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Alumina Membranes for Desalination and Water Treatment

Saad Alami Younssi, Majda Breida and
Brahim Achiou

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Abstract

In recent years, there has been a growing interest in utilizing inorganic membranes, particularly alumina (Al_2O_3) ceramic membranes (CMs), and to address a variety of separation problems in miscellaneous industry. Al_2O_3 membranes are commercially predominant in CMs market. Al_2O_3 material is generally used either as membrane support and/or as membrane layer due to advantages provided by this material and its derivatives such as availability in tonnage quantities, chemical inertness, good hardness, and thermal stability of the porous texture during elaboration steps. In this chapter, we comprehensively look at the recent studies related to desalination and water treatment by ultrafiltration (UF), nanofiltration (NF) Al_2O_3 membrane, and highlight the separation properties of the membrane in specific environmental pollution. The influences of membrane operating conditions and water quality on the rejection of pollutant by Al_2O_3 membrane are reported through a series of bench-level experiments.

Keywords: Al_2O_3 , ceramic membrane, nanofiltration, ultrafiltration, desalination, wastewater treatment

1. Introduction

The rapid increase in urbanization and industrialization has led to the global economic development, which has significantly contributed to the human welfare, but led at the same time to severe environmental degradation that automatically affects sustainable development. Indeed, the uncontrollable rise of waste and wastewater discharges create a series of environmental issues, making difficulty to access to water of adequate quality for human consumption

and for industrial-scale production [1]. This strong dependence of pollution and water deterioration on industrial activities is well witnessed in developing countries, where 90% of raw sewage and 70% of untreated industrial wastewater are released into water sources (surface and groundwater) [2]. Furthermore, the influence of industrial activities along with the variability of effluents quality and the leak of information of the exact amount of the untreated effluents exacerbates the situation [3]. The physicochemical analysis of wastewater demonstrated a wide range of pollutants such as nitrates, nitrites, dyes, organic components, and toxic heavy metals has been reported [4]. In addition, the presence of different pollutants in water has a direct impact in increasing chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), and salinity. Furthermore, regulations related to the quality of drinking water and wastewater has increasingly become severe. Therefore, the aim of finding a balanced solution between environmental protection and industrial progress is an overarching objective for all policy-makers and scientific researchers. As a result, industries gained awareness of the importance of treating wastewater (recycle/reuse), and some treatment technologies have already been brought into practice [5]. However, the use of one technology over another depends on several factors. The efficiency of many current treatment technologies still needs significant improvements, from the energy point of view. Membrane technology has become a promising industrial alternative compared with traditional treatment techniques, such as distillation, absorption, adsorption, extraction, activated sludge, trickling filters, stabilization ponds, and constructed wetlands. In fact, membrane processes for water treatment such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been used in industrial-scale for years now [6, 7]. These membranes are divided (based on material nature) into two categories, organic membranes (or polymeric membrane) and inorganic membranes (also referred to as ceramic or mineral membranes).

Polymeric membranes (PMs) are considered to be the first membrane generation, and they are on the frontline of wastewater treatment [8], recognized as an integral part of treatment processes. However, PMs suffer from several limitations such as low-mechanical strength, low fluxes, restricted chemical and thermal stability, and the trade-off relationship between permeability (P) and selectivity as well as membrane fouling [9]. In contrast, the application of ceramic membranes (CMs) offers the advantage to work in harsh operating conditions due to their superior mechanical, thermal, chemical stability, and prolonged lifetime [10–12]. In addition, CMs are less exposed to the phenomenon of biofouling, caused by the membrane deterioration by bacteria [13]. Depending on the material nature, CMs can be elaborated in many configurations and with different pore size, which facilitates their use. Among the various mineral materials (titania (TiO_2), silica (SiO_2), and zirconia (ZrO_2)...) used in CMs elaboration. Alumina (Al_2O_3) is the most applied material due to economical consideration along with its ability to resist in high transmembrane pressures (TMP) [14]. Usually, Al_2O_3 CMs (Al_2O_3 -CM) are fabricated in a multi-layer structure, in other words, each layer is different than another in pore size and thickness. Furthermore, Al_2O_3 is known by two impressive characteristics, namely by its hydrophilic and covalent bonding characteristics [11, 15].

Al_2O_3 -CMs for UF and NF have shown an interesting efficiency in desalination and water treatment. As known in membrane technology, the efficient membrane should combine high permeability with high rejection. These membranes have found several industrial

applications, which cover sea water desalination, food production, gas and vapor separation, and domestic and oily wastewater treatment. Indeed, UF membranes demonstrate good performance in removing turbidity and pathogens, and they are very effective and reliable in removing microbiological parasites, dyes, and some ions in specific conditions. Mostly, Al_2O_3 -UF has been efficiently applied for the separation of components with a size ranging from 2 to 100 nm (like proteins and colloidal particles). The Al_2O_3 -NF membranes have been operated for separation of components with low-molecular weight (MWCO 200–1000) and electrolyte by optimization of operating conditions.

2. Development of ceramic membranes (CMs)

The word membrane in association with the separation phenomenon, purification or concentration processes is defined as a thin semi-permeable layer, which separates two phases. This semi-permeable layer is able to selectively restrict the transport of one or many components. In other words, a membrane is a thin layer that allows a component to pass more readily than others (**Figure 1**). The components that pass through the membrane are called permeate, whereas the components that are retained are defined as retentate [16]. Also, it should be noted that the first recorded research on membrane phenomenon appears to be done by French Abbe Nollet in 1748, and Fick is the first to synthesize membrane from nitrocellulose (organic). The first membrane filters were commercialized in 1927 by the Sartorius Company [17].

However, the elaboration of inorganic membranes only started around the 1940s, by the development of Vycor glass membranes [18]. The first application of the CM is related to the uranium isotopes separation by gaseous diffusion processes. In 1973, two companies Ceraver and Euroceral started to produce ceramic oxide support for nuclear fission industries, which still are operating in Eurodif plant (France) [19]. The intensive research and the continuous development of CMs have resulted in the elaboration of MF and UF membranes. The concept of liquid filtration was developed by Carre in 1960, and the filtration was done on dynamic zirconium hydroxide. In addition, SFEC is the first company to manufacture cross-flow filtration system equipped with the inorganic membrane (1978s) [18]. Recently, CMs have undergone notable development due to its different advantages and have been widely adopted.

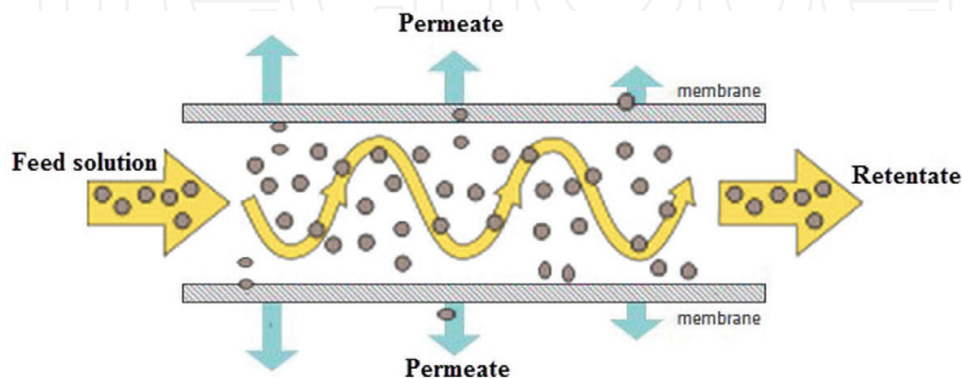


Figure 1. Principe filtration by membranes.

Membrane processes are categorized based on the types of driving force and pore size solution as well as the phases of permeate and feed. The driving force can take different forms; this force can be a concentration gradient, pressure, or voltage difference across the membrane. Depending on the driving force as well as the pore size, membrane processes are classified, therefore, to MF, UF, NF, RO, dialysis, electrodialysis (ED), and gas separation (GS) as in **Table 1**. However, it should be noted that even though dialysis, ED, and GS process are conducted in liquid phase, but CMs have not been yet applied to this kind of separation processes [20]. To overcome the problem of complexity of water pollution, as well as the limitations of individual systems, a combination of membrane techniques can be used.

2.1. Membrane materials

Inorganic membranes are generally classified into porous and amorphous membranes, porous and crystalline membranes, and dense membranes. The materials used in the elaboration of dense CMs are usually metals, such as palladium, nickel, silver, and zirconium, while porous CMs are produced from metallic oxides (Al_2O_3 , ZrO_2 , TiO_2 , and SiO_2), carbon, and zeolites. The use of a material than another depends on the preparation technique and the desired membrane structure. CMs with a large range of pores size can be obtained with different preparation techniques, as an example the slip-casting tape-casting technique, pressing, extrusion, the sol-gel, and dip-coating processes (**Table 2**).

Tighter UF and NF membranes are generally prepared by the sol-gel technique. In addition, alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) are the most common CMs materials. The attractive use of Al_2O_3 in membrane elaboration is mainly due to its properties, such as high resistance to organic solvent, narrow particle size distribution, high-surface area as well as a high-density. **Table 3** demonstrates the thermal and mechanical properties of Al_2O_3 as CMs material. In addition, the great abundance of this material, as well as its chemical stability and a small amount of shrinkage makes Al_2O_3 the most encouraging option in CMs elaboration [21–23].

Al_2O_3 powder (as a raw material) is principally produced by the Bayer process using the bauxite mineral. While Al_2O_3 porous membrane have been prepared by the holds method in which

Process	Nominal pore size	Driving force	Average permeability L/m ² h bar
Microfiltration	0.05–10 μm	1–3 bar	500
Ultrafiltration	0.001–0.05 μm	2–5 bar	150
Nanofiltration	<2.0 nm	5–15 bar	10–20
Reverse osmosis	<1 nm	15–75 bar	5–10
Gas separation	<0.5–1 nm		
Membrane distillation	0.5–2 nm		
Electrodialysis	MW < 200 Da	Electrical potential, 1–2 V/cell	

Table 1. Classification of membrane processes [8, 20].

Preparation techniques	Metallic oxides
Sol-gel	γ -Al ₂ O ₃ , SiO ₂ , TiO ₂ , ZrO ₂
Chemical vapor deposition	SiO ₂
Pyrolysis	SiC, Si ₃ N ₄
Hydrothermal treatment	Silicalite
Anodic oxidation	Al ₂ O ₃ (Amorphous)
Phase separation/ leaching	SiO ₂
Dynamic membranes	ZrO ₂ (Amorphous)

Table 2. Preparation techniques of CMs [8].

Mechanical properties	
Tensile Strength (MPa)	117–173
Bending Strength (MPa)	307–413
Modulus of Elasticity (E) × 10 ⁸ (MPa)	21.27–26.8
Compressive Strength (MPa)	1600–3733
Modulus of Rigidity (G) × 10 ⁸ (MPa)	8.67–11.3
Hardness on the Mohs scale	9
Thermal properties	
Melting point (°C)	2051 ± 9.7
Thermal coefficient at 200–1000°C	8.80 × 10 ⁻⁶
Boiling point (°C)	3530 ± 200

Table 3. Mechanical and thermal properties of alumina [21, 22].

boehmite sol is made by the hydrolysis of aluminum butoxide or aluminum propoxide in hot water (above 80°C) and peptized by acid (nitric acid) afterward [20]. Al₂O₃ is classified into two major groups depending on the purity of Al₂O₃, the first of high-grade with 99%, and the second grade between 80 and 99% of Al₂O₃. The color of Al₂O₃ changes along with the addition of additives or the presences of impurities, the sintering atmosphere, and by the interaction with ionizing radiation. In general, Al₂O₃ is characterized by a white color. However, in some cases, it can change the coloration to pink (when the purity of Al₂O₃ is equal to 88%) or brown (96% alumina).

Generally, the oxide of stoichiometry Al₂O₃ is well known by a large diversity of phases. The structural diversity of Al₂O₃ is emphasized in a series of transitions (α , γ , χ , κ , δ , θ , and η). Transition means that the crystal structure of Al₂O₃ depends on temperature. It is thermodynamically varied from unstable to stable, and it should be noted that α -Al₂O₃ (Corundum) is the most thermodynamically stable form of alumina (Al₂O₃) (**Figure 2**).

An increase in firing temperature above 1000°C leads to the phase transition of γ -Al₂O₃ to α -Al₂O₃. As a result, a conversion of UF membranes to MF membranes is obtained. Further, **Figure 3**

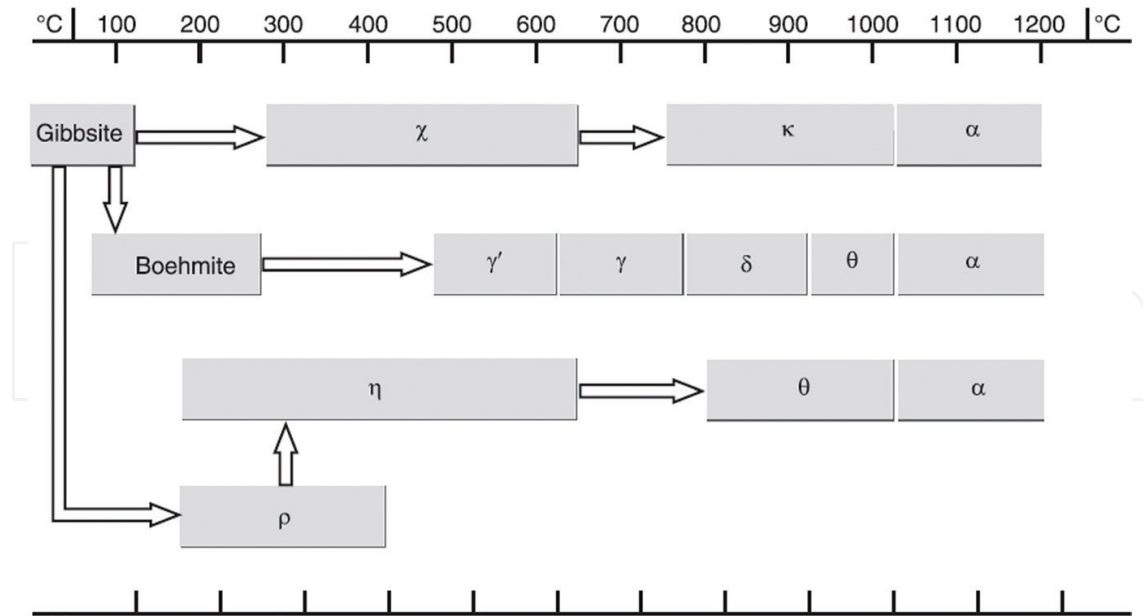


Figure 2. Transitions of alumina (Al_2O_3) [24].

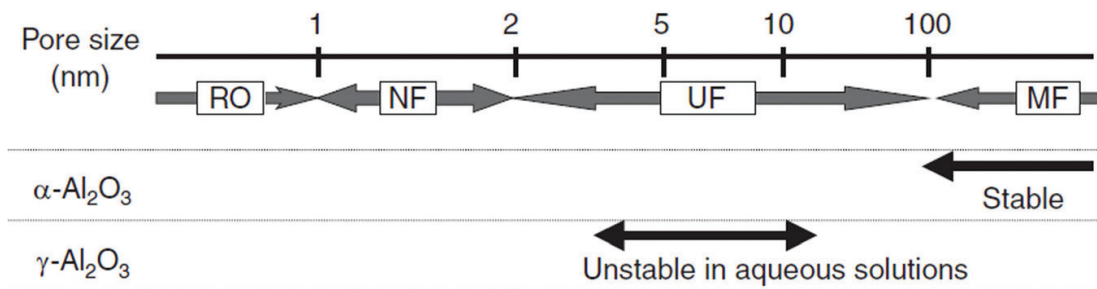
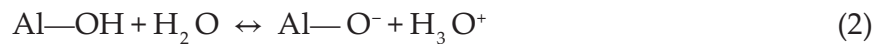
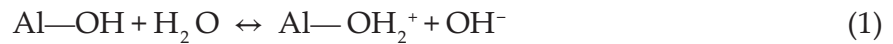


Figure 3. Material and pore sizes for use in liquid separation [20, 25].

shows a schematic diagram of pore sizes obtained with Al_2O_3 materials that have been used for liquid separation. α -Alumina has excellent stability in both acidic and basic pH; however, it has a limitation in pore size, which is in a range of MF (larger than 100 nm). On the other side, γ - Al_2O_3 is not stable as in the case of α - Al_2O_3 , however, it has a pore size as in UF range (4 nm).

When Al_2O_3 surface is hydrated, there is a finite solubility of Al_2O_3 into the water. The limit of solubility as well as the type of species in the solution depends upon the solution pH and temperature. Indeed, the hydrated surface of Al_2O_3 is known by amphoteric behavior, which means that the sign and the charge density of membrane surface can be controlled by controlling pH solution. The point of zero charge (pzc) is the value for which the electric charges of the fixed cations globally neutralize anions, which was found to be around 8 and 9. At pH above the pHpzc, the surface of membrane is negative, which is explained by the acidic dissociation of the surface hydroxyl groups Eq. (1). While the positive charge when the pH is below pHpzc is explained by proton addition to the neutral aquo complex due to the existence of $AlOH_2^+$ groups Eq. (2), depending on the following reactions (Eqs. (1) and (2)):



Application of Al_2O_3 membrane widely use a porous structure specially in solid–liquid and solid-GS, which is due to Al_2O_3 high structural durability, low-energy, easy cleaning, and mostly controllable microstructure [26]. In general, the elaboration of porous Al_2O_3 membrane implicates several techniques like green compact shaping and sintering, suspension preparation (by slurry or sol–gel processes). The preparation of Al_2O_3 -CMs by extrusion method is commonly applied for membrane with tubular or multi-channel membrane, whereas tape-casting technique is more suitable for Al_2O_3 -CMs with flat sheet structure. Furthermore, pressing and slip-casting methods are usually used for the production of symmetric structure of Al_2O_3 -CMs. The preparation of porous Al_2O_3 -CM of an asymmetric structure is achieved by tape-casting using phase-inversion techniques [27]. Furthermore, multi-layer composite membranes with an asymmetric structure can be processed using coating techniques [28]. It is worth to mention that Al_2O_3 membranes (MF, UF, and NF) have naturally hydrophilic character due to the presence of an oxide material in the hydroxyl group. The hydrophilic character presents extremely polar properties, which causes the absorption of water molecules by forming a hydrogen bond [29]. However, a strong adhesion between Al_2O_3 -CMs surface and foulants can mainly cause membrane fouling. Therefore, a superhydrophilic character of alumina’s membrane surface is more preferable [30].

2.2. Filtration modes

Membrane separation can be mainly operated in two modes (**Figure 4**), dead-end (frontal filtration) and cross-flow (tangential filtration). In dead-end filtration, feed solution flows perpendicularly

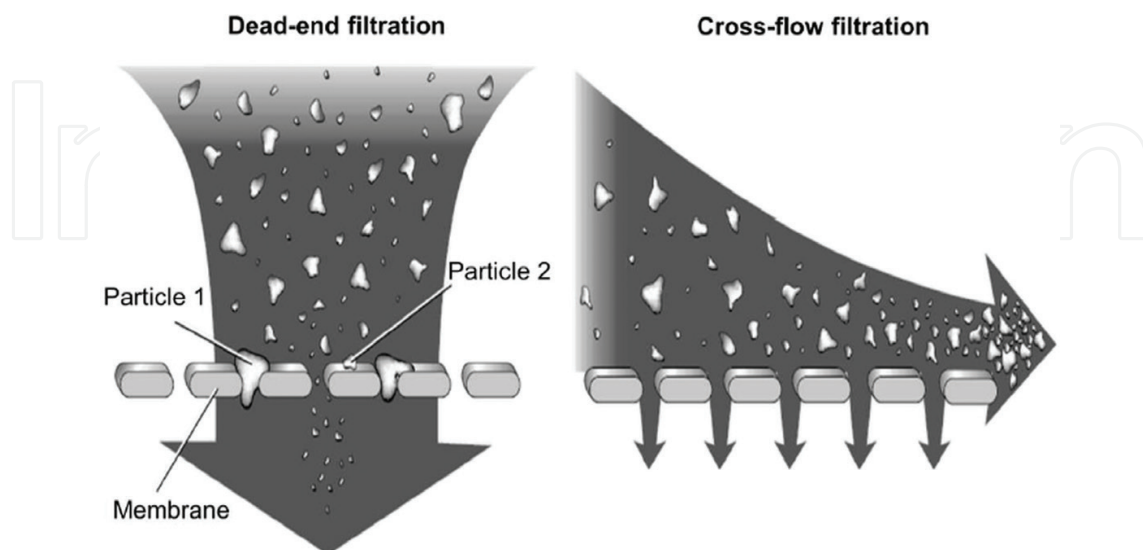


Figure 4. Schematic of dead-end and cross-flow filtrations [8].

on the membrane surface, which leads to the accumulation and disposition of the retained substance on membrane surface. In most filtration applications, the accumulation of particles on the membrane surface causes the formation of cake over the operating time. Consequently, the membrane performance is severely reduced and required a periodic backwash to control the cake formation and fouling phenomenon. Therefore, the dead-end mode is impractical for effluent highly charged with solid particles and it recommended for conventional filtration processes with dilute feed, such as filtration of surface water or secondary industrial effluents [10].

In another hand, in the cross-flow filtration, the feed solution flows tangentially (in a perpendicular direction) across the membrane. The cross-flow mode can result in higher permeation flux compare with the dead-end mode due that the stream continuously removes particles and simultaneously reduces the formation of cake layer as well as polarization layer [31]. Furthermore, the cross-flow filtration is extensively applied in most industrial large scales.

2.3. Membrane configuration

Large range of membrane devices is available for both cross-flow and dead-end modes. The expression “membrane configuration” makes reference to the membrane geometry and shape that depends on the flux of both permeate and feed solution pressure and fouling phenomenon. Generally, for CMs membrane, tree configurations are used in the water purification, namely tubular, flat disk and hollow fiber (as illustrated in **Figure 5**). These configurations are the commonly used the most in cross-flow mode [33].

In principle, the three types can be applied in dead-end configuration, however, there are susceptible to high fouling. For this reason, specific devices have been developed for dead-end

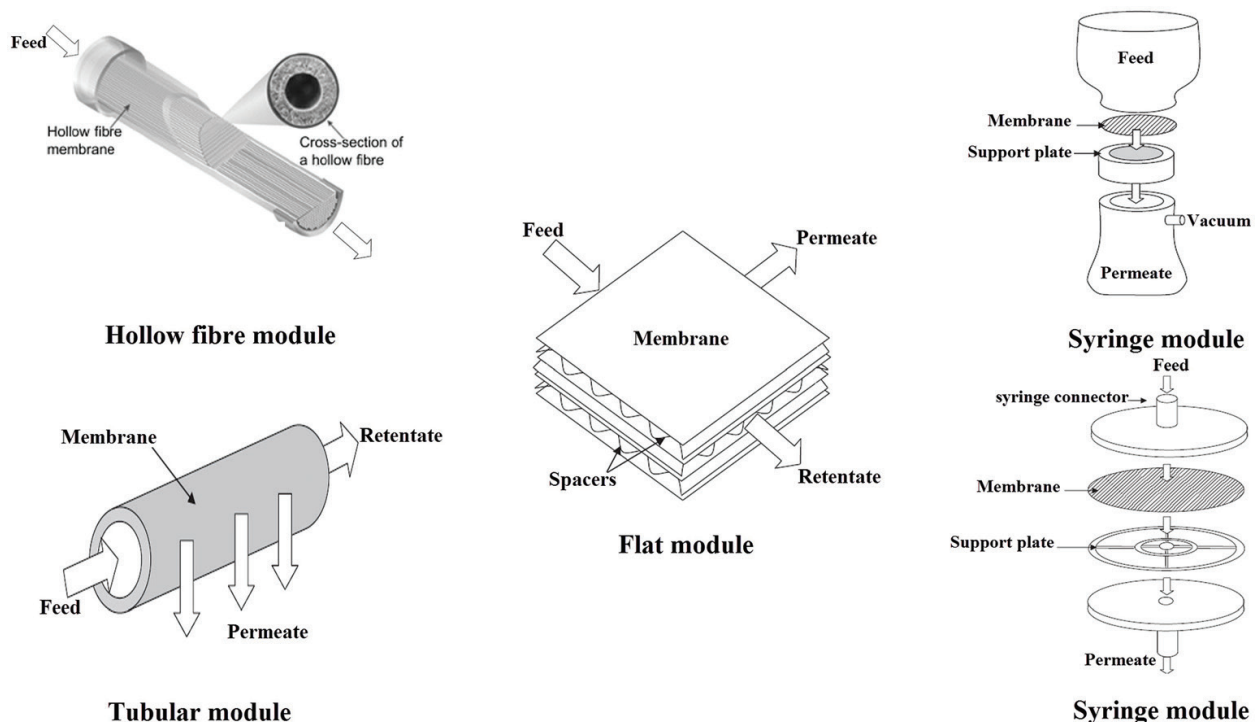


Figure 5. Membrane configurations [8, 32].

applications [34] such as syringe-end filters, centrifugal membrane, and vacuum filtration devices as illustrated in **Figure 5**. The most important properties for perfect membrane modules are high packing density, low-cost (operating and maintenance), good hydrodynamic propriety as well as cost-efficient production [35].

2.4. Membrane performance

For liquid separation, membrane performance is evaluated by simultaneous parameters, which are the permeate flux through the membrane and the rejection of soluble species, suspended or dispersed species. In order to characterize the rejection of membrane R generally, size exclusion technique is used, where R depends on the pore size and the membrane character (hydrophilic/hydrophobic), and the operation conditions (pH, pressure...).

Furthermore, dissimilar types of solute/solvent solutions can be applied. Usually, macrosolute solutions (as PEGs) or dextrans are employed for UF membranes, while for characterization of NF membranes, a mixture of mono- and multivalent salt solutions are used. The apparent rejection (R_a) and the intrinsic rejection (R_i) are defined, respectively, as follows (Eqs. (3) and (4)):

$$R_a = 1 - \frac{C_p}{C_f} \quad (3)$$

$$R_i = 1 - \frac{C_p}{C_w} \quad (4)$$

where C_p , C_f , and C_w are, respectively, the species concentration in the permeate (C_p), feed, and at the membrane wall. The R_a is measured by sampling the feed and permeate phase, R_i takes into consideration the solute concentration at the membrane interface. It should be noted that a difference between R_i and R_a is due to the hydrodynamic resistance. To reduce this difference control of concentration and velocity of the feed solution is needed. $R = 0$ indicates no separation acquired, whereas $R = 1$ reveals that solute is retained, and the only solvent passes through the membrane.

In the case of a pressure-driven process, the membrane hydraulic permeability (L_p) ($m/s Pa$) is an important indicator of the membrane functionality. Darcy's law of flow through porous materials and r laminar flow conditions allows the determination the value of L_p according to Eq. (5). It should be noted that the volumetric permeate flux (J_v) ($m.s^{-1}$) is related to the TMP.

$$L_p = J/\Delta TMP \quad (5)$$

In addition, membranes know by fouling phenomenon. The membrane fouling is defined as the progressive accumulation of particles at the surface or in the pores of the membrane, which cause a decrease of permeates flux. The decrease in membrane capacity is mainly caused by the formation of a boundary layer during the process of filtration (**Figure 6**). Membranes fouling come in two forms: external fouling, which is the accumulation of rejected particles (foulants) on the external surface of the membrane, and an internal membrane fouling that

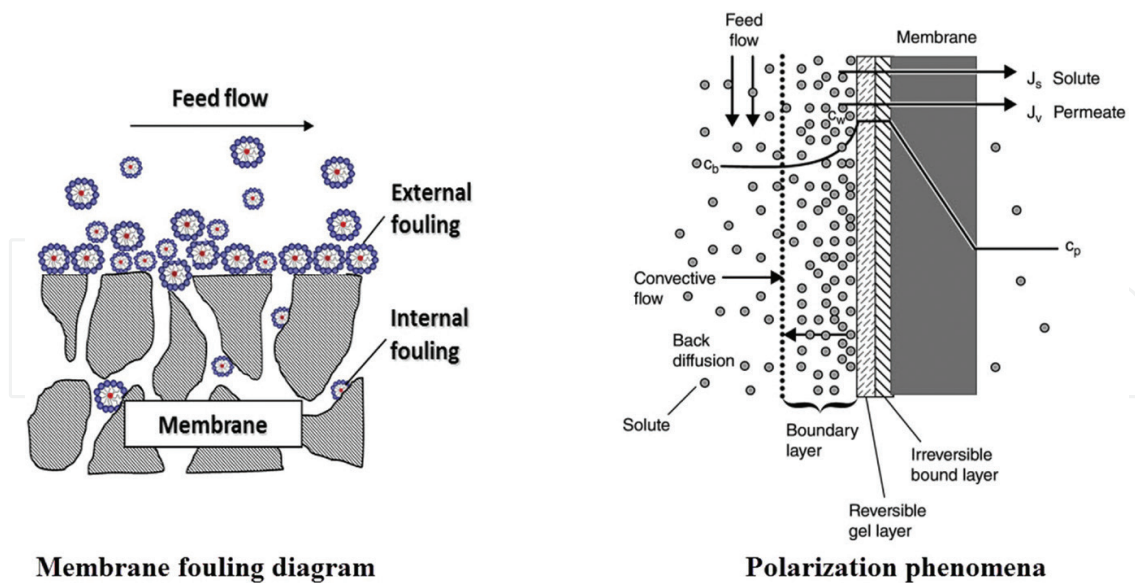


Figure 6. Schematic figure of membrane fouling and polarization phenomena [36].

represents the deposition or adsorption of microminiature particles or macromolecules within the internal pore structure of the membrane. The concentration polarization, during the initial period of filtering operation time, is one of the primary reasons for flux decline.

3. Different applications of Al_2O_3 UF, and NF ceramic membranes (CMs)

3.1. Desalination

Nowadays, desalination has become a very affordable solution to cope with the growing global water gap. However, even though water covers 70% of the earth surface but 97% of it has too high-salt content. The applications of separation techniques for desalination only cover 1% of the world's potable water supply. Desalination by membrane technology is commonly performed by RO membranes. The use of polymeric as material for membrane desalination has demonstrated some limitations such as membrane deterioration. For these reasons, research and development of new membrane materials could allow more opportunities for water desalination. Since the last decade, ceramic materials have known significant progress in desalination, especially using NF and UF membranes. The use of CMs especially $\gamma\text{-Al}_2\text{O}_3$ membranes in water desalination and water softening showed potential application [37, 38].

$\gamma\text{-Al}_2\text{O}_3$ NF membranes were primarily investigated in salt rejection by different authors. Baticle et al. [39] compared the filtering performance of two tubular $\gamma\text{-Al}_2\text{O}_3$ NF membranes, fired at 450–650°C, in terms of ion rejection and flux. The two NF membranes were prepared by a sol–gel process [40] having a pore size near to 1.3 nm for the membrane fired at 450°C (M1), and near to 2 nm for the membrane fired at 650°C (M2). The filtration tests were carried out in a tangential filtration setup. The tests were performed with different salts at a

concentration of 0.01 mol/l for M1 and 0.005 mol/l for M2 at applied pressure of 10 bar and pH (5, 0–5.6). For each salt, volume flux and rejection were measured at the steady state. In addition, an earlier work by Alami Younssi et al. [41] highlighted the rejection of mineral salts by a monotubular γ -Al₂O₃ NF membrane (M3) with a pore size of 0.7 nm obtained by sol-gel [40] and fired at 450°C. The filtration experiments of different salts at concentration of 0.01 mol/l were performed on tangential pilot and fixed pressure of 10 bar. The filtration results of the three membranes (M1, M2, and M3) are grouped in **Table 4**.

From **Table 4**, it can be concluded that the charge and size of different ionic species dramatically influence on the salt rejection. The ion valency has a dramatic effect, which can be manifested by an increase in salt rejection when the valency of the associated cation increase, M²⁺ (divalent cation) > M⁺ (monovalent cation). However, salt rejection decreases when the valency of the anion increases in the following order: NO₃⁻ > Cl⁻ > SO₄²⁻. Furthermore, the difference in rejection obtained for ions having the same charge (rejection of Na⁺ > K⁺) is mainly due to hydration effect. It was also found that the low permeation rates lead to negligence of the concentration polarization phenomenon. The effect of sintering temperature was marked by a small decrease of salt rejection, when the temperature is changed from 450 to 650°C. This decline is in agreement with weak electric interactions caused by larger pores. However, a variation in the density of the charges on the surface of the two membranes cannot be excluded.

In addition, the sintering temperature of the membrane has a profound effect on water permeability rather than salt permeability, which is not radically affected. The main responsible phenomenon for the electrolyte rejection in the different experiments is the electric repulsion or attraction happening between the dissolved ions and the membrane surface charge.

Anions	Cations	pH	R% of M1	R% of M2	R% of M3
NO ₃ ⁻	K ⁺	5.6	55	41	55
NO ₃ ⁻	Na ⁺	5.5	70		70
NO ₃ ⁻	Ca ²⁺	5.6	95		95
NO ₃ ⁻	Cu ²⁺	5.5	97		97
NO ₃ ⁻	Cd ²⁺	5.6	97		97
NO ₃ ⁻	Ni ²⁺	5.6	97		97
Cl ⁻	K ⁺	5.5	36		36
Cl ⁻	Na ⁺	5.6	50		50
Cl ⁻	Ni ²⁺	5.5	97	95	90
SO ₄ ²⁻	K ⁺	5.6	1		1
SO ₄ ²⁻	Na ⁺	5.6	20		20
SO ₄ ²⁻	Ca ²⁺	5.5	40		40
SO ₄ ²⁻	Cu ²⁺	5	45		45
SO ₄ ²⁻	Cd ²⁺	5.6	40		40
SO ₄ ²⁻	Ni ²⁺	5.9	40	20	40

Table 4. Rejection rate of different salts on γ -alumina NF membrane.

The typical behavior of Al_2O_3 NF membranes was also found during the filtration of different salt solutions, such as AlCl_3 , FeCl_3 , CaCl_2 , MgCl_2 , NaCl , NH_4Cl , MgSO_4 , and Na_2SO_4 , by a $\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ hollow fiber NF composite membranes (HFNF) prepared and characterized by Wang et al. [42]. The elaborated inorganic composite membranes were prepared by dip-coating $\gamma\text{-AlOOH}$ sol on $\alpha\text{-Al}_2\text{O}_3$ hollow fiber and sintered at 750°C . The optimal hollow fiber NF membrane has a mean pore size of 1.61 nm and permeability P equal to $17.4 \text{ L/m}^2 \text{ h bar}$; this permeance was found to be much higher than reported in the literature (**Table 5**) due to the relatively high-porosity (45%). Also, the membrane exhibited great chemical resistance in different solvents and harsh pH. Separation performance of the studied membrane, at applied pressure of 5.0 bar and fixed salt concentration of 2000 ppm, exhibited higher retentions of multivalent ions than monovalent ions, such as Fe^{3+} (97.1%) > Al^{3+} (90.9%) > Mg^{2+} (85.0%) > Ca^{2+} (84.1%) as in **Figure 7**. It could be explained by the dominance of Donnan exclusion mechanism and size exclusion mechanism [43].

Di Yu et al. [37] elaborated a thin homogeneous supported mesoporous $\gamma\text{-Al}_2\text{O}_3$ membrane on top of hybrid $\alpha\text{-Al}_2\text{O}_3$ support with a pore size of 4 nm. The preparation of the $\gamma\text{-Al}_2\text{O}_3$ membranes was obtained by dipping supports in a nanoparticle precursor dispersion and applied for water permeation and purification of salt solutions. The experiments were conducted on a dead-end mode (300 kPa), and the water flux was measured to calculate the permeability of the membrane ($7.7 \text{ L/m}^2 \text{ h bar}$). Aqueous solutions prepared from CaCl_2 and NaCl salts with a concentration of 10^{-3} mol/l along with an artificial sea water sample were used to demonstrate the perselectivity of the NF membrane. The pH of the synthesized salt solutions (except the pH of sea water is natural pH) was adjusted to be 4.6 to the surface of the $\gamma\text{-Al}_2\text{O}_3$ is properly charged with adsorbed positive ions, and not chemically attacked. The results showed a high-rate rejection for Ca^{2+} and Na^+ ions (98.7% for Ca^{2+} , > 79.0% for Na^+) and matched the typical behavior of NF membrane in the manner that retained hydrated ions ($\sim 0.5 \text{ nm}$) are much smaller than the NF membrane pore size ($\sim 4 \text{ nm}$). However, the rejection of sea water is weak and found to be 6.3%. These results were explained either by a surface adsorption chemistry and/or electrokinetic interaction between the ions in the solution and the adsorbed ions.

From the different parameters influencing the selectivity and permeability of NF and UF CMs filled with electrolytes, we found pressure and potential gradients the consequences of these parameters are the results of phenomena like streaming potential, electro-osmosis, and electroviscous retardation, which influences the flow of electrolyte solutions [48]. This was in coincidence with the results as Wang et al. [42] observed. The salts transport mechanism through this membrane, relied on diffusion and convection [49]. The diffusion which resulted from a concentration difference governed at lower pressure. Contrary, the convection which is due to a pressure gradient across the membrane dominates the filtration process at elevated applied pressures [50]. That is the drag forces are less important than the surface forces, when the pressure is low. In contrast, as the pressure increases the surface forces stays constant while increasing velocity in membrane pores leads to an increase of the drag forces toward the permeate.

For a fixed concentration it has demonstrated that the reflection coefficient (σ) and solute permeability (P), which are the phenomenological coefficients, depend on the nature of the cation

Type membrane	Sintering T°	Elaboration technique	Permeability	Experimental set-up	Pore size (nm)	CM Shape	Concentration	Rejection	Article
γ -Al ₂ O ₃ / hybrid α -Al ₂ O ₃ membrane	950°C	Dip-coating	7.7 L/m ² h bar	Dead-end filtration	4	Disk-shape	0,001 mol/l	Ca ²⁺ > 98.7% Na ⁺ > 79.0%	[37]
γ -Al ₂ O ₃ / α -Al ₂ O ₃	450°C	Sol-gel process		Cross-flow filtration	1.3	Tubular	0.01 mol/l	Ca ²⁺ > 95	[39]
γ -Al ₂ O ₃ / α -Al ₂ O ₃	650°C	Sol-gel process		Cross-flow filtration	2	Tubular module	0.005 mol/l		[39]
γ -Al ₂ O ₃ / α -Al ₂ O ₃	450°C	Sol-gel process	12 L/m ² h bar.	Cross-flow filtration	0.7	Tubular		Ca ²⁺ > 95%	[41]
γ -Al ₂ O ₃ / α -Al ₂ O ₃		Dip-coating	17.4 L/m ² h bar	Cross-flow filtration	1.61	Hollow fiber	2000 mol/l	Ca ²⁺ > 84.1%	[42]
A1100/TiO ₂ / γ -Al ₂ O ₃		Dip-coating	4.5 L/m ² h bar	Dead-end	4.4	Flat disk	005–0.1 mol/l	Ca ²⁺ > 80% Mg ²⁺ > 80%	[43]
γ -Al ₂ O ₃ / α -Al ₂ O ₃	600°C	Dip-coating	1.2 L/m ² h bar	Dead-end filtration	4.5–7.5	Flat disk			[44]
γ -alumina NF membrane	500°C	Dip-coating	5.4 L/m ² h bar	Cross-flow filtration	1.9	Flat disk	260–80 mg/kg	TOC (oil hydrocarbons) > 90%	[45]
N-membrane			7.4 L/m ² h bar		2.7	Tubular			
C8/ γ -Al ₂ O ₃ / anatase-TiO ₂	400°C	Sol-gel process	2.8 L/m ² h bar		1.5	Flat disk			[46]
A025/Si	500°C	Sol-gel process	2.2 L/m ² h bar	Dead-end filtration	0.5	Flat disk	50 mol/l	PEG400 > 90%	[47]
γ -Al ₂ O ₃ / α -Al ₂ O ₃	450°C	Sol-gel process	5 L/m ² h bar	Cross-flow filtration	5	Tubular	50 mol/l	Ca ²⁺ > 80% Mg ²⁺ > 87%	[1]
γ -Al ₂ O ₃ -clay composite	600°C	Dip-coating	0.02357 × 10 ⁻⁵ m/s kPa	Bubble point setup	5.4–13.6	Flat disk	3000 mol/l	AlCl ₃ > 88%	[48]

Table 5. Comparison of γ -Al₂O₃ membranes.

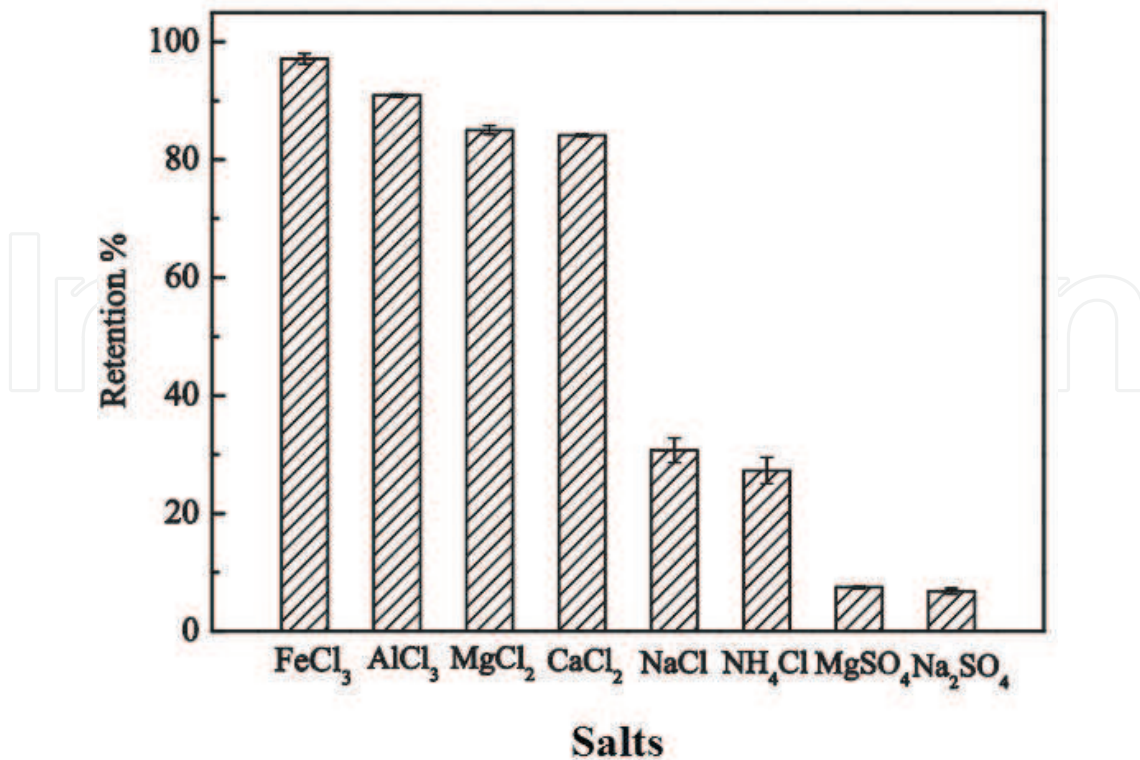


Figure 7. Retentions of various salts for HFNF membrane (at ΔP 5.0 bar and fixed salt concentration of 2000 ppm) [42].

and the anion of the solution [39]. In general, the highest σ along with the weakest permeabilities has been achieved with divalent cation associated to a monovalent anion. Contrary, salt with monovalent cation and divalent anion lead to an increase in salt permeability and a decrease of σ . Similar behavior was observed by Bejaoui et al. [51] with an Osmonics spiral module equipped with a thin film composite HL membrane, characterized by a molecular weight cut-off (MWCO) for the organic compounds of about 150–300 Da. The results of the studies are grouped in Table 6. The same founding was also reported for γ -Al₂O₃ UF membrane [52].

One of widespread behavior is the dependence of both flux and salt rejection on salt concentration. The osmotic effect governs the permeate, whereas increasing the feed concentration led to a decrease of the rejection rate caused by shielding of the effective charge of the membrane in the presence of a high electrolyte.

Among the first results appear to be promising in using γ -Al₂O₃ NF in water denitrification, is the study done by Alami Younssi et al. [41]. The removal of nitrate (NO₃⁻) ions in soft drinking water doped with NO₃⁻ was investigated using a NF tangential filtration pilot equipped with a membrane with 0.7 nm pore size and a fixed pressure of 10 bars. The preliminary results demonstrated that it is possible to reduce the concentration of NO₃⁻ from 50 to 31 mg/l, by a single filtration step.

A recent study by Breida et al. [1] was carried out to highlight and understand the transport mechanism that governs the tangential filtration of NO₃⁻ solutions through an UF γ -Al₂O₃

Salts	Membrane $\gamma\text{-Al}_2\text{O}_3$ NF (at 5×10^{-3} mol/l)			HL membrane (at 1×10^{-3} mol/l)		
	pH	σ	P (cm/s)	pH	σ	P (cm/s)
NaCl	5.5	0.65	1.86×10^{-4}	6	0.803	26.02
NaNO ₃	5.5	0.80	1.52×10^{-4}			
NaF	6			6	0.923	15.18
Na ₂ SO ₄	5.5	0.17	2.2×10^{-4}	6	0.947	1.29
NiCl ₂	5.6	0.86	0.13×10^{-4}			
NiSO ₄	5.6	0.37	3.1×10^{-4}			

Table 6. σ and P parameters in the presence of different salts for NF membranes.

membrane with a nominal pore size of 5 nm and water permeability of 5 L/m² h bar. The experimental filtration results were done on a series of various sources of NO₃⁻ solutions and operating conditions (as pH, applied pressure, the initial concentration of NO₃⁻, and cation valency). The effect of applied pressure on NO₃⁻ removal (the concentration of the different solution was equal to 50 mg/l, at natural pH) indicated that the rejection increased with pressure due to twofold force, the convection and friction forces. Furthermore, the rejection varies according to the associated cations and increases in the order of the following sequence Mg²⁺ > Ca²⁺ > Na⁺ > K⁺, with highest NO₃⁻ rejection above 80%, and at 6 bar for Mg (NO₃)₂ salts. Thereby, the hydrated radius and valency of associated cation had a dramatic effect on NO₃⁻ rejection. Further, the results demonstrated that the rejection and permeate fluxes gradually decreased when the initial NO₃⁻ concentration increased. The primary phenomenon that can justify the decrease in flux with concentration is the osmotic pressure difference and the partial plugging at higher concentration. In addition, the best ions rejections was obtained at low concentration (25 mg/l) with rate rejections equal to 87%, 80%, 60%, and 52%, respectively, for Mg(NO₃)₂, Ca(NO₃)₂, NaNO₃, and KNO₃. An increase of the water complexity, especially the presence of divalent anions such as SO₄²⁻, decreased the rejection of NO₃⁻.

The selectivity of the $\gamma\text{-Al}_2\text{O}_3$ UF membrane in NO₃⁻ removal strictly depended upon the pH [53–55]. Strong repulsion happened between the positive charged membrane and the multi-valent cations, which lead to a high rejection of ions (Mg²⁺, Ca²⁺...). The rejection of NO₃⁻ was found to grow with an increase of feed pH (range of pH from 3 to 9), due to electro-neutrality consideration. The high rejection of NO₃⁻ was obtained around pH_{pzc} by a rejection rate, which exceeded 80% for divalent cation Mg (NO₃)₂ and 50% for monovalent cation NaNO₃. The charge density and hence the Donnan exclusion changed depending on the pH and governed the NO₃⁻ separation (**Figure 8**. Electroneutrality).

The same UF membrane ($\gamma\text{-Al}_2\text{O}_3$ UF with a nominal pore size of 5 nm and water permeability of 7 L/m² h bar) showed similar behavior in the removal of heavy metals such as Cd(NO₃)₂, CdSO₄, and CdCl₂ [52]. The result obtained during the study of the variation of salt's retention

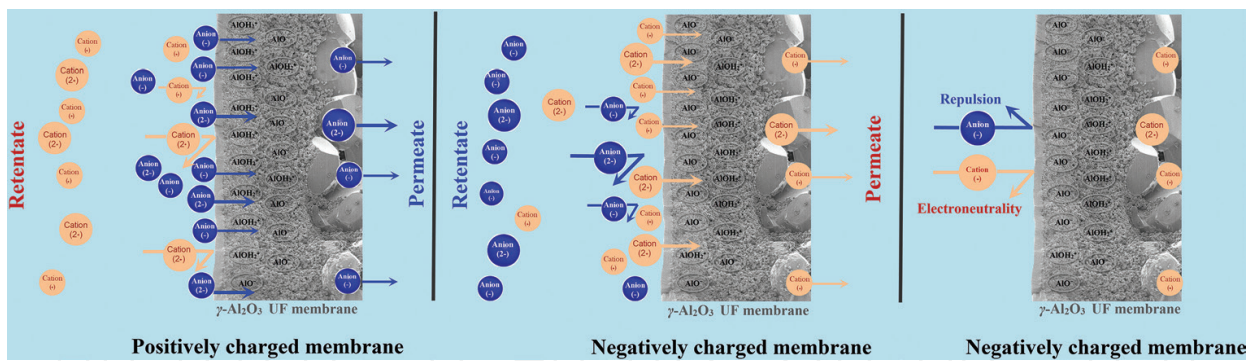


Figure 8. Electroneutrality phenomenon.

when the pH varies between 4 and 7 (concentration of 0.001 mol/l and pressure of 10 bar) demonstrate a greater dependency on pH irrespective of the heavy metals. However, no marked effect was observed with respect to flow variation as a function of pH.

To summarize, Al_2O_3 NF, and UF membranes can be successfully employed in ions separation, this separation is governed by size and charge effect.

In order to enhance the performance of organic membranes, nano Al_2O_3 could be introduced in polymeric membrane to form new generation of membranes (composite membranes) with new performances that combine organic and CM properties. García-Fernández et al. [56] introduced $\gamma\text{-Al}_2\text{O}_3$ nanoparticles to polyethersulfone (PES) membrane and evaluate the effect of nanoparticles in improving the membrane performance for copper ion removal from aqueous solutions. The obtained results showed that $\gamma\text{-Al}_2\text{O}_3$ nano-composite membranes prepared with 1.0 wt% of $\gamma\text{-Al}_2\text{O}_3$ nanoparticles possesses higher swelling and porosity compared to intact PES. In addition, the membrane could remove around 60% of copper.

3.2. Dyes removal

Textile industries are reported to be one of the most polluting industries out of the different industrial sectors, considering both volume and composition of the discharged effluents [57, 58]. The textile wastewater is composed of an elevated variability and complexity of pollutants, caused by the use of dyes, and several reactive agents. They are characterized by high COD, salts concentration, pH, and strong coloration [59]. In addition, recent survey conducted by FICCI [60] reported that the water demand for the textile sector is likely to witness an increase due to the forthcoming industrial growth beside the significant rise in population. In order to overcome the problems generated by these effluents and to reuse it in the processes for industrial production, different chemical, physical, and biological techniques have been devoted to eliminate dyes from wastewaters. However, these methods are reviewed as good solution to meet legislative requirements but not enough to allow water reuse.

The process of separation by membrane techniques are currently viewed as economically, and technologically lucrative options for industrial wastewater treatment and the textile industry is one of the principal beneficiaries of membrane process [26, 59]. UF had been efficiently used for recycling insoluble dyes (such as indigo) and high-molecular weight, auxiliary chemicals,

and water [61, 62]. Al₂O₃ UF, and NF membranes result in reducing the various contaminants present in textile effluents, especially dyes, below permissible levels.

DeFriend et al. [63] investigated the use of Carboxylate-aluminoxane nanoparticles as an alternative to the traditional sol–gel method, for forming UF Al₂O₃ membranes. Al₂O₃ membranes derived from A-alumoxane, prepared by the reaction of boehmite in acetic acid, and disposed on a α -Al₂O₃, were calcinated at 600°C. The average pore size was found to be 11 nm. The performance and rejection characteristic of the new A-alumoxane membranes along with the used support is described in the following **Table 7**.

The results presented in **Table 7**, demonstrate that the deposition of Al₂O₃, which was obtained from A-alumoxane, α -Al₂O₃ support results in a decrease in the permeability. Furthermore, the performance of the elaborated membrane was envisaged in the separation and discrimination of various synthetic dyes (Direct Red 81 (DR 81), Direct Red 75 (DR 75), Direct Blue 71 (DB 71), Direct Yellow 62 (DY 62), and Direct Yellow 50 (DY 50)), the studied dyes have different molecular weights, sizes, and formal charge. The dye solutions were passed through a dead-end filtration system (pressure of 5.5x10⁴ Pa (8 psi)), and the pH of these solutions was between 5.7 and 7.1 for all the dyes. The rate retentions obtained by the support, 40% for DB 71, 39% for DR 75, 38% DY 50, 20% for DY 62, and 0% DR 81, were much weaker than the retentions achieved by the membrane (88% for DB 71, 90% for DR 75, 73% DY 50, 20% for DY 62, and 90% DR 81), and this is for all dyes. The A-alumoxane membrane (7 nm) improves dye’s retention of about 40–90% over the support, without a significant increase in the total surface area. The used dyes are poly-sulfate salts characterized by a charge dependence on pH. Furthermore, the Al₂O₃ is well known for its dependency on the pH. On the basis of the amphoteric character of both dyes and membrane material, the authors study the effect of pH (an acidic pH = 1, 5, neutral pH = 6.5, and basic pH = 12, 5) on dyes removal. The results of this study are presented in **Table 8**.

Variations of pH value has no marked effect on the retention of dye by the support, but the alteration of pH has resulted either in increasing or decreasing the retention characteristics of the membranes. Under acidic conditions, there is a meaningful absorption of dyes on the

Performance measurements	α -Al ₂ O ₃ support	New A-alumoxane membranes
Particle size (nm)	100–500	7–25
Surface area (m ² /g)	3.85	111
Average pore size (nm)	50	7
Surface roughness (nm)	67	9
Permeate flux (10 ⁻⁶ m/s)	1.42	0.85
Permeability (nm ²)	36.7	22
MWCO (g/ mol)	>500,000	>1000
MWCO pore size (nm)	31	>4

Table 7. Characteristics of Al₂O₃ and aluminate UF membranes derived from Al₂O₃ nanoparticles [63].

Synthetic dyes	Dye MW (g/mol)	Dye charge	pH	Retention by membrane (%)	Retention by support (%)
DR 81	675	-2	1.87	100	0
			6.05	90	0
			12.52	94	0
DR 75	991	-4	1.63	97	20
			6.45	20	20
			12.56	66	20
DB 71	1030	-4	1.76	100	38
			6.95	90	38
			12.41	95	38
DY 62	771	-2	1.82	99	39
			7.07	73	39
			12.44	44	39
DY 50	957	-4	1.62	100	40
			5.73	88	40
			12.57	93	40

Table 8. Retentions of selected dyes by A-alumoxane-derived Al_2O_3 membranes at a specific pH [63].

Al_2O_3 surface leading to a high rejection. However, in the basic pH range, the retention is mainly due to the charge repulsion between membrane pore surfaces and the dyes.

In the past few years, several major reports highlighted the effect of changing the charge of Al_2O_3 surface on permeate flux [42, 49]. At the pzc, the membrane has a lower net charge, which assumed that the permeate flux is higher as the electroviscous effects should be reduced. In another study (using a single tubular $\alpha\text{-Al}_2\text{O}_3$ CMs) an increase in permeate flux with decreasing pH was either below or above the pzc [64]. Further, the study indicated that during the filtration of solutions containing SiO_2 on Al_2O_3 membrane, the highest permeation occurred at pH values of 2, and pH above 10. However, the lowest flux was obtained near a pH equal to 9.

Most recently, Oun et al. [65] prepared an UF membrane (mean pore diameter of about 50 nm) by simple deposition of TiO_2 nano-powder on the internal surface of the tubular porous clay- Al_2O_3 membrane support. The membrane is the result of a combination of extrusion, sintering, and slip-casting methods. Cross-filtration membrane tests were conducted to estimate the permeability and rate rejection of alizarin red dye. The decolorization efficiency of the membrane was studied as a function of the initial dye concentration, pH of the dye solutions, and the TMP. UF membrane demonstrated a water permeability of 117 L/m^2 h bars. The highest retention of about 99% was observed at TMP of 5 bars, which is due to the dual functionality of the TiO_2 layer, namely adsorption and filtration. Giving that the efficiency of the UF process of dyes removal dramatically depends on the pH of the feed solution, the alizarin dye showed a significant dependence on pH. Indeed, the best rejection (above 98%) was obtained in alkaline solution at pH = 9. However, in acidic feed solution pH = 2 the rejection decreased to a value of 40%.

3.3. Application of Al₂O₃ NF and UF membranes in food applications

The demand for products with higher nutritional value and of processing procedures less harmful to the environment and to human health has recently known a tremendous growth. Furthermore, transferring of membrane processing to food industries has been the objective of many studies [18, 66]. The choice of working with CMs technologies in the food industry is mainly based on the different advantages obtained by these techniques such as ease of cleaning, food safety [67, 68], and the acquisition of newly food fractions that can be used for other food process. CMs allow simplifying the different production stages, by avoiding complex, and chemically stressful steps. This section investigates the application of Al₂O₃ NF and UF CMs in the field of food processing.

3.3.1. Filtration of dietary fats

Authors such as, Alicieo et al. [69] investigated the purification of crude soybean oil from several components (like pigments, sterols, phospholipids, free fatty acids, carbohydrates, proteins...), by use of UF membranes. The applied ceramic UF is a tubular membrane made of α -Al₂O₃/TiO₂, with nominal pore size of 10 nm. The filtration tests were performed in cross-flow configuration at 6 bar pressure. The UF membranes provide a high rejection for most of components. The rate rejection for phospholipids is 99.14%, 97.91% for soaps, along with a medium rejection for both free fatty acids, and color (54 and 42%, respectively).

In another work [70], Al₂O₃ multi-channel CMs with an average pore size of 50 nm was used to UF vegetable oil miscella (specifically removal of phospholipids from a mixture of extracted corn oil and solvent). The influence of TMP (0.5 and 1.5 bar) and the composition of miscella (between 25 and 35% w/w of corn oil) on phospholipids and permeates flux were studied. The increase of crude oil percentage into the miscella negatively influenced the flux of permeate. However, it favored the retention of phosphorus (P). In addition, it has been demonstrated that high TMP results in high retentions, however, when it comes to permeate flux, the tangential velocity had a greater influence on flux than TMP. UF of 35% w/w of crude corn oil at 1.5 bar resulted in 93.5% w/w rejection of the phospholipid.

3.3.2. Filtration of proteins

The purpose of protein separation and purification by membrane technologies is to ameliorate the stability and purity by removing pollutants. Furthermore, the membrane allows increasing the range of products that can be offered and reduced waste treatment costs. Some works have been carried out to upgrade liquids effluents by recovering proteins using UF and NF membranes [71].

Fist work on fish proteins recovering from the use of CMs was reported in 2003 [72]. The wastewaters were pretreated by a Al₃O₂ MF and filtered with NF membrane made of TiO₂ and deposited on a Al₃O₂-TiO₂ support. The applied pressures in the MF tests were ranging from 3 to 5 bars with a cross-flow velocity (CFV) ranging from 2 to 4 m/s. Permeate and concentrate were recycled to the feed tank, in order to maintain the feed at an approximately constant concentration. The optimal conditions used during the effluent filtration by NF membrane

were obtained from previous microfiltrated fish meal effluent, and the subsequent concentration experiment was carried out at 4 bar, 4 m/s, ambient temperature, and pH = 6.3. Due to the deposition and adsorption of proteins on the surface and pore walls of Al_2O_3 membranes, the flux was found to decrease to 21% of the pure water values.

Recent research highlighted the potential use of ceramic modified nanofiber membrane for protein recovery [73]. The elaboration of the membrane was done through steps. Firstly, the boehmite nanofibres were prepared by a hydrothermal reaction from Al_2O_3 colloidal gels [74, 75] and calcined at 500°C for 5 h to form $\gamma\text{-Al}_2\text{O}_3$. The prepared boehmite nanofibers were coated on the surface of α -alumina supports, calcinated at 500°C. Furthermore, silane groups were introduced to change the surface proprieties of the prepared $\gamma\text{-Al}_2\text{O}_3$ nanofiber membranes. The pore size distribution indicated that the addition of nanofiber had improved remarkably the pore size of the support, from 700 to 11 nm and through reduced the permeability. However, the silane-grafted fiber membrane had no marked effect on pore size, but it changed the membrane surface from hydrophilic to hydrophobic. Both $\gamma\text{-Al}_2\text{O}_3$ fiber membranes and silane-grafted fiber membrane demonstrated good separation efficiency with the MWCO of 70 kDa (90%). The performance of the support and the resultant fiber membranes was investigated by tangential flow filtrations of proteins such as bovine serum albumin (BSA), cellulose, and trypsin. The rejection ability has been improved by 30% when Al_2O_3 nanofibres were coated on the support and this for all protein and concentrations. Furthermore, the silane-grafted Al_2O_3 fiber membrane rejected 100% BSA protein, 92% cellulase protein, and 75% in case of trypsin protein (at a concentration of 400 ppm). Inconstancy, the efficiency of $\gamma\text{-Al}_2\text{O}_3$ fiber membrane in rejecting BSA is between 58 and 36% with various feeding concentrations. The difference in rate rejection of the two membranes can be attributed to the differences of pore size.

Because of ceramic fouling phenomena, more particularly in the case of whey proteins separation, Svetlana Popovi et al. [76] studied the flux recovery procedure for ceramic tubular membrane fouled with whey proteins. The study evaluated the effect of the choice of rinsing, cleaning agents and concentration, and on CM cleaning efficiency. The experiments were done on two membranes of different pore size, an UF membrane made of ZrO_2 filtering layer on an $\alpha\text{-Al}_2\text{O}_3$ support (with a pore size of 50 nm), and a MF membrane of a 200 nm mean pore size made of an $\alpha\text{-Al}_2\text{O}_3$ filtering layer on an $\alpha\text{-Al}_2\text{O}_3$ support. The synthesized effluents were made by dissolving whey powder (the powder composition was 11.8% (w/w) proteins, 75.0% (w/w) lactose, 3.3% (w/w) fat, 9.5% (w/w) ash, and 2.3% (w/w) water) in deionized water with a concentration of 10 g/l. The pH of solutions was kept at a neutral value (pH = 6.0). The retentate and permeates were both recycled to the feed tank. Experiments have been conducted following steps, pure water flux measurement, fouling, rinsing, chemical cleaning, rinsing, and pure water flux measurement. Furthermore, the chemical cleaning and rinsing was carried out for 30 min with full recycle. The sodium hydroxide solution was used as an alkaline cleaning agent, different concentrations of NaOH was studied. In addition, the caustic cleaning was done with commercially available detergents P3-ultrasil 67 and P3-ultrasil 69.

Chemical cleaning (**Figure 9**), by caustic solution (1.0% (w/w)) of the UF membrane gives a flux recovery equal to 97%, in the other hand the cleaning of MF with (0.6% (w/w)) caustic solution achieved a best flux recovery of 78% (regardless of the applied concentration). The

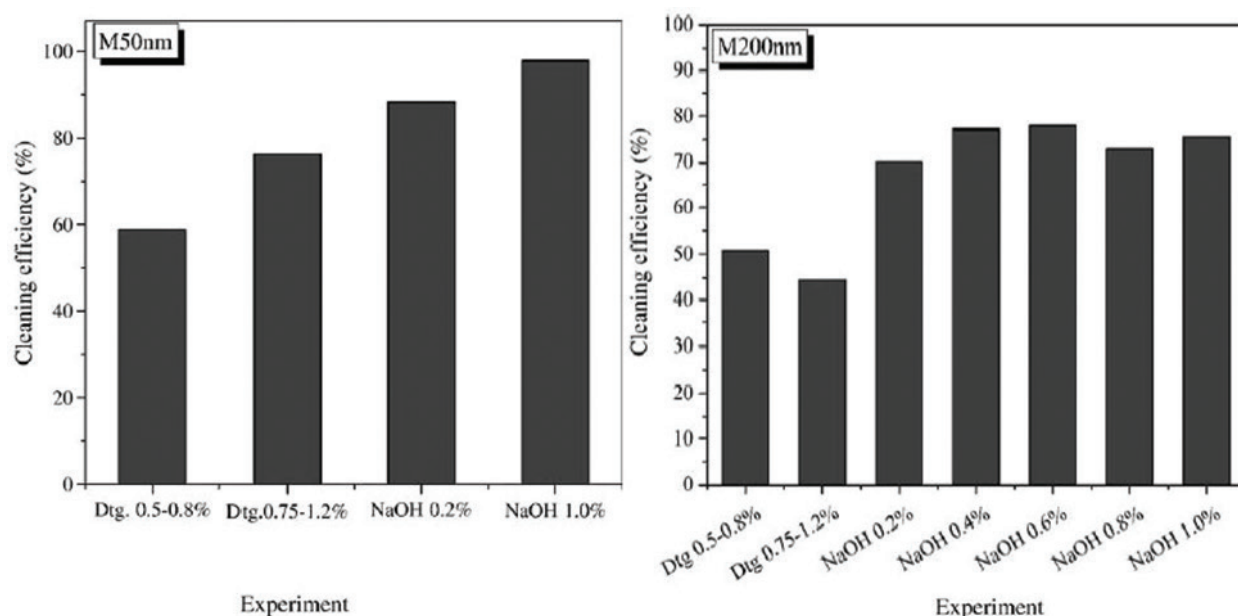


Figure 9. Cleaning efficiency for the 200–50 nm membranes on the pure water flux measurements before fouling and after cleaning at the same conditions 25°C, TMP [76].

application of commercial detergents in the cleaning of both membranes is less efficient than the caustic solution. However, it was noted that the flux recovery risen with increasing of detergent concentration from 60 to 75%.

Beside the different methods used for membrane cleaning and fouling prevention, membrane fouling can be reduced by improving the preparation methods and modifying the membrane in a way to decrease the surface interaction between the membrane material and the proteins [77]. Recently, researchers targeted two potentials in the modification of Al_2O_3 surface, which are the super-hydrophobicity (contact angle $>150^\circ$) and super-hydrophilicity (contact angle $<5^\circ$), that enhance the anti-fouling, and self-cleaning applications. Furthermore, graphene derivatives are viewed as having high-potential to serve as modified materials [30, 78, 79].

3.4. Oily wastewater treatment

Oily industrial wastewaters are highly heterogeneous, due to the different pollutants (hydrocarbons, surfactants, metals, acids, etc.) coming from the diverse stages of oil production. The most challenging in terms of effective treatment is the stable oily effluents consisting of highly chemically and physically emulsified oils. The classical separation processes used for oily effluents does not meet the established standards (The European standard for effluent from onshore petroleum activities is, 5 mg/l total hydrocarbons (HC) and less than 10 mg/l suspended solids). Membrane technology is used in both, industrial processes, and oily effluents treatment [12, 80]. Application of membrane in the petroleum industry is mostly done in hydrogen recovery and olefins such as ethylene and propylene in polyolefin production beside the removal of aromatics from gasoline [81]. Furthermore, major studies on filtration of industrial oily wastewaters were performed in the 1990s and research has continuously increased in recent years.

The research done by Ebrahimi et al. [82] is one of the primary works in oil separation by CM. The application of a combination of commercially ceramic, MF, UF, and NF was evaluated for the removal of oil from used model solutions and oil-field produced water, respectively. The study aimed to investigate the variation of permeates flux and the removal efficiency of total organic carbon (TOC) and oil. The studied UF and NF membranes had TiO_2 as active layer and Al_2O_3 as membrane support. Cross-flow filtration (velocities ranged from 1.3 to 6 m/s) processes were conducted using a continuous stirred tank reactor. The experiment showed that the average percentages of oil removal by UF and NF are 80 to 84%, respectively. However, the TOC removal is relatively low (27% for UF and 13% for NF). Furthermore, the MF, UF, and NF membranes used in combination were able to provide a total oil removal percentage of 82% in terms of initial feed concentration at 1 bar TMP. The same authors [83] reported that TOC removal was modest (27% for UF, and 13% for NF), as pretreatment for wastewater. The efficiency of single application of dissolved air flotation (process in removing oil pollutants) was found to be up to 90% in 90 min with airflow rate of 0.8 NI/s. In addition, the combination of the two techniques allowed 99.5% oil removal and 50% TOC elimination. The NF in oil industry has replaced RO in many applications due to higher flux rates and lower energy consumption [84].

Sadeghian et al. [45] prepared supported $\gamma\text{-Al}_2\text{O}_3$ NF membrane from colloidal dispersions of bonhomie, through a sol-gel method. The pore size at the support and $\gamma\text{-Al}_2\text{O}_3$ layer was determined to be 22 and 0.99 nm, respectively. The $\gamma\text{-Al}_2\text{O}_3$ NF was applied for removal of oily hydrocarbon wastewater, via a cross-flow NF pilot. The applied TMP pressure was in the range of 0.7–1.1 MPa and the CFV was between 0.56 and 2.8 m/s. The membrane efficiency was determined based on the measurements of permeate flux and rejection of TOC. The permeation of flux increased with an increase of pressure (from 0.7 to 1.1 MPa), the highest flux was obtained at 1.1 MPa with 46.3 L/m² h. Furthermore, the flux increased when the CFV increases and when the concentration of oily effluent was minimum (260 ppm, concentration of TCO in feed solution). Under the various operation conditions, the TOC rejection efficiencies were higher than 90%.

In another work done by Zhang et al. [85], CMs with different membrane pore sizes and materials were studied in the treatment of oilfield produced water. Membranes of 200–500 nm pore size were made from $\alpha\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$, beside two other membranes with a pore size of 20–50 nm made from $\text{ZrO}_2/\alpha\text{-Al}_2\text{O}_3$ materials. The study investigated the effects of NaCl and Polyacrylamide (PAM) on the membrane performance. The effect of pore size was primarily seen during the measure of pure water flux. The permeability of both membrane (M) increased with an increase of the pore size from 200 to 180 L/m² h, respectively, for M 20 nm and M 50 nm (at, PAM 5 mg/l, NaCl 3% (w/w), TMP 0.1 MPa, CFV 2 m/s, T 25°C).

For the $\text{ZrO}_2/\alpha\text{-Al}_2\text{O}_3$ UF membranes, the average MW of PAM in the permeate experienced a little change with the different concentrations of PAM. In addition, it was found that an increase of NaCl concentration led to a decrease of PSF of the membrane because the increased viscosity of the feed water and the change in the PAM morphology causes strong membrane fouling. Moreover, in alkali solutions, the PAM was easily hydrolyzed and degraded, and the membrane fouling can be avoided with a simple cleaning by aqueous NaOH solutions (pH > 12).

Overview of the experimental results indicates that Al_2O_3 UF and NF membranes can be applied to offer high-efficiency in oil HC removal as well as a relatively high-flux. Despite the difference in operational conditions, the flux of permeate was found to rise with increasing TMP, CFV, and low oil concentration in the feed (Cf) solution. Furthermore, TOC rejection was higher than 90% and this for all experiments. It is worth mentioning that the concept of MF of oily wastewater by Al_2O_3 -MF membrane (where cleaned permeate can be obtained and recycled/reused in the oil refining process), showed promising results and possibly large-scale application [86].

Many studies showed the high-efficiency of Al_2O_3 -MF membranes in oil removal. Recently, Zita-Sere et al. [87] demonstrated that a Al_2O_3 ceramic tubular membrane with a pore size of 200 nm is an adequate secondary treatment technique to decontaminate wastewater from an oil refinery. The wastewater was characterized by turbidity in the range of 200–2500 NTU and COD ranging from 5000 to 18,000 mg O_2 /l. Batch cross-flow MF runs were performed at TMP in the range of 1–3 bar and a flow rate of 100–300 L/h. The MF of the oily effluents provided satisfactory removal, expressed by the good COD retention (75%), and the significant turbidity removal (99%). The characteristics of the obtained permeate allow the circulation of the water in the process.

Yeom et al. [88] prepared Al_2O_3 -coated clay–diatomite composite membranes using inexpensive raw materials by a simple pressing and dip-coating method. The study of raw material compositions demonstrate that the optimal membrane support was obtained with, 48.6% Diatomite, 18.8% Kaolin, 14.8% bentonite, 14.8% Talc, 2.0% sodium borate, and 1.0% BaCO_3 . Meanwhile, the pore size of the Al_2O_3 -coated clay– diatomite composite membrane (with optimal support) is equal to 120 nm, and the steady state flux was $6.91 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$, at an applied pressure of 101 kPa. The membrane performance in oily wastewater filtration was excellent with rate rejection of 99.9% with a feed oil concentration of 600 mg/l and an applied pressure of 101 kPa.

Chang et al. [89] studied the hydrophilic modification of a tubular Al_2O_3 -MF membrane (with a 19 channels configuration) by nano- TiO_2 coating, using the in situ precipitation method, and evaluated the modified membrane in treating stable oil in water emulsions. The membrane modified with 2 mol/l $\text{Ti}(\text{SO}_4)_2$ solutions, was the best for water MF. The results of nano-coating on the membrane surface allowed an increase of the membrane hydrophilic character; however, no marked influence was observed in the layer pore size. The stable flux of the modified membrane was higher by 30–40% compared to the unmodified membrane, and this when the feed temperature was 40°C, a CFV of 5 m/s, and TMP of 0.16 MPa. The increase of flux is mainly due to the presence of hydrophilic nano- TiO_2 . The elimination of oily contamination was demonstrated by a fall in concentration from an initial feed concentration of 4 g/l to a concentration of 10 mg/l in the permeate.

3.5. Domestic wastewater treatment

Domestic or municipal wastewater (MWW) is now considered more as a resource than as a waste. The MWW can be used a resource for energy, for plant fertilizing, and recovery of both

nitrogen (N) and P [90]. Moreover, the reclaimed wastewater of MWW is widely accepted for landscape and crop irrigation thereby preserving the water sources. The anaerobic membrane bioreactor (AnMBR) systems have become an advantageous technique for treating domestic MWW. Giving the advantages of CMs, recent studies targeted the use for fouling control of anaerobic ceramic MBR (AnCMBR) [91, 92].

In this context, Jeong et al. [93] are the first to suggest the application of CMs for the anaerobic treatment of domestic wastewater (AnCMBR). In this study, The membrane bioreactor holds either a flat sheet Al_2O_3 -based anaerobic ceramic membrane (AnCMBR-ACM) or a flat-sheet Pyrophyllite-based anaerobic ceramic membrane (AnCMBR-PCM), the AnCMBR-ACM has a pore size of 100 nm, pure water permeability of $1104.2 \text{ L/m}^2 \text{ h bar}$, and were operated in the inside-out mode. The performance of CMs was principally done by evaluating the filtering efficiency and treatment performances. For AnCMBR-ACM, at longer hydraulic retention time (HRT) condition (44 ± 3.1 for 1–45 days), the efficiencies of COD, DOC (Dissolved Organic Carbon), and methane content removal reached values of $90.5 \pm 6.8\%$, $95.9 \pm 5.3\%$, and $56.2 \pm 5.3\%$, respectively. Furthermore, the reactor performance was not significantly affected by changes in HRT, which is seen by the rate rejection of COD ($96.1 \pm 5.1\%$), DOC ($98.5 \pm 0.5\%$), and methane ($60.2 \pm 4.9\%$) when the HRT was (18 ± 1.3 for 46–80 days). Both CMs were successfully operated and been suggested as a treatment technique for domestic wastewater treatment.

The following study confirms the applicability of ceramic membrane bioreactor (CMBR) for urban wastewater, C.-H. Xing et al. [94] used an UF membrane to address wastewater treatment. The UF membrane is composed of a top layer of ZrO_2 and a support made of $\gamma\text{-Al}_2\text{O}_3$. It had a tubular configuration with seven channels that have a diameter of 4.5 mm. Performance of the UF-CMBR was examined with a HRT of 5 h, membrane flux between 75 and $150 \text{ L/m}^2 \text{ h}$, and a sludge retention time (SRT) of 5. The removal efficiency of COD, $\text{NH}_3\text{-N}$, and suspended solid was on the average as high as 97, 96.2, and 100%, respectively. In addition, the bioreactor was found to be responsible for 85% of COD removal, while 12% was due membrane separation.

The study done by Ali Farsi et al. [95] focuses on the treatment of effluents, from a secondary municipal wastewater treatment plant (MWWTP), by mean of different CMs. The wastewater was characterized by a conductivity of $1120 \mu\text{S/cm}$, 2.8 mg/l organic compounds matters and 5 mg/l inorganic N. The efficiency of MF $\alpha\text{-Al}_2\text{O}_3$, TiO_2 -UF membrane (with MF $\alpha\text{-Al}_2\text{O}_3$ support), $\gamma\text{-Al}_2\text{O}_3$ NF membrane (with $\alpha\text{-Al}_2\text{O}_3$ MF a support), TiO_2 -NF membrane (with TiO_2 -UF interlayer and $\alpha\text{-Al}_2\text{O}_3$ MF support), and hybrid silica membrane (with $\gamma\text{-Al}_2\text{O}_3$ NF on a $\alpha\text{-Al}_2\text{O}_3$ MF support) were investigated to assist the membranes ability to remove toxic compounds. The samples from MWW plant were filtered by cross-flow setup at room temperature. The comparative study shows that the NF $\gamma\text{-Al}_2\text{O}_3$ membrane was the most promising membrane, in terms of its selectivity, and flux for wastewater treatment plants. The permeability of the treated MWW effluent ($6.6 \text{ L/m}^2 \text{ h bar}$) by $\gamma\text{-Al}_2\text{O}_3$ NF was lower than deionized water ($12.8 \text{ L/m}^2 \text{ h bar}$). In addition, the NF $\gamma\text{-Al}_2\text{O}_3$ removed the UV254-absorbing components by 75, and 15% of the total ions. During the cross-filtration of the spiked MWWTP effluent (copper concentration was set at approximately $1 \pm 0.1 \text{ mg/l}$). The membrane was able to reject CuCl and CuSO_4 by 40 and

25%, respectively. The treatment by NF γ -alumina membrane was also efficient in reducing the toxicity present in the WWTP effluent with elevated concentrations of toxic ions.

4. Conclusion

The increase in energy costs and the demands of products with high quality, that answers consumer needs, and which are less toxic to the environment are all reasons to apply membrane process in industrial activities and water treatment. Current applications of membrane technologies have shown their high-potential to answer the industrial needs. CMs materials with good thermal and chemical stability, such as Al_2O_3 , would allow their use in different chemical processes, which are not largely explored with membranes process. Knowledge of the chemistry of Al_2O_3 UF and NF membranes elaboration and performance their characteristics were reported. The choice of Al_2O_3 material is due to the different advantages (chemical, physical characteristics) over other mineral materials and mostly over the organic material. Furthermore, the chapter summarizes studies available in treatment by UF and NF Al_2O_3 membranes of wastewater from different industrial activities such as desalination, dyes effluents, discharges from the food industry (namely dietary fats and proteins), oily wastewater effluents, and domestic wastewater. The results obtained by Al_2O_3 -CMs during desalination and water treatment can be explained by membrane dependency on the complexity of the ionic composition of the solution, and the interaction solute-solute and membrane-solute, and the influence of parameters such as the solute hydration radius and its energy. The UF- Al_2O_3 or NF- Al_2O_3 membranes can successfully eliminate the dyes from industrial waste. It can reach 100% of dye elimination and simultaneously contribute to the progress of the textile industrial activity. The use of CMs in the food industry is gradually increasing, however, particular efforts are needed to understand and reduce membrane fouling, which enables the gains in productivity. The experimental results indicate that the Al_2O_3 ceramic UF and NF membranes can be applied to offer a high relative flux and high-oil HC removal efficiency, especially if they are used as secondary treatment. In the other hands, the use of Al_2O_3 -CMs for AnCMBR was found to be effective in COD and DOC removal with rejection exceeded 90%.

Competing interest statement

The authors declare no conflict of interest.

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Nomenclature

COD	chemical oxygen demand
BOD	biological oxygen demand
TDS	total dissolved solids
MF	microfiltration
UF	ultrafiltration
NF	nanofiltration
RO	reverse osmosis
PM	polymeric membranes
CM	ceramic membrane
TiO ₂	titania
SiO ₂	silica
ZrO ₂	zirconia
Al ₂ O ₃	alumina
Al ₂ O ₃ -CM	Al ₂ O ₃ ceramic membranes
ED	electrodialysis
GS	gas separation
α-Al ₂ O ₃	alpha alumina
γ-Al ₂ O ₃	gamma alumina
pHpzc	the point of zero charge
Lp	the membrane hydraulic permeability
R	the membrane rejection
C _p	concentration in the permeate
C _f	concentration in the feed
C _w	concentration at the membrane wall
Ra	the observed solute rejections
TMP	transmembrane pressure
Jv	the volumetric permeate flux
HFNF	γ-Al ₂ O ₃ /α-Al ₂ O ₃ hollow fiber NF composite membranes

PES	polyethersulfone
PAI	γ -Al ₂ O ₃ nanocomposite membranes
MWCO	molecular weight cut-off
NO ₃ ⁻	nitrate
VRF	volume reduction factor
BSA	proteins as bovine serum albumin
HC	hydrocarbons
CFV	cross-flow velocity
MWW	municipal wastewater
N	nitrogen
P	phosphorus
AnMBR	anaerobic membrane bioreactor
AnCMBR	anaerobic ceramic MBR
AnCMBR-ACM	Al ₂ O ₃ -based anaerobic ceramic membrane
AnCMBR-PCM	pyrophyllite-based anaerobic ceramic membrane
DOC	dissolved organic carbon

Author details

Saad Alami Younssi*, Majda Breida and Brahim Achiou

*Address all correspondence to: alamiyounssisaad@yahoo.fr

Laboratory of Materials, Membranes and Environment, Faculty of Sciences and Technologies of Mohammedia, University Hassan II, Casablanca, Morocco

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