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COMPOSITES THEORY AND PRACTICE

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CERAMIC POROUS MATERIALS MADE OF ZnO INTENDED FOR ELIMINATING PARTICLES IMITATING VIRUSES FROM WATER

In water there are several pollutants having a significant impact on human health. The greatest difficulties are associated with the removal of viruses due to their small size (generally in the range of 20 to 400 nm). Currently, the most effective ways of removing of viruses from water are filters based on electrostatic adsorption. In this method, negatively charged viruses (in the pH of drinking water, pH 5÷9) are retained on an oppositely charged filter surface. These filters are characterized by large pores allowing a much more efficient flow of liquid through the filters and also eliminating the blockage of pores. In order to provide ceramic filters with a positive charge, their inner surface is modified. The purpose of this study was to obtain ceramic composite materials on the basis of zinc oxide with active layers from zinc oxide and simulate the filtration process using a polymer dispersion characterized by a similar size of particles to that of viruses and a negative charge in the pH of drinking water, as is in the case of viruses, was carried out. In order to obtain ceramic composite materials, two types of zinc oxide were used. The average grain sizes of the powders were different - an average particle size of about 200 nm for the powders which were purchased from NanoTek and about 7 μm for those which were purchased from POCH. Porous ceramic composite materials were formed by unilateral pressing. A 10 wt.% aqueous solution of poly(vinyl alcohol) with a molecular weight of 67 000 and degree of hydrolysis of 88% was used as the binder in the ceramic materials. Zinc acetate ($(CH_3COO)_2Zn$) was used to obtain the active layer of the ceramic composite materials while 0.01 wt.% solutions of polymer dispersion with a negative electrokinetic potential - Rokryl SW 4025 (Rokita S.A.) - was used to simulate the process of filtration. During the study, measurements characterizing the ceramic powders, measurements of the physical and mechanical properties of the samples were performed. The influence of the pressure (10 and 30 MPa) and additive of nano-ZnO (0 to 10 vol.%) on the tensile strength, open porosity and distribution of the pore size in the samples after sintering at 900°C were determined. Moreover, the effectiveness of the filtration process using the porous ceramic materials with an active layer of ZnO, which was formed by the impregnation of ceramic samples by zinc acetate and sintered at 430°C, were evaluated.

Keywords: zinc oxide, zinc acetate, filtration of particles imitating viruses, ceramic porous materials, polymer dispersion

CERAMICZNE TWORZYWA POROWATE Z ZnO DO USUWANIA Z WODY CZĄSTEK IMITUJĄCYCH WIRUSY

W wodzie występuje wiele zanieczyszczeń mających znaczący wpływ na zdrowie człowieka. Największe jednak trudności związane są z usuwaniem wirusów ze względu na ich niewielkie rozmiary (na ogół w zakresie od 20 do 400 nm). Najskuteczniejszym sposobem usuwania wirusów mogą stać się filtry działające na zasadzie elektrostatycznej adsorpcji. W metodzie tej ujemnie naładowane wirusy (w zakresie pH wody pitnej, tj. pH 5÷9) są zatrzymywane na przeciwnie do nich naładowanych powierzchniach filtrów. Filtry te odznaczają się dużymi porami, pozwalając na efektywniejszy przepływ cieczy przez nie, a także eliminację blokowania porów. W celu nadania filtrom ceramicznym ładunku dodatniego ich powierzchnie wewnętrzne są modyfikowane. Celem niniejszej pracy było otrzymanie ceramicznych tworzyw porowatych na bazie tlenku cynku z aktywną warstwą filtracyjną również z tlenku cynku, a także przeprowadzenie symulacji procesu filtracji z zastosowaniem dyspersji polimerowej odznaczającej się wielkością cząstek zbliżoną do wielkości wirusów oraz ładunkiem ujemnym w zakresie pH wody pitnej podobnie jak to jest w przypadku wirusów. W badaniach nad otrzymaniem ceramicznych tworzyw porowatych zastosowano dwa rodzaje proszków tlenku cynku (ZnO). Proszki różniły się średnią wielkością ziarna - 200 nm firmy NanoTek i 7 μm firmy POCH. Tworzywa były formowane metodą prasowania jednostronnego. Jako spoiwo zastosowano 10% wodny roztwór poli(alkoholu winylu) o masie cząsteczkowej 67 000 i stopniu hydrolizy wynoszącym 88%. Do otrzymania aktywnej warstwy filtracyjnej z ZnO zastosowano octan cynku, natomiast w symulacji procesu filtracji wykorzystano dyspersję polimerową Rokryl SW 4025 o ujemnym potencjale zeta w całym zakresie pH. Wykonane w pracy badania obejmowały swoim zakresem pomiary charakteryzujące proszki ceramiczne, jak również pomiary parametrów fizycznych i mechanicznych kształtek po procesie wypalania. Określono wpływ ciśnienia prasowania (10 i 30 MPa) i dodatku ZnO o nanometrycznej wielkości cząstek (0 i 10 vol.%) na wytrzymałość mechaniczną na rozciąganie, porowatość otwartą i rozkład wielkości porów w kształtkach po procesie wypalania w temperaturze 900°C. Oceniono również skuteczność procesu filtracji z zastosowaniem opracowanych w ramach pracy ceramicznych tworzyw porowatych z aktywną warstwą filtracyjną z ZnO, powstałą w wyniku impregnacji kształtek ceramicznych octanem cynku i wypaleniu w temperaturze 430°C.

Słowa kluczowe: **tlenek cynku, octan cynku, filtracja cząstek imitujących wirusy, ceramiczne tworzywa porowate, dyspersja polimerowa**

INTRODUCTION

The progress of human activity has a significant impact on the environment, particularly on water - mainly on drinking water in less developed nations. In the water there are numerous pathogens, inorganic substances and substances having a significant impact on health. The major problem is with the occurrence of microorganisms, especially viruses, in water. The occurring microorganisms lead to millions of deaths per year [1-4]. Their small size causes problems with removing them from water. The technologies used to remove viruses from water, for example ozone, UV-irradiation or membrane processes consume large amounts of energy and all leading to high costs [5]. A better solution are filters that retain viruses on the basis of electrostatic adsorption. Viruses are negatively charged, thus the filter surface should have a positive charge. The advantages of using these filters is that they remove particles due to their charge not their size. In this method, the materials are characterized by large pores, which allow the flow of liquid and eliminate the blockage of pores [6-9].

The aim of this study was to design ceramic porous materials with active layers from ZnO. Two types of zinc oxide were used to obtain new filters. Their application is also beneficial because of their low toxicity to humans and antibacterial properties. In this study, two types of ceramic porous materials were obtained. One of the types of samples was prepared from ZnO POCH while the other from 10 vol.% ZnO NanoTek and 90 vol.% ZnO POCH.

EXPERIMENTAL PROCEDURES

Two types of zinc oxide were used in order to obtain ceramic composite materials. One of the powders was purchased from POCH (average particle size $D_{50} \sim 7$ μm) while the other was purchased from NanoTek (average particle size $D_{50} \sim 200$ nm). The size of the powder particles was determined by the dynamic light scattering method. A 10 wt.% aqueous solution of poly(vinyl alcohol) (Aldrich) with a molecular weight of 67 000 and degree of hydrolysis of 88% was used as the binder in the ceramic materials. Zinc acetate ($(CH_3COO)_2Zn$) (POCH) was used to obtain the active layer of the ceramic composite materials. 0.01 wt.% solutions of the polymer dispersion type, Rokryl SW 4025 (38 wt.% solution) (Rokita S.A.), were used to simulate the filtration process. Their particles are negatively charged in the whole pH range just as viruses which have a negative charge in the pH of drinking water and their particles are similar in size ($D_{50} \sim 170$ nm) since viruses range from 20 to 400 nm. The zeta potentials of the powder particles and polymer dispersions were measured. These measurements were set using a zeta potential analyzer (Zetasizer Nano ZS, Malvern Instruments). The substances were dispersed in deionized water. The water was supplied by the MilliQ (Millipore) water purification system. The prepared diluted suspensions were treated with ultrasonification for 10 minutes before the measurements took place. The pH value was altered from pH 2 to 12 using HCl and NaOH solutions. The concentration of the solutions equaled 0.2 mol·dm^{-3}.

During the study, two types of ceramic porous materials were obtained. One of the samples was prepared from ZnO POCH while the other from 10 vol.% ZnO NanoTek and 90 vol.% ZnO POCH. The binder was added to the dry mixture of powders. Then the samples were unilaterally pressed at the pressure of 10 and 30MPa in a hydraulic press. These composites were made with a diameter of 30 mm and a height of 5 mm. The ready composites were dried at 105°C to a constant mass. Then they were sintered in a chamber furnace, which was purchased from Carbolite (type RHF 14/15). The samples were sintered at 900°C for 1 h. The heating rate was 3°C/min. At this stage of measurements, the open porosity, tensile strength and pore diameter distribution were defined. The measurements of tensile strength ("Brazilian test" method) were carried out using the Tinius Olsen H10KS apparatus. The hydrostatic method was used to measure the open porosity. The pore diameter distribution was estimated using mercury porosimetry and was carried out by using AutoPore II by Micrometrics. This method is based on the introduction of mercury under controlled pressure and temperature conditions. The measurements consist of injecting mercury at increasing pressures.

The samples obtained during this study were impregnated by a 10% solution of zinc acetate. A vacuum desiccator was used under the pressure of 10 hPa to remove the air from the whole volume of the porous samples and afterwards, they were filled with the solution. After impregnation, the samples were dried for 24 h at 105°C and then sintered for 30 min at 430°C. At this stage, an active layer (ZnO) of the samples was obtained and the ZnO particles were fixed on the filter surface. The decomposition temperature of zinc acetate to zinc oxide was selected on the basis of the thermogravimetric analysis of zinc acetate.

In this study, simulation of the filtration process was performed on the so prepared samples to determine the effectiveness of the prepared materials. The effectiveness was calculated based on the concentration of polymer dispersion before and after the filtration process. In order to determine the concentrations of polymer dispersion, the calibration curve was determined. The curve is constructed by measuring the absorbance of several prepared solutions of a known concentration. In this method, the unknown concentration of samples is determined through the record of absorbance and referring it to the calibration curve (Fig. 1). The measurements of absorbance were carried out using the Spektrophotometer V-3300 apparatus.

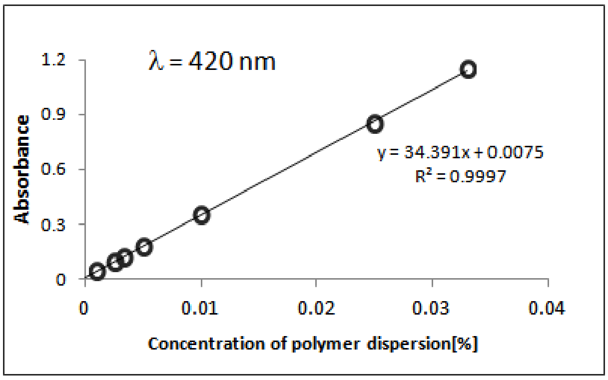

Fig. 1. Calibration curve for wavelength 420 nm

Rys. 1. Krzywa kalibracyjna dla długości fali 420 nm

RESULTS AND DISCUSSION

In Figure 2, the results of the zeta potential of ZnO NanoTek, ZnO POCH and Rokryl SW 4025 are presented.

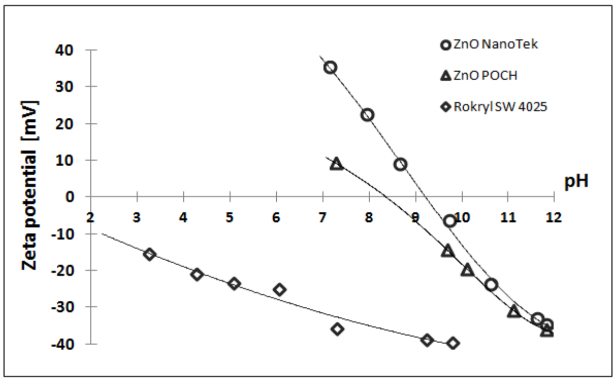

Fig. 2. Zeta potential of ZnO NanoTek, ZnO POCH and Rokryl SW 4025 as a function of pH

Rys. 2. Potencjał zeta ZnO NanoTek, ZnO POCH i Rokrylu SW 4025 w funkcji pH

The zinc oxide (NanoTek and POCH) powder and polymer dispersion particles show great difference in their electrokinetic behavior. Zinc oxide (NanoTek) in water shows a point of zero charge at a pH of about 9.1; zinc oxide (POCH) - 8, while the particles of the polymer dispersion have negative charges in the whole pH range (Fig. 2). This combination of powders and polymer dispersion will lead to adsorption of the polymer dispersion particles at the zinc oxide particle surface.

Porosity and tensile strength play an essential role when considering materials applicable to the process of removing viruses from drinking water (Table 1). The samples which were obtained during the study are characterized by good mechanical properties in the green state. The samples which were formed in the pressing process at the pressure of 30 MPa have higher values of tensile strength and therefore are characterized by a lower porosity than the samples pressed at the pressure of 10 MPa. The obtained results indicate that the materials after being sintered at 900°C achieved significant values of tensile strength, while retaining a high and desirable level of porosity. The value of porosity for the sintered samples was decreased. Samples consisting of ZnO POCH which were formed in the pressing process at the pressure of 10 MPa achieve the highest porosity equal to ca. 57%, while the samples consisting of 90 vol.% ZnO POCH - 10 vol.% ZnO NanoTek which were formed in the pressing process at the pressure of 10 MPa, are characterized by a slightly lower value of porosity equal to ca. 55%.

TABLE 1. **Porosity (P) and tensile strength (σ_t) of green and sintered ZnO POCH and 90 vol.%ZnO POCH - 10 vol.% ZnO NanoTek samples depending on pressing pressure**

TABELA 1. **Porowatość i wytrzymałość mechaniczna na rozrywanie kształtek surowych oraz spieków z ZnO POCH and 90 vol.%ZnO POCH - 10 vol.% ZnO NanoTek w zależności od ciśnienia prasowania**

	ZnO POCH		**90 vol.%ZnO POCH 10 vol.%ZnO NanoTek**	
	Pressing pressure			
	10 MPa	**30 MPa**	**10 MPa**	**30 MPa**
	Green bodies properties			
P [%]	59,3 ± 0,7	48 ± 2	58 ± 2	48,3 ± 0,8
σ_t [MPa]	0,86 ± 0,07	1,9 ± 0,2	0,8 ± 0,1	1,50 ± 0,09
	Properties of bodies sintered at 900°C			
P [%]	56,7 ± 0,7	47,6 ± 0,8	55,4 ± 0,7	42,3 ± 0,5

In Figures 3 and 4, the distributions of the pore sizes of ceramic porous materials, containing two types of zinc oxide (one of the types of samples was prepared from ZnO POCH while the other from 90 vol.% ZnO POCH and 10 vol.% ZnO NanoTek) which were sintered at 900°C, are shown. The results obtained for the sample pressed at the pressure of 10 MPa are shown in Figure 3. Figure 4 presents the distributions of the pore sizes for the sample pressed at the pressure of 30 MPa. The samples pressed at the pressure of 30 MPa are characterized by slightly wider distributions of pore sizes in comparison to the distributions of the pore sizes in the samples pressed at the pressure of 10 MPa. The samples pressed at the pressure of 10 MPa have pores of a diameter between 0.3 to 2.5 μm. However, the samples pressed at the pressure of 30 MPa are characterized by pores of a diameter between 0.3 and 1.5 μm. It is generally known that a higher pressing pressure leads to a more uniform sample structure. Samples formed by pressing at the higher pressure are characterized by having more pores of a smaller size. Based on the graphs in Figures 3 and 4, it can be concluded that the addition of ZnO NanoTek (nanoparticles) has practically no effects on the size of the pores.

The samples obtained during this study were impregnated by a 10% solution of zinc acetate and sintered at 430°C. In order to evaluate the effectiveness of the composite materials obtained during the studies, a simulation of the filtration process was carried out. Rokryl SW 4025 was used to imitate viruses. Figure 5 shows the preliminary results of the filtration process. The effectiveness of the filtration process was calculated based on the concentration of the polymer dispersion before and after filtration.

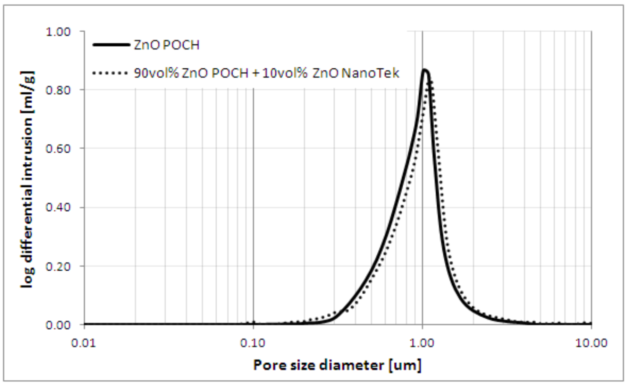

Fig. 3. Distributions of pore sizes of ceramic porous materials pressed at pressure of 10 MPa and sintered at 900°C

Rys. 3. Rozkład wielkości porów dla ceramicznych tworzyw porowatych prasowanych pod ciśnieniem 10 MPa i wypalonych w temperaturze 900°C

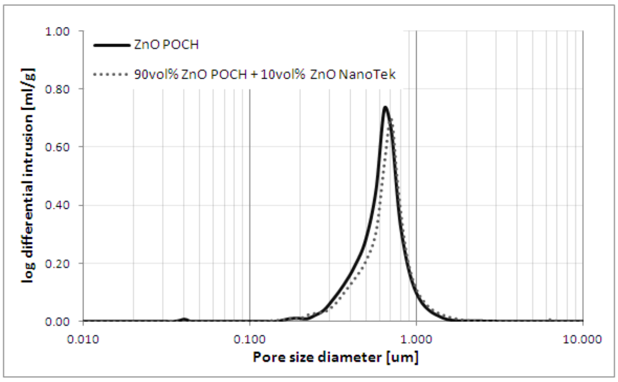

Fig. 4. Distributions of pore sizes of ceramic porous materials pressed at pressure of 30 MPa and sintered at 900°C

Rys. 4. Rozkład wielkości porów dla ceramicznych tworzyw porowatych prasowanych pod ciśnieniem 30 MPa i wypalonych w temperaturze 900°C

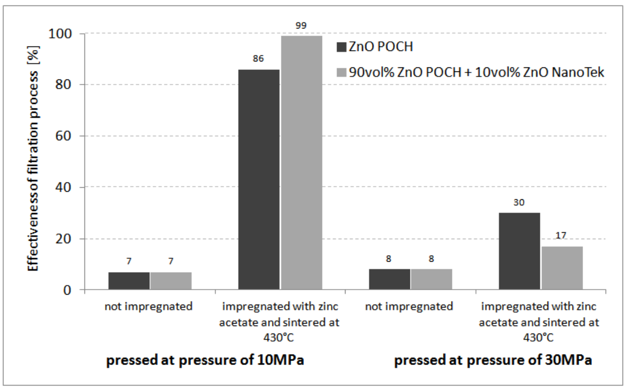

Fig. 5. Effectiveness of filtration process of polymer dispersion particles using samples formed by pressing at 10 and 30 MPa, sintered at 900°C and impregnated with zinc acetate and finally sintered at 430°C

Rys. 5. Skuteczność procesu filtracji cząstek dyspersji polimerowej z zastosowaniem kształtek prasowanych przy ciśnieniu 10 i 30 MPa, wypalonych w 900°C, impregnowanych octanem cynku, a następnie wypalonych w 430°C

On the basis of the measurements, it was discovered that modifying ceramic materials which were formed by pressing at 10 MPa gives good results. The addition of ZnO NanoTek (nanoparticles) to the samples has practically has no influence on the effectiveness of the filtration process. The effectiveness of the samples modified by zinc oxide is higher than that of the unmodified samples. In the mentioned samples, the polymer dispersion particles are attracted to the walls of the filter.

X-ray diffraction, the composition of the obtained filters, will be analysed in order to verify the changes in the structure of the samples after modification - the impregnation of zinc acetate and sintering at 430°C.

CONCLUSION

The aim of this study was to develop porous ceramic materials which could be applied in the process of eliminating particles imitating viruses from water. On the basis of the experimental route, it can be concluded that good results are obtained by using both samples (one of the types of samples was prepared from ZnO POCH while the other from 90 vol.% ZnO POCH and 10 vol.% ZnO NanoTek), which were pressed at the pressure of 10 MPa, sintered at 900°C and then were impregnated with a solution of zinc acetate and sintered at 430°C in order to achieve an active filter layer from ZnO. The samples prepared during the study effectively attract negatively charged polymer dispersion particles which imitate viruses in water. ZnO, which was obtained on the surface of the ceramic composite, plays the role of promotor in the process of adsorption of negatively charged particles imitating viruses. Additional studies should be carried out. X-ray diffraction, the composition of the obtained filters, will be analysed in order to verify the changes in the structure of the samples after modification - the impregnation of zinc acetate and sintering at 430°C.

Acknowledgements

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