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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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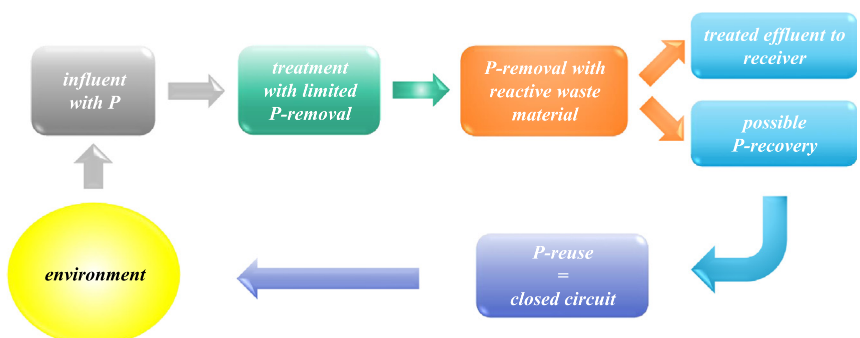
HIGHLIGHTS

- Paper presents a possible method for P-removal to explore recovery potential.
- Two sorption materials of different characteristic were assessed.
- Material M1 shown significant influence on solution pH.
- Material M2 can be disqualified as filling of sedimentation clarifier in multiple uses.

GRAPHICAL ABSTRACT



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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.

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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 analyzed 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 mg P/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 mg P/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 >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 >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).

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: 3.64%, 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

Table 1
Characteristics of M1 (Product Data Sheet).

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

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