

Comparative analysis of phosphorus removal efficiency from water on selected filter beds for use in the natural swimming pond filtration systems

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ABSTRACT

This study aimed to compare the adsorption efficiency of phosphorus and its possible removal using three types of filter materials: modified rock opoka (Rockfos[®]), iron grit (Sulfur E), and limestone, based on laboratory column studies. Adsorption studies of phosphorus were carried out in laboratory conditions at two concentration levels (2 mg P/L and 5 mg P/L), and phosphorus concentration analyses in eluate were conducted using a spectrophotometer. For the assessment of adsorption capacity and potential, changes in phosphorus concentrations in eluate (P_{tot}) per operating cycle of each filter were analyzed, including calculations of phosphorus adsorption efficiency and capacity. In case of possible eluate leaching from the bed, seven other parameters were additionally analyzed, including: pH, electrical conductivity (EC), water hardness (mval/L), ammonium ions ($N-NH_4$), nitrate ions ($N-NO_3$), iron ions (Fe), and manganese ions (Mn) in mg/L. Based on the results of eluate analysis, it was observed that the tested filtration materials were able to remove phosphorus from water. The highest and most stable adsorption efficiency was shown by the material Rockfos[®] (90–99%), followed by Sulfur E (20–89%), and the lowest by limestone (24–70%). The tested granulate used in the study also showed very favorable parameters of sorption effectiveness and eluate leaching. The tested minerals were characterized by the release of various parameters from the deposit and/or change in their values to a minimal extent without exceeding the water quality standards for FLL eco-pools. The potential for use in filtration systems of natural swimming ponds applies in particular to modified rock (Rockfos[®]). The material Sulfur E, despite its lower adsorption effectiveness, was also highlighted due to its significant Fe content, which could be a phosphorus availability regulator for microorganisms in water and eco-pool systems.

Keywords: modified rock opoka, iron grit, limestone, eco-pools, mineral filtration.

INTRODUCTION

In the perspective of ecological technological solutions, natural swimming ponds (eco-pools, biopools) are becoming increasingly popular in every sphere of socio-economic life as an environmentally friendly alternative to typical swimming pool basins [Littlewood 2005; Casanovas-Massana and Blanch 2013; Walczak et al., 2023].

Eco-pools are artificial water reservoirs with high landscape values (quasi-mini lakes), used recreationally without the use of advanced chemical water treatment techniques. These ponds rely on the natural processes of self-cleaning of water [Casanovas-Massana and Blanch, 2013; Bus

and Karczmarczyk, 2015], based on the treatment properties of treatment wetlands (TWs) – a living substratum of an ecosystem [Langergraber and Dotro, 2019; Walczak et al., 2023].

A typical natural swimming pond is built from a water-filled basin with a bottom covered with hydro-insulation material (e.g., PVC, bentonite, EPDM). It is divided into three zones with differentiated functionality. The regeneration zone – shallow, covered with specific aquatic vegetation – is placed on a specially selected mineral bed (TWs). This zone facilitates the assimilation of substances and the biocumulatory removal of toxic compounds by macrophytes – aquatic vascular plants [Serafin et al., 2019; Walczak et al., 2023].

Additionally, the zone of microorganic biofilm in the bed aids in the mineralization of organic compounds and the physico-chemical sedimentation of suspensions. The swimming zone, in turn, is the deepest and intended for recreational use [Radic et al., 2013; Bus and Karczmarczyk, 2015; Walczak et al., 2023].

Efficient water treatment in the TWs system is linked to actively functioning ecosystems, supported by the complementary role of macrophytes and regeneration zones, as well as the properties of root systems of higher aquatic plants. A crucial aspect is also the biological, chemical, and physical sorption of biogenic compounds in the plant bed, which influences the efficiency of phosphorus sorption and the potential activity of the microorganic biofilm [Wolski et al., 2001; Walczak et al., 2023]. The result of the purifying function of TWs is to maintain bio-physico-chemical water parameters at levels suitable for recreational use, limiting the development of harmful algae, fungi, and bacteria and increasing the diversity of aquatic organisms, improving shore biodiversity, and creating optimal conditions for aquatic flora growth [Pilon-Smits, 2005; Vymazal et al., 2017; Langergraber and Dotro, 2019; Walczak et al., 2023; 2024].

Improving the capabilities of TWs in the regeneration zone of a swimming pond sometimes needs to be supported by dedicated filtration systems that mimic the natural processes occurring in the environment. These systems eliminate physical contaminants (mechanical filtration) but primarily address biogenic substances that cause water reservoir eutrophication.

The problem particularly concerns the phosphorus (P) level, which can have negative effects by overloading ecosystems in natural swimming ponds. For this reason, it is essential to explore various techniques and materials that could contribute to its removal from water used by people [Molle et al., 2005; Ádám et al., 2007].

The efficiency of phosphorus removal in water treatment systems for natural swimming ponds is linked to the use of filtration chambers with various porous mineral materials that operate based on the principles of physical adsorption (less durable) occurring due to van der Waals forces and chemical adsorption (more durable), which uses covalent and ionic bonding [Nawrocki and Biłozor, 2000; Kowal and Świdorska-Bróz, 2007]. The effectiveness of this process also depends on the granulometric characteristics of the mineral

material, including its size, grain shape, and porosity, which influence the capillary action associated with adsorption [Patil and Kulkarni 2012; Skoczko 2019; Walczak et al., 2024].

Physical and chemical adsorption primarily concerns biogenic compounds and other associated compounds, for which minerals may exhibit selective ion exchange properties [Anielak and Piaskowski, 2000; Brzychczyk et al., 2015; Bus and Karczmarczyk, 2015]. An example may be clinoptilolite, which demonstrates ion exchange selectivity relative to specific ions, such as $\text{Pb}^{2+} > \text{NH}_4^+ > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$ [Ciciszwili et al., 1990]. According to other authors, $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+}$ [Kaleta et al., 2007]. Typical adsorbents can also include substances of artificial origin (modified materials like fly ash, clays, or ceramics) as well as natural substances like lignite, sand, and specific mineral groups whose adsorption efficiency is utilized in both simple household and advanced filtration systems [Szczykowska and Siemieniuk, 2020]. Among the adsorption materials used in filtration, a wide range of carbon adsorbents is applied: wooden charcoal, anthracite, semi-coke, brown coal, or stone coal, as well as various mineral adsorbents: silica sand, activated alumina, zeolites – especially clinoptilolite and keramsite, mainly used to capture heavy metals and ammonium ions that occur naturally in mineral raw materials [Brzychczyk et al., 2015; Szczykowska and Siemieniuk, 2020].

The issue with using some natural or synthetic mineral materials is the release of ions from the bed during water filtration, which can significantly affect their quality and aesthetic values [Chorover and Brusseau, 2008; Miura et al., 2018].

The aim of the study was to determine the relationship between the physical and chemical properties of water with filtration materials and the potential utility of these materials in the functioning of water treatment systems in eco-pools, such as modified rock marketed under the trade name Rockfos[®], iron slag Sulfur E, and limestone grit. The first part of the study examined the efficiency of phosphorus removal from water in long-term filtration processes, and the second focused on the potential leaching of various chemical compounds from the materials into water. The materials were chosen to meet criteria of market availability, relatively low acquisition costs, and functional potential based on product datasheets and results of prior research.

MATERIALS

The material Rockfos® (Figure 1a) is produced by the Ceramika KUFEL company through the calcination process (decarbonization) of natural marl rock. It contains significant amounts of the following chemical elements: calcium (CaO – 43.4%), silicon (SiO₂ – 36.04%), aluminum (Al₂O₃ – 5.93%), iron (Fe – 1.34%), magnesium (MgO – 0.94%), and manganese (MnO – 0.12%). These chemical properties result in a high mineral alkalinity (pH=11–12), which can increase the pH of treated water. The material's features indicate its high porosity. The bulk density is 730 kg/m³, internal porosity is approximately 50%, and the granule size is 2–6 mm. Rockfos® has wide applications for wastewater and water treatment, particularly as a final filter in septic tanks to remove residual phosphorus in pre-treated sewage [www.ceramika-kufel.pl/rockfos/].

The material Sulfur E (Figure 1b), an iron slag granulate, comes from the EKOWAVE company [www.ekowave.pl]. In terms of physical features, it has a light brown color, cylindrical grain shape, a bulk density of 700–800 kg/m³, and a grain length of 5–15 mm. The material specification indicates a chemical composition rich in iron oxides. Its content of iron oxides determines its phosphorus-binding properties, with a potential phosphorus binding capacity of up to 40% of its active sites [product datasheet from EKOWAVE]. This material is commonly used for the removal of phosphorus in treatment biogas system, which is a product of anaerobic digestion of sludge in municipal and agricultural wastewater treatment

plants, for the purification of landfill biogas, coke gas, and synthetic gas. Due to its high porosity, the material demonstrates high efficiency in phosphorus binding under minimal flow conditions [EKOWAVE company product datasheet].

Limestone grit (Figure 1c) – limestone grit, also known as filtration limestone grit, is obtained from its own Jurassic limestone deposit by the Trzuskawica S.A. Industrial Limeworks in Sitkówka near Kielce (Poland). The material is a natural calcium carbonate produced by the mechanical processing of raw material, including crushing and fraction sorting. It contains: min. 97.0% CaCO₃, max. 0.7% Al₂O₃ + Fe₂O₃, max. 1.2% MgCO₃, and max. 2.5% SiO₂. Its physical properties include a bulk density of 1540 kg/m³, a grain density of 2710 kg/m³, and a grain size of 4–8 mm. Limestone grit has wide applications in chemistry, energy, sugar production, metallurgy, environmental protection, and the building materials industry (product datasheet). Its chemical composition indicates potential sorption capabilities for phosphorus; however, such potential has not been experimentally confirmed [www.trzuskawica.pl/wp-content/uploads/2021/01/przemysl.pdf].

METHODS

To conduct the study on the efficiency of sorption of selected parameters, a setup consisting of three filtration columns was designed, one of which served as a reference example as shown

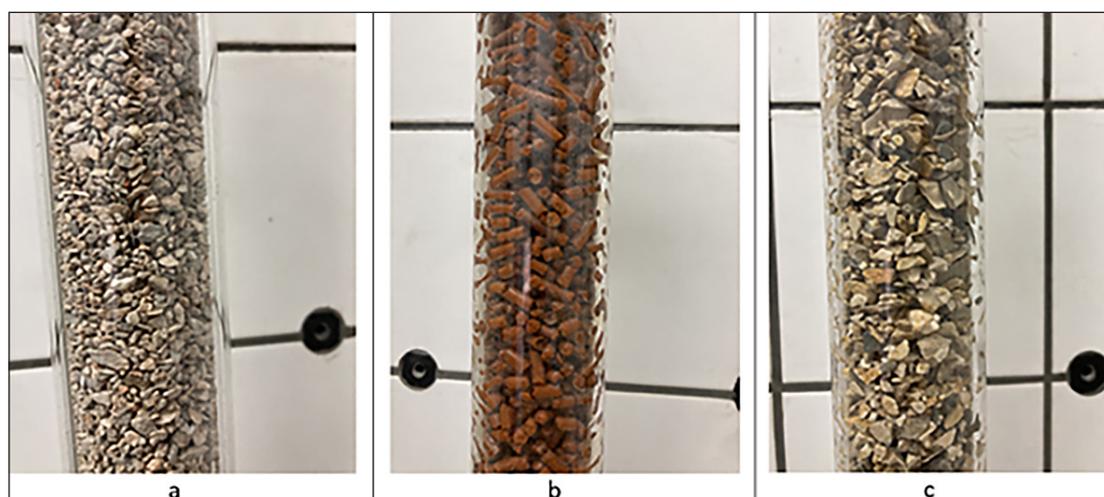


Figure 1. Filtration materials in research columns: (a) modified marl rock opoka (Rockfos®), (b) iron granulate, (c) limestone grit (photo by Walczak)

in Figure 2. In each of the columns, the tested bed was placed in the section indicated, which was subjected to an analysis of its phosphorus sorption potential.

The filtration columns were made from plexi-glass pipes with a height of 2 m, an external diameter of 60 mm, and a wall thickness of 5 mm. They were equipped with a perforated drain grate, a system of hoses and valves, adjustable clamps, a dosing pump, and an outflow reservoir for flow kinetics analysis (as per the work by Walczak et al., 2024), as well as additional piezometers and other equipment, according to the presented diagram (Figure 2).

Inside each column, at the bottom, there was a perforated grate on which a support layer composed of quartz gravel was placed, arranged in decreasing particle size. The layers were built from progressively smaller grains, such that the bottom layer had a grain size of 3–4 mm, the middle layer 2–3 mm, and the top layer 1.5–2 mm, with each layer having a height of 10 cm. The grain sizes were selected to ensure they would not block the grate's openings and were also larger than the grains of the tested bed.

On top of the support layer, the tested filtration material bed with a thickness of 70 cm was applied in each measurement cycle.

In the upper part of the column, there was an inlet pipe with an installed regulating valve, allowing the adjustment of the inflow rate of water or a laboratory solution. A similar valve was located below the column and was used to regulate

the outflow rate. The stabilization of flow conditions relied on setting the water level in the column throughout the entire study cycle so that the inflow and outflow rates of water were balanced.

Throughout the entire study cycle, due to ongoing clogging, it was necessary to correct the inflow and outflow rates as well as the water level in the column to maintain stable filtration speeds between the water and the bed.

Research methods

The first part of the study, determining the efficiency of phosphorus removal on the described materials, involved passing water with elevated phosphorus concentrations through filtration columns filled with the tested materials. Laboratory solutions with stable physical-chemical parameters were prepared: $P_{\text{total}} = 2 \text{ mg/dm}^3$; $N\text{-NO}_3 = 1.0 \text{ mg/dm}^3$; $\text{pH}=7,2$ (first series) or $P_{\text{total}} = 5 \text{ mg/dm}^3$; $N\text{-NO}_3 = 1.0 \text{ mg/dm}^3$; $\text{pH} = 7,34$ (second series). Tap water and a concentrated Na_2HPO_4 solution were used to prepare the appropriate solutions. Prepared solutions were introduced to each filter column at a rate of 5 m/h, and control samples (3 samples of effluent) were collected at 24-hour intervals, i.e., at 24, 48, 72, 96, 120, and 144 hours after the filter started operating. Effluent samples were analyzed for P_{total} , $N\text{-NO}_3$, and pH. The results obtained were presented as averaged values. A new bed was applied in each series.

In analyzing the efficiency of phosphorus removal by the filtration materials, the formula

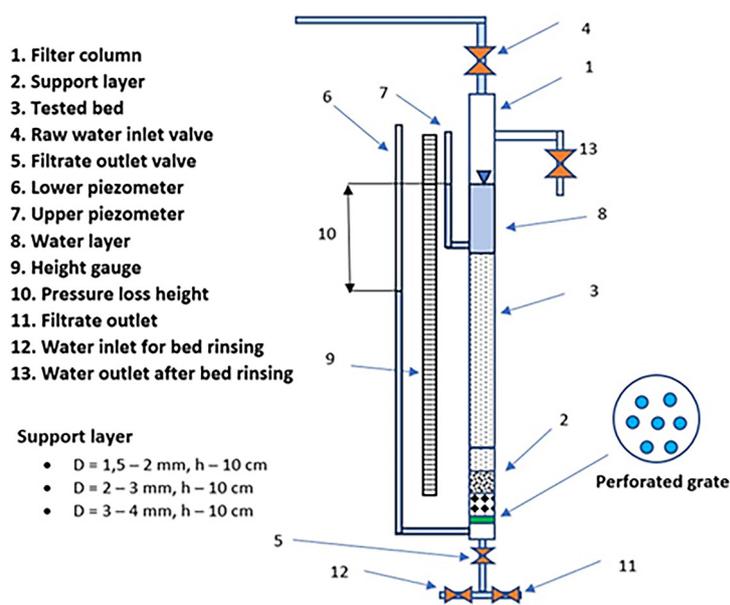


Figure 2. Water filtration testing setup – schematic (from Walczak et al., 2024, modified)

[based on Józwiakowski, 2012; Marzec et al., 2019] was used:

$$\eta = 100 \cdot (1 - C_o/C_d) \quad (1)$$

where: C_o is the concentration of the contaminant in the effluent, and C_d is the concentration of the contaminant in the influent water.

Phosphorus retention, understood as the load of phosphorus retained by the filtration bed, was calculated using the formula:

$$L = (C_d - C_i) \times V_f \quad (2)$$

where: C_d represents the concentration of contaminants in the inflowing water, C_i is the concentration of contaminants in the effluent after a given number of hours of filtration, and V_f is the volume of filtered water over a specific period, calculated as the product of the flow rate and filtration time.

In the second experiment, to assess the potential release of chemical compounds from the bed materials into the effluent water, tap water with known physical-chemical parameters, free from any additives, was also used.

The laboratory analysis of selected physical-chemical factors in the water (both raw and effluent) was conducted in three series of repetitions. It concerned the following parameters: pH, electrical conductivity EC ($\mu\text{S}\cdot\text{cm}^{-1}$), total hardness (mval/L), total phosphorus (P_{tot}), nitrates (N-NO_3), ammonium nitrogen (N-NH_4), iron (Fe), and manganese (Mn) in mg/L. Samples of raw and effluent water were collected at 8, 16, and 24 hours after the filter's operation began, with a flow rate of 5 m/h (fast filter).

The results presented as reference points were arithmetic averages of the parameters analyzed in the samples.

Laboratory measurements

Laboratory analyses of water samples were conducted in the laboratory of the Department of Environmental Engineering at the University of Life Sciences in Lublin using certified methods in accordance with standardized procedures. The following parameters were examined, depending on the experiment - conditions 8 physicochemical factors important for the use of eco-pools were examined (according to FLL 2011): reaction (pH) - by potentiometric method (PN-EN ISO 10523); electrolytic conductivity (EC) - by conductometry

method (PN-EN ISO 27888); water hardness – EDTA titration method (PN-ISO 6059:1999); ammonium nitrogen (N-NH_4) content by spectrophotometric method (PN-ISO 7150-1:2002; NANOCOLOR UV/VIS spectrophotometer by Macherey-Nagel); nitrate (N-NO_3) concentration by colorimetric method with sodium salicylate (PN-C-04576-08:1982); total phosphorus content (P_{tot}) by spectrophotometric method (PN-EN ISO 6878); and the concentration of iron (Fe) cations by the spectrometric method with 1,10-phenanthroline (PN-ISO 6332:2001) and manganese (Mn) – by the permanganate method (PN-C-04590/02:1992).

RESULTS

The results of phosphorus adsorption efficiency for the individual beds are shown in Figure 3. The efficiency of phosphorus removal for the various tested beds was very high. Phosphorus concentrations in the effluent from columns filled with the modified marl rock Rockfos® were significantly lower.

The final concentration after 144 hours of filtration with the solution containing 2 mg P/L was 0.0012 mg P/L, while with the solution containing 5 mg P/L, it was 0.45 mg/L. Due to this, and at such initial concentrations, the results presented in Figure 3a are displayed on a logarithmic scale. The phosphorus removal efficiency in the other columns did not demonstrate such high effectiveness. The decrease in phosphorus concentration during filtration in the column filled with the sulfur material was initially noticeable during the first 48 hours, as the concentration dropped to about 0.2 mg P/L from 2 mg P/L and to about 1.7 mg P/L from 5 mg P/L. After about 60 hours of filtration, a gradual increase in phosphorus concentration was observed.

Ultimately, after 144 hours, the phosphorus concentration in the filter effluent increased to 1.60 mg P/L and 3.14 mg P/L (Figure 3b). Phosphorus removal on the limestone grit beds was minimal. The reduction of phosphorus concentration during filtration with the 2 mg P/L solution dropped to 1.07 mg P/L after 24 hours and to 1.8 mg P/L after 144 hours. Similarly, for the 5 mg P/L solution, the concentration dropped to 4.55 mg P/L and 4.90 mg P/L (Figure 3c).

To illustrate the sorption potential for phosphorus in the tested filtration minerals, Figure

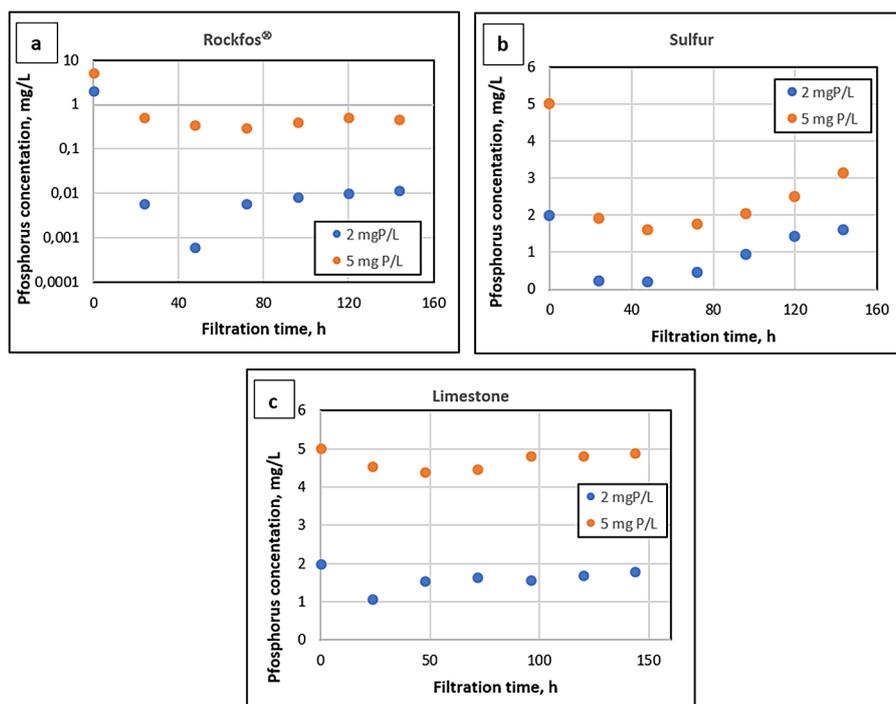


Figure 3. Changes in phosphorus concentration during flow of the research solution through analyzed filter beds: (a) Rockfos® (due to its very high efficiency in phosphorus retention this plot is presented on a logarithmic scale), (b) sulfur, (c) limestone

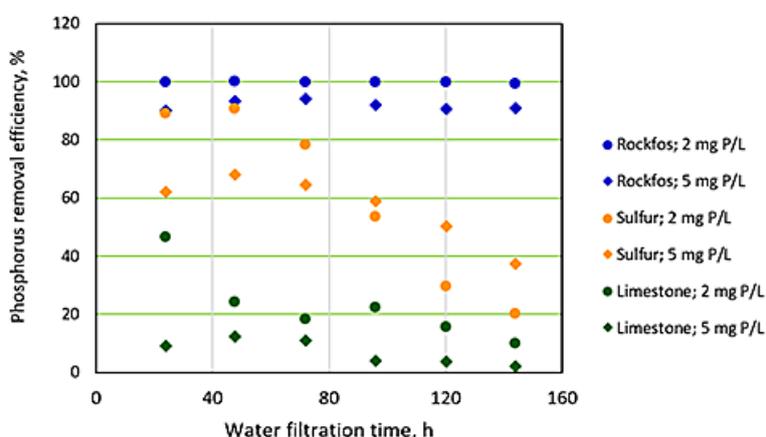


Figure 4. Phosphorus removal efficiency as a function of filtration time and initial phosphorus concentration for all tested filter beds

4 shows the phosphorus removal efficiency (%) calculated using formula 1. The efficiency of phosphorus removal for the material Rockfos® was very high. For the solution with an initial concentration of 2 mg P/L, it oscillated between 99.7% at the beginning of the filtration process and 99.4% at the end. For the solution with 5 mg P/L, it reached 90% to 91%, achieving 94% at 72 hours of filtration. Other materials were not as effective. For Sulfur E, for the solution with 2 mg P/L, the efficiency ranged between 89% to 20%,

while for the solution with 5 mg P/L, it ranged between 62.2% to 37.2%. Limestone grit demonstrated even lower efficiency, which ranged from 46.5% to 10% for the 2 mg P/L solution and from 9% to 2% for the 5 mg P/L solution. These trends indicate a consistent process, where, in different test conditions, filtration efficiency does not show pronounced peaks. For example, during the filtration of the solution with 2 mg P/L, Rockfos® achieved a maximum efficiency of 99.97% at 24 hours, Sulfur E achieved 90.5% at 24 hours, and

limestone grit achieved 46% at 24 hours. Meanwhile, during filtration with the solution of 5 mg P/L, the maximum efficiency of Rockfos® was 94% at 72 hours, Sulfur E was 68% at 48 hours, and limestone grit was 12.4% at 48 hours. This shows that for higher phosphorus concentrations, the highest filtration efficiency is shifted in time.

The evaluation of the retention capacity of individual beds, expressed in grams of phosphorus over consecutive days, calculated using formula 2, is shown in Figure 5, while the cumulative values are presented in Figure 6. The analysis of the phosphorus load retained by the beds also confirmed the differences among the tested minerals (Figure 5). The retention capacity of Rockfos® was very high, and during the experiment, no saturation of its capacity was observed. The differences in capacity per day for each bed were minimal, ranging for the solution with a concentration of 2 mg P/L from

0.468–0.471 g P/kg, and for the solution with a concentration of 5 mg P/L, from 1.060–1.107 g P/kg. This indicates a high sorption potential of this material for phosphorus.

The other materials behaved differently, as shown by the retained phosphorus loads, which exhibited a declining trend. The sulfur material, for the solution with 2 mg P/L, retained 0.419 g P on the first day, 0.426 g P on the second day, and in subsequent days, the retained phosphorus mass gradually decreased, until only 0.094 g P was retained on the last day. During filtration of the concentrated solution (5 mg P/L), the retained phosphorus masses changed similarly. On the first day, it retained 0.733 g P, on the second day, 0.801 g P, and at the end, 0.438 g P. Both of the aforementioned materials exhibited higher capacity when the inflowing solution contained a higher phosphorus concentration.

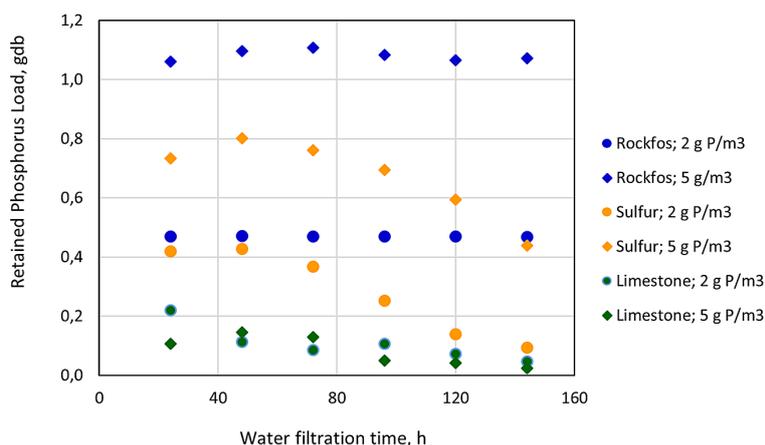


Figure 5. Phosphorus load retained by the analyzed beds over consecutive days of testing as a function of phosphorus concentration in the inflowing solution

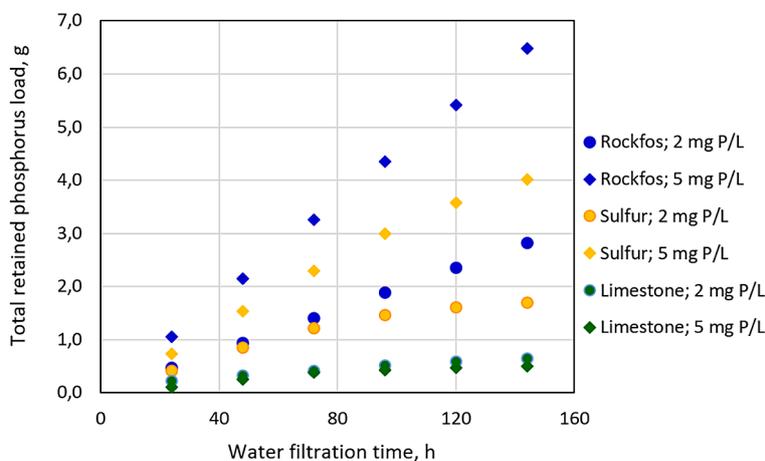


Figure 6. Cumulative phosphorus load retained by the analyzed beds over consecutive days of testing as a function of phosphorus concentration in the inflowing solution

Completely different characteristics were exhibited by limestone grit, whose sorption potential for phosphorus was the lowest. In the case of the solution with a low concentration (2 mg P/L), the mass of phosphorus retained during filtration by the bed changed from 0.219 g P on the first day to 0.047 g P, with a continuous downward trend. In the case of the concentrated solution (5 mg P/L), the retained phosphorus mass on the first day was 0.106 g P, followed by 0.146 g P on the second day, then 0.130 g P, and later, only 0.024 g P.

A significant property in the practical applications of filters is their cumulative capacity, as shown in Figure 6. The trend in the graph indicates an upward trajectory, as each day, each of the materials retained a smaller but increasing cumulative mass of phosphorus. The highest phosphorus mass retained during the study was observed for Rockfos[®], which retained 4.684 g P/kg of bed material during filtration of the concentrated solution (5 mg P/L) and 2.817 g P/kg for the solution with a lower concentration (2 mg P/L). Using the density values of the materials – Rockfos[®]: 730 kg/m³, sulfur: 750 kg/m³, and limestone grit: 1540 kg/m³ – the phosphorus load was calculated per unit of volume depending on the phosphorus concentration in the inflowing solution. Rockfos[®] from a 2 mg P/L solution retained 2.81 g P/kg grains, and from a 5 mg P/L solution 6.484 g P/kg grains. The Sulfur material retained 1.65 g P/kg grains and 3.984 g P/kg grains, respectively, and the limestone grit retained 0.3 g P/kg grains and 2.35 g P/kg grains.

The analysis of measurement points presented in Figure 6 shows that the process proceeds predictably. The points for Rockfos[®] align along a single line, indicating a relatively stable retention

capacity of the bed material. On the other hand, the points describing the behavior of Sulfur and limestone grit reveal variability along the curves. The initial points align along a straight line with a constant slope, and from a certain value, the slope decreases. This indicates the saturation of the phosphorus adsorption capacity of these materials.

One of the most important parameters that changes during the contact of water with various active filtration materials is pH. Therefore, during the discussed tests, every phosphorus concentration measurement in the filtration process was correlated with pH measurements, the changes of which are shown in Figure 7.

From the analysis of the results shown in Figure 7, it follows that the material Rockfos[®] had the greatest impact on pH changes. The highest values were recorded for the concentrated solution (5 mg P/L) after 72 and 96 hours of filtration, amounting to pH=8.61 and pH=8.62, respectively. In the other samples, the pH was below 8,6, and the lowest value was 8.45. This is clearly due to the increase in pH during filtration, as the initial solution pH was 7.35. In the case of filtration with the lower-concentration solution, the maximum pH value was 8.25, and the minimum was 8.05, while the initial solution pH was 7.2.

For the sulfur, the pH values during filtration were in the range of 7.23–7.44, while for limestone grit, they ranged from 7.44–8.15, both within the acceptable range for drinking water.

Considering the potential for using the tested materials in filters to improve water quality in natural pools, it was important to verify not only their sorption capabilities but also whether substances leaching from these materials could affect water users. This study was important to

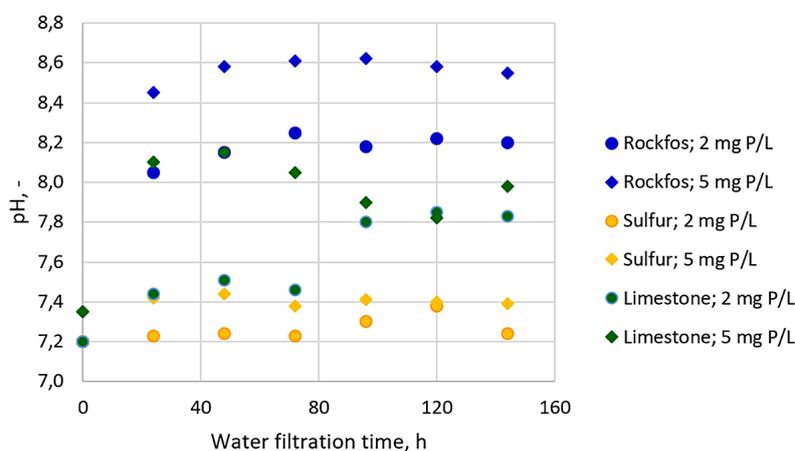


Figure 7. pH values in subsequent measurement samples

determine whether, over a long period, any leaching of compounds could occur that might be harmful to people swimming in the pool.

After constructing such a pool, the first step during commissioning is filling it with water. Since the most readily available water comes from the water supply system, samples of this water were taken and analyzed in this study to determine its composition concerning the parameters listed in the “Laboratory Measurements” section. Three samples were collected at 8-hour intervals, and the results of the tests are presented in Table 1.

The values of the analyzed parameters fell within the limits specified for water intended for human consumption (in accordance with the Regulation of the Minister of Health of December 7, 2017, Journal of Laws, item 2294).

The water between individual samples showed practically no changes. Only slight differences were observed in terms of hardness. The analysis of the obtained laboratory results indicates that, in terms of essential indicators from the perspective of human impact, the risks are very low. The observed variations in values for some factors fall within the margin of measurement error. The results of the mean values shown in the last column were used as the reference point for measurements of water passing through individual beds, as presented in Figure 8.

The pH of the effluent water ranged from 7.23–7.29 and was slightly higher than the values in tap water (mean pH of 7.22) for all tested minerals. The electrolytic conductivity (EC) ranged from 749.2 to 845.0 $\mu\text{S}/\text{cm}$ (with an average EC of tap water being 752.2 $\mu\text{S}/\text{cm}$), and the highest values in the effluent water were recorded for the material Sulfur E. For the other analyzed minerals, only slightly higher values were observed compared to tap water, and in the case of the material

Rockfos[®], after 24 hours, the values were slightly lower (Figure 8).

Total phosphorus P_{total} showed slight variations across the entire study cycle for all the filtration beds, ranging from thousandths of mg P/L in the effluent (range: 0.001–0.008 mg P/L, with an average value for raw water being 0.006 mg P/L). The only statement linked to the measurements is that none of the tested minerals leached phosphorus ions into the effluent, and slight differences in values across the different beds likely result from the methodological precision limitations applied.

For N-NO₃ ions, the range of values was between 0.7–1.2 mg/L. For all the mineral materials, slightly higher concentrations were observed after 8 hours of filter operation. After 16 hours, the concentrations were lower, which persisted until the 24-hour cycle, stabilizing for Sulfur E and Rockfos[®]. For limestone grit, during this time, the concentration of N-NO₃ ions rose again, suggesting a potential for slight leaching into the effluent.

No migration of N-NH₄ ions was observed for any of the tested filtration materials. Their concentrations were 0.01 mg/L for both raw and effluent water, regardless of the filter operation time. For Fe ions (range: 0.01–0.08 mg/L) over the 24-hour cycle, a decrease in this parameter was observed for Sulfur E; for limestone grit, an increase (after 8 hours), a decrease (after 24 hours), and another increase (after 24 hours). For modified marl rock (Rockfos[®]), two peaks of reaction (after 8 and 16 hours) were observed, indicating an increase in this parameter during these periods.

For Mn ions (range: 0.01–0.09 mg/L), no changes in reaction were noted over the 24-hour test cycle for Sulfur E and limestone grit, whereas for Rockfos[®], slight increases were observed at the same time intervals. Water hardness over the entire test cycle for all beds ranged from 5.78–8.89

Table 1. Values of physical-chemical parameters of tap water

| Tap water | Units | Samples number | | | Mean |
|--------------------------------|-------------------------|----------------|-------|-------|-------|
| | | 1 | 2 | 3 | |
| Reaction (pH) | - | 7.21 | 7.22 | 7.22 | 7.22 |
| Electrolytic conductivity (EC) | $\mu\text{S}/\text{cm}$ | 749.2 | 752.4 | 754.9 | 752.2 |
| Water hardness | mval/L | 6.57 | 6.18 | 7.25 | 6.67 |
| P_{total} | mg/L | 0.002 | 0.008 | 0.008 | 0.006 |
| N-NO ₃ | mg/L | 0.80 | 1.10 | 1.00 | 0.97 |
| N-NH ₄ | mg/L | 0.01 | 0.01 | 0.01 | 0.01 |
| Fe | mg/L | 0.04 | 0.06 | 0.04 | 0.05 |
| Mn | mg/L | 0.01 | 0.01 | 0.01 | 0.01 |

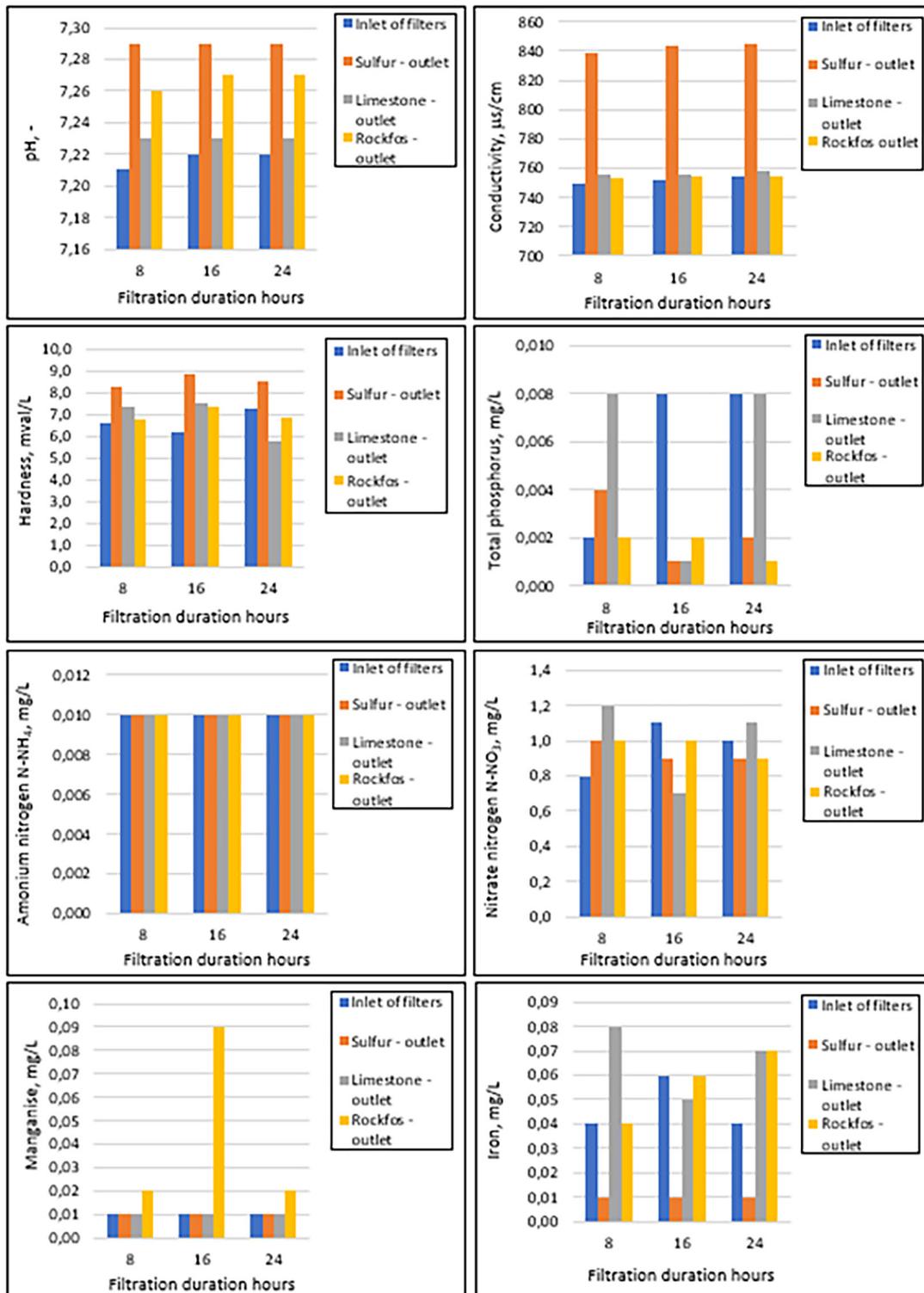


Figure 8. Values of selected physical-chemical parameters of the effluent after filter operation compared to the values of raw water parameters

mval/L, with an average tap water hardness of 6.67 mval/L. For Sulfur E, hardness values were higher than raw water values across all test times, whereas for limestone grit and modified marl rock (Rockfos®), higher values were noted only during the 8- and 16-hour periods.

DISCUSSION

Natural swimming ponds, despite their anthropogenic origins, function as quasi-natural lake ecosystems. Maintaining the proper quality parameters of water in eco-pools is facilitated by

a range of natural bio-physical-chemical processes occurring in the regeneration zone of the reservoir with the involvement of micro- and macro-organisms in the water and the filtration properties of the mineral substrate. These elements shape the metabolism of biogenic substances, which significantly determines the limnological status and trophic character of the water reservoir [Augustyniak and Serafin, 2021; Walczak et al., 2023].

The utility values of swimming ponds are related to maintaining appropriate ranges of many physical-chemical water quality factors, the norms for which are described in materials from the German Research Association for Landscape Development and Construction (FLL, 2011). Although these do not have a binding legal character, they are used in many European countries. They constitute a set of recommendations and references to regulations defining the technical requirements and parameters of materials used for the construction and operation of swimming ponds. They are intended to meet the guidelines of the German Institute for Standardization (DIN) and align with standards in green building.

However, natural processes occurring in the reservoir do not always ensure the optimal metabolism of biogenic substances and stable utility parameters of eco-pools according to their primary function. Excessively high levels of biogenic substances result in water eutrophication, increase the rate of primary phytoplankton production (algal blooms), and can lead to the intoxication of the water reservoir, causing fundamental changes to water quality parameters [Wetzel 2001; Serafin et al., 2019]. The utility values of such a reservoir deteriorate, and using the water body can result in significant health problems for users [Walczak et al., 2023].

A key element in controlling negative processes of water eutrophication, which affect many other water quality parameters, is primarily phosphorus (P). In natural and anthropogenic waters, phosphorus occurs as mineral and organic compounds, in both dissolved states and in forms of sediment and colloids. As a biogenic component, phosphorus is also a component of aquatic organisms. The natural source of phosphorus compounds in waters includes micro- and macro-organisms. Anthropogenic sources of phosphorus compounds in surface waters include runoff from overly fertilized agricultural lands, insufficiently treated sewage, municipal waste, and industrial activities, as well as atmospheric precipitation, introducing phosphorus into recreational waters

that are seasonal and intensively used [Ho et al., 1992; Wetzel, 2001; Serafin et al., 2019].

Many methods of treating water reservoirs have thus aimed to modify the cycle of this element. It is worth noting that phosphorus in water reservoirs should remain in accordance with Liebig's Law of the Minimum, where its limited presence is necessary for sustainable aquatic development bacterioplankton and phytoplankton (primary production). The threshold level of phosphorus in water to limit primary production is very low – 0.01 mg P/L (FLL 2011 standard for swimming ponds), and an even greater role in adsorption and desorption processes is played by bottom sediments, which store 90% of the phosphorus pool in the ecosystem. This property may have a significant impact on water quality [Orihel et al., 2017; Augustyniak and Serafin, 2021].

With elevated levels of anthropogenic phosphorus in the water, aimed at mitigating negative phenomena associated with excessive eutrophication of the reservoir (e.g., improving the organoleptic properties of water: taste, smell, clarity, etc.), the need for inactivating excess phosphorus using dedicated filtration systems containing minerals with significant adsorption properties becomes crucial [Walczak et al., 2023; 2024]. However, developing appropriate and cost-effective technologies that are easy to operate and maintain at low costs poses a significant challenge.

One of the barriers for budget-conscious options to fully functional filtration systems is the specification of reactive materials. These materials must ensure high sorption efficiency for phosphorus and other allochthonous substances, demonstrate stable properties with minimal ion release, and be economically accessible for all eco-pool users [Bus and Karczmarczyk, 2015]. Such requirements can be met by selected mineral materials tested in this study (limestone grit, iron material Sulfur E, and modified marl rock Rockfos®), whose filtration efficiency potential is the subject of this work.

The effectiveness of filters in technological processes was determined based on water quality indicators before and after the filtration process and by analyzing the filtration bed's permeability under pressure and its durability [Siwiec, 2007; Walczak et al., 2024].

For the proper verification of such effectiveness, the selected filtration materials were subjected to column experiments, which are currently the best-known and widely used technique

to determine adsorption capacity and design TWs [Del Bubba et al., 2003; Dalahmeh et al., 2014; Hamisi et al., 2022]. Column experiments provide valuable data on the interaction of polluted water with the mineral bed and allow for monitoring changes in pollutant concentration as a function of time and filtered volume. This makes them highly useful in delivering reliable information on the level of pollutant retention and the characteristics of the filter's adsorption matrix [Hamisi et al., 2022; Walczak et al., 2024].

In addressing the fundamental research problem of analyzing the filtration efficiency of selected mineral materials for phosphorus, column experiments have shown that all tested materials exhibit potential activity for this process. Filtration materials characterized by their calcium, aluminum, and iron compound content confirm that the adsorption properties of many minerals for phosphorus depend mainly on the presence of these primary compounds in the bed [Aulenbach and Meisheng, 1988; Czerwionka, 2002]. The efficiency of phosphorus removal, as well as the retention capacity in relation to the initial phosphorus concentration in the effluent, varied among the individual minerals.

Modified marl rock opoka (Rockfos®) is a transitional rock between marl and siliceous rocks. It is formed mainly from fine-grained organic detritus, which gives it a heterogeneous structure with scattered remains of fragmented detritus [Pinińska, 2008]. It contains significant amounts of chemical elements with reactive potential for phosphorus adsorption, including calcium, silicon, aluminum, iron, and manganese.

The process of phosphorus removal takes place in an alkaline environment via chemical sorption [Zawadzka et al. 2024A, Zawadzka et al., 2024B]. During this process, calcium phosphates, including hydroxyapatite, are formed. Recent studies on the applicability of this material for water and wastewater filtration indicate that its high calcium (Ca) content is particularly responsible for its phosphorus sorption properties [Cucarella et al., 2007; Bus and Karczmarczyk, 2014]. A similar content of magnesium and aluminum oxides indicates high sorption values in contrast to magnesium oxide alone, whose presence does not influence the process [Bus and Karczmarczyk, 2014]. The phosphorus sorption potential of modified marl rock makes it suitable not only as a filtration material for purifying wastewater and runoff but also as a secondary stage in

cleaning effluents in household hydrofilters [Renman and Renman, 2010; Józwiakowski, 2012; Wąsik and Chmielowski, 2013].

In the operating conditions of the constructed wetland treatment plant under initial phosphorus concentrations of 1.9–4.9 mg P/L, was high, ranging from 87–91% [Renman and Renman, 2010]. It was also consistent with the filtration results obtained during this study, where Rockfos® achieved phosphorus removal efficiency from 90% to 99.7%, depending on the total phosphorus (P_{total}) concentration in the effluent. For the 2 mg P/L solution, the final phosphorus concentration after 144 hours was 0.0012 mg P/L (respectively, for 5 mg P/L, 0.45 mg P/L). The results confirm that the use of Rockfos® leads to increased sorption potential with rising phosphorus concentration in the inflowing solution, further highlighting its application potential utility. This observation is confirmed by the analysis of the bed's capacity, which can be considered very high. The daily differences in capacity were negligible, around 0.003 g P/L for the 2 mg P/L solution and approximately 0.047 g P/L for the 5 mg P/L solution. The cumulative capacity of this material also indicates the highest amount of progressively accumulated phosphorus in the bed throughout the entire study, regardless of the initial concentration of the solution used.

It is worth adding that the adsorption potential of marl rock depends on the chemical specification of the material. It may vary depending on the nature of the raw material and the extent of modifications performed by the manufacturer, which rarely, as information, reaches consumers [Bus and Karczmarczyk, 2014; 2015].

The experimental studies conducted also tested the utility of iron material (Sulfur E). Its adsorption capacity for phosphorus is largely attributable to its high 40% iron (Fe) content, which provides the chemical capability to precipitate orthophosphate ions from the solution in the form of iron salts (chlorides and sulfates). There is no information on the full chemical composition of this product, which limits understanding of its functionality in the process. From the perspective of eco-pool operation, the large amounts of iron introduced into the water due to the use of this type of bed may influence the potential to increase the biological availability of phosphorus for microorganisms and aquatic vegetation. Studies have shown that when the Fe:P ratio is 1,6, the biological availability of phosphorus is highest

and decreases for ratios of Fe:P equal to 9,8 [Kahiluoto et al., 2015].

During the laboratory experiments, it was found that the retention efficiency of phosphorus on this material ranged from 20–89%, depending on the study cycle. However, its phosphorus adsorption potential decreased over time during the filter operation. In the first 48 hours, a significant decrease in phosphorus concentration was observed: from 2 mg P/L to around 0.2 mg P/L, and from 5 mg P/L to around 1.7 mg P/L. Over the entire experimental cycle, the efficiency decreased (after 144 hours, the phosphorus concentration in the filter effluent increased to 1.60 mg P/L and 3.14 mg P/L). These results are reflected in the low capacity of this material, where slight increases in retained phosphorus were observed only during the 20–24 and 48-hour periods. The significant, successive growth of phosphorus concentration in the effluent at the end of the experiment resulted from the saturation of the material relative to the inflowing phosphorus concentration. The utility potential of this material should be considered not only from the perspective of its effectiveness as a sorption bed (retention) but also its ability to make phosphorus available to microorganisms and aquatic plants in the regeneration zone of the swimming pond.

The sorption potential for phosphorus of limestone grit was minimal. Despite the high content of calcium, magnesium, and iron compounds in its chemical composition, the sorption efficiency of this material did not exceed 46.5% throughout the study cycle. After 144 hours of filter operation, the phosphorus concentration for the 2 mg P/L solution in the effluent was 1.8 mg P/L, and for the 5 mg P/L solution, it was 4.90 mg P/L. This also corresponded to the low capacity of the bed over the entire experimental cycle, regardless of the initial phosphorus concentration, indicating a rapid saturation of this material's sorption capacity. In the framework of the filtration system dedicated to eco-pools, processes of ion exchange and surface sorption are therefore incompatible with user expectations, giving the lowest evaluation of the utility potential for this material.

The highest and most stable sorption capacity for phosphorus was shown by the filter with modified marl rock (Rockfos®).

Analyzing the maximum phosphorus removal efficiency for all tested filtration beds yields certain observations. At low concentrations of the initial solution (2 mg P/L), the maximum adsorption

efficiency was observed after 24 hours, while at higher initial concentrations (5 mg P/L), the timing was shifted. The above information confirms observations that highly efficient filtration materials show improved phosphorus removal efficiency over time with the gradual saturation of the bed [Kaleta et al., 2011].

The utility potential of the tested filtration beds is also linked to analyzing the possibility of ion release from the compounds of the applied materials. This could destabilize the natural self-purification processes of water due to the functioning of the regeneration zone in eco-pools, as well as the interaction of the micro-biocoenosis in swimming ponds. This would then translate into changes in the values of key physical-chemical factors in water, which should not exceed the limits specified by FLL.

The above problem may also concern biogenic nitrogen compounds. Their concentrations in nature are linked to the metabolism of the internal ecosystem of the water reservoir, simultaneously influenced by the processes of organic matter mineralization and the biological retention of nutrients through the interactions of aquatic plants and animals [Serafin et al., 2019].

No N-NH₄ ions resulting from the mineralization of organic compounds containing ammonium nitrogen were detected during the entire study period or during filtration through the Rockfos® material or other tested beds. This indicates a lack of adverse interactions related to ion exchange or surface desorption from the beds. Their content in eco-pools should remain in the range of 0.0–0.03 mg N-NH₄/L [FLL 2011].

For nitrate ions (N-NO₃) formed in the process of microbial nitrification (from ammonium ions to nitrate) or deposition from the atmosphere, the reactivity of the tested materials was negligible. This was reflected in the stable values of this parameter during subsequent cycles of laboratory testing, where, relative to the initial solution specification (N-NO₃ = 0.8–1.1 mg/L), the measured values ranged from 0.7–1.2 mg/L, with the highest variation observed for limestone grit. According to FLL [2011], the nitrate ion content in eco-pool water should not exceed 30 mg/L.

In natural swimming pools, the nitrogen compound content should primarily be linked to regulating the metabolic activity of the water ecosystem. This is achieved by controlling and intensively modifying the structure of the biocoenosis, including aquatic vegetation in the regeneration

zone, as well as phytoplankton and bacterio-plankton in the reservoir water. For manganese ions (Mn), whose excess has a negative impact not only on human health but also on the organoleptic properties of water (taste, smell, transparency), no significant increases in concentration were observed during filtration with Sulfur E and limestone grit. For Rockfos[®], manganese stock values ranged from 0.02–0.03 mg Mn/L, insignificant in physical-chemical terms and therefore treated as a margin of error. The Mn content in eco-pool water should not exceed 0.05 mg/L (FLL 2011). For iron ions (Fe), similar to Mn in their impact on organoleptic water properties and effects on human health, the sorption properties of the iron material Sulfur E proved significant. This demonstrates its potential for ion exchange and chemical precipitation in the bed material. The Fe content in eco-pools should not exceed 0.3 mg/L (FLL 2011). It should be noted that for increased concentrations of Fe and Mn ions in swimming pools, regulatory filters are often used. Their role is to eliminate excess Fe and Mn compounds, causing precipitation of these ions in the form of sediment and trapping them on their surfaces.

Water hardness, defined as the concentration of calcium, magnesium, iron, and manganese cations in the solution, for all tested materials generally did not deviate from raw water values (average = 6.67 mval/L). Slightly higher values were recorded only for the Sulfur E material (average = 8.54 mval/L), which could indicate slight migration of these cations into the effluent water. This parameter in eco-pool water should not exceed 30 °d (10.7 mval/L) [FLL 2011].

With regard to pH, for the material Rockfos[®], its chemical specification associated with a high content of calcium and magnesium compounds – primary alkaline components – corresponds to its high alkalinity (pH=11–12). This could influence the alkalization of the effluent solution, but no such effect was observed for tap water with a pH of 7.22. The effluent pH assumed an average value of around 7.27, which does not indicate alkalization of the effluent. The process was more significantly noticeable with solutions of varying phosphorus concentrations (range: 8.45–8.62, compared to pH values for laboratory solutions in the range 7.22–7.35). For the Sulfur E material and limestone grit, the pH values in the effluent ranged between 7.23–7.29, while for laboratory solutions, they ranged between 7.23–8.15, meaning they remained within ranges acceptable

even for drinking water. Electrolytic conductivity (EC), an indirect measure of mineralization and contamination, for Rockfos[®] and limestone grit had average values very close to tap water (EC=752.17 μ S/cm for raw water, with material ranges between 746.3–752.4 μ S/cm). The highest values in the effluent were recorded for Sulfur E (average EC=842.57 μ S/cm for the effluent), indicating a slightly higher level of ion dissociation from this material.

The final effect of the mineral filtration process depends on: the quality of the raw water supplied to the filter, the type of filtration material used, its chemical structure, the thickness of the material layer, the filter flow rate, and the speed of water flow through the bed [Cucarella and Renman, 2009; Bus and Karczmarczyk, 2014; Karczmarczyk et al., 2015; Walczak et al., 2023; 2024].

As the duration of water contact with the bed increases, the adsorption efficiency also increases. The water flow rate through filtration-absorption beds is typically limited to a filtration speed of 5–10 m/h, depending on the technology used [Kowal and Świdorska-Bróz, 2007]. It is worth noting that reducing the flow rate positively influences biofilm development on the adsorbent's surface, which determines its reactive properties and thus its filtration usefulness. This is also related to the issue of bed regeneration, which includes washing, drying, and rinsing the bed. The results of studies by [Karczmarczyk et al., 2019] indicate that reducing the flow rate to below 50% to 100% of the initial value suggests that the bed is no longer active for regeneration.

The sorption activity of each filter material should therefore be determined in relation to the relevant chemicals in eco-pool water, a specific reactive material under a specific manufacturer's name, taking into account its chemical specification and granulometric fraction. It is also necessary to take into account the regeneration capabilities of the adsorbent, filtration parameters, filter system equipment and the characteristics of a given water object, therefore, best in field conditions and under full load.

CONCLUSIONS

Based on the obtained research results, the following conclusions are presented below:

- laboratory analyses showed that all tested filtration materials (limestone grit, modified marl

rock, and iron material) were characterized by phosphorus sorption potential. However, the efficiency of phosphorus binding by limestone grit was so low that it cannot be recommended as a material for future applications;

- among all the tested parameters, the highest sorption capacity, confirmed by the efficiency of phosphorus removal from the water, as well as the capacity of the bed, was demonstrated by the filter with modified marl rock (Rockfos®), followed by the iron material (Sulfur E) and, to a negligible extent, by limestone grit;
- the tested materials to a minimal extent exhibited ion leaching processes or changes in their values that would exceed FLL standards for natural swimming ponds;
- the potential use of the iron material (Sulfur E) in filtration beds for eco-pools is associated with its sufficient adsorption capabilities for phosphorus and its potential ability to make phosphorus available to microorganisms and aquatic plants in the regeneration zone of the pond.

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