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Possibilities of Phoslock® application to remove phosphorus compounds from wastewater treated in hybrid wetlands

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ABSTRACT

Treatment wetland technologies for wastewater treatment can be easily applied for removal of all pollutants except phosphorous. They are applicable in a small towns and rural areas, places where conventional wastewater treatment plant cannot properly operate because of common economic constraints. In Poland only the 8% of rural areas are equipped with sewer system, thus treatment wetlands might be an alternative, effective and low-cost method to treat wastewater from households. The aim of this study was to optimise the operational parameters for Phoslock® application on treated wastewater and to prove that Phoslock® may also be successfully used to remove phosphorus compounds from treated wastewater and possibly recover them. Phoslock® also known as lanthanum-modified bentonite (LMB) is an adsorbent material developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and Industrial Research Organization). Experimental trials were carried out in the laboratory with batch reactors pilot units in three separate stages to establish sorption capacity of material, define characteristic constants of isotherms of adsorption and verify kinetic parameters by using pseudo-second order model. Carried out research confirmed high sorption capacity of LMB – Phoslock® for removal of phosphorous compounds from wastewater both synthetic and effluent from treatment wetland. Performed kinetic studies have shown that LMB is much less effective in case of real effluent from WWTP (2.09 mg/g) than in synthetic wastewater (4.31 mg/g). Langmuir and Freundlich adsorption models have shown relatively good matching of isotherms in graphical. Results obtained for kinetic studies have shown correlation coefficient close to 1.0 both for synthetic and effluent from WWTP. Application of LMB caused not only a rapid decrease of PO_4^{3-}-P concentration, but also no other meaningful influence on the water solution was discovered.

1. Introduction

Baltic Action Plan (HELCOM 28E/5, 2007; HELCOM 28E/6, 2007) enhances to remove phosphorus compounds from the wastewater treatment plants (WWTPs) effluents above 300 person equivalents (p.e.) to the level of 1 mgP/l. In such installations (300 p.e. up to 10.000 p.e.), treatment wetland technologies for wastewater treatment can be easily applied for removal of all pollutants except phosphorous (Kadlec and Wallace, 2009; Vymazal, 2011; Gajewska and Obarska-Pempkowiak, 2011; Gajewska et al., 2011). In these conditions, selection of substrates for wetland systems can be critical (Drizo et al., 1999; Drizo et al., 2002).

Treatment wetlands (TWs) are applicable in small towns and rural areas, places where conventional wastewater treatment plant cannot properly operate because of common economic constraints. In Poland only the 8% of rural areas are equipped with sewer system, thus treatment wetlands might be an alternative, effective and low-cost method to treat wastewater from households. The effluent from treatment wetlands usually does not meet the FWD/2000/EU and national requirements as far as phosphorous concentration (Vymazal, 2011; Obarska-Pempkowiak et al., 2015).

Phoslock® also known as lanthanum-modified bentonite (LMB) is an adsorbent material developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and Industrial Research Organization). Phoslock® significant abilities to remove phosphorus compounds are well known, due to using this material to reverse eutrophication and to reduce algae growth in about 200 water bodies all over the world (Copetti et al., 2015; Douglas et al., 1999; Douglas et al., 2016).

Also, it is worth to mention that Phoslock Water Solution Ltd (PWS)

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is planning to create a constructed wetland to treat wastewater from large Chinese canals. PWS is using Phoslock® into the wetlands to reduce concentration of nutrient compounds in the water. Due to that fact lanthanum modified bentonite is foreseen as material to treat not only eutrophic inland waters, where phosphates concentrations are relatively low (0.1 mg/L), but also for wastewater treatment with much higher concentrations of phosphates (PWS Media Center Blogs, 2018).

Mechanism of LMB operation is lean on binding phosphorus ions on the surface of the material particles. Binding processes are consider as adsorption, although special research is need to be performed to define if absorption processes are not occurs simultaneously. Also phosphates removal by Phoslock® application is characterized with lack of by-products during rhabdophane ($LaPO_4 \cdot nH_2O$) formation. Rhabdophane is a highly stable rare-earth mineral of low solubility (Douglas et al., 2000). Several tests have been conducted to assess eco-toxicity of Phoslock® due to possible toxic character of lanthanum to some aquatic organisms (dependent on used media) (Barry and Meehan, 2000). Although specific of material allow to classified LMB as not hazardous and confirm applicability in water/wastewater environment (Martin and Hickey, 2004).

The physical properties of Phoslock® are making it as a possible filling material to be used in TWs schemes, both as placed directly inside the wetland beds or into a final P-recovery treatment stage.

Thus the aim of this study is to optimise the operational parameters for Phoslock® application on treated wastewater and to prove that Phoslock® may also be successfully used to remove phosphorus compounds from treated wastewater and possibly recover them. First stage of the study was conducted to assess sorption capacity of LMB and also investigate the influence of mixing time on material operation. Second stage of research was aimed at finding parameters of adsorption isotherms both Langmuir and Freundlich. While the last stage of described laboratory trials, performed on model solution (KH_2PO_4) and hybrid treatment wetland effluent, was carried to analyzed the effect of real wastewater and interaction of presence of other contaminations on material ability to phosphates removal.

2. Materials and methods

2.1. Materials

The process of removing phosphorus by Phoslock® is based on binding phosphate ions in 1:1 ratio according to reaction (Haghseresht et al., 2009):

$$La^{3+} + PO_4^{3-} \rightarrow LaPO_4 \quad (1)$$

The average size of Phoslock® particles is small and equal 22 µm but the large specific surface area (39.3 m^2/g) and pore volume (0.171 cm^3/g) are causing a very high sorption capacity for this material (Haghseresht et al., 2009). The LMB can be used in a wide pH range, from 4 to 11, but the optimal range for PO_4^{3-}-P removal is 5.0–7.0 with pH of the adsorption material equal 7–7.5 (Ross et al., 2008). Phoslock® consists mainly of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) (almost 80%). Also, other compounds as MgO (2.76%), Fe_2O_3 (3.64%), CaO (1.79%) and La_2O_3 (0.058%) are appearing in analyzed material (Haghseresht et al., 2009).

2.2. Methods

Some experimental trials were carried out in the laboratory with batch reactors pilot units. First stage of the studies (Table 1) was a preliminary evaluation of Phoslock® to remove phosphorus compounds from synthetic wastewater. Also influence of mixing time (magnetic stirrer: 1000 rpm) was tested (5, 10, 20 and 30 min). Sampling was made after 0.5, 1, 2, 3, 4, and 24 h of sedimentation.

Sorption capacity of Phoslock® was defined after exhaustion of sorption area for 100 g of material. The test was repeated 5 times with the same concentration of PO_4^{3-}-P (~15 mg/L) in each series. The total load of PO_4^{3-}-P in all series was equal to 77 mg.

Second stage of the studies was about the sorption equilibrium in order to determine parameters for the Langmuir and Freundlich isotherms of adsorption (Table 1). Research was conducted at various concentrations of PO_4^{3-}-P (5, 10, 20, 50 and 100 mg/L). Samples were taken after 1 h contact time. The amount of Phoslock® tested in each batch reactor was equal to 10 g. Due to economic reasons and the findings obtained in the first stage of research, mixing time was reduced to 5 min and was kept the same in each batch.

Last stage of the experiment was carried out with two batch reactors with synthetic wastewater and effluent collected after treatment wetland (Table 1). 1 g of Phoslock® was added in a batch reactor containing 1 L of synthetic wastewater with a concentration of PO_4^{3-}-P equal to 10 mg/L. To the batch reactor with 1 L of real wastewater, because of the low concentration of PO_4^{3-}-P, only 0.50 g of Phoslock® were added.

Samples from wetland for domestic wastewater treatment were collected before and after treatment process. The inflow sample was taken from inspection chamber before Hybrid Treatment Wetland (HTW), while the effluent was collected from inspection chamber after treatment process with 48 h retention time.

An example of an operative hybrid treatment wetland is Kniewo (Northern Poland, Pomerania Region). Kniewo is located close to the Puck Bay, severely contaminated water body, attached indirectly with Baltic Sea. This location causes difficulties with fresh water access and contributes to the eutrophication in that area.

Hybrid treatment wetland was designed for 60 pe and consisted of subsurface vertical flow bed (SS VF) followed by subsurface horizontal flow bed (SS HF). Because of a non-sufficient reduction level of phosphates concentration after wastewater treatment (~4 mg/L) an additional treatment unit should be applied.

The assumed technology of the treatment wetland in Kniewo provides wastewater treatment in mechanical processes (sedimentation, flotation) and biochemical processes (microbiological decomposition of contaminants in oxidation and reduction processes as well as absorption and adsorption). The treatment processes take place both in the mechanical part (three chamber sedimentation tank with 3 days retention time) and in the biological part – HTW. After the HTW treated effluent is discharged to drainage system. As filling material in both beds (SSVF and SSHF) gravel of granulation 2–8 mm was used. Beds were planted with local species of common reeds (*Phragmites australis*) with density 4 pcs/m^2. At this moment, after three years of operation, almost 80% of beds area are covered with reeds.

Quality of effluent after HTW, before the drainage system in Kniewo is shown in the Table 2. Samples were taken after 5, 10 30, 60, 120 and 300 min to describe adsorption kinetics of material by pseudo-second order model. Also, others parameters (pH, conductivity, color, turbidity, TSS) were tested to evaluate the influence of Phoslock® over the wastewater quality.

2.3. Physical and chemical analysis

The concentration of total suspended solids (TSS) was calculated on the basis of the standard formula. Turbidity and color were designated by HACH Lange DR 3900 laboratory VIS spectrophotometer with Radio Frequency Identification (RFID), calibrated to achieve a value of color in mgPt/l. The temperature, pH and conductivity were defined by WTW Multi 350i compact precision portable meter.

Phosphates concentration was tested by the cuvette tests HACH Lange and HACH Lange DR 3900 laboratory VIS spectrophotometer with RFID. All measurements were conducted in temperature 21 ± 1 °C.

Based on given results, the series of analyses were conducted to identify the suitability in phosphorus compounds removal of Phoslock® in adsorption processes. The effectiveness of PO_4^{3-} -P removal was calculated by equation (Bus and Karczmarczyk, 2015).