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ANTIBACTERIAL PROPERTIES OF CERAMIC MEMBRANES WITH TiO_2 SELECTIVE LAYER

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Abstract

The use of ceramic membranes is an effective way to reduce microbial contamination of water without chemicals. Ceramic membranes have a longer service life and more environmentally friendly disposal methods. Creating inexpensive ceramic membranes significantly reduces the load on fine filtration installations, which is especially important for the pharmaceutical, biotechnological and food industries. The aim of the work was to manufacture ceramic membranes of asymmetric configuration based on a matrix and a TiO_2-containing selective layer and to investigate the ability of ceramic matrices/membranes to reduce turbidity, chemical oxygen demand and the level of microbial pollution. Two samples of ceramic membrane matrices were synthesized: CM-1 based on aluminium oxide, silicon carbide, borax, ammonium carbonate, and CM-2 based on kaolin, silicon carbide, borax, ammonium bicarbonate and silicon oxide. Various selective coatings were applied to the ceramic matrices by the spin-coating method. To determine and compare the characteristics of the obtained ceramic matrices/membranes, the raw (natural) and purified water were analyzed for the presence of suspended solids (nephelometric method), chemical oxygen demand (photometric method) and the level of microbial contamination (CFU/mL). The antibacterial properties of ceramic membranes were evaluated using the zone of inhibition test, namely the diffusion method in agar. Features of membrane morphology were also studied using scanning electron microscopy. It was determined that the turbidity, chemical oxygen consumption and microbial contamination of the treated water after filtration were reduced. The CM-1.10 ceramic membrane with TiO_2 selective layer showed greater efficiency in reducing suspended solids contaned and microbiological pollution indicators. The prospect of using ceramic matrices and ceramic membranes with TiO_2 selective layer for natural water purification to eliminate bacterial contamination and contamination with organic substances and improve the organoleptic qualities of water has been confirmed.

Keywords: ceramic matrix; membrane; selective layer; bacterial contamination; antibacterial properties; titanium(IV) oxide.

АНТИБАКТЕРІАЛЬНІ ВЛАСТИВОСТІ КЕРАМІЧНИХ МЕМБРАН З СЕЛЕКТИВНИМ ШАРОМ НА ОСНОВІ TiO_2

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Анотація

Використання керамічних мембран є ефективним способом зменшення мікробного забруднення води без застосування хімічних речовин. Керамічні мембрани мають помітно довший термін служби та більш екологічні методи утилізації порівняно з полімерними. Створення низьковартісних керамічних мембран значно зменшує навантаження на установки тонкої фільтрації. Метою роботи було виготовлення керамічних мембран асиметричної конфігурації на основі матриці та TiO_2-вмісного селективного шару й дослідження здатності керамічних матриць/мембран зменшувати каламутність, хімічне споживання кисню та рівень мікробного забруднення води. Синтезовані два зразки керамічних мембранних матриць: КМ-1 – на основі алюміній оксиду, силіцій (IV) карбіду, бури, амонію карбонату; та КМ-2 – на основі каоліну, силіцій (IV) карбіду, бури, амонію бікарбонату та силіцій (IV) оксиду. На них методом спін-коатингу наносили селективні шари різного складу. Для визначення та порівняння характеристик отриманих керамічних матриць/мембран вихідну природну та очищену воду аналізували на наявність завислих речовин, хімічне споживання кисню та рівень мікробного забруднення (КУО/мл). Антибактеріальні властивості керамічних мембран оцінювали за допомогою тесту зони інгібуванняі. Особливості морфології керамічних мембран вивчали за допомогою скануючої електронної мікроскопії. Встановлено, що каламутність, хімічне споживання кисню та мікробне забруднення очищеної води після фільтрації через мембрани зменшуються. Керамічна мембрана СМ-1.10 з селективним шаром на основі TiO_2 показала найбільшу ефективність у зниженні вмісту завислих речовин та показників мікробіологічного забруднення води.

Ключові слова: керамічна матриця; мембрана; селективний шар; бактеріальне забруднення; антибактеріальні властивості; титан(IV) оксид.

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Introduction

The use of ceramic membranes in water and wastewater treatment technologies is increasing every year. The advantages of ceramic membranes, including their chemical/thermal/ mechanical stability, good corrosion resistance, high porosity, low susceptibility to fouling, high hydrophilicity, distinct pore size distribution, high permeability at low pressures, and long service life, make them attractive. The market for ceramic membranes achieved compound annual growth rate of 11.2 %, in particular, it showed growth of about 8.9 % in 2023 [1; 2]. Wastewater treatment is the largest industry that defines the importance of ceramic membranes because they can be integrated into technological schemes along with advanced water treatment processes that cannot be applied in the case of polymer membranes due to their sensitivity to oxidizing agents, for example – in the ozonation process. In addition, hybrid-ceramic membrane systems, such as the ceramic membrane bioreactor, outperform polymer counterparts due to higher flux, more efficient pollutant removal, and less membrane fouling [3].

It is known that ceramic membranes are also resistant to the presence of bacteria, which cause the degradation of polymer membranes [4]. Such properties of ceramic materials make them unique for removing bacterial contamination in water. Effective removal of a number of pollutants, such as suspended solids and pathogens by membranes, can be achieved due to the regulation of membrane pore sizes, pollutants adsorption on the membrane, and electrostatic repulsion of pollutants from the membrane charged surface [6]. Such properties of ceramic materials make them unique for removing bacterial contamination in water. The ability to adjust the properties of ceramic membranes also allows them to be regenerated after use, that is, to remove contaminants such as suspended solids and microorganisms before reuse.

Using ceramic membranes with kaolin, limestone and bentonite in different ratios was studied [5]. Membranes were tested while detaining both Escherichia coli and Staphylococcus aureus. Limestone served as a pore former; membranes containing up to 7% limestone showed complete rejection of both bacteria. The study [1] describes the method of manufacturing ceramic membranes using Egyptian raw materials: Aswan ball clay, Aswan kaolin, and a mixture of potassium feldspar and quartz. The ceramic membranes produced were low-cost and used for water and wastewater treatment. The membranes were heat treated at 900 °C. Membrane samples showed good turbidity removal efficiency and a significant decrease in the bacterial load in water from 70 to 14 CFU/100 mL, which indicates the feasibility of using such membranes for antibacterial microfiltration. Scientists from Luxembourg synthesized [6] and tested ceramic membranes based on a mixture of clay and ash in different ratios. Ceramic membranes were produced by sintering at a temperature of 700 °C. This study aimed to remove *E. coli bacteria* from municipal water. Experimental results showed that the membrane with the following composition showed the best characteristics: clay (40 %) + ash (60 %). The pore size of this membrane was from 1.6 to 2.0 µm, which allowed to retain up to 99 % of *E. coli* at an operating pressure of 0.25 bar. A group of scientists conducted research [7] on the purification of river water using a ceramic membrane based on ash clay sintered at 950 °C. Studies have shown that this membrane at an operating pressure of 0.75 bar can retain Pb, Fe, and *E. coli* by 96.59 %, 95.55 %, and 99.29 %, respectively.

The article by Mohit Kumar C and co-authors [8] describes the preparation of ceramic membranes using inexpensive precursors (Chinese clay, quartz, calcium carbonate) at different temperatures (900–1100 °C). Membranes were studied in the microfiltration process by removing bacteria and polyethylene glycol (PEG) from the aqueous medium. The membrane, which was burned at a temperature of 900 °C, provided 90.24 % retention of bacteria and 40 % retention of PEG. The paper also focuses on the problem of membrane cleaning. Cleaning from biofouling using simultaneous chemical and ultrasonic treatment showed effectiveness, and alkaline treatment together with distilled water effectively cleaned the membranes from PEG.

It should be noted that ceramic membranes' chemical and thermal stability greatly facilitates the cleaning and regeneration process of membranes due to their much lower sensitivity to aggressive chemicals, particularly oxidants [9]. If necessary, acids (HCl, HNO_3 and H_2SO_4), alkalis (NaOH), chelating agents (Ethylenediamine-tetraacetic acid – EDTA), surfactants (SDS) and their combinations are used. Ceramic membranes can easily withstand cleaning even with such aggressive reagents as NaClO and O_3.

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Another advantage of ceramic membranes compared to polymer membranes is the possibility of using natural raw materials from agricultural production for their manufacture. Such ceramic membranes have shown their effectiveness in simplicity, cheapness and environmental friendliness. Thus, ceramic membranes made of kaolinite clay (75 %), coconut shell (15 %) and eggshell (10 %) were developed and investigated in [10] in the process of removing *E. coli* bacteria from the water environment. Membranes were subjected to heat treatment at different heating rates. As a result of work using a synthesized membrane, which was sintered at the highest speed up to 1000 °C, it was possible to achieve 100 % retention of *E. coli*. The water permeability of such a membrane was the highest, and no biological contamination was detected on it. The membrane pore diameter was 0.060 nm, and the porosity was 31%.

Recently, various modifications have been used to improve the filtering properties of ceramic filters to eliminate pollutants of various origins. For example, applying an additional coating to the membrane with substances that have antimicrobial properties: compounds of silver, zinc, copper, titanium, and organic compounds [11; 12].

A study [13] used a low-cost porous ceramic membrane made of clay and rice husk and modified with Fe/TiO_2 nanocomposites to remove *E. coli* from water. Due to the presence of nano-TiO_2 and Fe^{2+}, a double synergistic bactericidal effect on *E. coli* removal is provided. It was shown that the ceramic membrane coated with Fe/TiO_2 nanocomposites can retain bacteria up to 97 % at an initial concentration of 105 CFU/cm^3 (colony-forming unit/mL) and simultaneously inhibit their growth. Previous research results also indicate 90 % removal of *E. coli* by unmodified ceramic membranes due to the smaller pore size compared to the size of the bacteria. The results of such research can help find a cost-effective and safe solution to drinking water problems.

According to laboratory research [14], water purification processes using a bioreactor with an installed inexpensive ceramic membrane showed promising results. The ceramic membrane was made of clay, potato starch, calcium carbonate, almond shell, chamotte and selective layer of titanium (IV) oxide. The membrane with thin TiO_2 film also demonstrated high fouling resistance and good retention capacity for *E. coli*, *Cryptosporidium* cysts, and *Giardia* cysts.

This study [15] investigated the reduction of *E. coli* using ceramic filters containing rice husk (29.03 %) and decorated with nano-TiO_2 (mass fraction of nano-TiO_2 – 2.21 %). Deactivation and bacteria removal were carried out using UV irradiation on a ceramic membrane. The results are essential for finding a safe and cost-effective approach to solving drinking water problems in developing countries. Thus, the use of natural materials as the main components of matrices and selective layers based on TiO_2 raises many questions and remains a relevant topic for research [16; 17].

Some physicochemical processes, such as coagulation and UV irradiation, can be easily integrated into ceramic membrane systems, such as bioreactors, to improve the removal of organic compounds, suspended solids and color from anaerobically treated dairy wastewater [18]. It was established that due to the adsorption of organic matter on the membrane, the chemical oxygen demand (COD) decreases by 3–18 %. Colour removal was 96–98 % for all tested membranes, and almost all total suspended solids (TSS) were removed.

It should be noted that using membrane technologies to remove various pollutants from water significantly reduces the need for chemicals. Ceramic membranes, especially those made from inexpensive natural materials and industrial waste, are widely used in various industries for water and wastewater treatment. Compared to conventional filtration processes, separation processes based on membrane technologies are compact, reliable, provide high-quality purification, and can realize many environmental applications [19; 20]. An interesting idea is the application of the modern trend of developing 3D-printed ceramic membranes, which has attracted the attention of researchers due to its high versatility [21].

It is known that the use of ceramic membranes in full-scale water purification technologies is still limited due to the high cost of their production. [22]. However, the successful use of ceramic membranes in bacteria removal processes during the microfiltration of food products, particularly dairy products [23] or filtration of fermentation broths in the biotechnology and pharmaceuticals industry [24], has been demonstrated.

It is known that the use of ceramic membranes in full-scale water treatment technologies is still limited due to the high capital costs of their manufacture. But, although the production of ceramic membranes is associated with significant

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capital costs, the life cycle cost of ceramic membranes is less. Moreover, chemicals and backwash are reduced when ceramic membranes are implemented in water treatment technology. For example, Sunkist Growers, a leader in the citrus juice industry, uses Membralox ceramic membrane purchased from GEA Filtration in 1994 at its Tipton, California processing plant [4].

Natural materials such as pyrophyllite, kaolin, natural zeolites, clay materials and various industrial and agricultural wastes (animal bones, fly ash waste, glass waste, corn starch, eggshell) are used to reduce the capital costs of the ceramic membrane production process [19; 25–28]. An important economic advantage of using natural clays is that they require lower sintering temperatures than metal oxide materials such as alumina, silica, and zirconium (IV) oxide. The sintering temperature of aluminium and zirconium oxides, as materials for the synthesis of ceramic membranes, requires a temperature of more than 1100 °C, compared to natural clay, which is sintered in the range of 800 to 900 °C. In this way, it is possible to reduce capital costs for the manufacture of ceramic membranes significantly. Additionally, it's worth mentioning that current recycling programs for ceramic membranes present various methods for repurposing them into new components or other construction-related products. In this way, it is possible to reduce disposal costs, as well as to overcome environmentally threatening challenges associated with the existence of membrane waste landfills [4].

Silicon carbide (SiC), which is one of the few natural hydrophilic membrane materials, is also gaining popularity. It effectively passes water, in contrast to organic compounds, which allows us to assert its promise in water purification processes [29]. At the same time, SiC is a compound with a strong covalent bond, which makes it an excellent means of reinforcing the membrane. However, the sintering temperature of SiC ceramics is quite high, which makes the process of manufacturing membranes expensive and prevents their mass production. At the same time, the addition of some additives (borax, liquid glass, etc.) to the original ceramic mixture, which have a lower melting point, allows you to significantly lower the sintering temperature and make the production process of ceramic membranes more cost-effective. Thus, the use of silicon carbide can provide both high strength and good permeability of aqueous solutions [30].

Thus, compared to other separation processes, processes based on the use of ceramic filters have many advantages: they are reliable, environmentally friendly, and provide high-quality cleaning. Therefore, using ceramic membranes to remove various substances, especially microorganisms, from water for its purification and disinfection holds considerable promise. Nevertheless, developing new, cheaper ceramic filters and identifying coatings that offer enhanced filtering and antimicrobial features, among other improvements, continues to be necessary.

This study aimed to investigate the ability of ceramic matrices without a selective layer and with a selective layer based on TiO_2 to reduce the values of the following indicators of natural water: turbidity, chemical oxygen demand, and the level of microbial contamination.

Experimental part

Preparation of ceramic matrices. The following components were chosen for the synthesis of ceramic matrices: kaolin ($Al_2O_3·2SiO_2·2H_2O$, Hlukhovetske`s deposit, Vinnytsia region), silicon carbide (SiC), aluminium oxide (Al_2O_3), ammonium carbonate $(NH_4)_2CO_3$), ammonium bicarbonate (NH_4HCO_3), silicon oxide (SiO_2) and borax ($Na_2B_4O_7$). The choice of such components is based on the following known facts: kaolin is a clay material that has significant deposits throughout Europe, including in Ukraine, and has great prospects for use in the production of ceramic membranes; the use of silicon carbide allows obtaining sufficiently strong ceramic membranes; aluminum oxide is added as a traditional component for the synthesis of ceramic membranes; borax is an agent for improving the mechanical charac-teristics of samples after sintering; ammonium carbonate and bicarbonate were used to form pores due to their thermal decomposition with the release of carbon dioxide [31].

Ceramic matrix 1 (CM-1). The dry components of the mixture for the manufacture of the ceramic matrix (aluminium oxide (Al_2O_3), silicon carbide (SiC), borax ($Na_2B_4O_7$), ammonium carbonate ($(NH_4)_2CO_3$) were thoroughly ground in an agate mortar until a uniform consistency. Then, the calculated masses of all components of the mixture were weighed on an analytical balance and mixed in one container. After that, a 10 % starch solution was added to the crushed mixture, calculated so that the mass content of starch in the mixture was 10 %. Next, the mixture was thoroughly mixed with starch, after which 0.5 mL of liquid glass was added.

Ceramic matrix 2 (CM-2). Dry powdery components of a mixture of kaolin, silicon carbide (SiC), borax ($Na_2B_4O_7$), ammonium bicarbonate (NH_4HCO_3) and silicon oxide (SiO_2) after careful grinding in an agate mortar to uniformity were weighed on an analytical balance according to the calculated mass of each component and mixed in one container. After that, a 10 % starch solution was added to the crushed mixture, so that the mass content of starch in the mixture was 10 %. Next, the mixture was thoroughly mixed with starch, after which 2 drops of liquid glass were added.

Method for creating ceramic membranes. The method of uniaxial pressing was used to form samples of ceramic matrixes. The powders of the ceramic matrix ingredients were thoroughly ground in an agate mortar, weighed on an analytical balance and thoroughly mixed until homogenous. The resulting mixture was placed in a mould and uniaxially pressed with a load equivalent to 8 tons. As a result, a flat matrix with diameter of 46 mm and a thickness of 3 mm was obtained. The received pressed ceramic matrix was sintered with a gradual temperature increase of 1 °/min to 95 °C with isothermal holding time of 30 min, at rate of 3 °/min to 350 °C and rate of 2 °/min to 950 °C with further holding at this temperature for 60 min.

The obtained matrices CM-1 and CM-2 were checked for flexural strength [32] and porosity [33].

Method of forming TiO_2 selective layer on the ceramic matrix surface. Two types of solutions were used to obtain a selective layer. The first solution (solution 1) was prepared by sequentially mixing diethanolamine ($C_4H_{11}NO_2$), titanium isopropoxide ($Ti(OC_3H_7)_4$), distilled water and glycerin ($C_3H_8O_3$) in the following volume ratios: 2 : 1.5 : 1.5 : 1. The "spin-coating" method was used to form a selective layer on the surface of the ceramic matrix, for which the prepared solution (solution 1 or solution 2) was applied dropwise to the matrix during its rotation (from 100 to 1000 rpm), 1 mL of solution was used to apply one selective layer. Next, the membrane samples were dried at 100 °C for 1 hour, and the next selective layer was applied according to a similar procedure. After applying the appropriate number of selective layers, the membrane samples were sintered at 500 °C for 1 hour. The selection of the sintering temperature of the selective layer is based on the following literature sources [34–36].

Determination of membrane permeability. After heat treatment, the membranes were checked for permeability on a special filter laboratory unit (Fig. 1). First, the membranes were placed in container with distilled water and subjected to ultrasonic treatment for 300 s, after which the membrane was placed in a Petri dish and dried in an oven for 30 min at 80 °C. Later, a similar membrane-washing procedure was carried out in an ethyl alcohol solution (70 %). The membrane dried after washing in alcohol was installed in a filter unit, distilled or natural water was passed through the membrane under pressure, and the volume of water that passed through the membrane in 1 minute was measured.

Determination of antibacterial properties of ceramic membranes – «Zone of Inhibition Test». The antibacterial properties of ceramic membranes were evaluated using the zone of inhibition test, namely the diffusion method in agar [24; 37]. The following cultures were used as test microorganisms from Danylo Zabolotny Institute of Microbiology and Virology of National Academy of Science of Ukraine: gram-negative bacteria *Escherichia coli* (UKM B-906), gram-positive bacteria *Bacillus subtilis* (UCM B-506T), and pathogenic fungi *Candida albicans* (шифр штаму). Before the study, the test strains *E. coli, B. subtilis* and *C. albicans* were cultured in a meat-peptone broth for 6 hours at 37 °C. The resulting suspensions were diluted with water to an optical density of 0.5 on the McFarland standard scale, which is equivalent to $1.5 \cdot 10^8$ colony-forming units (CFU) per mL. Standardized suspensions were inoculated onto sterile nutrient agar in Petri dishes using a swab. Then, ceramic membranes were placed on the agar surface. Petri dishes were incubated at 37 °C for 24 hours. An indicator of antibacterial activity was the presence of a zone of no growth of the test culture around the ceramic membrane.

Determination of microbial contamination of water samples. The colony-forming unit and coliform index determined microbial contamination in water/suspension samples. Colony-forming unit (CFU) – the number of microorganisms in 1 mL of liquid. Coliform index – the number of coliform bacteria in 1 L of liquid. Water was analysed before filtration and in the filtrates. Liquid/suspension samples were collected in sterile plastic containers with a volume of 100 mL. Determination of the CFU and coliform bacteria was carried out by the method

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of surface sowing of liquids on meat-peptone nutrient agar (MPA) and Endo agar respectively, with previous serial dilutions (100 and 1000 times) in aseptic conditions. Inoculation of each dilution of each sample on the surface of nutrient agar and Endo agar was carried out in triplicate. Incubation was carried out in thermostats at (37 ± 1) °C for (24 ± 2) hours and then moved to (28 ± 1) °C, where they were incubated for another (48 ± 2) hours. After incubation, the number of microorganism colonies was counted, the dilution was taken into account, and the arithmetic mean value of the number of colonies in the samples was determined [38].

Determination of the turbidity of water samples by the nephelometric method. The method of determining water turbidity consisted of measuring the intensity of light scattered at an angle of 90° by particles weighed in a water sample using the "Fluorat-02-3m" liquid analyzer. A state standard sample with a turbidity of 4000 FTU (formazin polymer turbidity units per liter) was used as a standard to determine turbidity [39].

Determination of the chemical oxygen demand (COD) in water samples by the photometric method. Determination of COD was carried out by treating a water sample with sulfuric acid (H_2SO_4, conc.) and potassium dichromate ($K_2Cr_2O_7$, $C(1/6K_2Cr_2O_7)$ = 0.05 mol/L) at 150 ± 5 °C, in the presence of a catalyst – argentum sulfate (Ag_2SO_4) and the addition of hydrargyrum sulfate ($HgSO_4$), which reduces the effect of chlorides [40]. Aliquots of water samples were placed in vials, and a prepared solution of potassium dichromate with a solution of argentum sulfate in sulfuric acid was added to them in a volume ratio of 1 : 1. The vials were placed in a thermoreactor and kept at 150 °C for 2 hours. After cooling, solution samples were poured from the vials into cuvettes, and the optical density of the samples was determined in the wavelength range from 340 to 380 nm using the "Fluorat-02-3m" liquid analyzer [41].

Scanning electron microscopy study of the matrix samples morphology. The morphology of the obtained matrix samples was studied by scanning electron microscopy (SEM) using a Tescan Vega 3 LMU electron microscope (Czech Republic).

Method of assessment of change in the quantity of pollutants in water. The natural and purified water were analyzed for suspended solids (turbidity), chemical oxygen demand (COD) and microbial contamination (CFU/mL) according to the above methods. The results were evaluated by the degree of change (X) in turbidity, organic substances capable of chemical oxidation, and the level of microbial contamination according to the formula:

$$X = \frac{A_0 - A_k}{A_0} \cdot 100\%, \quad (1)$$

where A_0 and A_k are the initial and resulting certain optical characteristics of the solution obtained by measurement using liquid analyzer.

Methods of statistical analysis of the obtained results were used in the work. Namely, dilution was considered when the CFU and coliform bacteria were determined, and the average arithmetic value of the number of colonies in the samples was determined.

Results and their discussion

Study of selective characteristics of ceramic matrices. Membranes were manufactured according to the methodology described in the Preparation of ceramic matrices section. The percentage content (wt. %) of each of the main components of ceramic matrices is shown in Table 1.

Table 1

Composition of ceramic matrices, wt.%

	SiC, %	Al_2O_3, %	$Na_2B_4O_7$, %	$(NH_4)_2CO_3$, %	SiO_2, %	Kaolin, %	NH_4HCO_3, %
CM-1	55	25	10	10	-	-	-
CM-2	20	-	5	-	10	40	25

The flexural strength and porosity of the obtained ceramic matrices were determined [32; 33]: CM-1 – 46.8 MPa and та 49 %; CM-2 – 10.5 MPa and 64 %, respectively.

Water as an object of purification was taken from natural reservoirs of the city of Kyiv (sample № 1 and sample № 2). Table 2 shows the main characteristics of the raw (natural) water, according to which the quality of its treatment was evaluated, namely, turbidity (Nephelometric Turbidity Unit – NTU), COD (%) and microbial contamination (CFU/mL). Each indicator's first and second values correspond to water samples taken on different days, namely, 03/10/2023 and 17/10/2023.

The natural water was passed through a matrix (ceramic matrices CM-1 and CM-2) installed on a laboratory setup (Fig. 1).

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Table 2

Characteristics of samples of natural water

Date	Sample of natural water № 1			Sample of natural water № 2		
	Turbidity, NTU	COD, %	CFU/mL	Turbidity, NTU	COD, X %	CFU/mL
03/10/2023	11.54	125.4	$1.7{\cdot}10^4$	40.72	134.10	$2,.3{\cdot}10^4$
17/10/2023	19.96	174.63	$2.4{\cdot}10^4$	22.16	142.75	$4.4{\cdot}10^4$

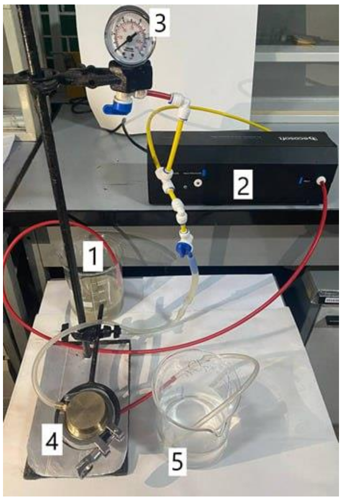


Fig. 1. Laboratory setup for determining the permeability of a ceramic membrane: a glass vessel with a capacity of 1 L for initial water (1), reverse osmosis pump (2), manometer for measuring pressure in the system (3), filter cell (4), a glass vessel with a capacity of 1 L for filtered water (5)

The results of removal degree studies and COD indicators in filtering water samples on ceramic matrices are shown in Table 3.

Table 3

The removal degree of turbidity and COD reducing of natural water samples, X %

Sample of natural water № 1			Sample of natural water № 2		
Sample	Turbidity, X %	COD, X %	Sample	Turbidity, X %	COD, X %
CM-1	10.05	55.15	CM-1	18.22	12.60
CM-2	0	9.09	CM-2	0	6.60

The results of the studies of change in the indicator of microbial contamination in the process of filtering water samples on ceramic matrices are shown in Table 4.

Table 4

The removal degree of microbial contamination of natural water samples, X %

Sample of natural water № 1		Sample of natural water № 2	
CFU/mL, X %		CFU/mL, X %	
CM-1	88.23	CM-1	39.13
CM-2	7.00	CM-2	8.70

The membrane permeability of CM-1 and CM-2 ceramic matrices was 310 mL/min and 675 mL/min, respectively.

Study of selective characteristics of ceramic matrices with applied TiO_2 layers. Since the CM-1 matrix showed a better reduction of all types of investigated pollutants in water after filtration, it was chosen as a matrix for creating membranes with applied selective layers. The raw water was passed through the membranes made by applying solution 1 to the CM-1 matrix, using 6 layers (CM-1.6) and 10 layers (CM-1.10), respectively. Raw and treated water were analyzed for suspended solids (turbidity), COD and microbial contamination (CFU/mL) according to the above methods. The results were evaluated by changes in turbidity indicators, changes in the amount of organic substances capable of chemical oxidation, and the level of microbial contamination according to formula 1.

The results of studies of changes in turbidity and COD indicators in water filtration on ceramic matrices with applied selective layers are presented in Table 5.

Table 5

The removal degree of turbidity and COD reducing of natural water samples, X %

Sample of natural water № 1			Sample of natural water № 2		
Sample	Turbidity, X %	COD, X %	Sample	Turbidity, X %	COD, X %
CM-1.6	6.11	8.10	CM-1.6	31.00	26.00
CM-1.10	21.44	12.80	CM-1.10	66.90	45.43

The study results of changes in the level of microbial contamination in the process of filtering water on ceramic matrices with applied selective layers are shown in Table 6.

Table 6

The removal degree of microbial contamination of natural water samples, X %

Sample of natural water № 1		Sample of natural water № 2	
CFU/mL, X %		CFU/mL, X %	
CM-1.6	0	CM-1.6	37.50
CM-1.10	20.45	CM-2.10	58.33

Tables 7 and 8 compare the characteristics of purified water after filtration through matrices and membranes.

Table 7

The removal degree of turbidity and COD reducing in natural water samples after filtration on ceramic matrices and membranes, X %

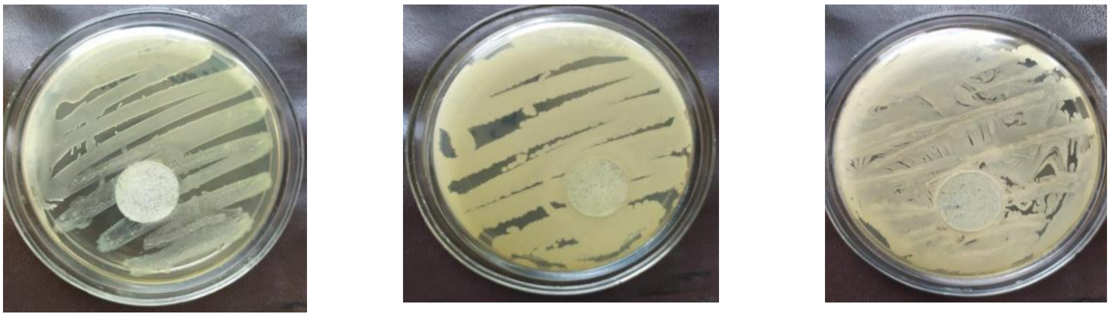
Sample of natural water № 1			Sample of natural water№ 2		
Sample	Turbidity, X. %	COD, X %	Sample	Turbidity, X %	COD, X %
CM-1	10.05	55.15	CM-1	18.22	12.6
CM-1.6	6.11	8.10	CM-1.6	31.00	26.00
CM-1.10	21.44	12.80	CM-1.10	66.90	45.43

Table 8

The removal degree of microbial contamination of natural water samples after filtering on ceramic matrices and membranes, X %

Sample of natural water № 1		Sample of natural water № 2	
CFU/mL, X %		CFU/mL, X %	
CM-1	88.23	CM-1	39.13
CM-1.6	0	CM-1.6	37.50
CM-1.10	20.45	CM-2.10	58.33

Antibacterial activity of ceramic membranes. The antibacterial properties of the CM-1 ceramic matrix without an selective layer and with a TiO_2 selective layer (CM-1.10) were investigated. Determination of the antibacterial activity of the CM-1 did not reveal an antimicrobial effect on the test cultures (Fig. 2).



Escherichia coli ***Bacillus subtilis*** ***Candida albicans***

Fig. 2. Determination of antibacterial action of ceramic matrix (CM-1 sample) against *E. coli, B. subtilis* and *C. albicans* after 24 h of incubation

On the other hand, samples of CM-1.10 ceramic membrane with TiO_2 layer on the surface show inhibition of *E. coli* growth and no growth inhibition of *B. subtilis* and *C. albicans* test cultures (Fig. 3).

Escherichia coli ***Bacillus subtilis*** ***Candida albicans***

Fig. 3. Determination of antibacterial action of ceramic membranes with TiO_2 selective layer (CM-1.10 sample) against *E. coli, B. subtilis* and *C. albicans* after 24 h of incubation

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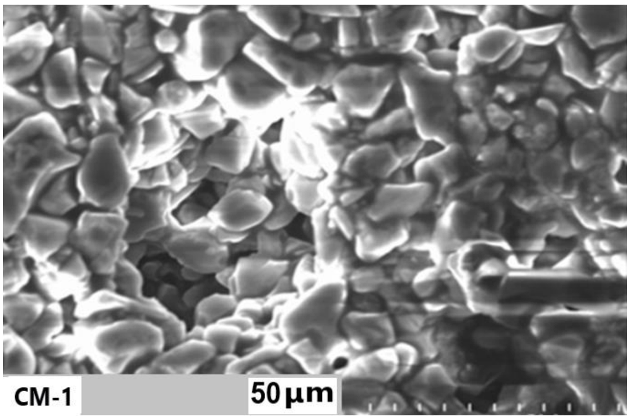
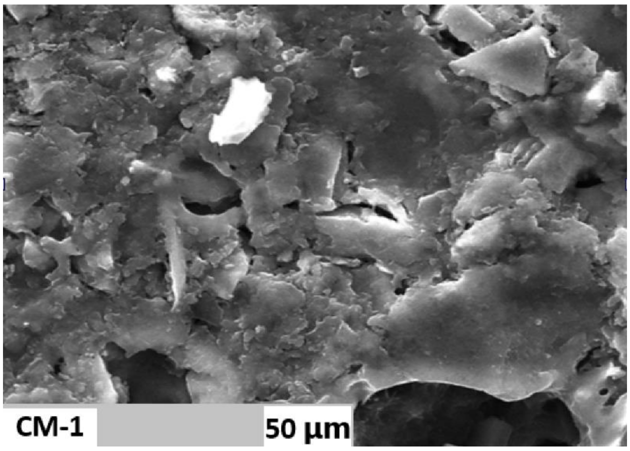
The obtained results indicate that the antibacterial properties of ceramic membranes are exhibited with the appearance of TiO_2 on their surface. The obtained data on the antibacterial effect of TiO_2 are consistent with the results of other authors [42]. Thus, ceramic membranes with a TiO_2 selective layer show antibacterial activity against *E.coli* bacteria, which is an additional factor for increasing the antibacterial effect of filters when purifying water from microbial contamination.

Study of the morphology of matrix samples. SEM images of the studied samples of CM-1 and CM-2 matrices are presented in Figure 4. The figure shows that the morphology of the samples is significantly different. A granular structure characterizes the CM-1 matrix and consists of small particles of arbitrary shape of almost the same size. The CM-2 matrix has a dense structure, characteristic of clay materials, and contains large macroporous channels. Using the GIMP graphic editor, the estimated average pore size of the matrices was determined, which is for samples CM-1 – 20 μm and CM-2 – 170 μm.

The morphological structure of the CM-1 and CM-2 matrix revealed by scanning microscopy is consistent with the established transport properties. It explains the difference in the determined permeability of the CM-1 and CM-2 samples – 310 mL/min and 675 mL/min, respectively.



a



b

Fig. 4. SEM images of matrix samples: CM-1 (a); CM-2 (b)

According to the data in Table 3, it should be noted that the CM-1 ceramic matrix shows much better selective properties in terms of reducing the turbidity and COD (10.05 % and 55.15 % (CM-1) respectively compared to 0 % and 9.09 % (CM-2) for water sample № 1 and 18.22 % and 12.60 % (CM-1) respectively compared to 0 % and 6.60 % (CM-2) for water sample № 2). This effect can be explained by the difference in the permeability values of these matrices (the permeability of CM-1 is approximately 2 times lower than the permeability of CM-2), which may indicate a smaller diameter of the pores of the CM-1 matrix compared to the CM-2 matrix or a lower pore density per unit area of the matrix. In addition, a lower water flow rate throughout the matrix contributes to an increase in the contact time of water pollutants (suspended substances and organic molecules) with the surface of the ceramic membrane, which, in turn, increases the chances of pollutants being retained in the pores or adsorbed on the surface of the matrix due to the formation of adsorption physical-chemical bonds. This fact is confirmed by a significant decrease in the indicator of microbial contamination of purified water after the CM-1 membrane (88.23 % and 39.13 % for water sample № 1 and water sample № 2, respectively) compared to a similar indicator for the CM-2 membrane (7.00 % and 8.70 % for water sample No. 1 and water sample No. 2, respectively) (Table 4). It can be assumed that certain types of microorganisms in water can attach to the dispersed colloidal suspended particles and thus be retained on the matrix during filtration.

The study of membranes with applied selective layers (CM-1.6, CM-1.10) showed a logical correlation between the number of applied selective layers on the matrix and the degree of reduction in the investigated parameters after filtration for water sample № 2 (Tables 5, 6). Thus, the more layers of the selective layer applied, the greater the degree of pollutant removal.

The abnormally low level of retention of all types of pollutants under investigation on the CM-1.6 membrane during the filtration of water sample № 1 (Tables 7, 8) can probably be associated with the occurrence of microdefects and cracks in the membrane itself, which allowed the unimpeded passage of water pollutants into purified water. This assumption is well consistent with the fact that the change in all water parameters after filtration through the CM-1.6 membrane is small.

In addition, increasing the contact time of microorganisms with the TiO_2 selective layer helps to strengthen its antibacterial properties on the microbial flora, which is confirmed by the "Zone of Inhibition Test". Therefore, the CM-1 matrix was chosen to manufacture membranes with applied selective layers, which showed lower permeability and ensured longer contact of natural water with the TiO_2 layer.

Conclusions

The article examines the efficiency of using a matrix and a matrix with applied TiO_2-selective layer to reduce turbidity, chemical oxygen demand and the level of microbial pollution of natural water.

Two types of ceramic matrices were produced: CM-1 (aluminium oxide (Al_2O_3), silicon carbide (SiC), borax ($Na_2B_4O_7$), ammonium carbonate ($(NH_4)_2CO_3$); CM-2 (kaolin, silicon carbide (SiC), borax ($Na_2B_4O_7$), ammonium bicarbonate (NH_4HCO_3), silicon oxide (SiO_2)). After filtration, the matrix efficiency for the pollutants' removal degree of natural water in the Kyiv reservoirs was checked. The CM-1 matrix was more effective in the filtration process. It shows much better selective properties in terms of reducing the turbidity and COD (10.05 % and 55.15 % (CM-1) respectively compared to 0 % and 9.09 % (CM-2) for water sample № 1 and 18.22 % and 12.60 % (CM-1) respectively compared to 0 % and 6.60 % (CM-2) for water sample № 2). The CM-1 membrane also shows a significant decrease in the parameters of microbial contamination of purified water after (88.23 % and 39.13 % for water sample № 1 and water sample № 2, respectively).

Conducted studies of the antimicrobial properties of ceramic membranes with different coatings on a number of test cultures using the "Zone of inhibition" test showed the presence of antibacterial action against the Gram-negative culture of *E. coli* in the CM-1 membrane with a TiO_2 coating. Ceramic membranes, which were made by applying solution 1 (based on TiO_2) to the
CM-1 matrix, respectively 6 layers (CM-1.6) and 10 layers (CM-1.10), and were also investigated in the process of filtration for changes in the parameters (turbidity, chemical oxygen demand and the level of microbial pollution) of natural water in Kyiv reservoirs. The study of the CM-1.6 and CM-1.10 membranes for filtering water sample № 2 showed a logical correlation between the number of selective layers applied to the matrix and the degree of reduction of all investigated water parameters after filtration – the more layers applied selective layer, the greater the reduction degree in the water pollution according to all indicators (31.00 % and 66.90 % (turbidity), 26.00 % and 45.43 % (chemical oxygen demand), 37.50 % and 58.33 % (the level of microbial pollution), respectively).

Thus, the work results confirm the effectiveness of using ceramic matrices and ceramic membranes with an applied selective layer based on TiO_2 to purify natural water, eliminate bacterial contamination and contamination with organic substances, and improve the organoleptic qualities of water. The presented results confirm the relevance of research on the creation of new ceramic materials and ceramic membranes, in particular, to improve the degree of separation of microbiological contaminants and suspended particles in water treatment processes.

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References

[1] Rashad, D., Amin, Sh.K., Mansour, M.S., Abdallah, H. (2022). Fabrication of low-cost antibacterial microfiltration tubular ceramic membranes. *Ceramics International*, *48*(8), 11489–11501. https://doi.org/10.1016/j.ceramint.2022.01.005

[2] Samadi, A, Gao, L, Kong, L, Orooji, Y, Zhao, S. (2022). Waste-derived low-cost ceramic membranes for water treatment: Opportunities. challenges and future directions, Resources. *Conservation and Recycling*. 185, 106497. https://doi.org/10.1016/j.resconrec.2022.106497

[3] Asif, M.B, Zhang, Z. (2021). Ceramic membrane technology for water and wastewater treatment: A critical review of performance, full-scale applications, membrane fouling and prospects. *Chemical Engineering Journal*, *418*, 129481. https://doi.org/10.1016/j.cej.2021.129481

[4] Azaman, F., Nor, M.A.A.M., Rafizah Wan, A.W., Razali, M.H, Zulkifli, R.C, Zaini, M.A.A, Ali, A. (2021). Review on natural clay ceramic membrane: Fabrication and application in water and wastewater treatment. *Malaysian Journal of Fundamental and Applied Sciences*. *17*(1), 62–78. https://doi.org/10.11113/mjfas.v17n1.2169

[5] Mountoumnjou, O., Szymczyk, A., Lyonga Mbambyah, E.E., Njoya, D., Elimbi, A. (2022). New Low-Cost Ceramic Microfiltration Membranes for Bacteria Removal. *Membranes, 12*, 490. https://doi.org/10.3390/membranes12050490

[6] Diana, S., Fauzan, R., Elfiana, E. Removing Escherichia Coli Bacteria in River Water using Ceramic Membrane from Mixed Clay and Fly Ash Material. *IOP Conference Series: Materials Science and Engineering, International Conference on Science and Innovated Engineering (I-COSINE)*, 536, 012089. https://doi.org/10.1088/1757-899X/536/1/012089

[7] Diana, S., Munawar, M., Saifuddin, S., Nahar, N., Silmina, S., Razi, F,. Arahman, N. (2023). Ceramic Membrane-Based on Fly Ash-Clay For River Water Treatment. *Biointerface Research in Applied Chemistry*. *13*(5), 430, 25640944900. https://doi.org/10.33263/BRIAC135.430

[8] Mohit Kumar, C., Roshni, M., Vasanth, D. (2019). Treatment of aqueous bacterial solution using ceramic membrane prepared from cheaper clays: A detailed investigation of fouling and cleaning. *Journal of Water Process Engineering*. 29, 100797. https://doi.org/10.1016/j.jwpe.2019.100797

[9] Zuo, X., Zhang, Sh., Ma, G., Lv, Y., Li, P. (2020). Analysis of ceramic membrane fouling behavior and cleaning Technology. *E3S Web of Conferences ICAEER 2020*. 194, 04048. https://doi.org/10.1051/e3sconf/202019404048

[10] Kamgang-Syapnjeu, P., Njoya, D., Kamseu, E., Balme, S. (2022). Bechelany, M., Soussan, L. Bio-Based Ceramic Membranes for Bacteria Removal from Water. *Membranes*. *12*, 901. https://doi.org/10.3390/membranes12090901

[11] da Silva Biron, D., Santos, V., Bergmann, C. P. (2021). Tubular ceramic membranes coated with ZnO and applied in the disinfection of water contaminated with Staphylococcus aureus. *Ceramics International*, *47*(19), 27082–27090. https://doi.org/10.1016/j.ceramint.2021.06.121

[12] Xu, J., Pan, Z., Peng, S., Zhao, Y., Jiang, S., Chen, Y.J., Xie, Z.H., Munroe, P. (2020). Remarkable bactericidal traits of a metal-ceramic composite coating elated by hierarchically structured surface. *iScience*. *24*(1), 101942. https://doi.org/10.1016/j.isci.2020.101942

[13] Zhao, Y., Huang, G., An, Ch., Huang, J., Xin, X., Chen, X., Hong, Y., Song, P. (2020). Removal of Escherichia Coli from water using functionalized porous ceramic disk filter coated with Fe/TiO_2 nano-composites. *Journal of Water Process Engineering*, *33*, 101013. https://doi.org/10.1016/j.jwpe.2019.101013

[14] Ugarte, P., Ramo, A., Quílez, J., Bordes, M.C., Mestre, S., Sánchez, E., Peña, J. Á., Menéndez, M. (2022). Low-cost ceramic membrane bioreactor: Effect of backwashing, relaxation and aeration on fouling. Protozoa and bacteria removal. *Chemosphere*. 306, 135587. https://doi.org/10.1016/j.chemosphere.2022.135587

[15] He, Y., Huang, G., An, Ch., Huang, J., Zhang, P., Chen, X., Xin, Xi. (2018). Reduction of Escherichia Coli using ceramic disk filter decorated by nano-TiO_2: A low-cost solution for household water purification. *Science of The Total Environment*. 616–617:1628–1637. https://doi.org/10.1016/j.scitotenv.2017.10.149

[16] Serhiienko, A., Dontsova, T., Yanushevska, O., Vorobyova, V., Vasyliev, G. (2023). Characterization of ceramic membrane support based on Ukrainian kaolin. Molecular *Crystals and Liquid Crystals*, *752*(1), 128–141. https://doi.org/10.1080/15421406.2022.2091279

[17] Dontsova, T., Kyrii, S., Yanushevska, O., Suprunchuk, V., Kosogina, I. (2022). Physicochemical properties of TIO_2, ZrO_2, Fe_3O_4 nanocrystalline adsorbents and photocatalysts. *Chemical Papers*. 76, 7667–7683. https://doi.org/10.1007/s11696-022-02433-4

[18] Zielińska, M., Galik, M. (2017). Use of Ceramic Membranes in a Membrane Filtration Supported by Coagulation for the Treatment of Dairy Wastewater. *Water Air Soil Pollut.*, *228*, 173. https://doi.org/10.1007/s11270-017-3365-x

[19] Amin, Sh.K., Abdullah, H.A.M., Roushdy, M.H., El-Sherbiny, S.A. (2016). An overview of production and development of ceramic membranes. *International Journal of Applied Engineering Research*. *11*, 7708–7721.

[20] Issaoui, M., Limousy, L. (2019). Low-cost ceramic membranes: Synthesis, classifications, and applications. *Comptes Rendus Chimie*, 22, 175e187. https://doi.org/10.1016/j.crci.2018.09.014

[21] Dommati, H., Sinha Ray, S., Wang, J-Ch., Chen, Sh-Sh. (2019). A comprehensive review of recent developments in 3D printing technique for ceramic membrane fabrication for water purification. *RSC Advances*, 9, 16869–16883 | 16869. https://doi.org/10.1039/c9ra00872a

[22] Sun, H., Liu, H., Wang, S., Cheng, F., Liu, Y. (2018). Ceramic membrane fouling by dissolved organic matter generated during on-line chemical cleaning

with ozone in MBR. *Water Research*. 146, 328–336. https://doi.org/10.1016/j.watres.2018.09.001

[23] Tomasula, P.M., Mukhopadhyay, S., Datta, N., Porto-Fett, A., Call, J.E., Luchansky, J.B., Renye, J., Tunick, M. (2011). Pilot-scale cross flow microfiltration and pasteurization to remove sporesof Bacillus anthracis (Sterne) from milk. *Journal of Dairy Science*, *94*(9), 4277–4291. https://doi.org/10.3168/jds.2010-3879

[24] Waszak, M., Gryta, M. (2016). The ultrafiltration ceramic membrane used for broth separation in membrane bioreactor. *Chemical Engineering Journal*. 305, 129–135. https://doi.org/10.1016/j.cej.2015.11.058

[25] Abdullayev, A., Bekheet, M.F., Hanaor, D.A.H., Gurlo, A. (2019). Materials and Applications for Low-Cost Ceramic Membranes. *Membranes*. *9*, 105. https://doi.org/10.3390/membranes9090105

[26] Kuzminchuk, A., Burmak, A., Litynska, M. et al. (2023). New diatomaceous earth and kaolinite ceramic membranes for turbidity reduction in water. *Applied Nanosci*ence. *13*, 5335–5343. https://doi.org/10.1007/s13204-023-02792-8

[27] Yanushevska, O. I., Dontsova, T. A., Aleksyk, A. I., Didenko, O. Z., Nypadymka, A. S. (2020). Surface and structural properties of clay materials based on natural saponite. *Clays and Clay Minerals*. *20*(5), 465–475. https://doi.org/10.1007/s42860-020-00088-4

[28] Maryani, E., Nurjanah, N. S., Hadisantoso, E P., Wijayanti, R. B. (2020). The Effect of TiO_2 additives on the antibacterial properties (Escherichia coli and Staphylococcus aureus) of glaze on ceramic tiles. *IOP Conf. Ser.: Mater. Sci. Eng.*, *980*, 012011. https://doi.org/10.1088/1757-899X/980/1/012011

[29] Boffa, V., Lunghi, C., Quist-Jensen, C.A., Magnacca, G., Calza, P. (2019). Fabrication and surface interactions of super-hydrophobic silicon carbide for membrane distillation. *Nanomaterials (Basel)*. *9*(8), 1159. https://doi.org/10.3390/nano9081159

[30] Juan, W., Xiaoyu, W., Qianlong, F., Jinxiu, F., Fengrui, Z., Shuang, L. (2023). Silicon carbide ceramic membrane support sintered at 800 °C with low-temperature sintering aid. *Ceramics International*. *49*(15), 25612–25619. https://doi.org/10.1016/j.ceramint.2023.05.102

[31] Dontsova, T. A., Kuzminchuk, A. V., Yanushevska, O. I., Litynska, M.I., Kyrii, S.O. (2023). *Membrane technologies: Ceramic membranes based on mineral raw materials: monograph*, Kyiv: Igor Sikorsky Kyiv Polytechnic Institute, Polytechnic Publishing House.

[32] International Organization for Standardization (2006). High quality ceramics (ceramics and technical ceramics of improved type). (DSTU ISO 14704:2006). Geneva, Switzerland: International Organization for Standardization.

[33] International Organization for Standardization (2014). DSTU ISO 5017:2014 Fire-resistant, dense molded products. Method for determining apparent density, open porosity and total porosity. (DSTU ISO 5017:2014. ISO 5017:1998, IDT). Geneva, Switzerland: International Organization for Standardization.

[34] Guesmi, Y., Ounifi, I., Khabbouchi, M., Agougui, H., Hafiane, A., Rodríguez, M. A. (2023). Cost-efficient natural apatite–metakaolin supported TiO_2 mesoporous membrane for dye removal applications. *Boletín de la Sociedad Española de Cerámica y Vidrio*. https://doi.org/10.1016/j.bsecv.2023.10.002

[35] Dongdong, W., Likun, H., Haiyang, S., Shaofang, L., Guangzhi, W., Rui, Z., Simin, Z., Xiyu, S. (2024). Enhanced photogenic self-cleaning of super hydrophilic Al_2O_3@GO-TiO_2 ceramic membranes for efficient separation of oil-in-water emulsions. *Chemical Engineering Journal, 486*, 150211. https://doi.org/10.1016/j.cej.2024.150211

[36] Ajenifuja, E., Ajao, J. A., Alayande, S. O., Bakare, M. K., Taleatu, Bidini A. E., Ajayi, O. B. (2016). Synthesis and characterization of pure and Ag-TiO_2-modified diatomaceous aluminosilicate ceramic membranes for water remediation. *Journal of Water Resource and Protection. 8*(5). https://doi.org/10.4236/jwarp.2016.85049

[37] Benkova, M., Soukup, O., Marek, J. (2020). Antimicrobial susceptibility testing: currently used methods and devices and the near future in clinical practice. *Journal of Applied Microbiology, 129*, 806–822. https://doi.org/10.1111/jam.14704

[38] International Organization for Standardization (1999). *Water quality. Enumeration of culturable micro-organisms – Colony count by inoculation in a nutrient agar culture medium,* Geneva, Switzerland: International Organization for Standardization.

[39] International Organization for Standardization (2016). *Water quality – Determination of turbidity – Part 1: Quantitative methods*, Geneva, Switzerland: International Organization for Standardization.

[40] Dhanjai, A.S., Huimin, Z., Jiping, Ch., Samuel, M.M. (2019). Water Analysis | Determination of Chemical Oxygen Demand. Encyclopedia of Analytical Science (Third Edition). *Academic Press*. 258–270. https://doi.org/10.1016/B978-0-12-409547-2.14517-2

[41] International Organization for Standardization (1989). *Determination of the chemical oxygen demand (COD) in water samples by the photometric method* Geneva, Switzerland: International Organization for Standardization.

[42] Lopez de Dicastillo, C., Correa, M., Martínez, F., Streitt, C., Galotto, M. (2020). Antimicrobial Effect of Titanium Dioxide, *Nanoparticles*, 90891. https://doi.org/10.5772/intechopen.