

Clay Ceramic Pellets for Water Treatment

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Abstract — Two different Quaternary clays from deposits Slucenieki and Prometejs were used for production of porous ceramic pellets. 3 wt % of sawdust additive was used to increase porosity of the obtained ceramic. Porosity and surface area of pellets was determined by mercury porosimetry. pH values after water immersion of fired pellets were determined using a pH meter. Pellets produced from both clays after sintering at similar temperatures had different pore size distribution and different sorption properties. Sorption properties were determined for a molecular substance (iodine) and anionic organic substance (methyl orange dye).

Keywords — Ceramic pellets, pH of water immersion, porosity, sorption of pollution.

I. INTRODUCTION

Environment is polluted with various substances such as heavy metal ions, solvents, pesticides, etc. and demand of various sorbents, filters, sorption and filtering membranes and the like increases. Suitable materials for environmental technologies are clays and clay ceramic materials. Natural clays are characterised with sorption ability of different chemical compositions [1]–[6]. However, such materials have a weak point. Considering colloidal character of clay minerals, after purification of polluted water such water contains other kind of pollution — colloidal particles of clay. As a result there other technological processes and equipment for purification of this water are needed. Sintered porous clay pellets help to resolve this disadvantage regarding water purification technologies. Binding of heavy metal ions in the ceramic materials from water solutions is widely studied [7]–[13]. Clay ceramics are known for their adsorptive properties that allow the use these materials in water treatment processes. Sorption properties can vary over a wide range, depending on mineralogical and chemical composition of clay, type of additives, firing temperature, porosity and the specific surface area of pores.

Some of the most common ways to improve sorption properties of clay ceramic are: the use of various additives and/or chemical treatment. Some properties of ceramic materials such as porosity and the specific surface area are changed in both cases. Previous studies show that different additives can either improve or decrease sorption properties. Sorption ability depends on the character of pollutant and its chemical properties [14], [15].

II. MATERIALS AND METHODS

Two different Quaternary clays from Slucenieki and Prometejs deposits were used for production of porous ceramic pellets. The main difference between both clays was the grain size distribution: clay from Slucenieki deposit is lean with a

large content of sand fraction $\varnothing \geq 0.05$ mm and both have large amount of clayey fraction $\varnothing \leq 0.005$ mm.

Pellets were formed from plastic body with 3 wt % saw dust additive with $\varnothing \leq 2$ mm. Diameter of pellets was 4–5 mm. In the case of clay Prometejs a second composition was made in which extra additive — 2 wt % glycerine — in was used together with sawdust. After drying, pellets were sintered at 800 °C, 900 °C, 1000 °C or 1100 °C temperature in accordance with results obtained by thermal analysis of clays. Sintering was done with heating rate 300 °C/h, holding time at the maximum temperature was 1 h.

Phase composition of obtained materials was characterised by X-ray diffraction (XRD *Rigaku Ultima+*, Japan) with Cu K α radiation. Mercury intrusion porosimetry was used to determine pore size distribution in ceramic; it was carried out using *Quantachrome Instrument PoreMaster*. pH of water immersion of fired pellets was determined using a pH-meter *Mettler Toledo Multi Seven*. Zeta potential of ceramic materials was determined using equipment *Malvern Zetasizer Nano Z*, light source was He-Ne laser with wavelength 633 nm. Sorption ability was determined using a titrimetric method for 0.01 N solution of iodine (a substance with a molecular bond). The sorption ability of soluble organic substances (dye methyl orange) was determined using UV-visible light spectrophotometer *GENESYS 10S UV — Vis* at 464 nm wavelength. On all occasions the sorption ability was determined depending on the sorption time.

III. RESULTS AND DISCUSSION

Chemical composition and grain size distribution of investigated clays (Table I and Table II) differed greatly between both raw materials.

Both investigated clays are carbonate containing Quaternary clays. CaO content in clay Slucenieki was two times larger and determined some of the ceramic properties such as porosity and pore size distribution of sintered pellets above decomposition temperature of carbonates — 800 °C. Iron (III) oxide content was two times larger in clay Prometejs than in clay Slucenieki. Iron oxide content also promoted sintering of clay Prometejs and properties of sintered pellets. The main reason for the differing properties and their result — differing sorption activities of pellets produced from these clays — was differences in grain size distribution for both raw materials. Clay Slucenieki is lean because sand and dust fractions together exceed 50 wt %, while sand and dust fractions together in clay Prometejs constituted only 15.1 wt %.

TABLE I
CHEMICAL COMPOSITION OF CLAYS, WT %

Oxides	Clay Slucenieki	Clay Prometejs
SiO ₂	49.16	45.95
Al ₂ O ₃	13.72	17.07
Fe ₂ O ₃	3.15	6.78
CaO	11.18	5.95
MgO	3.35	3.86
TiO ₂	0.55	0.58
Na ₂ O	0.80	0.17
K ₂ O	2.65	3.93
LOI 1000 °C	14.87	14.48

TABLE II
GRAIN SIZE DISTRIBUTION IN INVESTIGATED CLAYS, WT %

Fraction, mm	Clay Slucenieki	Clay Prometejs
Sand $\varnothing > 0.05$	8.5	1.8
Dust $\varnothing 0.05-0.005$	45.5	13.3
Clay $\varnothing < 0.005$	46.0	84.9

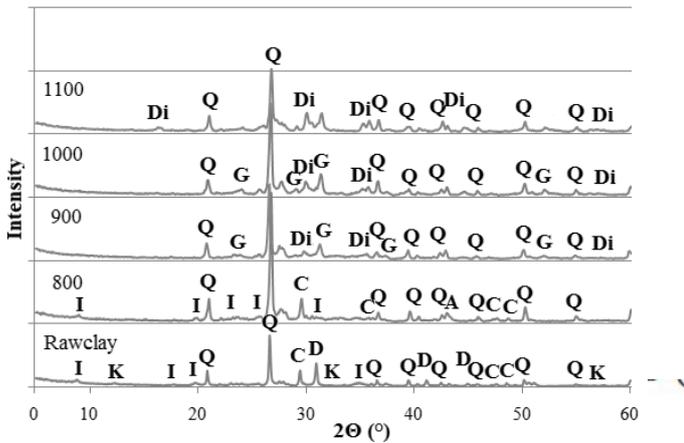


Fig. 1. Phase composition of clay Slucenieki and pellets sintered at various temperatures: K — kaolinite, I — illite, Q — quartz, D — dolomite, C — calcite, Di — diopside, G — gehlenite.

Phase composition in the fired ceramic pellets somewhat differed, although there was no difference in phase composition of raw clays. Gehlenite and diopside crystalline phases formed in ceramic pellets obtained from clay Slucenieki after sintering in the temperature range 900–1100 °C (Fig. 1).

Anorthite and hematite phases formed in pellets obtained from Prometejs clay at the same temperature range and at 1100 °C temperature diopside additionally forms (Fig. 2). Quartz phase remains in all ceramic pellets independently of clay composition and firing temperature.

Such difference between phase formations in the two carbonate containing Quaternary clays is connected with different content of calcium oxide (Table I). Diopside

(CaO·MgO·2SiO₂) and gehlenite (2CaO·Al₂O₃·SiO₂) form in the presence of more calcium oxide in clay Slucenieki.

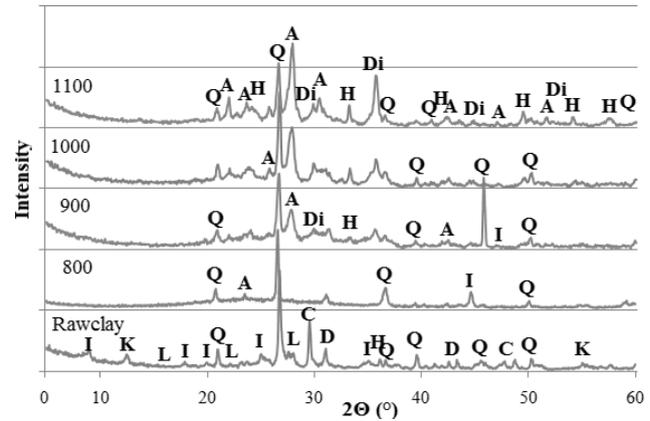


Fig. 2. Phase composition of clay Prometejs and pellets sintered at various temperatures: K — kaolinite, I — illite, Q — quartz, D — dolomite, C — calcite, A — anorthite, Di — diopside, H — hematite.

TABLE III
POROSITY AND CUMULATIVE SURFACE AREA OF PELLETS

Clay deposits	Porosity, %			
	800	900	1000	1100
Slucenieki	22.3	22.5	23.0	22.2
Prometejs	26.7	22.7	22.1	11.2
Prometejs with additive of glycerine	26.7	22.7	19.1	6.8
	Cumulative surface area, m ² /g			
Slucenieki	3.3	2.8	1.7	1.3
Prometejs	12.4	4.9	3.8	3.8
Prometejs with additive of glycerine	18.9	3.9	3.8	1.5

The sintering process of both clays was different; this could be characterised by results of open porosity obtained by mercury porosimetry (Table III). Open porosity of pellets obtained from clay Slucenieki changed in little. Some increase of porosity at the temperature range 900–1000 °C characterised decomposition of calcite and dolomite. Porosity of sintered pellets obtained from clay Prometejs changed considerably, especially at temperature above 1000 °C, and decreased to 11 %. High content of clayey minerals in the raw clay of deposit Prometejs provided such sintering process. Additive of glycerine increased porosity only at the lower sintering temperature — 800 °C.

Difference between ceramic pellets of both clays sintered at the same temperature characterises the volume of pores depending of pore diameter (Fig. 3 and Fig. 4).

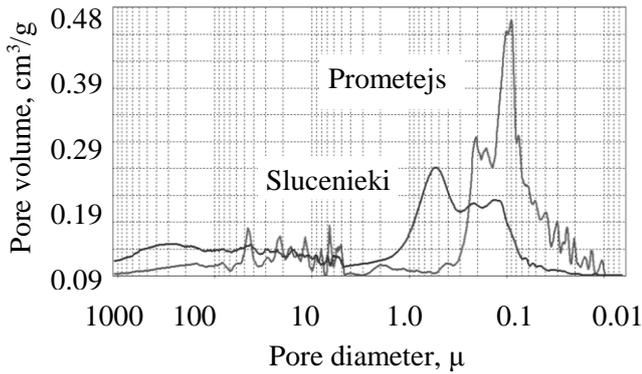


Fig. 3. Pore volume of clay pellets sintered at 800 °C temperature.

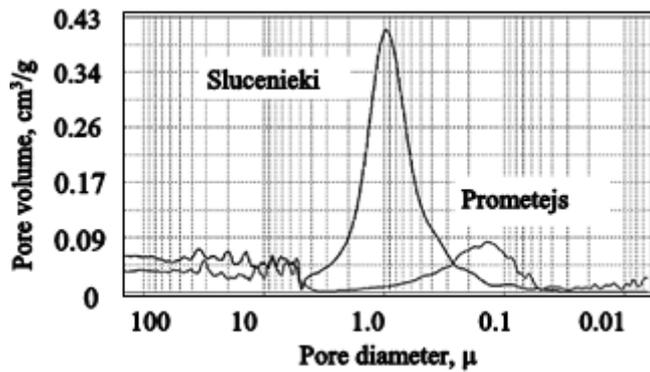


Fig. 4. Pore volume of ceramic pellets sintered at 1100 °C temperature.

Median mean pore size in pellets obtained from Slucenieki clay increased from 0.2 μm in pellets sintered at 800 °C temperature to 0.41 μm in pellets sintered at 1100°C but in pellets obtained from Prometejs clay the mean pore size was a little larger and increased from 0.45 μm to 1.0 μm, if by sintering temperature was increased from 800 °C to 1100 °C. These results correspond to values of cumulative surface area.

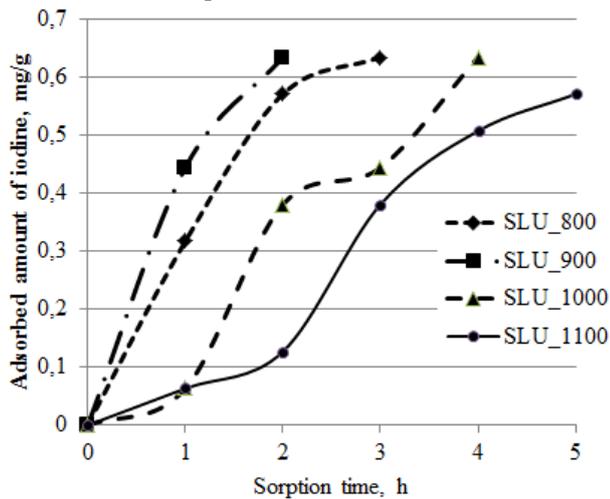


Fig. 5. Sorption ability of iodine on Slucenieki clay pellets.

The sorption ability of both investigated clay pellets was different. The sorption ability of ceramic pellets of clay Slucenieki is shown in Fig. 5. Pellets sintered at temperatures from 800 °C to 1000 °C absorbed all iodine from the solution, but the time in which sorption process was finished was

different. The faster sorption occurred on the pellets sintered at 900 °C temperature and it was 2 h, but the slower sorption occurred on pellets sintered at 1000 °C temperature — 4 h. Pellets sintered at 1100 °C temperature during 5 h adsorb 90 % of iodine from the solution.

Pellets of clay Prometejs sintered at the temperature range from 900 °C to 1000 °C adsorbed all iodine from solution, similarly to ceramic pellets of clay Slucenieki, but sorption was slow and sorption time reached 8 days (Fig. 6).

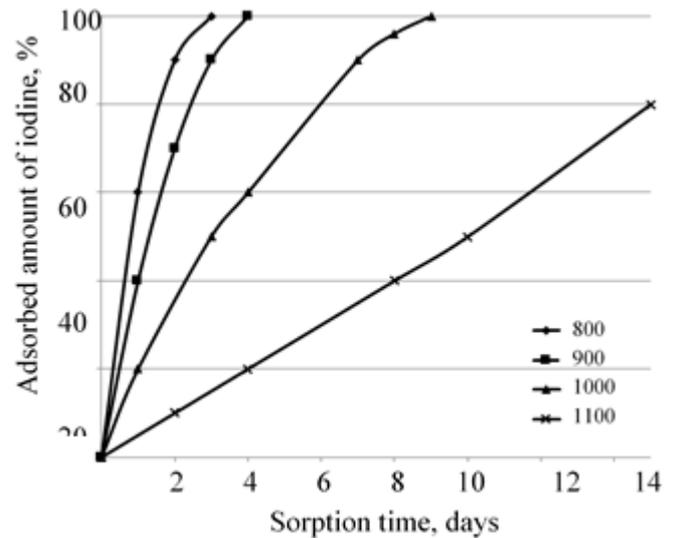


Fig. 6. Sorption ability of iodine on Prometejs clay pellets.

Sorption ability of iodine on ceramic pellets obtained from clay Prometejs with extra additive of glycerine is the same compared to sorption ability of pellets produced only with 3 wt % of sawdust additive to clay and only sorption time increased (Fig. 7), mainly for pellets sintered at lower temperature.

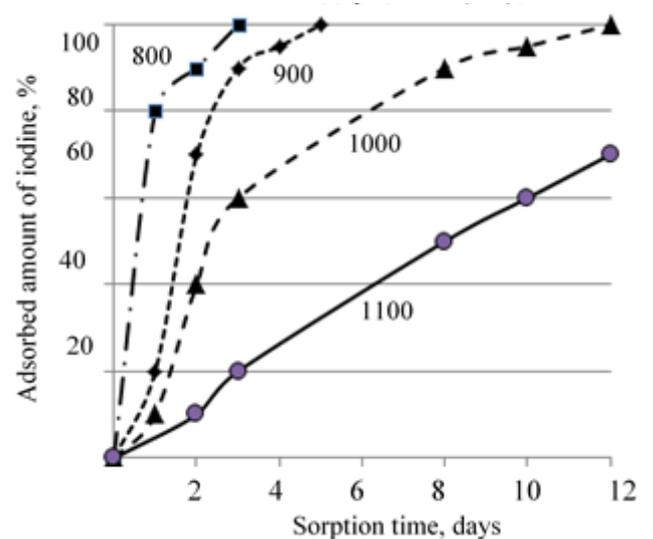


Fig. 7. Sorption ability of iodine on Prometejs clay pellets with additive of glycerine to raw clay.

The sorption ability also depended on pH of solution. Water immersion of sintered ceramic pellets changed pH in wide range depending on sintering temperature and kind of clay used. Results are given in Table IV. Water immersion of Sluceniaki clay pellets sintered at the temperature range from 800 °C to 1100 °C was characterised by alkaline medium in the water immersion, but in the case of clay Prometejs alkaline medium showed only pellets sintered at temperature 800 °C

TABLE IV
PH OF WATER IMMERSION OF SINTERED CLAY PELLETS

Clay	Sintering temperature, °C			
	800	900	1000	1100
Sluceniaki	11.2	11.5	10.7	9.7
Prometejs	9.8	7.0	6.7	6.4
Prometejs with additive of glycerine	10.3	7.1	7.1	6.6

The sorption ability of investigated pellets in regard to organic substances such as methyl orange dye was considerably lower. Sorption of methyl orange dye was detected only on the ceramic pellets of clay Sluceniaki sintered at 800 °C and 900 °C temperatures. Sorption ability was intermediate and reached only 0.07 mg/g and 0.09 mg/g (Fig. 8) or 64 % and 47 %, respectively.

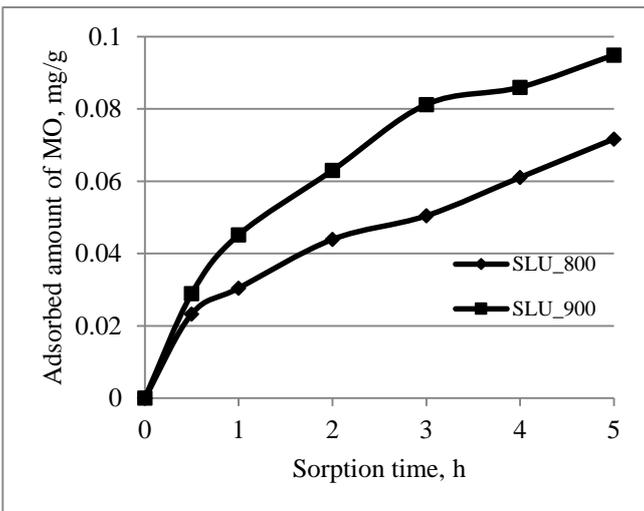


Fig. 8. Sorption ability of methyl orange dye on Sluceniaki clay pellets.

The sorption ability of methyl orange dye on the ceramic pellets from clay Prometejs was lower. Adsorbed amount reached the maximum of 6 % from methyl orange dye that was in the starting solution after 4 h sorption time. Some sorption of methyl orange dye on the pellets obtained from Prometejs clay only with the additive of sawdust was observed for pellets sintered at 800 °C temperature. Sorption of methyl orange dye was detected on Prometejs clay pellets obtained from clay with additive of glycerine sintered at three temperatures with the exception of pellets sintered at 1000 °C temperature (Fig. 9). A character of sorption was similar both in case of pellets without additive of glycerine and in case of raw clay sintered at 800 °C temperature and on pellets with additive of glycerine to raw clay. A little similarity of sorption processes was shown in case

of pellets sintered at 900 °C and 1100°C temperatures obtained from clay with addition of glycerine.

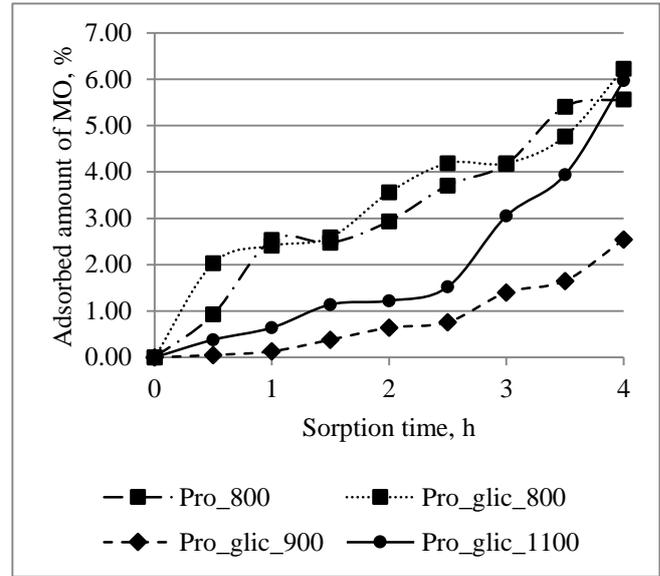


Fig. 9. Sorption ability of methyl orange dye (MO) on Prometejs clay pellets and on pellets obtained by addition of glycerine to raw clay.

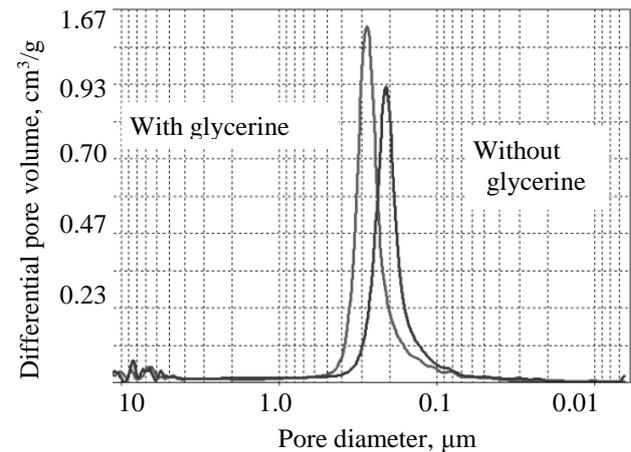


Fig. 10. Pore volume of pellets sintered at 900 °C temperature with and without addition of glycerine.

Difference concerning methyl orange dye between sorption ability of ceramic pellets obtained from clay Prometejs with addition of glycerine to raw clay and without this additive could not be explained only by results of mercury porosimetry. In the case of pellets sintered at 900 °C temperature (Fig. 10) some shift of characteristic pore diameter in direction of larger pores from 0.21 μm to 0.28 μm and larger pore volume from 0.93 cm³/g to 1.45 cm³/g was a small difference compared to the large difference in sorption ability. In addition some clarity was given in results after determination of zeta potential of sintered pellets in the water (Table V).

TABLE V
ZETA POTENTIAL OF CLAY CERAMIC PELLETS

Ceramic pellets of clay deposits	Sintering temperature, °C			
	800	900	1000	1100
Slucenieki	-11.5	-15.4	-18.9	-20.4
Prometejs	0.07	-0.77	0.17	0.09
Prometejs with glycerine	-23.0	-27.5	-33.7	-24.7

Zeta potential of ceramic pellets obtained from clay Prometejs was different depending on the composition of ceramic body for the ceramic pellets. The value of zeta potential of pellets obtained from raw clay only with additive of sawdust was very low. Very small particles of milled pellets were not charged. Charge of sorbent is not significant to sorption of molecular compound I₂ and this sorption is physical. By sorption of anionic organic dye (methyl orange dye) the charge of sorbent had important role and sorption process was more chemical than physical.

Sorption ability of obtained pellets depended at first both on chemical composition of clays and grain size distribution in clays. Clay with low content of carbonate formed porous structure with high water uptake and low density in the process of sintering. These properties of clays further determined structure and chemical properties of ceramic pellets and, in result, the sorption ability of these materials. Sorption of molecular compound iodine is a physical process which is characterised by formation of iodine layer on the surface of sorbent and on the wall of pores. Such process was going on in the case of pellets obtained from lean clay Slucenieki. Porosity of pellets changed a little all over the sintering range. Sorption ability of pellets reached 0.6 mg/g during 2–5 h. Quaternary clay from deposit Prometejs was characterized by comparatively low content of carbonates and high content of clayey fraction. Relatively dense structure with smaller pore size formed in the sintering process. Sorption of iodine on these clay ceramic pellets was going on very slowly and sorption process was longer.

Sorption process of anionic organic substance (methyl orange dye) differed from the sorption process of neutral substance. Important role was played in addition to pH of the solution and zeta potential of the sorbent in this case. Sorption of methyl orange dye on the both kinds of pellets differed less. On the ceramic pellets of clay Slucenieki sintered at 800 °C and 900 °C 64 % and 47 % of methyl orange dye dissolved in the starting solution was adsorbed, respectively. Immersion of these pellets in water showed larger pH values — 11.2 and 11.5, respectively, and larger cumulative surface area 3.3 m²/g and 2.8 m²/g, respectively, and similar value of zeta potential. The sorption ability of ceramic pellets from clay Prometejs was low and reached 6 % only. The determinative factor was the pH of these pellets in the water immersion. In spite of content of carbonates in this clay similar to clay Slucenieki alkaline medium of pellets immersion had pellets sintered only at 800 °C. Methyl orange dye adsorbs on these pellets only in a little amount. Similar sorption was established for the pellets

obtained from clay Prometejs with additive of glycerine to the raw clay.

IV CONCLUSION

Sorption of clay ceramic was selective and the sorption ability determined various factors depending on the composition of clay (chemical composition and grain size distribution) and the sintering temperature of ceramics. Sorption ability depended on the properties of polluted substances. In case of molecular composition with covalent unipolar binding (I₂) sorption ability depended mainly on the pore structure of sorbent, pore size and the value of surface area. In case of anionic organic substance (methyl orange dye) sorption ability depended on the pH of water after the immersion of pellets and surface charge of these pellets. Value of surface area and pore size did not play such an important role.

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Ruta Švinka, Visvaldis Švinka, Inga Pudže, Mārīte Damberga. Mālu keramikas granulas ūdens apstrādei.

Porainas keramikas granulas iegūva no diviem atšķirīgiem kvartāra māliem: liesiem Šļūcenieku un trekniem Prometeja atradnes māliem. Abi māli atšķiras gan ar karbonātu saturu (CaO saturs, attiecīgi, 11,18 % un 5,95 %), gan ar dažādu mālu frakcijas saturu (attiecīgi, 46,0 % un 84,9 %). Granulu porainības palielināšanai mālam pievienoja 3 masas% koksnes skaidu ($\varnothing \leq 2$ mm) un granulas ar diametru 5 mm veidoja no plastiskas masas ar ekstrūzijas paņēmienu. No Prometeja māliem izgatavoja divu veidu granulas — otrā veida granulu veidošanas masai pievienoja arī 2 masas% glicerīna. Granulas apdedzināja 800 °C, 900 °C, 1000 °C un 1100 °C temperatūrā. Granulu sorbcijas spēju noteica attiecībā uz jodu, kas ir molekulārs savienojums ar kovalentu saiti, un attiecībā uz anjonu tipa krāsvielu (metiloranžu), kurā starp katjonu un anjonu pastāv jonu saite. Pastāvēja atšķirība abu mālu sorbcijas spējās gan no granulu īpašību viedokļa, gan no atšķirīgo vielu sorbcijas rakstura. Šļūcenieku mālu granulu porainība bija lielāka, salīdzinot ar tādā pašā temperatūrā apdedzinātām Prometeja mālu granulām. Sorbējot vielas ar kovalentu nepolāru saiti, sorbcija bija fizikāla, t.i., sorbcijas spēja bija atkarīga no poru izmēriem un virsmas laukuma. Tāpēc Šļūcenieku mālu keramikas granulu sorbcijas spēja attiecībā uz jodu bija lielāka un notika ievērojami īsākā laikā, salīdzinot ar Prometeja mālu granulām. Attiecībā uz savienojumu sorbciju, kuros pastāv jonu saite, svarīga nozīme bija absorbcijas vides pH un daļiņu zeta potenciālam, t.i., virsmas lādiņam, bet porainība, poru izmēri un virsmas laukums mazāk ietekmēja šādu vielu absorbciju. Granulām, kuru veidošanas procesā mālu masai pievienoja arī glicerīnu, konstatēts vidēji liels zeta potenciāls (23–34, atkarībā no apdedzināšanas temperatūras), kas arī ietekmēja sorbciju savienojumos ar jonu saiti. Tomēr Prometeja mālu gadījumā metiloranža sorbcija bija maza un nepārsniedz 6 % no šķīdumā esošā metiloranža daudzuma salīdzinot ar metiloranža sorbciju uz Šļūcenieku mālu granulām, kas bija 40–60 %.