Operating Procedure :

- Measure the desired quantity (refer to the table below) using the graduated overflow flask and pour it into the clean bottle.
- Insert the magnetic stirrer into each bottle.
- Add a pinch of allylthiourea.

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- Place 2 potassium hydroxide tablets into each inner cap (black) using two tweezers.
- Screw the cap without sealing it tightly.
- Set the agitation system to 20 °C.
- Allow the equilibrium to establish for 30 minutes and then seal the cap tightly.
- Record the values after 5 days (Oxytop system).
- Use the measurements from other groups to determine the precision of the measurements.

- Place 2 potassium hydroxide tablets into each inner cap (black) using two tweezers.