

Phosphorus removal by application of natural and semi-natural materials for possible recovery according to assumptions of circular economy and closed circuit of P

Magda Kasprzyk^{a*}, Magdalena Gajewska^a

^aGdansk University of Technology, Faculty of Civil and Environmental Engineering, Narutowicza st. 11/12, 80-233, Gdansk, POLAND

*magkaspr@pg.edu.pl

Abstract

In the last few years the idea of circular economy has become essential. Thus, designing methods of nutrients removal should be based on using materials that make it possible to recover those nutrients. Recently, methods applied in wastewater treatment plants cannot provide optimal results; moreover, the application of commercial coagulants like ferric chloride and polyaluminum chloride can cause difficulties in potential recovery of phosphorus from sludge. Sorption materials, both natural and modified, are appearing as successful for wastewater treatment, especially for treatment wetland effluent. To pursue circular economy principles, the capacity of waste materials needs to be tested with regard to nutrients removal. If in addition a possibility to recover them appears, it will be possible to close the circuit. The aim of the investigation, according to HELCOM and EU Water Framework Directive recommendations, was to explore the possibility of ensuring good and stable quality of effluent by the application of natural materials for phosphorous removal with possible minimum energy and material consumption. The objective was to determine the sorption capacity of two selected materials (waste material and chemically modified material) in steady conditions. The research focused also on the time of mixing, a period of sedimentation of absorbent materials, and the influence of used materials on the basic parameters of the solution: pH, temperature, total suspended solids, conductivity, turbidity, and color. M1 was a waste material after thermal treatment of carbonate-siliceous rock in temperature above 700°C (Rockfos®). Material M2 was lanthanum-modified bentonite, a material of anthropogenic origin. Both selected materials have shown a high ability to reduce phosphates concentration in synthetic wastewater. Sorption capacity of materials M1 and M2 were 45.6 mg/g and 5.6 mg/g, respectively.

Keywords

calcium oxide; lanthanum-modified bentonite; phosphorus removal; sorption capacity; wastewater treatment

Corresponding author:

Magda Kasprzyk magkaspr@pg.edu.pl

1. INTRODUCTION

Phosphorus together with nitrogen limit plant growth, although nutrients in excess can be a major cause of eutrophication, blue-green algae expansion resulting in oxygen deficiency (Márquez-Pacheco et al., 2013; Zamparas et al., 2015). Thus, methods of wastewater treatment focus on the efficiency improvement of phosphorus and nitrogen compounds reduction.

48

49 Methods applied in wastewater treatment plants very often cannot provide optimal results,
50 while the requirements on limits for discharge are still getting more restricted (HELCOM,
51 2006). Moreover, commonly used chemical and biological methods of phosphorus removal are
52 not economic and cost-effective in small treatment plants or treatment wetlands (Gajewska
53 and Obarska-Pempkowiak, 2011; Józwiakowski et al., 2017; Obarska-Pempkowiak et al., 2015).
54 The application of commercial coagulants like ferric chloride (PIX) and polyaluminum chloride
55 (PAX) can cause difficulties in potential recovery of phosphorus from sludge. Especially P-
56 removal with PIX may disqualify sludge from wastewater treatment plant from P-recovery,
57 because phosphorus compounds that contain iron are almost insoluble in water solution and
58 thus cannot be used as fertilizers (are not bioavailable for plants) (Podewils, 2014).

59

60 In case of PAX, aluminum phosphate formed during P-removal process is also insoluble in
61 water solution and in addition requires pH level adjusting (5,5-6,5). Aluminum presence is
62 essential for plants growth, although in excess can be toxic, also for humans. Potable water
63 highly contaminated with aluminum (320 mg/L) can affect the digestive system, cause skin
64 rash and memory loss. The impact of aluminum on Parkinson and Alzheimer disease is also the
65 subject of many research studies (Zuziak and Jakubowska, 2016).

66

67 Thus, another efficient technology needs to be found. Recently, sorption materials, both
68 natural and modified, are appearing as successful for wastewater treatment, especially for
69 treatment wetland effluent that usually does not meet requirements concerning outflow
70 phosphates concentration, as well as for highly concentrated effluent like that from
71 sequencing batch reactor (SBR) with Anammox, or for reject water from centrifugation of
72 digest sewage (Brogowski and Renman, 2004; Bus et al., 2016; Karczmarczyk and Bus, 2014;
73 Renman and Renman, 2012; Vohla et al., 2011). To pursue circular economy principles, the
74 capacity of waste materials needs to be tested with regard to nutrients removal. If in addition
75 a possibility to recover them appears, it will be possible to close the circuit.

76

77 Obtained results should provide information on possible implementation of analysed sorbents
78 as materials for phosphorus removal in sedimentation clarifier. To provide good effluent
79 conditions, phosphorus concentration cannot exceed 2 mg/L in accordance with the Council
80 Directive 91/271/EEC (European Commission, 1991), while reduction level should achieve at
81 least 70% even for small wastewater treatment plants (up to 300 person equivalent) (HELCOM,
82 2006). In case of treatment wetlands, with an initial concentration of 12-15 mgP/L of
83 wastewater and P-reduction efficiency of 20-30%, final effluent quality does not meet these
84 requirements (Gajewska and Obarska-Pempkowiak, 2011; Gajewska et al., 2011; Kadlec and
85 Wallace, 2009; Vymazal, 2011). Besides, acceptable quality needs to be ensured despite
86 weather conditions or growing seasons.

87

88 Research conducted by Józwiakowski et al. (2016), where an additional P-filter was applied in
89 Hybrid Treatment Wetland system (HTW), can be indicated as implementation example.
90 Natural carbon silica rock treated in high temperature was used as a filling material. The P-
91 removal efficiency of this type of material reached 99% and should provide effluent with P-
92 concentration below the required limit (Bus and Karczmarczyk, 2014; Cucarella et al., 2007;
93 Nastawny et al., 2015).

94

95 Another example of sorption material application is lanthanum modified bentonite that has
96 already been used to treat lakes and other water bodies for eutrophication negative effects

97 (Copetti et al., 2015; Douglas et al., 2016). Surface waters are characterized by low P
98 concentration, although eutrophication phenomena occur with concentration above 0.03
99 mgP/L. Granules of LMB can easily disperse after addition to the eutrophied water body and
100 bind phosphates ions during sedimentation process (Phoslock in Ponds and Small Lakes, 2012).

101

102 The aim of the investigation, according to HELCOM and EU Water Framework Directive (WFD)
103 recommendations, was to explore the possibility of ensuring good and stable quality of
104 effluent by the application of natural materials for phosphorous removal with possible
105 minimum energy and material consumption.

106

107 To buffer the quality of effluent, selected materials for phosphorus binding have been tested.
108 The objective was to determine the sorption capacity of two selected materials (waste
109 material and chemically modified material) in steady conditions. The research focused also on
110 the time of mixing, a period of sedimentation of absorbent materials, and the influence of
111 used materials on the basic parameters of the solution: pH, temperature, total suspended
112 solids (TSS), conductivity, turbidity and color. The maximum sorption capacity and parameters
113 of adsorption were estimated through approximation of the Langmuir and Freundlich
114 isotherms.

115 2. MATERIALS AND METHODS

116 2.1 Materials

117 M1 was a waste material after thermal treatment in temperature above 700°C of carbonate-
118 siliceous rock called opoka. Opoka with high content of calcium carbonate CaCO_3 was
119 subjected to thermal treatment to increase P-sorption capacity. After process of
120 decarbonization, CaCO_3 was transformed into calcium oxide CaO , which is a more reactive
121 form (Bus and Karczmarczyk, 2014; Cucarella et al., 2007). In this way the Rockfos® material
122 (registered under No. 014188338) was obtained. This material has a granulation of 2-5 mm
123 and a porosity of more than 50%. While the very fine-grained fraction of 0-2 mm is a by-
124 product that is usually wasted, it consists of over 80% of CaO (Table 1). Due to the increased
125 concentration of calcium after thermal treatment, pH level of material M1 can be very high
126 and reach more than 12, i.e. the level causing alkaline solution. Thus the process of removing
127 phosphorus was carried out in the alkaline environment. In the chemical sorption reaction
128 phosphate ions are cumulated to form calcium phosphates $\text{Ca}_3(\text{PO}_4)_2$ (Table 1).

129

130 **Table 1. Characteristics of M1 (Product Data Sheet)**

Properties	Value
Average particle size (mm)	0–2
CaO content (%)	~80
pH	11– 12

131

132 M2, lanthanum-modified bentonite (LMB), was the material of anthropogenic origin
133 developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and
134 Industrial Research Organization) (Douglas et al., 1999). LMB is characterized by pH level close
135 to neutral, but an operative pH range of 4-9 (Table 2). The chemical composition of LMB is as
136 follows: SiO_2 : 61.36%, Al_2O_3 : 14.73%, MgO : 2.76%, Fe_2O_3 : 3.6%, CaO : 1.79%, and La_2O_3 :
137 0.058% (Haghseresht et al., 2009; Ross et al., 2008). Lanthanum contained in bentonite clay

138 binds phosphorus in molar ratio 1:1 and forms rhabdophane (LaPO_4), an insoluble rare-earth
139 mineral and the only product of the reaction (Douglas et al., 2000).
140

141 **Table 2. Characteristics of M2**

Properties	Value
Specific surface area (m^2/g)	39.3
Total pore volume (cm^3/g)	0.171
Average particle size (μm)	22
pH	7 – 7.5

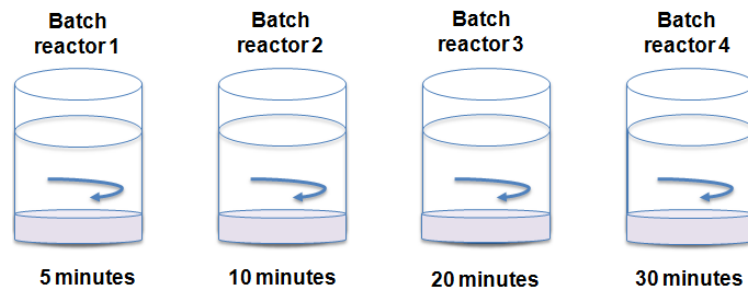
142

143 2.2 Methods

144 Two materials were selected to remove phosphorous compounds: powder/dust by-product
145 (calcium oxide) – M1, and lanthanum-modified bentonite – M2. In order to determine the
146 sorption capacity of those materials the laboratory trials were conducted. Research was
147 carried out in batch reactors in steady conditions (Figure 1). To produce synthetic wastewater,
148 distilled water and a solution of di-potassium hydrogen phosphate KH_2PO_4 was used.
149

150 1.5 L of model solution with a given concentration of $\text{PO}_4\text{-P}$ was added to four batch reactors
151 filled with 100 g of tested material each. The concentration of phosphate phosphorus was the
152 same in each of performed series of repetition and amounted to approx. $15 \text{ mgPO}_4\text{-P/L}$, which
153 is close to the concentration of untreated wastewater or treatment wetland effluent. Upon
154 phosphate load removal the treated solution was decanted and the process was repeated. The
155 tested material in the amount of 100 g was left in each batch reactor. Once again each batch
156 reactor was filled with 1.5 L of synthetic wastewater (concentration of $\text{PO}_4\text{-P}$: $\sim 15 \text{ mg/L}$). The
157 experiment was repeated until the exhaustion of sorption capacity of the material.
158

159 The research focused also on the time of mixing – it was different for each batch reactor and
160 equaled respectively 5, 10, 20, and 30 minutes. Every series lasted for 24 hours. During that
161 time samples were taken after assumed sedimentation period (0.5, 1, 3, and 24 hours). The
162 same conditions were maintained for both tested materials (M1 & M2).



163

164 **Figure 1. Experiment design with batch reactors**

165

166 To estimate parameters of adsorption isotherms another research was conducted with
167 different concentrations of $\text{PO}_4^{3-}\text{-P}$ (5, 10, 20, 50, and 100 mg/L). Contact time was 1 hour. A
168 tested dose of sorption material in each batch reactor was 10 g.
169

170 2.3 Physical and chemical analysis

171 To evaluate the influence of selected materials on synthetic wastewater solution, basic
172 parameters were tested before and after contact with analyzed materials. Study was

173 conducted at room temperature of approx. 20±1°C. All determinations were carried out
174 according to Polish Standards (Table 3).
175

176 **Table 3. Scope of analysis and methodology used**

Parameter	Methodology/Test procedure
PO ₄ ³⁻	Method accredited according to PN-EN ISO 6878:2006+Ap1:2010+Ap2:2010 (spectrophotometric method)
TSS	Method accredited according to PN-EN 872:2007+Ap1:2007 (weighing method)
pH	PN-EN ISO 10523:2012 (potentiometric method)
Conductivity	Method accredited according to PN-EN 27888:1999 (conductometric method)
Color	Method accredited according to PN-EN ISO 7887:2012, C method (spectrophotometric method)
Turbidity	Method accredited according to PB-09 (03 edition) of 09 January 2012 (spectrophotometric method)

177
178 Measurements of phosphates concentration in synthetic wastewater were carried out with the
179 HACH Lange DR 3900 laboratory VIS spectrophotometer with RFID and cuvette tests (LCK 348,
180 LCK 349, LCK 049). Measurements of turbidity and color were also performed with HACH
181 Lange DR 3900 laboratory VIS spectrophotometer with RFID. The temperature, pH and
182 conductivity were measured using WTW Multi 350i compact precision portable meter. The
183 amount of total suspended solids (TSS) of the model solution was defined using formula (1):

$$Z = (m_2 - m_1) / V * 1000 \quad (1)$$

184 where: Z – concentration of TSS [mg/L], m₁ – mass of the filter before filtration [g], m₂ – mass
185 of the filter after filtration [g], V – sample volume [L].
186

187 Sorption capacity of each material with regard to phosphate reduction was calculated
188 according to equation (2) (Nastawny et al., 2015; Liu and Zhang, 2017):

$$q = (C_0 - C) \cdot V / m \quad (2)$$

189 where: q – sorption capacity [mg/g], V – volume of solution [L], C₀ – initial concentration of
190 PO₄-P [mg/L]; C – final concentration of PO₄-P [mg/L], m – mass of sorption material [g].

191 **2.4 Adsorption isotherms**

192 Maximum sorption capacity at equilibrium was verified based on the correlation between
193 mass of adsorbed phosphates q_e [mg/g] and final concentration of phosphates C_e [mg/L].
194 Adsorption isotherms are described by mathematical equations (Bus, Karczmarczyk, 2015;
195 Cucarella, Renman, 2009; Del Bubba et al., 2003; Xu et al., 2013; Limousin et al., 2007):

196 a) Langmuir isotherm

$$q_e = (K_L \cdot C_e) / (1 + a_L \cdot C_e) \quad (3)$$

197 where: q_e – sorption capacity [mg/g]; a_L [L/mg], K_L [L/g] – constants in Langmuir model of
198 adsorption; C_e – concentration of PO₄³⁻-P at equilibrium [mg/L], K_L/a_L = q_{max} – maximum
199 sorption capacity [mg/g].

200 In linear form:

$$1/q_e = 1/K_L \cdot 1/C_e + a_L/K_L \quad (4)$$

201 b) Freundlich isotherm

$$q_e = a_F \cdot C_e^{b_F} \quad (5)$$

202 where: q_e – sorption capacity [mg/g]; C_e – concentration of $\text{PO}_4^{3-}\text{-P}$ at equilibrium [mg/L]; a_F
203 [L/g], b_F [L/mg] – constants in Freundlich model of adsorption.

204 In linear form:

$$\log q_e = \log a_F + b_F \cdot \log C_e \quad (6)$$

205 3. RESULTS AND DISCUSSION

206 3.1 P-sorption capacity

207 Both selected materials have shown high ability to reduce phosphates concentration in
208 synthetic wastewater. Multiple use of the same dose (batch) of analyzed material in each
209 series of repetition made it possible to define sorption capacity upon exhaustion.

210

211 M1 appears to be the material with significant sorption capacity. To identify the value of
212 sorption capacity, 14 series of repetition were conducted, which gives a total load of
213 phosphates over 220 mg and volume of added model solution above 20 L. In consequence
214 sorption capacity after 14 series reached almost 46 mg $\text{PO}_4\text{-P/g}$ and was not exhausted so far
215 (Table 4). Potential amount of removed phosphorus could be much higher. According to
216 Brogowski and Renman (2004), maximum value of sorption capacity for opoka heated in 900°C
217 (material called Polonite) could be almost 120 mg $\text{PO}_4\text{-P/g}$. Obtained results were similar for
218 each mixing time.

219

220 **Table 4. Average sorption capacity and removal efficiency of the analyzed material**

	Mass of material [g]	Total $\text{PO}_4\text{-P}$ load [mg]	Average final concentration [mg/L]	Load of adsorbed $\text{PO}_4\text{-P}$ [mg]	Sorption capacity [mg/g]	Removal efficiency [%]
M1	100	223.0	0.5	222.5	45.6	99.0
M2	100	77.0	2.7	74.3	5.6	96.0

221

222 In case of material M2 sorption capacity was possible to define and equaled 5.6 mg $\text{PO}_4\text{-P/g}$
223 (Table 4). These results were obtained after 5 series of repetition, with 77 mg of phosphates
224 load and 7.5 L of treated solution. Study with lanthanum-modified bentonite performed by
225 Haghseresht et al. (2009) indicates that the theoretical adsorption capacity of the product
226 cannot exceed 10.6 mg P/g. Other studies show a maximum sorption capacity of LMB at the
227 level 14.4±4.7 mg $\text{PO}_4\text{/g}$ (Kurzbaum and Bar Shalom, 2016). In our research stirring had no
228 effect on sorption capacity and P-removal efficiency (Table 5). Thus, for economic reasons
229 mixing time should be reduced.

230

231 **Table 5. Mixing time influence on sorption capacity and P-removal efficiency**

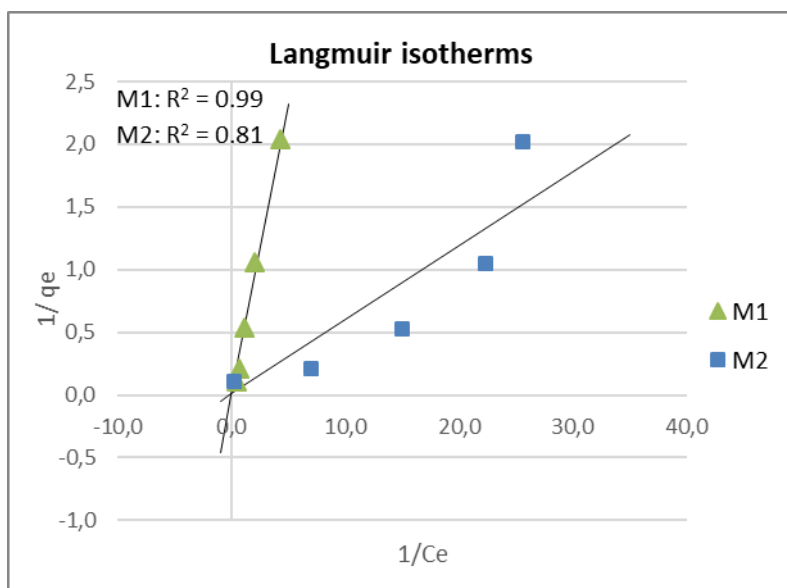
Mixing time	Number of series	Sorption capacity [mg/g]	Removal efficiency [%]
-------------	------------------	--------------------------	------------------------

M1			
5 min	14	45.6	0.99
10 min		45.7	0.99
20 min		45.7	0.99
30 min		45.7	0.99
M2			
5 min	5	5.6	0.97
10 min		5.6	0.97
20 min		5.5	0.96
30 min		5.6	0.96

232

233 3.2 Adsorption isotherms

234 Both analyzed materials indicate that efficiency of phosphates reduction and sorption capacity
 235 increased with the increase of initial concentration of P-PO₄ (5-100 mg/L). For material M1, at
 236 the highest concentration of P-PO₄ sorption capacity reached 9.6 mg/g with reduction
 237 efficiency close to 98% (Kasprzyk et al., 2018a). For material M2, obtained sorption capacity
 238 equaled 9.1 mg/g, with efficiency of 95%, after 1 hour of contact time (Kasprzyk et al., 2018b).
 239

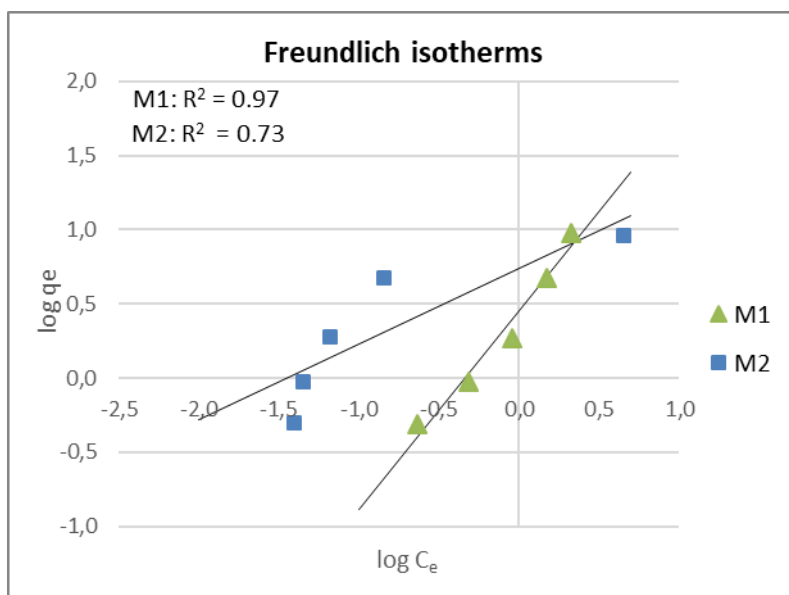


240

241

242

Figure 2. Langmuir isotherms of adsorption for both materials M1 and M2



243

244 **Figure 3.** Freundlich isotherms of adsorption for both materials M1 and M2

245

246 Graphical analysis of Langmuir and Freundlich isotherms of adsorption show good matching
 247 for material M1 ($R^2= 0.99$ and 0.97 , respectively) and relatively good matching for material M2
 248 ($R^2= 0.81$ and 0.73 , respectively), and can describe the sorption process for both sorption
 249 materials (Figures 2 and 3). Maximum sorption capacity obtained from parameters of
 250 Langmuir isotherm was significant and equaled 294.12 mg/g for material M1, and 158.7 mg/g
 251 for material M2 (Table 6) (Kasprzyk et al., 2018a; Kasprzyk et al., 2018b).

252

253 **Table 6.** Parameters of adsorption isotherms

Langmuir isotherm				
	K_L [dm ³ /g]	a_L [dm ³ /mg]	q_{max} [mg/g]	R^2
M1	2.16	0.01	256.4	0.99
M2	14.98	0.09	158.7	0.81
Freundlich isotherm				
	a_F [dm ³ /g]	b_F [dm ³ /mg]	R^2	
M1	2.84	1.34	0.97	
M2	5.48	0.51	0.73	

254 3.3 Impact of the materials on pH

255 The influence of the materials on pH value was quite different. pH of model solution, prepared
 256 from distilled water, was similar in each series (from 6.5 to 7.5).

257

258 M1, with significant content of calcium oxide, caused – as it had been expected – a significant
 259 pH increase of model solution (Figure 4). After the first application pH level reached almost 13,
 260 and it dropped slightly with each subsequent series. In the last performed series pH of the
 261 model solution was still over 9, which still means a negative impact on the effluent. Multiple
 262 use of the same amount of the material did not provide satisfactory results with regard to pH
 263 level. Obtained values were confirmed in other conducted researches in which values of
 264 heated opoka pH were reaching 12.4 – 12.6 (Brogowski and Renman, 2004; Cucarella et al.,
 265 2007). As a pro, high pH values give an opportunity to remove pathogens from wastewater

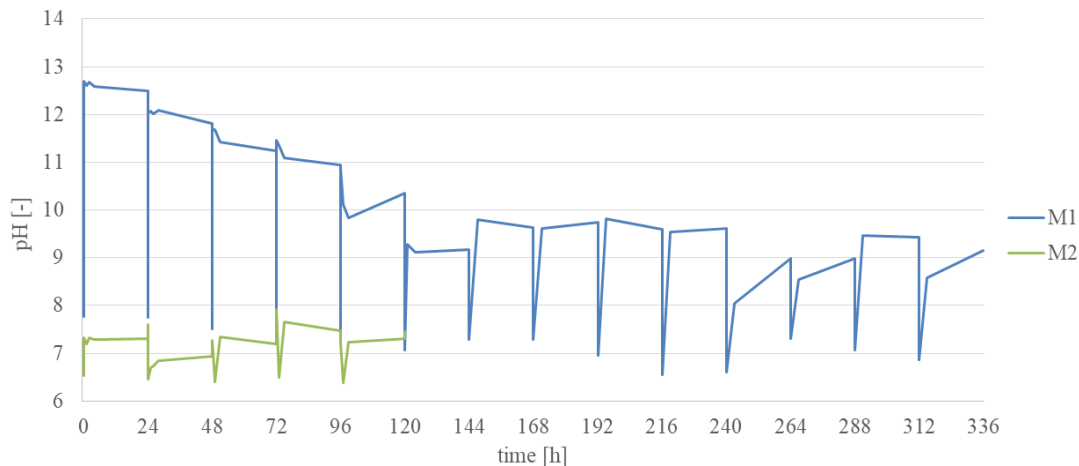
266 due to adverse conditions for bacteria. According to Józwiakowski et al. (2016), the application
267 of P-filter with regular Rockfos® as the last stage of wastewater treatment (after hybrid
268 constructed wetland) ensures the removal of 100% of even Faecal type *coli* group bacteria.

269

270 M2, lanthanum-modified bentonite, did not cause a significant pH fluctuation during the
271 investigation (Figure 4). An inconsiderable increase in pH values was observed. With initial pH
272 values of 6.5, pH of the final effluent reached almost 7.5 and was still close to neutral. Thus,
273 application of material M2 is not needed to provide special treatment for pH level reduction.
274 Investigations described by Haghseresht et al. (2009) also show that lanthanum-modified
275 bentonite application does not change the pH of the solution. However, LMB activity is
276 vulnerable to solution pH, as reduction efficiency of phosphates significantly decreases when
277 pH is not optimal. An operative range of pH for phosphates removal using material M2 was
278 oscillating between 6.0 and 9.0 (Ross et al., 2008).

279

280 No mixing time influence on pH fluctuations was observed in case of either selected material.



281

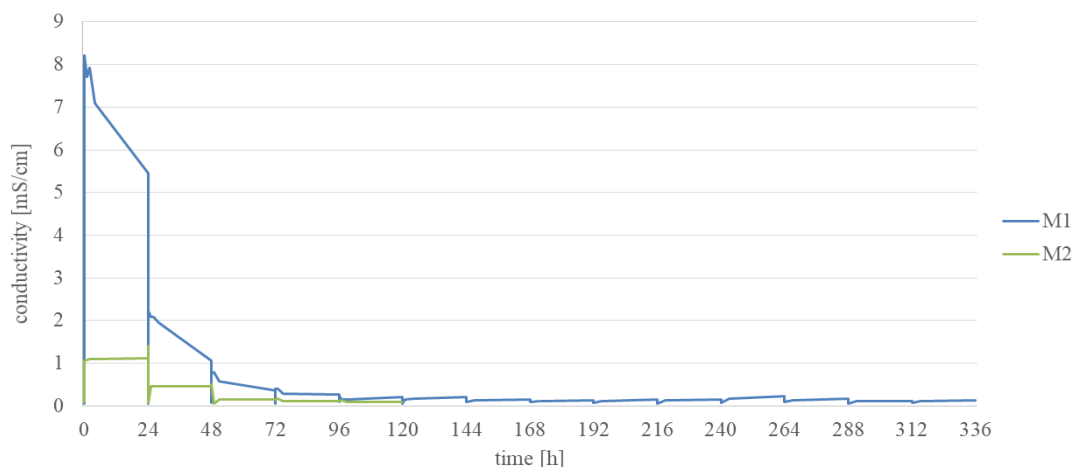
282 **Figure 4. The influence of selected material on pH level during the investigation**

283 3.4 Impact of the materials on conductivity

284 No correlation was noticed between mixing time and the impact of sorption materials on the
285 values of conductivity. The initial conductivity of the model solution was approx. 0.1 mS/cm. In
286 both cases after the first application material M1 caused a large increase in conductivity.
287 Influence of M1 was significantly higher (over 8 mS/cm) than M2 (~1 mS/cm) on conductivity
288 results. In each of subsequent series the increase was not that meaningful and after 4 series
289 did not exceed 0.3 mS/cm (Figure 5).

290

291 Those observations indicate that dissolution of matter from the sorption material caused an
292 increase in solution conductivity. Multiple use of the same dose of materials caused a gradual
293 rinsing of released substances. Thus, values of conductivity decreased along with subsequent
294 series and in the final stage of investigation tested materials hardly affected the effluent at all.

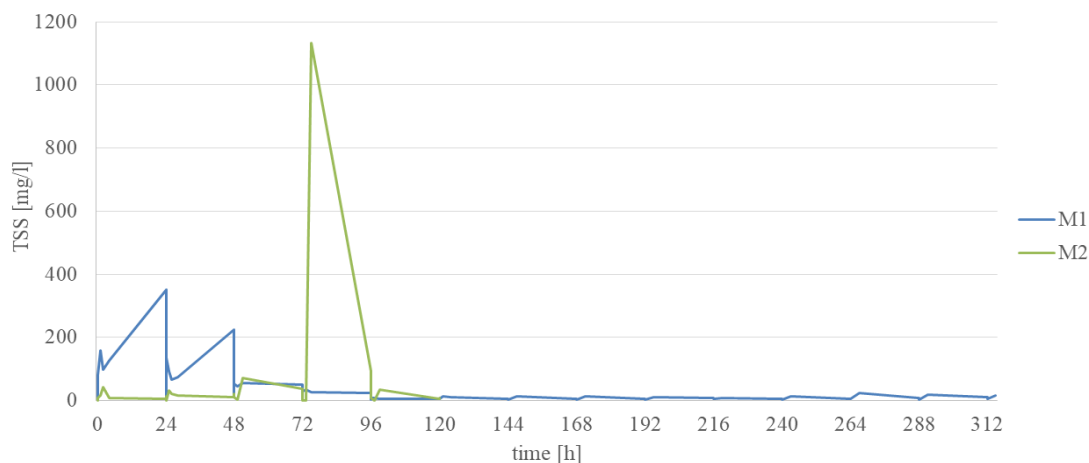


295

296 **Figure 5.** The influence of selected material on conductivity during the investigation

297 **3.5 Impact of the materials on total suspended solids**

298 In early stages of the experiment material M1 caused an increase in total suspended solids
 299 (TSS) concentration. After the first series TSS values reached almost 350 mg/L (Figure 6). It is
 300 also worth noticing that during the first series of repetition a layer of suspended solids was
 301 formed on the surface of each batch reactor. Each following series showed smaller influence of
 302 the material on TSS results and finally after the 5th series the concentration of total suspended
 303 solids was slightly higher than initial value. Similarly to conductivity, those observations could
 304 be explained by rinsing of released substances.

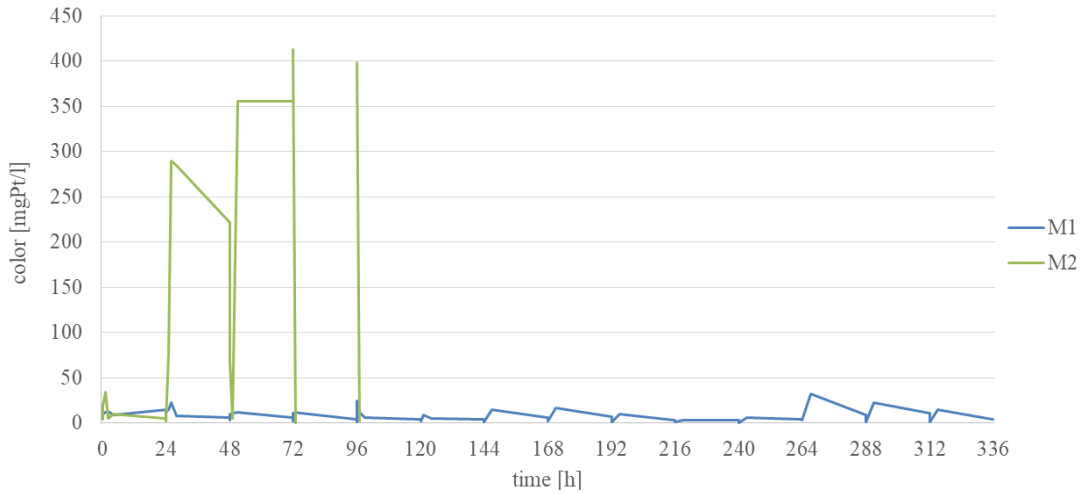


305

306 **Figure 6.** The influence of selected material on total suspended solids during the
 307 investigation

308 Conversely to M1, material M2 did not significantly affect TSS in the first few series, but along
 309 with the study duration a significant dose of suspended solids was released. In the 4th series
 310 the amount of TSS clogged the filter during the filtration of the samples with short
 311 sedimentation time (0.5 h). In this case the period of mixing affected the amount of dissolved
 312 substances – an increase of TSS concentration with longer mixing time was observed (Figure
 313 6).

314 **3.5 Impact of the materials on color and turbidity of the solution**



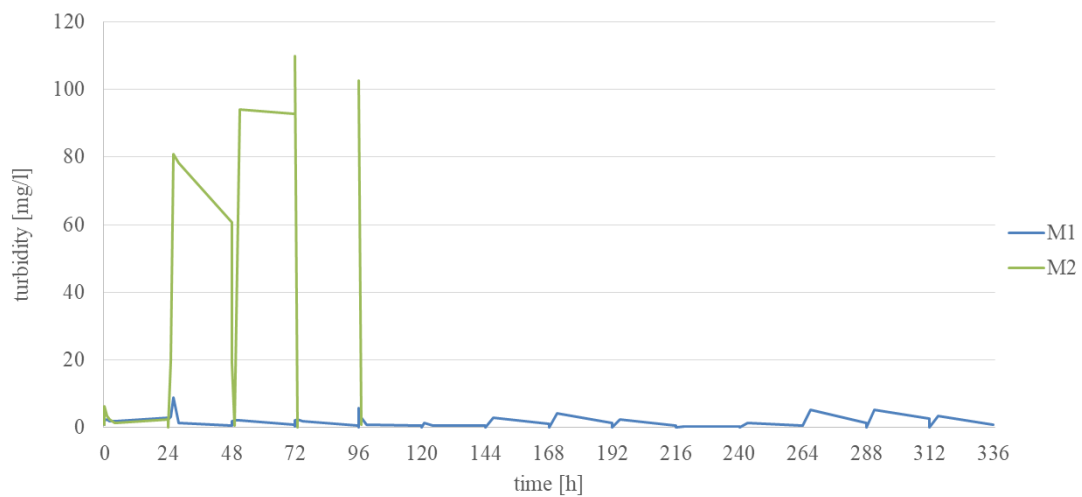
315

316 **Figure 7. The influence of selected material on color of the solution during the investigation**

317 Investigation conducted with material M1 demonstrated a minor influence on color and
318 turbidity of the solution. Slight increase of those results was observed after short period of
319 sedimentation. Samples collected after 3 hours of sedimentation or later were characterized
320 by values close to initial ones (~3 mgPt/L) (Figure 7). Time of mixing was not an issue in case of
321 material M1 influence on the effluent color.

322

323 The same conclusions can be made about the turbidity of the solution. Obtained results did
324 not exceed 9.0 mg/L; and even after sedimentation time longer than 1 hour turbidity values
325 were lower than 1.0 mg/L (Figure 8).



326

327 **Figure 8. The influence of selected material on turbidity of the solution during the**
328 **investigation**

329 The experiment with lanthanum-modified bentonite (M2) has shown that multiple use of the
330 material and longer mixing time adversely affect color and turbidity of the solution. Each
331 subsequent series caused a significant increase in physical parameters. The worst results were
332 obtained with 30 minutes of mixing time, where after the 3rd series of repetition no results
333 could be defined (absorbance > 3.5). After 24 hours of sedimentation those measurements
334 were possible and reached values for color – over 300 mgPt/L, and for turbidity – close to 100

335 mg/L (Figures 7 and 8). At the last (5th) performed series values of color and turbidity were
336 measurable only for 20 minutes mixing time (color: 372 mgPt/L, turbidity: 96 mg/L), in any
337 other case results were out of the calibration range.

338

339 Similar results were described in several papers on lanthanum-modified bentonite. It was
340 found that LMB caused a high increase in turbidity at the early stage after stirring, but values
341 of turbidity were also decreasing due to rapid settlement of material particles (Copetti et al.,
342 2015; Van Oosterhout and Luring, 2013; Van Oosterhout et al., 2014).

343 **4. CONCLUSIONS**

344 The main conclusion from conducted research is that both materials have got a significant
345 ability to remove phosphorus compounds from model solution. Phosphates removal efficiency
346 of material M1 was much higher than that of material M2 – it equaled 45.6 mg/g and 5.6
347 mg/g, respectively.

348

349 No influence of stirring period on phosphates reduction effectiveness of those materials can
350 also be considered to be an advantage. Thanks to that knowledge, time of mixing can be
351 reduced to 5 minutes. It can improve process economy, as facilities of smaller volume/size can
352 be used and retention time in the system can be shortened.

353

354 In case of material M1, high values of pH can be an issue, although performed investigation
355 has shown a decrease in pH from almost 13 to 9. Obtained results of conductivity and TSS can
356 indicate a necessity to primary rinsing of the material, but also a need to verify influence of
357 rinsing on phosphates removal.

358

359 High values of color and turbidity received after multiple use of the same amount of material
360 seem to be the disadvantages of material M2. In that case, time of sedimentation should not
361 be shorter than 24, which can disqualify material M2 as fit for reusing.

362

363 Nevertheless, these sorption materials after using are a potential source of recovery
364 phosphorus and could be used as fertilizer components, e.g. M1 on acidic soils due to alkaline
365 character. These P-recovery abilities will be further investigated with the use of materials from
366 the study described in that paper.

367 **ACKNOWLEDGEMENTS**

368 This research is carried out within the subtask 2.3 of the project entitled “Integrated
369 technology for improved energy balance and reduced greenhouse gas emissions at municipal
370 wastewater treatment plants” with the acronym “BARITECH” co-funded by the Norwegian
371 funds, under the Polish-Norwegian Cooperation Research carried out by the National Centre
372 for Research and Development (197025/37/2013).

373

374 Special thanks to KUFEL Ceramics Company, the sole producer of Rockfos® in Poland for the
375 free of charge sharing of research material.

376 **REFERENCES**

377 Brogowski, Z., Renman, G., (2004) Characterization of opoka as a basis for its use in
378 wastewater treatment. Polish J. Environ. Stud. 13, 15–20.

- 379 Bus, A., Karczmarczyk, A., (2014). Charakterystyka skały wapienno-krzemionkowej opoki w
 380 aspekcie jej wykorzystania jako materiału reaktywnego do usuwania fosforu z wód i
 381 ścieków [Properties of lime-siliceous rock opoka as reactive material to remove
 382 phosphorous from water and wastewater]. *Infrastruktura i Ekologia Terenów*
 383 *Wiejskich*. Nr II/1/2014, 227–238, (in Polish).
- 384 Bus, A. Z., Karczmarczyk, A. A. (2015). Kinetic and sorption equilibrium studies on phosphorus
 385 removal from natural swimming ponds by selected reactive materials, *Fresenius*
 386 *Environmental Bulletin* 24(9), 2736–2741.
- 387 Bus A., Karczmarczyk A., Baryła A., (2016). The use of reactive material for limiting P-leaching
 388 from Ggreen roof substrate. *Water Science & Technology* 73.12, 3027-3032.
- 389 Copetti, D., Finsterle, K., Marziali, L., Stefani, F., Tartari, G., Douglas, G., Reitzel K., Spears, B.M.,
 390 Winfield, I.J., Crosa, G., D'Haese, P., Yesseri, S., Lüring, M. (2015). Eutrophication
 391 management in surface waters using lanthanum modified bentonite: A review, 1–13.
 392 <https://doi.org/10.1016/j.watres.2015.11.056>
- 393 Cucarella, V., Renman, G. (2009) Phosphorus Sorption Capacity of Filter Materials Used for On-
 394 Site Wastewater Treatment Determined in Batch Experiments - A Comparative Study.
 395 *J. Environ. Qual.* 38, 381–392.
- 396 Cucarella, V., Zaleski, T., & Mazurek, R. (2007). Phosphorus sorption capacity of different types
 397 of opoka, *Annals of Warsaw University of Life Sciences - SGGW, Land Reclamation*, No
 398 38, 11–18.
- 399 Del Bubba, M., Arias, C. A., Brix, H. (2003). Phosphorus adsorption maximum of sands for use
 400 as media in subsurface flow constructed reed beds as measured by the Langmuir
 401 isotherm. *Water Research*, 37(14), 3390–3400. [https://doi.org/10.1016/S0043-](https://doi.org/10.1016/S0043-1354(03)00231-8)
 402 [1354\(03\)00231-8](https://doi.org/10.1016/S0043-1354(03)00231-8)
- 403 Douglas, G.B., Adeney, J.A., Robb, M., (1999). A novel technique for reducing bioavailable
 404 phosphorus in water and sediments. *Int. Assoc. Water Qual. Conf. Diffuse Pollut.* 517-
 405 523.
- 406 Douglas G.B., Adeney, J.A, Zappia LR (2000) Sediment Remediation Project: 1998/9 Laboratory
 407 Trial Report. CSIRO Land and Water. Report No. 6/00 2000 CSIRO.
- 408 Douglas, G. B., Lurling, M., & Spears, B. M. (2016). Assessment of changes in potential nutrient
 409 limitation in an impounded river after application of lanthanum-modified bentonite.
 410 *Water Research*, 1–8. <https://doi.org/10.1016/j.watres.2016.02.005>
- 411 European Commission, 1991. Council directive 91/271/EEC of 21 May 1991 concerning urban
 412 wastewater treatment. *Off. J. Eur. Union* L135, 40–52.
- 413 Gajewska M., Kopeć Ł, Obarska-Pempkowiak H. (2011). Operation of small wastewater
 414 treatment facilities in a scattered settlement, *Annual Set of Environment Protection*,
 415 vol. 13 (vol. 1) 207–225.
- 416 Gajewska M., Obarska-Pempkowiak, H. (2011). Efficiency of pollutant removal by five
 417 multistage constructed wetlands in a temperate climate, *Environment Protection*
 418 *Engineering*, 37(3), 27–36.
- 419 Haghseresht, F., Wang, S., Do D.D., (2009). A novel lanthanum-modified bentonite, Phoslock®,
 420 for phosphate removal from wastewaters, *Applied Clay Science* 2009, 46, 369–375.

- 421 HELCOM Thematic Assessment in 2006 Eutrophication in the Baltic Sea, HELCOM Stakeholder
422 Conference on the Baltic Sea Action Plan Helsinki, Finland, 7 March 2006.
- 423 Józwiakowski, K., Gajewska, M., Pytka, A., Marzec, M., Gizińska-Górna, M., Jucherski, A., Wal-
424 czowski, A., Nastawny M., Kamińska, A., Baran, S., (2017). Influence of the particle size
425 of carbonate-siliceous rock on the efficiency of phosphorous removal from domestic
426 wastewater, *Ecological Engineering* 98, 290–296.
- 427 Józwiakowski K., Gajewska M., Marzec M., Gizińska-Górna M., Pytka A., Kowalczyk-Juśko A.,
428 Sosnowska B., Baran S., Malik A., Kufel R. (2016). Hybrid Constructed Wetlands for the
429 National Parks in Poland – The Case Study, Requirements, Dimensioning and
430 Preliminary Results// *Natural and Constructed Wetlands Nutrients: heavy metals and
431 energy cycling, and flow* / ed. Jan Vymazal: Springer Nature, 2016, 247–267
- 432 Kadlec, R.H., & Wallace, S. (2009). *Treatment wetlands* (2nd edn, pp. 1016). Boca Raton:
433 London/ New York: CRC Press/Taylor & Francis Group, ISBN 978-1-56670-526-4.
- 434 Karczmarczyk, A., Bus, A., (2014). Testing of reactive materials for phosphorus removal from
435 water and wastewater – comparative study. *Annals of Warsaw University of Life
436 Sciences - SGGW Land Reclamation*. 02/2014, 46 (1), 57–67.
- 437 Kasprzyk, M., Węgler, J., Gajewska, M. (2018a). Analysis of efficiency of phosphates sorption
438 by different granulation of selected reactive material. In *E3S Web of Conferences* (Vol.
439 26). <https://doi.org/10.1051/e3sconf/20182600002>
- 440 Kasprzyk, M., Obarska-Pempkowiak, H., Masi, F., Gajewska, M. (2018b). Possibilities of
441 Phoslock® application to remove phosphorus compounds from wastewater treated in
442 hybrid wetlands. *Ecological Engineering*, 122, 84–90.
443 <https://doi.org/10.1016/j.ecoleng.2018.07.020>
- 444 Kurzbaum E., Bar Shalom O., (2016). The potential of phosphate removal from dairy
445 wastewater and municipal wastewater effluents using a lanthanum-modified
446 bentonite. *Applied Clay Science*, 123, 182–186.
- 447 Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthea, V., Krimissa, M. (2007). Sorption
448 isotherms: A review on physical bases, modeling and measurement, *Applied
449 Geochemistry* 22, 249–275. <https://doi.org/10.1016/j.apgeochem.2006.09.010>
- 450 Liu, X., Zhang, L. (2015). Removal of phosphate anions using the modified chitosan beads:
451 Adsorption kinetic, isotherm and mechanism studies. *Powder Technology*, 277, 112–
452 119. <https://doi.org/10.1016/j.powtec.2015.02.055>
- 453 Márquez-Pacheco, H., Hansen, A. M., & Falcón-Rojas, A. (2013). Phosphorous control in a
454 eutrophied reservoir. *Environmental Science and Pollution Research*, 20(12), 8446–
455 8456. <https://doi.org/10.1007/s11356-013-1701-2>
- 456 Nastawny, M., Jucherski, A. Walczowski, A., Józwiakowski, K., Pytka, A., Gizińska-Górna, M.,
457 Marzec, M., Gajewska, M., Marczuk, A., Zarajczyk, J. (2015) Preliminary evaluation of
458 selected mineral adsorbents used to remove phosphorus from domestic wastewater.
459 *Przemysł Chemiczny*, 10 (94), 1000–1004. (in Polish)
460 <https://doi.org/10.15199/62.2015.10.XX>
- 461 Obarska-Pempkowiak H., Gajewska M., KołECKA K., Wojciechowska E., Ostojcki A. (2015).
462 Sustainable Sewage Management in Rural Areas. *Annual Set of Environmental
463 Protection*, vol. 17, 585-603. (in Polish)
- 464 Phoslock in Ponds and Small Lakes. (2012).

- 465 [http://www.phoslock.eu/media/48944/Phoslock%20for%20Ponds%20and%20Small%20Lakes.](http://www.phoslock.eu/media/48944/Phoslock%20for%20Ponds%20and%20Small%20Lakes.pdf)
466 [pdf](http://www.phoslock.eu/media/48944/Phoslock%20for%20Ponds%20and%20Small%20Lakes.pdf)
- 467 Podewils W. (2014) Recykling fosforu w Niemczech – stan aktualny i perspektywy. *Wodociągi –*
468 *Kanalizacja 1* (119), 26–30 (in Polish)
- 469 Product Data Sheet of Rockfos®
- 470 Renman, G., Renman, A., (2012). Sustainable use of crushed autoclaved aerated concrete
471 (CAAC) as a filter medium in wastewater purification, WASCON 2012 Conference
472 proceeding.
- 473 Ross, G., Haghseresht, F., Cloete, T. E. (2008). The effect of pH and anoxia on the performance
474 of Phoslock, a phosphorus binding clay. *Harmful Algae*, 7(4), 545–550.
475 <https://doi.org/10.1016/j.hal.2007.12.007>
- 476 Van Oosterhout, F., Lürling, M., (2013). The effect of phosphorus binding clay (Phoslock®) in
477 mitigating cyanobacterial nuisance: a laboratory study on the effects on water quality
478 variables and plankton, *Hydrobiologia* 2013, 710, 265–277.
- 479 Van Oosterhout, F., Goitom, E., Roessink, I., Lürling, M., (2014). Lanthanum from a Modified
480 Clay Used in Eutrophication Control is Bioavailable to the Marbled Crayfish, *PLoS One*
481 July 2014, Volume 9, Issue 7, e102410.
- 482 Vohla, C., Kõiv, M., Bavor, H.J., Chazarenc, F., Mander, Ú. (2011). Filter materials for
483 phosphorus removal from wastewater in treatment wetlands – A review. *Ecological*
484 *Engineering* 37, 70–89.
- 485 Vymazal J. 2011 Constructed wetlands for wastewater treatment: five decades of experience.
486 *Environ. Sci. Technol.* 45, 61–69.
- 487 Xu, Z., Cai, J., Pan, B. (2013). Mathematically modeling fixed-bed adsorption in aqueous
488 systems, *Journal of Zhejiang University-SCIENCE A, Applied Physics & Engineering*,
489 14(3), 155–176. <https://doi.org/10.1631/jzus.A1300029>
- 490 Zamparas, M., Gavriil, G., Coutelieres, F. A., & Zacharias, I. (2015). A theoretical and
491 experimental study on the P-adsorption capacity of Phoslock™. *Applied Surface*
492 *Science*, 335, 147–152. <https://doi.org/10.1016/j.apsusc.2015.02.042>
- 493 Zamparas M., Gianni A., Stathi P., Deligiannakis Y., Zacharias I. (2012). Removal of phosphate
494 from natural waters using innovative modified bentonites. *Applied Clay Science*, 62–
495 63, 101–106. <https://doi.org/10.1016/j.clay.2012.04.020>
- 496 Zuziak J, Jakubowska M. (2016). Aluminum in the environment and its influence on living
497 organisms. *Analit 2*, 110–120.