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## MODIFIED CERAMIC POROUS MATERIALS INTENDED FOR RETENTION VIRUSES IMITATING PARTICLES FROM WATER

### MODYFIKOWANE CERAMICZNE TWORZYWA POROWATE PRZEZNACZONE DO USUWANIA Z WODY CZĄSTEK IMITUJĄCYCH WIRUSY

The main purpose of this study was to perform ceramic composite materials with active filter layers which could be applied in the process of elimination viruses imitating particles from water. In this study, the method of obtaining the active layer on the surface of the ceramic porous materials was developed and simulation of the filtration process using polymer dispersion characterized by similar size of particles to the size of viruses and negative charge at the pH of drinking water as it is in the case of viruses was carried out. In order to obtain ceramic composite materials, two types of zinc oxide were used. Application of ZnO is also beneficial because of their low toxicity to human and antibacterial properties.

*Keywords:* zinc oxide, zeta potential, electrostatic adsorption, water purification

Głównym celem badań było wykonanie ceramicznych tworzyw porowatych z aktywną warstwą filtracyjną, które mogłyby skutecznie usuwać z wody cząstki imitujące wirusy. Opracowano metodę otrzymywania aktywnej warstwy na powierzchni tworzywa ceramicznego oraz przeprowadzono symulację procesu filtracji. Zastosowano dyspersję polimerową odznaczającą się wielkością cząstek zbliżoną do wielkości wirusów oraz mającą ładunek ujemny w zakresie pH wody pitnej podobnie jak to jest w przypadku wirusów. W badaniach zastosowano dwa rodzaje proszków tlenku cynku. Zastosowanie ZnO jest korzystne ze względu na ich niską toksyczność oraz właściwości antybakteryjne.

#### 1. Introduction

Safe drinking water, sanitation and hygiene are crucial to health, growth and development of all living organisms. However, these basic needs are still a goody for many people. In the countries, where a big problem with access to pure water there is, a high percentage of mortality from diarrhea and a high incidence of diseases such as ascaris, dracunculiasis, hookworm, schistosomiasis and trachoma appears. All of these diseases are associated with the occurrence of microbial pollution in water. The small size of viruses causes huge problems with their removal from water. The technologies which are used in developing countries consume large amounts of energy and all leading to high costs. A good solution in poor countries are filters which retain viruses on the basis of electrostatic adsorption. The advantages of using these filters is that they remove particles due to their surface charge not pore size. In this method, the materials are characterized by large pores, which allow the easy flow of liquid, to eliminate the blockage of pores and to reduce the cost of water purification process [1-7].

The goal of this study was to design and test of modified ceramic porous materials made of ZnO with electropositive zinc oxide coating for the removal of particles imitating viruses from the water. Zinc oxide was chosen on the basis

of its high value point of zero charge. Zeta potential measurement shown that this powder exhibits a positive surface charge across wide pH range.

#### 2. Experimental

**Materials.** In order to obtain ceramic porous materials, two types of zinc oxide powder of different particle size, were used. One of the powders had an average particle size of  $7\mu\text{m}$  (powder which was purchased from POCh S.A., Poland) while the next had about 200nm (powder which was purchased from NanoPhase Technologies Corporation, US). The dynamic light scattering method was used to measure the size of the powder particles. 10<sub>wt.%</sub> aqueous solution of poly(vinyl alcohol) (Aldrich) with a molecular weight of 67 000 and the degree of hydrolysis of 88% was used as a binder. The substance, which was used to obtain the active layer of the composite materials was zinc acetate  $((\text{CH}_3\text{COO})_2\text{Zn})$  (POCh S.A.). 0,01<sub>wt.%</sub> solutions of polymeric dispersion Rokryl SW 4025 (38<sub>wt.%</sub> solution) (Rokita S.A., Poland) were used in the simulation of the filtration process. The particles of the dispersion were negatively charged in the whole pH range just like viruses and their particles are similar in size ( $D_{50} \sim 170 \text{ nm}$ ) since viruses particles range from 20 to 400 nm.

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**Method.** The samples consisting of only ZnO POCh and of the mixture of 10<sub>vol.%</sub> of ZnO NanoTek and 90<sub>vol.%</sub> ZnO POCh were prepared by uniaxial pressing at 10 and 30 MPa in a hydraulic press with binder addition. The prepared samples were dried at 105°C to the constant mass and then sintered at 1000°C (for 1h) in a chamber furnace (RHF 14/15 Carbolite UK). The obtained samples were impregnated by 10% solution of zinc acetate ((CH<sub>3</sub>COO)<sub>2</sub>Zn). After impregnation, the samples were dried for 24h at 105°C and then sintered at 430°C for 30 min. Decomposition temperature of zinc acetate to zinc oxide was selected on the basis of thermogravimetric analysis of zinc acetate using derivatograph with graphic recorder (Q-1500D, MOM, Germany). During this stage an active layer (ZnO) of the samples was received and particles of ZnO were fastened on the samples surface. The microstructure of the sample was observed using scanning electron microscope (LEO 1530, Carl Zeiss, Germany). Finally the simulation of the process of filtration was performed to determine the effectiveness of the materials. In this process 0,01<sub>wt.%</sub> solutions of polymeric dispersion Rokryl SW 4025 (38<sub>wt.%</sub> solution) were used. The efficiency of the prepared materials was determined basing on the concentration of the polymeric dispersion before and after filtration process. Zeta potential of the powders suspensions and polymeric dispersions was measured using zeta potential analyzer (Zetasizer Nano ZS, Malvern Instruments, UK). The substances were dispersed in deionized water. The prepared diluted suspensions were ultrasonicated for 10 minutes before the measurements were taken. HCl and NaOH solutions were used as titrating agents.

### 3. Results and discussion

The results of zeta potential measurements are presented in Fig. 1. Generally zeta potential defines electrokinetic potential on the particles surface. This is a physical property which characterizes particle in a suspension.  $pH_{IEP}$  is the point at which the net electrical charge density on a surface is zero.

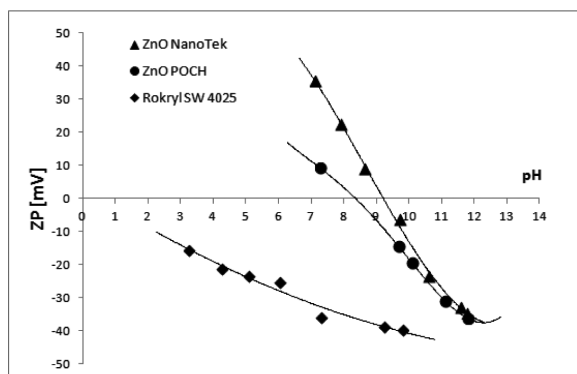


Fig. 1. Zeta potential curves of ZnO NanoTek, ZnO POCh and Rokryl SW 4025

Isoelectric point (IEP) of ZnO (NanoTek) in water was found to lie at  $pH=9,1$  while the ZnO (POCh) powder was found at  $pH=8,0$ . These difference in pH (IEP) indicates that size has influence on the pH of point of zero charge. Particles surface is positively charged when pH of the medium is below this pH, value while the pH of the medium is above this pH the

surface is negatively charged. The particles of the polymeric dispersion have negative charge in the whole pH range. This combination of powders and polymeric dispersion leads to adsorption of particles of polymeric dispersion at zinc oxide particles [8].

The materials consisting of ZnO POCh and also 10<sub>vol.%</sub> of ZnO NanoTek and 90<sub>vol.%</sub> of ZnO POCh were modified by using 10% solution of zinc acetate, then dried and finally sintered at 430°C to obtain zinc oxide on the surface. The SEM images (Fig. 2) show the microstructure of the sample (sintered at 1000°C) fracture surface obtained from 10<sub>vol.%</sub> of ZnO NanoTek and 90<sub>vol.%</sub> of ZnO POCh.

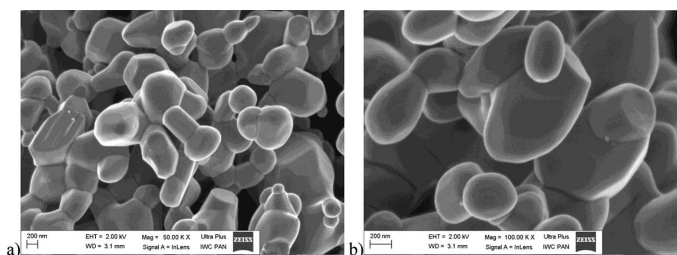


Fig. 2. SEM images of the sample containing 10<sub>vol.%</sub> of ZnO NanoTek and 90<sub>vol.%</sub> of ZnO POCh, sintered at 1000°C (without impregnation). Picture from a scanning electron microscope; a) magnification 50 000x, b) magnification 100 000x

The SEM images in Fig. 3 show the microstructure of the samples sintered at 900°C, which were impregnated and then resintered at 430°C to obtain an active layer.

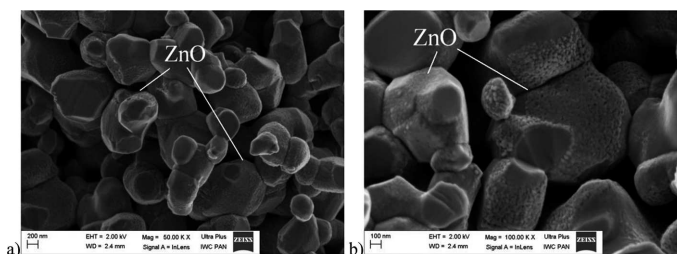


Fig. 3. SEM images of the sample containing 10<sub>vol.%</sub> of ZnO NanoTek and 90<sub>vol.%</sub> of ZnO POCh, sintered at 1000°C, impregnated and then resintered at 430°C. Picture from a scanning electron microscope; a) magnification 50 000x, b) magnification 100 000x

After impregnation and sintering process the samples surface was definitely modified. The surface of these samples was much more developed which is associated with the new phase of nanoparticles ZnO surface. There are zinc oxide nanoparticles resulting from the decomposition of zinc acetate. Basing on the literature and thermal analysis zinc acetate decomposes to zinc oxide at 430°C. The obtained surface may have a significant impact on the activity of these materials during filtration process.

In order to evaluate effectiveness of the samples (after zinc acetate modification) simulation of filtration process was carried out. In this process 0,01<sub>wt.%</sub> solution of polymeric dispersion Rokryl SW 4025 (38<sub>wt.%</sub> solution) was used. The filtration efficiency of the prepared materials was determined basing on the concentration of polymeric dispersion before and after the process. In Fig. 4 the results of the filtration process were shown. Basing on these results, it can be concluded that

by modifying ceramic materials better results can be obtained than by using of unmodified materials. The samples which were formed by pressing at 10MPa are removing particles imitating viruses better than samples which were pressed at 30 MPa. The addition of ZnO NanoTek (nanoparticles) to the samples has influenced on the effectiveness of the filtration process. When the samples were pressed at 10 MPa the addition of ZnO NanoTek caused the increase of efficiency a while for materials which were pressed at 30 MPa, the addition of nanopowder leads to the decrease of efficiency.

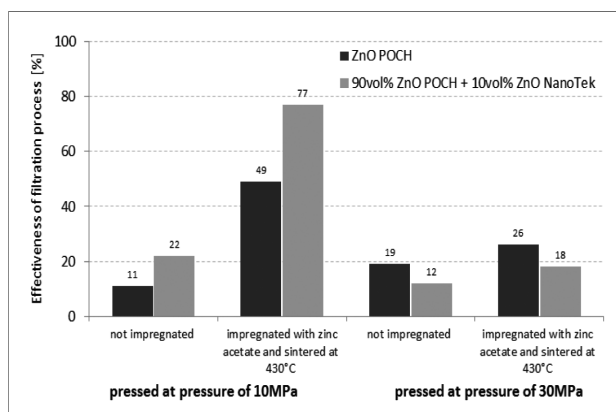


Fig. 4. Effectiveness of filtration process of polymer dispersion particles using samples formed by pressing at 10 and 30 MPa, sintered at 1000°C and impregnated with zinc acetate and then finally sintered at 430°C

EDS analysis and X-ray diffraction analysis, the final composition of as-obtained filters, should be done to verify the changes in their structure after modification – i.e. the impregnation of zinc acetate and sintering at 430°C.

#### 4. Conclusion

The aim of this work was to create a ceramic porous materials with active layer obtained from particles with high value of zero charge, point which is capable of removing particles imitating viruses from water. This study shown that modifying a ceramic porous materials from zinc oxide with electropositive nanoparticles coating can be used in the process of remov-

ing viruses from water. The samples consisting of 90<sub>vol.%</sub> of ZnO POCh and 10<sub>vol.%</sub> of ZnO NanoTek, which were pressed at 10MPa, 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 quite effectively attract negatively charged particles of polymer dispersion which imitate viruses in water. Additionally X-ray diffraction analysis and specific surface area measurement of the obtained filters should be done in order to verify the changes in their structure after modification.

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#### REFERENCES

- [1] J.M. Brown, Effectiveness of ceramic filtration for drinking water treatment in Cambodia, PhD thesis, University of North Carolina, Chapel Hill, 2007.
- [2] B. Michen, Virus removal in ceramic depth filters: The electrostatic enhanced adsorption approach, PhD thesis, Technical University "Bergakademie", Freiberg, 2010.
- [3] A.L. Kowal, M. Świdorska-Bróź, *Oczyszczanie wody*, Wydawnictwo Naukowe PWN, Warszawa, 2005.
- [4] M. Wegmann, B. Michen, T. Graule, Nanostructured surface modification of microporous ceramics for efficient virus filtration, *Journal of the European Ceramic Society* **28**, 1603-1612 (2008).
- [5] N. Kattamuri, J.H. Shin, B. Kang, C.G. Lee, J.K. Lee, C. Sung, Development and surface characterization of positively charged filters, *Journal of Materials Science* **40**, 4531-4539 (2005).
- [6] C.P. Gerba, Applied and theoretical aspects of virus adsorption to surfaces, *Advances in Applied Microbiology* **30**, 133-168 (1984).
- [7] M. Zalewska, E. Bobryk, A. Pędzikiewicz, M. Szafran, Porous ceramic materials for virus filtration, *Archives of Metallurgy and Materials* **56** (4), 1193-1197 (2011).
- [8] A.B. Garcia et al., Zeta – potential as a tool to characterize plasma oxidation of carbon- fibers, *Journal of Colloid and interface science* **192** (2), 363-367 (1997).