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INFLUENCE OF THE PARTICLE SIZE OF CARBONATE-SILICEOUS ROCK ON THE EFFICIENCY OF PHOSPHOROUS REMOVAL FROM DOMESTIC WASTEWATER

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ABSTRACT

The aim of the study was to determine the influence of the particle size of carbonate–silica rock (opoka) used in rock filters on the efficiency of phosphorus removal from domestic wastewater. The investigations were carried out in a laboratory using a model consisting of three vertical flow filters with carbonate–silica rock of different particle sizes (G_1=1–2 mm; G_2=2–5 mm; G_3=5–10 mm). The tested rock was subjected to decarbonising at 900 °C and consisted primarily of 51.7% SiO_2, 23.2% CaO, and 7.6% Al_2O_3. In the first three weeks of the study (1–3), the hydraulic load of each filter was Q_1=0.72 l/day and the hydraulic residence time was HRT_1=24 hours; in the next three weeks (4–6) Q_2=1.08 l/day and HRT_2=16 hours, and during the last three weeks (7–9) Q_3=1.44 l/day and HRT_3=12 hours. A significant influence of the size of rock particles and the hydraulic load (hydraulic residence time) on the efficiency of total phosphorus removal and on phosphorus concentration in the wastewater discharged from the system was observed (α=0.05). Statistically, the best removal of phosphorus from wastewater – an average of 97%, was found in the substrate with the smallest particle size (rock G_1, 1–2 mm) at the lowest hydraulic load of 0.72 l/day and at a hydraulic residence time of 24 hours. The lowest phosphorus removal efficiency was observed in the filter containing rock G_3 with a particle size of 5–10 mm (mean <60%). The average concentration of total phosphorus in wastewater flowing out from filter G_1 was 0.23 mg/l, which was much below the limit values specified by EU regulations. The overall phosphorus load removed during the study period (nine weeks) in the filter with fraction G_1 was 0.38 g/kg of rock, in the filter with G_2-0.30 g/kg of rock, in the filter G_3-0.28 g/kg of rock. The load of phosphorus removed during this period not characterized the full sorption capacity of the rock. The study showed that the rock subjected to decarbonising at 900 °C could be successfully used to remove phosphorus from domestic wastewater, especially in areas where phosphorus removal requirements are very high ($P_{tot.}< 2$ mg/l).

Key words: phosphorus removal, domestic wastewater, carbonate−siliceous rock (opoka), mitigation of eutrophication

1. Introduction

The problem of removal of biogenic compounds from wastewater is still unresolved, in particular with regard to small and local treatment plants. Around the world, researchers are looking for innovative ways of eliminating biogenic elements (nitrogen and phosphorous) from wastewater with a view to reducing the process of eutrophication of surface waters. The main element responsible for the fertility of fresh water is phosphorus. It may come from various sources: 1) natural – organic compounds of animal and plant origin, and 2) anthropogenic – agriculture (aerial sources) and different types of insufficiently treated wastewater (point sources). Among point sources, the most important ones are: industrial wastewater, e.g. discharged from plants producing fertilizers and cleaning agents based on detergents, municipal wastewater, wastewater from pig farming and domestic wastewater. Total phosphorus concentrations in raw domestic wastewater are in the range from a dozen to several dozen mg/l (Metcalf and Eddy, 2003).

Discharge of improperly treated wastewater may cause many problems in the recipient body. The most important of those problems include oxygen depletion due to mineralization of organic matter and oxidation of ammonium nitrogen (nitrification) (Jóźwiakowski et al., 2017). When the concentration of the two biogenic compounds in the discharged wastewater is too high, oxygen depletion accelerates due to the intensive growth and death (decomposition) of algae. An increase in phosphorus concentration in surface waters up to over 15 μg/l may lead to an intense growth of algae (Yang et. 2008). It is estimated that large amounts of biogenic compounds contained in sewage can increase secondary oxygen consumption more than five-fold, compared with primary consumption associated with the disposal of organic matter contained in wastewater. Therefore, it is crucial to reduce the content of biogenic compounds in the effluent discharged from treatment plants to receivers (Mikosz and Mucha, 2014).

Phosphorus concentration in the effluent can be reduced using biological and chemical purification methods (Clark et al., 1997; Wei and Zhi, 2002; Ren-Jie and Yi-Rong, 2008; Wei et al., 2013). Biological removal consists in creating optimal conditions in a sewage treatment plant for the growth of microorganisms capable of collecting an excess of phosphorus, and then removing the accumulated phosphorus with excess sludge (Morse et al. 1998). Chemical processes rely, instead, on the use of coagulants, e.g. coagulants of iron and aluminium. The removal of phosphate with reactive media as sorption filters has been more and more frequently used over the recent years in small wastewater treatment plants (Renman and

Renman 2010; Bus and Karczmarczyk 2014; Nastawny et al. 2015; Jucherski et al. 2016). In this method, wastewater filtering through a substrate bed remains in contact with a reactive material, which facilitates chemical precipitation and sorption of phosphorus compounds (Eveborn, 2013). The biological method usually guarantees the elimination of required amounts of phosphorus/reduction of phosphorus to a required level, but is only effective when used in large (over 100 000PE) wastewater treatment plants (WWTP). The use of aluminum or iron coagulants is cumbersome and relatively expensive, especially for small and medium wastewater treatment plants. The main disadvantage of chemical precipitation of phosphorus is production of chemical sludge which needs to be disposed of, increasing the cost of WWTP operation. Given these difficulties, there is a need to study materials capable of absorbing large amounts of phosphorus, both natural and man-made, such as rock, granulated blast furnace slag, fly ash, gravel, or brick covered with iron (Vhola, et al. 2009).

Studies on the use of carbonate–silica rock (opoka) to remove phosphorus from wastewater have been carried out for many years now (Brogowski and Gworek, 1996; Brogowski and Renman, 2004; Cucarella et al., 2007; Jóźwiakowski, 2006, 2012; Renman and Renman, 2010; Karczmarczyk and Bus, 2014; Bus and Karczmarczyk, 2014). This rock material is highly reactive to phosphorus because it contains large amounts of calcium and silicon. The content of these components varies in different types of opoka from 14 to 56% CaO and from 5 to 75% SiO_2 (Kozłowski, 1986; Brogowski and Renman, 2004; Bus and Karczmarczyk, 2014). Carbonate–silica rock is characterised by more than 50% porosity (Brogowski and Gworek, 1996). This material is of organic origin and consists mainly of small organic debris with some addition of silica. Thus opoka is assumed to be an intermediate form between rocks containing carbonate and those containing silica (Pinińska, 2008, Brogowski and Renman, 2004). The composition and properties of the rock favour chemical sorption of phosphorus. The good sorption properties of the material could be enhanced in an alkaline environment since in such conditions phosphorus forms chemical bonds with calcium to give calcium phosphates (Reddy and D'Angelo, 1997; McGechan and Lewis, 2002).

So far, it has been established that thermal treatment increases the sorption capacity of rocks. A study by Brogowski and Renman (2004) shows that a natural carbonate–silica rock is characterized by a sorption capacity of 19.6 g P/kg, but after firing at 250 °C the capacity increases to 60.5 g P/kg, and at 1000 °C to 119.6 g P/kg. Additionally, experiments conducted by Cucarella et al. (2007) and Bus and Karczmarczyk (2014) demonstrate that sorption capacity of rocks is also closely related to their calcium content (Table 1).

Table 1. Relationship between sorption capacity of carbonate–silica rock fired at 900 °C and Ca content (Cucarella et al. 2007).

Element	Rock 1	Rock 2	Rock 3
Ca [g/kg]	220.79	364.39	419.75
Sorption capacity [mg P/g]	79.37	136.99	181.82

For a few years now, a rock excavated in the village of Bełżec in Poland (50°3'04" N, 23°26'18" E), heated at a temperature of about 900 °C, with a particle size of 2.0–6.0 mm, bearing the trade name Polonite®, has been used, primarily in Sweden, as a sorbent for the removal of phosphorus from wastewater (Bus and Karczmarczyk, 2014).

The reports cited above have shown that using this rock as a substrate in phosphorus-removal filters gives very good results. Up till now, however, only one grain size of Polonite® (2.0–6.0 mm) has been shown to have a high (over 90%) phosphorous removal capacity. Researchers believe that the main mechanism of phosphorous removal is chemical sorption, and if so the process is strongly dependent on the availability of calcium for binding to P (Karczmarczyk, 2000, 2003; Karczmarczyk and Mosiej, 2003; Karczmarczyk et al., 2003; Brogowski and Renman, 2004; Jóźwiakowski, 2006; Renman, 2008; Cucarella, 2009, Nilson, 2012). Unfortunately, there are few studies regarding the effect of the composition of rocks and their particle size on phosphorus removal. To investigate this problem, we decided to conduct experiments with different particle sizes (different surfaces) of carbonate–silica rock and different hydraulic retention times. Both of these parameters were hypothesized to have an influence on the efficiency of phosphorus removal from domestic wastewater.

2. Material and method

The experiments were conducted using a laboratory model consisting of three vertical-flow wastewater filters filled with opoka as a substrate (Fig. 1). The rock was obtained from a mine in the town of Chrzanów, located in south-eastern Poland (50°46'26" N, 22°36'19" E) and was characterized by a different composition in comparison to those described by Karczmarczyk, 2000, 2003; Karczmarczyk and Mosiej, 2003; Karczmarczyk et al., 2003; Brogowski and Renman, 2004; Jóźwiakowski, 2006; and Renman, 2008. The substrate rock was dried, crushed and sorted, to obtain three types of samples differing in particle size: G_1, 1–2 mm; G_2, 2–5 mm; and G_3, 5–10 mm (Fig. 2).

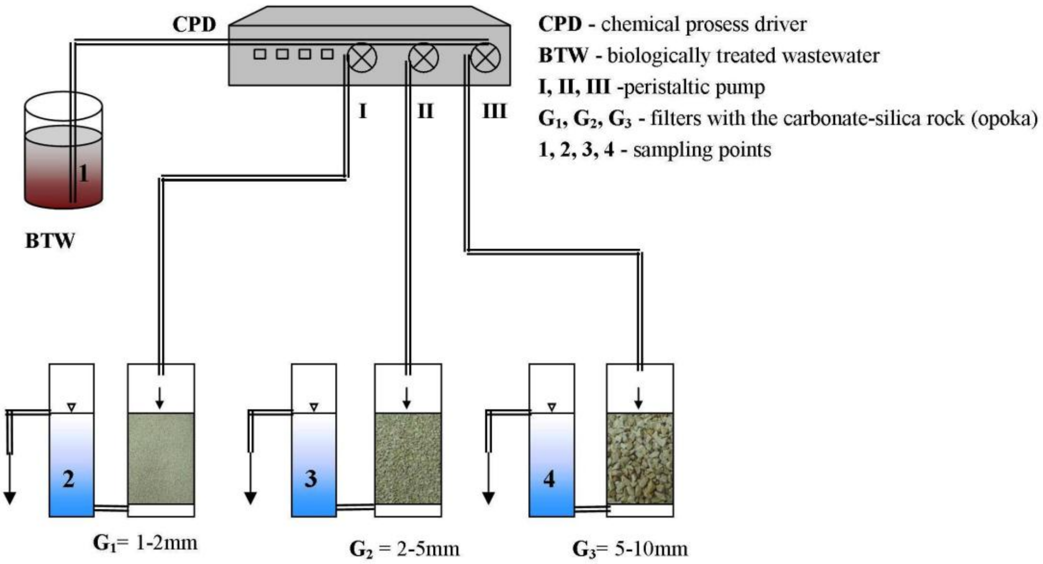

Figure. 1. A schematic showing vertical-flow filters with rock substrate (G_1, G_2, G_3) and storage tanks for treated wastewater (2, 3, 4)

Figure. 2. Images of three grain sizes of the rock substrate used in filters

Then, the three particle-size fractions of rock were heated in a muffle furnace at 900 °C, as treatment at this temperature had been reported to ensure the highest sorption capacity and thus the most effective removal of phosphorous. Prepared in this way, the granular substrate, sorted by grain size, was packed into three filters with a volume of 1.4 l each (Fig. 1). The chemical composition of the rock, estimated using a ground mixture of samples is shown in Table 2. The effect of the size of substrate on its composition was not investigated. Studies performed using an X-ray spectrometer (fluorescence spectrometry, MINIPAL 4 from PANALYTICAL) showed that the test rock consisted primarily of 51.7% SiO_2, 23.2% CaO, and 7.6% Al_2O_3. Its composition was therefore different from that of Polonite® used in phosphorus removal plants in Sweden, which comprises 40.2% SiO_2 and 42.6% CaO (Bioptech; Bus and Karczmarczyk, 2014). The tested rock contained about 11.5% more SiO_2 and 19.4% less CaO than Polonite®.

The specific density of the material applied in investigation was 2.54 g/cm^3. The bulk density of individual fractions of the rock used in the experiment ranged from 0.85-0.91 g/cm^3 and the porosity - 54,2-56,5%. The chemical composition of the material is presented in Table 2.

Tab. 2. The chemical composition of the examined substrate fired at 900 °C

Components	Content [in % of weight]
SiO_2	51.729
CaO	23.159
Al_2O_3	7.586
Fe	2.246
Na_2O	0.836
TiO_2	0.973
MgO	1.388
K_2O	0.917
S	0.634
P	0.358
Cl	0.285
MnO	0.118

Biologically treated domestic wastewater, transported from a hybrid treatment wetland through vertical and horizontal flow beds (VF-HF), was used to investigate the phosphorus removal efficiency of filters filled with the test rock as a substrate. The experiments were carried out for nine weeks (63 days) at different hydraulic loads in the range of 0.72 to 1.44 l/day. The wastewater was discharged 24 hours per day throughout the study period by peristaltic pumps, as shown in Fig. 1. In the first three weeks of the study (1–3), the hydraulic load of each filter was Q_1=0.72 l/day and the hydraulic residence time HRT_1=24 hours; in the next three weeks (4–6), Q_2=1.08 l/day and HRT_2=16 hours; during the last 3 weeks (7–9), Q_3=1.44 l/day and HRT_3=12 hours. The content of total phosphorus and the pH of the wastewater supplied to the rock filter and treated wastewater flowing out of the filter were analyzed during the study.

Throughout the study period, 18 series of analyses were performed, during which 18 samples of wastewater flowing into the rock filter and 54 samples of treated wastewater were examined. The content of total phosphorus in the wastewater samples collected was determined using a WTW MPM 2010 photometer, and pH was measured with Multi meter 340 from WTW.

The results of the analyses allowed us to determine the efficiency of removal of phosphorus from wastewater in the three rock filters with different granulometric composition at different hydraulic loads. The results were statistically analyzed using STATISTICA 10. Two-way analysis of variance (ANOVA) was used to study the effects of granulated carbonate–silica rock and hydraulic load on the rate of removal of phosphorus from domestic sewage. Homogeneous groups were determined using Fisher's procedure. In addition, regression analysis was used to describe the relationships between the examined variables. For all the statistical analyses, the level of significance was set at $\alpha=0.05$.

3. Results and discussion

Phosphorus removal efficiency

Table 3 and Figure 3 show phosphorus removal efficiency of the test rock filters used for the treatment of domestic wastewater at varying hydraulic loads.

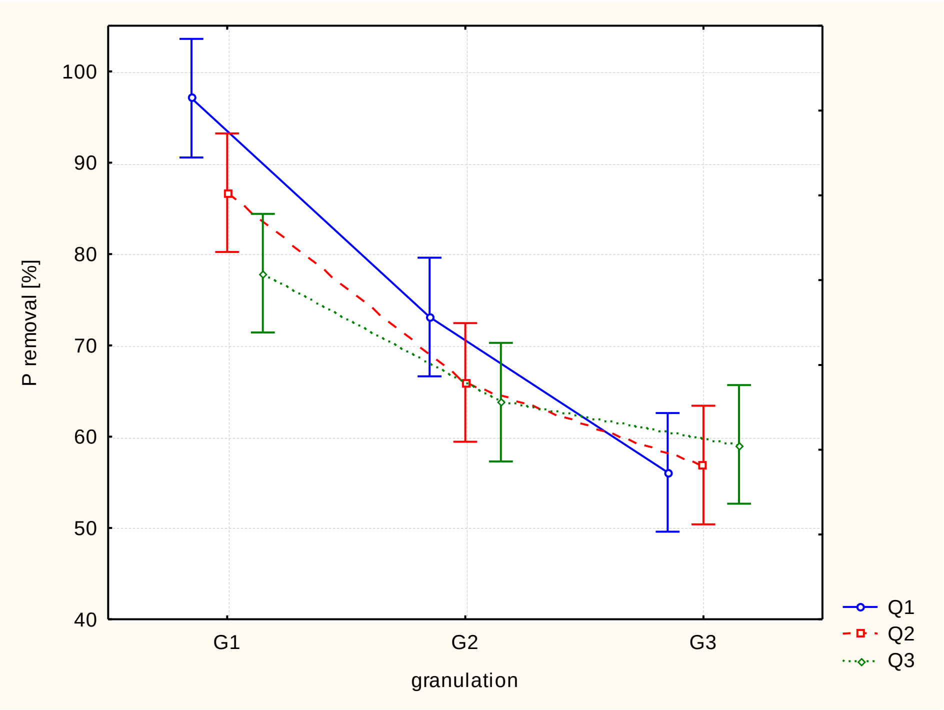

Fig. 3. Changes in average total phosphorus removal efficiency of filters as a function of substrate grain size (G_1, G_2, G_3) at three different hydraulic loads (Q_1, Q_2, Q_3)

The experiments showed that total phosphorus removal efficiency of the tested filters was significantly affected by both the diameter of rock particles and the hydraulic load. Also, a significant interaction effect between these two factors was observed. The division into homogeneous groups with respect to phosphorus removal efficiency established on the basis of the Fisher Test is shown in Table 3. The study showed that increasing of the diameter of substrate particles resulted in a significant decrease in total phosphorus removal efficiency ($\alpha=0.05$). The highest efficiency of removal was noted for the substrate with a grain size of 1–2 mm (G_1). The average removal efficiency of G_1 ranged from 77.9% at a hydraulic load of 1.44 l/day (HRT=12h) to 97.1% at a load of 0.72 l/day (HRT= 24h) (Table 3, Fig. 3).

Tab. 3. Phosphorus removal efficiency, concentrations of phosphorus, and pH of the influent and effluent of the rock filters with different particle diameters

Hydraulic Load/ Hydraulic residence time	Inflowing wastewater		Outflowing wastewater						Phosphorus removal efficiency [%]		
			pH			Total phosphorus (mg/l)					
	Total phosphorus (mg/l)	pH	G_1	G_2	G_3	G_1	G_2	G_3	G_1	G_2	G_3
Q_1 / HRT_1	6.94-8.66* **7.78**	7.21–7.66	9.02–9.94	8.77–9.15	8.86–9.26	0.12-0.42 **0.23**^{a}	0.78-2.70 **2.12**^{cd}	2.54-3.98 **3.41**^{f}	94.7-98.6* **97.1**^{a}	64.8-88.8 **73.1**^{cd}	48.8-63.4 **56.1**^{f}
Q_2 / HRT_2	7.42-8.64 **8.00**	7.32–7.61	8.48–8.78	8.48–8.81	8.67–9.16	0.83-1.39 **1.07**^{b}	2.08-3.57 **2.70**^{de}	2.59-4.63 **3.43**^{f}	83.9-89.4 **86.7**^{b}	51.9-74.4 **65.9**^{de}	42.1-68.5 **56.9**^{ef}
Q_3 / HRT_3	7.14-10.84 **8.73**	7.16–7.69	8.22–8.46	8.36–8.47	8.37–8.56	0.88-2.31 **1.85**^{c}	2.57-3.27 **3.06**^{ef}	2.97-3.94 **3.46**^{f}	71.1-91.3 **77.9**^{bc}	54.2-74.6 **63.7**^{ef}	44.8-69.9 **60.4**^{ef}

Values labelled with different letters are significantly different ($p<0.05$).

Min – Max*
Average

Similar efficiency of phosphorus elimination has been observed in Sweden, where a test was conducted using a 4 l column filled with Polonite® at a hydraulic residence time of 5.5 h (Nilsson et al., 2013). Also other laboratory tests with Polonite® have shown that it has a very high (96.7%) phosphorus removal efficiency, but the investigations were carried out with synthetic wastewater (Gustafsson et al., 2008). Another investigation conducted using filters with granulated rock with a particle diameter of 2–5 mm has shown that they had a lower phosphorus removal efficiency than the Polonite® used in the Swedish study (Nilsson et al., 2013). The average phosphorus removal efficiency in filters with 2–5-mm rock particles, at hydraulic residence times of 12, 18 and 24 hours, was 64.9, 66.3, and 72.8%, respectively (Table 3).

Our investigation demonstrated that the filter containing substrate with particle sizes in the range of 5–10 mm (G_3) was characterized by the lowest phosphorus removal efficiency. At HRT of wastewater of 12, 18 and 24 hours, the average efficiency of removal was 56.1, 57.2, and 60.4%, respectively. These results suggest that filters filled with large-particle substrate (5–10 mm) do not exhibit a sufficiently high total phosphorus removal efficiency and so should not be used in full-scale wastewater treatment plants.

It was also found that an increase in the hydraulic load of wastewater caused a decrease in total phosphorus removal efficiency, regardless of the particle size of the rock used. The highest statistically significant removal efficiency (an average of 97%) was recorded for bedrock G_1 with the smallest grain diameter (1–2 mm), at the lowest hydraulic load of 0.72 l/day (Tab. 3).

The results obtained in the present study confirmed the findings of Cucarella and Renman (2009), who demonstrated that the efficiency of phosphorus removal by reactive materials depended not only on their chemical composition (presence of Ca, Al and Fe), but also the hydraulic retention time of wastewater in the filter, the initial concentration of phosphorus in wastewater, the particle size of the substrate, as well as the hydraulic load ($\alpha=0.05$).

Concentration of phosphorus in treated wastewater

Table 3 and Figure 4 show the concentrations of total phosphorus in the wastewater flowing into and out of the rock filters at different hydraulic loads. The concentration of total phosphorus in wastewater carried from the soil-plant VF-HF hybrid treatment plant into the tested rock filters ranged from 6.9 to 10.8 mg/l (a mean of 8.2 mg/l) (Table. 3). Similar concentrations of total phosphorus have been quoted for biologically treated wastewater discharged from other facilities of this type (Vymazal, 2005; Gajewska and Obarska-Pempkowiak, 2011).

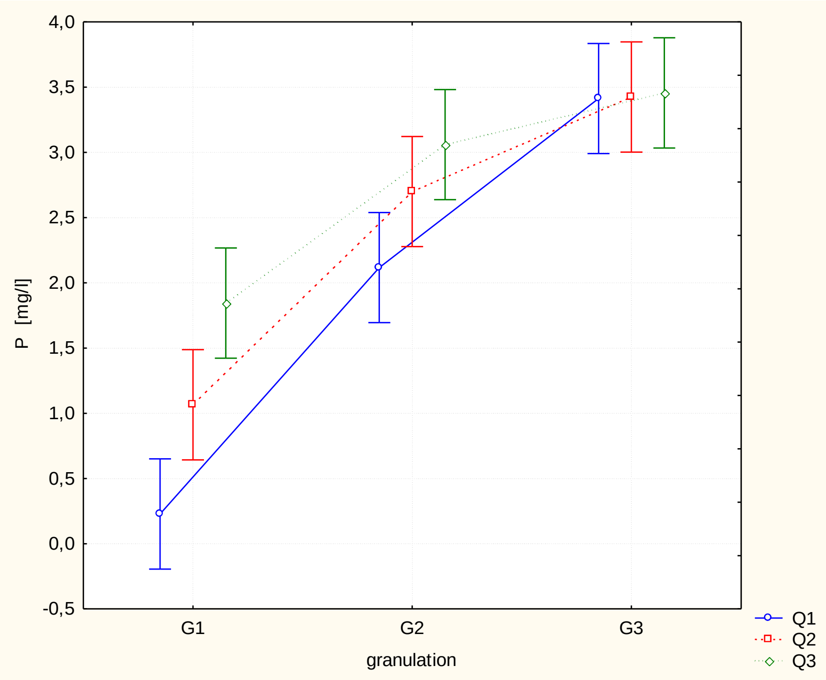

Fig. 4. Changes in the average concentration of total phosphorus in the wastewater flowing out of the tested rock filters at different hydraulic loads

A significant impact of both substrate particle size and hydraulic load on phosphorus concentration in the treated effluent as well as a significant interaction effect between these two factors were observed (α=0.05). The division into homogeneous groups obtained using the Fisher test for concentrations of total phosphorus is shown in Table 3.

The present study showed that increasing of the diameter of rock particles in a filter resulted in a significant increase in the concentration of total phosphorus in the effluent, regardless of the hydraulic load of wastewater. The concentration of total phosphorus was statistically significantly the lowest in the wastewater flowing out from the filter with rock G_1 (1–2 mm) at hydraulic load Q_1 (0.72 l/day) and ranged from 0.12 to 0.42 mg/l, an average of 0.23 mg/l (Table 3, Fig. 4). With the increase in the hydraulic load, the concentration of phosphorus in the treated wastewater also increased. At load Q_2 (1.08 l/day), it ranged from 0.83 to 1.39 mg/l, an average of 1.07 mg/l; and at load Q_3 (1.44 l/day), it ranged from 0.88 to 2.31 mg/l, an average of 1.85 mg/l (Table 3, Fig. 4).

Average concentrations of total phosphorus in the wastewater flowing out from the filter with rock G_1 with a particle diameter in the range of 1–2 mm were lower than 2 mg/l, a level which many countries of the European Union define in accordance with the Council Directive

91/271/EEC (European Commission, 1991) as allowable in wastewater discharged from municipal wastewater treatment plants serving 10,000 to 100,000 PE. The concentrations of total phosphorus recorded for wastewater discharged from filters G_2 and G_3 were much higher (>2 mg/l) (Table 3, Fig. 4).

A significant negative correlation was found between hydraulic residence time and concentration of total phosphorus in the wastewater discharged from filters with rock G_1 (r_{O1}=0.91) and G_2 (r_{O2}=0.59). This means that for these filters, total phosphorus concentration in treated wastewater increased linearly with an increase in hydraulic load.

The main mechanism which forms the basis for the discussion in this paper is adsorption of phosphorus, a subject that is described extensively in the literature (Drizo et al. 2006; Gustafsson et al. 2008; Renman and Renman, 2010). Brogowski and Renman (2004) have shown that carbonate–silica rock with a particle size of 0.25 mm subjected to heat treatment at a high temperature has a maximum sorption capacity of about 120 g/kg. However, this fraction cannot be used in filtration treatment, because the particulate material causes clogging, which impedes hydraulic flow. A study by Yao and colleagues (1971) has demonstrated that the optimum particle size that ensures adequate treatment conditions is 1–2 mm. Polonite® with a particle size of 2–6 mm has very good flow properties (800 m/d), which, however, can be greatly reduced by the large concentration of 1 mm particles formed during the manufacture of this material (Renman and Renman 2010). In the present study, experiments were performed using rock of different grain sizes from 1 to 10 mm; no bed clogging was observed.

pH of the treated wastewaters

Table 3 shows the fluctuations in the pH of the wastewater flowing into and out of the rock filters at the different hydraulic loads. At hydraulic load Q_1 (0.72 l/day), an elevated pH (>8.5) was observed in the effluent from all the investigated rock filters. Particularly high pH values – from 9.02 to 9.94, were found in the effluent from filter G_1 containing rock with the finest grains of 1–2 mm in diameter. In the following weeks of the study (4-9), when the hydraulic load was increased to 1.08 and 1.44 l/day, a decline in pH in the effluent from filter G_1 to values below 9 pH was recorded (Table 3, Fig. 6).

The EU Water Framework Directive does not set limits on the pH of the effluent discharged to the environment. However, monitoring of effluent pH is especially important in biological processes, where microbial survival rates depend on pH. Most organisms can grow in a pH range of 6.5–8.5, which is why this range is recommended for secondary (treated) effluent (USEPA, 1997). Treated wastewater with a pH outside this range, when discharged into the aquatic environment, may reduce the survival, growth and productivity of the organisms living there. Discharge of low-pH sewage can increase the mobility of toxic elements taken up by aquatic organisms. This may have an impact on the health of these organisms and organisms higher in the food chain, and, ultimately, humans, due to bioaccumulation of heavy metals (Fairbrother et al. 2007; Muirhead, 2005; USEPA 1997).

A similar tendency for effluent pH to decrease (from above 12 to below 9) over several weeks of exploitation has been observed by Albright and Waterfield (2010), and Renman and Renman (2010) for a filter filled with Polonite®. The increase in the pH of the treated wastewater relative to that of the inflowing wastewater observed by these authors was associated with the pH of the rock which increased from 6.8 pH (natural rock) to 12.4 (rock heated at a temperature of 900 °C) as an effect of decarbonisation [Brogowski and Renman, 2004; Cucarella et al., 2007; Bus and Karczmarczyk, 2014]. The lower pH of the wastewater discharged from the rock filters (<10 pH) tested in the present study can be explained by the fact that the tested rock contained about 19.4% less CaO than did Polonite®.

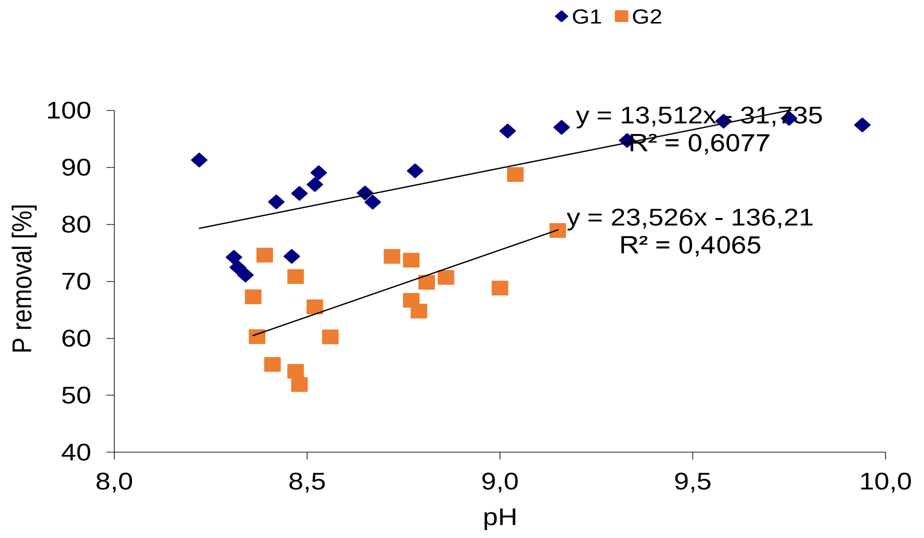

Fig. 5. The dependence of phosphorus removal efficiency on pH, in wastewater flowing out of rock filters of different grain sizes

Based on a statistical analysis, a significant positive correlation was shown between phosphorus removal efficiency and pH of the wastewater discharged from filters with rock G_1 with a grain diameter of 1–2 mm (r_{O1}=0.78) and G_2 with a particle size of 2–5 mm (r_{O2}=0.64). This means that the efficiency of phosphorus removal increased linearly for these filters along with the increase in the pH of the treated wastewater. Figure 5 shows fitted linear regressions with coefficients of determination (R^2) for the individual filters with different rock grain sizes.

Also, a statistically significant negative correlation was found between hydraulic residence time and pH of the wastewater discharged from the rock filters ($r_{O1}= -0.88$, $r_{O2}=-0.87$, $r_{O3}= -0.88$). This means that the pH of the treated wastewater decreased linearly with an increase in hydraulic load.

In our experiments the velocity has been of less importance since investigation were carried out with the different contact times (12, 18 and 24 h respectively). During further investigations influence of velocity needs to be investigated most likely this parameter has also a great importance for efficiency of phosphorous removal and the working condition of the filter with substrate.

Based on carried out investigation it could be concluded that double contact time do not influence much on better efficiency. For smaller diameters of the substrate the differences in efficiency removal could be better countered act by contact time while for bigger one prolonging of contact time do not significantly improve the efficiency. In case of hydraulic load the tendency is similar – higher load caused decreased in efficiency removal but the differences were significant (Table 3, Fig 3). Generally the best efficiency removal was hydraulic load 0.72 l/day. The adoption of the above assumption into full scale facility will be too big simplification. A study by Jucherski and colleagues (2006) has shown that a small diameter of the material used has a positive influence on phosphorus removal from wastewater, but may reduce the hydraulic conductivity of the bed due to faster degradation of the material and deposition of eluted particles in spaces between the grains (mechanical clogging). This makes filtration in the bed more difficult, at the same time shortening the useful life of the filter. For functional reasons, it is advisable to use particles of larger diameters, which should ensure a stable and environmentally acceptable level of phosphorus emissions over the year from a 600 dm^3 filter designed to treat about 800 dm^3/day of domestic sewage (Jucherski et al. 2016).

In many cases the efficiency removal and in consequence concentration of phosphorous achieved with application of G_3 (5-10 mm) fraction of analysed substrate will be sufficient to meet the legal requirements and in the same time could be the least burdensome in operation. Applying of G_3 fraction should ensure trouble-free operation and should prevent clogging (both mechanical and biological).

4. Conclusions

1. The present study indicates that the investigated rock material subjected to decarbonising at 900 °C can be successfully used to remove phosphorus from domestic wastewater, especially in areas where phosphorus removal requirements are very high.
2. The grain size of the rock and the hydraulic load used had a significant influence on total phosphorus removal efficiency of the tested filters, and a significant interaction effect between these factors was observed. Increasing of the diameter of the particles filling a rock filter resulted in a significant decrease in total phosphorus removal regardless of hydraulic load.
3. Statistically the best removal of phosphorus from wastewater (an average of 97%) was achieved in the bed with rock G_1 with the smallest grain diameter (1–2 mm) at the lowest hydraulic load of 0.72 l/day and a hydraulic residence time of 24 h.
4. The lowest phosphorus removal efficiency was observed in the filter containing rock G_3 with a grain diameter of 5–10 mm (mean < 60%); this level of efficiency seems sufficient from both the functional (a lower risk of clogging of the bed) and the environmental perspective (only slightly higher concentration of phosphorus in the effluent), which increases the chance of using this material in domestic sewage treatment filters.
5. Rock grain diameter and hydraulic load had a significant impact on phosphorus concentration in the effluent, and an interaction effect between these factors was observed. Increasing of the diameter of the particles filling the filter and increasing of the hydraulic load, resulted in a significant increase in the concentration of total phosphorus in the effluent.
6. The lowest statistically significant concentrations of total phosphorus (an average of 0.23 mg/l) were found in the wastewater flowing out from the filter with rock G_1 (1–2 mm) at hydraulic load Q_1 of 0.72 l/day.
7. The average concentration of total phosphorus in the wastewater flowing out from filter G_1 with a rock particle diameter in the range of 1–2 mm was considerably lower than 2 mg/l, a limit that the European Union sets on wastewater discharged from municipal wastewater treatment plants.
8. There were significant positive correlations between the efficiency of phosphorus removal and pH of the wastewater discharged from filters containing substrate G_1 with a grain diameter of 1–2 mm (r_{O1}=0.78) and $G_{2,}$ 2–5 mm (r_{O2}=0.64). This means that the efficiency

of phosphorus removal with the tested filters increased early with an increase in the pH of treated wastewater.

9. There were significant negative correlations between hydraulic residence time and the pH of the wastewater discharged from the investigated rock filters ($r_{O1}= -0.88$, $r_{O2}=-0.87$, $r_{O3}=-0.88$). The increase in the hydraulic load and the shorter time of residence caused a linear decrease in the pH values of treated wastewater.

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