

Article

Use of Natural Sorbents in the Processes of Removing Biogenic Compounds from the Aquatic Environment

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Abstract: This paper presents the results of the evaluation of the possibility of using a selected sorbent of natural origin, mineral (opoka rock), for the removal of biogenic compounds from aqueous solutions. The analyzed opoka rock contains approximately 70% calcium carbonate (CaCO₃) and from 26 to 27% silicon dioxide (SiO₂) and has been classified as heavy opoka rock. The experiment focused on the sorption of organic components, including phosphorus (P), nitrogen (N) and carbon (C). It was carried out for two treatment systems, column tests and batch tests, for three samples of water—water from a water supply system, water from a fish pond and water from a garden pond—located in the region of Silesia (Poland). The results showed that the P removal efficiency was equal to 96.6% for the fine-grained sorbent (grain size < 2 mm) and 90.8% for the coarse-grained sorbent (2–4 mm) in the batch tests, while lower effectiveness was observed for the column tests, reaching 67.8% and 54%, respectively. The efficiency of N (NH₄⁺) removal was equal to 84% for both types of sorbents in the batch tests, while it was 47.7% for the fine-grained sorbent and 26.3% for the coarse-grained sorbent in the column tests. The efficiency of the removal of nitrate-nitrogen (NO₃[−]) was higher for the fine-grained sorbent in all analyzed water samples. The use of materials of natural origin in industrial applications is a recommended direction, part of the green transition. The analyzed samples of opoka rock come from deposits, and opoka rock has so far not been analyzed in terms of its possible use in water and sewage treatment technology. Therefore, further research is recommended for this low-cost sorbent, which may be a competitive material for commercial products.

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1. Introduction

Water is one of the most important resources in the world, necessary for the life of all organisms, including humans [1,2]. Over 70% of the earth's surface is covered by water, which suggests that water resources are very large [3]. However, of all the water resources on earth, only about 2.5% are freshwater fit for consumption [4]. The remainder of the water, mainly found in oceans and seas, is saltwater, which is not used for drinking purposes. It is also worth mentioning that the majority of freshwater, approx. 70%, is stored in glaciers and snow, mainly in Antarctica [5]. These freshwater resources should be sufficient to meet the needs of the world's growing population [6]. However, this is the cause of the growing concerns over the availability of sufficient water supplies to accommodate the future needs of society. This requires taking further measures to protect water resources, as well as to recover clean water from wastewater. This is especially important due to the fact that human use of natural waters (especially freshwater resources) has increased steadily in recent decades [7]. Moreover, it is to be expected that this trend will

continue, as there is an observed rapid increase in the world's population, as well as urbanization and the ever-widening utilization of water for industrial, agricultural and recreational purposes [8].

Water scarcity is a problem that is increasing worldwide, and regions and cities such as Cape Town in South Africa [9] and Cairo in Egypt [10] are already facing severe water shortages. The current use of surface water resources has already reached maximum capacity in some regions of the world, such as the southwestern United States (US) [11]. The problem of water deficit affects millions of people around the world, including over 100 million citizens in Europe [12], despite the fact that this continent has many large rivers and lakes. In Europe, around 80% of freshwater consumed for drinking and other uses comes from rivers and groundwater, making these sources extremely vulnerable to the dangers of overexploitation, pollution and climate variability [13].

Currently, a problem with water scarcity is related not only to the drinking water quantity available but also to its quality, which is a result of intensive human activity [14]. The major cause of contamination of the aquatic environment is surface runoff from agricultural lands, where the excessive use of fertilizers [15] and insufficiently treated municipal and industrial wastewater are discharged into natural reservoirs [16]. The infiltration of mineral fertilizers (such as nitrates and phosphates), herbicides and pesticides into surface and subsurface waters contributes to water pollution (unfit for drinking) and disrupt the aquatic ecosystems in various regions [17]. Moreover, natural reservoirs, such as lakes and rivers, are also contaminated by inadequate sewage disposal, the discharge of untreated industrial and municipal wastewater (including toxic wastewater such as polychlorinated biphenyls) and the release of heated wastewater from industrial facilities (such as power plants), resulting in thermal pollution and associated problems [18]. There are also biogenic compounds that occur in the aquatic environment, such as phosphorus (P) and nitrogen (N), which are the main causes of eutrophication in water reservoirs [19]. As a result of the increase in the content of these two biogenic compounds in water, algae multiply massively, creating huge biomass. After algae cells die, their biomass decomposes, which releases even larger amounts of phosphorus and nitrogen into the water and additionally deteriorates the oxygen conditions in reservoirs. The lower amount of dissolved oxygen in water increases the release of nutrients from the bottom sediments and reduces the biodiversity of reservoirs. The lack of availability of light causes an increase in the intensity of cell death that ends up in the form of biomass at the bottom of reservoirs. This, in turn, is the initiator of the last stage of eutrophication [20]. The accumulation of large amounts of dead plant parts, algae and other living organisms within the bottom layers, combined with oxygen deficiency and the lack of light availability, creates ideal conditions for the promotion of the growth of putrefying bacteria. Organisms of this nature, through anaerobic biodegradation reactions, are responsible for the formation of unpleasant odors. They are also the cause of the emission of toxins and changes in the pH of water. The consequences of the above-discussed phenomenon of eutrophication include the disturbance of the balance of the food chain in local ecosystems, changes in the physical and chemical parameters of water, toxin synthesis, turbidity of water and the appearance of green color, emission of an unpleasant odor, intensification of competition processes for living space in the ecosystem and shallowing of the bottom of water reservoirs [21]. In general, eutrophication resulting from runoff from agricultural land and the discharge of insufficiently cleaned sewage is an undesirable phenomenon in water reservoirs.

The effects of pollution of the aquatic environment, including eutrophication, are commonly considered to be the source of very important ecological, economic and even social problems [22]. Aspects such as water turbidity, the green color of reservoirs, water toxicity or unpleasant odor have a very strong impact not only on the state of the environment and biodiversity but also on tourism and industry related to fishing. In many cases, facilities with blooms are taken out of service and significantly limit both the earning and recreational opportunities of society [23]. The excessive content of biogenic raw materials

in water reservoirs (ponds and swimming pools) could be a threat to the biological balance of aquatic ecosystems. Moreover, in tourist areas, it can also contribute to emerging social and economic problems resulting from the inability to use water reservoirs for recreational purposes. Therefore, it is important to undertake wide-ranging activities to prevent and reduce the negative consequences of the eutrophication effect of water reservoirs.

In recent years, more and more attention has been paid to the removal of biogenic compounds and minimizing their negative impact on receiving waters [24]. Physical, chemical and biological methods, as well as integrated processes combining the above methods, are used to remove nutrients from the aquatic environment [25]. Nitrogen can be removed from water by physical (desorption and ion exchange), chemical (chlorine oxidation) and biological (nitrification) methods [26]. Phosphorus can be removed from water solutions via conventional methods, including chemical precipitation (with aluminum, iron and lime salts) and biological nutrient removal (BNR) [27]. In many cases, the above-mentioned methods of removing nutrients turn out to be very expensive [28], prompting the search for so-called low-cost sorbents in water and wastewater treatment technology [29]. Among them, materials of natural origin, such as clays, siliceous materials and natural zeolites, deserve special attention. It is also possible to use industrial waste materials in the adsorption process, e.g., ashes, sludges and sediments [30,31]. The main requirements for modern sorbents are their easy availability, high efficiency and economic efficiency [32]. Natural and waste materials are of particular interest, as they are easy to obtain and do not require complicated prior preparation. Biosorbents are a very wide group, including chitosan and biomass (hulls of various types of grains, leaves of trees and shrubs, seaweed and natural fibers such as coconut, sisal and raffia), which is of great interest because they are easily available in various regions of the world [33,34].

The objective of this work was to evaluate the possibility of using a selected sorbent of natural origin, opoka rock, to remove biogenic compounds from aqueous solutions. This work also includes a comparison of the effectiveness of using this mineral material with other methods of N and P removal from aqueous solutions. The scope of this paper includes the characteristics of the material used from the region in Poland, conducting the process of N and P sorption in two filtration systems and comparing the results with other authors. The use of materials of natural origin in industrial applications is a recommended direction, part of the green deal strategy [35], which is being promoted in various regions of the world, such as America, Europe, Asia and Australia.

2. Materials and Methods

This study was conducted in three successive stages. The research framework is presented in Figure 1.

Stage 1—Characterization of the natural-origin sorbent. In the first stage, the natural mineral used in the analysis was characterized. For this purpose, tests were carried out on the physicochemical properties of the limestone fraction from the Silesia region in Poland. The mineral was sent for direct mineralogical analysis (X-ray technique), a method allowing the determination of the mineralogical composition of solid materials. Two test fractions of minerals were analyzed: Fraction A—fine (grain size < 2 mm) and B—coarse (2–4 mm). The samples of materials were ground for approx. 5 min in an agate mortar. The obtained powder was pressed into a metal window to perform an X-ray powder diffraction (XRD) analysis. Measurements were made using a PANalytical X-ray diffractometer, model X'Pert Pro MPD PW3040/60. The obtained diffraction pattern was processed in the HighScore + program by PANalytical (version 4.9), based on the pattern databases: PDF4 + (commercial database of the International Center for Diffraction Data, version 2019) and Inorganic Crystal Structure Database (ICSD, version 2015). This stage of research also included an analysis of the physicochemical properties of the natural sorbent, including an analysis of pH in H₂O, reactivity (according to norm: PN-EN 13971) and determination of the neutralization value (according to norm: PN-EN 12945 + A1). The results of this stage are presented in Section 3.1.

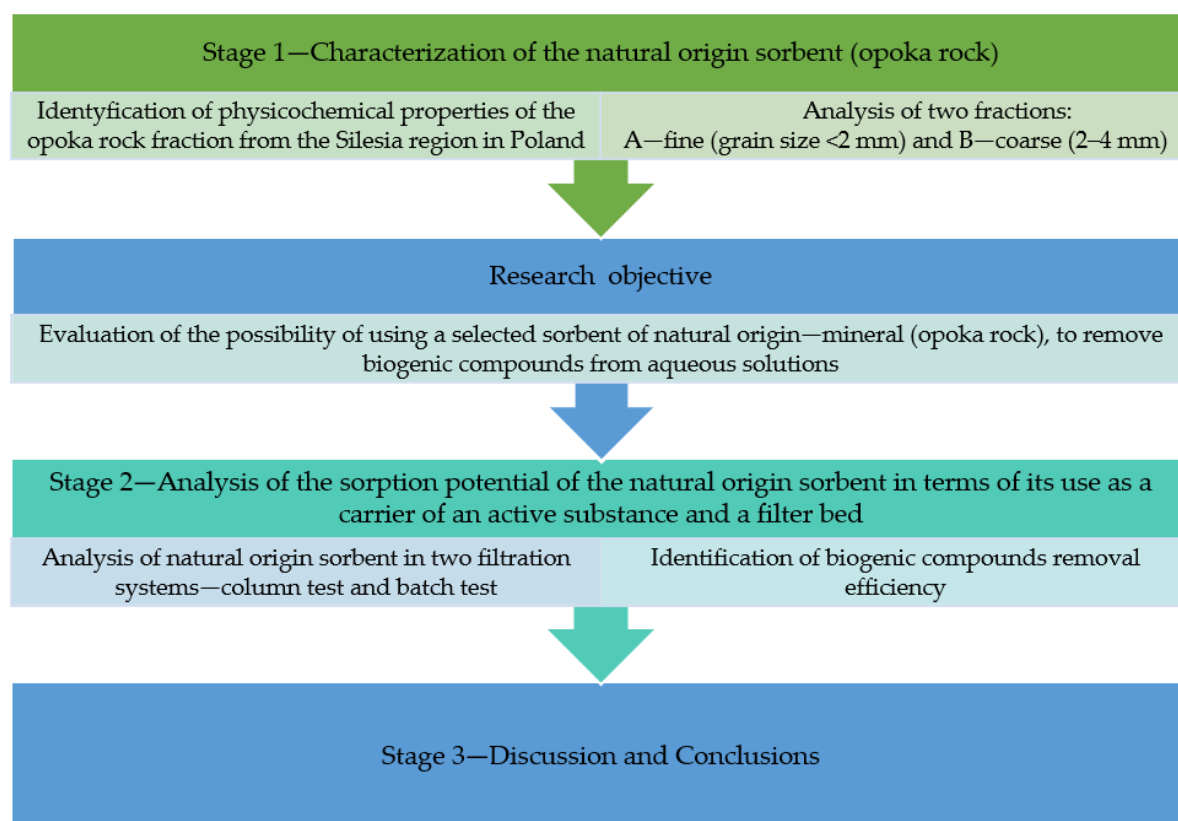


Figure 1. The assumed research framework.

Stage 2—Analysis of the sorption potential of the natural-origin sorbent in terms of its use as a carrier of an active substance and a filter bed. The aim of this stage was to determine the sorption potential of the mineral (natural-origin sorbent—opoka rock) in relation to the basic nutritional elements used in agriculture (nitrogen and phosphorus) and total organic carbon. The analysis was conducted in two filtration systems—column analysis and batch tests. Three water solutions were used in this study: W1—tap water from a water supply system located in the region of Silesia, W2—water from a fish pond located in the region of Silesia, W3—water from a garden pond located in the region of Silesia. The chemical compositions of the water solutions were analyzed for determination, including an analysis of pH, total organic carbon (TOC), content of nitrogen (N) (in the form of NO_3^- , NH_4^+) and phosphorus (P) (in the form of PO_4^{3-}). Each sample was run in triplicate, and the results are presented as the mean. The research was conducted with the use of accredited methods: pH (potentiometric analysis), NH_4 content in water (according to the Nessler method), NO_3 content in water (according to EN 26777/1993), PO_4 content in water (spectrophotometric method, UV-VIS; wavelength, 690 nm) and total organic carbon (TOC) in water (according to EN 1484). The results of this stage are presented in Section 3.2.

The first system, column analysis, consisted of preparing a series of columns filled with the 2 types of tested materials. Then, three types of water (W1, W2, W3) were passed through the prepared filtration systems. The eluate obtained after filtration was subjected to chemical characterization. Each filtration procedure was performed three times for each tested sample. The columns used during the experiment have the following dimensions: $H = 1020$ mm, $r = 25$ mm. The effective volume of the individual column was equal to 2000 cm^3 . To each column, 1000 g of the tested fraction of opoka rock was introduced. Due to the differences in material properties, each tested fraction showed a different water retention time, which is presented below. This parameter also slightly differed along the different water sample types. However, in this case, differences were in the range below

0.01%. The retention time for the columns filled with Material A was equal to 1.42 L/min \pm 0.0, and the retention time for the columns filled with Material B was equal to 1.59 L/min \pm 0.03. The amount of water passed through the filtration columns was equal to 2 L per trial. As a result, the overall amount of filtrated water during the analysis was equal to 6 L per type of sample. After filtration, the eluate was collected and subjected to further analyses.

The second system, the batch test, consisted of the quantitative introduction of the tested material into glass containers with the tested water samples. The batch experiment was conducted in 1000 dm³ glass containers. To each container, 1000 cm³ of water subjected to study was introduced. Next to each prepared sample, 10 g of mineral material solution was introduced, in accordance with the similar order as in the case of column trials. After that, the prepared mixtures were shaken (25 rpm) for 1 h. In the final stage, samples were subjected to stabilization for 24 h. Then, the solid fraction was separated from the liquid fraction by filtration using membrane filters. After the process, the filtrate was sent for quantitative analysis to determine the concentration of N (in the form of NO₃⁻, NH₄⁺), P (PO₄³⁻) and TOC.

After the procedures described above, nutrient removal efficiency was calculated. This parameter refers to the effectiveness of the removal of biogenic raw materials from water, and it is shown as E—effectiveness of the adsorption process (the amount of nutrients that are adsorbed of filtration material). The following formula was used for the evaluation of the adsorption efficiency parameter:

$$E = \frac{C_o - C_{eq}}{C_o} * 100 [\%] \quad (1)$$

where E—effectiveness of the adsorption process (percentage, %); C_o—initial concentration (mg/ dm³); C_{eq}—equilibrium concentration (mg/dm³).

Stage 3—Discussion and comparison of the obtained results with the results of other authors. A desk research method was used. For this purpose, we analyzed scientific papers (peer-reviewed articles) available in scientific databases such as ScienceDirect, Google Scholar, BazTech, Multidisciplinary Digital Publishing Institute (MDPI) and the Polish Scientific Bibliography [36]. The keywords used were “adsorption”, “nitrogen”, “phosphorus”, “water purification”, “nutrient removal”, “N”, “P”, “removal” and “treatment”. The results of this stage of the research are presented in Section 4.

3. Results

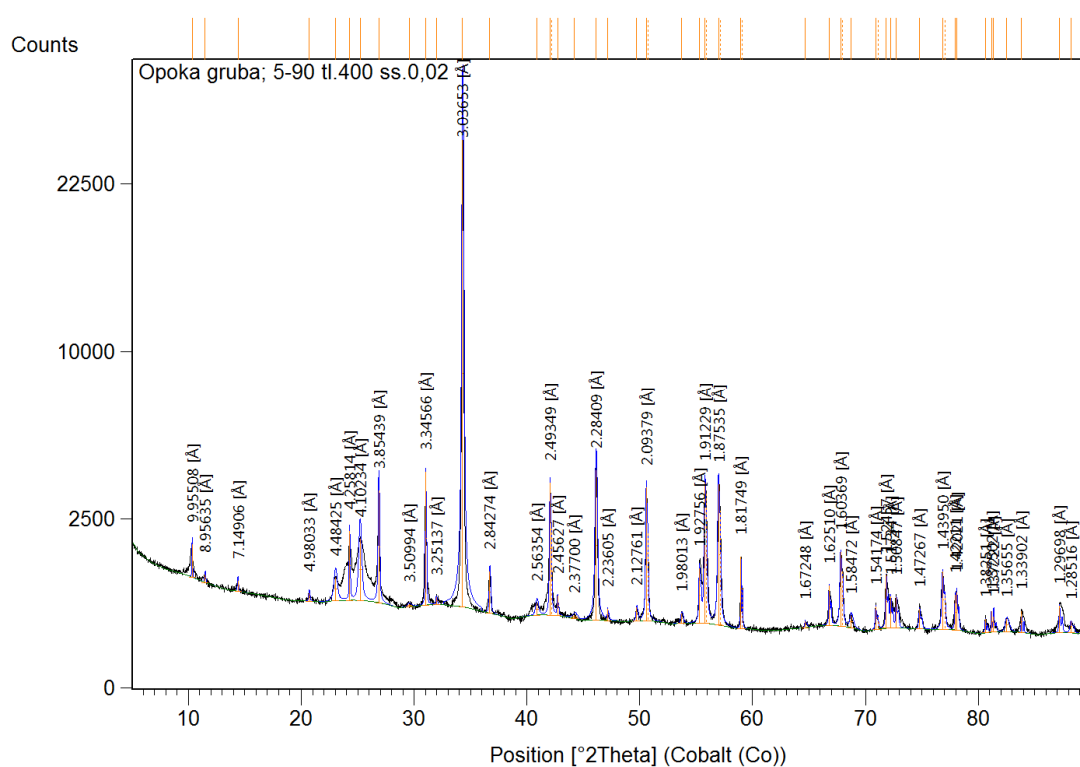
This section provides a description of the results.

3.1. Characterization of the Natural-Origin Sorbent

The results of the crystalline phases of the analyzed materials are presented in Table 1 and Figures 2 and 3. The dominant opoka rock components are always calcium and silica. The results obtained during the analysis show that the mineral contains approximately 70% calcium carbonate (CaCO₃) and from 26 to 27% silicon dioxide (SiO₂). Opoka rock, in which calcium has a dominant part in its composition, is called “heavy” or “calcareous” rock. There is also a small amount of illite in both materials, approx. 2–3%. The contents of kaolinite and clinoptilolite are below 1% in both samples.

Table 1. Quantitative fraction of crystalline phases in the sample—coarse-grained sorbent (2–4 mm) and fine-grained (0–2 mm) sorbent.

Mineral Name	Chemical Formula	SemiQuant (%)	
		Coarse-Grained	Fine-Grained
Calcite	CaCO_3	69	71
Quartz	SiO_2	9	7
Cristobalite low	SiO_2	10	11
Tridymite	SiO_2	8	8
Illite 2M1	$\text{K}(\text{Al}_4\text{Si}_2\text{O}_9(\text{OH})_3)$	3	2
Kaolinite 1A	$\text{Al}_4(\text{OH})_8(\text{Si}_4\text{O}_{10})$	0.2	0.5
Clinoptilolite	$\text{Ca}_{3.16}\text{Si}_{36}\text{O}_{72}(\text{H}_2\text{O})_{21.80}$	0.5	0.8

**Figure 2.** X-ray diffraction pattern of the sample—coarse-grained material (sorbent).

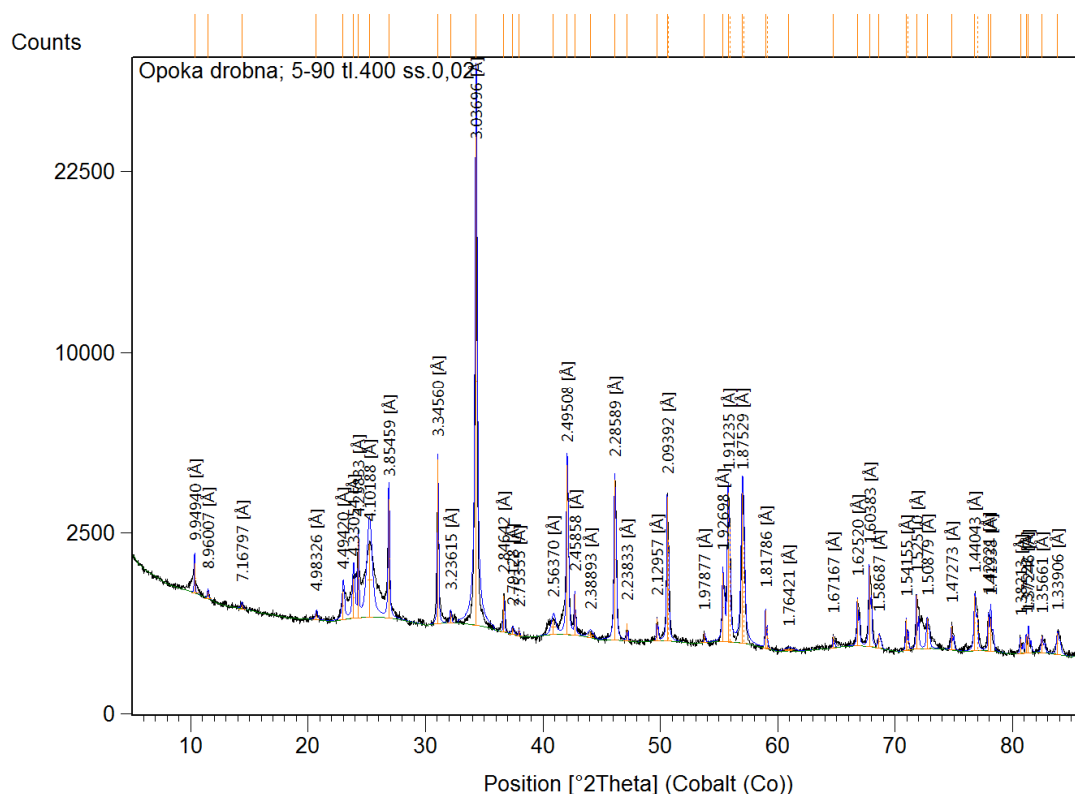


Figure 3. X-ray diffraction pattern of the sample—fine-grained material (sorbent).

The analysis also included identification of the pH, reactivity and neutralization value for both fractions of the mineral. The values presented in Table 2 indicate that the tested material is classified as chalk lime (reactivity of limestones, 65–100%).

Table 2. pH, reactivity and neutralization capacity of mineral.

Indicator	Type of Material	
	Fine-Grained	Coarse-Grained
pH	8.6	8.5
reactivity	0.7495	0.7022
Neutralization value	32.5 (for CaO)	30.5 (for CaO)

3.2. Removal of Biogenic Raw Materials from Aquatic Solutions with the Use of Natural-Origin Sorbent

The chemical composition of the aquatic solutions used in this study is presented in Table 3. In the experiment, three samples of water were analyzed: (i) tap water from a water supply system located in the region of Silesia, (ii) water from a garden pond located in the region of Silesia and (iii) water from a fish pond located in the region of Silesia. Water pH is one of the most important indicators determining the biological life conditions in aquatic solutions. The appropriate pH level, guaranteeing effective self-cleaning of reservoirs and creating an appropriate climate for the bodies in the pond, should be 7.4–8.4. The analyzed aquatic solutions were in the recommended range, while the pH of tap water from the water supply system was the lowest (7.5), and water from the reservoirs was equal to 8.1. The analysis of nutrients showed that tap water contains the lowest levels of nitrogen, phosphorus and carbon compounds, which results from the fact that this water must meet the conditions of water permitting its use, specified in the relevant legal acts in Poland.

The concentrations of ammonia and nitrates were the highest in the water coming from ponds. The highest concentrations of ammonium nitrogen (NH_4^+) and nitrate-nitrogen (NO_3^-) were found in the fish pond water, reaching 0.9 mg/dm^3 NH_4^+ and 4.4 mg/dm^3 NO_3^- . In this aqueous solution, the highest concentrations of phosphorus (33.3 mg/dm^3 of PO_4^{3-}) and organic carbon (41.7 mg/dm^3 of TOC) were also observed. A slightly lower content of these components was observed in the garden pond water samples, reaching 0.5 mg/dm^3 NH_4^+ , 2.1 mg/dm^3 NO_3^- , 16.7 mg/dm^3 of PO_4^{3-} and 27.5 mg/dm^3 TOC.

Table 3. Chemical composition of the aquatic solutions.

Water Sample	pH	NH_4^+ (mg/dm^3)	NO_3^- (mg/dm^3)	PO_4^{3-} (mg/dm^3)	TOC (mg/dm^3)
W1	7.5	<0.1	<3.0	0.02	1.1
W2	8.1	0.9	4.4	33.3	41.7
W3	8.1	0.5	2.1	16.7	27.5

W1—tap water from a water supply system located in the region of Silesia, W2—water from a fish pond located in the region of Silesia, W3—water from a garden pond located in the region of Silesia.

The results of the column test for the analyzed water samples are presented in Table 4 and for the batch experiment in Table 5. The phosphorus removal from tap water (W1), taken from the water supply system was equal to 100% for both types of sorbents (fine-grained sorbent, 0–2 mm; coarse-grained sorbent, 2–4 mm) in the column test and in the batch test.

The analysis of the effectiveness of phosphorus removal showed that the best results were observed for the batch experiments compared to the column tests. The highest effectiveness in P removal was observed for water from the ponds (W2 and W3), where the P content was the highest. The degree of adsorption of P compounds in the fine-grained sorbent reached 96.5% and 96.6%, while for the coarse-grained sorbent, it was equal to 90.8% and 83.0% in water from the fish pond (W2) and the garden pond (W3), respectively. The lower effectiveness in P removal was observed for the column tests, reaching 53.8% and 67.8% for the fine-grained sorbent and 38% and 54% for the coarse-grained sorbent.

Table 4. Removal efficiency of selected indicators from aquatic solutions—column test.

Water Sample	Sorbent Type	Removal Efficiency (%)			
		NH_4^+	NH_4^+	NH_4^+	TOC
W1	S1	-	-	100	66.4
	S2	-	-	100	27.3
W2	S1	47.7	33.0	53.8	52.6
	S2	26.3	27.0	38.0	46.5
W3	S1	55.4	49.2	67.8	62.9
	S2	18.9	30.3	54.0	28.2

W1—tap water from a water supply system located in the region of Silesia, W2—water from a fish pond located in the region of Silesia, W3—water from a garden pond located in the region of Silesia; S1—fine-grained (0–2 mm) sorbent; S2—coarse-grained (2–4 mm) sorbent.

Table 5. Removal efficiency of selected indicators from aquatic solutions—batch test.

Water Sample Sorbent Type		Removal Efficiency (%)			TOC
		NH ₄ ⁺	NH ₄ ⁺	NH ₄ ⁺	
W1	S1	-	-	100	69.7
	S2	-	-	100	63.4
W2	S1	84.3	49.0	96.5	79.1
	S2	86.1	42.8	90.8	65.4
W3	S1	39.2	51.7	96.6	69.3
	S2	66.9	33.7	83.0	55.0

W1—tap water from a water supply system located in the region of Silesia, W2—water from a fish pond located in the region of Silesia, W3—water from a garden pond located in the region of Silesia; S1—fine-grained (0–2 mm) sorbent; S2—coarse-grained (2–4 mm) sorbent.

The efficiency of nitrogen compound removal was also higher for the batch experiment than for the column experiment. In general, ammonia nitrogen (NH₄⁺) removal rates were higher than for nitrate-nitrogen (NO₃⁻). More than 84% ammonia nitrogen was adsorbed from the water samples coming from the fish pond for both types of sorbents in the batch tests, while 47.7% and 26.3% NH₄⁺ were adsorbed from the same water samples for the fine-grained sorbent and the coarse-grained sorbent, respectively, in the column test. Inconsistent test results were obtained for water samples from the garden pond. In the column test, the higher NH₄⁺ removal efficiency was observed for the fine-grained sorbent (55.4%) and for the batch test for the coarse-grained material (66.9%). The efficiency of the removal of nitrite nitrogen (NO₂⁻) was higher for the fine-grained sorbent in all analyzed water samples.

In both experiments, promising results were obtained in terms of the removal of carbon in the form TOC. Higher efficiency was observed for the fine-grained sorbent in all analyzed water samples, including tap water. The removal efficiency for the fine-grained sorbent was in the range of 52.6–66.4% in the column experiments and in the range of 69.3–79.1% in the batch experiment. The removal efficiency for the coarse-grained sorbent was in the range of 27.3–46.5% in the column experiments and 55–65.4% in the batch experiments.

On the basis of the column and batch studies, it can be observed that the natural form of calcareous rock, especially in fine-grained form, is characterized by very good sorption properties in relation to nitrogen, phosphorus and carbon compounds.

4. Discussion

An excessive amount of biogenic compounds in surface waters leads to an increase in water fertility and their exclusion from economic, recreational or natural use [37]. One of the methods of removing nutrients from surface waters is the use of sorbents, i.e., reactive materials with the ability to selectively remove certain substances by sorption or precipitation. In the green transformation [38], which includes individual strategies towards a clean environment [39], great attention is paid to the use of natural sorbents for the removal of various impurities from water solutions, including biogenic raw materials. Due to their origin, reactive materials can be divided into natural or anthropogenic, which in turn can be divided into commercial products dedicated to P removal (Pollytag®, Filtralite®, Leca®, Polonite®, Rockfos®, and Filtra P), as well as waste (or construction) materials, which due to their chemical composition, have P sorption properties (cellular concrete, expanded clay, slags and others) [40,41].

In the current study, it was indicated that the tested natural-origin sorbent, opoka rock, has high application potential for the removal of P and N from aquatic solutions. It is a consequence of the high calcium content in opoka rock, which causes this material to

be reactive to remove nutrients from aqueous solutions. As a reactive material for the removal of biogenic compounds from aquatic solutions and wastewater, the most used are calcium rocks, i.e., heavy opoka rocks [42], which were used in the current study.

In most of the studies available in the literature (Table 6), opoka rock was evaluated for the removal of P from water solutions, as ponds and sewage. There is a limited number of papers that have focused on N removal with the use of this sorbent.

Table 6. Removal efficiency of biogenic compounds from aquatic solutions with the use of opoka rock sorbent.

Treated Medium	Removal Efficiency		Source
	P	N	
Domestic sewage	90%	-	[43]
Domestic sewage	91%	-	[44]
Domestic sewage	90.9%	-	[45]
Septic tank effluent	80%	11%	[46]
Synthetic solution	>95%	-	[47]
Synthetic solution	99.3%	-	[48]
Synthetic sewage	<50%	-	[49]
Swim pond	95%	-	[50]

In Ref. [43], it was indicated that opoka rock has the ability to remove P from domestic sewage, as well as heavy metals. The conducted research shows a degree of P removal of up to 90%. Opoka rock, which removed P from the solution in the first minutes of the test (95% reduction after 5 min of contact), turned out to be very effective in the short contact time in the static experiment. In this work, opoka rock (Fraction 1–5 mm) was more effective at removing P from a swim pond than a commercial product FerroSorp® [50]. Ref. [45] confirmed the high efficiency of opoka rock for the removal of P from domestic sewage coming from a small home sewage treatment station. The research was carried out on a model sewage treatment station with a sand bed, with and without opoka rock. The average efficiency of total P removal with opoka rock (90.9%) was more than twice as high as in the sewage without opoka rock (42.4%). The high P removal efficiency was also indicated for commercial products, based on opoka rock (Polonite). In [44], Polonite was evaluated in domestic sewage in batch experiments. Polonite demonstrated high efficient sorption of P from the nutrient solution, reaching 91%. The assessment of P sorption capacity was evaluated for different filtration materials to be used for P removal from water and wastewater in Ref. [48]. The effectiveness of P removal with the use of Polonite, manufactured from bedrock opoka, was equal to 99.3% in the batch tests. In Ref. [49], more than 95% of P was removed from a synthetic solution in the column leaching experiment with the use of mineral-based sorbents Filtra P (produced after heating a mixture of limestone, gypsum and iron oxides) and Polonite (manufactured from siliceous sedimentary opoka rock in Poland that is heated to 900 °C). Ref. [46] presents an evaluation of mineral-based material (Polonite) for the removal of P, N and from a septic tank effluent. The efficiency of the opoka-based material in the removal of P was equal to 80%, inorganic nitrogen (TIN) 11% and TOC 72%. These results confirmed the high P removal efficiency with the use of an opoka-based material, as well as possible N removal, thereby providing superior performance of the material in the water and sewage treatment process. A detailed revision of reactive materials for the removal of nutrients from water solutions was conducted in [40]. It was also confirmed that among the natural materials, opoka rock has the highest sorption capacity in water solutions. Opoka-based materials can also be used for the removal of other compounds, such as aluminum [46], catechol [51], fluoride [52], polypropylene [53] or cadmium [54], as well as gases (carbon dioxide (CO₂) and sulfur dioxide (SO₂)) [55,56].

It is worth mentioning that Ref. [42] has shown that the ability of opoka rock to bind phosphorus is strongly correlated with the calcium content in its chemical composition. In Ref. [49], opoka rock showed a P removal efficiency $< 50\%$, although the extracts (synthetic sewage) were supersaturated with respect to hydroxyapatite. It could be associated with a too-low supersaturation to initiate Ca-P precipitation. The additional content of the silicate fraction may increase the sorption capacity of the material, giving it specific functional properties. These include, among others, the ability to absorb biogenic compounds from water solutions. The natural form of calcareous rock with a high content of calcium carbonate (CaCO_3) can also be used in the agriculture, construction, energy, food and chemical industries [41]. The wide range of applications is related to the specific property of this chemical for pH adjustment, chemical bond initiation and preservation activity. There are also some limitations in the usage of this solution for the removal of biogenic raw materials from the aquatic environment. The small particle size of the tested fractions may have a temporal effect on water clarity. The solution after direct introduction to water forms a semi-soluble mixture that is present on the reservoir surface for 2–4 days. In some cases, such an effect may have a negative impact on some biotic ecosystems.

One of the most important benefits of the usage of natural-origin sorbents is the fact that they are more environmentally friendly and more effective for releasing P to plants in agricultural production [57] after use in the treatment process compared to artificial precipitation chemicals. Moreover, the chemical composition of this silica-calcium rock is safe for soil environments. The heavy metal content is comparable to that normally found in most of the agricultural soils in Poland [58]. Additionally, the economic factors are encouraging. Apart from the fact that adsorption using natural or waste materials is considered one of the most effective methods of cleaning the environment from both organic and inorganic substances, the main economic advantage of this method is its low application costs [51].

In the current paper, the analyzed opoka rock comes from deposits in the Silesia region in Poland. So far, this material has not been analyzed in terms of its possible use in water and sewage treatment technology. The results of preliminary studies presented in this paper confirm that this material can be used for the treatment of water reservoirs and also as a sorbent in municipal sewage treatment processes. Comparing this analyzed sorbent to other materials in the discussion, this material has not been further processed. In the subsequent stages of the research, it is planned to calcine and obtain a sorbent that will be transferred for further analysis in terms of the effectiveness of removing biogenic materials from aqueous solutions. Further research on this material will continue.

5. Conclusions

In order to remove biogenic raw materials from the aquatic environment, this paper proposes the use of natural mineral, fine- and coarse-grained opoka rock fractions. The analysis of P and N removal efficiency was analyzed in batch and column tests. The results showed that the P removal efficiency was equal to 96.6% for the fine-grained sorbent and 90.8% for the coarse-grained sorbent in the batch test. The lower effectiveness in P removal was observed for the column tests, reaching 67.8% for the fine-grained sorbent and 54% for the coarse-grained sorbent. This is consistent with the results of other authors, who also used opoka rock for P removal from aquatic solutions (such as ponds and sewage) and achieved efficiencies of up to 99%. The ability of opoka rock to bind P is strongly correlated with the calcium content in its chemical composition. The efficiency of N (NH_4^+) removal was equal to 84% for both types of sorbents in the batch tests, while it was 47.7% for the fine-grained sorbent and 26.3% for the coarse-grained sorbent in the column test. The efficiency of the removal of nitrate-nitrogen (NO_3^-) was higher for the fine-grained sorbent in all analyzed water samples. The analyzed samples of opoka rock come from deposits in the Silesia region in Poland, which has so far not been analyzed in terms of its

possible use in water and sewage treatment technology. Therefore, further research is recommended for this low-cost sorbent, which may be a competitive material for commercial products.

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