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Phosphorus removal from wastewater using marl and travertine and their thermal modifications

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ABSTRACT

Due to non-renewable resources and the need to meet the world's food needs, phosphorus is considered a strategic resource. As a component of agricultural fertilizers, phosphorus is the main factor causing the eutrophication process, which makes it necessary to the efficient removal of phosphorus from wastewater, will also enable the recovery of this element remove it in wastewater treatment plants. Currently used wastewater treatment methods, based on biological phosphorus binding or its chemical precipitation, force high investment and operating costs, with simultaneous insufficient phosphorus removal. Modern technologies designed to purify wastewater from phosphorus compounds are based on reactive materials that bind phosphorus in adsorption and precipitation processes, while allowing its recovery in subsequent stages. The paper presents an analysis of two natural marl and travertine materials, their thermal modifications and filter material Polonite® in terms of phosphorus binding by sorption and precipitation under static conditions. The research took into account the influence of the elemental composition of the materials, the initial concentration of P, fraction size, process conditions and the temperature of thermal treatment of natural materials in terms of phosphorus retention. Marl showed a higher phosphorus binding efficiency with increasing the initial concentration, reaching a maximum of 91.93% phosphorus reduction. At a concentration of 188.72 mg P/L, the marl showed the highest sorption capacity at the level of 8.72 mg P/g. Travertine achieved the highest phosphorus binding efficiency of 89.82% at an initial concentration of 20.26 mg P/L, while the highest sorption capacity of travertine equal to 7.10 mg P/g was demonstrated at the initial concentration of 188.72 mg P/L. Commercial material Polonite® achieved the highest phosphorus binding efficiency (95.09%) at the initial concentration of 20.26 mg P/L. In terms of the process parameters under static conditions, the most optimal for marl, travertine and Polonite® are 350 rpm shaking speed and 24 h shaking time. Research using materials with different fraction sizes have shown that the most appropriate particle size is 1–2 mm due to the best phosphorus removal efficiency. Thermal treatment of both marl (at temperatures between 600°C–1,000°C) and travertine (at temperatures between 650°C–1,000°C) clearly increases their phosphorus binding efficiency up to 99% reduction. The high efficiency of thermally modified materials was maintained regardless of the process conditions and the size of the fraction.

Keywords: Wastewater treatment; Phosphorus sorption; Ecotechnology; Reactive materials; Adsorption; Phosphorus; Wastewater treatment

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1. Introduction

Phosphorus is an essential nutrient for the growth and functioning of life forms in most ecosystems. It is the basic component of proteins and participates in the transformation of carbohydrates and fats. Phosphorus is used in the pharmaceutical, metallurgical and food industries, as well as for the production of feed and animal feed [1]. Phosphorus as the main component of mineral fertilizers is the foundation of modern agricultural chemistry and agricultural development, based on stimulating plant growth [2]. For this reason, along with nitrogen, it is considered the main factor responsible for the eutrophication of water bodies. This process, as a result of oversize enrichment nutrients in water bodies, can seriously disturb the balance of organisms present in the water and adversely affect water quality, mainly by depleting the level of dissolved oxygen, leading to a threat to the preservation of biodiversity in aquatic ecosystems [3]. Elimination of the indicated problem is difficult and long-lasting because phosphorus in water bodies becomes part of the bottom sediments, from which it can be released under certain conditions, which causes a recurrence of the eutrophication process. As a consequence, there is a risk of a decrease in the quality of water intended for human consumption, which is affected by phosphorus compounds from wastewater, agricultural land, as well as from leachate from landfills [3,4]. In order to effectively minimize the impact of urban wastewater on the eutrophication process, increasingly stringent requirements are being placed on wastewater treatment plants in terms of phosphorus reduction [5]. In Poland, the minimum percentage of phosphorus reduction in wastewater treatment plants, with a P.E. value (Population equivalent is a number expressing the ratio of the sum of the pollution load in wastewater to the individual pollution load in household wastewater produced by one person in the same time) over 10,000 is equal to 80%. On the other hand, the concentration of phosphorus present in treated wastewater introduced into the receiver must not exceed 5 mg P/L at P.E. < 2,000, 2 mg P/L at P.E. in the range of 2,000–99,999 and 1 mg P/L at P.E > 100,000 [6].

On the other hand, there is now a steady increase in the demand for phosphorus to meet the world's food needs. In addition, in recent years there has been an increase in demand for fertilizers, and thus for phosphorus, due to the increased production of biofuels. Phosphorites, from which this element is mainly obtained, are a non-renewable raw material. Although the world's natural resources of phosphorus are rich, the reserves that can be exploited under the current economic and technical conditions may be depleted in the next 50–130 years [7–9].

Reaching a compromise between the contemporary demand for phosphorus, and its limited resources and impact on the environment, creates the need to cheat, among others, technologies for the purification of water used for domestic and economic purposes, which in addition to the efficient removal of phosphorus from wastewater, will also enable the recovery of this element [10].

Currently, the main methods of removing phosphorus from wastewater are biological and chemical methods – precipitation. Technologies of biological phosphorus binding are based on the accumulation of phosphates by groups of activated sludge bacteria, for example, *Acinetobacter*. A necessary condition for the controlled phosphorus binding by microorganisms is that the activated sludge is subjected to a combination of anaerobic, anoxic and aerobic conditions, allowing bacteria to accumulate orthophosphates in the form of polyphosphates thanks to their specific metabolism [11]. The effectiveness of this process depends, inter alia, on the amount of easily decomposable substrates in the raw sewage, which support phosphorus absorption, as well as the presence of nitrates and nitrites, which disturb the process in the anaerobic zone. Currently, thanks to the advanced measurement and control technology, the technological systems of the activated sludge allow for the simultaneous removal of nitrogen and phosphorus [11,12]. Nevertheless, maintaining an appropriate technological regime and the sensitivity of the system to changing conditions mean that biological methods are insufficient to effectively reduce the concentration of phosphorus in treated sewage, and thus prevent the eutrophication process [3]. In order to support the above-mentioned processes or as an alternative, methods based on chemical precipitation of phosphorus with lime or aluminum and iron salts are used, which remove phosphorus by precipitating it in the form of insoluble compounds. Chemical reagents can be used at the beginning of the treatment system (pre-precipitation), before or into the biological reactor chambers (simultaneous precipitation) or upstream of the secondary settling tank (post-precipitation). Consolidation of biological and chemical methods or only chemical methods causes that their use may be economically unjustified, especially taking into account the increasingly frequent need to increase the capacity of wastewater treatment plants and the increasingly higher requirements in terms of phosphorus removal [10,13].

Attempts to recover phosphorus from wastewater sludge from the biological treatment of wastewater, by fertilizing them to the ground surface, may negatively affect the quality of soils in terms of microbiology and contamination with heavy metals and microplastics [14]. The recovery of phosphorus from wastewater or from ashes from the thermal transformation of sewage sludge, using mineral acid extraction methods (including phosphoric acid), is still under discussion in ecological and economic terms, due to the complex conditions of the process and the amount of chemical reactants required. In addition, phosphorus recovery processes, due to their technological advancement, are currently unavailable in economic terms for sewage treatment plants of the smallest agglomerations < 2,000 P.E. [15,16].

In view of the above problems, research is currently underway on wastewater treatment ecotechnologies based on adsorption and precipitation processes, using green chemistry, that is, natural or waste materials, which, apart from phosphorus binding, will then be able to under certain conditions, desorb this element, releasing it to the environment, for example, during the process of soil fertilization [10]. Therefore, new reactive materials are currently being sought that have the ability to selectively remove phosphorus by adsorption or precipitation [17]. The process of binding phosphorus from wastewater or water consists in depositing it in the solid phase on the surface of the sorbent from the sediment-water phase, through chemical precipitation or chemical adsorption (creating a chemical bond between the adsorbent and the adsorbate) or physical adsorption (through van der Waals interactions) [10,17]. The reactive material intended for phosphorus removal should contain in its chemical composition elements with the natural ability to bind this element, that is, Ca (calcium), Mg (magnesium), Fe (iron) and Al (aluminum). The mechanism of phosphorus adsorption by Fe and Al may occur through ligand exchange, while for Ca and Mg, the removal of this element occurs through the precipitation of calcium or struvite phosphates [18,19].

The use of natural raw materials in the processes of sorption and precipitation of phosphorus compounds from wastewater, and then using them in agriculture as fertilizer, is in accordance with the principles of the circular economy and sustainable development. In addition, the use of natural sorbents in phosphorus removal and recovery, can reduce environmental losses and offer significant benefits in terms of resource use, which will also stabilize world prices of this commodity, which are constantly fluctuating [20–22].

The paper presents the results of research on the use of natural materials, that is, marl and travertine and their thermally modified forms, as well as the Polonite® material, in terms of phosphorus binding. The analysis took into account the influence of the following parameters on the retained amount of phosphorus: physicochemical properties, modification temperature, initial phosphorus concentration in the solution, fraction size and process conditions. The research was also aimed at assessing the materials in terms of their practical use in wastewater treatment technology.

2. Materials and methods

2.1. Reactive materials

The research was carried out using two natural materials and one commercial. The characteristics of the tested materials are presented in the Table 1.

The first natural material is marl – a natural sedimentary rock, consisting of carbonates and clay minerals, obtained from the Lublin Upland in Poland. Marl has a specific surface area of 24.402 m²/g and an average pore size of 165.62 nm. Scanning electron microscopy (SEM) micromorphological analysis allows us to conclude that marl has a non-uniform structure and uneven distribution of pores on the surface. The shape of the marl grains is irregular, both the sharp edges of the material grains and the low sphericity of the material particles are observed (Fig. 1a).

The second natural reactive material is travertine – a porous sedimentary rock consisting mainly of calcite and aragonite, taken from the mine of this raw material in Raciszyn in Poland. Travertine is characterized by an average pore size of 137.97 nm and a specific surface area of 0.182 m²/g. Micromorphological study of travertine SEM indicates the rounded shape of the grains and their average sphericity. This material is characterized by a moderately regular shape and proportional to the size of the grains, distribution of pores on the surface (Fig. 1b).

The third material is Polonite® a commercialized filter material consisting of reactive calcium silicate. Polonite® has a specific surface area of 10.616 m²/g and an average pore size of 117.96 nm. Analysis of the micromorphology of this material allows us to conclude that its surface is characterized by diversity in the shape and regularity of grains. Both spherical grain shapes of the material and elongated sharp edges of its particles were observed (Fig. 1c).

Natural materials were heated in a laboratory muffle furnace at temperatures of 500°C, 600°C, 650°C, 700°C, 800°C, 900°C, and 1,000°C for 1 h. Heat treatment contributed to the improvement of rounding and regularity of the structures of both marl and travertine (Fig. 2a and b). In the case of marl heated at 1,000°C, the appearance of medium spherical grains of the material was noted. In turn, travertine, after thermal modification at a temperature of 700°C, was characterized by high sphericity of grains. Heat treatment of marl and travertine resulted in an increase in their average pore size – travertine (from 137.97 to 174.07 nm), marl (from 137.97 to 187.29 nm). An increase in the specific surface area due to the heating process was observed only for travertine (from 0.182 to 0.255 m²/g).

In the case of marl, a decrease in the specific surface area and total pore volume was noted after the thermal treatment process, which may be due to the transition of SiO_2 and $CaCO_3$ into the form of $CaSiO_3$, $CaSiO_4$.

On the basis of the conducted research, 1,000°C for marl and 700°C for travertine were selected as the optimal material modification temperatures.

The effective size of the reactive materials used in the research was within the three fraction ranges <1 mm, 1–2 mm, and 2–5 mm.

2.2. Batch experiments

Studies of sorption and precipitation of phosphorus by selected materials included the determination of the

Table 1
Physico-chemical properties of materials

Parameter / Material	Raw travertine	Travertine heated at 700°C	Polonite®	Raw marl	Marl heated at 1,000°C
Density (g/cm³)	2.7859	2.7150	2.5290	2.7563	2.8865
Specific surface area BET (m²/g)	0.182	0.255	10.616	24.402	0.910
Phase composition	$CaCO_3$ 100%	$CaCO_3$ 100%	SiO_2 37.6% $CaCO_3$ 62.4%	SiO_2 6.5% $CaCO_3$ 93.5%	$CaSiO_3$, $CaSiO_4$, CaO
Total pore volume (cm³/g)	0.00126	0.00222	0.06261	0.20210	0.00852
Average pore size (nm)	137.97	174.07	117.96	165.62	187.29

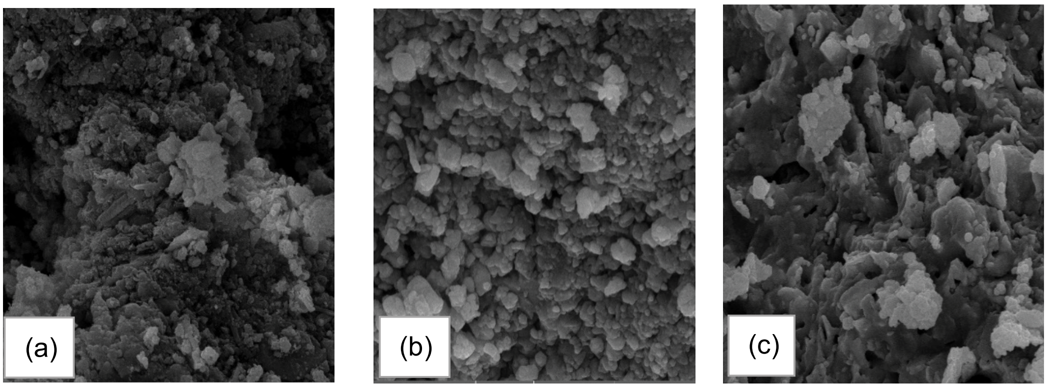

Fig. 1. Photographs from the study of the morphology of materials using SEM (magnification 10k) (a) natural marl and (b) natural travertine (c) Polonite®.

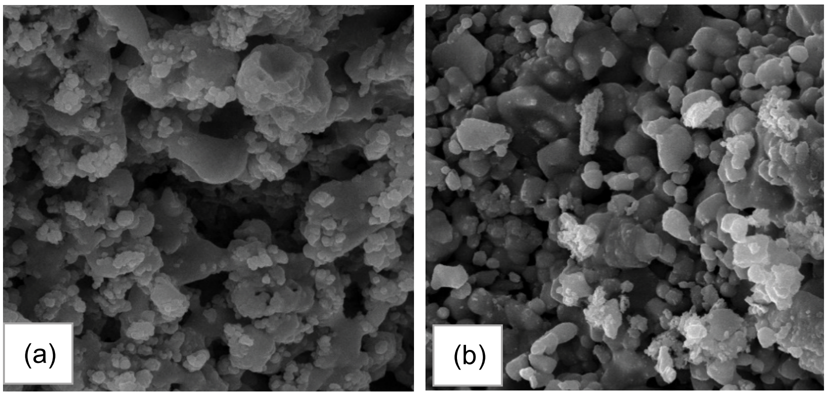

Fig. 2. Photographs from the study of the morphology of materials using SEM (magnification 10k) (a) marl heated at 1,000°C and (b) travertine heated at 700°C.

efficiency of phosphorus bonding and the influence of the heating temperature of materials on its size. The tests were carried out by the static method by shaking for 24 h at a rotational speed of 350 rpm 2 g weights of material with a fraction of 1 to 2 mm with a 100 mL solution KH_2PO_4 with a concentration of 20–200 mg P/L. In addition, studies were carried out on the influence of shaking speed (150, 250, and 350 rpm), shaking time (12 and 24 h) and fraction size (<1 mm, 1–2 mm, and 2–5 mm) on the phosphorus bonding efficiency, at an initial concentration of approx. 20 mg P/L. During the indicated tests, pH and conductivity were also determined by the potentiometric method. The determination of P concentrations was performed by spectrophotometric method, after prior mineralization of the samples, using Spectroquant® tests, the operation of which is based on the reaction in a sulfur solution, where orthophosphate ions react with molybdate ions to form molybdophosphoric acid. Ascorbic acid reduces this to phosphomolybdenum blue which is determined photometrically. The measuring range of the method is in the range of 0.05–5.00 mg P/L with an accuracy of ±0.06 mg P/L, coefficient of variation ±0.0093 mg P/L and a confidence interval (P = 95%) of ±0.05 mg P/L. Three repetitions were performed for each sample, the final result was determined as the arithmetic mean of the results not different by more than 5% of the less value.

The phosphorus binding efficiency of materials subjected to thermal treatment at various temperatures, was analyzed under static conditions, by shaking 2 g of material with a fraction of 1 to 2 mm, at a rotational speed of 350 rpm for 24 h with 100 mL of KH_2PO_4 solution with a concentration of 19.86 mg P/L.

The phase composition of the materials was determined using the X-ray diffraction method. Morphological analysis and elemental composition were determined by SEM. The specific surface area Brunauer–Emmett–Teller, volume and diameter of the pores were determined by the porosimetric method using the Nova Station A apparatus, while the density was determined by the pycnometric method using the ULTRAPYC 1200e pycnometer.

3. Results and discussion

3.1. *Influence of the elemental composition of the material on the nature of phosphorus binding*

Table 2 presents the results of research on the elemental composition of the tested materials.

It can be observed that in the composition of all materials, in the range of elements showing the ability to retain phosphorus, the content of Ca is the highest, which means that the binding process of this element takes place mainly by precipitation [18,19]. Comparing the composition of marl and travertine and their thermal modifications to the elemental composition of the Polonite® material, it can be noted that the commercialized material is characterized by the lowest content of Ca, but also the highest content of Fe and Al. This may indicate that phosphorus binding occurs both by ligand exchange and precipitation. The composition of marl and travertine also contains some contents of Mg, Al, Fe, but in a smaller amount, which does not exclude that these elements are also involved in the removal of phosphorus. In the case of heated marl, the heat treatment process increased the content of Ca (from 11.61% to 18.34%) and Fe (from 0.43% to 0.87%), which also translated into greater phosphorus bonding efficiency (Table 3).

3.2. Phosphorus binding efficiency by materials for different initial concentrations

The results of studies on the efficiencies of phosphorus binding by marl, travertine and Polonite® at different initial concentrations are presented in Table 3.

It can be seen from the presented results that the highest percentage of phosphorus reduction was achieved by the tested materials for the initial concentration of 20.26 mg P/L – Polonite® 95.09%, marl 89.98%, travertine 89.82%. For the highest initial concentration, amounting to 188.72 mg P/L, the marl turned out to be the most efficient, reaching 91.93% of phosphorus binding efficiency. The remaining materials showed a similar reduction efficiency for this concentration, that is, at the level of 75.27% by travertine and 74.07% by Polonite®. The decrease in the phosphorus binding efficiency of travertine and Polonite® at the highest initial concentration, compared to lower concentrations, may result from the depletion of the maximum sorption capacity of the tested materials, the determination of which should be the subject of further studies, that may confirm that these materials will not be highly effective for solutions with a high initial concentration of phosphorus.

For the lowest initial concentration, 1.95 mg P/L, the high efficiency of phosphorus binding was maintained by the Polonite® filter material (88.21%). Low values of phosphorus reduction were recorded at the level of 7.42% for marl and 30.88% for travertine, with the lowest initial concentration.

In terms of sorption capacity, the highest values were achieved by all materials at the initial concentration of 188.72 mg P/L – marl 8.67 mg P/g, travertine 7.10 mg P/g, commercial material Polonite® 6.99 mg P/g.

After the shaking process, for each tested sample, the pH increased. The greatest changes in pH were observed at baseline concentrations of 1.95 mg P/g (from 6.04 to 9.71 for travertine, from 6.04 to 9.24 for marl, from 6.04 to 9.92 for Polonite®), and they resulted from the presence in the phase composition of calcium carbonate materials, which has alkaline properties.

In the case of the conductivity of the solutions, the values lower than for the initial solution were recorded for all

Table 2
Elemental composition of materials

Material	Elemental composition (%)										
	C	O	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe
Raw marl	25.68	50.29	0.20	0.82	10.12	0.06	0.41	0.37	11.61	–	0.43
Marl heated at 1,000°C	17.74	46.89	0.17	0.74	14.58	0.05	0.04	0.57	18.34	0.02	0.87
Polonite®	23.62	51.00	0.25	1.89	11.71	0.10	0.07	0.62	8.30	0.12	2.32
Raw travertine	16.86	53.77	0.11	0.09	0.10	–	–	–	28.14	–	0.94
Travertine heated at 700°C	14.17	55.94	0.13	0.06	0.13	0.07	0.03	–	28.96	–	0.50

Table 3
Material test results for different initial concentrations of phosphorus

Material	Initial concentration	Final concentration	Removal efficiency	Sorption capacity	Initial pH	Final pH	Initial conductivity	Final conductivity
	(mg P/L)	(mg P/L)	(%)	(mg P/g)	(–)	(–)	(µS/cm)	(µS/cm)
Raw travertine	1.95	1.35	30.88	0.03	6.04	9.71	221	68
	20.26	2.06	89.82	0.91	5.30	8.41	77.2	164
	188.72	46.66	75.27	7.10	4.80	7.17	626	837
Raw marl	1.95	1.80	7.42	0.01	6.04	9.24	221	62
	20.26	2.03	89.98	0.91	5.30	8.30	77.2	149
	188.72	15.22	91.93	8.67	4.80	7.23	626	832
Polonite®	1.95	0.23	88.21	0.09	6.04	9.92	221	135
	20.26	0.99	95.09	0.96	5.30	9.70	77.2	139
	188.72	48.94	74.07	6.99	4.80	7.54	626	708

materials at the initial concentration of 1.95 mg P/L while in the remaining cases, the value of this parameter increased with the increase in the initial concentration.

3.3. Effect of material modification temperature on phosphorus binding capacity

The travertine has been heat treated at temperatures ranging from 500°C to 1,000°C by heating in a muffle furnace. The results of the research on the process of phosphorus binding by thermally modified travertine are shown in Fig. 3. The presented diagram shows that for the treatment temperatures of 500°C and 600°C there is a decrease in the efficiency of phosphorus removal as compared to natural material. This may be due to the low stability of the raw material, which, after an incomplete or unrealized calcination process, resulting from too low a roasting temperature, shows irregularities under certain conditions in the production of the adsorbent-solution equilibrium. In turn, from the temperature of 650°C, there is a rapid increase in the efficiency of the reduction of this element to the level of over 99%, which is maintained for subsequent, higher temperatures of 700°C, 800°C, 900°C and 1,000°C. The reason for the observed changes is the calcination process, as a result of which $CaCO_3$ is transformed into more reactive CaO, which is more effective in binding phosphorus [23]. In addition, the thermal process and the transformation of $CaCO_3$ to CaO, after the release of CO_2, increases the mean pore size (Table 1). Literature data confirm high efficiencies and a clear increase in the efficiency in phosphorus removal by heated materials with a similar composition. For example, calcined marble showed an efficiency of 99.91% at an initial concentration of 226.34 mg P/L [26]. On the other hand, other studies confirm that at the initial concentration of 1,000 mg P/L, powdered marble calcined at 1,000°C can achieve a phosphorus reduction efficiency of 66% [27]. Regarding the sorption capacity, tests using marble powder in a Continuous Stirred Tank Reactor (CSTR) showed a sorption capacity of 17.00 mg P/g [28]. Marine materials, which are a renewable source of calcium carbonate, after a thermal treatment process at the temperature of 750°C, they reached the efficiency of 99% at the initial phosphorus concentration of 30 mg P/L [24]. Moreover, the research conducted on the mussel shell powder proved that the process of thermal modification of this material at the temperature of 700°C increases the phosphorus removal capacity by 25% to 55% [29].

Along with the increase in the temperature of the thermal treatment, an increase in the conductivity of the solutions after the shaking process was also observed. In addition, studies have shown a significant increase in the pH of the final solutions from 650°C (from 5.38 to 11.01) to 1,000°C (from 5.38 to 12.55), which may be due to the presence of CaO, which has strongly alkaline properties. Tests carried out on thermally treated marine materials at a temperature of 750°C also confirm the change in the pH of the solutions (increased to 12) and indicate that the adsorption process dominates when phosphorus is removed with the use of raw materials, while with the use of heat-treated materials, the precipitation process dominates [24].

Moreover, the visual assessment of the solutions after the end of the process made it possible to state that the turbidity of the solutions increased as the heating temperature increased, which resulted from the change in the structure of the material. At the highest modification temperatures, travertine changed its properties towards a more soluble, brittle material compared to the raw form, which could be the reason for an increase in conductivity as a result of leaching calcium ions into the solution.

Marl was also modified by heating at 500°C, 600°C, 650°C, 700°C, 800°C, 900°C, and 1,000°C. The test results after the shaking process are shown in Fig. 4. At the temperature of 500°C, a decrease in the phosphorus binding efficiency

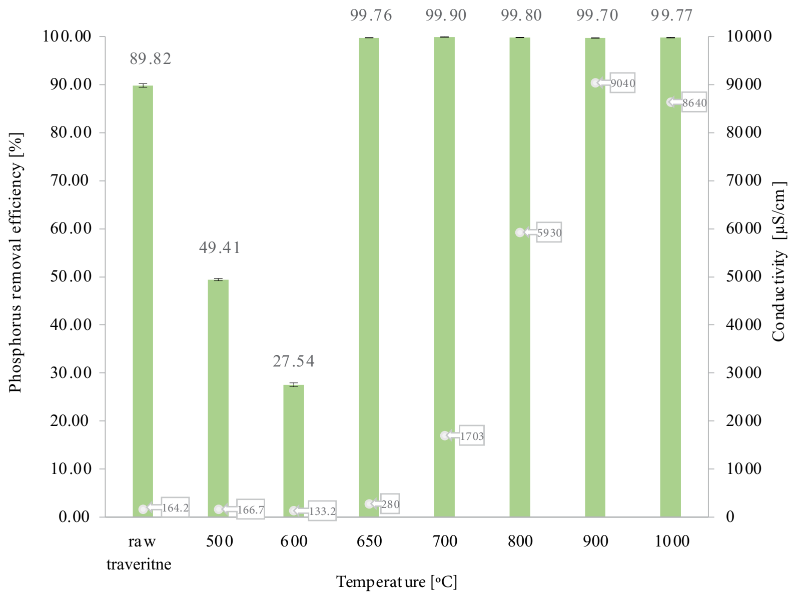

Fig. 3. Influence of travertine heating temperature on phosphorus binding efficiency and the conductivity of the solution after the process.

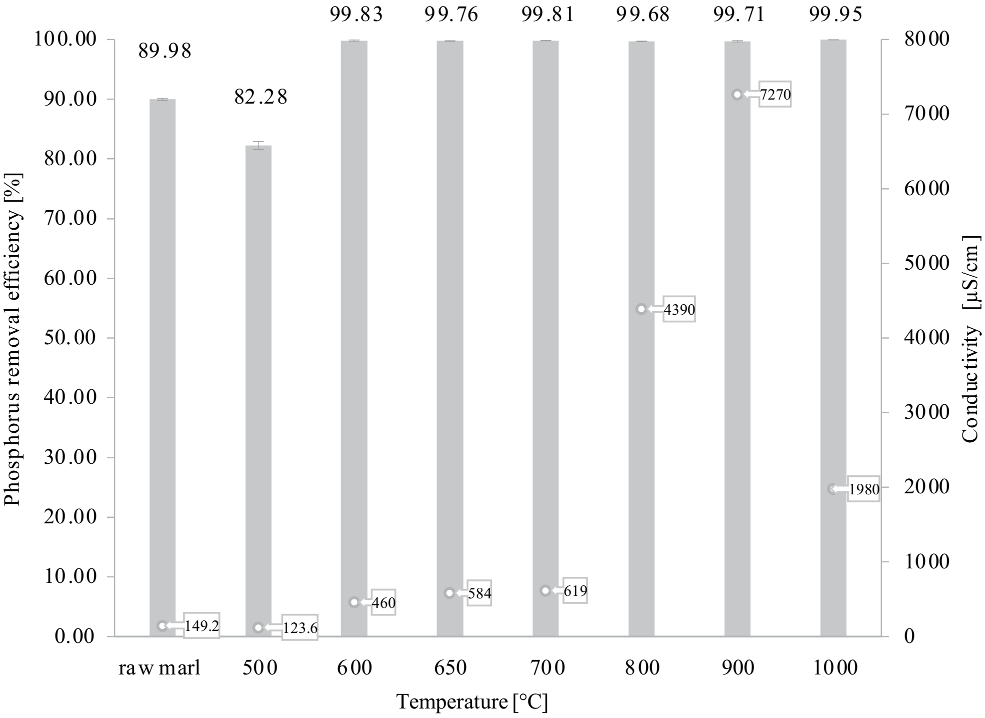

Fig. 4. Effect of marl heating temperature on phosphorus binding efficiency and conductivity solution after the process.

was observed from 89.98% to 82.28%, which may result from the low stability of raw marl in reaching the adsorption equilibrium under changing conditions or incomplete calcination process. At the temperature of 500°C, a decrease in the phosphorus binding efficiency was observed from 89.98% to 82.28%. With the use of higher temperatures of thermal treatment of the material, the efficiency was maintained at the level of over 99% reduction of this element. As in the case of travertine, there was a transformation of $CaCO_3$ into CaO, which has a greater affinity for phosphorus, which is manifested by greater efficiency in binding phosphorus on its surface. Additionally, in the modified marl, an increase in the mean pore size was observed, which also had a positive effect on phosphorus retention (Table 1).

The presented results are consistent with studies of similar materials, for example, opoka material, which after heating is a commercial material Polonite® [17,23,30–36]. Tests conducted with the use of opoka heated at a temperature of 700°C showed a reduction of phosphorus by this material at the level of 99% at the initial concentration 5–100 mg P/L [36]. For Polonite®, column experiments have proven a phosphorus binding capacity of 72.4% at an initial concentration of 4.41 mg P/L [34].

Along with the increase in the phosphorus removal efficiency, a change in the pH of the solution was observed after the process (from 5.38 to 10.85 for the modification temperature of 600°C, from 5.30 to 11.95 for the temperature of 1,000°C). The conductivity of the solutions increased significantly from the treatment temperature of 800°C. At the highest heating temperature, that is, 1,000°C, there is a smaller increase in the conductivity of the solution after the process (from 77.2 to 1,980 µS/cm) than at the temperature of 900°C, where this parameter reached the final value of 7,270 µS/cm.

Recognition of the properties of materials after thermal modification allowed to state that the marl changes its physical structure from brittle, slate, unstable raw form towards a compact, insoluble material with increasing processing temperature. The reason is the transition of SiO_2 and $CaCO_3$ into the form of $CaSiO_3$, $CaSiO_4$, which was observed during the analysis of the phase composition by X-ray diffraction (Table 1). In addition, after thermal treatment, the specific surface of the marl decreased, at the same time increasing the phosphorus binding efficiency. This may mean that the thermal process influenced the chemical properties of the elements of the marl, which in the form of $CaSiO_3$ and $CaSiO_4$ show high and stable reactivity towards phosphorus, which should be proven in subsequent research. This is confirmed by the literature data which show that, despite low specific surface area values, sorbents with the presence of characteristic functional groups capable of effective binding of a given group of pollutants may show high sorption capacity [37].

The turbidity of the solution after the phosphorus binding process carried out by the static method was imperceptible for the modification temperatures of 900°C and 1,000°C, where calcium silicates were present in the phase composition.

The efficiencies in the tested range of wollastonite present in thermally modified marl is consistent with the literature data on this material. Studies conducted with the use of calcium metasilicate have shown that its phosphorus removal efficiency at an initial concentration of 14–61 mg P/g is at the level of 90%–93% [38]. In turn, research conducted with the use of zeolite, showed the maximum phosphorus removal efficiency of 93.9% for the adsorbent dose of 25 g/L [39]. Other research conducted with use sodium functionalized ultrasonic-diatomite (U-D-Na) to remove phosphorus from an aqueous solution, showed the adsorption efficiency reached over 90% under optimal conditions [40].

3.4. Influence of the size of material fractions on the phosphorus reduction process

Raw materials and Polonite®, as well as their forms heat treated at temperatures of 700°C (travertine) and 1,000°C (marl), the fractions were divided into the following fractions: <1 mm, 1–2 mm, 2–5 mm and the shaking process was performed for the initial concentration of 19.63 mg P/L. The research results are presented in Table 4 and Fig. 5. For all materials, the best efficiency and sorption capacities were achieved for the 1–2 mm fraction. Heated materials, regardless of the size of the fraction, maintained a very high binding efficiency of this element, over 99% reduction each.

The least favorable fraction for raw materials and Polonite® in terms of phosphorus retention was the 2–5 mm fraction. For travertine it was a reduction of 17.74%, for marl 26.17%, and for Polonite® 13.05%, which in comparison to the results for the 1–2 mm fraction indicates a clear deterioration of the phosphorus binding capacity of larger fractions. The reason for the observed differences is the smaller contact area of the sorbent with the pollutant removed in the solution.

In case of fractions <1 mm, the materials showed satisfactory phosphorus removal efficiency. Marl achieved the lowest efficiency at the level of 50.96% reduction, travertine 78.13%, and Polonite® 59.38%. Nevertheless, in the aspect of wastewater treatment technology, after the conducted process with the use of fine fraction, it will be necessary to apply the filtration process due to the high turbidity of the solutions.

Studies conducted with the use of limestone have shown that with the reduction of the fraction size, the efficiency of the process increases – from 70% to 78% with the particle size reduction from 2 to 0.09 mm. Nevertheless, the authors also point to the necessity to choose a larger fraction (>0.09 mm) due to the possibility of clogging of the filter [41].

The conductivity and pH of the solutions after the performed process clearly increased, as in the previously presented results – only in the field of thermally treated materials. For modified travertine, the pH of the solution increased from 6.14 to 11.97 for the fraction <1 mm, while for material sizes 2–5 mm, the final pH was 12.08. The conductivity of the solutions after the application of this material was obtained at the level of 2,020 and 1,780 µS/cm, respectively. For heated marl, the final pH values increased to 12.08 (<1 mm) and 12.03 (2–5 mm). In the case of conductivity, there was an increase from 67.7 to 2,670 µS/cm for the

Table 4
Research results for materials with fractions <1 mm, 1–2 mm and 2–5 mm

Material	Initial concentration	Final concentration	Removal efficiency	Sorption capacity	Initial pH	Final pH	Initial conductivity	Final conductivity
	(mg P/L)	(mg P/L)	(%)	(mg P/g)	(–)	(–)	(µS/cm)	(µS/cm)
Raw marl <1 mm	19.63	9.63	50.96	0.50	6.14	8.05	67.7	149.6
Raw marl 1–2 mm	19.63	2.01	89.76	0.88	6.14	8.15	67.7	149.7
Raw marl 2–5 mm	19.63	14.50	26.17	0.26	6.14	8.06	67.7	148.2
Raw travertine <1 mm	19.63	4.29	78.13	0.77	6.14	8.55	67.7	137.2
Raw travertine 1–2 mm	19.63	2.05	89.50	0.88	6.14	8.40	67.7	153.4
Raw travertine 2–5 mm	19.63	16.15	17.74	0.17	6.14	8.13	67.7	141.9
Polonite® <1 mm	19.63	7.98	59.38	0.58	6.14	8.39	67.7	110.0
Polonite® 1–2 mm	19.63	0.96	95.09	0.93	6.14	9.70	67.7	138.7
Polonite® 2–5 mm	19.63	17.07	13.05	0.13	6.14	7.99	67.7	141.0
Marl heated at 1,000°C <1 mm	19.63	0.04	99.82	0.98	6.14	12.08	67.7	2,670
Marl heated at 1,000°C 1–2 mm	19.63	0.01	99.83	0.98	6.14	12.10	67.7	2,480
Marl heated at 1,000°C 2–5 mm	19.63	0.03	99.86	0.98	6.14	12.03	67.7	2,090
Travertine heated at 700°C <1 mm	19.63	0.03	99.85	0.98	6.14	11.97	67.7	2,020
Travertine heated at 700°C 1–2 mm	19.63	0.04	99.76	0.98	6.14	12.30	67.7	2,010
Travertine heated at 700°C 2–5 mm	19.63	0.02	99.90	0.98	6.14	12.08	67.7	1,780

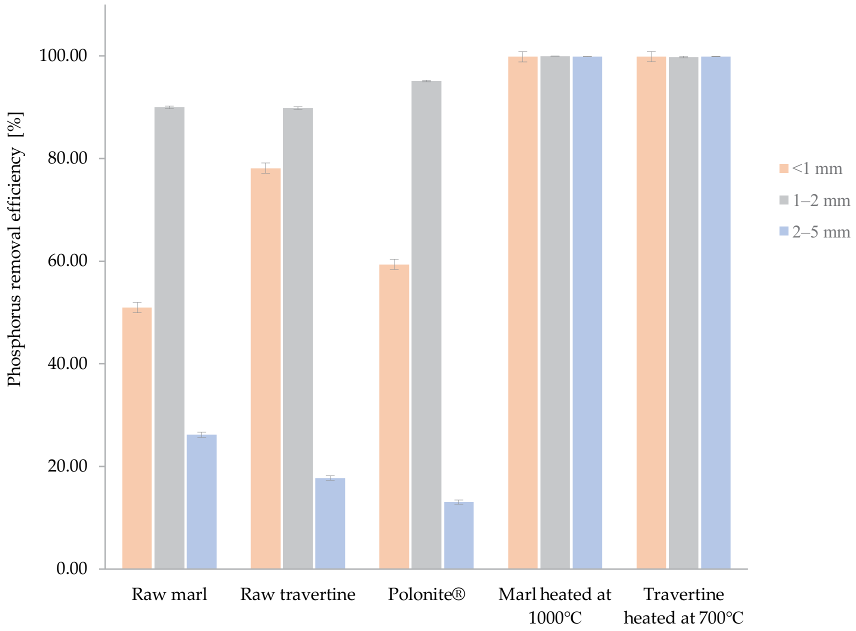

Fig. 5. Influence of material fraction size on phosphorus retention capacity.

Table 5
Results of the research on the efficiency of phosphorus binding at shaking speeds of 150 and 250 rpm

Material	Initial concentration	Final concentration	Removal efficiency	Sorption capacity	Initial pH	Final pH	Initial conductivity	Final conductivity	Shaking speed	Shaking time
	(mg P/L)	(mg P/L)	(%)	(mg P/g)	(–)	(–)	(µS/cm)	(µS/cm)	(rpm)	(h)
Raw marl	20.16	3.85	80.89	0.82	5.56	8.09	43.2	140	250	24
Marl heated at 1,000°C	20.16	0.05	99.75	1.01	5.56	11.60	43.2	657	250	24
Raw travertine	20.16	11.70	41.97	0.42	5.56	7.92	43.2	128.4	250	24
Travertine heated at 700°C	20.16	0.06	99.70	1.01	5.56	11.39	43.2	491	250	24
Polonite®	19.95	3.83	80.79	0.81	5.56	9.23	43.2	87.2	250	24
Raw marl	20.16	15.10	25.12	0.25	5.56	7.92	43.2	160.2	150	24
Marl heated at 1,000°C	20.16	0.05	99.75	1.01	5.56	11.36	43.2	435	150	24
Raw travertine	20.16	17.19	14.76	0.15	5.56	7.49	43.2	92.4	150	24
Travertine heated at 700°C	20.16	0.05	99.73	1.01	5.56	11.25	43.2	367	150	24
Polonite®	20.16	13.36	33.72	0.34	5.56	8.03	43.2	122.7	150	24

smallest fraction and from 67.7 to 2,090 µS/cm for the largest fraction.

3.5. Effect of shaking speed on the phosphorus reduction process

In order to determine the optimal conditions for the phosphorus binding process, raw and heated materials (travertine at 700°C and marl at 1,000°C) and Polonite® were additionally shaken at the rotational speeds of 150, 250 rpm for 24 h. The test results are presented in Table 5 and in Fig. 6. For the heated materials, as in the case of the fraction size, the agitation speed did not affect the efficiency of phosphorus removal. Thermally treated materials, regardless of speed, retain high phosphorus binding efficiencies of over 99%. Similar results were obtained for the removal of phosphorus from the stream water from the agricultural area with the use of aluminum coagulant where, with the optimal dose of the chemical reagent, the phosphorus value below 0.1 mg P/L was obtained after the process [42]. In the case of materials in natural form and commercial material, a clear decrease in the efficiency of phosphorus reduction was observed for the shaking speed of 150 rpm – marl 25.12%, travertine 14.76%, Polonite® 33.72%. The most optimal shaking speed for these materials is 350 rpm, because under such conditions the sorbents show the highest efficiency in terms of phosphorus removal. For the process carried out at 250 rpm, the raw marl maintained a satisfactory efficiency of 80.89%, along with Polonite® 80.79% reduction of this element. Only in the case of travertine, the phosphorus binding efficiency was at the lower level, amounting to 41.97%.

In terms of the sorption capacity of the tested materials, the highest value (1.01 mg P/g) was achieved for marl and heated travertine, regardless of the shaking speed. Polonite® achieved a sorption capacity of 0.81 mg P/g for a speed of 250 rpm, while for 150 rpm this parameter was only 0.34 mg P/g. Raw marl showed sorption at the level of 0.82 and 0.25 mg P/g, respectively. The lowest values of sorption capacities were demonstrated by raw travertine (0.15 mg P/g) for the rotational speed of 150 rpm.

The conductivity of the solutions after the process for the speed of 150 and 250 rpm increased significantly in the case of heated materials, but not as much as at the speed of 350 rpm. The solutions were characterized by a high pH (over 11) after the end of the process, also only for materials subjected to thermal treatment.

3.6. Influence of shaking time on the process of phosphorus binding by materials

Selected materials were also shaken at the rotational speed of 350 rpm for 12 h (Table 6) and compared with the results obtained for the shaking time of 24 h (Fig. 7). On the basis of the presented results, it can be seen that for the raw

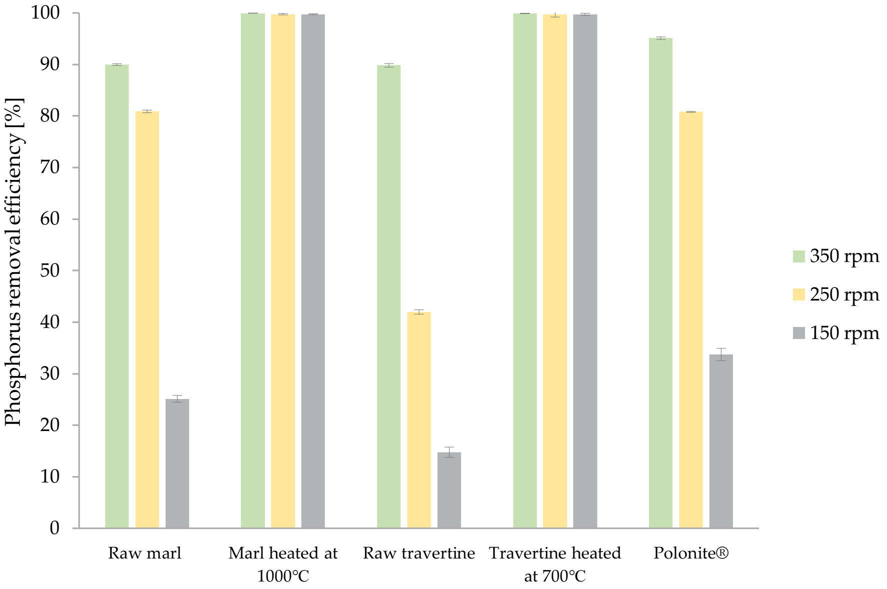

Fig. 6. Effect of shaking speed in 24 h on the ability to retain phosphorus.

Table 6
The results of the research on the efficiency of phosphorus binding at the shaking time of 12 h

Material	Initial concentration	Final concentration	Removal efficiency	Sorption capacity	Initial pH	Final pH	Initial conductivity	Final conductivity	Shaking speed	Shaking time
	(mg P/L)	(mg P/L)	(%)	(mg P/g)	(–)	(–)	(µS/cm)	(µS/cm)	(rpm)	(h)
Raw marl	19.95	9.19	53.94	0.54	5.56	7.98	43.2	161.1	350	12
Marl heated at 1,000°C	19.95	0.01	99.94	1.00	5.56	11.76	43.2	1385	350	12
Raw travertine	19.95	15.26	23.52	0.23	5.56	7.92	43.2	165.7	350	12
Travertine heated at 700°C	19.95	0.28	98.61	0.98	5.56	11.56	43.2	724	350	12
Polonite®	19.95	8.37	58.04	0.58	5.56	8.92	43.2	126	350	12

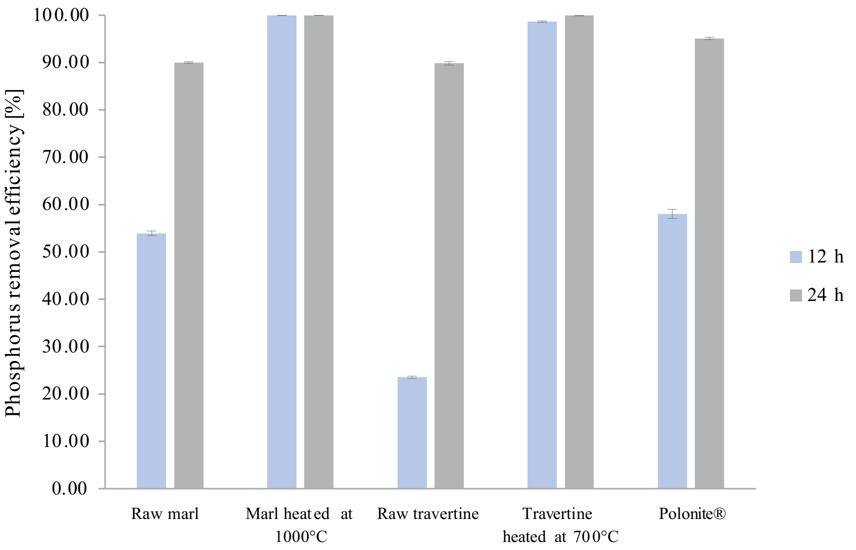

Fig. 7. Influence of shaking times 12 and 24 h on the phosphorus binding capacity.

materials and Polonite® there was a significant decrease in the phosphorus binding efficiency for the reaction time of 12 h. The raw travertine at the shaking time used showed the phosphorus removal efficiency at the level of 23.52%, and the marl 53.94%. As the contact time lengthens, the efficiency of the process increases, which was also confirmed by studies using limestone, where an increase in process efficiency from 16% to 71% for the contact time range of 1–24 h was noted [41].

As in the case of other analyzed parameters, the shaking time did not have a significant effect on the phosphorus binding efficiency of heated materials, which also show the highest sorption capacity (heated marl 1.00 mg P/g, heated travertine 0.98 mg P/g).

In the case of modified materials, an increase in pH was also observed (marl from 5.56 to 11.76, travertine from 5.56 to 11.56). In terms of conductivity, this parameter also increased for the heated materials – travertine (from 43.2 to 724 µS/cm) and marl (from 43.2 to 1,385 µS/cm), however not as high as in the case of shaking for 24 h (Figs. 3 and 4).

4. Conclusion

The results of research on new reactive materials have shown that in the elemental composition of marl and travertine, in the range of elements showing the ability to retain phosphorus, the Ca content predominates, which indicates the binding of this element by precipitation in the form of sparingly soluble calcium phosphates. In the conducted studies, the highest sorption capacity at the level of 8.72 mg P/g reached the marl at the initial concentration of 188.72 mg P/L. In terms of the parameters of the process under static conditions, the most optimal for marl, travertine and Polonite® was shaking speed of 350 rpm and shaking time 24 h, while the most appropriate particle size is 1–2 mm, at which sorbents achieve the best phosphorus retention efficiency. Heat-treated marl and travertine, regardless of the process conditions and fraction size, show much greater phosphorus binding efficiency than their raw forms. With the increase of the marl processing temperature, the structure of the material changed into a more compact and insoluble, which resulted in the reduction of the turbidity of the solutions after the process, compared to the tests with the use of raw marl. On the other hand, thermally modified travertine, with increasing modification temperature, changed its properties towards soluble, free-flowing material, increasing the turbidity of solutions after the process was carried out. The direction of further research will be to determine the stability of raw materials, that is, marl and travertine, which, under various process conditions, show variable in a wide range of phosphorus binding efficiency compared to their thermally treated forms, which maintain high, constant efficiency, regardless of the process parameters or fraction size.

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