

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

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19

20 **ABSTRACT**

21

22 The aim of the study was to determine the influence of the particle size of carbonate–silica rock  
23 (opoka) used in rock filters on the efficiency of phosphorus removal from domestic wastewater. The  
24 investigations were carried out in a laboratory using a model consisting of three vertical flow filters  
25 with carbonate–silica rock of different particle sizes ( $G_1=1-2$  mm;  $G_2=2-5$  mm;  $G_3=5-10$  mm). The  
26 tested rock was subjected to decarbonising at 900 °C and consisted primarily of 51.7% SiO<sub>2</sub>, 23.2%  
27 CaO, and 7.6% Al<sub>2</sub>O<sub>3</sub>. In the first three weeks of the study (1–3), the hydraulic load of each filter was  
28  $Q_1=0.72$  l/day and the hydraulic residence time was  $HRT_1=24$  hours; in the next three weeks (4–6)  
29  $Q_2=1.08$  l/day and  $HRT_2=16$  hours, and during the last three weeks (7–9)  $Q_3=1.44$  l/day and  $HRT_3=12$   
30 hours. A significant influence of the size of rock particles and the hydraulic load (hydraulic residence  
31 time) on the efficiency of total phosphorus removal and on phosphorus concentration in the  
32 wastewater discharged from the system was observed ( $\alpha=0.05$ ). Statistically, the best removal of  
33 phosphorus from wastewater – an average of 97%, was found in the substrate with the smallest  
34 particle size (rock  $G_1$ , 1–2 mm) at the lowest hydraulic load of 0.72 l/day and at a hydraulic residence  
35 time of 24 hours. The lowest phosphorus removal efficiency was observed in the filter containing rock  
36  $G_3$  with a particle size of 5–10 mm (mean <60%). The average concentration of total phosphorus in  
37 wastewater flowing out from filter  $G_1$  was 0.23 mg/l, which was much below the limit values specified  
38 by EU regulations. The overall phosphorus load removed during the study period (nine weeks) in the  
39 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  $G_3$ –  
40 0.28 g/kg of rock. The load of phosphorus removed during this period not characterized the full  
41 sorption capacity of the rock. The study showed that the rock subjected to decarbonising at 900 °C  
42 could be successfully used to remove phosphorus from domestic wastewater, especially in areas where  
43 phosphorus removal requirements are very high ( $P_{tot.} < 2$  mg/l).

44 **Key words:** phosphorus removal, domestic wastewater, carbonate–siliceous rock (opoka),  
45 mitigation of eutrophication

## 46 1. Introduction

47  
48 The problem of removal of biogenic compounds from wastewater is still unresolved, in  
49 particular with regard to small and local treatment plants. Around the world, researchers are  
50 looking for innovative ways of eliminating biogenic elements (nitrogen and phosphorous)  
51 from wastewater with a view to reducing the process of eutrophication of surface waters. The  
52 main element responsible for the fertility of fresh water is phosphorus. It may come from  
53 various sources: 1) natural – organic compounds of animal and plant origin, and 2)  
54 anthropogenic – agriculture (aerial sources) and different types of insufficiently treated  
55 wastewater (point sources). Among point sources, the most important ones are: industrial  
56 wastewater, e.g. discharged from plants producing fertilizers and cleaning agents based on  
57 detergents, municipal wastewater, wastewater from pig farming and domestic wastewater.  
58 Total phosphorus concentrations in raw domestic wastewater are in the range from a dozen to  
59 several dozen mg/l (Metcalf and Eddy, 2003).

60 Discharge of improperly treated wastewater may cause many problems in the recipient  
61 body. The most important of those problems include oxygen depletion due to mineralization  
62 of organic matter and oxidation of ammonium nitrogen (nitrification) (Józwiakowski et al.,  
63 2017). When the concentration of the two biogenic compounds in the discharged wastewater  
64 is too high, oxygen depletion accelerates due to the intensive growth and death  
65 (decomposition) of algae. An increase in phosphorus concentration in surface waters up to  
66 over 15 µg/l may lead to an intense growth of algae (Yang et. 2008). It is estimated that large  
67 amounts of biogenic compounds contained in sewage can increase secondary oxygen  
68 consumption more than five-fold, compared with primary consumption associated with the  
69 disposal of organic matter contained in wastewater. Therefore, it is crucial to reduce the  
70 content of biogenic compounds in the effluent discharged from treatment plants to receivers  
71 (Mikosz and Mucha, 2014).

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



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

92 Studies on the use of carbonate–silica rock (opoka) to remove phosphorus from wastewater  
93 have been carried out for many years now (Brogowski and Gworek, 1996; Brogowski and  
94 Renman, 2004; Cucarella et al., 2007; Józwiakowski, 2006, 2012; Renman and Renman,  
95 2010; Karczmarczyk and Bus, 2014; Bus and Karczmarczyk, 2014). This rock material is  
96 highly reactive to phosphorus because it contains large amounts of calcium and silicon. The  
97 content of these components varies in different types of opoka from 14 to 56% CaO and from  
98 5 to 75% SiO<sub>2</sub> (Kozłowski, 1986; Brogowski and Renman, 2004; Bus and Karczmarczyk,  
99 2014). Carbonate–silica rock is characterised by more than 50% porosity (Brogowski and  
100 Gworek, 1996). This material is of organic origin and consists mainly of small organic debris  
101 with some addition of silica. Thus opoka is assumed to be an intermediate form between rocks  
102 containing carbonate and those containing silica (Pinińska, 2008, Brogowski and Renman,  
103 2004). The composition and properties of the rock favour chemical sorption of phosphorus.  
104 The good sorption properties of the material could be enhanced in an alkaline environment  
105 since in such conditions phosphorus forms chemical bonds with calcium to give calcium  
106 phosphates (Reddy and D'Angelo, 1997; McGechan and Lewis, 2002).

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

113



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

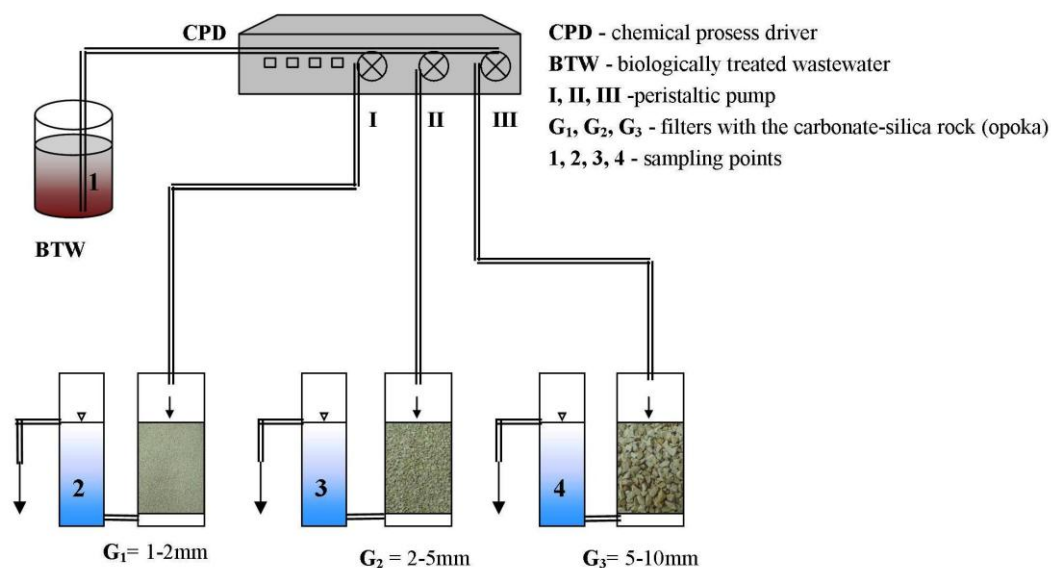
Element	Rock 1	Rock 2	Rock 3
Ca [g/kg]	220.79	364.39	419.75
Sorption capacity [mg P/g]	79.37	136.99	181.82

116  
117 For a few years now, a rock excavated in the village of Belżec in Poland (50°3'04" N,  
118 23°26'18" E), heated at a temperature of about 900 °C, with a particle size of 2.0–6.0 mm,  
119 bearing the trade name Polonite<sup>®</sup>, has been used, primarily in Sweden, as a sorbent for the  
120 removal of phosphorus from wastewater (Bus and Karczmarczyk, 2014).

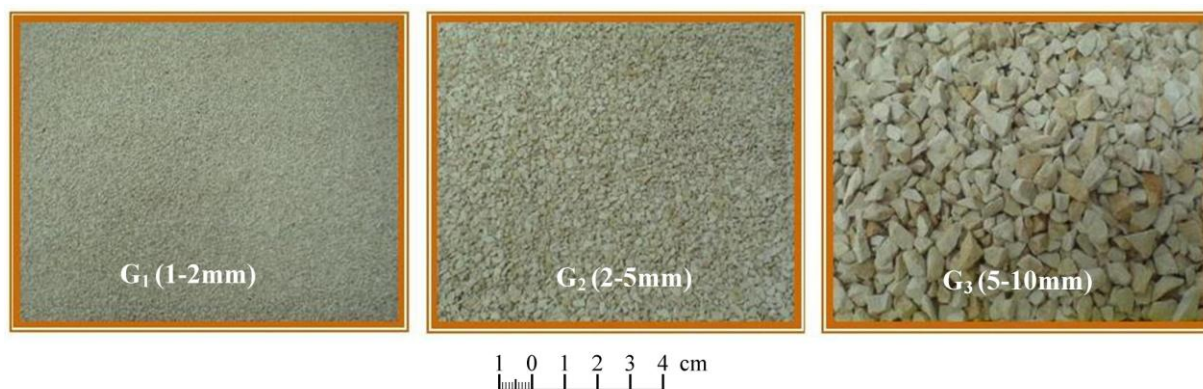
121 The reports cited above have shown that using this rock as a substrate in phosphorus-  
122 removal filters gives very good results. Up till now, however, only one grain size of Polonite<sup>®</sup>  
123 (2.0–6.0 mm) has been shown to have a high (over 90%) phosphorous removal capacity.  
124 Researchers believe that the main mechanism of phosphorous removal is chemical sorption,  
125 and if so the process is strongly dependent on the availability of calcium for binding to P  
126 (Karczmarczyk, 2000, 2003; Karczmarczyk and Mosiej, 2003; Karczmarczyk et al., 2003;  
127 Brogowski and Renman, 2004; Józwiakowski, 2006; Renman, 2008; Cucarella, 2009, Nilson,  
128 2012). Unfortunately, there are few studies regarding the effect of the composition of rocks  
129 and their particle size on phosphorus removal. To investigate this problem, we decided to  
130 conduct experiments with different particle sizes (different surfaces) of carbonate–silica rock  
131 and different hydraulic retention times. Both of these parameters were hypothesized to have  
132 an influence on the efficiency of phosphorus removal from domestic wastewater.

## 133 134 **2. Material and method**

135 The experiments were conducted using a laboratory model consisting of three vertical-flow  
136 wastewater filters filled with opoka as a substrate (Fig. 1). The rock was obtained from a mine  
137 in the town of Chrzanów, located in south-eastern Poland (50°46'26" N, 22°36'19" E) and was  
138 characterized by a different composition in comparison to those described by Karczmarczyk,  
139 2000, 2003; Karczmarczyk and Mosiej, 2003; Karczmarczyk et al., 2003; Brogowski and  
140 Renman, 2004; Józwiakowski, 2006; and Renman, 2008. The substrate rock was dried,  
141 crushed and sorted, to obtain three types of samples differing in particle size: G<sub>1</sub>, 1–2 mm; G<sub>2</sub>,  
142 2–5 mm; and G<sub>3</sub>, 5–10 mm (Fig. 2).



143  
144 Figure. 1. A schematic showing vertical-flow filters with rock substrate ( $G_1$ ,  $G_2$ ,  $G_3$ ) and  
145 storage tanks for treated wastewater (2, 3, 4)



146  
147 Figure. 2. Images of three grain sizes of the rock substrate used in filters

148  
149 Then, the three particle-size fractions of rock were heated in a muffle furnace at 900 °C, as  
150 treatment at this temperature had been reported to ensure the highest sorption capacity and  
151 thus the most effective removal of phosphorous. Prepared in this way, the granular substrate,  
152 sorted by grain size, was packed into three filters with a volume of 1.4 l each (Fig. 1). The  
153 chemical composition of the rock, estimated using a ground mixture of samples is shown in  
154 Table 2. The effect of the size of substrate on its composition was not investigated. Studies  
155 performed using an X-ray spectrometer (fluorescence spectrometry, MINIPAL 4 from  
156 PANALYTICAL) showed that the test rock consisted primarily of 51.7%  $\text{SiO}_2$ , 23.2%  $\text{CaO}$ ,  
157 and 7.6%  $\text{Al}_2\text{O}_3$ . Its composition was therefore different from that of Polonite<sup>®</sup> used in  
158 phosphorus removal plants in Sweden, which comprises 40.2%  $\text{SiO}_2$  and 42.6%  $\text{CaO}$   
159 (Biotech; Bus and Karczmarczyk, 2014). The tested rock contained about 11.5% more  $\text{SiO}_2$   
160 and 19.4% less  $\text{CaO}$  than Polonite<sup>®</sup>.



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

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

Components	Content [in % of weight]
SiO <sub>2</sub>	51.729
CaO	23.159
Al <sub>2</sub> O <sub>3</sub>	7.586
Fe	2.246
Na <sub>2</sub> O	0.836
TiO <sub>2</sub>	0.973
MgO	1.388
K <sub>2</sub> O	0.917
S	0.634
P	0.358
Cl	0.285
MnO	0.118

166  
167 Biologically treated domestic wastewater, transported from a hybrid treatment wetland  
168 through vertical and horizontal flow beds (VF-HF), was used to investigate the phosphorus  
169 removal efficiency of filters filled with the test rock as a substrate. The experiments were  
170 carried out for nine weeks (63 days) at different hydraulic loads in the range of 0.72 to 1.44  
171 l/day. The wastewater was discharged 24 hours per day throughout the study period by  
172 peristaltic pumps, as shown in Fig. 1. In the first three weeks of the study (1–3), the hydraulic  
173 load of each filter was Q<sub>1</sub>=0.72 l/day and the hydraulic residence time HRT<sub>1</sub>=24 hours; in the  
174 next three weeks (4–6), Q<sub>2</sub>=1.08 l/day and HRT<sub>2</sub>=16 hours; during the last 3 weeks (7–9),  
175 Q<sub>3</sub>=1.44 l/day and HRT<sub>3</sub>=12 hours. The content of total phosphorus and the pH of the  
176 wastewater supplied to the rock filter and treated wastewater flowing out of the filter were  
177 analyzed during the study.

178 Throughout the study period, 18 series of analyses were performed, during which 18  
179 samples of wastewater flowing into the rock filter and 54 samples of treated wastewater were  
180 examined. The content of total phosphorus in the wastewater samples collected was  
181 determined using a WTW MPM 2010 photometer, and pH was measured with Multi meter  
182 340 from WTW.

183 The results of the analyses allowed us to determine the efficiency of removal of  
184 phosphorus from wastewater in the three rock filters with different granulometric composition  
185 at different hydraulic loads. The results were statistically analyzed using STATISTICA 10.  
186 Two-way analysis of variance (ANOVA) was used to study the effects of granulated

187 carbonate–silica rock and hydraulic load on the rate of removal of phosphorus from domestic  
188 sewage. Homogeneous groups were determined using Fisher's procedure. In addition,  
189 regression analysis was used to describe the relationships between the examined variables.  
190 For all the statistical analyses, the level of significance was set at  $\alpha=0.05$ .

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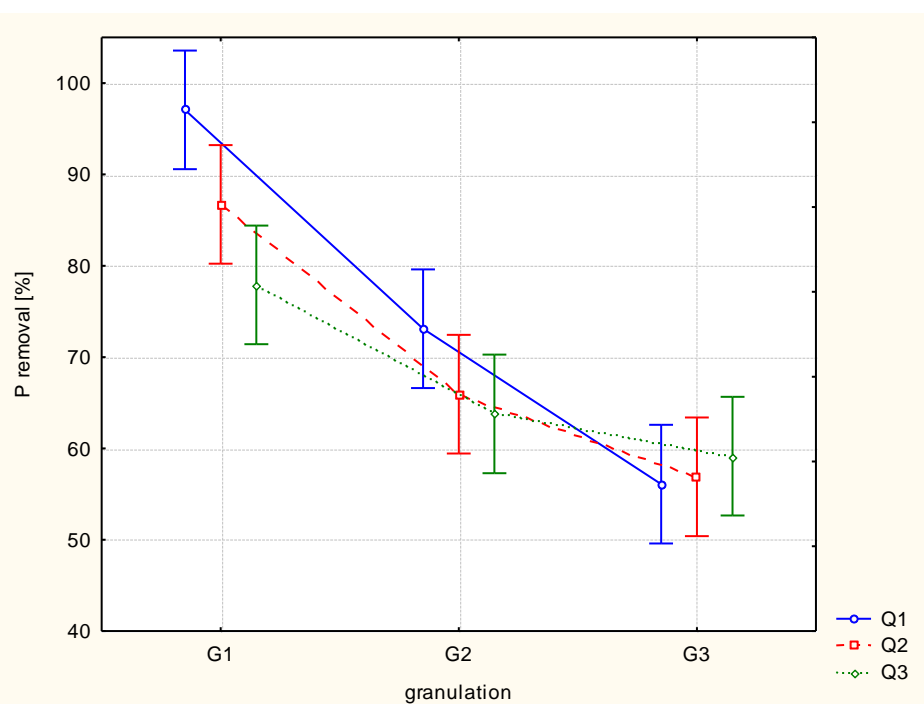
### 192 3. Results and discussion

193

#### 194 Phosphorus removal efficiency

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

197



198

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

201 The experiments showed that total phosphorus removal efficiency of the tested filters was  
202 significantly affected by both the diameter of rock particles and the hydraulic load. Also, a  
203 significant interaction effect between these two factors was observed. The division into  
204 homogeneous groups with respect to phosphorus removal efficiency established on the basis  
205 of the Fisher Test is shown in Table 3. The study showed that increasing of the diameter of  
206 substrate particles resulted in a significant decrease in total phosphorus removal efficiency  
207 ( $\alpha=0.05$ ). The highest efficiency of removal was noted for the substrate with a grain size of  
208 1–2 mm ( $G_1$ ). The average removal efficiency of  $G_1$  ranged from 77.9% at a hydraulic load of  
209 1.44 l/day (HRT=12h) to 97.1% at a load of 0.72 l/day (HRT= 24h) (Table 3, Fig. 3).

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211  
212

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 <sub>1</sub>	G <sub>2</sub>	G <sub>3</sub>	G <sub>1</sub>	G <sub>2</sub>	G <sub>3</sub>	G <sub>1</sub>	G <sub>2</sub>	G <sub>3</sub>
Q <sub>1</sub> / HRT <sub>1</sub>	<u>6.94-8.66*</u> <b>7.78</b>	7.21–7.66	9.02–9.94	8.77–9.15	8.86–9.26	<u>0.12-0.42</u> <b>0.23<sup>a</sup></b>	<u>0.78-2.70</u> <b>2.12<sup>cd</sup></b>	<u>2.54-3.98</u> <b>3.41<sup>f</sup></b>	<u>94.7-98.6*</u> <b>97.1<sup>a</sup></b>	<u>64.8-88.8</u> <b>73.1<sup>cd</sup></b>	<u>48.8-63.4</u> <b>56.1<sup>f</sup></b>
Q <sub>2</sub> / HRT <sub>2</sub>	<u>7.42-8.64</u> <b>8.00</b>	7.32–7.61	8.48–8.78	8.48–8.81	8.67–9.16	<u>0.83-1.39</u> <b>1.07<sup>b</sup></b>	<u>2.08-3.57</u> <b>2.70<sup>de</sup></b>	<u>2.59-4.63</u> <b>3.43<sup>f</sup></b>	<u>83.9-89.4</u> <b>86.7<sup>b</sup></b>	<u>51.9-74.4</u> <b>65.9<sup>de</sup></b>	<u>42.1-68.5</u> <b>56.9<sup>ef</sup></b>
Q <sub>3</sub> / HRT <sub>3</sub>	<u>7.14-10.84</u> <b>8.73</b>	7.16–7.69	8.22–8.46	8.36–8.47	8.37–8.56	<u>0.88-2.31</u> <b>1.85<sup>c</sup></b>	<u>2.57-3.27</u> <b>3.06<sup>ef</sup></b>	<u>2.97-3.94</u> <b>3.46<sup>f</sup></b>	<u>71.1-91.3</u> <b>77.9<sup>bc</sup></b>	<u>54.2-74.6</u> <b>63.7<sup>ef</sup></b>	<u>44.8-69.9</u> <b>60.4<sup>ef</sup></b>

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

Min – Max\*  
Average





218 Similar efficiency of phosphorus elimination has been observed in Sweden, where a test  
219 was conducted using a 4 l column filled with Polonite® at a hydraulic residence time of 5.5 h  
220 (Nilsson et al., 2013). Also other laboratory tests with Polonite® have shown that it has a very  
221 high (96.7%) phosphorus removal efficiency, but the investigations were carried out with  
222 synthetic wastewater (Gustafsson et al., 2008). Another investigation conducted using filters  
223 with granulated rock with a particle diameter of 2–5 mm has shown that they had a lower  
224 phosphorus removal efficiency than the Polonite® used in the Swedish study (Nilsson et al.,  
225 2013). The average phosphorus removal efficiency in filters with 2–5-mm rock particles, at  
226 hydraulic residence times of 12, 18 and 24 hours, was 64.9, 66.3, and 72.8%, respectively  
227 (Table 3).

228 Our investigation demonstrated that the filter containing substrate with particle sizes in the  
229 range of 5–10 mm (G<sub>3</sub>) was characterized by the lowest phosphorus removal efficiency. At  
230 HRT of wastewater of 12, 18 and 24 hours, the average efficiency of removal was 56.1, 57.2,  
231 and 60.4%, respectively. These results suggest that filters filled with large-particle substrate  
232 (5–10 mm) do not exhibit a sufficiently high total phosphorus removal efficiency and so  
233 should not be used in full-scale wastewater treatment plants.

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

239 The results obtained in the present study confirmed the findings of Cucarella and Renman  
240 (2009), who demonstrated that the efficiency of phosphorus removal by reactive materials  
241 depended not only on their chemical composition (presence of Ca, Al and Fe), but also the  
242 hydraulic retention time of wastewater in the filter, the initial concentration of phosphorus in  
243 wastewater, the particle size of the substrate, as well as the hydraulic load ( $\alpha=0.05$ ).

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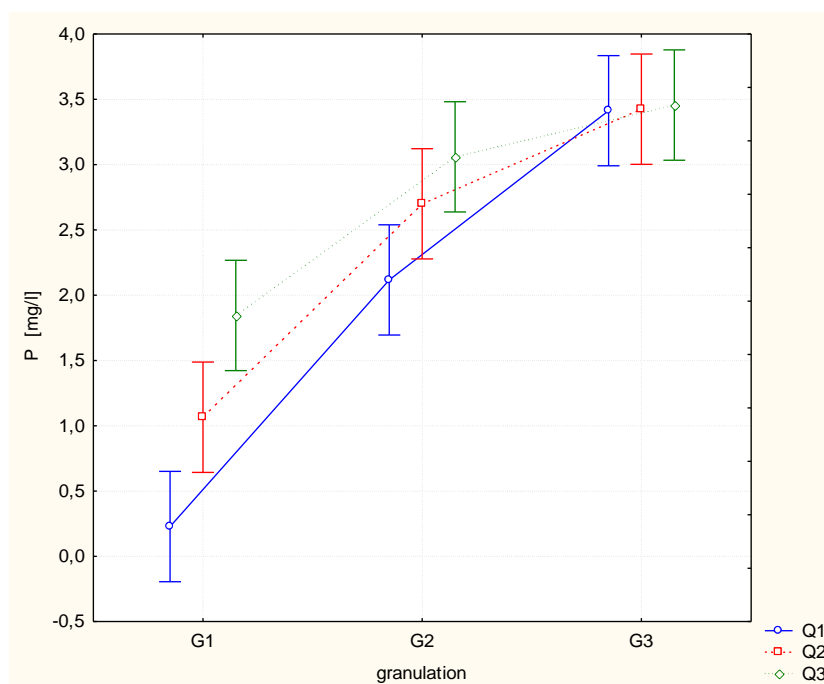
### 245 **Concentration of phosphorus in treated wastewater**

246 Table 3 and Figure 4 show the concentrations of total phosphorus in the wastewater  
247 flowing into and out of the rock filters at different hydraulic loads. The concentration of total  
248 phosphorus in wastewater carried from the soil-plant VF-HF hybrid treatment plant into the  
249 tested rock filters ranged from 6.9 to 10.8 mg/l (a mean of 8.2 mg/l) (Table. 3). Similar  
250 concentrations of total phosphorus have been quoted for biologically treated wastewater



251 discharged from other facilities of this type (Vymazal, 2005; Gajewska and Obarska-  
252 Pempkowiak, 2011).

253



254

255 Fig. 4. Changes in the average concentration of total phosphorus in the wastewater flowing out  
256 of the tested rock filters at different hydraulic loads  
257

258

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

262

263 The present study showed that increasing of the diameter of rock particles in a filter  
264 resulted in a significant increase in the concentration of total phosphorus in the effluent,  
265 regardless of the hydraulic load of wastewater. The concentration of total phosphorus was  
266 statistically significantly the lowest in the wastewater flowing out from the filter with rock G<sub>1</sub>  
(1–2 mm) at hydraulic load Q<sub>1</sub> (0.72 l/day) and ranged from 0.12 to 0.42 mg/l, an average of  
267 0.23 mg/l (Table 3, Fig. 4). With the increase in the hydraulic load, the concentration of  
268 phosphorus in the treated wastewater also increased. At load Q<sub>2</sub> (1.08 l/day), it ranged from  
269 0.83 to 1.39 mg/l, an average of 1.07 mg/l; and at load Q<sub>3</sub> (1.44 l/day), it ranged from 0.88 to  
270 2.31 mg/l, an average of 1.85 mg/l (Table 3, Fig. 4).

271

272 Average concentrations of total phosphorus in the wastewater flowing out from the filter  
273 with rock G<sub>1</sub> 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

274 91/271/EEC (European Commission, 1991) as allowable in wastewater discharged from  
275 municipal wastewater treatment plants serving 10,000 to 100,000 PE. The concentrations of  
276 total phosphorus recorded for wastewater discharged from filters G<sub>2</sub> and G<sub>3</sub> were much higher  
277 (>2 mg/l) (Table 3, Fig. 4).

278 A significant negative correlation was found between hydraulic residence time and  
279 concentration of total phosphorus in the wastewater discharged from filters with rock G<sub>1</sub>  
280 ( $r_{O1}=0.91$ ) and G<sub>2</sub> ( $r_{O2}=0.59$ ). This means that for these filters, total phosphorus concentration  
281 in treated wastewater increased linearly with an increase in hydraulic load.

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

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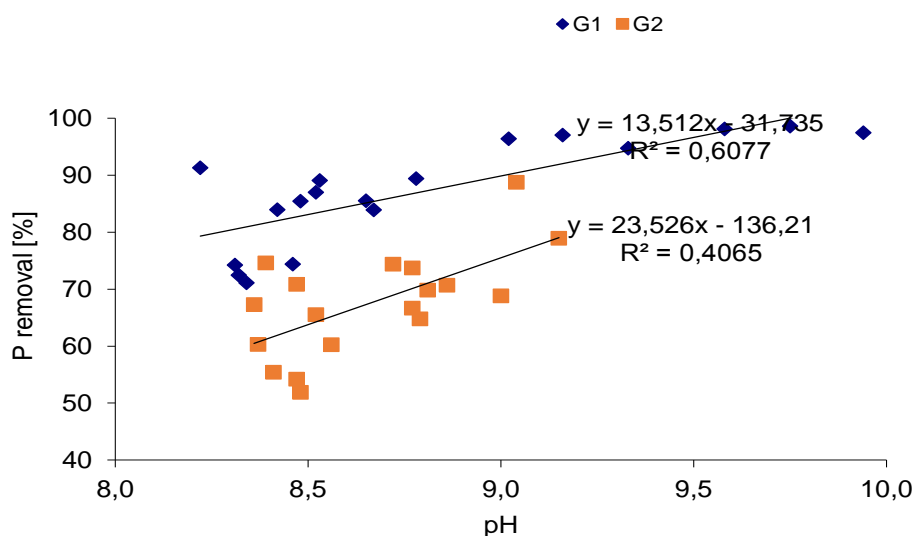
### 296 **pH of the treated wastewaters**

297 Table 3 shows the fluctuations in the pH of the wastewater flowing into and out of the rock  
298 filters at the different hydraulic loads. At hydraulic load Q<sub>1</sub> (0.72 l/day), an elevated pH  
299 (>8.5) was observed in the effluent from all the investigated rock filters. Particularly high pH  
300 values – from 9.02 to 9.94, were found in the effluent from filter G<sub>1</sub> containing rock with the  
301 finest grains of 1–2 mm in diameter. In the following weeks of the study (4-9), when the  
302 hydraulic load was increased to 1.08 and 1.44 l/day, a decline in pH in the effluent from filter  
303 G<sub>1</sub> to values below 9 pH was recorded (Table 3, Fig. 6).

304 The EU Water Framework Directive does not set limits on the pH of the effluent  
305 discharged to the environment. However, monitoring of effluent pH is especially important in  
306 biological processes, where microbial survival rates depend on pH. Most organisms can grow  
307 in a pH range of 6.5–8.5, which is why this range is recommended for secondary (treated)

308 effluent (USEPA, 1997). Treated wastewater with a pH outside this range, when discharged  
 309 into the aquatic environment, may reduce the survival, growth and productivity of the  
 310 organisms living there. Discharge of low-pH sewage can increase the mobility of toxic  
 311 elements taken up by aquatic organisms. This may have an impact on the health of these  
 312 organisms and organisms higher in the food chain, and, ultimately, humans, due to  
 313 bioaccumulation of heavy metals (Fairbrother et al. 2007; Muirhead, 2005; USEPA 1997).

314 A similar tendency for effluent pH to decrease (from above 12 to below 9) over several  
 315 weeks of exploitation has been observed by Albright and Waterfield (2010), and Renman and  
 316 Renman (2010) for a filter filled with Polonite®. The increase in the pH of the treated  
 317 wastewater relative to that of the inflowing wastewater observed by these authors was  
 318 associated with the pH of the rock which increased from 6.8 pH (natural rock) to 12.4 (rock  
 319 heated at a temperature of 900 °C) as an effect of decarbonisation [Brogowski and Renman,  
 320 2004; Cucarella et al., 2007; Bus and Karczmarczyk, 2014]. The lower pH of the wastewater  
 321 discharged from the rock filters (<10 pH) tested in the present study can be explained by the  
 322 fact that the tested rock contained about 19.4% less CaO than did Polonite®.



323 Fig. 5. The dependence of phosphorus removal efficiency on pH, in wastewater flowing out of rock  
 324 filters of different grain sizes  
 325  
 326

327 Based on a statistical analysis, a significant positive correlation was shown between  
 328 phosphorus removal efficiency and pH of the wastewater discharged from filters with rock G<sub>1</sub>  
 329 with a grain diameter of 1–2 mm ( $r_{01}=0.78$ ) and G<sub>2</sub> with a particle size of 2–5 mm ( $r_{02}=0.64$ ).  
 330 This means that the efficiency of phosphorus removal increased linearly for these filters along

331 with the increase in the pH of the treated wastewater. Figure 5 shows fitted linear regressions  
332 with coefficients of determination ( $R^2$ ) for the individual filters with different rock grain sizes.

333 Also, a statistically significant negative correlation was found between hydraulic residence  
334 time and pH of the wastewater discharged from the rock filters ( $r_{O1} = -0.88$ ,  $r_{O2} = -0.87$ ,  $r_{O3} =$   
335  $-0.88$ ). This means that the pH of the treated wastewater decreased linearly with an increase  
336 in hydraulic load.

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

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

358 In many cases the efficiency removal and in consequence concentration of phosphorous  
359 achieved with application of G<sub>3</sub> (5-10 mm) fraction of analysed substrate will be sufficient to  
360 meet the legal requirements and in the same time could be the least burdensome in operation.  
361 Applying of G<sub>3</sub> fraction should ensure trouble-free operation and should prevent clogging  
362 (both mechanical and biological).

363  
364



#### 365 4. Conclusions

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





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

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

403

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408

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