# Physicochemical Properties of Marl and Travertine and their Thermally Modified Forms in the Perspective of Phosphorus Removal from Wastewater

Sylwia Gubernat[1,2*], Adam Masłoń[3], Joanna Czarnota[3], Piotr Koszelnik[3]

[1] Doctoral School of Engineering and Technical Sciences, Rzeszow University of Technology, aleja Powstańców Warszawy 12, 35-959 Rzeszów, Poland

[2] Inżynieria Rzeszów S.A., ul. Podkarpacka 59A, 35-082 Rzeszów, Poland

[3] Department of Environmental and Chemistry Engineering, Rzeszow University of Technology, aleja Powstańców Warszawy 6, 35-959 Rzeszów, Poland

* Corresponding author's e-mail: pkoszel@prz.edu.pl

**ABSTRACT**

The paper presents physicochemical studies of nine reactive materials for removing phosphorus from wastewater and water. The materials under analysis are raw forms of marl and travertine along with their thermally treated forms at temperatures of 500 °C, 650 °C, 700 °C (travertine), 700 °C, 900 °C, 1000 °C (marl) and the commercial material Polonite®. The scope of the research included morphological analysis and elemental composition, specific surface area, pore volume and diameter, losses on ignition and the amount of elements leached from materials. The results of the research allowed assessing the impact of physicochemical properties and thermal modification on the efficiency of phosphorus binding by these materials. All the tested sorbents show the highest calcium content among the elements with the ability to bind phosphorus. The size of the specific surface does not determine the efficiency of phosphorus retention by the tested materials; therefore it is advisable to study the mechanism of its binding. The thermal modification process, along with the increase in the treatment temperature, improves the regularity of marl and travertine structures, which also manifests itself in increasing the efficiency of phosphorus removal.

**Keywords:** wastewater treatment; green chemistry; ecotechnology; reactive materials; adsorption; phosphorus.

## INTRODUCTION

The high requirements placed on new technologies of wastewater and water treatment in terms of phosphorus removal, coupled with the simultaneous high demand for it, make it necessary to look for new, effective sorption materials that will also enable the recovery of raw materials, e.g. by using in agriculture their form with adsorbed phosphorus, which meets the assumptions of the circular economy, and also reduces the problem related to the availability of this element [Chen et al., 2016; Golroudbary et al., 2019; Zhu et al., 2023].

In the search for new sorbents, physical and chemical properties should be taken into account, which may determine the choice of particular materials for testing. In the case of phosphorus removal, it should be determined whether the potential material contains the elements with a natural ability to bind it. In this respect, they have been classified depending on the type of reaction mechanism into two groups: Ca/Mg and Al/Fe [Wu et al., 2006; Gubernat et al., 2020]. Other physicochemical properties should indicate the characteristics of the material in terms of its use as a filtering medium/aiding purification, which, apart from not interfering with the operation of the purification device, should not adversely affect the chemical parameters and physicochemical properties of the purified medium [Jucherski et al., 2017; Bus et al., 2022]. For newly identified phosphorus sorbents beyond the materials included in

the review [Gubernat et al., 2020], consideration should be given to: biochars [Almanassra et al., 2021; Luo et al., 2022], silica nanoparticles prepared from rice husk ash [Nguyen 2022], cockle shell powder [Nayeem et al., 2023], eggshells and calcined eggshells [Park et al., 2022] agnetite/zirconium-comodified attapulgite (Fe/ZrATP) [Deng et al., 2023]. The basic properties of sorbents/filter materials include structural properties, i.e. porosity and surface area. These parameters increase the pollution holding capacity, as well as extend the filtration speed or the duration of the filtration cycle. The density of the material is of particular importance in the case of multi-layer beds and in determining the hydraulic conditions of bed rinsing. The granulometric composition is selected depending on the type and properties of the suspension in the medium to be purified, as well as the purification technology. Specific surface area, pore volume and diameter are most often determined by the Brunauer-Emmett-Teller (BET) method, which consists in determining the $N_2$ adsorption isotherm on the tested material. These parameters inform about the number and size of pores, which play a fundamental role in the intensification of the adsorption process, but in order to confirm it unequivocally, it is necessary to know the nature of the binding, whether it takes place through a physical or chemical process [Garbarczyk, 2010]. Due to a number of properties of materials that allow it to be characterized in physical and chemical terms, the influence of the chemical composition of the purified medium and the conditions of the binding process, it is impossible to clearly indicate the most important factor determining the effectiveness of purification or the probability of implementing a given sorbent on a real scale [Gubernat et al., 2020].

The aim of the work was to study the physicochemical properties of marl and travertine and their thermally treated forms in terms of phosphorus removal from wastewater. The research also included the commercial material Polonite®, which has already been used many times in research on phosphorus sorption [Bus et al., 2022; Hamisi et al., 2022; Renman et al., 2022] from aqueous solutions, enabling a better comparison of the obtained results.

## MATERIAL AND METHODS

The materials tested in the field of physicochemical properties in terms of phosphorus

binding were marl and travertine with their thermal modifications and the commercial material Polonite®.

Travertine is a carbonate sedimentary rock that was formed in specific geological processes as a result of chemical or biochemical reactions of organic and inorganic compounds in the presence of groundwater resources rich in calcium and bicarbonates [Mesci 2013; Kalender et al., 2015]. The material for the tests was taken from the mine of this raw material in Poland, in the city of Raciszyn. Travertine was thermally treated at the following temperatures of 500 °C, 650 °C, 700 °C in a laboratory muffle furnace for 1 hour. The modification temperatures were selected in the indicated range because further increase of the modification temperature (700 °C, 900 °C, 1000 °C) resulted in the transformation of the solid material into a soluble powder, which caused changes in the parameters of the purified medium [Gubernat et al., 2022].

Marl is a sedimentary rock consisting of carbonates and clay minerals, and in smaller amounts of quartz pelite and other allogeneic and autogenous sedimentary rock minerals. Marls are formed in the marine and lake environment. Depending on the ratio of the carbonate to the clay part, marly claystones, clay marls, marls and marly limestones can be distinguished [Kurdowski 1981; Ryka et al., 1982]. The material for the study was collected from the area of the Lublin Upland in Poland. Marl was heated in a laboratory muffle furnace for 1 hour at temperatures of 700 °C, 900 °C, and 1000 °C. Lower modification temperatures (500 °C, 650 °C, 700 °C) did not change the properties of the material towards a stable, insoluble sorbent [Gubernat et al., 2022].

Polonite® is a commercialized filter material that is produced in a fraction of 2–6 mm after crushing and screening, from sedimentary bedrock through its thermal treatment at 900 °C. This material is used to treat wastewater and surface runoff from agricultural fields, where it can be reused in adsorbed phosphorus form [Renman et al., 2010].

Selected materials were tested in terms of physicochemical properties in terms of phosphorus binding from wastewater. Morphological analysis and elemental composition were determined by scanning electron microscopy (SEM). The BET surface area, pore volume and diameter were determined using the porosimetric method using the Nova Station A apparatus. The true density of the materials was determined by

the pycnometric method using the ULTRAPYC 1200e pycnometer.

Morphological analysis of the materials after the study of the sorption process, which is discussed in detail in the publication [Gubernat et al., 2022], was carried out using a scanning electron microscope MIRA3 by TESCAN, with an X-ray spectroscopy (EDS) adapter by Panalytical, using scanning electron microscopy SEM-EDS (Scanning Electron Microscopy – Energy Dispersive Spectroscopy).

The amount of elements leached from materials, per unit of their mass, was determined in accordance with the PN-EN 1744-3 standard. Four-gram samples of material with a diameter of 1–2 mm were shaken for 24 hours with 40 ml of distilled water (at a ratio of 1:10). The resulting aqueous extract was filtered through a 0.45 μm membrane filter. The concentrations of released elements were determined by total reflection X-ray fluorescence (TXRF) using the X-ray spectrometer S2 PICOFOXTM by Bruker AXS Microanalysis GmbH.

Losses on ignition at temperatures of 700 °C, 900 °C, 1000 °C for marl and 500 °C, 650 °C, 700 °C for travertine were determined as the difference in the weight of the tested material before and after heating, related to the weight of the material before heating.
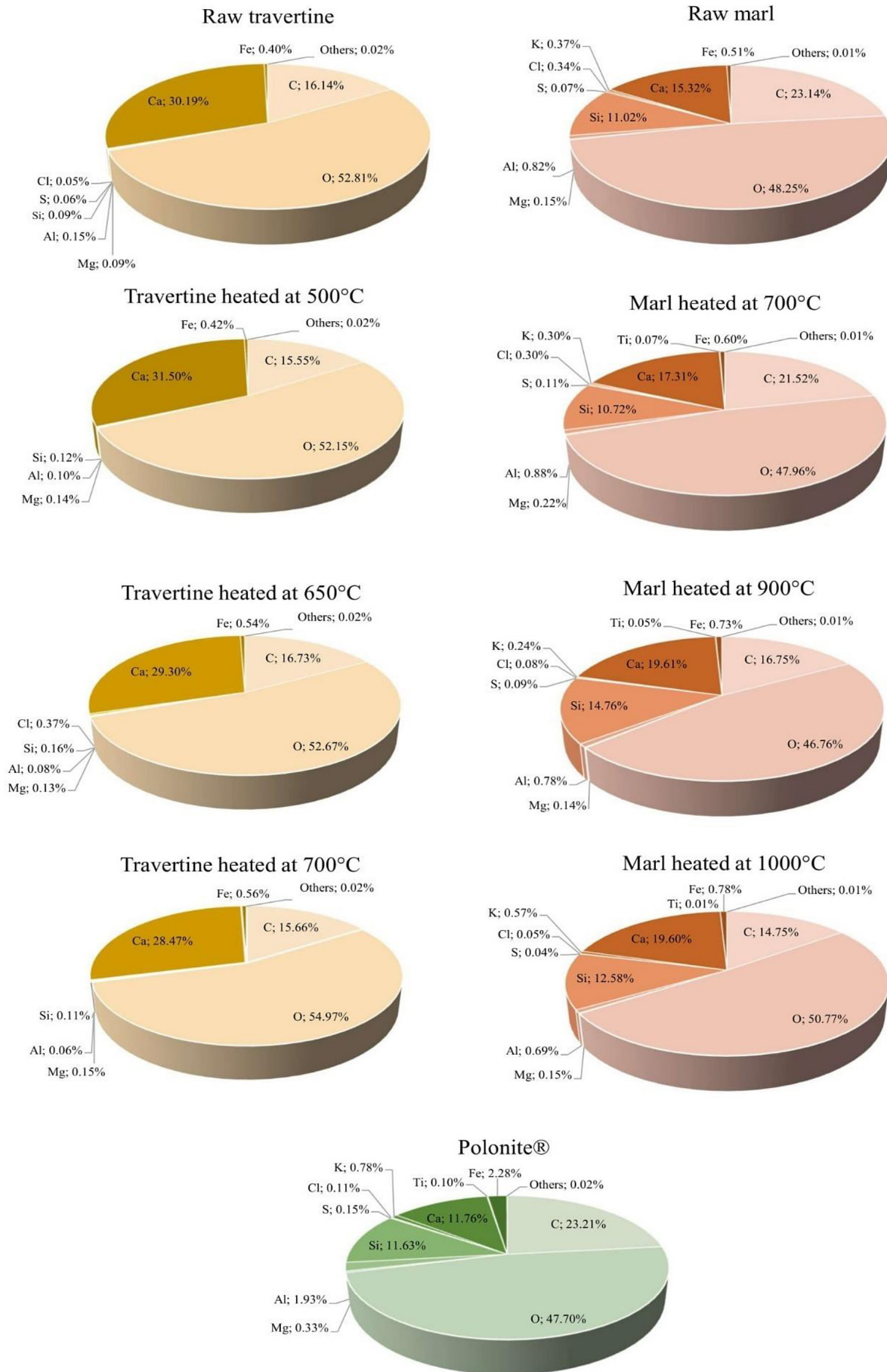
## RESULTS AND DISCUSSION

In the search for new materials as sorbents to remove phosphorus, the first step is to identify the chemical composition in order to determine the presence of compounds with a natural ability to bind phosphorus, i.e. Al, Fe, Mg, Ca. The elemental composition of the materials is shown in Figure 1.

Raw travertine with its thermally treated forms is characterized by high calcium content - in the range of 30.19–28.47%, which decreases with increasing modification temperature. A similar trend was observed in the case of aluminum, present in the chemical composition of travertine and its modifications in the range of 0.15–0.06%. The iron content in these materials increased with the processing temperature in the range of 0.40–0.56%, as did magnesium, the share of which oscillated from 0.09 to 0.15%.

Raw marl, for which the phase composition was determined at an earlier stage of research [Gubernat et al., 2022], with a calcium carbonate content of 93.5% and a silica content of 6.5%, it represents marl limestone or chalk marl. The assessment of the elemental composition showed that the calcium content in marl and its modifications is lower than in travertine and ranges from 15.32 to 19.60%. Aluminum, on the other hand, is an element present in a greater amount than in travertine, i.e. at the level of 0.82–0.69%, and its content also decreases with increasing processing temperature. Iron in the elemental composition of marl and its thermally treated forms increases with the modification temperature and is present at the level of 0.51–0.78%. Magnesium is present in marl and its modifications in amounts from 0.15 to 0.22% as well as no effect of temperature on its content were observed. Polonite®, a clay-carbonate rock, has the lowest calcium content (11.76%). On the other hand, aluminum, iron and magnesium are present in this material in greater amounts than in other tested sorbents (1.93%, 2.28%, 0.33%, respectively), which is confirmed by research [Cucarella et al., 2009].

The physical properties of the materials, i.e. density, BET surface area, pore diameter and volume, were shown in Figures 2 and 3. In terms of density, the effect of the treatment temperature was observed especially for marl, where the value of this parameter increased from 2.78 g/cm$^3$ for the raw form to 2.99 g/cm$^3$ for the sample subjected to heat treatment at a modification temperature of 700 °C. The BET specific surface area for travertine and its modifications was in the range of 0.20–0.34 m$^2$/g, where for thermally treated forms, an increase in this parameter was observed relative to the raw form, but with an increase in the modification temperature, the value decreased. For raw marl and its thermal modification at 700 °C, the BET specific surface area is equal to 24.40 and 23.26 m$^2$/g, respectively; however, with a further increase in the heating temperature, a clear decrease of this parameter is observed, which was described by [Gubernat et al., 2022] as a result of transition of $CaCO_3$ and $SiO_2$ into $CaSiO_3$, $CaSiO_4$ forms. The Polonite® material, which is also a thermally treated material but with a higher silica content than marl, has a density of 2.52 g/cm$^3$ and a surface area of level 10.61 m$^2$/g, which differ from the results of research on the opoka and its thermal modifications [Brogowski et al., 2004; Cucarella et al., 2009], which may be due to the heterogeneity of the composition of mineral materials taken from their natural place of occurrence.

**Raw travertine**

Fe; 0.40%  Others; 0.02%
C; 16.14%
Ca; 30.19%
O; 52.81%
Cl; 0.05%
S; 0.06%
Si; 0.09%
Al; 0.15%
Mg; 0.09%

**Raw marl**

K; 0.37%  Fe; 0.51%  Others; 0.01%
Cl; 0.34%
S; 0.07%  Ca; 15.32%  C; 23.14%
Si; 11.02%
Al; 0.82%
O; 48.25%
Mg; 0.15%

**Travertine heated at 500°C**

Fe; 0.42%  Others; 0.02%
C; 15.55%
Ca; 31.50%
O; 52.15%
Si; 0.12%
Al; 0.10%
Mg; 0.14%

**Marl heated at 700°C**

K; 0.30%  Ti; 0.07%  Fe; 0.60%  Others; 0.01%
Cl; 0.30%
S; 0.11%  Ca; 17.31%  C; 21.52%
Si; 10.72%
Al; 0.88%
O; 47.96%
Mg; 0.22%

**Travertine heated at 650°C**

Fe; 0.54%  Others; 0.02%
C; 16.73%
Ca; 29.30%
O; 52.67%
Cl; 0.37%
Si; 0.16%
Al; 0.08%
Mg; 0.13%

**Marl heated at 900°C**

Ti; 0.05%  Fe; 0.73%  Others; 0.01%
K; 0.24%
Cl; 0.08%  Ca; 19.61%  C; 16.75%
S; 0.09%
Si; 14.76%
O; 46.76%
Al; 0.78%
Mg; 0.14%

**Travertine heated at 700°C**

Fe; 0.56%  Others; 0.02%
C; 15.66%
Ca; 28.47%
O; 54.97%
Si; 0.11%
Al; 0.06%
Mg; 0.15%

**Marl heated at 1000°C**

Fe; 0.78%  Others; 0.01%
Ti; 0.01%
K; 0.57%  C; 14.75%
Cl; 0.05%  Ca; 19.60%
S; 0.04%
Si; 12.58%
O; 50.77%
Al; 0.69%
Mg; 0.15%

**Polonite®**

K; 0.78%  Fe; 2.28%
Cl; 0.11%  Ti; 0.10%  Others; 0.02%
S; 0.15%  Ca; 11.76%  C; 23.21%
Si; 11.63%
Al; 1.93%
O; 47.70%
Mg; 0.33%

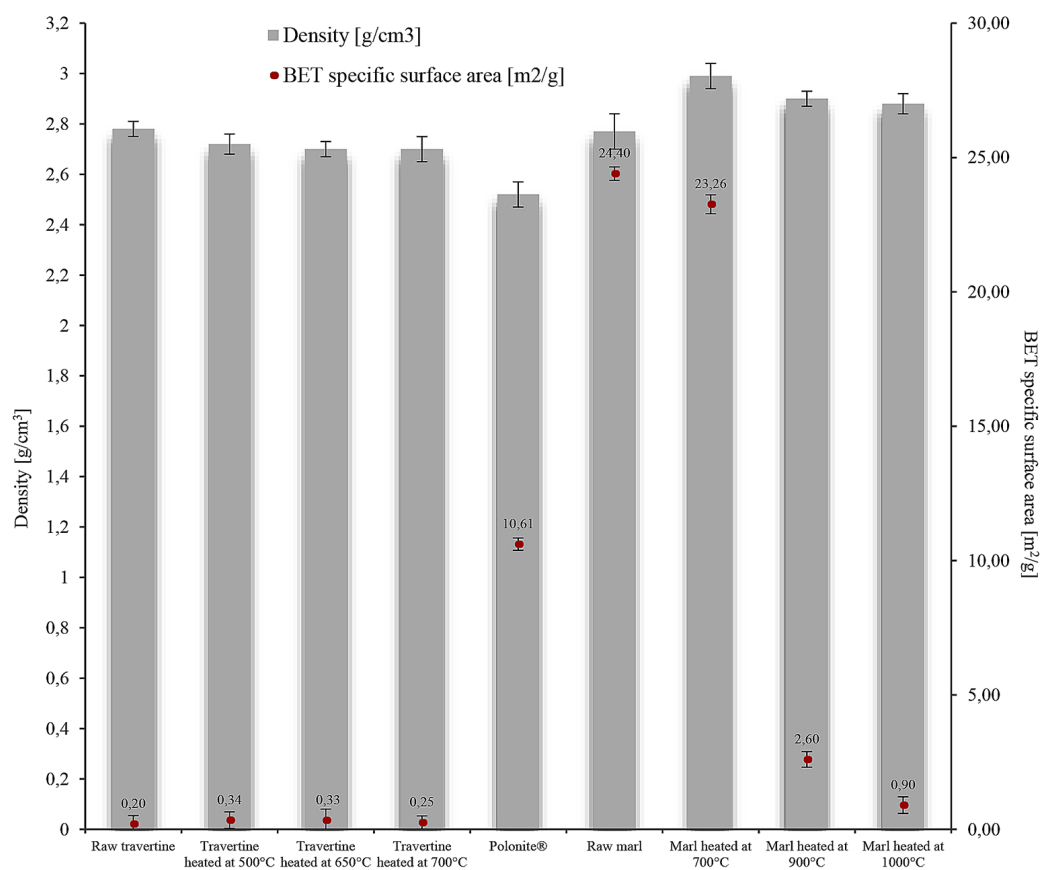**Figure 1.** Elemental composition of the tested materials

**Figure 2.** Density and BET surface area of the tested materials
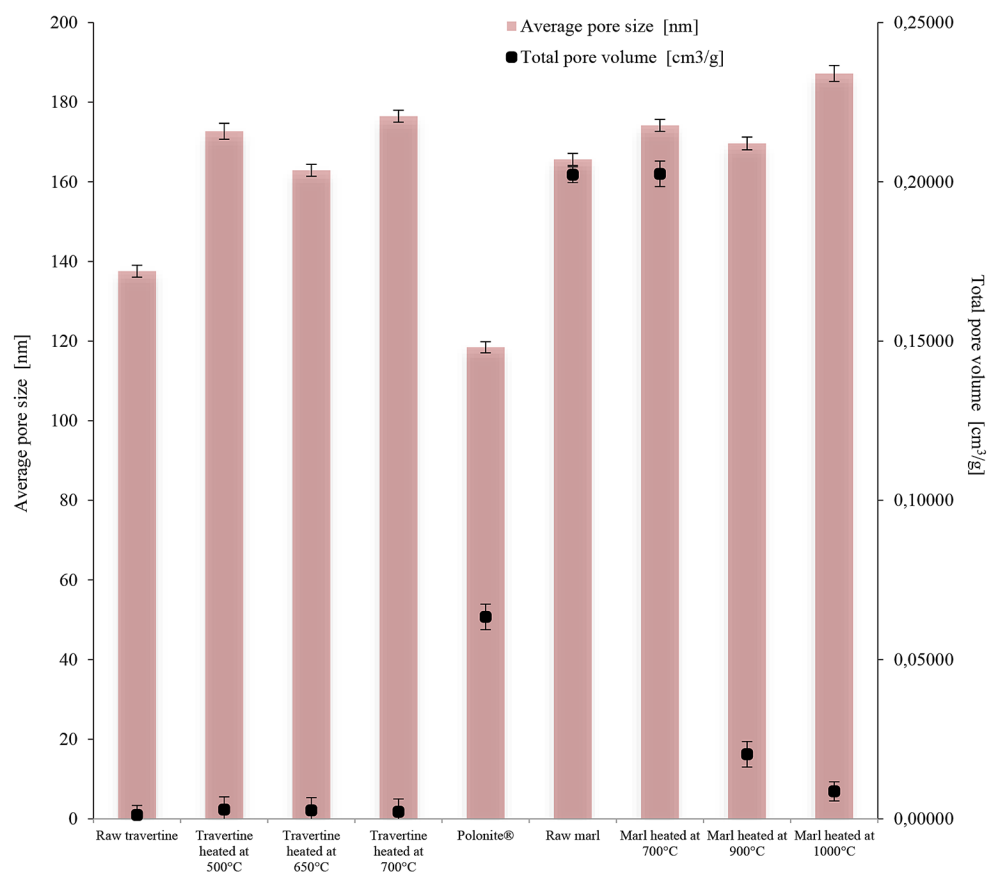


**Figure 3.** Average pore size and volume of the tested materials

The available literature data on phosphorus sorbents allow concluding that increasing the specific surface of materials, for example by thermal modification of bauxite [Altundogan et al., 2003], biochars [Zhu et al., 2020], deposition of ferrihydrite [Xiong et al., 2008], lanthanum [Xie et al., 2013] on diatomite, modification of bentonite with hydroxyAl [Yan et al., 2010] or lanthanum III [Kuroki et al., 2014], increases the sorption capacity of these materials. However, as in the present study, there are cases such as acadama clay, the modification of which reduced the specific surface area while increasing the sorption capacity [Wang et al., 2018], confirming that each material must be identified individually and that the nature of the phosphorus binding is of importance.

The analyses carried out in terms of the diameter and volume of pores allow concluding that the thermal treatment of materials increases their value; however, in the case of pore volume, a decrease in this parameter is observed with the increase of the modification temperature. All the average pore sizes of the materials fall into the class of macropores, which may explain the low specific surface area, e.g. in relation to activated carbon, which reaches the value of this parameter up to 1500 $m^2/g$, through high microporosity [Garbarczyk 2010].

During subjecting the materials to heat treatment, the values of losses on ignition were determined. Travertine was characterized by a very low value of these losses, which amounted to 0.21%,
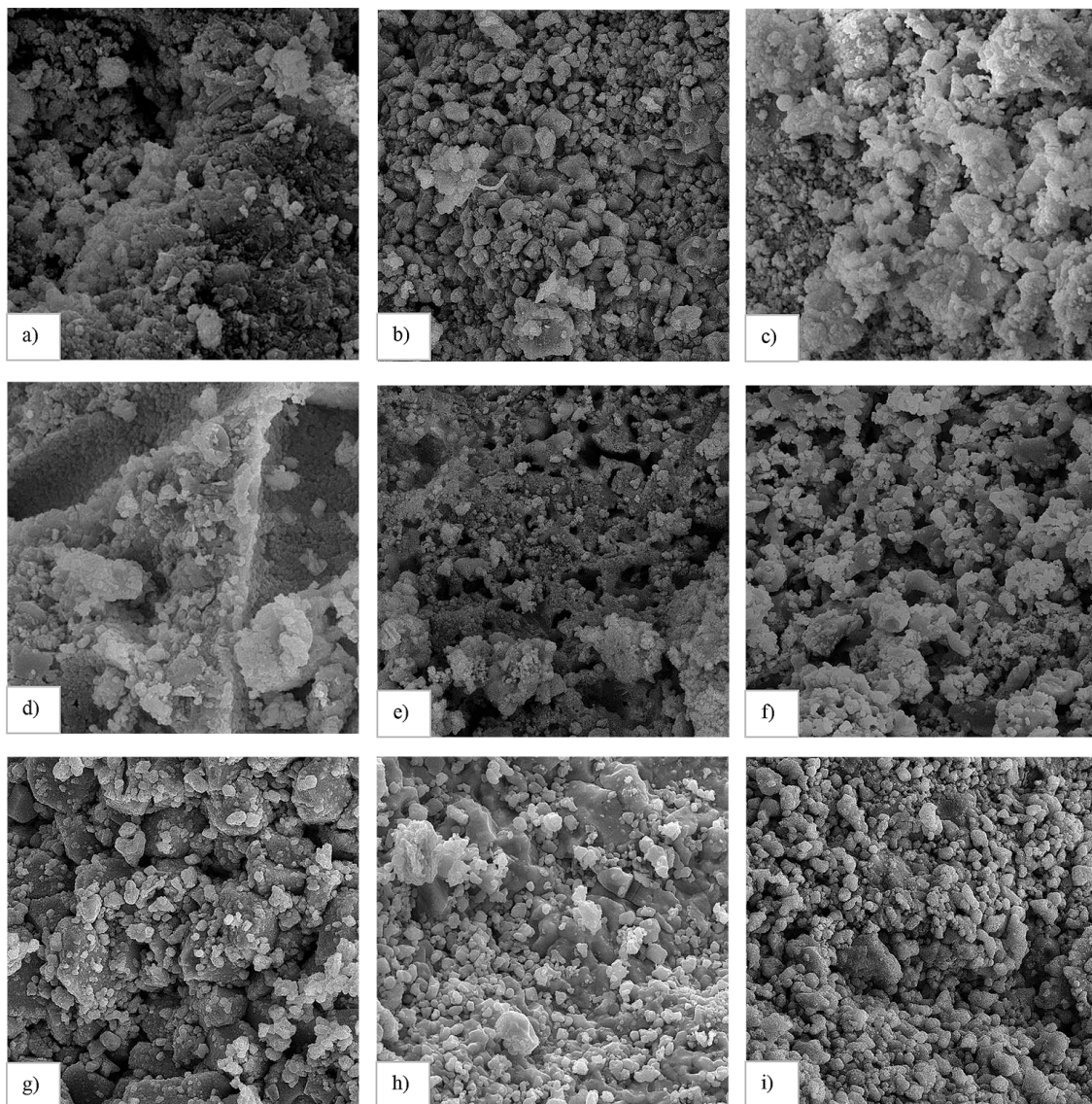


**Figure 4.** Photographs of materials using scanning electron microscopy SEM (magnification 5k) a) raw marl, b) raw travertine, c) Polonite®, d) marl heated at 700 °C, e) marl heated at 900 °C, f) marl heated at 1000 °C, g) travertine heated at 500 °C, h) travertine heated at 650 °C, i) travertine heated at 700 °C

1.47%, 2.66%, respectively, for processing temperatures of 500 °C, 650 °C, 700 °C. Marl also showed an increase in losses on ignition with increasing modification temperature (700 °C, 900 °C, 1000 °C) of 29.44%, 40.23%, 40.48%, respectively, which may indicate that marl in relation to travertine may contain more organic matter. However, it should be emphasized that the loss of mass also
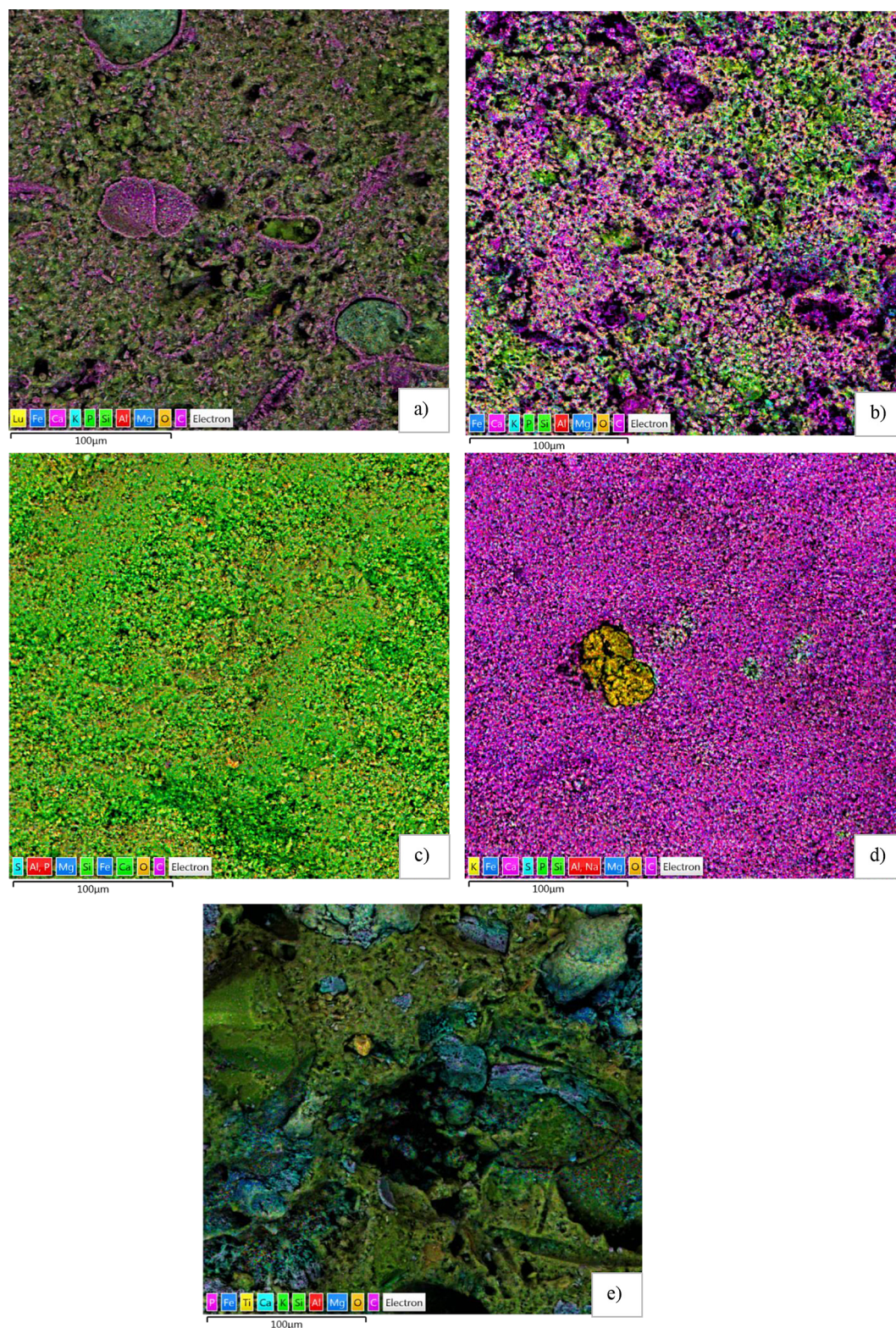


**Figure 5**. Map of the distribution of chemical elements on materials after sorption process, using scanning electron microscopy SEM-EDS (magnification 1k), a) natural marl, b) natural travertine, c) travertine heated at 700 °C, d) marl heated at 1000 °C, e) Polonite®

**Table 1.** The amount of leached elements from materials

| Material | Ca | S | Cl | K | Fe | Ni | Cu | Zn | Br | Sr | P | Pb | Si | Al | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | µg/g | | | | | | | | | | | | | | |
| Raw travertine | 107.34 | 21.23 | 35.46 | 12.37 | 0.52 | 0.01 | 0.04 | 0.92 | 0.20 | 0.23 | 0.95 | - | - | - | 0.19 |
| Travertine heated at 500 °C | 113.06 | 23.39 | 60.57 | 26.53 | 0.93 | 0.02 | 0.10 | 1.21 | 0.45 | 0.31 | 1.68 | 0.00 | - | 1.88 | 0.55 |
| Travertine heated at 650 °C | 237.75 | 18.95 | 50.25 | 19.94 | 0.29 | 0.01 | 0.05 | 0.35 | 0.37 | 0.65 | - | - | - | - | 0.20 |
| Travertine heated at 700 °C | 5589.31 | 7.57 | 28.32 | 32.83 | 0.25 | - | 0.05 | 0.69 | 0.38 | 1.14 | - | 0.03 | - | - | 0.21 |
| Polonite® | 212.61 | 145.89 | 67.13 | 57.99 | 2.05 | 0.73 | 2.52 | 0.24 | 0.84 | 2.31 | 4.86 | 0.63 | 440.20 | - | - |
| Raw marl | 341.17 | - | - | - | 43.38 | 2.88 | - | 2.47 | - | - | - | - | - | - | - |
| Marl heated at 700 °C | 734.41 | - | 144.49 | 170.23 | 4.33 | - | - | 0.80 | 1.31 | 7.63 | - | - | - | - | - |
| Marl heated at 900 °C | 9057.69 | - | - | 115.44 | 9.46 | - | - | 0.51 | 0.46 | 19.15 | - | - | - | - | - |
| Marl heated at 1000 °C | 1271.75 | - | - | - | 61.98 | - | - | - | - | - | - | - | - | - | - |

results from the release of $CO_2$ due to the thermal decomposition of $CaCO_3$ [Liu et al., 2012, Zapater-Pereyra et al., 2014, Tomaszewicz et al., 2016].

The morphological analysis of the SEM materials, shown in Figure 4, illustrates the structural changes occurring under the influence of the modification temperature. With the increase of the treatment temperature, a clear improvement in the regularity of the marl structures was observed. The grains of the raw form of the material are characterized by irregular, sharp edges, and already at the modification temperature of 700 °C they begin to take on more spherical shapes. Raw travertine grains are characterized by greater regularity of spherical structures than marl, and thermal treatment brings out more repetitive, even shapes. The SEM-EDS analysis, presented in Figure 5, shows the difference in the binding of phosphorus on its surface by individual materials. In the case of natural materials, phosphorus binding takes place evenly over the entire surface, while forms subjected to thermal treatment (including Polonite® material) are additionally characterized by high saturation of specific places. On the basis of SEM and SEM-EDS studies, it can be concluded that thermal treatment increases or uncovers new active sites where phosphorus can be deposited as a result of a chemical or physical process, which at the same time increases the sorption capacity of the material [Carrillo et al., 2020, Zhu et al., 2020].

In terms of leaching of elements from materials (Table 1), it can be seen that the main leached element is calcium. The largest amounts of it, in relation to the mass of the material, were leached from marl heated at 900 °C and from travertine thermally treated at 700 °C. In terms of phosphorus binding, this allows concluding that the released calcium may additionally increase the efficiency of the phosphorus removal process, because it will bind phosphorus as a result of precipitation in the form of insoluble compounds in the treated medium, but not on the surface of the sorbent.

Summing up the assessment of the physico-chemical properties of materials in comparison with their efficiency in binding phosphorus under static conditions, which was described in detail by [Gubernat et al., 2022], it can be concluded that the quantitative advantage of a given element with the ability to bind phosphorus does not have a significant impact on the effectiveness removal, as marl showed a better efficiency despite having a lower calcium content than travertine. The physico-chemical parameters also did not indicate a direct correlation between the phosphorus removal efficiency and their values. For example, both in the case of raw marl and travertine heated at 500 °C, these materials achieved low (compared to other materials) phosphorus retention efficiency, despite the highest values of specific surface areas. In terms of average pore size, it was observed that higher values of these parameters correspond to

higher phosphorus binding efficiency. The exception is travertine heated at 500 °C, which may indicate that the effect on phosphorus binding and sorption capacity of the tested materials, apart from their physicochemical properties, is also the mechanism of phosphorus binding.

## CONCLUSIONS

Physicochemical studies of marl and travertine and their thermally treated forms in terms of phosphorus binding allow concluding that the recognition of physicochemical properties is one of the stages in assessing the possibility of their use in wastewater or water treatment technology, because the values of these parameters do not determine the efficiency of phosphorus binding. On the basis of the physicochemical properties, it is possible to clearly indicate the influence of the temperature of marl and travertine modification in the perspective of retaining phosphorus on their surface – thermal treatment regulates the structure of materials and increases or reveals active sites, consequently improving the efficiency of phosphorus binding by these materials. In order to comprehensively assess marl and travertine with their modifications as phosphorus sorbents, tests should be carried out to determine the nature of the binding process of this element on their surface.

## REFERENCES

1. Chen, M.P., Graedel, T.E. 2016. A half-century of global phosphorus flows, stocks, production, consumption, recycling, and environmental impacts. Glob. Environ. Change-Human Policy Dimens, 36, 139–152. DOI: 10.1016/j.gloenvcha.2015.12.005

2. Golroudbary, A.S.R., El Wali, M., Kraslawski, A. 2019. Environmental sustainability of phosphorus recycling from wastewater, manure and solid wastes. Sci. Total Environ., 672, 515–524. DOI: 10.1016/j.scitotenv.2019.03.439

3. Zhu, F.Y., Cakmak, E.K., Cetecioglu, Z. 2023. Phosphorus recovery for circular Economy: Application potential of feasible resources and engineering processes in Europe. Chem. Eng. J., 454, 15. DOI: 10.1016/j.cej.2022.140153

4. Wu, D.Y., Zhang, B.H., Li, C.J., Zhang, Z.J., Kong, H.N. 2006. Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. J. Colloid Interface Sci., 304, 300–306. DOI: 10.1016/j.jcis.2006.09.011

5. Gubernat, S., Masłoń, A., Czarnota, J., Koszelnik, P. 2020. Reactive Materials in the Removal of Phosphorus Compounds from Wastewater-A Review. Materials. 13, 3377. DOI: 10.3390/ma13153377

6. Jucherski, A., Nastawny, M., Walczowski, A., Jóźwiakowski, K., Gajewska, M. 2017. Suitability studies of alkaline filtration materials for phosphates removal from biologically treated domestic sewage. Environmental Protection, 39, 33–38.

7. Bus, A., Karczmarczyka, A., Baryla, A. 2022. Phosphorus reactive materials for permeable reactive barrier filling - lifespan estimations. Desalin. Water Treat., 245, 9–15. DOI: 10.5004/dwt.2022.27905

8. Almanassra, I.W., McKay, G., Kochkodan, V., Atieh, M.A., Al-Ansari, T. 2021. A state of the art review on phosphate removal from water by biochars. Chem. Eng. J. 409, 15. DOI: 10.1016/j.cej.2020.128211

9. Luo, D., Wang, L.Y., Nan, H.Y., Cao, Y.J., Wang, H., Kumar, T.V., Wang, C.Q. 2022. Phosphorus adsorption by functionalized biochar: a review. Environ. Chem. Lett. 28. DOI: 10.1007/s10311-022-01519-5

10. Nguyen, T.T. 2022. Effective Removal of Phosphate from Waste Water Based on Silica Nanoparticles. J. Chem. 2022, 8. DOI: 10.1155/2022/9944126

11. Nayeem, A., Mizi, F., Ali, M.F., Shariffuddin, J.H. 2023. Utilization of cockle shell powder as an adsorbent to remove phosphorus-containing wastewater. Environ. Res. 216, 8. DOI: 10.1016/j.envres.2022.114514

12. Park, J.H., Choi, A.Y., Lee, S.L., Lee, J.H., Rho, J.S., Kim, S.H., Seo, D.C. 2022. Removal of phosphates using eggshells and calcined eggshells in high phosphate solutions. Appl. Biol. Chem. 65, 10. DOI: 10.1186/s13765-022-00744-4

13. Deng, C.X., Xue, J.H., Wu, Y.B. 2023. Using magnetite/zirconium-comodified attapulgite as a novel phosphorus (P) sorbent for the efficient removal of P and the adsorption mechanism allowing this effect. Appl. Water Sci. 13, 14. DOI: 10.1007/s13201-022-01821-1

14. Garbarczyk, C. 2010. Hydromechanics of water filtration Scientific and Technical Publishing House, Warsaw.

15. Hamisi, R., Renman, A., Renman, G., Worman, A., Thunvik, R. 2022. Long-term phosphorus sorption and leaching in sand filters for onsite treatment systems. Sci. Total Environ., 833, 14. DOI: 10.1016/j.scitotenv.2022.155254

16. Renman, A., Renman, G. 2022. Removal of Phosphorus from Hypolimnetic Lake Water by Reactive Filter Material in a Recirculating System-Laboratory Trial. Water. 14. DOI: 10.3390/w14050819

17. Mesci, B.L. 2013. Travertines with original features and their importances: Examples from the Sivas travertines. Turk. Jeol. Bult., 56, 23–37.

18. Kalender, L., Okan, O.O., Inceoz, M., Cetindag, B., Yildirim, V. 2015. Geochemistry of travertine deposits in the Eastern Anatolia District: an example of the Karakocan-Yogunagac (Elazig) and Mazgirt-Dedebag (Tunceli) travertines, Turkey. Turk. J. Earth Sci. 24, 607–626. DOI: 10.3906/yer-1504-27

19. Gubernat, S., Masłoń, A., Czarnota, J., Koszelnik, P. 2022. Phosphorus removal from wastewater using marl and travertine and their thermal modifications. Desalin. Water Treat., 275, 35–46. DOI: 10.5004/dwt.2022.28529

20. Kurdowski, W. 1981. Poradnik technologa przemysłu cementowego. Arkady Warszawa.

21. Ryka, W., Maliszewska, A. 1982. Słownik petrograficzny. Wydawnictwa Geologiczne, Warszawa.

22. Renman, A., Renman, G., 2010. Long-term phosphate removal by the calcium-silicate material Polonite in wastewater filtration systems. Chemosphere, 79, 659–664. DOI: 10.1016/j.chemosphere.2010.02.035

23. Cucarella, V., Zaleski, T., Mazurek, R. 2009. Phosphorus sorption capacity of different types of opoka J. Environ. Qual., 38, 381–392.

24. Brogowski, Z., Renman, G. 2004. Characterization of opoka as a basis for its use in wastewater treatment. Pol. J. Environ. Stud., 13, 15–20.

25. Altundogan, H.S., Tumen, F. 2003. Removal of phosphates from aqueous solutions by using bauxite II: the activation study. Journal of Chemical Technology and Biotechnology, 78, 824–833. DOI: 10.1002/jctb.860

26. Zhu, D.C., Chen, Y.Q., Yang, H.P., Wang, S.H., Wang, X.H., Zhang, S.H., Chen, H.P. 2020. Synthesis and characterization of magnesium oxide nanoparticle-containing biochar composites for efficient phosphorus removal from aqueous solution. Chemosphere, 247. DOI: 10.1016/j.chemosphere.2020.125847

27. Xiong, W.H., Peng, J. 2008. Development and characterization of ferrihydrite-modified diatomite as a phosphorus adsorbent. Water Research, 42, 4869–4877. DOI: 10.1016/j.watres.2008.09.030

28. Xie, F.Z., Da, C.N., Zhang, F.J., Zhang, J., Han, X., Ge, Y.J., Li, G.L. 2013. Phosphorus Removal from Eutrophic Waters with a Novel Lanthanum-Modified Diatomite. Asian J. Chem., 25, 5759–5761. DOI: 10.14233/ajchem.2013.OH84

29. Yan, L.G., Xu, Y.Y., Yu, H.Q., Xin, X.D., Wei, Q., Du, B. 2010. Adsorption of phosphate from aqueous solution by hydroxy-aluminum, hydroxy-iron and hydroxy-iron-aluminum pillared bentonites. Journal of Hazardous Materials, 179, 244–250. DOI: 10.1016/j.jhazmat.2010.02.086

30. Kuroki, V., Bosco, G.E., Fadini, P.S., Mozeto, A.A., Cestari, A.R., Carvalho, W.A., 2014. Use of a La(III)-modified bentonite for effective phosphate removal from aqueous media. Journal of Hazardous Materials, 274, 124–131. DOI: 10.1016/j.jhazmat.2014.03.023

31. Wang, Y., He, H., Zhang, N., Shimizu, K., Lei, Z.F., Zhang, Z.Y. 2018. Efficient capture of phosphate from aqueous solution using acid activated akadama clay and mechanisms analysis. Water Sci. Technol., 78, 1603–1614. DOI: 10.2166/wst.2018.441

32. Liu, Y., Sheng, X., Dong, Y.H., Ma, Y.J. 2012. Removal of high-concentration phosphate by calcite: Effect of sulfate and pH. Desalination, 289, 66–71. DOI: 10.1016/j.desal.2012.01.011

33. Zapater-Pereyra, M., Malloci, E., van Bruggen, M.A., Lens, P.N.L. 2014. Use of marine and engineered materials for the removal of phosphorus from secondary effluent. Ecol. Eng., 73, 635–642. DOI: 10.1016/j.ecoleng.2014.09.112

34. Tomaszewicz, M., Kotyczka-Morańska, M., Zuwała, J. 2016. Analysis of the possibility of using thermogravimetric analysis for quick determination of ignition losses in fly ash. Energy ashes, Zakopane, Polish Union of Combustion By-products.

35. Carrillo, V., Fuentes, B., Gomez, G., Vidal, G. 2020. Characterization and recovery of phosphorus from wastewater by combined technologies. Rev. Environ. Sci. Bio-Technol., 19, 389–418. DOI: 10.1007/s11157-020-09533-1