

## PREPARATION AND CHARACTERIZATION OF MICROFILTRATION CERAMIC MEMBRANES BASED ON NATURAL QUARTZ SAND

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**Abstract.** The effect of phase and chemical composition of natural quartz sand, binder and burnable additives was studied. The conditions of application of the membrane and biocide layers on the formation of porous ceramic and microfiltration membranes were investigated. It is shown that a crystalline oxide of Si(IV) is determinant for obtaining the ceramic materials. The presence of carbonates (calcite, dolomite, aragonite, *etc.*) and crystalline aluminosilicates (microcline, albite, phlogopit, *etc.*) leads to a decrease in mechanical strength of ceramics. The ceramic samples with porosity 30-34% and mechanical strength >35 MPa were obtained. Microfiltration membranes are characterized by an average pore size of 4.3  $\mu\text{m}$  and water permeability of 36.3  $\text{m}^3/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ . The biocide coating designed to protect the ceramic membrane surfaces from biofouling was applied and its anti-bacterial activity was shown.

**Keywords:** ceramic, membrane, microfiltration, quartz sand.

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### Introduction

Nowadays, the interest in the development and wide use of the membrane technology in natural and wastewater treatment, the food industry, biotechnology, and gas separation has continuously increased [1–3]. To large extent, these applications have become possible owing to the development of relatively inexpensive high-performance polymeric membranes. The main impediments to wider practical use of ceramic membranes are the lower packing density of membrane elements than that of hollow-fiber polymeric membranes and high cost [4]. Due to this, the growth of the number of publications dedicated to the study of cheap ceramic membranes on the basis of natural raw materials (clay minerals, natural zeolites and *etc.*) and their use in the processes of purification of natural and industrial sewage waters is observed [5-8].

Natural quartz sand that is a widely used raw material around the world predominantly consist of crystalline silicon dioxide, which makes them attractive for the creation of ceramic membranes. Considering the low plasticity of quartz as well as phase transition from  $\alpha$ - to  $\beta$ -form (573°C) accompanied by significant change in specific volume followed by the destruction of

quartz grains, the preparation of mechanically durable porous and permeable materials can be quite complicated task. In the case of using natural quartz raw materials of various deposits, it is important to take into account the effect on the membrane structure and performance characteristics that is exerted not only by the particle size and shape, compaction pressure, and drying and heat treatment conditions, but also by the phase and chemical transformations that occur during the heat treatment of the porous substrate and the fixation of the membrane layers [9].

Biofouling of membrane materials, which takes place during filtration of natural water, is one of the challenges of this method. Ordinary, for solving this task the biocide compounds are added into filtered water. But this method is not suitable for utilizing in case of treatment of drinking water. For this reason the surface modification of ceramic membranes by the insoluble biocide composites can be used [10].

The purpose of this work is the development of ceramic microfiltration (MF) membranes with biocide properties based on natural quartz sand. For this reason it is necessary to study the influence of phase and chemical

composition of quartz sand, binder and burnable additives and the conditions of application of the membrane and biocide layers on physical-chemical properties of MF membranes.

### Experimental

A tubular porous ceramic substrate (a diameter of 65 mm, a length of 500 mm, and a wall thickness of 3–4 mm) was prepared by isostatic radial compression at pressure of 60 MPa using an URP 02.00 setup. Quartz sand (fraction 200–630  $\mu\text{m}$ ) was used as the main component of the mixture for obtaining of ceramic supports. Inorganic binder (water solution of sodium aluminosilicate, silicate and aluminate), organic burning additive (wheat flour, starch, micro cellulose and soot) and non-ionogenic surface-active substance (1% water solution of oxyethylated alcohols OS-20) were used as components of ceramic mixture. Heat treatment of the final samples was conducted in laboratory oven SNOL 7.2/1100 in air atmosphere at 850°C.

MF membrane layers were applied using 30–50 wt.% aqueous suspension of fine-dispersed crystalline silicon dioxide (particle size 40–70 and 1–40  $\mu\text{m}$ ) with aluminosilicate binder (10 wt%). Then the samples were dried at room temperature during 24 h and calcined at 600°C for 5 h at heating rate of 5 °/min.

High biocide properties of the composites are reasoned by the presence of polyhexamethylene guanidine complexes with  $\text{Cu}^{2+}$  ions in their composition [11]. The process of obtaining of colloidal biocide composite included the following stages: (1) synthesis of polyhexamethylene guanidine hydrochloride (PHMG HCl); (2) preparation of aluminophosphate matrix (APM) and its conversion to its copper salt (CSAPM), and (3) mixing solutions of PHMG HCl and CSAPM with the formation of colloidal solution ready for membrane application. Before application of the composite, MF membrane was heated at 180°C during 40 min and submerged in colloidal composite for 2 min followed by drying in the oven at 120°C for 1 h.

The XRD patterns of natural quartz sand and ceramic samples were recorded using a DRON-3 diffractometer with Cu-K $\alpha$  monochromatized radiation with  $2\theta$  from 20 to 80°. The structure and morphology ceramics samples and initial powders of crystal silicon dioxide were studied on scanning electron microscope (SEM) JSM-5610 LS (Japan).

The estimation of the compressive mechanical strength of the samples in tablet form

(diameter 19 mm, height 10–13 mm) was performed on laboratory hydraulic press by measuring the value of pressure, destroying the unity of sample during the process of testing. The average values of mechanical strength were determined using 5 parallel tests.

Porosity ( $P$ ) of the samples were determined by the method of hydrostatic weighing according to the increase in their weight and calculated by the Eq.(1) [12]:

$$P = 1 - \left( \frac{\rho_{app.}}{\rho_{true}} \right) \times 100 \quad (1)$$

where,  $P$  is the open porosity (%);

$\rho_{true}$  - the true density of the porous ceramics was determined pycnometrically *via* immersing the ceramics in benzene;

$\rho_{app.}$  - the apparent density was found from the volume of benzene displaced by the sample impregnated with water.

The medium pore size of the ceramic membranes was determined by the bubble point method and calculated by the Eq.(2) [4]:

$$r = 2\gamma \cos\theta / P \quad (2)$$

where,  $r$  is the pores radius (m);

$\gamma$  is the surface tension of liquid (for the water - 72 N/m);

$\theta$  is the edge angle of the wetting of the material;

$P$  is the pressure (Pa), when the uniform flow of bubbles from the entire surface of the sample is observed.

Anti-bacterial activity of the samples was investigated by the methods of respiratory activity in relation to obligate aerobic micrococusses AA1 [9]. The investigated material was placed in a vial tube with the test culture ( $\sim 10^7$  CFU/mL) and aged for 30 min, and then determined the concentration of oxygen in the environment using a portable oxygen meter AZHA-101MA. The determination of dissolved oxygen concentration in the nutrient medium was carried out before and after the addition of biocidal material.

### Results and discussion

Inorganic binders have a great influence on the porous structure and strength of silicate ceramics. True and apparent densities provide important information on the porous structures of the obtained materials. The true density of a composite material is an additive sum of the densities of its constituents. This statement holds

when the initial constituents do not undergo substantial phase or chemical transformations during high-temperature treatment of the sample. To a first approximation, this is valid for porous silicate ceramics. With respect to the dry residue, the binder content of the samples does not exceed 5 wt.% and its density after thermal treatment at 850°C approximates to 2.4 g/cm<sup>3</sup>, while the density of crystalline SiO<sub>2</sub> is 2.6 g/cm<sup>3</sup>. Therefore, the theoretically calculated true density of the silicate samples should be close to 2.6 g/cm<sup>3</sup>. It can be seen in Table 1 that the true density measured by the picnometric method is somewhat lower than the calculated value for all the obtained samples. According to [12], this discrepancy can be associated with the presence of a small number of “closed” and separate pores in the porous structures. This effect is the most pronounced for the aluminate-based samples ( $\rho_{true} = 2.37$  g/cm<sup>3</sup>) and less pronounced for the aluminosilicate ( $\rho_{true} = 2.42$  g/cm<sup>3</sup>) and silicate-based materials ( $\rho_{true} = 2.45$  g/cm<sup>3</sup>).

The samples with the aluminate binder are characterized by the highest open porosity (~37%). For the samples with the silicate and aluminosilicate binders, the open porosity is 33 and 34 vol.%, respectively. Thus, the integral porosity (with consideration of closed pores) of the aluminate materials exceeds 40 vol.% (Table 1). The binder nature strongly influences not only the porosity, but also the strength and water resistance of the obtained materials. The aluminate-based samples show the lowest strength

(6 MPa) among the studied ceramics. This can be associated with the loose of structure of aluminum oxide released from the mixed system during its thermal treatment and distributed among skeletal silicate particles and their contacts, which cannot provide the required strength. This is illustrated by SEM image shown in Figure 1(a). The porous silicate-based materials are also characterized by relatively low strengths (18 MPa). During thermal treatment, the silicate binder is transformed into highly dispersed SiO<sub>2</sub>, which is an actual binder. In this case, the low strength is due to micro cracks and cavity defects formed in the binder material during the thermal treatment, because water evaporation from the bulk of the silicate binder is followed by “swelling” of sodium silicate (Figure 1(b)). The porous aluminosilicate-based materials are the strongest (35 MPa) ones. This is explained by the perfect structure of the aluminosilicate binder subjected to thermal treatment (Figure 1(c)) [13].

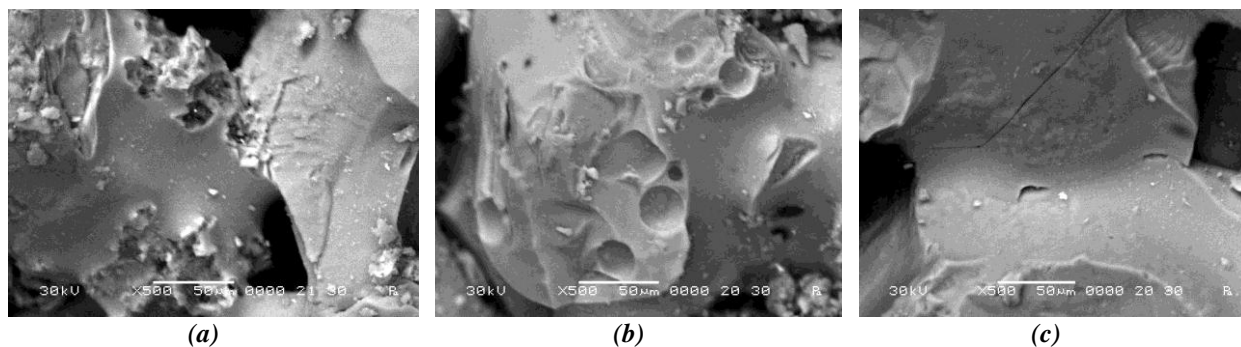
One effective approach to raising the porosity of ceramic materials is to introduce burnable (pore formers) substances, which can be removed by external influences and produce voids, thereby increasing the porosity of the material. In choosing burnable additives, the following was taken into account: (i)- the pore former must have a plasticizing effect to insure good formability of the starting mixture; (ii)- the particle size of the additive must be comparable to the size of pores forming between matrix particles.

Table 1

**Influence of the binder on the structural and mechanical properties and water resistance of porous silicate ceramics.**

Binder	$\rho_{true}$ , g/cm <sup>3</sup>	$\rho_{app.}$ , g/cm <sup>3</sup>	P, %	Compressive strength, MPa		Strength loss, %
				Initial	After reflux	
Sodium silicate	2.45	1.64	33	18	6	67
Sodium aluminate	2.37	1.50	37	6	*	100
Sodium aluminosilicate	2.42	1.60	34	35	35	0

\*The sample loses its integrity upon the reflux.



**Figure 1. SEM images of porous ceramic samples based on crystalline SiO<sub>2</sub> and (a) aluminate, (b) silicate, and (c) aluminosilicate binders.**

The following burnable additives were introduced into the starting mixture: wheat flour, starch, microcellulose, and soot. Wheat flour particles had the form of platelets by 10-20  $\mu\text{m}$  in length and no more than 2  $\mu\text{m}$  in thickness. Starch consisted of spherical particles of 5-70  $\mu\text{m}$  in diameter. Microcellulose consisted of fibers from 10 to 30  $\mu\text{m}$  in length and  $\sim$ 2-5  $\mu\text{m}$  in diameter. All these additives are natural polysaccharides and swell in the presence of moisture. Soot is a hydrophobic powder consisting of spherical particles  $\sim$ 50 nm in size (Figure 2).

The effect of the amount and nature of burnable additives on the porosity and mechanical strength of ceramic samples was considered. The present experimental data (Figure 3(a)) indicate that the porosity is proportional to the initial additive content, independent of the nature of the additive. Figures 3(c) and (d) show SEM micrographs of samples with different wheat flour contents, which clearly illustrate that the porosity of the samples increases notably with increasing initial burnable additive content. The highest porosity (25 to 51%) was achieved using soot as a pore former. The samples prepared with wheat flour and microcellulose had similar porosity because those additives were similar in microstructure and chemical composition (Figures 2(a) and (b)). The samples prepared with

starch as a burnable additive gave higher porosity than those with wheat flour and microcellulose.

The highest strength was achieved in the samples prepared using flour as the pore former (9-65 MPa). The strength of samples prepared with microcellulose ranged between 12-48 MPa, while those prepared with soot had the lowest strength (1.5-30 MPa). This can be explained in terms of the microstructure of the ceramic samples with soot additive. As mentioned above, we failed to obtain strong porous ceramics with starch: the samples containing more than 5 wt.% swelled during sintering [14].

The phase and chemical composition of natural quartz sands are the key parameters that are responsible for the properties of porous ceramic sand MF membrane based on samples. According to X-ray analysis data (Table 2), the highest silica content (95-100 wt.%) was found in the natural sand of Belarus, Vietnam, Saudi Arabia and Turkmenistan. The quartz sand from Azerbaijan, Mongolia and Qatar is characterized by the lowest purity; the quartz content is 48-62 wt.%; this finding almost immediately casts doubt on the possibility of using its to prepare porous ceramics suitable for further application in pressure-driven membrane processes.

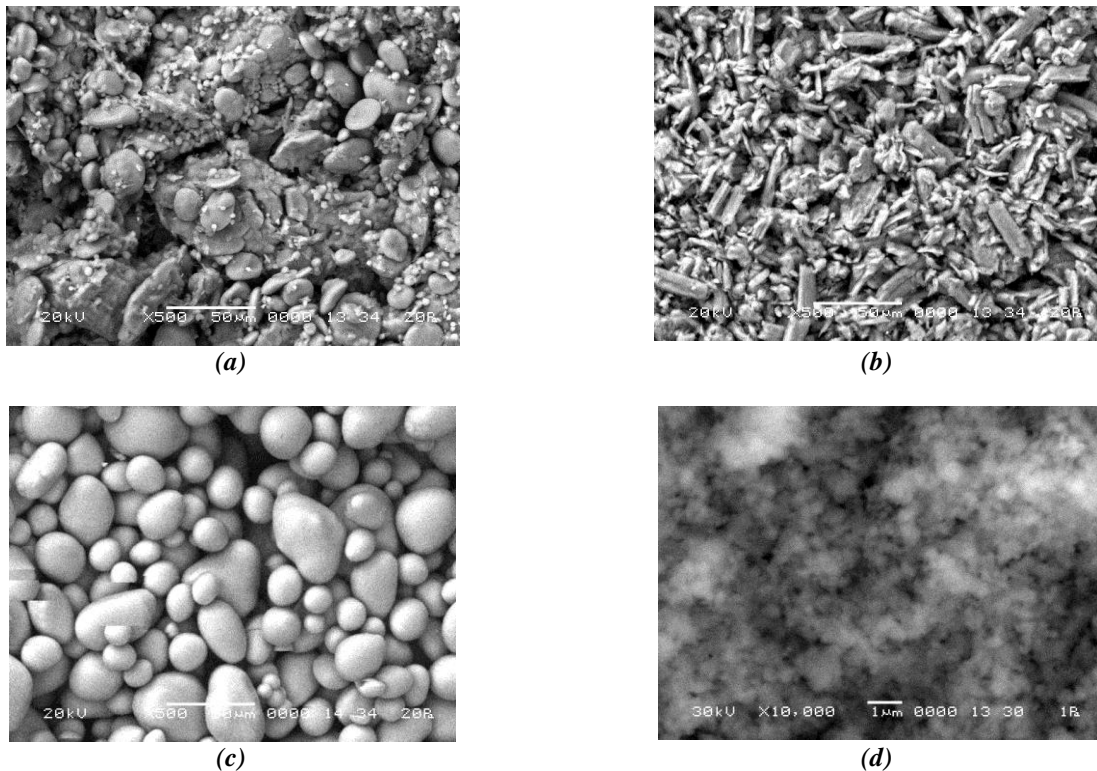


Figure 2. SEM images of burnable additives: (a) wheat flour, (b) microcellulose, (c) starch, (d) soot.

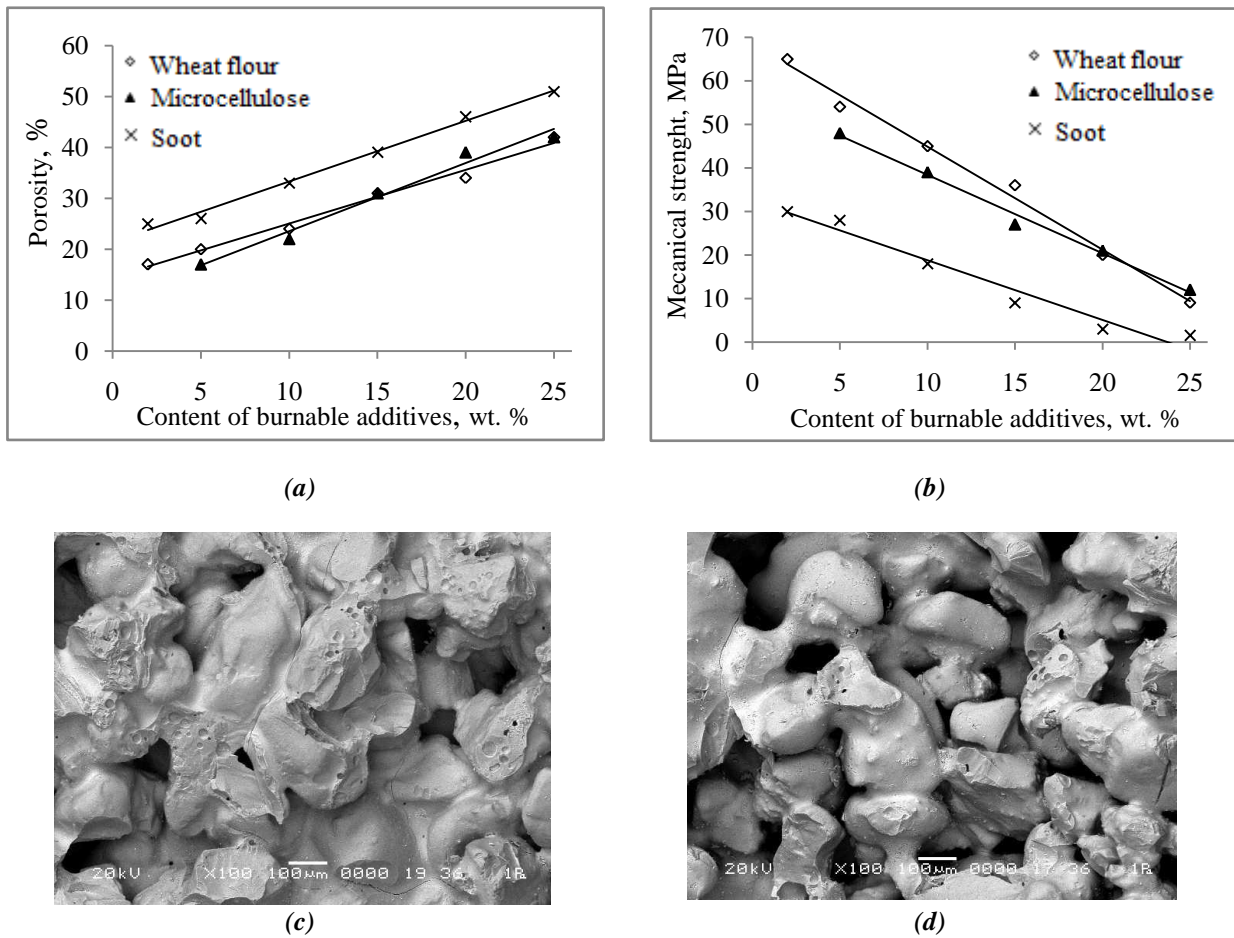


Figure 3. Effect of (a) porosity and (b) mechanical strength depending on content of burnable additives and SEM images of ceramics break containing (c) 2 and (d) 25 wt. % wheat flour.

Table 2

Country of origin	Phase content according to XRD, wt. %		Porosity, %	Mechanical strength, MPa
	Quartz	Others		
Belarus	99	gematite $Fe_2O_3$ - 1	34.0	35.0
Azerbaijan	48	calcite $CaCO_3$ - 48; sillimante $KAlSi_3O_8$ - 3; aragonite $CaCO_3$ - 1; phlogopit $KMg_3AlSi_3O_{10}(OH)_2$ - 1	-	-
Qatar	62	sillimante $Al_2SiO_5$ - 14; calcite $Mg_{0.1}Ca_{0.9}CO_3$ - 10; gypsum $CaSO_4$ - 8; onorthoclase $(Na, K)(Si_3Al)O_8$ - 6	32.8	6.1
Vietnam	99	albite $NaAlSi_3O_8$ - 1	31.3	24.8
Saudi Arabia	92	kaolinite $Al_4[Si_4O_{10}](OH)_8$ -5;	27.5	25.6
		calcite $Mg_{0.1}Ca_{0.9}CO_3$ - 3	27.2**	48.4**
Mongolia	72	albite $NaAlSi_3O_8$ -22; microcline $KAlSi_3O_8$ - 3;	33.2	13.6
		phlogopit $K(Mg,Fe)_3(Al, Fe)Si_3O_{10}(OH, F)_2$ - 3	28.5***	30.5***
		microcline $KAlSi_3O_8$ - 8;	29.3****	20.8****
Turkmenistan	88	nontronite $Na_{0.3}Fe_2Si_4O_{10}(OH)_2 \cdot 4H_2O$ -3; montmorillonite $Ca_{0.2}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 4H_2O$ - 1; traces of muscovite, clinocllore, and orthoclase	23.0***	55.6***

\* samples lost integrity at calcinations;

\*\* the ceramics optimized for quartz sand of Saudi Arabia;

\*\*\* the composition of the ceramic is optimized for quartz sand of Mongolia;

\*\*\*\* most of the specimens stratified.

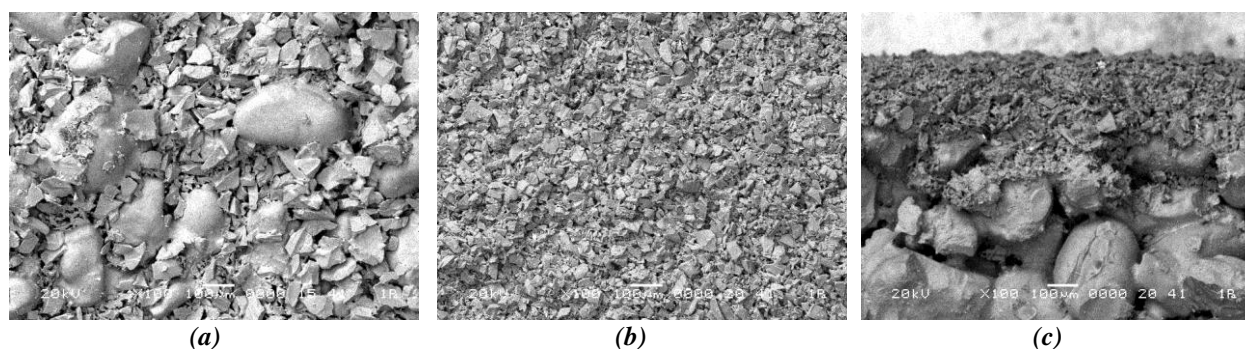
Since all of the tested samples are sedimentary rocks, the main attendant impurities are carbonates and aluminosilicates. The primary comparison of the properties of the ceramics was conducted using the same composition as for the samples based on the Belarus sand. Comparative characteristics of the resulting materials (Table 2) confirm the preliminary conclusions to a large extent. The use of the Belarusian sand provides obtaining the samples with high porosity (34%) and mechanical strength (35 MPa). It is shown that a crystalline oxide of Si(IV) is determinant for obtaining the ceramic materials, and the presence of carbonates (calcite, dolomite, aragonite, *etc.*) and crystalline aluminosilicates (microcline, albite, phlogopit, *etc.*) leads to a decrease in mechanical strength of ceramics [15].

The deposition of oxide powders on a porous substrate is widely used method for obtaining multilayer porous ceramic materials. An advantage of this method is that the substrate and the membrane layer can have similar compositions differing only in the particle size of the original powders; this feature makes it possible to minimize differences in the shrinkage of the particles of the layers during sintering and provide high adhesion. By varying the particle size of the oxide powder, it is possible to effectively control the pore size of the resulting layer. Taking into account the pore size of the

ceramic support (50–100  $\mu\text{m}$ ), the formation of a membrane layer was conducted by sequential deposition of suspensions of crystalline silica with the different particle sizes of 40–70 (intermediate layer) and 1–40  $\mu\text{m}$  (microfiltration layer). It is evident that the repeated deposition of intermediate (Figure 4 (a)) and membrane (Figure 4 (b) and (c)) layer leads to the formation of a defect-free homogeneous membrane layer with thickness 150–200  $\mu\text{m}$  that completely covers the porous support.

The deposition of an intermediate layer leads to a considerable decrease in the average pore size of the samples and, as a consequence, to a decrease in the water permeability (Table 5). The application of microfiltration layer allows to produce the ceramic membrane with an average pore size of 4.3  $\mu\text{m}$  and water permeability 36.3  $\text{m}^3/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ .

The prepared ceramic membranes were tested for biocidal activity (Figure 5). It should be noted a slight consumption of oxygen by cells of strain AA1 while maintaining together with the modified membrane (Figure 5, sample 1), while in the case of the initial membrane (Figure 5, sample 2) after 6 min in nutrient solution the oxygen is not detected. This suggests that only modified ceramic membranes demonstrated the high biocidal activity against the cells of strain AA1, which is especially important for the microfiltration of drinking water.



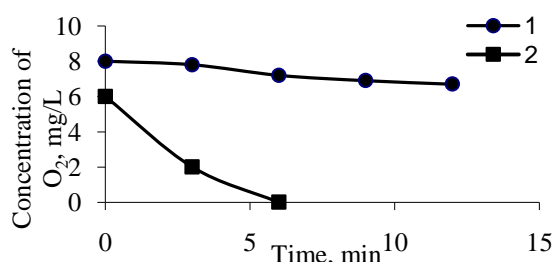
**Figure 4. SEM images of surface of porous ceramics with (a) the intermediate and (b) membrane layers, and (c) structure of break MF membrane.**

Table 5

**Characteristics of porous ceramic materials.**

Sample	$r_{average}$ $\mu\text{m}$	$r_{maximum}$ $\mu\text{m}$	Water permeability, $\text{m}^3/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Support	20.6	25.3	89.0
Support with intermediate layer	12.6	23.1	83.0
Support with microfiltration layer	4.3	11.8	36.3





**Figure 5. The consumption of oxygen by strain AA1 cells depending on the time of incubation with samples of (1) modified and (2) initial ceramic membranes.**

## Conclusions

It was established that the best characteristics of porosity (30-34%) and mechanical strength (>35 MPa) have ceramics prepared with the aluminosilicate binder content of 10-12 wt.% and burnable additives (wheat flour) 12-15 wt.%. It is shown that crystalline oxide of Si(IV) is determinant for obtaining the ceramic materials. The presence of carbonates (calcite, dolomite, aragonite, *etc.*) and crystalline aluminosilicates (microcline, albite, phlogopit, *etc.*) leads to a decrease in mechanical strength of ceramics. The microfiltration membranes with an average pore size of 4.3  $\mu\text{m}$  and water permeability of 36.3  $\text{m}^3/(\text{h}\cdot\text{m}^2\cdot\text{bar})$  were obtained. The modification of the microfiltration membrane with biocide composite was performed and high anti-bacterial activity was achieved.

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