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Long-term operating conditions for different sorption materials to capture phosphate from domestic wastewater

Andrzej Jucherski[a], Andrzej Walczowski[a], Piotr Bugajski[b], Krzysztof Jóźwiakowski[c,]*
Joanna Rodziewicz[d], Wojciech Janczukowicz[d], Shubiao Wu[e], Magda Kasprzyk[f,g],
Magdalena Gajewska[f,g], Artur Mielcarek[d]

[a] Mountain Centre of Research and Implementations in Tylicz, Institute of Technology and Life Sciences – the National Research Institute in Falenty, Poland, Pułaskiego St. 25A, 333-83 Tylicz, Poland
[b] Department of Sanitary Engineering and Water Management, University of Agriculture in Kraków, Al. Mickiewicza St. 24/28 30-059 Kraków, Poland
[c] Department of Environmental Engineering and Geodesy University of Life Sciences in Lublin, Leszczyńskiego St. 7, Lublin 20-069, Poland
[d] Department of Environment Engineering, University of Warmia and Mazury in Olsztyn, Warszawska St. 117a, Olsztyn 10-719, Poland
[e] Department of Agroecology, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark
[f] Department of Water and Wastewater Technology, Gdańsk University of Technology, Narutowicza St. 11/12, 80-233 Gdańsk, EcoTech Center, Poland
[g]EkoTech Center, Narutowicza St. 11/12, 80-233 Gdańsk, Poland

*Correspondence: krzysztof.jozwiakowski@up.lublin.pl

Abstract

This paper presents the results of a study on the possibility of applying various configured filters filled with a mixture of Rockfos® and Leca® material for the effective capture of phosphate from domestic wastewater. The tests were carried out for two years at two wastewater flow rates (20 and 40 L/day) in three pairs of filtration columns with a volume of filter material equal to 20 liters each. Columns 1A and 1B were filled only with Rockfos®. Columns 2A and 2B contained Rockfos® and two 5-cm layers of Leca®. Columns 3A and 3B were filled with Rockfos® and a 10% addition of Leca®. A high phosphate removal efficiency was obtained at a level of 93.2 – 94.9% for all columns tested at a flow rate of 20 L/day with a retention time of 12 h. After 250 days of the experiment, the efficiency of phosphate removal decreased significantly, which was associated with a drop in the temperature of the inflowing wastewater (<10°C). The alkaline characteristic (11–12 pH) of the filter material promoted the removal of phosphate from the wastewater. The pH value of the treated wastewater gradually decreased from pH 12 on the first days of an experiment to pH below 9.0 after about 300 days of operation. Studies showed that Rockfos® material can be used successfully to capture phosphate from wastewater for the sustainable development of rural areas in the circular economy. When designing and building phosphate removal filters, it is recommended to use 1 m^3 Rockfos® with the addition of Leca® in 1 m^3/day of wastewater inflow.

Keywords: circular economy; filter medium; Rockfos®; Leca®; phosphate removal; domestic wastewater

1. Introduction

Phosphorus is one of the main elements responsible for the development of the water eutrophication process, which can begin with as little as 10 µg/L of phosphorus in water [1-3]. An increase in the concentration of phosphorus in surface water above 15 µg/L can lead to an intense growth of algae [4]. The phosphate in surface and groundwater can come from natural and anthropogenic sources [5]. Animal and plant organic compounds are natural sources of phosphorus in waters. Agriculture is considered a major anthropogenic source of area pollution and a high concentration of phosphorus in surface waters [6-8]. Among the point sources of phosphorus are industrial or municipal wastewater, pig farming wastewater, and domestic wastewater [5, 9]. A significant impact on limiting the process of surface water eutrophication and reducing the degradation of groundwater quality is the proper management of water and wastewater management that should be developed following the principles of sustainable development [10-13].

Effective sanitation in catchment areas requires that the concentration of soluble phosphorus in surface watercourses should be reduced to 0.02–0.1 mg/L [14]. In Poland, the target concentration of total phosphorus is 0.1 mg/L for stagnant water and 0.25 mg/L for flowing water [15].

According to the Polish legal requirements from 2019 [16], the allowed concentration of total phosphorus in wastewater discharged from municipal wastewater treatment plants serving 2,000 to 100,000 PE (person equivalent) is 2 mg/l. On the other hand, in small WWTPs (<2000 PE), from which wastewater outflows to lakes and their tributaries allowed the concentration of total phosphorus to be below 5 mg/l. Furthermore, HELCOM [17] recommends that the total phosphorus concentration in the effluent of household wastewater treatment plants should be below 5 mg/L (the required efficiency of phosphorus reduction >70%).

In wastewater treatment plants, phosphorus can be removed from wastewater either by biological methods or by precipitation in primary settling tanks with the application of chemical reagents, as well as by using various mineral filtration materials at different treatment stages [18-20]. Adequate phosphorus removal efficiency can be achieved in household wastewater treatment plants by using special filters (at the final stage of treatment) filled with materials with a high capacity to retain and precipitate phosphorus compounds [21].

In recent years, a variety of materials have been used in phosphorus removal filters, eg, crushed marble [22], dried peat soils [23], and blast furnace slag [24]. Studies have also been conducted on the usefulness of various types of rock, such as calcite [25] and carbonate-siliceous rocks [26-27]. Comparisons of various filter materials that have been tested for use in the removal of phosphorus were made, among others, by Ballantine and Tanner [28] and Vohla, et al. [29]. Kasprzyk and Gajewska [30] showed that the application of natural and semi-natural materials for the possible recovery of phosphorus is compatible with the assumptions of circular economy and closed circuits. Furthermore, the requirements of the European Commission, along with increasing awareness of the limited natural resources of phosphorus, direct the implementation of particular technologies that make phosphorus recovery possible. Many assumptions showed that the critical period can be 2030, when worldwide phosphorus production will reach its peak [31-33]. According to the communication of the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Regions Committee on the 2017 list of Critical Raw Materials for the EU [34], the critical raw materials are phosphorus and phosphates. Europe is entirely dependent on external importers, and thus the ability to recover phosphorus from, for example, domestic wastewater can be crucial.

The preliminary results of laboratory studies [30, 35-37] have shown that a very promising material for the recovery of phosphorus from wastewater can be Rockfos®, which is produced in the decarbonization process (calcination at high temperature ~ 700°C) of natural carbonate-siliceous rock (opoka). The sorption capacity of this material with a very fine-grained fraction (0–2 mm) has been shown to be 45.6 mg/g [36]. In another article [37], the Rockfos® powder by-product was shown to provide a theoretical P-sorption capacity calculated from the Langmuir isotherm equal to 256.4 mg/g. Wastewater flowing through a filter bed should have a fixed time of contact with the reactive material in which phosphorus compounds are precipitated and adsorbed. The advantage of this method is that it can be easily applied in existing domestic wastewater treatment plants and that the used filter material can be utilized as fertilizer [38-39].

This paper aims to assess the possible application of filters filled with a Polish mineral material named Rockfos® to capture phosphorus from real domestic wastewater (previously biologically treated). As a filling of the filters, the addition of granular clay material was used, known as Leca® (light expanded clay aggregate). The authors of this study decided to use Leca® because previous studies of Rockfos® and similar materials have shown that filters filled with these materials become clogged during long-term operation. This is especially true for materials with small grain sizes <5 mm [27, 30, 35-37].

Research has been carried out on filtration columns filled with three different configurations of Rockfos® and Leca® materials, at various flow rates Q_1 = 20 L/day and Q_2 = 40 L/day and retention time 6 and 12 hours, respectively. During the research, the following objectives were investigated:

- phosphate removal efficiency under various conditions (flow rates, retention time, temperature),
- influence of wastewater temperature on phosphate concentration,
- changes in the pH values of the effluent along with the time of the experiment.

The study conducted introduces the application of the proposed filter configurations for the removal of phosphates from wastewater, which have not been investigated in any other paper. Furthermore, Rockfos® material is known in the scientific literature for only 3 years [30, 35-37].

2. Materials and Methods

2.1. Experimental facility

During the planning of the experiment, it was assumed that the Rockfos® and Leca® materials used in various configurations can be an attractive contribution to the filters used for the removal of phosphate from wastewater. The tests were carried out using the filtration column model shown in Figure 1.

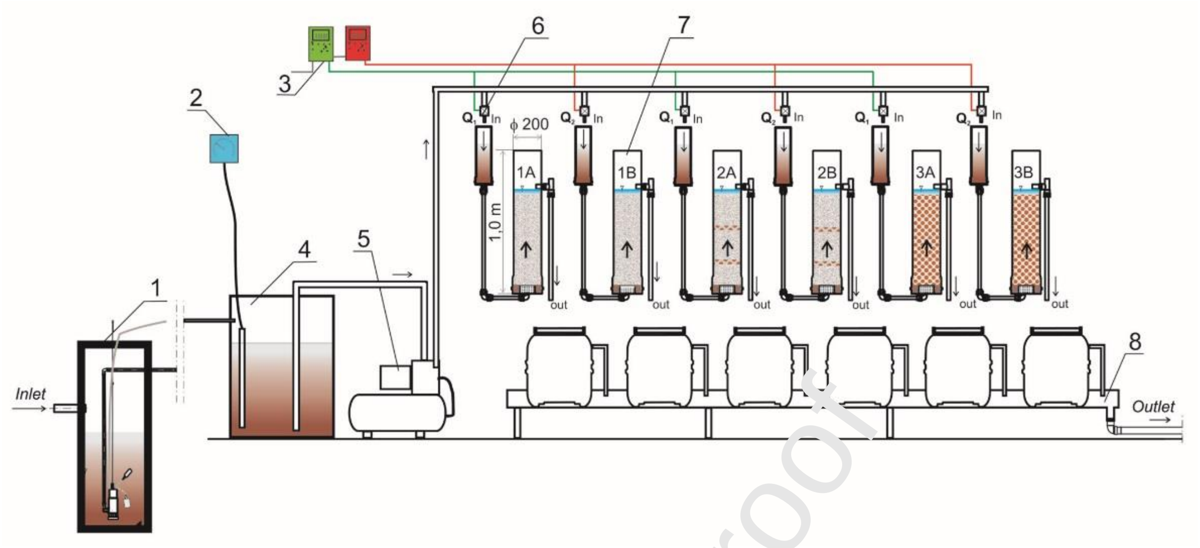


Figure 1. Scheme of the installation of the model studied.
1 - pumping chamber; 2 – wastewater level meter; 3 – programmer; 4 – distribution tank; 5 - compressor; 6 – electromagnetic valves; 7 – columns with filtration materials; 8 - the outflow of the treated wastewater

The model consists of three pairs of columns made of PVC pipes with a height of H = 1.0 m and a diameter of DN = 0.2 m. The columns (1A, 1B), (2A, 2B) and (3A, 3B) were filled with a 70 cm layer of filter material (volume 20 dm^3) as follows:

- columns 1A and 1B – 100% Rockfos®,
- columns 2A and 2B – Rockfos® with two 5 cm layers of Leca®,
- columns 3A and 3B – a mixture of Rockfos® and 10% of Leca®.

The research model was constructed in the laboratory of the Mountain Centre of Research and Implementations in Tylicz, Department of the Institute of Technology and Life Sciences – the National Research Institute in Falenty, Poland.

2.2. Materials

Rockfos®, the base material used in the study, is highly reactive to phosphorus compounds as it contains large amounts of compounds such as CaO – 43.34% and SiO_2 – 36.05% (Table 1). According to the producer's recommendations, it can be used to build filters to remove phosphorus and bacteriological contaminants from domestic and industrial wastewater. Rockfos® comes in grains of 2 to 5 mm and has a high pH of 11 to 12 [40].

The second material used as filling for the filter columns was light expanded clay aggregate Leca® with grain sizes of 10 to 20 mm. This material is produced by heating clay with a high loam content at a temperature of 1150 ° C [41]. The chemical composition of Leca® of pH 8,4 is presented in Table 1. The sorption properties of Leca® have been studied in connection with the removal of phosphorus by various authors [42-44]. In the current study, this material was used only for its ability to improve the hydraulic conductivity of Rockfos® filled filtration columns as the basic material.

The selected physical parameters of Rockfos® and Leca® are shown in Table 2 based on the manufacturer's data [40, 41]. Figure 2 presents the grain size characteristics of these materials.

Table 1. The chemical composition of Rockfos® and Leca® [40, 41, 45]

Parameter	Unit	Rockfos®	Leca®
CaO	%	43.34	10.44
SiO_2		36.05	59.12
Al_2O_3		5.93	12.24
Na_2O		2.86	-
Fe_2O_3		1.34	9.81
K_2O		1.00	2.74
TiO_2		0.37	0.58

Table 2. Selected physical parameters of the filter materials: Rockfos® and Leca® [40, 41, 45]

Parameter	Unit	Rockfos®	Leca®*
Specific mass	kg/L	2.41	2.59
Bulk density		1.12	1.25
Poured density		0.81	0.69
Tightness	%	46.7	48.3
Porosity		53.3	20.0 – 50.0
Absorption		32.2	18.0 – 30.0

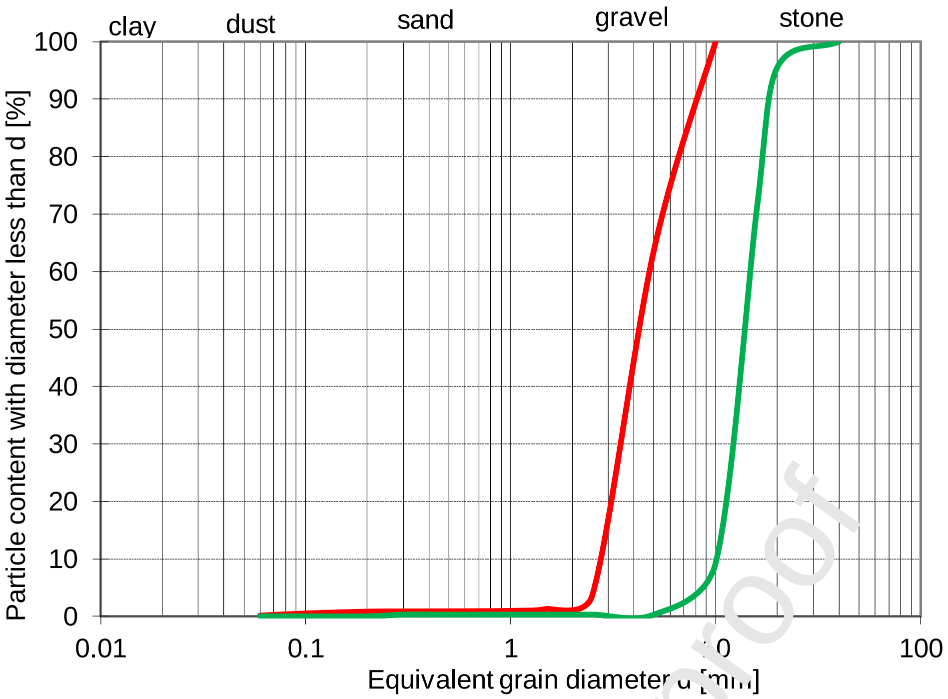


Figure 2. Grain size distribution of the materials used in the filtration columns

🟥 ROCKFOS® U*=d_{60}/d_{10}=1.72

🟩 LECA® U*=d_{60}/d_{10}=1.60

*/ granulation homogeneity coefficient

2.3. Analytical and statistical methods

The study was carried out for almost two years (659 days). During the tests, domestic wastewater was fed into columns 1A, 2A, and 3A at a flow rate Q_1= 20 L/day, and into columns 1B, 2B, and 3B at flow rate Q_2 = 40 L/day. The hydraulic retention time (HRT) was 12 hours for columns 1A, 2A, and 3A and 6 hours for columns 1B, 2B, and 3B.

The household wastewater used in the tests was previously biologically purified by the real household wastewater treatment plant with a daily capacity of up to 2,0 m^3, consisting of a preliminary septic tank and a biological bed. Biologically treated wastewater from the WWTP was successively delivered by pipeline to the distribution tank in the test stand, from where it was periodically fed to the filtration columns in equal doses every 30 minutes during the day and flowed through them from bottom to top, as shown in Figure 1.

During the study period, 65 test runs were performed and 65 samples of the influent and effluent of each column were taken. To make the test conditions as similar as possible to natural conditions, the filter columns were placed in an unheated but frost-proof room.

The influent wastewater samples were collected from the distribution tank (point 4) and the effluent wastewater samples were collected from the discharge pipes from each of the six columns (point 8) (Figure 1). The concentration of P-PO_4^{3-}, the pH, and the temperature was determined for each sample. P-PO_4^{3-} levels were determined using a MERCK Spectroquant Prove 100 spectrophotometer with the detection limit of P-PO_4^{3-}=0,05 mg/L. pH and temperature were measured using a WTW pH-METR 320 meter.

The concentration of P-PO_4^{3-} in the influent (C_{in}) and effluent (C_{out}) from the filtration columns were used to calculate the phosphate removal efficiency by formula 1:

$$Ŋ = 100 \cdot (1 - C_{out}/C_{in})\ [\%] \tag{1}$$

Pearson's linear correlation analysis was used to assess the effect of influent wastewater temperature on P-PO_4^{3-} concentration in treated wastewater. The strength of the relationship between two variables was measured by the scale [-1; 1] proposed by Stanisz [46]. Where the simultaneous effect of two independent variables (temperature of wastewater flowing into the columns and duration of the experiment) on one dependent variable (concentration P-PO_4^{3}- in wastewater flowing out of columns) was tested partial correlation analysis for the three variables was performed. The correlations were shown graphically in correlation plots. The significance of the correlations was tested using the Student's t-test at a confidence level of α=0.05. The results of the tests were statistically analyzed using STATISTICA 8 software (StatSoft, Inc., USA).

3. Results and discussion

Table 3 shows the concentration, temperature, and pH of P-PO_4^{3-} of wastewater flowing into the filtration columns.

Table 3. Statistical characteristics of the influent wastewater parameters investigated (n = 65)

Parameter	Unit	Statistics					
		Mean	Median	Min	Max	Standard deviation	Coefficient of variation
P-PO_4^{3-}	mg/L	7.12	7.10	2.20	15.62	3.05	43%
Temperature	°C	10.30	9.90	2.90	18.30	4.58	44%
pH	-	-	-	6.36	7.94	0.34	5%

During the investigation carried out, the concentration of P-PO_4^{3-} in the influent of the filtration columns ranged from 2.20 to 15.62 mg/L. The mean value of this parameter was 7.12 mg/L and the median was 7.10 mg/L. As Jucherski et al. [47] and Jówiakowski et al. [48] stated, these are the typical concentrations of phosphate in treated domestic wastewater discharged from household wastewater treatment plants in Poland. The coefficient of variation was C_V=43%, which means that there was high variability in the phosphate level in the wastewater that flows into the tested model according to the scale proposed by Mucha [49]. The influent temperature ranged from 2.9 to 18.3°C, which according to Bugajski et al. [50] is a typical range for domestic wastewater. The mean influent temperature was 10°C, and the median influent temperature was 9.9°C. Variability in the temperature of the wastewater flowing into the filtration columns was high, as evidenced by the CV = 44% coefficient of variation. The pH of the influent ranged from 6.36 to 7.94, with little variation (C_V = 5%).

The efficiency of phosphorus compounds removal from domestic wastewater depends on many factors. The critical one is the presence of reactive Ca^{2+} cations on the surface of the column filling material [51]. The chemical activity of the medium used to remove phosphorus may also depend on the hydraulic load, the retention time of the wastewater and the fraction of the filter material used [27, 52]. These issues are addressed later in the paper.

3.1. Effect of wastewater inflow rate and its retention time on phosphate removal efficiency

An analysis of the impact of wastewater inflow rates (Q_1 and Q_2) supplied to the filtration columns on P-PO_4^{3-} removal efficiency showed that the highest phosphate removal efficiency, ranging from 93.2 to 94.9%, was obtained for the wastewater inflow rate of Q_1 = 20 L/day throughout the study period (Figure 3). Much lower P-PO_4^{3-} removal efficiency values (76.8 – 84.1%) were obtained at the inflow rate Q_2 = 40 L/day. However, the filtration columns tested provided more than 70% phosphate removal efficiency, and therefore complied with HELCOM Recommendation 28E/6 [17].

In a study conducted in Sweden, a filtration column filled with a similar material called Polonite® with a particle diameter of 2–6 mm and a retention time of 5.5 h provided a phosphorus removal efficiency of 76% [53]. Jówiakowski [27] obtained a similar phosphorus removal efficiency of 77.9% at a retention time of 12 hours in a filter filled with carbonate-siliceous rock with grain sizes of 1 to 2 mm, fired at 900°C similar to Polonite®, which is higher than the calcination temperature of Rockfos® and creates a larger environmental footprint. These authors found that the same material showed a significantly lower efficiency (63.7%) when larger grain sizes were used in the range of 2-5 mm. They also pointed out that although smaller fractions of carbonate-siliceous rock (1 to 2 mm) remove phosphate more efficiently than larger fractions, they can expose a higher risk of clogging, which is essential for the practical application of these filters in engineering solutions. The same conclusion was obtained from a batch study conducted by Kasprzyk et al. [35] using Rockfos® material and the powder waste fraction of Rockfos® production.

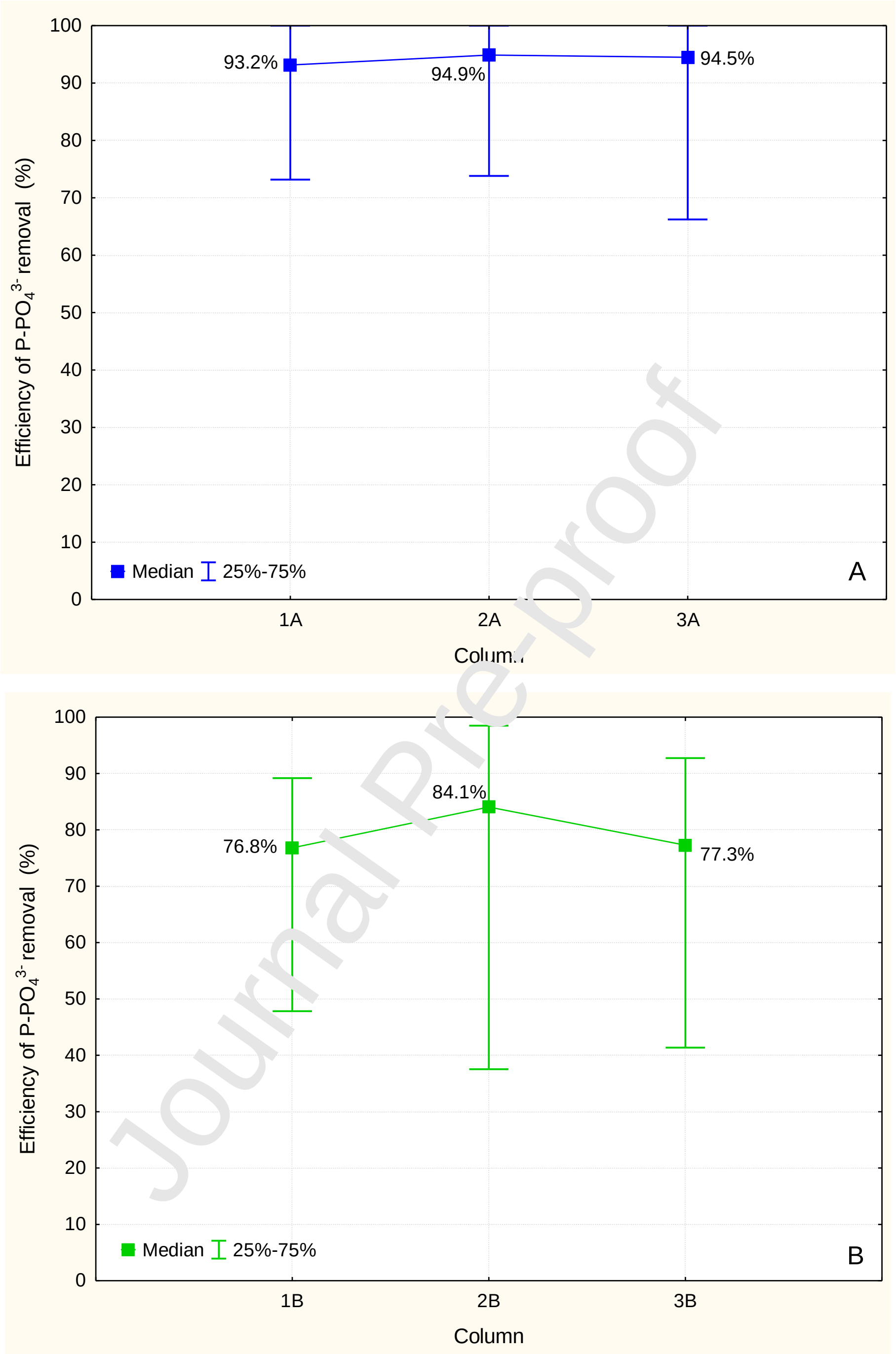


Figure 3. Median removal efficiency of phosphate in columns at different daily inflow volumes (inflow rates): A – Q_1 = 20 L/day; B – Q_2 = 40 L/day (1 – 100% Rockfos®, 2 – Rockfos® and two 5-cm layers of Leca®, 3 – Rockfos® and 10% Leca®).

The median phosphate concentration in the effluent of columns 1A, 2A and 3A were identical, at 0.40 mg/L, throughout the study period (Figure 4). The concentration of $P\text{-}PO_4^{3-}$

in the effluent from columns A was characterized by a high variability according to Mucha's scale [49], as evidenced by the coefficient of variation C_V, which ranged from 1.33 to 1.40.

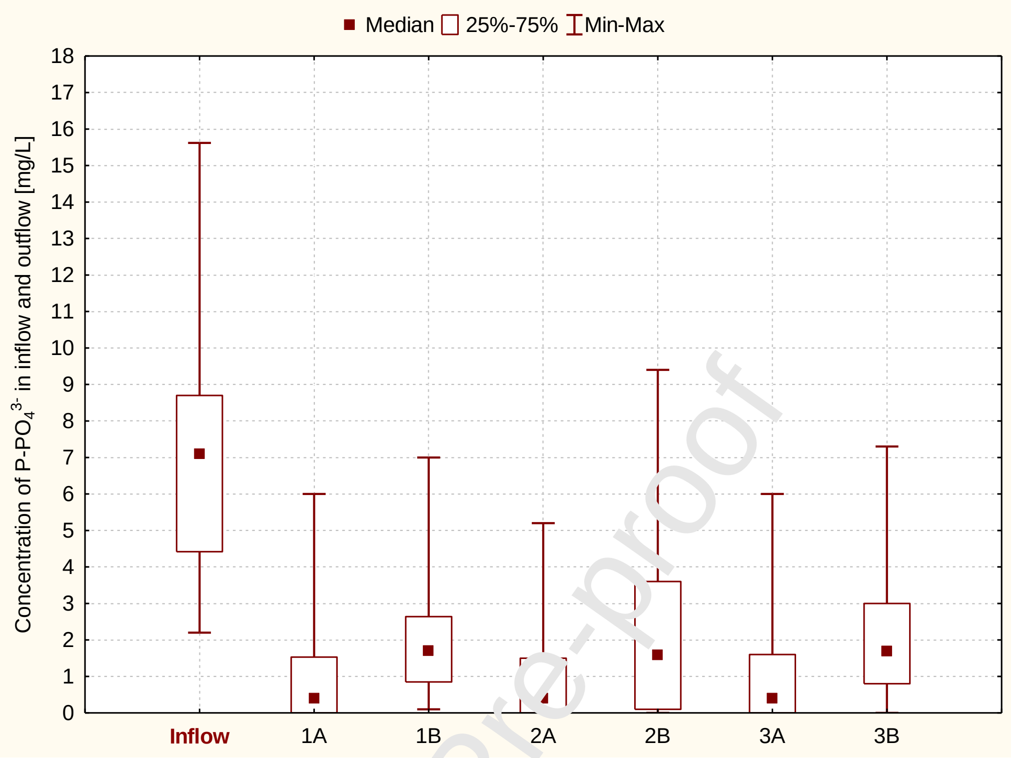


Figure 4. P-PO_4^{3-} concentration in the influent and effluent from columns A ($Q_1 = 20$ L/day) and B ($Q_2 = 40$ L/day)

The median phosphate concentration in the outflow from columns 1B, 2B, and 3B was several times higher at the inflow rate $Q_2 = 40$ L/day than in columns 1A, 2A, and 3A at $Q_1 = 20$ L/day, and ranged from 1.59 to 1.70 mg/L (Figure 4).

These data show that the amount of wastewater supplied to the columns, and thus also the time over which they were retained in the columns, had an impact on the effluent concentration of P-PO_4^{3-}. The lowest phosphate concentration was recorded for the inflow rate of $Q_1 = 20$ L/day. The results show that the phosphate concentration in the effluent of all filtration columns, both at the 6- and 12-hour wastewater retention time, was significantly lower than the discharge quality limit (TP<5 mg/L) recommended by HELCOM [17] for wastewater discharged from household wastewater treatment plants.

3.2. Influence of filter medium on phosphate removal efficiency

The authors, based on previous experience of the study on similar materials [52, 54], applied, respectively, in two columns No. 2 and No. 3 the additives of Leca® to Rockfos®

material. The aim was to verify whether it would minimize the negative impact of wastewater sediments precipitated on the hydraulic conductivity of the beds tested under specific column conditions. However, previously, the material was rinsed with water to remove the dust that remained on the grain surfaces after the crushing process.

In general, it was found that the Leca® material used in columns No. 2 and No. 3 had practically no effect in reducing clogging in both pairs of the filter columns analyzed. There was no difference between the hydraulic conductivity of these columns and those of columns filled with homogeneous filter material. The clogging of the filters studied in the initial period of the study occurred equally frequently in columns No.1 and No.3, but slightly less frequently than in column No. 2. However, the general frequency of the occurrence of clogging was higher in this period in the columns with the flow Q_2 = 40 L/day than with Q_1 = 20 L/day.

It is worth to be pointed out, that it is very unlikely to filter columns clogging could be caused by total suspended solids. Study was concerning on biologically treated wastewater, where the concentration of total suspended solids usually does not exceed 20-30 mg/L. Thus, it could be assumed that not total suspended solids present in wastewater, but the properties of the substrate materials in the filter could mainly cause the clogging effect. It is very likely that small particles were released during the filtration process and could block the flow. Thus, to prevent such a phenomenon, the material should be carefully rinsed out before use.

Analysis of the effect of the filter filling on the efficiency of phosphate removal provided no significant differences in the efficiency of its removal in filters with different filling configurations. However, the performance of the beds in all columns with a flow of Q_1 = 20 L/day was significantly higher. Only slightly higher phosphate removal effects were found in filter No. 2 filled with Rockfos® and two 5 cm Leca® layers, respectively: 94.9% and 84.1%, at the Q_1 and Q_2 inflow. Slightly lower effects of phosphate removal were found in filter No. 3 filled with the Rockfos® and 10% Leca® mixture, respectively: 94.5% and 77.3%, at the entry of Q_1 and Q_2 (Figure 3). On the other hand, in filters No. 1, filled with 100% Rockfos® material, the efficiency of 93.2% and 76.8% respectively, was achieved at the inflow of Q_1 and Q_2 (Figure 3).

3.3. Influence of the inflowing wastewater temperature on $P\text{-}PO_4^{3-}$ concentration in the effluent

Figure 5 shows the effect of the temperature of inflowing wastewater on the concentration of P-PO$_4^{3-}$ in the effluent from filtration columns 1A, 2A, and 3A at Q_1 = 20 L/day. Very low effluent P-PO$_4^{3-}$ concentration (< 1 mg/L) was observed during the first 36 weeks of the study (257 days). During this period, no correlation was found between the variables analyzed.

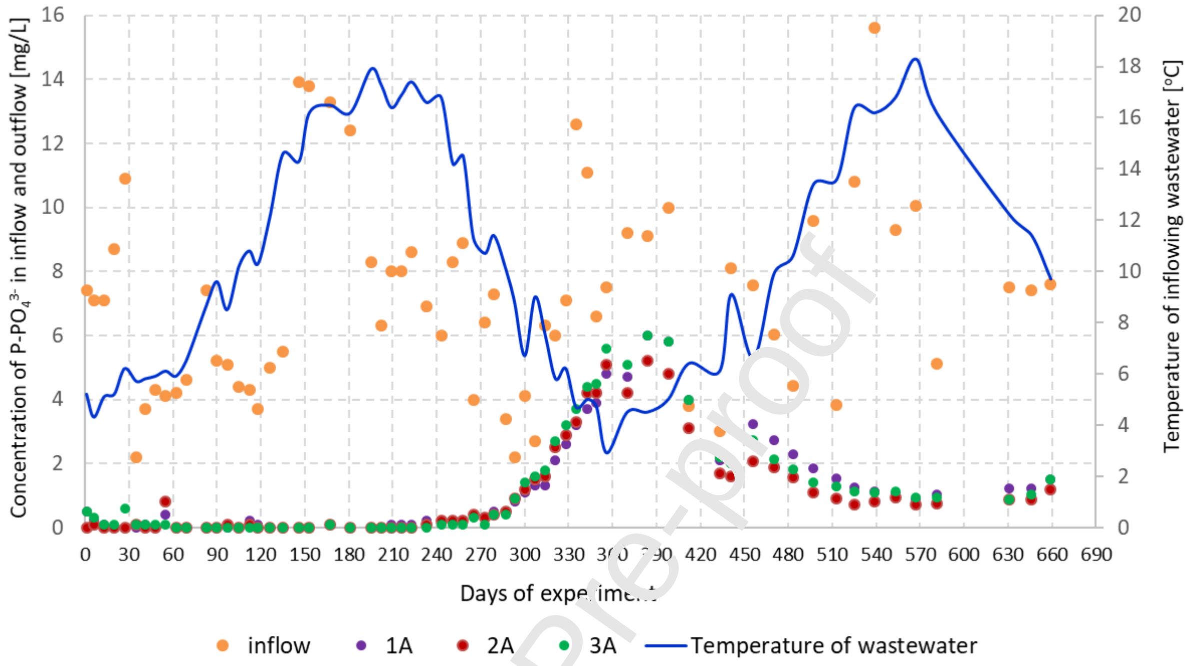


Figure 5. Effect of influent temperature on P-PO$_4^{3-}$ concentration in the effluent of filtration columns 1A, 2A and 3A

From week 37 onward (after day 264 of the experiment), there is a visible correlation between the concentration of P-PO$_4^{3-}$ in treated wastewater and the temperature of the inflowing wastewater, which is confirmed by the correlation coefficients for columns A: $r_{x,y}$ = -0.70 for column 1A, $r_{x,y}$ = - 0.78 for column 2A and $r_{x,y}$ = - 0.75 for column 3A. In all cases, the correlation was statistically significant at $\alpha = 0.05$. These correlations are high and very high according to the scale proposed by Stanisz [46], which means that the decrease in air temperature caused an increase in P-PO$_4^{3-}$ concentration in treated wastewater. The regression line equations shown in Figure 6 indicate that a change in wastewater temperature by 1°C increased the concentration of P-PO$_4^{3-}$ in treated wastewater by 0.26 mg/L in the case of column 1A (blue line), by 0.28 mg/L for column 2A (red line) and by 0.31 mg/L for column 3A (green line).

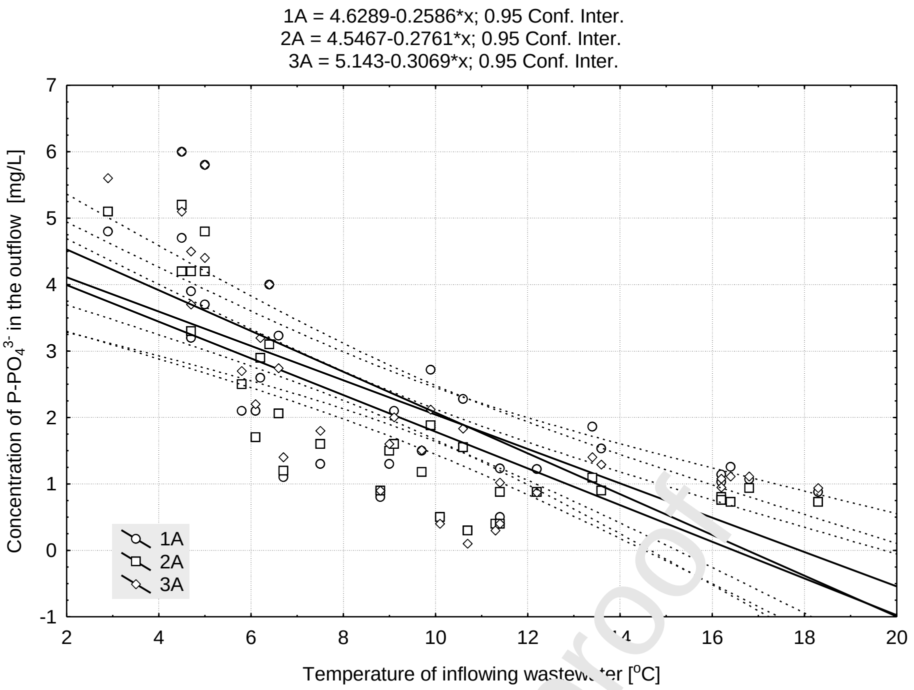


Figure 6. Scatter plot with a regression line and a 95% confidence level for the influence of temperature of inflowing wastewater on P-PO$_4^{3-}$ concentration in effluent from filtration columns A

Figure 7 shows the influent influence of the temperature of the influent on the concentration of P-PO43- in the effluent of the filtration columns 1B, 2B, and 3B (at Q_2 = 40 L/day). In this case, low concentrations of P-PO$_4^{3-}$ (< 2 mg/L) were recorded during the first 35 weeks (242 days) of the experiment. During this period, no correlation was found between the analyzed variables. However, the ability of the tested filters to remove phosphate was lower at Q_2 = 40 L/day than at Q_1 = 20 L/day. This can be explained by the fact that columns B were loaded with twice as much wastewater as columns A.

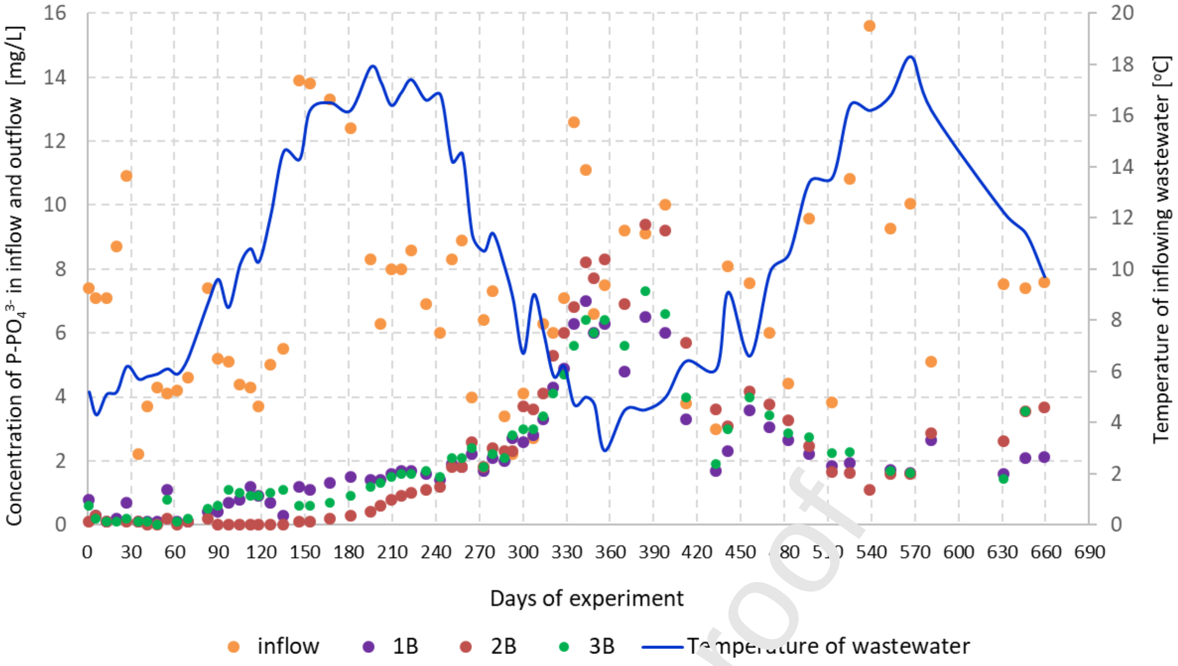


Figure 7. Effect of influent temperature on effluent concentration of P-PO_4^{3-} in filtration columns 1B, 2B, and 3B

From week 36 (after day 250 of the experiment), a clear increase in P-PO_4^{3-} concentration was observed in the effluent of the Q2 three columns at the inflow rate of Q_2 = 40 L/day (Figure 7). From day 250 of the experiment onward, a high correlation was observed between the concentration of P-PO43- in the effluent and the temperature of the influent. The effect of this relationship is confirmed by the correlation coefficients: $r_{x,y}$ = - 0.77 for effluent from column 1B, $r_{x,y}$ = - 0.84 for column 2B and $r_{x,y}$ = - 0.80 for column 3B. According to the Stanisz scale [46], these are very high correlations. In all cases, the correlations were statistically significant at $\alpha = 0.05$, which means, as in the case of filters in series A, that the decrease in air temperature caused an increase in P-PO_4^{3-} concentration in treated wastewater. The regression line equations shown in Figure 8 show that a change in wastewater temperature by 1°C caused an increase in the concentration of P-PO_4^{3-} in treated wastewater by 0.30 mg/L in the case of column 1B (blue line), 0.43 mg/L in the case of columns 2B (red line), and 0.28 mg/L in the case of column 3B (green line).

The present study shows that wastewater temperature was a significant factor affecting the efficiency of phosphate removal. During cold periods (temperature < 10^{o}C), a sharp increase in P-PO_4^{3-} levels in treated wastewater (Figures 5-8) and a significant decrease in its removal efficiency was observed in all filters tested in both Q_1 = 20 L/day and Q_2 = 40 L/day (Figure 9A and 9B). These data demonstrate that the decrease in air temperature in winter considerably slows down the chemical and biochemical processes that are crucial for the effective removal of phosphate from wastewater.

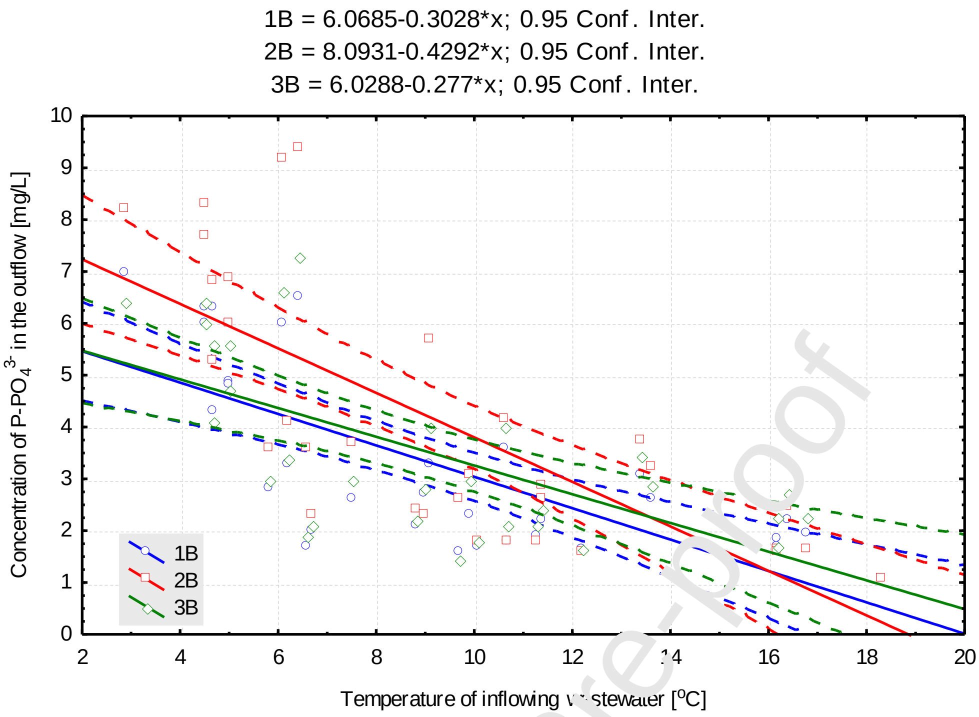
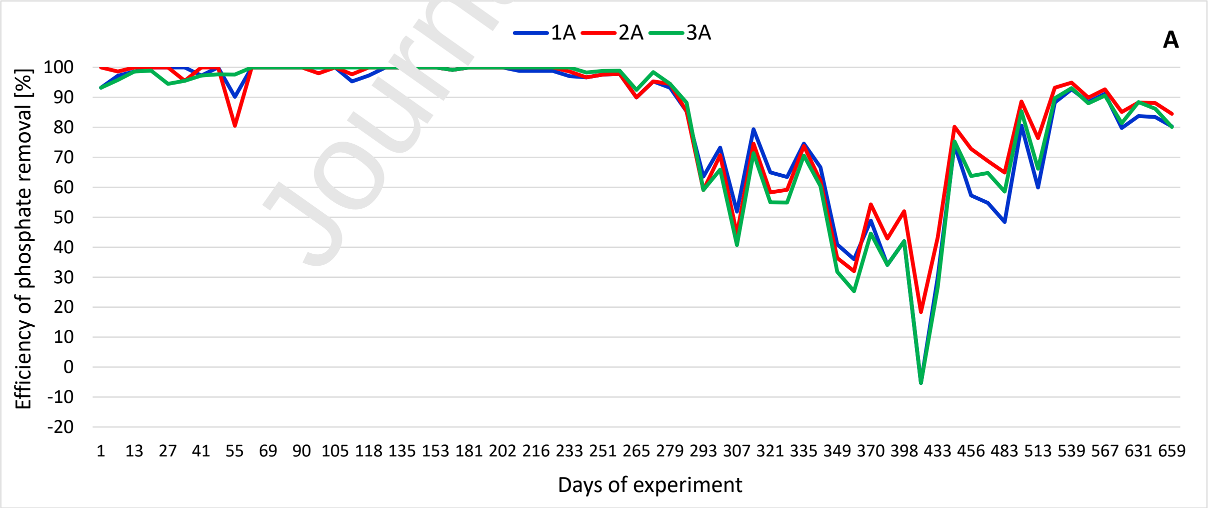


Figure 8. Scatter plot with a regression line and a 95% confidence level for the influence of the temperature of inflowing wastewater on P-PO_4^{3-} in the effluent of the filtration columns B



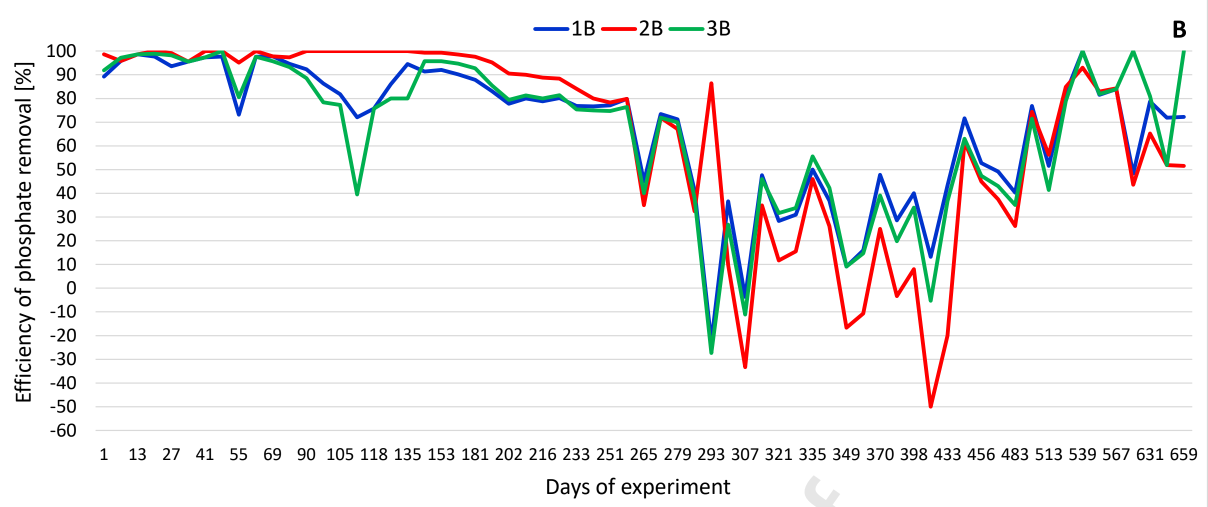


Figure 9. Phosphate removal efficiency of the filter columns during the study period, A - Q_1 = 20 L/day; B – Q_2 = 40 L/day (1 – 100% Rockfos®, 2 – Rockfos® and two 5-cm layers of Leca®, 3 – Rockfos® and 10% Leca®)

According to Herrmann et al. [54], the temperature is the main factor that affects the rate of chemical reactions, the growth and development of microorganisms, and the mechanical retention of phosphorus. Dissolved phosphorus is retained in limestone-filled filters as it reacts with calcium ions which are released from the surface of the filter medium into the aqueous solution, where they precipitate in the form of calcium phosphate [55]. According to Wajima and Rakovan [56], calcium phosphate precipitation is a spontaneous endothermic reaction; and because the equilibrium constant of an endothermic reaction increases with increasing temperature [57] phosphorus precipitation reactions occur faster at the higher temperature.

Thus, the sorption processes dominate chemisorption (as occurred in our research). Higher sorption at a higher temperature is expected until the process reaches an equilibrium. Bouamra et al. [58] while testing the phosphate removal processes of wastewater with the use of marble waste, confirmed that the mechanisms for the removal of phosphate mainly involved adsorption and precipitation, which varied with the pH of the solution, and that the sorption yield increased with the increase of temperature. Similarly, Yagi and Fukushi [59] during the phosphate removal testing process by adsorption and precipitation of calcium phosphate onto monohydrocalcite stated that the formation of amorphous calcium phosphate is strongly dependent on the ionic strength, temperature and reaction time. Oguz [60] also confirmed that the increase in temperature positively affects phosphate removal and suggested a high dependence of the precipitation reaction rate on the temperature.

The types of calcium phosphate forms precipitated from wastewater are influenced by the physicochemical conditions of the solution, while the contribution of temperature relates to its influence on the characteristics of the speciation of phosphate and calcium ions. The conversions of phosphorus compounds and forms in the mineral environment are generally referred to as sorption but are not delimited. This means that the removal of phosphate from wastewater during filtration by highly alkalizing mineral materials occurs in a continuous process, including (depending on the pH of the solution) nonspecific (ion exchange) adsorption, specific adsorption (chemisorption), precipitation of amorphous compounds, and crystallization of phosphorus compounds such as calcite and hydroxyapatite [61-62].

Our research results and observations may also confirm the findings of Kõiv [62]. They found that the processes of removal of P-PO_4^{3-} from wastewater during filtration in columns filled with Rockfos material rich in reactive CaO occur primarily through the precipitation of weakly crystallized or amorphous phases of di-calcium phosphate dihydrate, octa-calcium phosphate, and tri-calcium phosphate. These compounds form phases in solutions containing Ca and P by heterogeneous deposition on the grain surfaces of the material and are precursors (bridgeheads) for further recrystallization to thermodynamically stable hydroxylapatite.

In this study, it was confirmed that two main factors affect the efficiency of the removal of phosphate from biologically treated wastewater before it is filtered in column beds. The first was the supply and availability of reactive Ca^{2+} cations on the large grain surface area of the column filling material, which directly influenced the increase in the highly alkaline pH of wastewater (pH>11) and which was important to create the phosphates of the various products in these processes. The temperature of the treated wastewater was another significant factor. In the initial period of 250 days of testing the "fresh" material, no correlation was found between the analyzed variables, i.e. temperature and concentration of P-PO_4^{3-}. The drop in wastewater temperature in the first winter period had practically no effect on reducing the initially high efficiency of phosphate removal from wastewater. In this period of research, the large supply of easily accessible Ca^{2+} on grain surfaces, not yet occupied by sorption products in the beds, probably effectively eliminated the potentially negative impact of the temperature factor on the quantitative results of treatment processes. However, in the later period of the research, when the availability of reactive calcium on the grain surfaces was exhausted, due to its use as a substrate in precipitation reactions and the successive occupation of grain surfaces by sorption products, the influence of temperature on the efficiency of phosphate removal from wastewater became strongly noticeable. The drop in wastewater temperature to 5°C in the second winter period resulted in a radical limitation of the ability of the beds to remove phosphate. However, on the other hand, the increase in wastewater temperature in the next summer period activated the reactive properties of the sorbate in the solution. Although both the availability of Ca^{2+} ions and the pH of the solution were lower, a periodic increase in the efficiency of phosphate removal was found, but at a significantly lower level than in the initial period of the research at the same time of year.

3.4. Influence of the duration of the experiment on the pH value in the effluent

The pH of the wastewater discharged from the individual test columns ranged from 7.76 to 11.84 during the study period. As time passed, the pH value of the effluent from all filters decreased. pH is a practical parameter that helps to determine the moment of saturation of a medium with phosphorus, showing when the medium has to be replaced. Studies conducted by Vidal et al. [63] showed that the filter material should be replaced when its pH drops below 9.

The high pH of the wastewater at the beginning of the experiment (Figure 9, Figure 11) was conducive to the high accumulation of phosphate in the material that fills the tested filtration columns, ensuring a high (more than 90%) phosphate removal efficiency (Figure 9). According to many authors [27, 52, 55] the alkaline reaction of wastewater promotes the precipitation of calcium phosphate. Chemical precipitation is the main process leading to phosphate retention in Rockfos® material-filled filters. However, observations show that this process sometimes leads to the clogging of filter columns.

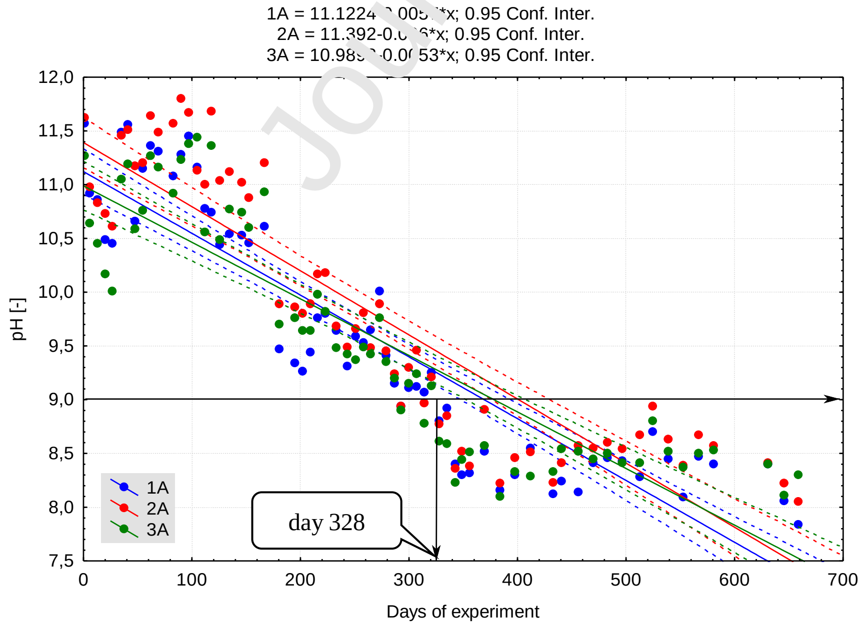


Figure 10. Scatter plot with a regression line and a 95% confidence level for the effect of the duration of the experiment on the pH of the effluent of columns A

It was found that in the initial test period, the reaction of the wastewater flowing from columns 1A, 2A, and 3A (Q_1 = 20 L/day) was strongly alkaline at approximately pH 11. However, over time, the pH gradually decreased to reach the value of 9.0 on day 328 of the experiment (Figure 10). In the following days until the end of the experiment, the pH value was below 9. Based on the calculated correlation, it was found that there was a strong relationship between the duration of the experiment and the pH of treated wastewater. In the case of columns 1A and 2A, the correlations between these variables were $r_{x,y}$ = -0.91 and $r_{x,y}$ = -0.90, respectively, which according to the Stanisz scale [46] are nearly perfect correlations. In the case of column 3A, the correlation was very high, $r_{x,\,y}$ = -0.89. In all cases, the correlation was statistically significant at α = 0.05. The regression line equations presented in Figure 10 show that every 10 days of the experiment, pH decreased by 0.057 in column 1A, by 0.06 in column 2A, and by 0.053 in column 3A.

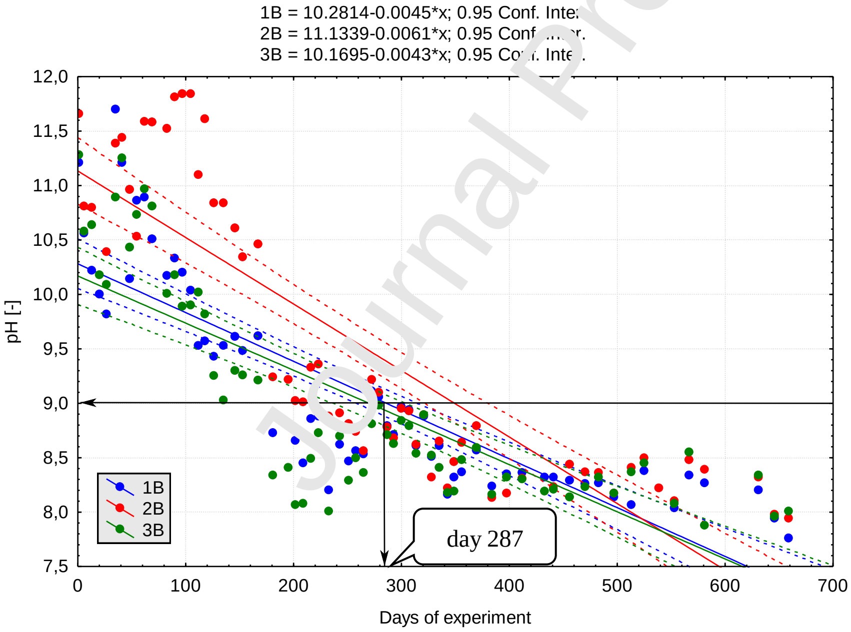


Figure 11. Scatter plot with a regression line and a 95% confidence level for the effect of the duration of the experiment on the pH of the effluent from columns B

At the beginning of the experiment (the first 100 days) conducted at Q_1=40 L/day the reaction of the wastewater discharged from columns 1B, 2B, and 3B was also strongly alkaline and oscillated between pH 10.0 and 11.8. However, as time passed, the pH value gradually decreased to a level of 9.0 after 287 days of the experiment (Figure 11). Similar to the effluent from column A, wastewater collected at the outflow from column B had a pH value below 9 until the end of the experiment. For all B columns, the correlation between the duration of the experiment and the pH value of the effluent was very high according to the Stanisz scale [46]: $r_{x,y}$ = - 0.85 for column 1B, $r_{x,y}$ = - 0.86 for column 2B, and $r_{x,y}$ = - 0.81 for column 3B. In all three cases, the correlation was statistically significant at the level of significance $\alpha = 0.05$. The regression line equations presented in Figure 11 show that every 10 days of the experiment, pH decreased by 0.045 for column 1B, 0.061 for column 2B, and 0.043 for column 3B.

3.5. Dependence of P-PO_4^{3-} concentration in the effluent on the duration of the experiment and the temperature of the influent

Multiple regression analysis was used to determine the strength of the simultaneous effect of the duration of the experiment and the influent temperature (independent variables) on the concentration of P-PO_4^{3-} in the effluent (dependent variable). Only columns 1A and 1B were analyzed because there were no significant changes in the concentration of P-PO_4^{3-} in the wastewater treated in the remaining pairs of columns A and B.

In the case of column 1A, we analyzed the data from day 265 to 669 of the experiment (404 days), during this period significant correlations were found between the P-PO_4^{3-} removal efficiency and the temperature of inflowing wastewater. During this period, 33 series of influent and effluent analyzes were performed from filtration column 1A.

Multiple regression analysis of the data for column 1A showed that not only the influent temperature (Rc = - 0.77) affected the concentration of P-PO_4^{3-} in treated wastewater but also the duration of the experiment affected the concentration of P-PO_4^{3-} in the effluent (R_c = 0.48). In terms of the Stanisz scale [46], the first correlation was very high and the second one was moderate. The significance of the calculated correlation coefficients was tested using Student's t-test at a significance level of $\alpha = 0.05$. In both cases, significant relationships were found. The results of multiple regression analysis for column 1A are shown in detail in Table 4.

Table 4. Results of multiple regression analysis of correlations between the concentration of P-PO_4^{3-} in wastewater discharged from column 1A and the experiment time and the influent temperature

Statistic	Group size	Partial correlation coefficient	Coefficient of determination	t-test of significance R	t-test at α = 0.05
Symbol Correlation	N	R_c	R^2	t	$t\alpha_{kr}$
Concentration of P-PO_4^{3-} Influent temperature	33	- 0.77	0.33	- 6.67	0.000000
Concentration of P-PO_4^{3-} Duration of experiment	33	0.48	0.33	2.97	0.005812

Partial correlation results were used to create the nomogram shown in Figure 12. The nomogram can be used to predict the concentration of P-PO_4^{3-} in the effluent from column 1A when the wastewater temperature (ordinate axis) and the time of filter operation during the experiment (abscissa axis) are known. The model can be described by the equation shown in Figure 12.

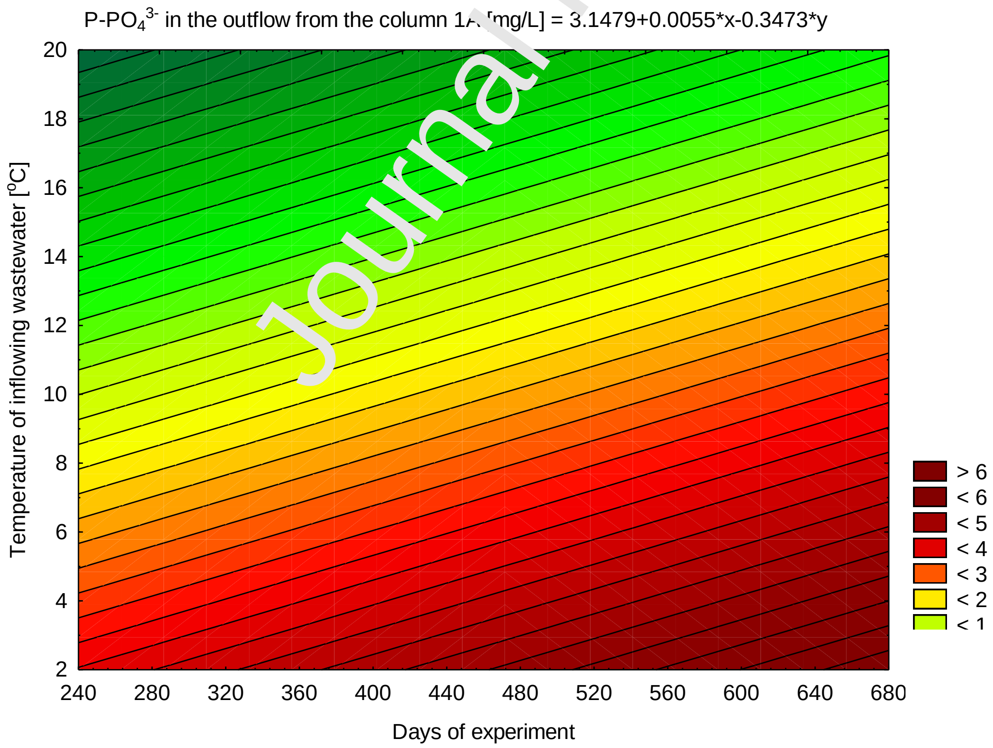


Figure 12. Nomogram to predict the concentration of P-PO_4^{3-} in treated wastewater discharged from column 1A based on the time of the experiment and the temperature of inflowing wastewater

Multiple regression analysis for column 1B was performed using data from day 251 to 669 of the experiment, a period of 418 days during which a significant relationship was observed between the P-PO_4^{3-} removal efficiency and the temperature of the influent. During this period, 35 series of analyses of influent and effluent samples were performed from the filtration column 1B.

Multiple regression analysis for column 1B showed that the concentration of P-PO_4^{3-} in treated wastewater was highly dependent (according to the Stanisz scale [46]) on the temperature of the influent, as shown by the value of the partial correlation coefficient $R_c = -0.75$. In contrast, no relationship was found between the duration of the experiment and the concentration of P-PO_4^{3-} in the effluent, as evidenced by the value of the coefficient $R_c = 0.06$. The significance of the calculated correlation coefficients was tested using Student's t-test at a significance level of $\alpha = 0.05$. The relationship between the concentration of P-PO_4^{3-} in the effluent and the temperature was significant, but no statistical significance was found for the correlation between the level of P-PO_4^{3-} in the effluent and the duration of the experiment. This finding can be explained by the fact that the amount of wastewater, and thus also the load of P-PO_4^{3-}, fed to column 1B was twice as large as that supplied to column 1A, which means that the sorption capacity for P-PO_4^{3-} was depleted faster in column 1B. The results show that the absorption capacity of the P-PO_4^{3-} infiltration column 1B (with a retention time of 6 hours) was exhausted in the first 10 months of the experiment.

The results of multiple regression analysis for column 1B are shown in detail in Table 5. The results of partial correlation were used to create the nomogram shown in Figure 13. The nomogram can be used to predict the concentration of P-PO_4^{3-} in column 1B effluent when the wastewater temperature (ordinate axis) and the filter operation time during the experiment (abscissa axis) are known. The model developed in the study can be described by the equation given in Figure 13.

Table 5. Results of multiple regression analysis of the correlation between the concentration of P-PO_4^{3-} in wastewater discharged from column 1B and the experiment time and the influent temperature

Statistic	Group size	Partial correlation coefficient	Coefficient of determination	t-test of significance R	t-test at α = 0.05
Symbol Correlation	N	R_c	R^2	t	$t\alpha_{kr}$
Concentration of P-PO_4^{3-} Wastewater temperature	35	- 0.75	0.19	- 6.39	0.000000
Concentration of P-PO_4^{3-} Duration of experiment	35	- 0.06	0.19	- 0.33	0.740563

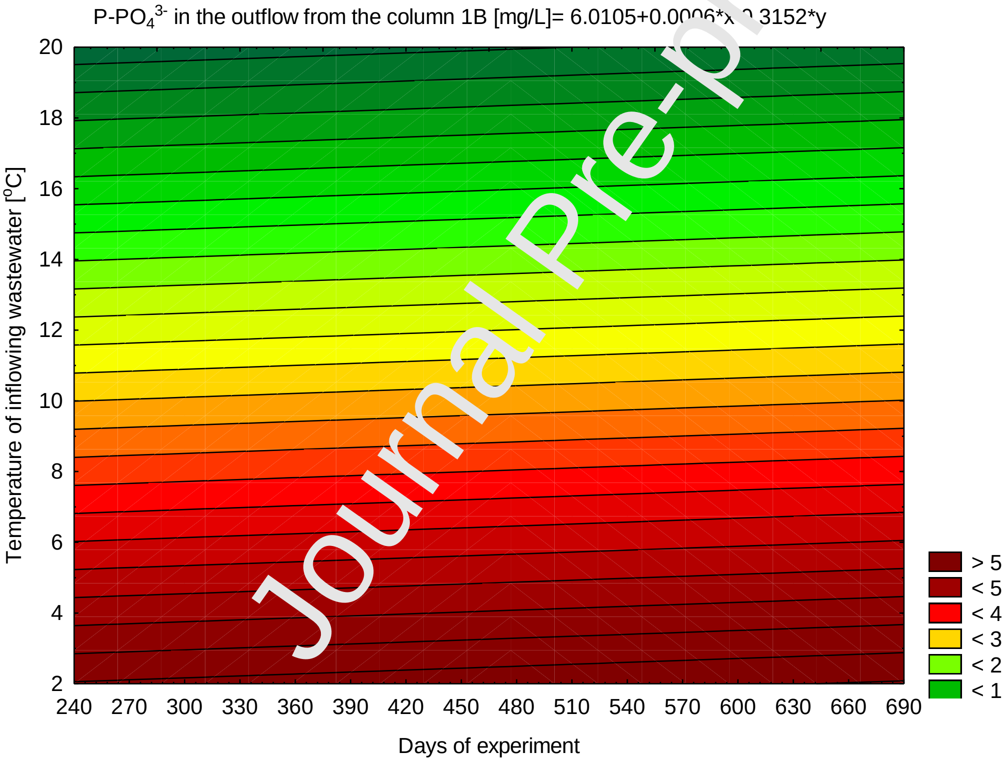


Figure 13. Nomogram to predict P-PO_4^{3-} concentration in treated wastewater discharged from column 1B based on experiment time and influent temperature

During the 250-day test cycle, in columns A (mean of 3 columns) with a nominal wastewater flow of 20 l/day and a retention time of 12 h, on average 2.04 g of P-PO_4^{3-} per 1 kg of filling material were removed. In columns B with a nominal flow of 40 l/day and a retention time of6 h, an average of 3.70 g of P-PO_4^{3-} was removed per 1 kg of filler material.

After a complete 659 day cycle of experiment, the columns A (mean of 3 columns) were removed: an average of 4.48 g P-PO_4^{3-} per 1 kg of filling material, and columns B: an average of 7.26 P-PO_4^{3-} per 1 kg of filling material.

The utilization rates of the sorption capacity of the tested materials specified after a 250-day cycle were generally: 3.64% in columns "A" and 6.58% in columns " B". After a 659-day test cycle, these rates were generally: 7.97% in columns "A" and 12.91% in columns "B". It was estimated based on the index of the maximum sorption capacity of a similar opoka material in a finely divided form (0,1-0,2 mm), determined by Nastawny et al. [61] as 56.2 mg P-PO_4^{3-}/g, from the Langmuir and Freundlich adsorption isotherm equations.

The influence of expanded clay aggregates on the general level of sorption of the materials used in the columns can be considered to be insignificant. This is due to its much lower potential sorption capacity: 0.59 mg/g [45], 2.4 mg/g [61], which is 1% and 4%, respectively.

The current rate of utilization of the sorption capacity of the filter materials analyzed, tested in columns in the form of grits, indicates still potentially large possibilities of their further use for the effective removal of P-PO_4^{3-} even at a drop in pH < 9, but preferably at a temperature above 10°C (Figure 6, 8, Figure 11, Figure 12). This is also confirmed by previous studies [61], conducted with similar materials.

Based on the regression analysis, it was estimated that assuming that the concentration of P- P-PO_4^{3-} in the treated wastewater does not exceed 5 mg/l, the possible period of use of the column A filling materials is 1160 days (on average columns A).

On this basis, the amount of P-PO_4^{3-} removed from wastewater (on average in columns A) after 1160 days of operation was estimated at 5.99 g per 1 kg of bed material with the utilization rate of the potential sorption capacity of 10.66%. The operational capacity of column B was exhausted after 658 days.

3.6. Implications for the practical use of Rockfos® and Leca® mixture as filtration bed to capture phosphate from domestic wastewater

Tested filter columns can only be used for the treatment of biologically treated wastewater and are not recommended for the treatment of raw domestic wastewater with a total suspended solids concentration over 100 mg/L, because such wastewater may cause column clogging. Moreover, to prevent the filter from the clogging effect, the substrate material should be carefully rinsed out before use.

Research results show that the use of Rockfos® with two 5 cm Leca® layers can be recommended infiltration beds for the removal of phosphate in household wastewater treatment plants. A better solution, for practical reasons, will be to use fillers that are not less effective according to patterns No. 1 and 2.

The research carried out showed that while designing and constructing phosphorus removal filters, it is recommended to use 1 m^3 of a filter on 1 m^3/day of inflowing wastewater, filled (for practical reasons) with mixture No. 3 - Rockfos® and 10% Leca®), as well as homogeneous material No. 1 – 100% Rockfos®. These materials remove phosphate at only a slightly lower level than material No. 2. Furthermore, it is recommended to provide 12 h of wastewater retention time in the filtration bed. For functional reasons, it is also recommended to feed the filter from the bottom to the upper outflow of treated wastewater. This generates a space in the lower part under the grate and allows for the accumulation of sediments and their periodic removal. Based on the research, it can be assumed that the practical life span of the filter bed, after which it should be replaced, should not be longer than 3 years.

Mixed fillers tested can be used in practice for phosphorus removal from wastewater after biological treatment in the vicinity of lakes, national parks, and other protected areas, as well as in areas of protection zones for drinking water intake, where the phosphorus removal requirements are increasing. Particularly protected areas Natura 2000 is the largest coordinated network that spans more than 18% of the European Union’s territory and includes more than 8% of the marine area. In Poland, Natura 2000 sites include over 20% of areas both on land and at sea [64, 65].

4. Conclusions

Based on the research conducted, it can be stated that the efficiency of phosphate removal was the highest at the lower inflow rate and equal to 93-95%. All columns provided a phosphate removal efficiency of over 70%, which was in accordance with HELCOM Recommendation 28E/6 [17]. A high removal efficiency of $P\text{-}PO_4^{3-}$ (90 to 100%) was observed in all columns analyzed during the first 250 days of the experiment and the effects were determined by the high availability of reactive Ca^{2+}. After this time, the removal efficiency was decreasing and more dependent on the temperature of the inflowing wastewater.

This research shows that the process of chemical precipitation of phosphate creates a tendency to block the filtration columns. However, this may be influenced by the specific structure of the column arrangement. In practical solutions, it is less important.

A strong relationship was also found between the duration of the experiment and the pH value of the treated wastewater. These findings demonstrate that $P\text{-}PO_4^{3-}$ can be effectively removed even at pH < 9, but only when the temperature is higher than 10°C. Furthermore, the temperature of the inflowing wastewater had a greater impact on the concentration of P-PO_4^{3-} than the duration of the experiment.

CREDIT AUTHOR STATEMENT

Andrzej Jucherski – Conceptualization; Methodology; Investigation; Resources; Data Curation; Writing - Original Draft; Writing - Review & Editing; Funding acquisition; Validation.
Andrzej Walczowski – Resources; Data Curation; Visualization; Supervision; Project administration.
Piotr Bugajski – Methodology; Software, Formal analysis, Writing - Original Draft, Visualization.
Krzysztof Jóźwiakowski – Formal analysis; Writing - Original Draft; Writing - Review & Editing.
Wojciech Janczukowicz – Formal analysis; Writing - Review & Editing.
Joanna Rodziewicz – Formal analysis; Writing - Review & Editing.
Shubiao Wu – Formal analysis; Writing - Review & Editing.
Magda Kasprzyk – Formal analysis; Writing - Original Draft; Writing - Review & Editing.
Magdalena Gajewska – Formal analysis; Writing - Original Draft, Writing - Review & Editing.
Artur Mielcarek – Formal analysis; Writing - Review & Editing.

DECLARATION OF INTEREST STATEMENT

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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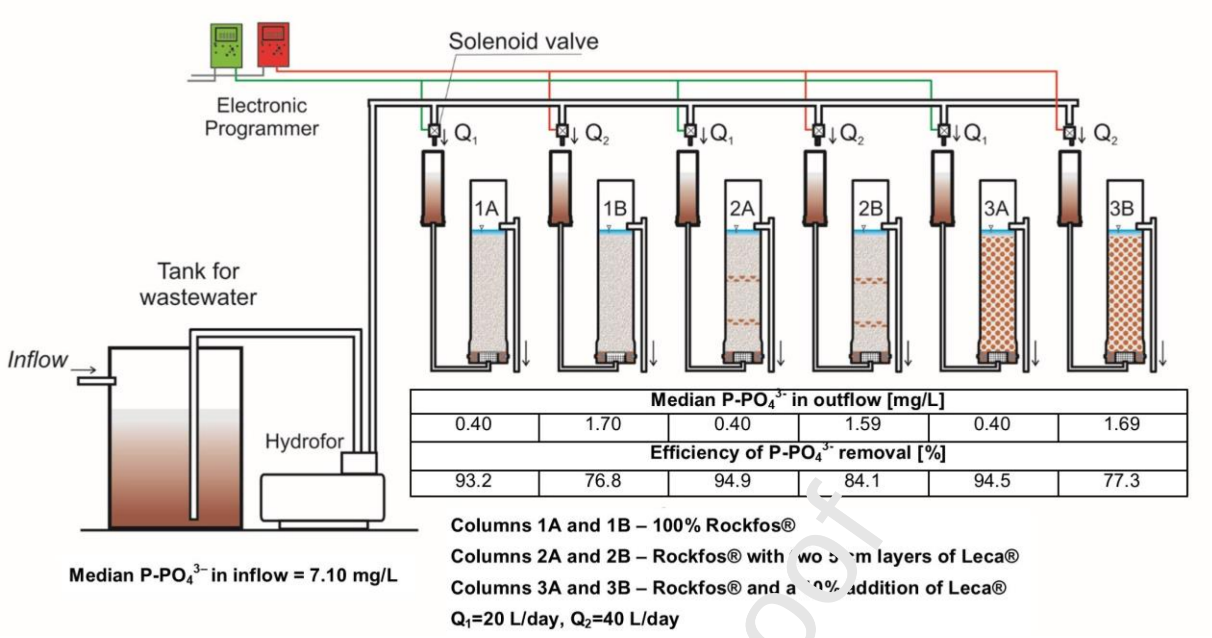

Median P-PO$_4^{3-}$ in outflow [mg/L]					
0.40	1.70	0.40	1.59	0.40	1.69
Efficiency of P-PO$_4^{3-}$ removal [%]					
93.2	76.8	94.9	84.1	94.5	77.3

Median P-PO$_4^{3-}$ in inflow = 7.10 mg/L

Columns 1A and 1B – 100% Rockfos®
Columns 2A and 2B – Rockfos® with two 5 cm layers of Leca®
Columns 3A and 3B – Rockfos® and a [illegible]0% addition of Leca®
Q_1=20 L/day, Q_2=40 L/day

Graphical abstract