CERAMIC MEMBRANES: NEW TRENDS AND PROSPECTS

(SHORT REVIEW)

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Abstract

This review is devoted to the features of the formation and application of ceramic membranes in
water treatment technologies. The structure, composition and geometric configuration of ceramic
membranes were analyzed. A comparison with polymer membranes was made, as a result of which
it was determined that the use of ceramic membranes is safer for the environment and will
contribute to the creation of sustainable water treatment technologies, which can be completely
closed. Despite their widely recognized shortcomings – fragility and cost, the use of ceramic
membranes can pay off quickly due to higher performance and longer service life. Besides, a
promising direction in overcoming these shortcomings is the fabrication of cheap and highly
functional ceramic membranes using nanotechnology, modification of their surface against
biofouling and for disinfection and creation of hybrid membranes. Additionally, the perspective
direction of ceramic membranes creation based on low-cost raw materials and the development of
cheap anisotropic inorganic membranes is outlined. In general, it is noted that membrane
technologies, while eliminating certain shortcomings, will be recognized as a universal and "green"
method of wastewater treatment, which will address a wide range of water treatment issues.

Key words: ceramic membranes; fouling; membrane processes; membrane technology;
wastewater treatment.

Introduction

Long ago membrane technologies have confidently entered the leading position among modern
water treatment technologies due to the possibility of the deep purification degree of water bodies
when using them. In addition, membrane processes are widely used in filtration and separation
processes in chemical (Yalcinkaya 2020 and Samaei 2018), oil (Aani 2020) food (Aani 2020 and More 2012), pharmaceutical (Aani 2020 and Yang 2018), medical (Aani 2020), environmental (Zhu 2016), textile (Silva 2016 and Aani 2020) industries, etc. Non-standard design, compactness, and portability of membrane installations make their use promising in any remote and hard-to-reach places, in various complex projects with non-classical production scheme geometry. Practically minimized use of chemical reagents in membrane cleaning technologies minimizes sludge and demonstrates their high environmental friendliness with a low degree of secondary environmental pollution. At the same time, membrane technologies are commercially viable, durable, and economically feasible for use in various industrial processes compared to other purification and concentration technologies. According to the literature (Nqombolo 2018), the combination of membrane technologies can be successfully used for the effective treatment of various wastewaters of any enterprise. However, membrane fouling and sensitivity to toxicity are still major drawbacks of membrane technologies. From this point of view, ceramic membranes are more desirable, as they are more resistant to contamination, have high permeability, and nanotechnology usage allows to purposefully change their properties in the desired direction (Li 2020). Also, in comparison with polymer membranes, ceramic membranes have many advantages that allow them to be used in specific technological conditions, and, therefore, they do not replace but complement polymer membranes, which also expand the usage range of membrane technologies (Amin 2016). Ceramic membranes have the following advantages: they can be used in the separation of mixtures and solutions at high temperatures; they are stable in chemically and biologically aggressive environments, various solvents; they can easily be given special properties such as catalytic, hydrophobic-hydrophilic and positive-negative surface charge; they retain their properties up to almost 1000 °C; they can be regenerated by sterilization and calcination, and spent inorganic membranes in contrast to the polymer can be regenerated by burning organic sludge that has penetrated their pores (Buekenhoudt 2008, Ciora 2003, Benfer 2004 and Padaki 2015). However, significant disadvantages of inorganic membranes are their high cost and fragility. To overcome such a shortcoming as fragility, in the literature it is proposed to create composite or hybrid membranes based on ceramic materials. The high cost of ceramic membranes (3-5 times higher than polymer) is partially offset by their higher permeability and service life compared to polymer membranes (Cai 2015, Sondhi 2003, Chougui 2019, Fard 2018 and Lin 2018). Given these shortcomings, researchers are looking for ways to improve ceramic membranes properties while reducing their cost. Modern directions of the development of the ceramic membrane are obtaining nanocomposite or hybrid materials with certain porous characteristics, nanotechnologies application in their production, use of nanosized ceramic materials, the addition of various functional additives such as
graphene oxide, metals or photocatalytically active metal oxides (e.g. zinc and titanium oxides), modification of ceramic surfaces to provide certain hydrophilicity/ hydrophobicity or positive/negative charge (Zielińska 2017, Arzani 2018, Malzbender 2016 and Dontsova 2018, 2019).

In this paper, based on modern sources, ceramic membranes, their role in membrane technologies were considered; their structure, composition, and geometric configuration are presented; prospects and progress that can be achieved in the future in the development of ceramic-based membranes were identified.

Water membrane technologies

There are several requirements for industrial water membrane installations. First, they must be easy in the system installation and maintenance, have a minimum pressure drop in the installation, be highly corrosion-resistant, and with a sufficient margin of mechanical strength. Secondly, the membranes must be characterized by a large working surface, and the liquid must be distributed evenly over the membrane elements and have a sufficiently high flow rate (to reduce the concentration polarization). Hence, it is obvious that satisfying all the requirements is quite a difficult task, so in industrial conditions provide optimal conditions for a particular process. In this regard, the organization of membrane technologies has many options, which are based on the use of various membrane elements that differ in structure, composition, and geometric configuration.

The general principle of using membrane processes is to separate the stream, which contains pollutant impurities of different origin and size, into a pure stream of solvent (permiate) and a contaminants precipitate. The process takes place under pressure appropriate to the nature, character, and degree of contamination. Depending on the working pressure, membrane processes are divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO). A brief description of membrane processes is given in Table 1.

MF is a filtration process in which large microorganisms and micron particles are removed. MF is usually used as a pre-treatment before NF or RO. UF is used to remove colloidal and nanoparticles, large molecular substances, and viruses (including bacteria that do not retain by MF). Organic molecules such as dyes and multi charged ions are successfully removed by NF. Reverse osmosis allows the retention of inorganic ions and organic molecules that are not retained by nanofiltration (Merlet 2020 and Erdem 2017).

The choice of the membrane geometric configuration (module) is often a difficult task because the correctly chosen type of membrane depends on whether the required performance and economic efficiency of the whole process will be achieved. Also, it is important to solve a problem in water treatment is the choice of material of the membrane element. As can be seen from Table 1, the
Materials and equipment for water treatment

Materials used to create membranes are quite diverse, but according to the classics are divided into polymer and ceramic membranes. The influence of the material and its structure on membrane processes will be considered in more detail in the next section.

**Table 1.** Characteristics of membrane processes (Amin 2019, Berk 2018, Hutten 2007, Erkan 2018, Qin 2016, Rastogi 2011 and Pal 2017)

| Membrane process   | Pore size [nm] | Working pressure [bar] | Membrane elements                                                                 | Configuration                  |
|--------------------|----------------|------------------------|------------------------------------------------------------------------------------|--------------------------------|
| Microfiltration    | 50–500         | <2                     | Polymers (polycarbonate, cellulose acetate butyrate, cellulose acetate propionate, polyacrylic, nylon; polyamide, polyvinylidene difluoride, polyethylene, polypropylene, polysulfone, polyacrylonitrile); ceramics (Al₂O₃, TiO₂, ZrO₂) | tubular; spiral-wound; hollow fiber; plate-and-frame |
| Ultrafiltration    | 2–50           | 1-10                   | Polymers (polycarbonate, cellulose acetate butyrate, cellulose acetate propionate, polyacrylic, nylon; polyamide, polyvinylidene difluoride, polyethylene, polypropylene, polysulfone, polyacrylonitrile); ceramics (Al₂O₃, TiO₂, ZrO₂) | tubular; spiral-wound; hollow fiber; plate-and-frame |
| Nanofiltration     | 0.6–2          | 5-35                   | Polymers (polycarbonate, cellulose acetate butyrate, cellulose acetate propionate, polyacrylic, nylon; polyamide, polyvinylidene difluoride, polyethersulfone, polyethylene, polypropylene, polysulfone, polyacrylonitrile); ceramics (TiO₂, SiO₂) | tubular; spiral-wound; hollow fiber |
| Reverse osmosis    | 0.3–0.6        | 10-70                  | terminally functionalized polypropylene; polyurethane; cellulose acetate butyrate; cellulose acetate propionate; cuprammonium rayon; polyamide; polyacrylonitrile | tubular; spiral-wound; hollow fiber |

**Types of membranes**

According to the manufacturing material, membrane materials are divided into two classical groups – inorganic and organic. On the other hand, membranes are classified by membrane matrix, in which case there are isotropic and anisotropic (Fig. 1). In addition to the main types, membranes have many subtypes, which indicate their diversity and continuous improvement of their composition and structural organization. This diversity is explained by the simultaneous influence of the material and the matrix of the membrane on its final performance in the separation process (Le 2016).
Fig. 1. Types of membranes by material and matrix.

The type of material (organic or inorganic) determines the separation mechanism, as well as the morphology (structure) of the manufactured membrane. The choice of material is based on: material selectivity and permeability; hydrophobicity and hydrophilicity; chemical resistance; heat resistance; mechanical stability; economic and engineering feasibility (Hors 2011 and Thibault 2017).

Recently, the greatest demand for organic (polymer) membranes, because they have several advantages in practical use. Polymer membranes, various aspects of their synthesis, modification, and use have been thoroughly studied and presented in (Choudhury 2018, Taheran 2016, Mohammad 2015, Liu 2017, Krause 2003, Yoshida 2003, Visakh 2016, Kaldis 2007 and Rynkowska 2018).

Despite the much greater popularity of polymer membranes, inorganic (namely ceramic) membranes have recently become more and more popular due to the possibility of regulating their structure, electrochemical and catalytic properties in a wide range; their high temperature, mechanical and chemical stability in a wide pH range; hydrophilicity and resistance to biofouling, etc. (Oun 2017, Zuriaga-Agusti 2014, Wise 2017 and Li 2020). Due to this, they can be used in more specific areas of water treatment or separation, for example, in production processes that have high temperatures of solutions, and, therefore, the use of ceramic membranes allows not to reduce their temperature before cleaning or separation.

Equally important is the choice of membrane matrix, which directly affects the separation mechanism. Isotropic membranes are homogeneous throughout the volume and are divided into macroporous, nonporous dense films, and electrically charged membranes (Fig. 2 a, b, and c,
respectively). Despite the homogeneity, all three types of membranes have different separation mechanisms. Solutions are filtered through macroporous membranes. When using non-porous film membranes, there is a diffusion mechanism, i.e., the solvent is transported under the action of driving forces (pressure, concentration, or electric field gradients). Electrically charged membranes or ion exchange membranes have negatively or positively charged surfaces. They are made either of non-porous dense films or microporous layers. The transport mechanism in these membranes is controlled by the concentration and charge exclusion.

![Image](https://example.com/image.png)

**Fig. 2.** Types of isotropic (**a**, **b**, **c**) and anisotropic (**d**, **e**) membranes: macroporous (**a**), non-porous dense (**b**), electrically charged (**c**), Loeb-Sourirajan (**d**), composite (**e**).

Anisotropic membranes, as can be seen from Fig. 2, have a heterogeneous morphology in both chemical composition and structure. They are divided into Loeb-Sourirajan membranes (Fig. 2 d) and composite membranes (thin-film, coated films, and self-assembled structures). Loeb-Sourirajan membranes have a homogeneous chemical composition but are heterogeneous in porosity and pore size. Composite membranes (Fig. 2 e) are inhomogeneous for chemical compositions and structures (Lee 2016).

Based on the above, we can conclude that membrane technologies have many varieties, due to variations in type, configuration, material, and matrix, as a result of which it is possible to solve any problem in water purification and water treatment. The most popular in the industry today are polymer membranes, but they have significant disadvantages, such as low mechanical strength, chemical degradation due to hydrolysis and oxidation, temperature limitations, microbial and radiation destruction, which reduces the life of polymer membranes. Ceramic membranes are virtually deprived of these disadvantages, but their significant disadvantage is the fragility, which
limits their geometric configuration (plates, tubes, or multi-channel blocks). To overcome this shortcoming in modern literature it is proposed to create hybrid or nanocomposite membranes based on ceramics, which will be discussed in the following sections. No less important disadvantage of ceramic membranes is their high cost. But the longer service life and reduced cost of replacing ceramic membranes to some extent compensate this shortcoming (Erdem 2017). Besides, the material of ceramic membranes is safe for both products and the environment. Therefore, the use of ceramic membranes is likely to contribute to the creation of "green" membrane water treatment technologies that will be safe, closed, and stable in management.

**Ceramic membranes**

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

Typically, ceramic membranes are a layer of the ceramic material on a base matrix, ie, they have a sandwich structure (Fig. 3), which consists of a supporting layer, a middle layer, and an active layer (also known as a selective layer). The supporting layer is responsible for the membrane mechanical stability, it has a large enough pore size to reduce the resistance to fluid flow and maintain the flow rate throughout the membrane at a given level (He 2019). The intermediate layer serves to regulate the flow and structural transition from the supporting layer with a large pore size to the active membrane layer, which is responsible for the separation process of components and has the smallest pore size. The active layer, which consists of a ceramic material and determines the membrane functional properties (selectivity and degree of components separation), is the most important layer and has a thickness of tens to hundreds of nanometers.

![Fig. 3. Ceramic membrane structure.](image-url)
Consider in more detail the structure and materials of ceramic membranes, their synthesis, and application features.

**Structure**

The morphology, porosity, and pore diameter of the active layer of ceramic membranes are primarily due to the properties of the materials used for synthesis and the technological features of their manufacture. According to the active layer pore size, ceramic water treatment membranes are classified into microfiltration (pore size greater than 50 nm), ultrafiltration (pore size 2-50 nm), and nanofiltration (pore size less than 2 nm) membranes (Erdem 2017).

The creation of certain membranes, which will be characterized by a certain porosity and pore size, is usually possible with the participation of different ceramic materials and is achieved by using certain processing temperature modes of the obtained membranes during drying and calcination (Erdem 2009). There are certain patterns of obtaining the desired porosity. For example, with increasing calcination temperature increases the ceramic material pore size, and, therefore, by varying only the calcination temperature, it is possible to synthesize either micro-, ultra-, or nanomembranes (Das 2016). Also, these modes significantly affect the mechanical properties of the membranes. Besides, the porosity of ceramic membranes can be regulated by adding reagents, the so-called pore formers, which prevent particle agglomeration. Researchers have shown that the starch addition allows obtaining a higher porosity of ceramic materials. The use of pore-forming additives is discussed in more detail in (Yang 2008 and Nishihora 2018). On the other hand, controlling the conditions of the synthesis of the selected membrane can achieve a variety of structures of ceramic membranes. Thus, the synthesis method is often decisive in the creation of a ceramic membrane for baromembrane processes. It should be noted that in addition to the porosity, size, and separation property are also the surface charge, hydrophilicity, and hydrophobicity, etc.

**Materials**

As can be seen from Fig. 4, ceramic membranes are divided into common-type and composite-type. Common-type ceramic membranes include Al₂O₃, ZrO₂, TiO₂, SiO₂, zeolites, etc., or their combinations. Features of ceramic membranes based on oxides of aluminum, zirconium, titanium, and silicon are the ability to create a controlled porous structure of the active membrane layer (Anderson 1988 and Ghouil 2015). α-Al₂O₃ and γ-Al₂O₃ are the main candidates for the creation of ceramic membranes for water and wastewater treatment on their bases (Zou 2017). Due to its lightness, high strength, and thermal stability, alumina can be used for the synthesis of the supporting layer, intermediate layer, and active layer of ceramic membranes. Alumina membranes are produced in different shapes with a wide range of pore sizes and in different modular configurations.
Titanium (IV) oxide and zirconium (IV) oxide are promising ceramic materials due to photocatalytic properties and chemical resistance in various aggressive environments, respectively. Membranes based on them have not gained such popularity in the industry as in the case of alumina-based membranes (He 2019). Silica is the least stable among the above oxides, so its use in ceramic membranes is reduced to the creation of composites based on it and other oxides, mainly such as Al₂O₃ and ZrO₂.

Zeolites are unique in that they have molecular sieving properties that have regulated pore sizes. The use of modern synthesis methods has led to the creation of zeolite membranes, characterized by different morphology, composition, and characteristics of the separation process (Tsapatsis 1999). It should be noted that at the beginning of its history common-type ceramic membranes have not found large-scale industrial applications due to their fragility, as well as the likelihood of microcracks in the synthesis and operation processes. However, the need for thermally and chemically stable membrane materials has led to the active involvement of researchers in the development of methods for obtaining stronger and defect-free ceramic membranes (Otitoju 2020).

To this end, researchers have begun to study actively composite materials which include ceramic materials. The result was the following subspecies composites: ceramic-ceramic composites, nanocomposites with incorporated metal nanoparticles, metal oxides or nanocarbon particles, metal-ceramic membranes, and nanocomposites based on ceramics and polymers.

Ceramic-ceramic composites have better properties than individual ceramic phases. Such mixed oxides, for example, ZrO₂–SiO₂, have greater chemical and mechanical resistance, which allows expanding the scope of inorganic membranes (Agoudjil 2005).

Recently, nanotechnology is increasingly used in the manufacture of membranes for water treatment (He 2019). Typically, nanoparticles are added to the active layer of ceramic membranes by attaching to the surface and/or to the wall of the inner pores. With the inclusion of nanoparticles, the microstructure (particle size, pore size, and porosity) and properties (such as hydrophilicity and stability) of ceramic membranes change, so the addition of certain nanoparticles can purposefully change their structure and properties. The addition of nanoparticles such as silver or TiO₂ can give ceramic membranes new characteristics such as photoactivity and antibacterial properties. The addition of incorporated nanocarbon particles allows manipulating such characteristics as conductivity and mechanical strength.

Due to the unique design of metal-ceramic membranes, they demonstrate high adsorption rates, no defects, stability, and selectivity (Li 2005 and Wang 2016).

Ceramic-polymer membranes are a polymeric active layer formed on a ceramic substrate (or intermediate layer, if any). Compared to polymeric substrates, ceramic substrates can provide high porosity, chemical, thermal and mechanical resistance. Such ceramic-polymer composite
membranes can purify oil from water and can be regenerated (Faibish 2001). Due to this, ceramics-polymer composites are given a lot of attention today.

![Diagram of Ceramic Membrane Types]

**Fig. 4.** Ceramic membrane types.

**Synthesis**

Technologies for producing a porous inorganic ceramic membrane have made significant progress in recent decades. The most popular methods of ceramic membranes fabrication include such methods as extrusion, sol-gel technology, hydrothermal approach, chemical deposition, chemical deposition from the gas phase (CVD), "green" technology, and others. All these methods allow obtaining an active membrane layer with specified characteristics by controlling various parameters during synthesis. Also, most of these methods are used to obtain intermediate and supporting layers. In (Arzani 2018), monolithic membranes for microfiltration made of powdered SiO₂, formed by the extrusion method, were created. Kaolin was chosen as the main source of inorganic membranes component, polyvinyl alcohol was used as a binder substance. It was found that in this case, the temperature regime of drying and calcination of ceramic material is significant, which is directly responsible for its morphological structure (homogeneity, porosity, pore size, no cracks, and holes). The application of this method allowed authors to obtain high-quality ceramic material with the porosity of 49% and the pore size of 1.2 μm.
The sol-gel method in the manufacture of composite membranes is implemented through the formation of fine particles (from 1 nm to 0.1 mm) in a liquid medium (sol) with their subsequent consolidation and agglomeration with moisture loss (formation of a three-dimensional gel), followed by application to the support surface and subsequent heat treatment. It is the sol particles (their size and distribution) that determine the future micro-, ultra- and nano-structures of the membrane layer after calcination. This method allows obtaining homogeneous structures of the applied coatings. Organometallic compounds, alkoxides \((\text{Me(OR)}_n, \text{Me is Zr, Ti, Al, Si, etc., R is an alkyl group})\) and highly soluble inorganic metal salts are used as precursors for sol-gel synthesis (Erdem 2017).

Variation of the precursors' type and additives allows controlling the structure of ceramic materials at the molecular level, which provides the creation membranes with a given porosity and pore range in the appropriate direction. The sol-gel method allows to precisely regulate the chemical composition of membranes and to carry out their modification.

Therefore, the sol-gel method is a convenient and widely used tool for adjusting the dispersion of the obtained particles by controlled process parameters: temperature, pH, nature of precursors, the addition of modifiers, etc. (Erdem 2017, Dontsova 2015, Kutuzova 2017 and Kutuzova 2018).

Obtaining particles of different sizes makes it possible to use a sol-gel method for the synthesis of monolithic membranes and all layers types of anisotropic membranes, ie this method is a tool for a wide range of applications.

Thus, (Bockute 2015) shows the application of the sol-gel method for the manufacture of isotropic ceramic membranes based on \(\text{Al}_2\text{O}_3\) and \(\text{TiO}_2\). In this work, the effect of calcination temperature on the porosity of the obtained ceramic materials was investigated, which also confirmed the previously mentioned increase in pore size with increasing calcination temperature. It is also shown that as a result of using the sol-gel method a homogeneous suspension is formed, which with the correct temperature choice allows obtaining rhombohedral and tetragonal structures of ceramic membrane for \(\text{Al}_2\text{O}_3\) and \(\text{TiO}_2\), respectively.

Another example of sol-gel method application indicates the prospects of obtaining \(\text{MgO}\) nanoparticles on a diatomite substrate, the main component is \(\text{SiO}_2\) (Meng 2016). The obtained membrane was used in the nanofiltration process, as a result of which the degree of tetracycline removal was achieved at the level of 99.7%. The results of energy dispersive spectroscopy (EDS), TEM, and SEM confirm the existence of \(\text{MgO}\) particles in the nano form – 50 nm, which guarantees a large specific surface area of the membrane. Photoelectron spectroscopy (XPS) showed strong adhesion of the nano-\(\text{MgO}\) coating to the substrate through binding to \(\text{Si-O}\), which ensures stable membrane operation.
The controllability of the formation of the nanostructured particles is the most attractive property of the hydrothermal method, which is one of the easiest to use methods for the synthesis of the membranes active layer nanoparticles (Zhang 2017 and Kutuzova 2018). The hydrothermal method allows obtaining particles of different morphology. The authors of (Zhang 2017) obtained an active layer in the form of TiO$_2$ nanorods on the Al$_2$O$_3$ substrate, which showed high photocatalytic activity against methylene blue under ultraviolet irradiation.

There are many examples of nanoparticle synthesis, including TiO$_2$, of different morphology: nanotubes, nanospheres, nanoflowers, etc. (Zhang 2017 and Sviderskyi 2018). Incidentally, researchers are paying more attention to the properties of TiO$_2$ nanorods. They are characterized by high electrical transport characteristics and chemical stability. The low recombination rate of $e^-$ and $h^+$ provides the high photocatalytic activity. Thus, in (Zhang 2017) authors showed 1.9-2.2 times greater photoactivity of TiO$_2$ nanorods in comparison with TiO$_2$ nanospheres and nanowires in the process of methylene blue photodegradation.

Hydrothermal synthesis is promising among other methods in obtaining metal-organic frameworks (MOF) (Qiu 2014). Organometallic frameworks are formed from metal salts (zirconium, zinc, etc.) and organic molecules that act as linkers. Variations in the ratio of organic and inorganic components allow obtaining a kind of metal frame structures with high adsorption properties. Zr-MOF membrane with a specific surface area of 740 m$^2$/g was obtained by the hydrothermal method in (He 2016). It was used in the nanofiltration process to remove fluorine ions, the withdrawal rate of which reached 98%. SEM and TEM images indicate elementary frame Zr-MOF structures with a size of 120 nm, which formed a solid polycrystalline layer with the 20 μm thickness on the substrate surface.

The solvothermal method was also used by researchers in (Liu 2015), resulting in Zr-MOF frameworks on hollow Al$_2$O$_3$ fibers. The membranes showed high efficiency in removing Cr$^{2+}$ (86%), Mg$^{2+}$ (98%), and Al$^{3+}$ (99%) ions over a long period (170 hours). Thus, the above data indicate the prospects of using the hydrothermal/solvothermal method to create active layers and MOF-membranes based on ceramics for use in nanofiltration water treatment processes.

The chemical deposition method is considered a valuable method of "adjusting" the size of the membrane pores in situ and was investigated in (Chen 2018). A multi-channel membrane for nanofiltration with an active TiO$_2$ layer on a ceramic substrate was obtained. Titanium isopropanoxide and isopropanol were used as a precursor and solvent, respectively, resulting in a membrane with an average pore radius of 0.9 nm to 2.3 nm while maintaining a sufficiently high flux of 20 dm$^3$/(m$^2$·h). The total manufacturing time was 46.5 hours, which is less than the duration of the sol-gel method.
Thus, the chemical deposition method in situ has great potential as a technique for "adjusting" the pore size for multi-channel nanofiltration membranes, which can be easily scaled.

The method of "linker crosslinking" by chemical deposition was successfully used to apply a catalytic active layer on a ceramic substrate to create ceramic membranes with different catalytic properties (Sun 2018). Various oxides have catalytic properties: iron-containing materials (α-FeOOH, Fe₃O₄), titanium (IV) oxide, zinc oxide, zirconium (IV) oxide, etc. (Sun 2018, Makarcuk 2017, Kutuzova 2020, Vlasenko 2019 and Vlasenko 2020).

In (Sun 2018), a catalytic active layer based on goethite (a-FeOOH) on a ceramic substrate was obtained by "crosslinking" method at ambient. Zirconium/titanium (Zr/TiO₂) coating on alumina (α-Al₂O₃) was used as a substrate. Using electron microscopy, X-ray diffraction spectroscopy, and infrared Fourier transform spectroscopy, the structure of the surface active layer was characterized as a homogeneous and smooth coating. The active layer with the addition of H₂O₂ and UV irradiation resulted in a high degradation degree for bovine serum albumin (76%) and humic acid (86%). The method "linker crosslinking" proves the possibility of low-temperature active layer deposition, which avoids high-temperature sintering and largely prevents potential changes in the catalyst crystallinity. This, in turn, reduces the process of membrane biofouling due to the passing of photocatalytic reactions by the Fenton mechanism.

Therefore, the chemical deposition method with "linker crosslinking" is important and promising for the manufacture of structures resistant to pollution and materials used for water purification and disinfection.

CVD is successfully used when necessary to obtain a thin layer of active substance (Hubadillah 2019). The advantages of this method in contrast to the above are the use of a small amount of substance to obtain an active layer on the ceramic membrane. This method is mainly used to obtain a thin layer of SiO₂ to hydrophobized the surface. It is also reported that this method is not environmentally friendly due to the formation of hazardous gases during synthesis.

Thanks to their "friendliness" to the environment, "green" technologies are attracting more and more attention. In (Choudhury 2018), the "green" technology using the Catharanthus Roseus leaf extract for the synthesis of ceramic membrane active layer, copper (II) oxide nanoparticles on a macroporous silica-alumina substrate, is proposed. The structural properties of CuO nanocoating were studied using FESEM (Field emission scanning electron microscopy) analysis, which indicates high adhesion of CuO nanoparticles on a silica-alumina substrate, resulting in a homogeneous structure of the active layer without defects. Studies of the porous structure before and after the application of the active layer revealed a decrease in the membrane pore size from 1-1.5 mm to 3.2 nm. The efficiency of the obtained membrane was determined using model...
chromium (VI) solutions, the withdrawal of which was 88%. This is a new and environmentally friendly method of fabricating membranes for wastewater treatment.

Therefore, as can be seen in practice, all methods allow obtaining an active layer of ceramic materials. The variation of process parameters allows to purposefully synthesize membranes with certain porosity and pore size. The choice of method is an important task, which is solved by researchers based on a wide range of initial data.

Application

Ceramic membranes are widely used in harsh conditions, such as cleaning/separation of water bodies at high temperatures and in aggressive chemical environments (various solvents, strongly acidic or alkaline solutions) and in the oily effluents treatment (Goh 2018). But recently, more often ceramic membranes began to be used in the production of drinking water. In this case, ceramic membranes can be used to provide high capacity and to create mobile membrane systems for local use (Staff 2011), among which are popular autonomous and hybrid systems in the water purification process. Such systems are able to remove completely suspended solids, microorganisms, and harmful chemicals. Besides, mobile ceramic membranes in MF/UF systems, which can improve tap water quality, treat local domestic wastewater, and provide safe drinking water in areas with limited water resources (eg camping or hiking), have recently received special attention. The mobility and compactness of membrane systems also make it possible to provide safe drinking water in emergencies or during crises.

The most widespread use of ceramic membranes is observed in the field of micro- and ultrafiltration, but recently there are more and more studies that indicate the high prospects for the use of ceramic nanocomposite membranes for nanofiltration (Wang 2018). It should be noted that materials based on α-Al₂O₃, TiO₂ and ZrO₂ (porosity 40-55%) are usually used for microfiltration, materials based on γ-Al₂O₃, TiO₂ and ZrO₂ (porosity 30-55%) for ultrafiltration, and materials based on SiO₂ and TiO₂ (porosity 30-40%) for nanofiltration (Qin 2015).

Besides drinking water treatment technologies, ceramic membranes have been successfully introduced in the paper industry (wastewater treatment and removal of valuable components), textile industry (wastewater treatment and fractionation), petrochemical industry, food, pharmaceutical and mining industries (Samaei 2018). Membrane technologies with the participation of ceramic membranes in wastewater treatment of the paper industry have demonstrated high reliability and longer performance compared to polymer membranes (Ordóñez 2011 and Mänttäri 2015). The separation of wastewater from the petrochemical industry is successfully carried out when using ceramic MF and UF membranes. In this case, ceramic membranes provide better stability under operating conditions compared to polymer membranes. However, despite the
obvious advantages of membrane technology over other cleaning methods, there are some problems with membrane filtration: accumulation of oil droplets on the membrane surface and membrane fouling (Abdelrasoul).

The food industry consumes a huge amount of water and depending on the processes these effluents can be different, the composition of which is sometimes difficult to predict. Typically, food wastewater contains BOD and COD, nutrients, fats, hormones, surfactants, and so on. Also, antibiotics and pesticides may be present. Therefore, the wastewater of the food industry is a threat to the environment, which must be purified before discharge into the sewer or reuse. The use of ceramic membranes in the wastewater treatment of the food industry has shown that multi-channel tubular membranes are much better than single-channel and are generally an effective treatment method, among which the use of UF ceramic membranes is economically feasible on an industrial scale (Afonso 2004).

Pharmaceutical effluents have become one of the main problems in recent years. Polymeric membranes are mainly used in the pharmaceutical industry, but they are sensitive to aggressive cleaning agents, so they are replaced much more often (Pabby 2015). This causes the growing usage of ceramic membranes in the pharmaceutical industry. Also, ceramic membranes are much easier to clean with aggressive chemicals compared to polymer membranes. When testing ceramic membranes, it was found that it is most appropriate to use a ceramic UF-membrane as part of a hybrid system. In general, according to preliminary estimates, the introduction of new polymer-ceramic composite membranes will be implemented in the future, which will be able to guarantee high selectivity and high tolerance to aggressive conditions (Samaei 2018).

Mine water is the most common issue of water pollution in the mining industry. They are characterized by low pH, high specific conductivity, and high concentrations of heavy metals and other toxic elements (Peppas 2000). Therefore, the use of ceramic membranes for mine water treatment is quite promising due to their chemical, mechanical, and thermal stability under strict operating conditions, which are present in actual mining operations.

**General progress in the ceramic membrane fabrication**

Today the main progress in ceramic membrane fabrication scientists and engineers achieve by varying the technique of manufacturing membranes, the use of nanotechnology, modification and functionalization of ceramic membranes, the creation of hybrid and nanocomposite ceramic membranes.

Innovations in the manufacturing technology of ceramic membranes in the field of membrane geometry (configuration) variation, molding techniques in the obtaining process, and properties such as matrix structure and porosity lead to increased separation efficiency at the lowest cost.
The greatest popularity in scientific literature was given to the use of nanotechnology. A wide range of nanomaterial properties such as adjustable particle and pores size; large specific surface area and the associated active energy state of the surface; light sensitivity; optical and magnetic activity, as well as the ability to catalytic and antimicrobial action provides powerful opportunities for the nanomaterials use in membrane fabrication.

The use of nanotechnology in the process of manufacturing ceramic membranes is primarily associated with the production of membranes for nanofiltration, which allows obtaining homogeneous and clearly sustained nanosized pores (1-2 nm). Such membranes are able to retain pollutants of a certain size, ie with the help of these membranes, it is possible to solve complex and specific problems, for example, to retain ions and molecules of small radii without the use of foreign chemicals and agents. At the same time, NF ceramic membranes have been studied to a lesser extent in comparison with MF and UF membranes, but already showed prospects for their water purification usage (Mohammad 2015).

Another way to apply nanotechnology is the impregnation of ultrafiltration polymer membranes with nanoparticles (silica, TiO$_2$, etc.), which demonstrate improved resistance to biological fouling (Aani 2020). The methods of improvement of the UF membrane based on TiO$_2$ and its transformation into the NF membrane due to nanotechnologies have already been described (He 2019 and Chen 2018). Such an approach allowed to significantly increase the retention degree of organic pollutants in comparison with traditional membranes. Therefore, nanotechnology can significantly change the properties of ceramic materials to eliminate their shortcomings.

It was stated that ceramic-composite NF-membranes from silicon (IV) oxide and zirconium (IV) oxide, which showed high stability in aqueous medium and non-aqueous solvents, were synthesized by sol-gel method (Bockute 2015). The addition of other metals (Co, Ni, Fe) to the silica system allowed to reduce the hydrothermally-induced motion of the SiO$_2$ lattice, increase its hydrostability, obtain the exact pore size in the nanoscale, which allowed to successfully desalinate water.

The authors (Da 2016) synthesized the upper layer of the composite nanofiltration membrane based on yttria-stabilized-zirconia using the sol-gel technique. Such a membrane provided deep desalination of water.

These examples prove that nanotechnology allows to "adjust" the size and distribution of pores for nanofiltration, thereby modeling the membrane porous texture.

The method of atomic layer deposition (ALD) is even more accurate in the formation of the active layer with a given nanoporosity compared to other nanotechnologies. This method also allows applying homogeneous layers of matter with a controlled thickness (less than 1 Å). Thus, in (Zhang 2017) the application of titanium (IV) oxide on a porous ceramic substrate by ALD method...
allowed to narrow the pore size from 0.7 nm to 0.5 nm, and make their distribution more uniform. This provided highly selective retention of molecules and ions.

The use of the ALD method for vacuum deposition of titanium (IV) oxide on a ceramic substrate \( \text{Al}_2\text{O}_3/\text{TiO}_2 \) (Chen 2017) provided the manufacture of NF-membrane with high water permeability and the retention degree of organic matter.

Control of pore size and pore distribution, and accordingly the permeability of the ceramic membrane, was implemented by the number of deposition cycles, and hence the thickness of the application. Thus, the ALD nanotechnology method is a high-precision tool in the process of modeling the texture of ceramic materials to bring micro- and ultra-structures closer to the nano-level (Shang 2017).

Thus, the involvement of nanotechnology in the synthesis of ceramic membrane materials allows creating fundamentally new materials with nanostructured properties that meet the needs of nanofiltration: pore size and porosity, hydrostability, hydrophilicity and permeability of membranes. The use of nanotechnologies in the synthesis of the ceramic membrane opens wide, provided opportunities for the creation of nanostructures by modification with various elements. Moreover, variations in synthesis methods, temperature regimes, pH, pressure, application frequency, combination of precursors, etc. lead to high-tech results in membrane technologies, including the provision of membranes with high photoactivity and antibacterial properties.

Modification or functionalization is a powerful method of varying surface chemistry and its charge. Modification of membranes is most often carried out by particles of \( \text{TiO}_2 \), \( \text{ZnO} \), argentum, and others. Then received modified structures and indicators of membranes pollution at ultrafiltration are investigated (Aani 2020). Studies show that such modification is promising, as water disinfection improves.

The method of grafting (functionalization) of the surface involves fixing organic molecules on the ceramic surface. The process of "growing" (called in the literature "grafting-to") organic polymer chains can occur separately or directly on the surface of the ceramic base (Yoshiba 2003). To achieve precise control of the polymerization degree so-called atom transfer radical polymerization methods are used in the process of growing polymers with low specific molecular weight on the surface of the ceramic material. And the grafting method of such low molecular weight organic molecules on a ceramic surface is called grafting-from. Therefore, the grafting method is modern and promising in achieving the desired results for the purification of solutions containing organic polar and non-polar solvents, and relevant in solving the problems of today's chemical industry.

The purpose of creating nanocomposite materials based on ceramics is to reduce the fragility and cost of ceramic membranes. For this purpose, ceramic-ceramic nanocomposite materials, nanocomposites with incorporated metal nanoparticles, metal oxides or nanocarbon particles, metal-
ceramic membranes, and nanocomposites based on ceramics and polymers are created. All these composites have their prospects when used in membrane technologies, which have much better properties than pure ceramic materials, mainly due to synergistic effects. Thus, a synergistic effect was found in the creation of nanocomposites with the participation of nanoparticles $\gamma$-Al$_2$O$_3$ and TiO$_2$. Such membranes were characterized by increased hydrophilicity, permeability, mechanical properties of membranes, better resistance to dirt in the ultrafiltration process (Aani 2020).

In (Das 2016) a method of composite monolithic membranes production of multicomponent composition (kaolin, feldspar, quartz, boric acid, activated carbon, sodium metasilicate, titanium (II) oxide) for microfiltration is proposed. The authors motivate the presence of a large component number and give each of them a certain functional purpose, which can significantly increase the overall mechanical properties and porosity. The manufacture of composite monolithic ceramic membranes is usually a multi-stage process, which usually consists of three steps: preparation of ceramics; forming a ceramic powder into the desired geometry; heat treatment. The choice of method and conditions for each step depends on the desired membrane configuration, quality, morphology, mechanical and chemical stability, and selectivity of the end membranes. The manufacturing method must also be economical and easy to scale without compromising the final membrane quality.

Other promising studies are related to the production of ceramic membranes from low-cost raw materials, or even from industrial waste (de Oliveira Henriques 2019 and Abdullayev 2019). Such low-cost raw materials include clays, zeolites, apatites, waste (ash), cement, etc. The microstructure, durability, and filtration characteristics of membranes made from low-cost raw materials can be significantly changed by using pore formers, binders, and other additives. The development of appropriate processing technologies, including heat treatment, further regulates the properties of the resulting membranes and affects the overall cost of the system.

Thus, it can be argued that great progress has been made in ceramic membrane fabrication, the development of which is still ongoing.

**Future development**

The demand for membrane technologies in the field of water treatment has recently become widespread around the world, and, consequently, the development of membrane technologies for wastewater treatment of chemical, pharmaceutical, food industry, water desalination will continue (Fard 2018). However, there are still problems with the membrane's efficiency and stability. That is why there is an urgent need to improve existing methods for the synthesis of the membrane adapted to more aggressive environments, which must be chemically inert/stable, selective in separating
nanosized molecules of polar/nonpolar solvents, have high permeability, long life, improved mechanical properties, and maximum low cost.

To achieve such characteristics, scientists are now studying a new generation of membranes – hybrids, which can combine chemical inertness, thermal stability, and mechanical strength of ceramic membranes with low cost and favorable modification of polymer membranes. Ways to create new composite hybrid membranes are divided into three types (Merlet 2020): inorganic (ceramic) material is dispersed on the surface of the polymer membrane with the formation of the mixed matrix membranes; the organic component is introduced directly into the ceramic mixture during gelation; the organic component is immobilized on the ceramic material surface by the formation of covalent or coordination bonds (grafting method).

In the development of the ceramic membrane for MF and UF, research on the resistance to fouling, high temperatures, solvents and solutions with a wide pH range is very important. The priority in the creation of membrane modules is to obtain inexpensive membranes, the design of which will be characterized by low energy consumption.

The development of cheap anisotropic inorganic membranes with high packing density can be considered as a possible solution to most of the problems listed above. In recent years, significant progress has been made in the technology of manufacturing ceramic membranes, which must be skillfully used to obtain membranes of the desired structure and properties. The main objectives of future research in this area should be to improve the density of packaging, manufacturing techniques, and coatings. Besides, future research should focus on the development of membrane models and processes with their participation, which allows to easily "transfer" the experimental results into real large industrial membrane cleaning and separation processes. In the fight against contamination and clogging of membranes with oil droplets, a promising direction is the development and control of surface roughness of the ceramic membrane (Kramer 2020).

Therefore, the future development of ceramic membranes will cover the following aspects: increasing selectivity and stability in nanofiltration processes; development of ceramic membranes with large pore size and high porosity to promote longevity and stability in high temperature separations; adjusting the ceramic membrane surface, expanding the application field by changing the surface hydrophilicity/hydrophobicity, surface charge, etc.; development of inexpensive productions of ceramic membrane and composites on its basis of necessary structure and geometry; obtaining membranes with improved separation efficiency (Xing 2017). In the future, this approach (but this is not a complete list of issues) will further expand the scope of membrane technologies, which will be able to solve various specific scientific and practical problems in water treatment processes.
Also, the use of nanotechnology opens up great opportunities for manipulating the properties and sizes of membrane technologies. Undoubtedly, analyzing the presented literature review shows that it is reasonable to say that in the future membrane technologies will be the universal methods of water treatment, which will also be safe for the environment and contribute to the creation of sustainable water treatment technologies that can be completely closed.

Conclusions

Membrane processes and features of ceramic membranes application were considered, based on which it can be stated that the material, geometric configuration, structure, and matrix significantly affect the properties of membranes, and hence their filtration capacity. The main advantages of ceramic membranes were outlined, which determine the perspective ways of their application. Methods of active layer synthesis, modification, fabrication of ceramic membranes were considered. It was shown that progress in the fabrication of ceramic membranes lies in the field of creating nanocomposite and hybrid membranes based on ceramic materials. It was noted that the modification of ceramic membranes by nanoparticles will allow manipulating their structure and properties. The use of modifiers TiO$_2$, ZnO, Ag, etc. will give ceramic membranes multifunctional properties. Additionally, a promising direction for the creation of ceramic membranes based on low-cost natural raw materials and man-made waste was indicated. Based on modern literature sources the main directions for the future development of ceramic membranes were generalized, among which the most perspective are creation of new composite hybrid membranes and development of cheap anisotropic inorganic membranes. In general, it can be argued that membrane technologies are technologies of the future that are able to create sustainable and "green" water treatment technologies.

Conflict of interests

The authors declare that they have no conflict of interest.

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**KERAMIČHNI MEMBRANI: NOVI TRENDENCIJA TА PERSEPCTIVI (KOROTKIY OGLED)**

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Реферат

Даний огляд присвячений особливостям формування та застосування керамічних мембран в водоочисних технологіях. У даній роботі на підставі сучасних джерел було розглянуто керамічні мембрани, їх роль у мембранних технологіях; представлено їх структуру, склад та геометричну конфігурацію; визначено перспективи та прогрес, що можна досягти у майбутньому, при розвитку мембран на керамічній основі. Проведено порівняння з
полімерними мембраними, в результаті якого визначено, що використання керамічних мембрани є більш безпечним для оточуючого середовища та буде сприяти створенню стійких технологій водоочищення, які можуть бути цілком замкнутими. Розглянуто методи синтезу активного шару, модифікування, фабрикування керамічних мембрани. Зазначено, що модифікація керамічних мембран наночастинками дозволить маніпулювати їх структурою та властивостями. Використання модифікаторів TiO₂, ZnO, Ag тощо дозволить надати керамічним мембранам поліфункціональних властивостей. Незважаючи на широко визнані їх недоліки – крихкість та вартісність, застосування керамічних мембран може швидко окупитись за рахунок більш високих експлуатаційних показників і тривалого терміну служби. До того ж, перспективним напрямком у подоланні цих недоліків є фабрикація дешевих та високо функціональних керамічних мембран з використанням нанотехнологій, модифікації їх поверхні проти біообростання та з метою знезараження та створення гібридних мембран. Додатково креслено перспективний напрямок створення керамічних мембран на основі низьковартісної сировини та розробка дешевих анізотропних неорганічних мембран. В цілому зазначається, що мембранны технології при усуненні певних недоліків будуть визнані універсальним та «зеленим» методом очищення стічних вод, який дозволить вирішувати велике коло питань водопідготовки.

Ключові слова: керамічні мембрани; фоулінг; мембранні процеси; мембранны технологія; очищення стічних вод.