www.czasopisma.pan.pl www.journals.pan.pl

A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 56 2011 Issue 4

DOI: 10.2478/v10172-011-0134-5

M. ZALEWSKA*, E. BOBRYK*, A. PĘDZIKIEWICZ*, M. SZAFRAN*

POROUS CERAMIC MATERIALS FOR VIRUS FILTRATION

ZASTOSOWANIE CERAMICZNYCH TWORZYW POROWATYCH DO FILTRACJI WIRUSÓW

The purpose of this study was to design and examine porous ceramic materials on the basis of diatomaceous earth, as well as carrying out preliminary model researches of the purification of drinking water. The conditions, parameters and methods of production of the ceramic samples have been selected on experimental way, in order to characterize them by suitable porosity and tensile strength. The authors have searched such porous ceramic materials, which exhibit positive charge, in contrast to viruses, which have a negative surface charge in pH o drinking water.

Celem pracy było zaprojektowanie i zbadanie ceramicznych tworzyw porowatych na bazie ziemi okrzemkowej, jak również przeprowadzenie wstępnych badań modelowych nad oczyszczaniem wody pitnej z wirusów. Na drodze eksperymentalnej zostały dobrane warunki, parametry i metody wytwarzania kształtek ceramicznych, tak aby cechowały sie odpowiednią porowatością otwartą oraz wytrzymałością mechaniczną. Autorzy poszukali takich ceramicznych tworzyw porowatych, które będą wykazywały dodatni potencjał, w stosunku do wirusów, które są ujemnie naładowane w zakresie pH wody pitnej (pH 5-9).

1. Introduction

Water is an essential substance for normal growth and development of all living organisms. Recent years, which were connected with the development of human activity, caused the shortage of drinking water in the world. There are many pollutants in the water: a lot of pathogens, organic substances, inorganic substances and substances having a significant impact on health [1]. The occurrence of viruses in the water is a major problem, which is connected to their small dimensions. At present, they are fully removed by nanofiltration or reverse osmosis. The mechanism of these methods is based on liquid filtration through membranes with pores smaller than the mentioned pollutants (Fig. 1). In these methods, the solution is forced through semipermeable membrane by an external stimulus e.g. concentration or the pressure difference. Consequently, they are quite expensive and time-consuming [2].

In recent years, there have been attempts to develop more efficient and cheaper membranes that remove viruses from the water. Membranes of the newest generation will stop viruses (negatively charge at pH of drinking water) on the basis of electrostatic adsorption onto oppositely charged surface filter (Fig. 2). Therefore, the surfaces of ceramic filters are modified in order to provide them with a positive charge. This modification can be done by introducing particles of ceramic powders with a high value of zero point charge at the stage of synthesis or after the stage of synthesis of ceramic materials [3].

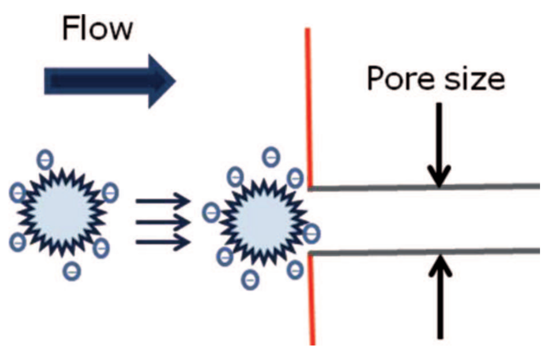

Fig. 1. The mechanism of the process of filtration in conventional filter [4]

The advantage of using these filters is that they abstract very small particles, which practically are not separated in conventional membranes and they remove viruses due to their charge not their size. They are much more efficient, than conventional filters. This is due to the presence of large pores, which allow increasing the flow of

* INORGANIC TECHNOLOGY AND CERAMICS DEPARTMENT, FACULTY OF CHEMISTRY, WARSAW UNIVERSITY OF TECHNOLOGY, 00-664 WARSAW, 3 NOAKOWSKIEGO STR., POLAND

the filtered water. The blockage with of pores is not an issue in this case [4-6].

In the paper the utilization of porous ceramics for virus potable water filtration was investigated. Porous samples were obtained from diatomaceous earth and bentonite, which are preferable from both economical and structural point of view. The high internal porosity of the used materials make them an excellent material for filters. Physical and mechanical properties of the obtained samples were measured. Selected samples were modified so that their surface attracted negatively charged dispersion (that simulated viruses), according to the filtration model schematically shown in Fig. 2.

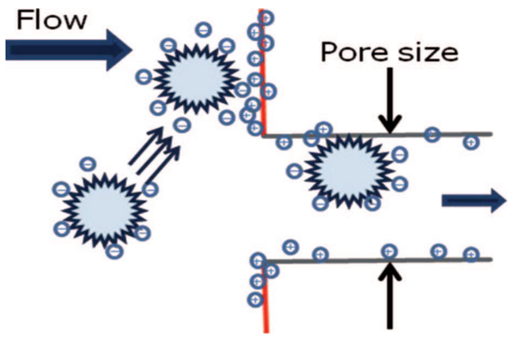

Fig. 2. The mechanism of the process of filtration on positively charged filter [3]

2. Experimental

Materials

In order to obtain porous ceramic materials, diatomaceous earth (2,34g/cm^3), which was purchased from *Desotec* and bentonite (2,39g/cm^3) purchased from *ZGM Zębiec* were used. 10$_{wt.}$% aqueous solution of poly(vinyl alcohol) (*Aldrich*) with a molecular weight of 67 000 and degree of hydrolysis of 88% was the binder. Yttrium nitrate (V) $Y(NO_3)_3$ obtained at Warsaw University of Technology was used to obtain the active layer of the filter. For means of research of the filtering process simulation 40$_{wt.}$% solution of polymer dispersion *Rokryl SW 4025* (*Rokita S.A.)* with a negative zeta potential of the whole pH range was used (Fig.3.).

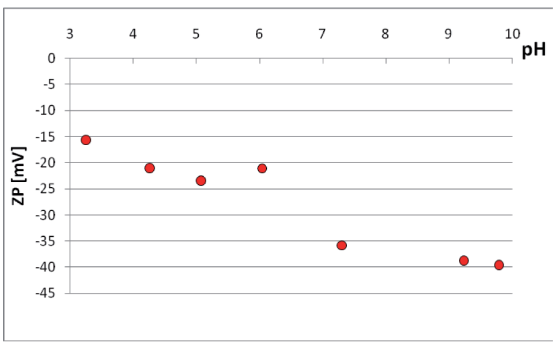

Fig. 3. Zeta potential curves of the polymer dispersion *Rokryl SW 4025*. Measurements of zeta potential were performed using *Nano ZS* by *Malvern Instruments*

Method

The studies were conducted according to the diagram, which is shown in Fig. 4.

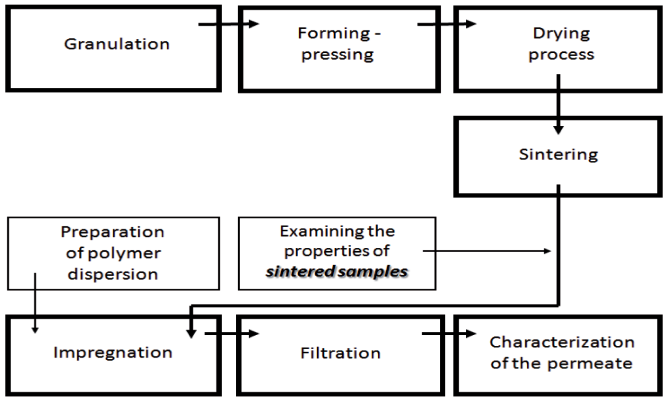

Fig. 4. Methodology of experimental work

Firstly, the composition of previously determined granulates was prepared. Three granulates were prepared containing respectively 20$_{vol.}$% bentonite and 80$_{vol.}$% diatomaceous earth, 30$_{vol.}$% bentonite and 70$_{vol.}$% diatomaceous earth and a 40$_{vol.}$% bentonite and 60$_{vol.}$% diatomaceous earth. Then samples were pressed in a hydraulic press at the pressure of 30MPa. These samples were made with a diameter of 30mm and a height of 5mm. Subsequently the prepared samples were dried at 105°C to the constant mass and then sintered at three temperatures: 1100°C, 1150°C and 1200°C in the chamber furnace, *Carbolite (type RHF 14/15)*. At this stage of measurements porosity and tensile strength were determined. The measurements of tensile strength ("brazilian test") were performed using the *Tinius Olsen H10KS* apparatus. Porous ceramic materials with the optimal properties were impregnated once or twice with a solution of yttrium nitrate (V) in a vacuum desiccator for 20 minutes. Then the samples were dried and sintered at two temperatures: 600°C and 1000°C. The simulation of the process of filtration was carried out in the designed filtration system and its effectiveness was evaluated depending on the parameters of the ceramic samples.

3. Results and discussion

The main problems occurring during the preparation of the porous ceramic materials are suitable choice of compositions of granulates at the stage of forming and the choice of the firing temperature. The composition of various powders mixtures that gives them the relevant properties should be considered. Porosity and tensile strength play an important role in the case of these materials, which find application in the process of removing viruses from drinking water. The results, obtained by authors, indicate that samples consisting of 40$_{vol.}$% bentonite and 60$_{vol.}$% diatomaceous earth are of the best properties, which in green state are of good mechanical properties and sintered at 1150°C achieve significant values of tensile strength (Fig. 5) while preserving a high and desirable level of porosity (Fig. 6).

These samples were impregnated with a solution of yttrium nitrate. Fig. 7 shows the percentage of cations of yttrium introduced into the pores of samples and sintered at 600°C and 1000°C for single and double impregnation.

The simulation of the process of filtration allowed evaluating the effectiveness of porous ceramic materials which were prepared during these studies (Fig. 8). Basing on these results and their visual examination, it can be concluded, that the best results are obtained whereas samples which were impregnated of solution of yttrium nitrate and sintered at 600°C were used. Therefore, it can be concluded that the sintering at 600°C leads to receiving cations of yttrium with higher activity, than when sintered at 1000°C, which is connected with the type of the compound formed in the pores of the porous ceramic material. After sintering at 600°C yttrium hydroxide was received in the pores, whereas when sintering at 1000°C yttrium oxide was obtained. X-rays diffraction, the composition of the obtained filters, will be affected.

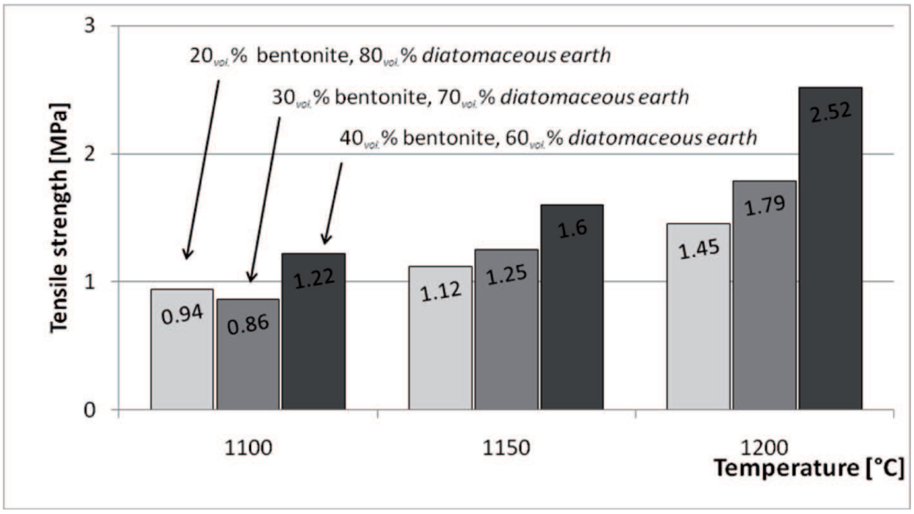

Fig. 5. The relationship between tensile strength and the sintering temperature of porous ceramic materials

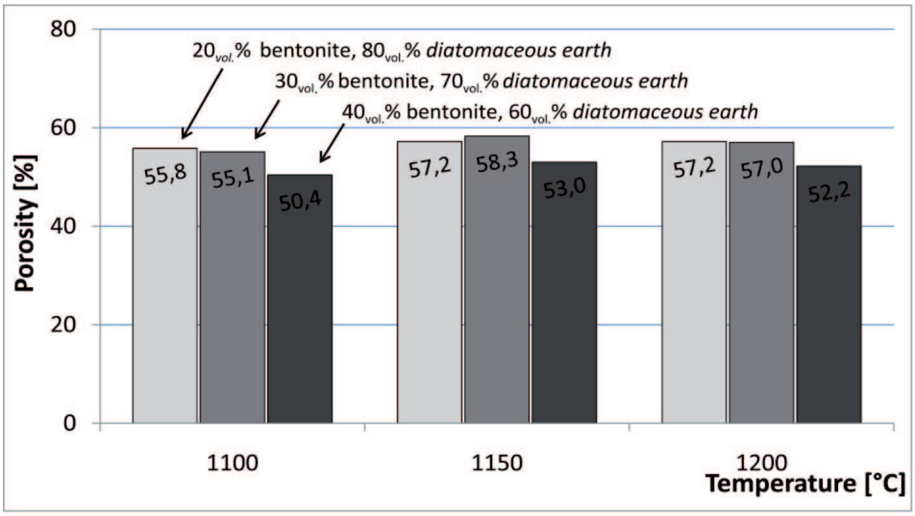

Fig. 6. The relationship between porosity and sintering temperature of porous ceramic materials

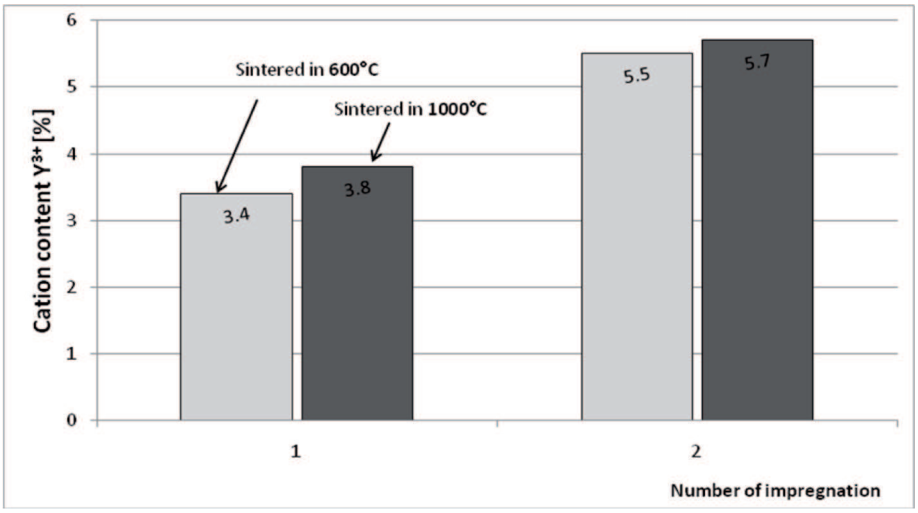

Fig. 7. The influence of the sintering temperature and number of impregnations on percentage of cations of yttrium in the samples

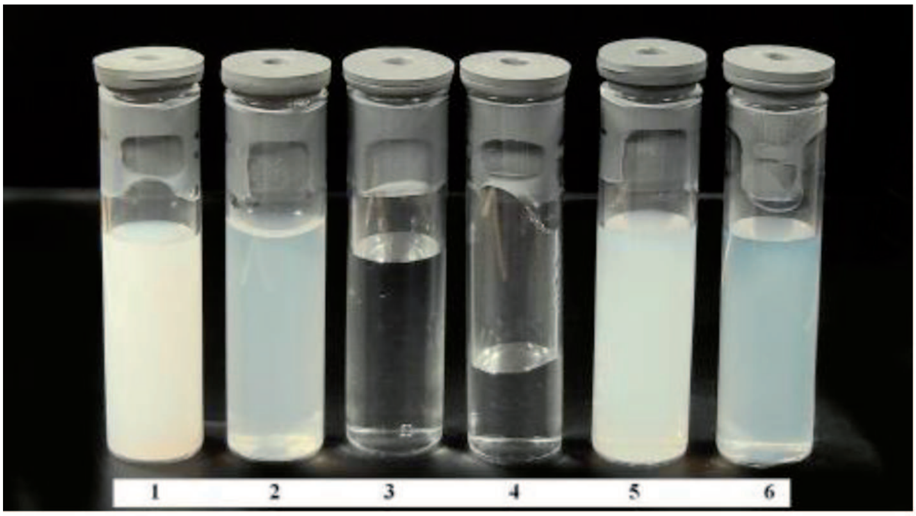

Fig. 8. The results of the process of filtration; 1- standard sample of 1% solution of polymer dispersion; 2- permeate after filtration through not impregnated sample; 3 i 4- permeates after filtration through once and twice impregnated samples, sintered at 600°C; 5 i 6- permeates after filtration through once and twice impregnated samples, sintered at 1000°C

4. Conclusions

The purpose of the study was to study if the mixture of diatomaceous earth and bentonite can be applied to the preparation of porous ceramic materials for virus filtration.

On the basis of experimental route conducted, it can be concluded that porous ceramic materials consisting of $40_{vol.}\%$ bentonite and $60_{vol.}\%$ of diatomaceous earth and sintered at 1150°C are characterized by the best applicable features. They can be successfully used in the process of removing viruses from the water. Samples impregnated with cations of yttrium which were sintered at 600°C effectively attract negatively charged particles of polymer dispersion that imitate viruses in water.

In future research, a method of evaluating the effectiveness of the filters should be developed. The full characteristic of the obtained filters can be reached only after conducting the complete process of filtration of viruses from drinking water by using these filters.

Acknowledgements

This work was financially supported by Warsaw University of Technology

REFERENCES

[1] R. Kocwa-Haluch, Wirusologia w inżynierii środowiska, Wydawnictwo PK, Kraków 2002.

[2] A.L. K o w a l, M. Ś w i d e r s k a - B r ó ż, Oczyszczanie wody, Wydawnictwo Naukowe PWN, Warszawa 2005.
[3] J. K i m, B. v a n d e r B r u g g e n, The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment; Environmental Pollution **158**, 2335-2349 (2010).
[4] N. K a t t a m u r i, J.H. S h i n, B. K a n g, C.G. L e e, J.K. L e e, C. S u n g, Development and surface charakterization of positively charged filters, Journal of Materials Science **40**, 4531-4539 (2005).
[5] M. W e g m a n n, B. M i c h e n, T. L u x b a c h e r, J. F r i s c h, T. G r a u l e, Modification of ceramic microfilters with colloidal zirconia to promote the adsorption of viruses from water, Water Research **42**, 1726-1734 (2008).
[6] M. W e g m a n n, B. M i c h e n, T. G r a u l e, Nanostructured surface modification of microporous ceramics for efficient virus filtration, Journal of the European Ceramic Society **28** 1603-1612 (2008).
[7] E. K a w e c k a - C e b u l a, Z. K a l i c k a, J. W y p a r t o w i c z, Filtration of nonmetallic inclusions in steel: Archives of Metallurgy and Materials **51**, 2, 261-268 (2006).

Received: 20 March 2011.