Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

A Systematic Literature Review of Ceramic Membranes Applications in Water Treatment

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Abstract

Ceramic membranes can be described as fine sieves used for separation. They are made from inorganic ceramic materials (zirconia, silicon carbide, alumina, titania, etc.), usually consisting of several layers of one or more ceramic materials. Chemical addition, coagulation, flocculation, sedimentation, filtration, and disinfection, commonly with chlorine, are all common methods for treating raw water for municipal drinking water supplies. Many attempts have been made to produce ceramic membranes with superior properties by varying used raw materials for the application of water treatment. Ceramic membrane exhibits good applications in microfiltration and ultrafiltration process for water treatment, which has many advantages like recycling, volume reducing of household wastewater, safe drinking water in remote areas and farms, help in limited drinking water production in developing nations or during humanitarian crises. Microfiltration / ultrafiltration ceramic membranes can be used to remove water turbidity, microorganisms, salinity, organic matter, and disinfection byproduct precursors. However, the hydrophilic surface of membranes can improve antifouling properties. This article reviews a summary on the traditional techniques and different uses of ceramic membranes in water treatment, characteristics of ceramic membranes and different manufacturing technologies of ceramic based membranes.

Keywords: Ceramic membranes, Preparation, Characterizations, Wastewater treatment, Standards

1. Introduction

One of the main and most important components in our life on this planet is water. Only around 2.5 percent of the world's total water content is pure water, which makes up roughly 71 percent of the overall water content (Fig. 1). Fresh water is required to keep life in our environment. As shown in Fig. (2), one of the biggest sources of pollution is industrial wastewater [1-3]. According to recent FAO study, to feed the world in 2050, around 20% more fresh water will be required to meet the demand [2]. Water scarcity is therefore becoming a global challenge needed to be solved.

Over 99.8% of death caused by poor quality of drinking water in the developing countries according to World Health Organization (WHO) which make an increased need for safe and adequate large amount of water which is free from physical, chemical, and biological contaminations [4] [5]. Traditional techniques are used for that purpose such as boiling and using UV lamps (heat and UV based systems), flocculation, precipitation, and adsorption (chemical treatment-based systems), settling and filtration (physical removal processes) [6].

2. Traditional Techniques for Water Treatment

2.1. Physical methods

These methods for treating water and wastewater do not depend on making chemical or biological changes but on relying physical ones. The most popular physical methods to control pollution of water are Sedimentation, Degasification and Filtration.

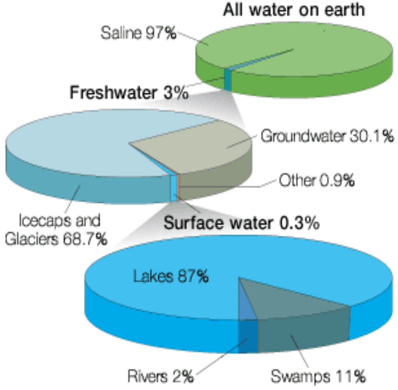

Fig. (1): Global water distribution [3]

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Receive Date: 13 November 2021, **Revise Date:** 05 December 2021, **Accept Date:** 12 December

DOI: 10.21608/EJCHEM.2021.105802.4871

Fig. (2): Major causes of Water Pollution [1]

2.1.1. Sedimentation

Sedimentation is one of the most important main wastewater treatment procedures. Gravity settling is the method for separating particles from a fluid. The suspended particles remain stable because the velocity of the water during the treatment process is low, following which the particles settle by gravitational force [7]. On the surface of the suspended particles, certain chemicals are adsorbed during organic chemical sedimentation. When Pollutants have density higher than that of water, they separate and settle at the bottom of the streamline. In the water stream, Solid suspended particles are exposed to shear forces so, they undergo hydrodynamic and physical processes, which affect the aggregation process and solid removal efficiency [8]. Gravity sedimentation, flocculation, and thickening all affect sedimentation efficiency.

2.1.2. Degasification

Degasification is defined as removing gases which is dissolved in solutions. The amount of gas dissolved in a liquid is proportional to the partial pressure of that gas which is called as Henry's law. Degasification process is based on this law. Degasification is a low-cost method of removing CO_2 gas from polluted water. The time it takes for the degasification process to complete is determined by the following factors: polluted water's temperature, as well as tank capacity.

2.1.3. Filtration

The technique of eliminating pollutants based on their size is known as filtration. Pollutant removal from wastewater permits water to be reused for a variety of purposes. The types of filters used in the procedure differ depending on the contaminants present in the water. Particle filtration and membrane filtration are the two main forms of wastewater filtration [9]. Particle filtering is one of the most important processes in the wastewater treatment process. It's made to get rid of solids that are bigger than one micron in size. The particle form, size, texture, density, and quantity all influence the type of filter employed in the filtration process. Used filters in dirty water filtration process are divided into two main types: bag and cartridge filters [10].

2.2. Chemical methods

An additional method for reducing discharge of pollutants and wastewater into water bodies is the chemical method. Flocculation and coagulation, Ozonation, Chemical precipitation, Adsorption and Ion exchange are different chemical methods used for safe disposal of contaminants.

2.2.1. Flocculation and Coagulation

In industrial wastewater treatment, a solid-liquid separation is done by coagulation and flocculation (Fig. 3). As shown in Fig. (4), adding certain coagulants cause destabilization for the colloidal suspensions leading to aggregation of smaller particles [8, 11].

2.2.2. Ozonation

Ozonation had great importance in industrial water treatment because of high disinfection and oxidation capacity of ozone. So, ozone is used in many applications in wastewater treatment including Odor, taste, and color removal from substances, obtaining higher oxidation state for inorganic compounds, Disinfection, splitting of rarely biodegradable compounds and Oxidation of organic pollutants.

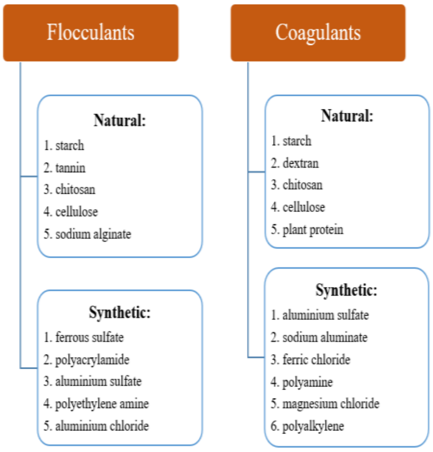


Fig. (3): Examples of natural and synthetic flocculants and coagulants

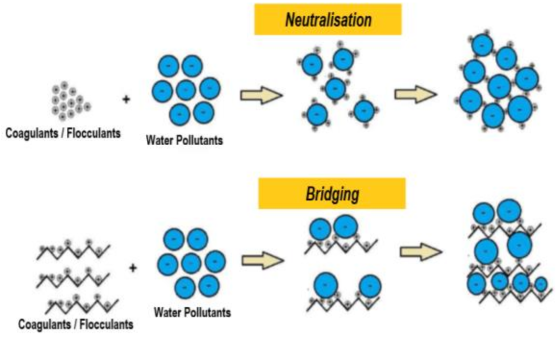


Fig. (4): Coagulation mechanism

2.2.3. Chemical precipitation

Heavy metals found in industrial effluents cause danger to the environment and chemical precipitation is a very effective process for removing it. Chemical formation between precipifying agents and dissolved metal components causes transformation of ionic metals into insoluble particles. Cationic metals are frequently removed using chemical compounds [12]. It can also eliminate living anions and molecules in some instances. Hydroxide precipitation, Carbonate precipitation and Sulphide precipitation are the three main types of precipitation in water treatment processes.

2.2.4. Adsorption

Removing organic and natural contaminants from the environment is done by adsorption process (Fig. 5). Chemical overlap or interphase between two phases processes is referred to as adsorption [13, 14]. According to interaction between adsorbents and adsorbate, adsorption extraction process can be categorized into two main categories: physisorption and chemisorption. Dosage of adsorbents, contaminant concentrations in polluted water, Temperature, pH, and Time of Contact are factors that affect the adsorbent's capacity in adsorption process.

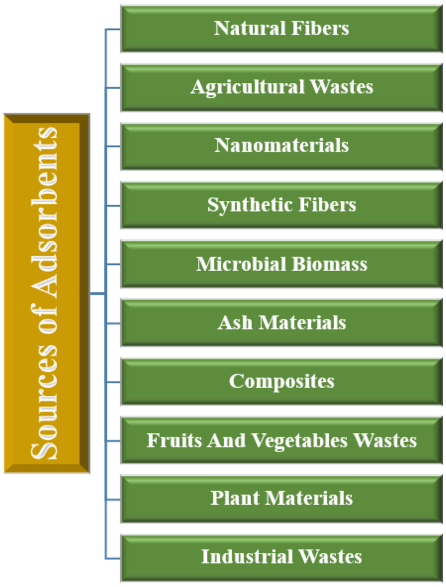


Fig. (5): Different sources for adsorbents

2.2.5. Ion exchange

The ion exchange procedure is a method of replacing ions in wastewater treatment. Resins are compounds that are utilized to identify impurities [15] [16]. The active groups that are covalently bonded to the resin frames generate a polymer matrix that is coupled to the building spaces and allows for proper ion transport. Ion exchange processes are divided into two categories: cation exchange and anion exchange.

Membrane technology is a promising method and have become widely used in our life due to their simplicity in operating, high effectiveness, and its low cost. Microfiltration (MF), ultrafiltration (UF), Nano filtration (NF) and reverse osmosis (RO) are membrane- based processes which are used for water treatment [17] such as treatment of textile wastewater [18].

3. Classification of Membranes

Researchers have classified membranes according to many parameters such as: used driving force, morphology, and structure of membrane (their pore sizes) [19], mechanism of separation, and materials used in membrane fabrication [20]. Fig. (6) shows membranes classifications according to the fabrication material.

The transport quality of solutes through the membrane is determined by the permeability of the used membrane and the driving force. Darcy's law of flow through porous materials under laminar flow conditions, which states that flux varies linearly with increase pressure, can be used to describe the pure water membrane flux, J, in pressure-driven processes [21].

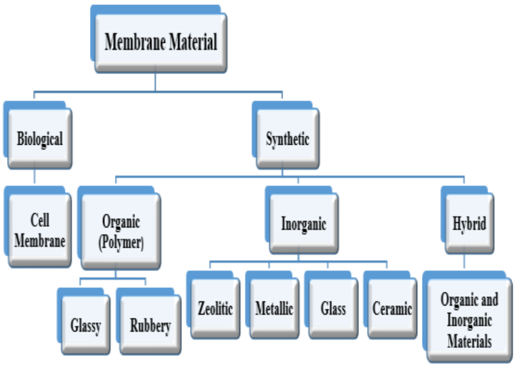


Fig. (6): Classification of membranes according to different materials used for membrane fabrication [20]

$$J = A(\Delta P) \qquad (1)$$

Where: A is a function of membrane porosity, pore size and tortuosity and membrane thickness, and ΔP is the hydraulic driving force.

Membranes can be formed out of a variety of different materials. The material required for membrane fabrication is chosen based on processing needs, thermal and chemical stability, and the tendency of fouling [22]. In membrane separations, there are two primary modes of operation: crossflow and dead end. The feed solution flows perpendicular to the membrane surface in the dead-end mode. There is no reject stream in crossflow (tangential flow) filtration, only a feed stream and a permeate stream, as shown in Fig. (7).

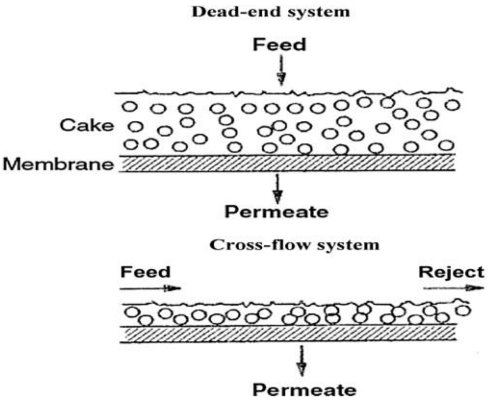


Fig. (7): Dead-end filtration and crossflow filtration [22]

Those used membranes are either polymeric or ceramic [23] and because of the nature of polymeric ones as they aren’t suitable in harsh conditions such as severe chemical environment and high temperatures, ceramic membranes have got great attention as they have superior characteristics and long lifetime [24] [25, 26]. To address the issue of commercial ceramic membranes' high cost, academics have proposed two primary techniques to dramatically reduce their cost: 1) use of less expensive materials and 2) energy conservation during heat treatment [27]. As a result, substantial work has gone into developing alternative nature-based ceramic membranes made from clay materials such kaolin, ball clay, bauxite, and bentonite. Other waste materials, such as rice husk ash and aluminum dross, have also been utilized to make ceramic membranes [28]. Asymmetric structures are common in ceramic membranes and used for water and wastewater treatment, with a thin selective layer, intermediate layer(s), and permeable supporting layer (Fig. 8). [29-34].

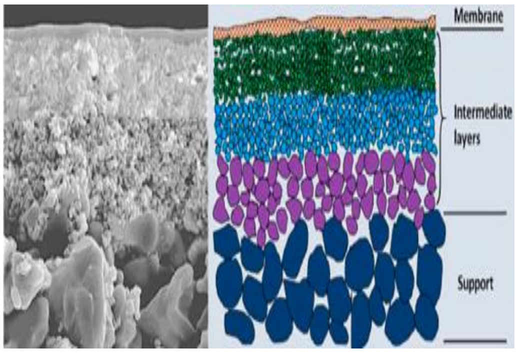


Fig. (8): The schematic of the ceramic membrane cross-section [29]

4. Categorization of Ceramic Membranes

Ceramic membranes can be categorized into two categories according to their structure [35]:
1. Porous membranes
2. Dense membranes

4.1. Porous membranes

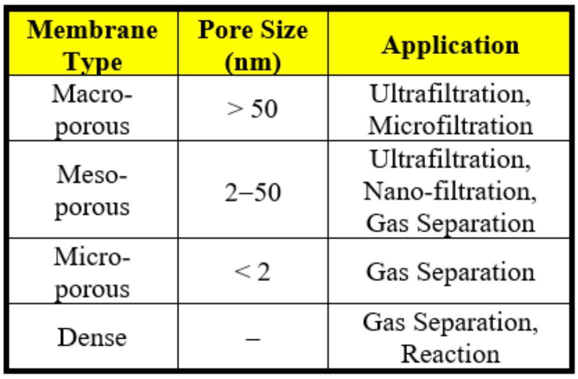
Porous ceramic membranes are usable in high temperature operations and aggressive environments because they have the advantages of high porosity, high temperature and chemical resistance. Pore diameter of microporous inorganic membranes is smaller than 2 nm (0.5–2 nm) and they are under the category of porous membranes. Microporous inorganic ceramic membranes may be amorphous or crystalline (zeolite) [36]. Many microfiltration applications depend on using porous ceramic membranes such as: gas purification, membrane distillation and separation of water and oil [37].

They have many fields of application, ranging from catalyst supports to filters for molten metals, aerosol filters and gas adsorbers, filters for hot corrosive gases and particulate- containing diesel engine exhaust gases [38]. Removing sand. Silt, bacteria and algae can be by choosing microfiltration membranes and viruses can be controlled also, although they can’t be removed completely. Fouling can be reduced also because MF membranes are able to remove organic matters so, it is a pretreatment step for RO and NF applications to reduce fouling hazards. Besides, it can reduce the demand for chlorine in water disinfection as it helps removing pathogens.

4.2. Dense membranes

When polycrystalline ceramics or metals are used to fabricate membranes, those produced membranes are called dense inorganic membranes. Dense inorganic membranes allow permeation of gases through its crystal lattice [36]. Dense membrane (<0.5 nm) materials are ideally selective for O_2 or H_2 molecules [39]. Table (1) shows different applications of ceramic membranes according to difference in their pore size.

Table (1): Types and applications of ceramic membranes [36]



Membrane Type	Pore Size (nm)	Application
Macro-porous	> 50	Ultrafiltration, Microfiltration
Meso-porous	2–50	Ultrafiltration, Nano-filtration, Gas Separation
Micro-porous	< 2	Gas Separation
Dense	–	Gas Separation, Reaction

Another categorization for ceramic membranes may be according to its shape (disk, pot, candle element) as shown in Fig. (9), combustible material used (flour, rice husk, saw dust), and type of clay used as a raw material (white kaolin, black clay, red clay).

5. Preparation of Ceramic Membranes

They're made by depositing one or more active layers of desirable materials (TiO_2, ZrO_2, $ZnAl_2O_4$, zeolite, and so on) on an inorganic membrane support made of mineral clays. Various membrane supports for microfiltration and ultrafiltration have been developed using a variety local mineral clay with unique qualities from Morocco, Tunisia, China, and Algeria (porosity and pores diameter) [40]. Ceramic membranes can be fabricated by different techniques such as slip casting, tape casting, pressing, extrusion, sol-gel process, dip coating, chemical vapor deposition, and anodic oxidation. The selected production method greatly depends on the desired membrane structure and the specific application [30, 33-34].

The following steps describe the preparation of ceramic membranes:

a) Formation of the suspension: by mixing a suitable liquid with the starting powder
b) Forming: Where the prepared suspension is packed into membrane precursor with the required shape such as flat sheet or tube.
c) Heat treatment: Consolidation of the prepared shaped precursor by a heat treatment process.

Firing step is noted to be the most important step in preparation of ceramic membranes.

On the other hand, sol-gel and CVD preparation methods can be used to produce multi-layers' membrane before being fired by coating a membrane support with the required layers [41].

The following section details the different methods used in ceramic membrane fabrication [30, 42-43].

Fig. (9): Types of Ceramic Water Filter Elements according to its shape

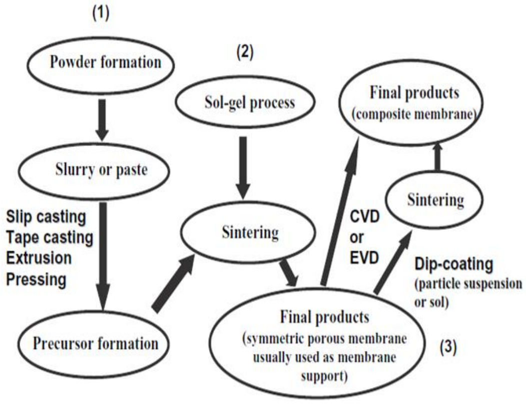


Fig. (10): General ceramic membrane preparation procedures [36]

6. Advantages of Ceramic Membranes

Ceramic membranes offer many advantages to polymer and inorganic membranes such as: [31-32, 41, 44-45]

a) They are environmentally friendly.
b) Ceramic membrane filtration is a mild and highly selective process without phase transformation.
c) They are usually characterized by low running costs whether through closed production cycles or continuous processes.
d) Owing to the very nature of ceramic materials, they are stable thermally, chemically, mechanically and physically. They can withstand very high temperatures, extremes of pH (0 to 14), and operating pressures up to 10 bar.
e) They are not affected by bacteria.
f) They are regenerated easily after being used.
g) The membrane support (aluminum oxide or silicon carbide) provides maximum permeability and excellent mechanical stability.
h) They usually show excellent separation properties and long working life.
i) Because of their elevated chemical durability, they are not affected by aggressive chemicals such as caustic, chlorine, hydrogen peroxide and other inorganic acids.
j) They also can be sterilized by steam and show a good ability for back flushing.
k) Their superior mechanical properties confer high abrasion resistance.
l) They are suitable for use whenever high fluxes are involved.

7. Disadvantages of Ceramic Membranes

Ceramic membranes suffer however from the following drawbacks compared to polymeric types:

a) They have small surface area per unit volume.
b) As compared to polymeric membranes, their densities are higher.
c) Also, the production costs are higher because of the use of costly raw materials and more complex fabrication procedures [31-32, 44-45].

8. Uses of Ceramic Membranes

Membranes are used in numerous applications such as water and wastewater treatment, desalination, MF and UF [46]. Despite their relatively elevated initial cost, ceramic membranes are economically suitable because they are available, have high flux, can be cleaned easily, and have relatively low operating cost [23]. One successful application of ceramic membranes is their use in the separation of oily wastewater generated in oil refining and in some metallurgical industries prior to drainage in the sewage system [47-49].

Dense ceramic membranes are known to be highly efficient in gas separation because of the compatibility between their pore size and the molecular size of gases. One main merit of ceramic membranes is the possibility of use at relatively high temperatures such as separating CO_2 from flue gas at 550–650°C [50], steam – methane reforming at 700ºC [51] and hydrogen separation using diverse oxides in their preparation (WO_3, La_2O_3, Al_2O_3, etc.) [52-53].
Ceramic membranes were also successfully used in food industries such as juice clarification [54-55] clarification of raw rice wine [56], corn syrup clarification [57], and liquor treatment collected from processing of sardine fish [58].

It should be mentioned that the application of ceramic membrane has gained impetus in the water treatment field. One of the main attracting points for further research is using low-cost raw material in the water treatment field to fabricate the membrane [59].

Likewise, desalination of seawater is one of the most promising applications of ceramic membranes [60-62] whereby three different mechanisms can operate:

a) Membrane distillation (MD): Where the membrane permits water vapor molecules pass after thermal treatment.
b) Reverse osmosis (RO): the membrane allows passage of water molecules and repels salt ions.
c) Pervaporation: Where the difference in water vapor pressure allows the passage of water molecules through molecular sieves.

The increasing demand for ceramic membranes in water desalination stemmed from the numerous inconveniences associated with the use of the classical polymeric membranes. Among these one may cite the swelling phenomenon, bio-fouling, and poor chemical and thermal stability. As previously mentioned, the use of ceramic membranes of elevated chemical and thermal resistance helps alleviating these defects [63]. A high quality of permeate and low fouling was obtained when using zirconium dioxide as a pretreatment for RO desalination [64], tri-cobalt tetroxide [65], zeolites [66-67] and silicon nitride [68-69].

9. Application of Ceramic Membranes in Water Treatment

In recent decades, the population growth and rarity of water due to drought and other reasons have led to an increased demand of potable water on one hand and an urgency to use as little water as possible in most industries. This latter concern has been the reason why a major industry such as the cement industry has totally shifted from the wet water consuming process to the dry process which uses a minimal amount of water. Other industries are currently recycling wastewater after treatment to the process, an ideal situation being that of "zero-discharge" condition. The advent of relatively cheap filtration membranes operating at low pressures played a key role in economically solving problems associated with the old conventional methods of treatment which were costly and time consuming (coagulation, sedimentation, and filtration) [70-73].

Ceramic membranes are an excellent choice owing to their stability at high temperature, high pressure, chemical attack, and pH resistance [29]. On the other hand, the application of micro-filtration and ultra-filtration for water treatment has become standard procedure during the last two decades [46]. Ceramic membranes are more effective and using them is more advantageous than other common steps [70].

Since water scarcity is a critical concern in many areas worldwide, there is an increasing concern about the problems that arise due to water shortage and the possible solutions available [74]. Particularly, in Egypt, where most of water is supplied from Nile River, the quality and quantity of supplied water from the Nile is seriously threatened. On one hand the untreated industrial and agricultural wastes affect water quality while on the other, the quantity of inflowing water is threatened by the misuse of available resource and the construction of the Renaissance Dam of Ethiopia [75].

The current water deficit in Egypt amounts to about 7 billion cubic meters [76]. The United Nations have even warned that Egypt may run out of water by 2025, Countries in arid regions started to apply water desalination on a large scale to turn available seawater into drinkable water. Water desalination currently represents less than 1% of water production in Egypt but it should be a vital element in its water future policy. It could offer a secure potable water source using the available resources in Red and Mediterranean seas [77]. Although there are many desalination plants in Egypt in tourism resorts (Hurgada, Sharm El Sheikh…), they have limited application in urban and industrial sections. Therefore, it is strongly recommended to start applying desalination plants in Egypt to help in solving the water crisis that we are facing [78].

9.1. Oily wastewater treatment

Ceramic membranes could be used in oily wastewater treatment and provide anti-fouling properties and chemical stability [48, 79]. In comparison between different types of ceramic membranes for using in oily wastewater treatment, zirconia ceramic membranes performed a flux which is higher than that when using alumina and titania ceramic membranes [80]. The pore size within 0.1 μm could provide high oil separation percentage with good permeate flux [81-82]. Lahiere et al. reported the first use of ceramic membranes for oily wastewater separation [83]. They achieved oil rejection performance of 94 percent with a flux of 12.26 m^3/day when they employed commercial alumina ceramic membrane (Membralox technology) manufactured by Societe des Ceramiques Techniques.

Alftessi et al. successfully fabricated Hollow fibre ceramic membranes (HFCMs) from a low-cost ceramic material (silica sand) using the phase inversion/sintering technique for oil water separation with a flux of 12.6 L/m^2h within the first 10 minutes of operation and mechanical strength of 78.5 MPa using 55 wt. percent silica sand content and sintering temperature of 1300 ºC with rejection of 99.7% [28].

Surface roughness of ceramic membranes is considered the control parameter of the anti-fouling properties [78]. Zhong et al. have discussed that manipulating the templates particle size led to control in the membrane surface roughness, that could serve like an alternative method to polishing method, which makes problem on the surface like inhomogeneity of morphology [84-85].

For example, increasing the particle size of poly (methyl methacrylate) template on alumina membrane surface leads to increase the roughness of the surface. Smoother membrane surface provides high and stable permeate flux, that due to minimizing the fouling layer formation. γ-Al_2O_3 UF ceramic membrane provided good membrane performance due to thin top alumina layer that was fabricated by dip-coating technique using boehmite solution [86]. This method provided homogeneity and best adhesion without cracks or pinholes. γ-Al_2O_3 multilayer ceramic membranes was used in wastewater from petroleum refinery and provided standard discharge of 10 mg/L, and the TSS (total suspended solids) reached to 84%.

Mullite hollow fibre composed of TiO_2 ceramic membrane was prepared from coal fly which is a low-cost industrial waste and dip-coating method has been used to coat it to be used in oily water treatment [87]. Mullite is mostly composed of SiO_2 and Al_2O_3, with minor amounts of metal oxide impurities like Fe_2O_3 and TiO_2 [88]. Coating ceramic membrane by titania thin layer leads to increase in surface hydroxyl groups on membrane surface that enhancing hydrophilicity of the surface and leads to repel of oil droplets from adhering onto the surface. this membrane was used in oil-in-water (O/W) emulsion separation, where the feed solution of 200 $mg \cdot L^{-1}$ synthetic (O/W) emulsion, the total organic removal reached to 97% and the membrane can be reused by simple backwash using NaOH solution and the flux recovery reached to 96%.

Hydrophilic modification of ceramic membrane surface leads to reduction in the fouling formation [89-90]. Using nanomaterials on the dip coating solution performs uniform distribution of them on the membrane surface [89]. Some researchers studied that using graphene oxide as a Nanoparticles on coating of alumina ceramic membranes enhanced the membrane performance, where flux was 667 $L.m^{-2}.h^{-1}.bar-1$ with rejection of 98.7% that due to hydrophilicity improvement. Hu et al. and Chen et al. [90] [91] studied that fabrication of hybrid ceramic membrane by implementing CNT network on zirconia CMs for treatment of oil emulsion which is surfactant stabilized.

The feed solution was prepared from various type of surfactants (anionic and non-ionic) and oil concentrations (100–600 ppm) [91]. (CNTN) built their network into the channels of pore for ceramic membrane by catalytic reaction (Fig. 11 (a)). Fig. 11 (b), indicates that there are three mechanisms in play in treatment of emulsified oily water, i.e. 1) size-exclusion, 2) surface adsorption through interaction with the membrane and 3) multi-layer adsorption by carbon nanotubes, where this hydrophilic macro-mesoporous CM is able to separate molecules of oil, but dissolved oil passes through membrane pores leading to minimum fouling.

Zhao et al. obtained a 100% rejection when using pristine and CNTN-ZrO membranes but the flux of CNTN-ZrO membrane was higher as shown in Fig. 11 (c) and (d) [92]. Using CNTs improved the membrane performance because they reduced the formation of gel layer, then reduce the flow resistance. The high surface area of CNTNs can adsorb emulsified oil and remove it. (CNTN) incorporation within the pores of the zirconia ceramic matrix in the ceramic-hybrid membrane, (b) three mechanisms that are in play in treatment of emulsified oily water and (c, d) pristine (PM) and CNTN-ZrO ceramic membranes steady state rejection and flux for as a function of feed concentration [93].

Some modified ceramic membranes were used in dye removal. Anodized alumina membrane was modified using azobenzene to be used for removal rhodamine B [94]. Azobenzene group was grafted on the surface of anodized alumina ceramic membrane, as shown in Fig. 12 (a), which indicates the effect of simultaneous UV and visible light radiation that cause continuous photo-cistrans isomerization. Rhodamine B is non-volatile dye, so it removed efficiently by membrane (after grafting by active functional group) especially after using solar-driven filtration as shown in (Fig. 12 (b) & (c)) [94].

Perfluoro-octyl tri-ethoxy-silane hydrophobized titania membranes were used in pervaporation techniques to separate methyl tert-butyl ether (MTBE) which is volatile and hazardous from water, where the separation factor reached to 91 with removal percentage 98.5%. Kujawa et al. [95] fabricated composite ceramic polymeric membrane using zinc nitrate precursor with 2-methylimidazole linker during interfacial polymerization technique on a polyether-sulfone (PES) as a substrate and 1-Octanol was used as linker/metal solvent source. During the top layer growth, a fine layer of ZIF-8 was formed that has a thickness of about 250–300 nm.

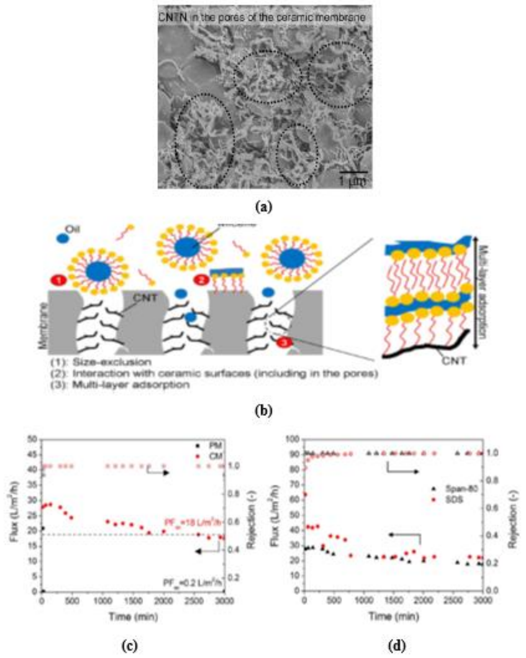


Fig. (11): Carbon-Nanotube Network

Using 1-octanol as a solvent lead to faster formation of the top layer and the crystals took place on the surface to make a sealing for any defects. The dense top layer of ceramic ZIF-8 was formed with increase in rejection percentage and reduction in flux because of its high dense packing and it has small spaces between particles. When raising the amount of 2-methylimidazole to that of zinc nitrate at the interface from 1.9 to 15.9, it will be noted that the layer of ceramic will be denser and the flux will reduce from 37.5 to 5.6 L.m^{-2}.h^{-1}.bar^{-1}, but with rejection 98%. Some previous experiments were carried out on humic acid removal using macro-porous anodic alumina support coated with reduced graphene oxide (RGO) intercalated CNT network [96]. using CNTs with block copolymers by dispersion technique leads to less defect's formation. However, using CNT with graphene sheets allowed to formation of repeated nanostructure which provide channels facilitate mass transfer through them, leading to increasing the permeability to 20 L.m^{-2}.h^{-1}.bar^{-1} with rejection of 99% fulvic acid. On the other hand, the RGOCNTs improved the membrane hydrophilicity leading to formation of antifouling membranes.

GO sheets provides negative charges on the membrane surface due to carboxyl groups on the edges of the GO sheet that facilitate the water permeation through Nano channels leading to high permeability of 695 L.m^{-2}.h^{-1}.bar^{-1} [97].

9.2. Heavy metal and radioactive ions removal

9.2.1. Heavy metal removal

Using a charged membrane surface, Badawy et al. [98] were able to remove Fe (III) and Cr (III) ions from a waste stream by means of forming water-soluble positively charged hydrolyzed species that were adsorbed on the surface of the membrane. Heavy metals occur as hydrated ions in aqueous systems, resulting from the interaction of water molecules with metal ions via electrostatic ion–dipole interactions. Their hydrated radii, however, are still too small for microporous membranes to hold Abdullah [99].

Fabricated silica ceramic membranes were used as charged membranes depending on an abundance of surface reactive functional groups, which can be used in heavy metal ions removal. However, the divalent heavy metal like Pb^{+2}, Cu^{+2} and Cd^{+2} ions were removed using silica ceramic membranes in alkaline aqueous environment [100]. This membrane was fabricated using low-cost materials of local clay mixed with various sawdust percentages of 0.5%, 2.0%, and 5.0%. the aqueous solutions of heavy metals were prepared in lab. The removal efficiency reached to 99% for the concerned heavy metals that due to the adsorption of the ions of heavy metals (positively charged ions) on the membrane surface which carries OH$^-$ functional groups (negatively charged).

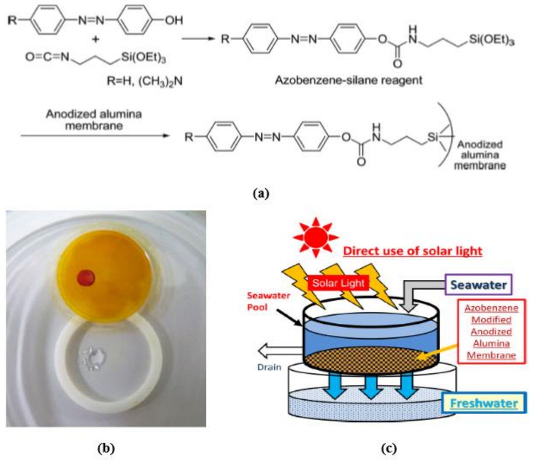


Fig. (12): (a) Using anodized alumina membranes for preparation of azobenzene, (b) Photo-induced filtration process for filtration of rhodamine B solution using the azobenzene modified membrane, (c) Applying of solar driven filtration system on the azobenzene modified anodized alumina membrane [94]

9.2.2. Chromium removal

Many kinds of CMs have been tested for removal of chromium [101]. Kumar et al. [102] used situ crystallization technique to manufacture a membrane for removing chromium by coating a ceramic support with analcime-C. The produced membrane is called analcime-C zeolite-ceramic composite membrane. Zeolite particles have a good adhesion due to formation of multiple layers of coating which is up to three layers. Zeolite particles were dispersed on the ceramic support making a dense film. This membrane provided Cr^{+4} rejection of 84% with solution concentration of 250 ppm. Where the charges of this membrane surface can be manipulated using various pH solutions, where the best rejection of chromium

(Cr^{+4} and Cr^{+3}) was at high pH of 11.

Ultrafiltration ceramic membrane was prepared from zeolite that was supported on circular porous ceramic disk was prepared from clay exhibited good removal for Cr^{+4} [103]. The membrane performance depends on hydrophilicity of the surface, porosity, and surface charges. The removal of Cr^{+4} through this membrane depends on the interaction according to the charged zeolite membranes and chromium ions.

9.2.3. Arsenic removal

Sklari et al. [104] studied removal of arsenic (As^{+3}/As^{+5} ions) using integrated hybrid ceramic membranes were prepared from Alumina, where the feed solution was 70 ppb As^{+3}/As^{+5}. The first ceramic module made from alumina that was used as a contractor for ozone which was supplied to the inner water stream from an external surface to make oxidation for As^{+3}/As^{+5}. Tri chloro-methyl-silane was used to make functionalization of membrane surface in this case to reduce hydrophobicity of the surface to make the ozone stream's flow easier. Then, produced water went through second module. Second module was fabricated from alumina and modified at the interior pore structure by the in-situ generation of Fe_3O_4 nanoparticles. This structure of ceramic membrane leads to adsorbent for As^{+5}. The membrane regeneration was carried out by heat treatment at 110 ºC for 24 h [104].

9.3. Radioactive wastewater treatment

Lu et al. used modified colloidal sol-gel technique to Fabricate ceramic membrane from TiO_2 doped ZrO_2 for using it in treatment of radioactive wastewater [105]. Zirconium ceramic membranes can be coated by TiO_2 doping sol-gel to modify the microstructure of ZrO_2 membrane that reduced the pores size, enhance the hydrophilicity, improve mechanical properties and the membrane performance was enhanced, where the permeability reached to 40 $L.m^{-2}.h^{-1}.bar^{-1}$ with rejection of 99.6% for Co^{+2}, 99.2% for Sr^{+2}, and 75.5% for Cs^{+}.

9.4. Inorganic Waste Removal

9.4.1. Fluoride removal

Ceramic membrane, which were manufactured using metal organic framework (MOF) was considered new kind of membranes with high performance. He et al. [106] studied defluoridation from water using MOF zirconium ceramic membranes. These kinds of membranes represent high adsorption capacity for fluoride leading to removing of fluoride from solutions [106]. Other new ceramic membrane was fabricated using alumina support with polycrystalline Zr-MOFs has a thickness of 20 μm. This membrane was prepared by situ solvothermal technique. Solution of initial fluoride concentration of 5 mg/L was used as a feed for this kind of membrane with 15 ml min^{-1} as a flow rate. Zr-MOF membrane with alumina support provided maximum fluoride removal of 99%, that due to presence of hydroxyl groups and Zr(IV) active sites on the surface which lead to the fluoride adsorption.

9.4.2. Phosphate removal

Shang et al. [107] studied that using ultrafiltration ceramic membrane was fabricated from tight TiO_2 before reverse osmosis membranes as a pre-treatment step for phosphate removal provided high rejection percentage [107]. The rejection of phosphate anion depends on electrostatic repulsion, where a high percentage of rejection is obtained when the negative charge density increases on the surface. This kind of ceramic membrane has smaller pore sizes and great density of negative surface charge, so high rejection percentage of anions which are less diffusive such as phosphate was achieved. The maximum rejection percentage of phosphate reached to 87% at solution with pH 8.5.

9.4.3. Ammonia removal

Yang et al. [108] studied removal of ammonia from the water using ceramic membrane by pervaporation technique. This kind of membrane was fabricated using a cobalt-doped molecular sieve silica membrane. Silica membrane was fabricated by controlled hydrothermal treatment to reduce the pore size. This membrane was applied using pervaporation technique, where the water passes by molecular sieving mechanism. The results exhibited high ammonia selectivity up to 60, which was higher 5 times compared with hydro-phobic polypropylene membrane [108].

Yang et al. [109] investigated that using hydro-stable organo-silica ceramic membranes in pervaporation technique for alkaline ammonia solution treatment. Silanol groups are formed on the silica surface because of hydrolysis of siloxane due to presence of high concentration of ammonia in the used solution.

9.5. Ceramic membrane for desalination

Most studies for desalination using ceramic membranes were carried out using membrane distillation technique [60, 110]. Krajewski et al. [111] studied desalination by Air gap membrane distillation (AGMD) using fluoro-silanes grafted ceramic membranes. The results indicate that high salt rejection close to 100% and high flux 6.67 L/m^2h. Cerneaux et al. [110] studied desalination by direct contact membrane distillation (DCMD) and made a comparison between zirconia and titania ceramic membranes. Fig. (13) indicates the salt rejection and permeate flux for two membranes [110]. The Figure indicates reduction in permeate flux due to reduction in driving force by the effect of concentration polarization which was happened due to increasing in salt concentrations in the feeding water during the application test [110, 112]. The results indicated that zirconia membrane provides highest performance than titania membrane due to the lower resistance of water vapor transfer, these experiments were carried out at feed temperature 40°C under vacuum pressure 3 mbar. Other studies have been performed with different configurations of MD using ceramic membranes as shown in Table (2).

Abdallah et al. [113] studied fabrication of ceramic membrane has Nano-pores size that fabricated from ceramic factory wastes powder, this powder was treated using hydrothermal treatment. The produced powder was Nano–sized and have rosette–like segregations structure. Poly-vinyl-alcohol was used as a binder during ceramic membrane fabrication. Firing temperatures ranging from 1100 to 1300°C for 1, 2, and 3 h soaking time were the most important parameters effect on the formation of ceramic membrane with Nano pore size. The best ceramic membrane (fired at 1250 °C) was applied on dead end filtration system for desalination of 5000 ppm synthetic solution. It exhibited salt rejection reached to 99% with a flux of 244.5 $Lm^{-2}h^{-1}$.

Belgada et al. [114] investigated the use of Moroccan natural phosphate in the dry pressing method for preparation of a new flat MF membrane. From 900 to 1100 ºC, the influence of sintering temperature on membrane properties, including porosity, pore size, mechanical strength, and permeability, was examined. The improved seawater quality in terms of total organic carbon (TOC), turbidity, and silt density index (SDI) was used to evaluate the efficacy of the modified membrane for pre-treatment of raw seawater for RO desalination. The produced membrane has excellent permeability, pore size, and flexural strength, making it ideal for use in MF applications. The manufactured phosphate membrane has a high efficiency for MF pre-treatment of raw saltwater, eliminating 73 and 98 percent of TOC and turbidity, respectively, and lowering SDI to 3.25 [114].

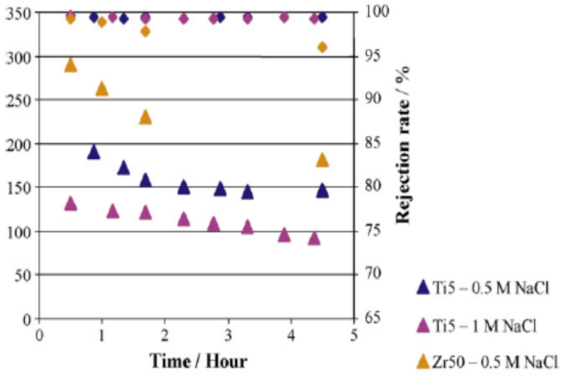


Fig. (13): Flux on left vertical axis and rejection rate on right vertical axis as a function of time in vacuum membrane distillation (VMD) of NaCl solutions (0.5 and 1 M) using Ti5 and Zr50 [110]

10. Conclusion

This article gives a comprehensive review on importance of ceramic based membranes for water and wastewater treatment. Therefore, a substantial improvement of the quality of water which is delivered to the consumer's tap was obtained. CMs showed remarkable improvements compared to polymeric membranes and traditional techniques in water treatment according to the systematic review of the existing literature. CMs are categorized according to many factors such as their structure and raw material to be used in fabrication. They have many preparation techniques producing different CMs differ in their shape and pore size which allow them to be used in many applications such as removing oil, heavy metals, organic and in organic wastes and salt from sea water.

Table (2): Summary of studies related to the use of ceramic membranes in membrane distillation (MD) applications [112]

Ceramic Material	**Feed Temperature (°c)**	**Flux (Kg/m^2.h)**	**Rejection**	**Reference**
TiO_2	65	13.44	92.3	Cerneaux et al., 2009 [109]
	85	57.74	99.8	
Clay Alumina	20	5.48	99.1	Krajewski et al., 2006 [110]
	60	98.66	99.96	
ZrO_2	55	15.7	100	Larbot et al., 2004 [60]
	85	82.7	100	
Al_2O_3	58	18.2	100	Larbot et al., 2004 [60]
	90	129.5	100	
B-Sialon	50	100	99	Wang et al., 2016 b [114]
	80	290	99	

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