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

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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

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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.

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

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

Thus, another efficient technology needs to be found. Recently, sorption materials, both natural and modified, are appearing as successful for wastewater treatment, especially for treatment wetland effluent that usually does not meet requirements concerning outflow phosphates concentration, as well as for highly concentrated effluent like that from sequencing batch reactor (SBR) with Anammox, or for reject water from centrifugation of digest sewage (Brogowski and Renman, 2004; Bus et al., 2016; Karczmarczyk and Bus, 2014; Renman and Renman, 2012; Vohla et al., 2011). 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.

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

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

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

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

The aim of the investigation, according to HELCOM and EU Water Framework Directive (WFD) 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.

To buffer the quality of effluent, selected materials for phosphorus binding have been tested. 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 (TSS), conductivity, turbidity and color. The maximum sorption capacity and parameters of adsorption were estimated through approximation of the Langmuir and Freundlich isotherms.

2. MATERIALS AND METHODS

2.1 Materials

M1 was a waste material after thermal treatment in temperature above 700°C of carbonate-siliceous rock called opoka. Opoka with high content of calcium carbonate $CaCO_3$ was subjected to thermal treatment to increase P-sorption capacity. After process of decarbonization, $CaCO_3$ was transformed into calcium oxide CaO, which is a more reactive form (Bus and Karczmarczyk, 2014; Cucarella et al., 2007). In this way the Rockfos® material (registered under No. 014188338) was obtained. This material has a granulation of 2-5 mm and a porosity of more than 50%. While the very fine-grained fraction of 0-2 mm is a by-product that is usually wasted, it consists of over 80% of CaO (Table 1). Due to the increased concentration of calcium after thermal treatment, pH level of material M1 can be very high and reach more than 12, i.e. the level causing alkaline solution. Thus the process of removing phosphorus was carried out in the alkalescent environment. In the chemical sorption reaction phosphate ions are cumulated to form calcium phosphates $Ca_3(PO_4)_2$ (Table 1).

Table 1. Characteristics of M1 (Product Data Sheet)

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

M2, lanthanum-modified bentonite (LMB), was the material of anthropogenic origin developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and Industrial Research Organization) (Douglas et al., 1999). LMB is characterized by pH level close to neutral, but an operative pH range of 4-9 (Table 2). The chemical composition of LMB is as follows: SiO_2: 61.36%, Al_2O_3: 14.73%, MgO: 2.76%, Fe_2O_3: 3.6%4, CaO: 1.79%, and La_2O_3: 0.058% (Haghseresht et al., 2009; Ross et al., 2008). Lanthanum contained in bentonite clay binds phosphorus in molar ratio 1:1 and forms rhabdophane ($LaPO_4$), an insoluble rare-earth mineral and the only product of the reaction (Douglas et al., 2000).

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

2.2 Methods

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

1.5 L of model solution with a given concentration of PO_4-P was added to four batch reactors filled with 100 g of tested material each. The concentration of phosphate phosphorus was the same in each of performed series of repetition and amounted to approx. 15 mgPO_4-P/L, which is close to the concentration of untreated wastewater or treatment wetland effluent. Upon phosphate load removal the treated solution was decanted and the process was repeated. The tested material in the amount of 100 g was left in each batch reactor. Once again each batch reactor was filled with 1.5 L of synthetic wastewater (concentration of PO_4-P: ~15 mg/L). The experiment was repeated until the exhaustion of sorption capacity of the material.

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

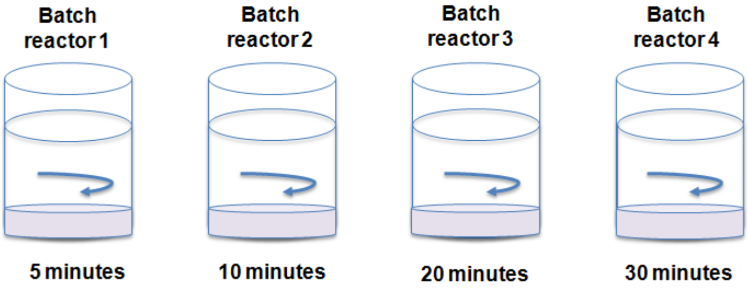

Figure 1. Experiment design with batch reactors

To estimate parameters of adsorption isotherms another research was conducted with different concentrations of PO_4^{3-}-P (5, 10, 20, 50, and 100 mg/L). Contact time was 1 hour. A tested dose of sorption material in each batch reactor was 10 g.

2.3 Physical and chemical analysis

To evaluate the influence of selected materials on synthetic wastewater solution, basic parameters were tested before and after contact with analyzed materials. Study was conducted at room temperature of approx. 20±1°C. All determinations were carried out according to Polish Standards (Table 3).

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)

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

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

where: Z – concentration of TSS [mg/L], m_1 – mass of the filter before filtration [g], m_2 – mass of the filter after filtration [g], V – sample volume [L].

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

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

where: q – sorption capacity [mg/g], V – volume of solution [L], C_0 – initial concentration of PO_4-P [mg/L]; C – final concentration of PO_4-P [mg/L], m – mass of sorption material [g].

2.4 Adsorption isotherms

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

a) Langmuir isotherm

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

where: q_e – sorption capacity [mg/g]; a_L [L/mg]., K_L [L/g] – constants in Langmuir model of adsorption; C_e – concentration of PO_4^{3-}-P at equilibrium [mg/L], $K_L/a_L = q_{max}$ – maximum sorption capacity [mg/g].

In linear form:

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

b) Freundlich isotherm

$$q_e = a_F \cdot C_e^{bF} \qquad (5)$$

where: q_e – sorption capacity [mg/g]; C_e – concentration of PO_4^{3-}-P at equilibrium [mg/L]; a_F [L/g], b_F [L/mg] – constants in Freundlich model of adsorption.

In linear form:

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

3. RESULTS AND DISCUSSION

3.1 P-sorption capacity

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

M1 appears to be the material with significant sorption capacity. To identify the value of sorption capacity, 14 series of repetition were conducted, which gives a total load of phosphates over 220 mg and volume of added model solution above 20 L. In consequence sorption capacity after 14 series reached almost 46 mgPO_4-P/g and was not exhausted so far (Table 4). Potential amount of removed phosphorus could be much higher. According to Brogowski and Renman (2004), maximum value of sorption capacity for opoka heated in 900°C (material called Polonite) could be almost 120 mgPO_4-P/g. Obtained results were similar for each mixing time.

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

	Mass of material [g]	Total PO_4-P load [mg]	Average final concentration [mg/L]	Load of adsorbed PO_4-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

In case of material M2 sorption capacity was possible to define and equaled 5.6 mgPO_4-P/g (Table 4). These results were obtained after 5 series of repetition, with 77 mg of phosphates load and 7.5 L of treated solution. Study with lanthanum-modified bentonite performed by Haghseresht et al. (2009) indicates that the theoretical adsorption capacity of the product cannot exceed 10.6 mg P/g. Other studies show a maximum sorption capacity of LMB at the level 14.4±4.7 mg PO_4/g (Kurzbaum and Bar Shalom, 2016). In our research stirring had no effect on sorption capacity and P-removal efficiency (Table 5). Thus, for economic reasons mixing time should be reduced.

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

3.2 Adsorption isotherms

Both analyzed materials indicate that efficiency of phosphates reduction and sorption capacity increased with the increase of initial concentration of P-PO_4 (5-100 mg/L). For material M1, at the highest concentration of P-PO_4 sorption capacity reached 9.6 mg/g with reduction efficiency close to 98% (Kasprzyk et al., 2018a). For material M2, obtained sorption capacity equaled 9.1 mg/g, with efficiency of 95%, after 1 hour of contact time (Kasprzyk et al., 2018b).

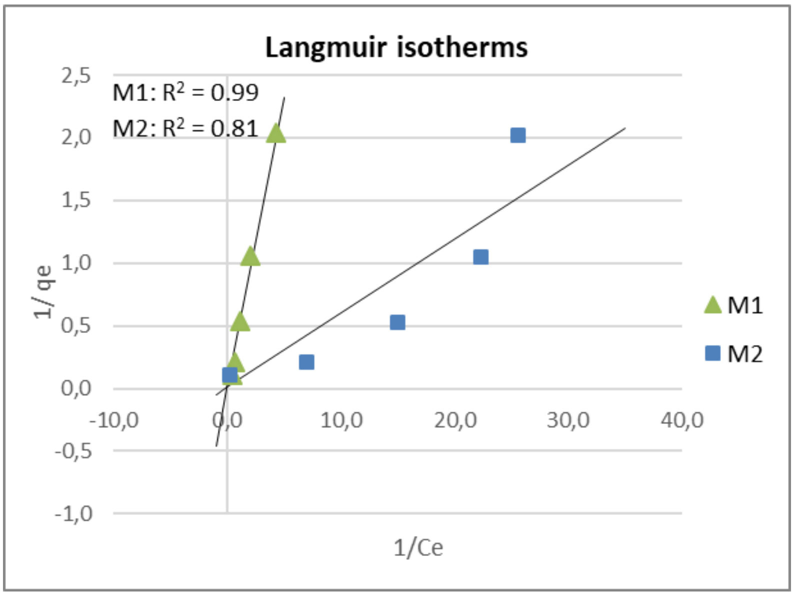

Figure 2. **Langmuir isotherms of adsorption for both materials M1 and M2**

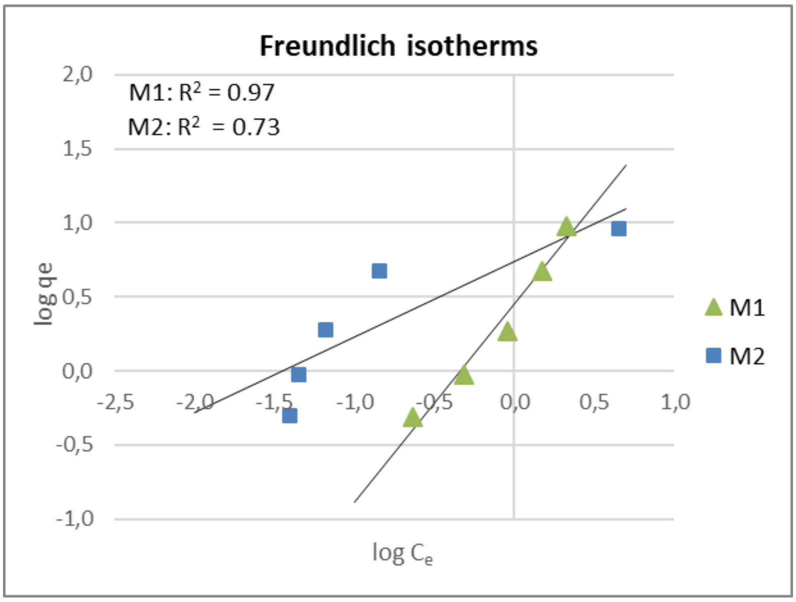

Figure 3. **Freundlich isotherms of adsorption for both materials M1 and M2**

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

Table 6. **Parameters of adsorption isotherms**

	Langmuir isotherm			
	K_L [dm³/g]	a_L [dm³/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 [dm³/g]	b_F [dm³/mg]	R^2	
M1	2.84	1.34	0.97	
M2	5.48	0.51	0.73	

3.3 Impact of the materials on pH

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

M1, with significant content of calcium oxide, caused – as it had been expected – a significant pH increase of model solution (Figure 4). After the first application pH level reached almost 13, and it dropped slightly with each subsequent series. In the last performed series pH of the model solution was still over 9, which still means a negative impact on the effluent. Multiple use of the same amount of the material did not provide satisfactory results with regard to pH level. Obtained values were confirmed in other conducted researches in which values of heated opoka pH were reaching 12.4 – 12.6 (Brogowski and Renman, 2004; Cucarella et al., 2007). As a pro, high pH values give an opportunity to remove pathogens from wastewater due to adverse conditions for bacteria. According to Jóźwiakowski et al. (2016), the application of P-filter with regular Rockfos® as the last stage of wastewater treatment (after hybrid constructed wetland) ensures the removal of 100% of even Faecal type *coli* group bacteria.

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

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

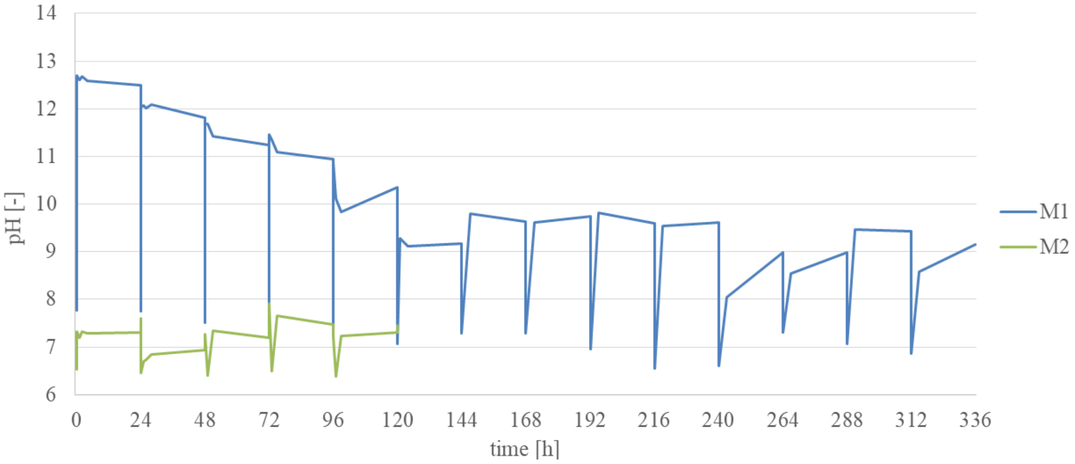

Figure 4. **The influence of selected material on pH level during the investigation**

3.4 Impact of the materials on conductivity

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

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

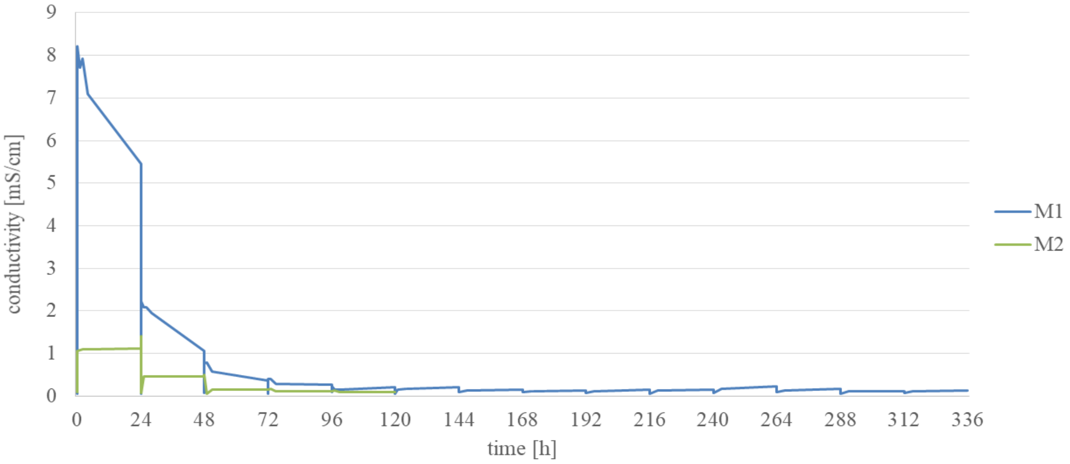

Figure 5. **The influence of selected material on conductivity during the investigation**

3. 5 Impact of the materials on total suspended solids

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

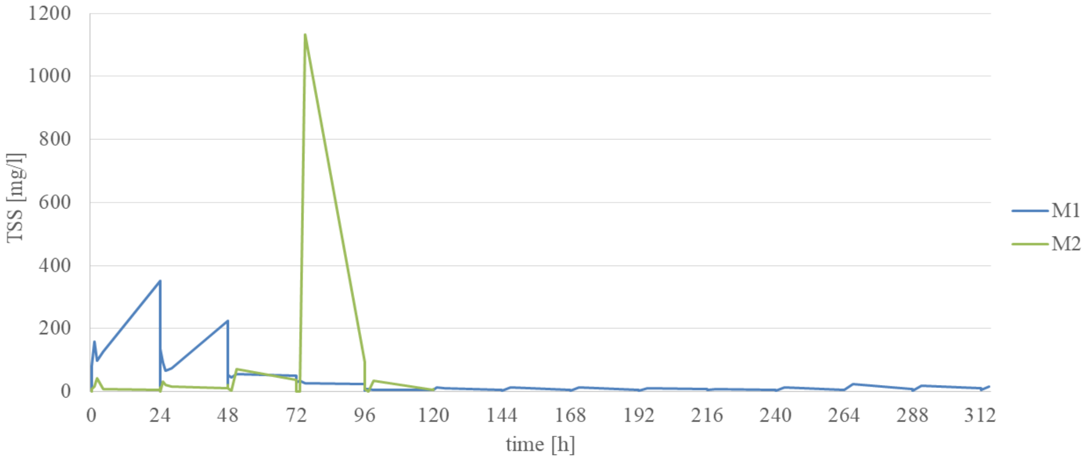

Figure 6. **The influence of selected material on total suspended solids during the investigation**

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

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

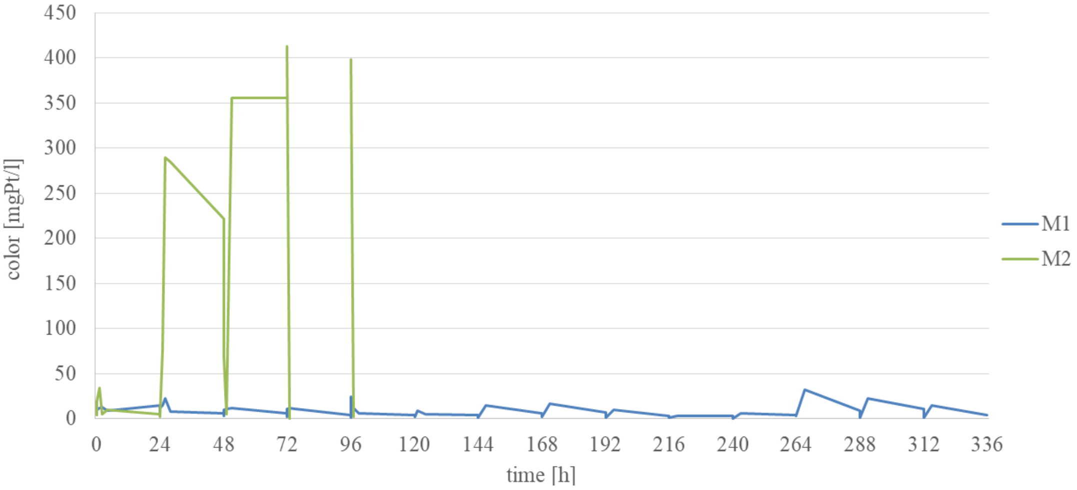

Figure 7. The influence of selected material on color of the solution during the investigation

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

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

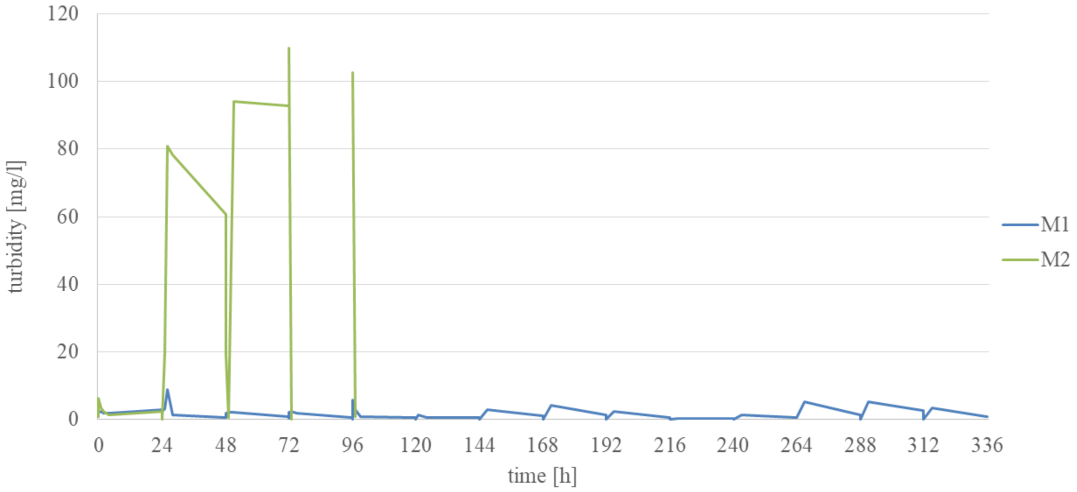

Figure 8. The influence of selected material on turbidity of the solution during the investigation

The experiment with lanthanum-modified bentonite (M2) has shown that multiple use of the material and longer mixing time adversely affect color and turbidity of the solution. Each subsequent series caused a significant increase in physical parameters. The worst results were obtained with 30 minutes of mixing time, where after the 3rd series of repetition no results could be defined (absorbance> 3.5). After 24 hours of sedimentation those measurements were possible and reached values for color – over 300 mgPt/L, and for turbidity – close to 100 mg/L (Figures 7 and 8). At the last (5th) performed series values of color and turbidity were measurable only for 20 minutes mixing time (color: 372 mgPt/L, turbidity: 96 mg/L), in any other case results were out of the calibration range.

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

4. CONCLUSIONS

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

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

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

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

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

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