

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

Magda Kasprzyk<sup>a</sup>, Hanna Obarska-Pempkowiak<sup>a</sup>, Fabio Masi<sup>b</sup>, Magdalena Gajewska<sup>a</sup>

<sup>a</sup> Department of Water and Wastewater Technology, Faculty of Civil and Environmental Engineering, Gdańsk University of Technology, Poland

<sup>b</sup> IRIDRA Srl, Via La Marmora 51, Florence 50121, Italy

## 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  $\text{PO}_4^{3-}\text{-P}$  concentration, but also no other meaningful influence on the water solution was discovered.

**Keywords:** Freundlich isotherm; Langmuir isotherm; lanthanum-modified bentonite; phosphorus removal; sorption capacity; treatment wetland.

## Introduction

Baltic Action Plan (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, 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<sup>®</sup> 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<sup>®</sup> 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) is planning to create a constructed wetland to treat wastewater from large Chinese canals. PWS is using Phoslock<sup>®</sup> 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<sup>®</sup> application is characterized with lack of by-products during rhabdophane (LaPO<sub>4</sub>·nH<sub>2</sub>O) 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<sup>®</sup> due to possible toxic character of lanthanum to some aquatic organisms (dependent on used media) (Barry, Meehan, 2000). Although specific of material allow to classified LMB as not hazardous and confirm applicability in water/wastewater environment (Martin, Hickey, 2004).

The physical properties of Phoslock<sup>®</sup> 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<sup>®</sup> application on treated wastewater and to prove that Phoslock<sup>®</sup> 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<sub>2</sub>PO<sub>4</sub>) 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.

## Materials and methods

### 1.1 Materials

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



The average size of Phoslock<sup>®</sup> particles is small and equal 22 μm but the large specific surface area (39.3 m<sup>2</sup>/g) and pore volume (0.171 cm<sup>3</sup>/g) are causing a very high sorption capacity for this material (Haghsresht et al., 2009). The LMB can be used in a wide pH range,



from 4 to 11, but the optimal range for  $\text{PO}_4^{3-}\text{-P}$  removal is 5.0 - 7.0 with pH of the adsorption material equal 7-7.5 (Ross et al., 2008). Phoslock<sup>®</sup> consists mainly of silicon dioxide ( $\text{SiO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) (almost 80%). Also, other compounds as MgO (2.76%),  $\text{Fe}_2\text{O}_3$  (3.64%), CaO (1.79%) and  $\text{La}_2\text{O}_3$  (0.058%) are appearing in analyzed material (Haghseresht et al., 2009).

## 1.2 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<sup>®</sup> to remove phosphorus compounds from synthetic wastewater. Also influence of mixing time (magnetic stirrer: 1000 rpm) was tested (5, 10, 20 and 30 minutes). Sampling was made after 0.5, 1, 2, 3, 4, and 24 hours of sedimentation.

Sorption capacity of Phoslock<sup>®</sup> was defined after exhaustion of sorption area for 100 g of material. The test was repeated 5 times with the same concentration of  $\text{PO}_4^{3-}\text{-P}$  (~15 mg/L) in each series. The total load of  $\text{PO}_4^{3-}\text{-P}$  in all series was equal to 77 mg.

**Table 1.** Experiment design in each stage of study

	Sorbent dose	Batch reactor 1	Batch reactor 2	Batch reactor 3	Batch reactor 4	Batch reactor 5
Stage 1 - - time of mixing (1000 rpm)	100 g	5 minutes	10 minutes	20 minutes	30 minutes	--
Stage 2 - - $\text{PO}_4^{3-}\text{-P}$ concentration	10 g	5 mg/L	10 mg/L	20 mg/L	50 mg/L	100 mg/L
Stage 3 - - type of wastewater	1 g /0.5 g	synthetic wastewater	effluent from HTW	--	--	--

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  $\text{PO}_4^{3-}\text{-P}$  (5, 10, 20, 50 and 100 mg/L). Samples were taken after 1 hour contact time. The amount of Phoslock<sup>®</sup> 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 minutes 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<sup>®</sup> was added in a batch reactor containing 1 L of synthetic wastewater with a concentration of  $\text{PO}_4^{3-}\text{-P}$  equal to 10 mg/L. To the batch reactor with 1 L of real wastewater, because of the low concentration of  $\text{PO}_4^{3-}\text{-P}$ , only 0.50 g of Phoslock<sup>®</sup> 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 48h 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 4pcs/m<sup>2</sup>. 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 minutes 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<sup>®</sup> over the wastewater quality.

**Table 2.** Quality of wastewater from HTW in Kniewo (Pomerania Region, Poland)

Parameter	Unit	Inflow	Effluent from TW
PO <sub>4</sub> <sup>3-</sup> -P	mg/L	26.6	4.34
NO <sub>3</sub> <sup>-</sup> -N	mg/L	0.75	36.1
NO <sub>2</sub> <sup>-</sup> -N	mg/L	0.13	0.42
NH <sub>4</sub> <sup>+</sup> -N	mg/L	138.9	18.9
COD	mg/L	329.0	20.8
Temperature	°C	20.8	18.9
pH	-	7.17	7.17
Conductivity	μS/cm	1656	1226
Color	mgPt/L	392	34
Turbidity	mg/L	104.4	6.5
TSS	mg/L	28.0	9.0

### 1.3 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<sup>®</sup> in adsorption processes. The effectiveness of PO<sub>4</sub><sup>3-</sup>-P removal was calculated by equation (Bus, Karczmarczyk, 2015).

Amount of adsorbed phosphorus compounds from solution was determined according to equation (2) (Nastawny et al., 2015; Liu, Zhang, 2017)

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

where: q – quantity of adsorbed PO<sub>4</sub><sup>3-</sup>-P [mg/g], V – volume of solution [L], C<sub>0</sub> – initial concentration of PO<sub>4</sub><sup>3-</sup>-P [mg/L]; C – final concentration of PO<sub>4</sub><sup>3-</sup>-P [mg/L], m – mass of sorption material [g].

## 1.4 Adsorption models

Sorption capacity of Phoslock<sup>®</sup> was verified based on the relation between the quantity of adsorbed phosphates  $q_e$  [mg/g] and equilibrium concentration of phosphates  $C_e$  [mg/L]. This relation is described by mathematical equations of adsorption isotherms. Adsorption isotherms equations are the following (Bus, Karczmarczyk, 2015; Cucarella, Renman, 2009; Del Bubba et al., 2003; Xu et al., 2013; Limousin et al., 2007):

a) Langmuir isotherm

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

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  $\text{PO}_4^{3-}$ -P at equilibrium [mg/L],  $K_L/a_L = q_{\max}$  – maximum sorption capacity [mg/g].

Equation (3) in linear form becomes:

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

b) Freundlich isotherm

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

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

Equation (5) in linear form becomes:

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

## 1.5 Kinetic model

The objective of kinetic analysis is to understand the saturation period of the filtering material and particularly the more efficient contact time for ensuring an acceptable adsorption while reducing as much as possible the filter size and the related investment cost. Biochemical reactions are best approximated by this reaction.

The kinetics data of Phoslock<sup>®</sup> were presented by the pseudo-second order model to predict sorption capacity and the rate constant of sorption (Ho and Chiang, 2001; Haghseresht et al., 2009; Ross et al. 2008). The equation used to describe the adsorption process is the following:

$$dq_t/dt = k(q_e - q_t)^2 \quad (7)$$

where:  $q_t$  – adsorption capacity of Phoslock<sup>®</sup> at time  $t$  [mg/g],  $q_e$  – adsorption capacity of Phoslock<sup>®</sup> at equilibrium [mg/g],  $k$  – equilibrium rate constant of pseudo-second order reaction [g/mg·min].

For the boundary condition  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , equation (7) becomes:

$$1/(q_e - q_t) = 1/q_e + k_t \quad (8)$$

Equation (8) can be converted to linear form:

$$t/q_t = 1/kq_e^2 + t/q_e \quad (9)$$

From analysis of linear plot of  $t/q_t$  against time (Fig.3,4), the value of  $k$ ,  $q_e$  and the correlation coefficients  $R^2$  were obtained.



Interpretation of equations (4), (6) and (9) shown in figures 1, 2, 3 and 4 is presented in linear form (10):

$$y = a \cdot x + b \quad (10)$$

where:

for Langmuir isotherm:

$$y = 1/q_e \quad x = 1/C_e \quad a = 1/K_L \quad b = a_L/K_L$$

for Freundlich isotherm:

$$y = \log q_e \quad x = \log C_e \quad a = b_F \quad b = \log a_F$$

for pseudo second order model:

$$y = t/q_t \quad x = t \quad a = 1/q_e \quad b = 1/kq_e^2$$

## Results and discussion

### 2.1 Chemical analysis – phosphates removal and sorption capacity of Phoslock®

Sorption capacity results obtained in first stage of the study are presented in Table 3. The value of sorption capacity was equal to 5.60 mg/g in case of multiple use the same dose (100g) of adsorbing material. Also, in this case, an influence of mixing time on phosphorus removal effectiveness was not observed. Due to this knowledge and economic considerations, following studies were conducted with short mixing time (5 minutes).

Research conducted by Zamparas (2015) at pH 7 and room temperature of  $25 \pm 1^\circ\text{C}$  showed reduction efficiency of 87% after 250 minutes of contact time. Results obtained in each series of this experiment (except the last one when sorption capacity was exhausted) was equal over 99%, and in last one reached almost 85%. The whole experiment efficiency of sorption capacity was equal to 97%

**Table 3.** Average sorption capacity of Phoslock® in multiple use for 5 minutes of mixing time (Gajewska, Kasprzyk, 2017)

Total load of $\text{PO}_4^{3-}\text{-P}$ $L_0$ [mg]	Final load of $\text{PO}_4^{3-}\text{-P}$ $L$ [mg]	Quantity of adsorbed $\text{PO}_4^{3-}\text{-P}$ [mg]	Sorption $q$ [mg/g]	E [%]
77.0	2.4	74.6	5.6	97.0

**Table 4.** Sorption capacity and effectiveness of phosphorus compounds removal

Initial concentration of $\text{PO}_4^{3-}\text{-P}$ $C_0^*$ [mg/L]	Final concentration of $\text{PO}_4^{3-}\text{-P}$ $C$ [mg/L]	Sorption $q$ [mg/g]	E [%]
4.98	0.04	0.50	99.2
9.54	0.05	0.95	99.5
18.80	0.07	1.90	99.6
47.80	0.14	4.80	99.6
95.60	4.53	9.10	95.3

\*Actual concentrations of the prepared solutions of 5, 10, 20, 50 and 100 mg / L

Second stage of the study has shown better results in phosphorus removal with single use of Phoslock®. With the highest concentration, amount of adsorbed  $\text{PO}_4^{3-}\text{-P}$  was over 90 mg/L, which concludes in a sorption capacity value of over 9 mg/g and efficiency of 95.% in phosphorus removal with relatively short contact time (1 hour) (Table 4).

Considering chemical composition of lanthanum-modified bentonite (LMB) and 1:1 molar ratio of lanthanum and phosphorus, adsorption capacity of Phoslock<sup>®</sup> cannot exceed 10.6 mgP/g (Haghsresht et al., 2009).

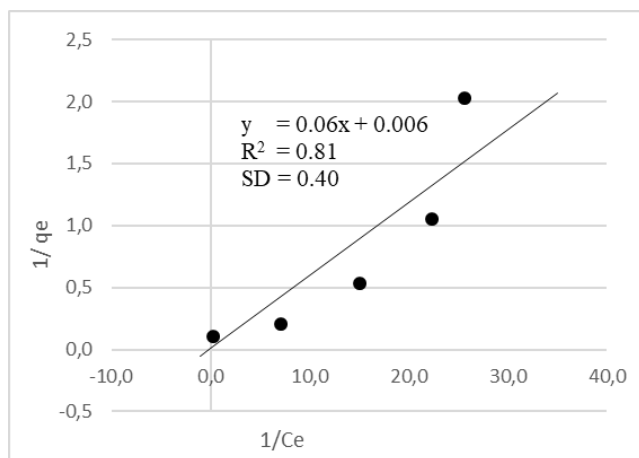
## 2.2 Adsorption models

Performed research has shown better and relatively good matching of applied mathematical Langmuir model for adsorption (Fig.1). Maximum theoretical sorption capacity reached value of 158.7 mg/g (Table 5). Correlation coefficient for Langmuir isotherm was equal  $R^2 = 0.81$ . Such situations happened on occasion due to described method of the experimental research. Standard deviation (SD) in both cases was relatively high and equal to 0.40 and 0.31 for Langmuir and Freundlich isotherms respectively.

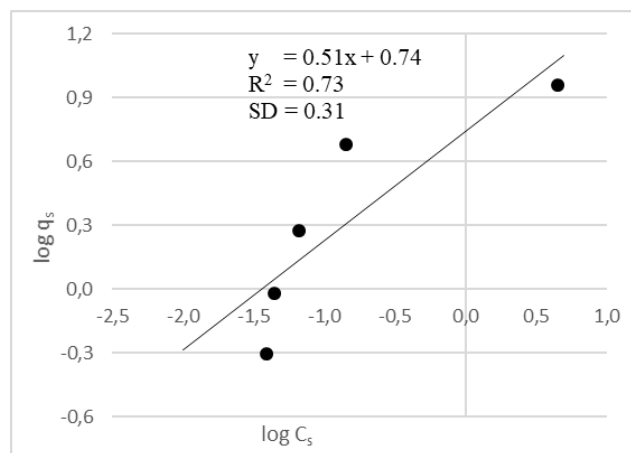
Specific models of adsorption are used to verify and compare constants of adsorption for both Langmuir and Freundlich isotherms (Fig.1,2) despite to their approximate values and not always high linear correlation coefficients. Linear forms of the isotherms equations are favorable to find characteristic parameters of adsorption process.

**Table 5.** Parameters of the Langmuir and Freundlich adsorption isotherms

Langmuir isotherm					Freundlich isotherm			
constant parameters in Langmuir model of adsorption		maximum sorption capacity	Statistical data		constant parameters in Freundlich model of adsorption		Statistical data	
$K_L$ [L/g]	$a_L$ [L/mg]	$q_{max}$ [mg/g]	$R^2$	SD	$a_F$ [L/g]	$b_F$ [-]	$R^2$	SD
14.98	0.094	158.7	0.81	0.40	5.48	0.51	0.73	0.31



**Fig. 1.** Langmuir isotherm of adsorption



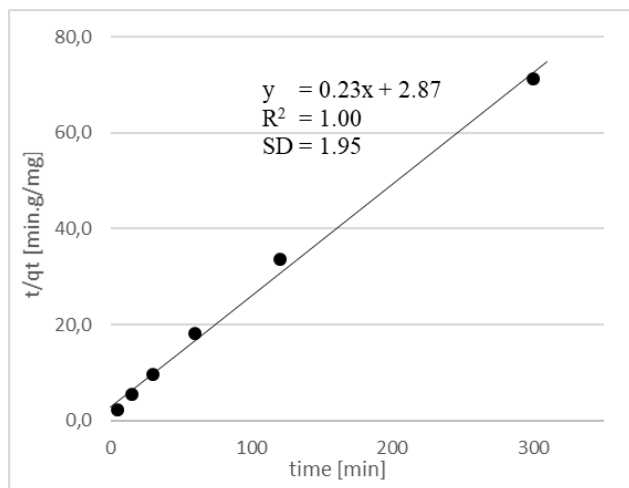
**Fig. 2.** Freundlich isotherm of adsorption

## 2.3 Kinetic model

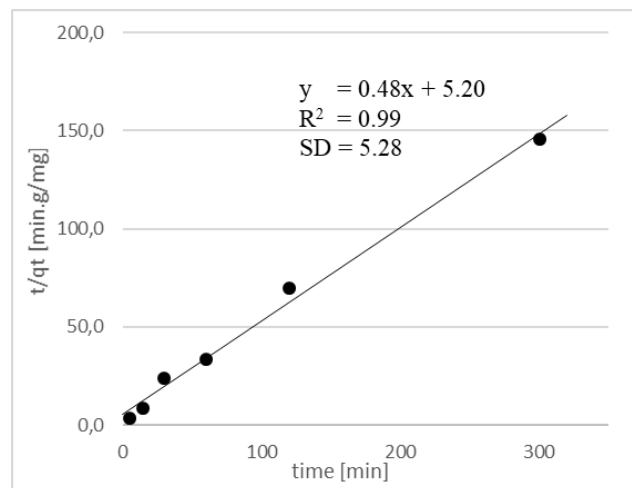
Based on conducting kinetic studies it can be concluded that pseudo-second order model might be successfully used to describe adsorption process of lanthanum modified bentonite (Fig.3,4). Correlation coefficient was oscillating above 0.99 both for synthetic and effluent from HTW. Standard deviation (SD) in both cases was relatively low and equal to 1.95 and 5.28 for synthetic and real wastewater, respectively. Obtained results for sorption capacity of synthetic wastewater was equal to 4.31 mg/g after 5 hours of contact time. Also, it has been found that the adsorption capacity of LMB is significantly lower for effluent from HTW and equal 2.09 mg/g (Table 6).

**Table 6.** Kinetic parameters for phosphorus adsorption for synthetic and effluent from HTW

Kinetic parameters							
synthetic wastewater				effluent from HTW			
$q_e$ [mg/g]	$k$ [g/mg*min]	$R^2$	SD	$q_e$ [mg/g]	$k$ [g/mg*min]	$R^2$	SD
4.31	0.054	1.00	1.95	2.09	0.228	0.99	5.28



**Fig. 3.** Pseudo-second order kinetics of phosphorus adsorption from synthetic wastewater

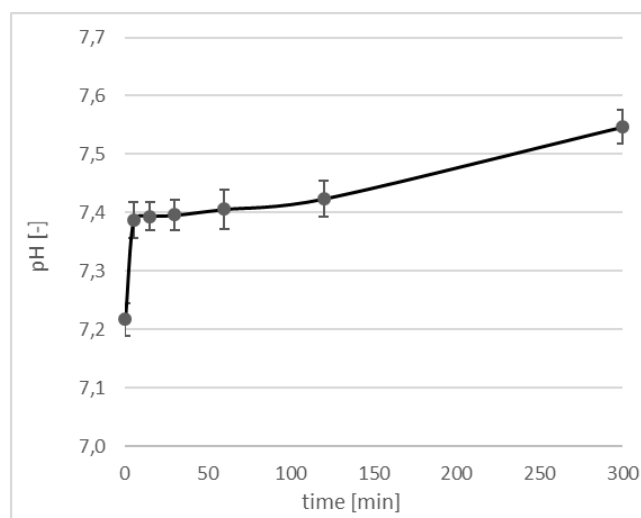


**Fig. 4.** Pseudo-second order kinetics of phosphorus adsorption from real wastewater

## 2.4 Physical analysis

In Figures 5-9 the influence of LMB to parameters on the effluent from HTW are presented. Effect of Phoslock® on pH of the solution was not substantial (Fig.5). The initial pH value of 7.22 reached the value of 7.55 after 5 hours of contact time. Several studies have indicated that LMB caused none or little effect (mainly increase) on pH (Van Oosterhout, Lürling, 2013).

Also, it is worth to notice that maximum efficiency in phosphates binding is obtained in a pH range of 5-7 and decrease at pH above 9 (Copetti et al., 2015; Haghseresht et al. 2009; Ross et al., 2008).

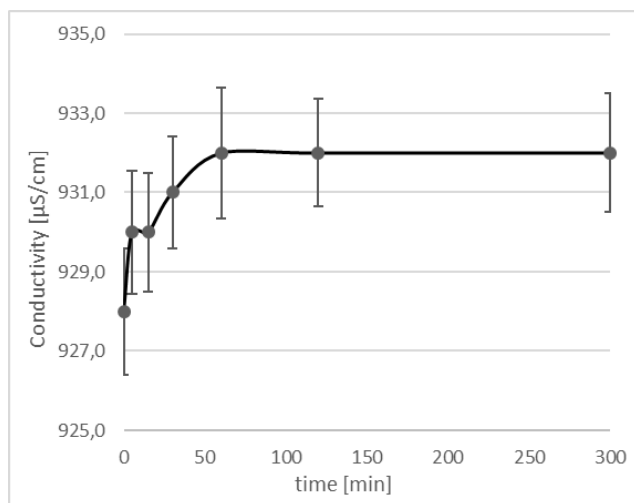


**Fig. 5.** Effect of LMB on pH

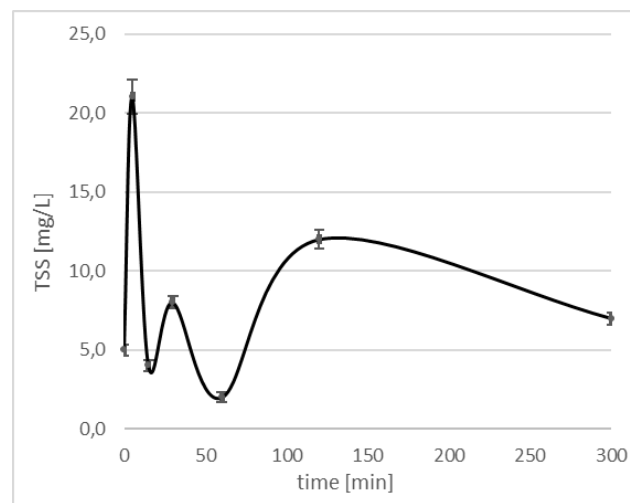
Conductivity of the effluent from HTW after application of Phoslock® was slightly higher (from a value of 928  $\mu\text{S}/\text{cm}$  to 932  $\mu\text{S}/\text{cm}$ ) (Fig.6). However, investigation (first stage of the studies) performed on synthetic wastewater with multiple use of the same dose of LMB has



shown a significant increase of conductivity in the early stage of action from a value of approx. 100  $\mu\text{S}/\text{cm}$  to over 1000  $\mu\text{S}/\text{cm}$  (Gajewska, Kasprzyk, 2017).



**Fig. 6.** Effect of LMB on conductivity



**Fig. 7.** Effect of LMB on total suspended solids

After the research conducted by Van Oosterhout (2013), it might be concluded that conductivity increases with increasing concentration of Phoslock<sup>®</sup>. In the first stage of studies described in this paper, when a large increase of conductivity was observed a 100 g of Phoslock<sup>®</sup> were added to 1.5 L of the solution. Studies on effluent from HTW were performed with small amount of adsorption material (0.5 g) added to 1.0 L of effluent from HTW. Thus the same conclusion can be found.

Figure 7 shows the changes in total suspended solids. The initial concentration of TSS was low and equal to 5.0 mg/L. After the addition of LMB the increase of TSS was observed and was influenced by mixing period and short sedimentation time (5 minutes). Along with sedimentation time a concentration of TSS was fluctuating and after 5 hours dropped to almost initial value (7 mg/L).

Investigation performed with multiple use of the same amount of Phoslock<sup>®</sup> has shown that resuspension caused significant increase of TSS to value of 1000 mg/L, however along with time of sedimentation, the concentration of TSS dropped to approx. 10 mg/L (Gajewska, Kasprzyk, 2017).

Influence of LMB on color and turbidity of the effluent from HTW was not substantial but for both parameters application of Phoslock<sup>®</sup> was causing increase of their values (Fig.8,9). In case of color of the solution an increase from 24 mgPt/L to 36 mgPt/L was observed, while for turbidity an increase from a value of 5.3 mg/L to 7.1 mg/L was noticed.

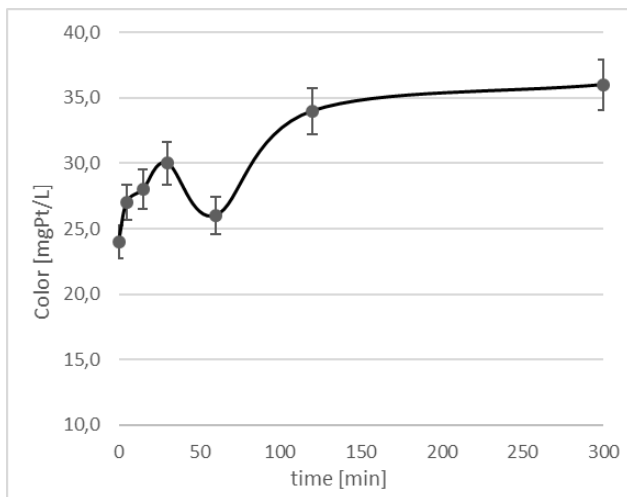


Fig. 8. Effect of LMB on color

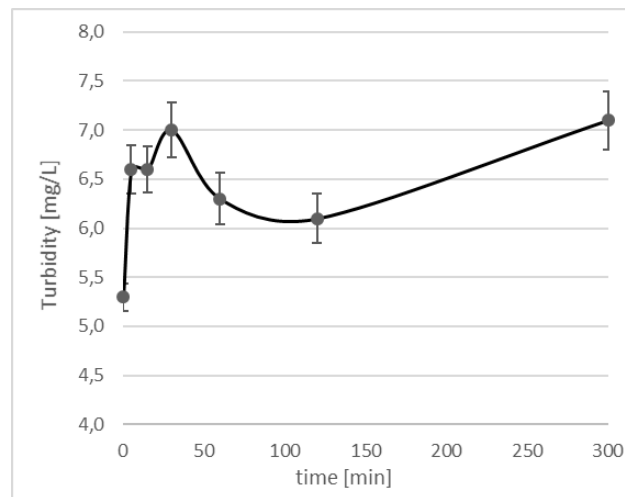


Fig. 9. Effect of LMB on turbidity

## 2.5 Limitations, costs and maintenance analysis

In case of HTW in Kniewo, according to assumption of the design project, total daily inflow of wastewater was equal to 7.0 m<sup>3</sup>/d which gives annual inflow of wastewater to HTW about 2,500 m<sup>3</sup>/year.

For mitigating the infiltration impacts and the risk of exposing the Puck Bay to discharged large load of phosphates the idea of implementing the post treatment filter became reasonable. Potential location of Phoslock<sup>®</sup> filter unit is just before the drainage system (Fig. 10). It will be equipped with a dosage pump and a stirrer with ON/OFF system. After a Phoslock<sup>®</sup> application, the stirrer will be mixing for 5 minutes followed by 2 hours of sedimentation time post treated effluent will be decanted to drainage system.

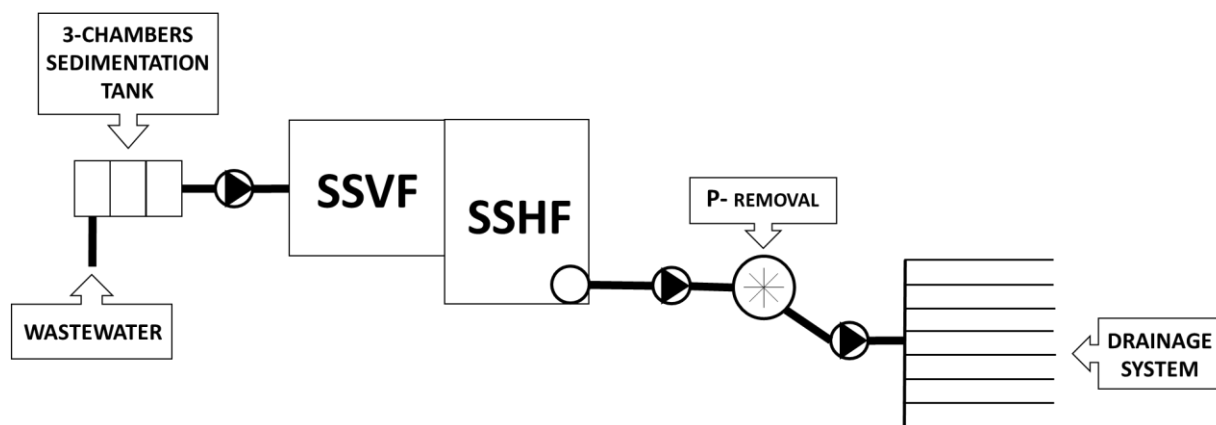


Fig. 10. Potential location of Phoslock<sup>®</sup> filter unit

Based on assumed annual wastewater inflow and concentration PO<sub>4</sub><sup>3-</sup>-P of the effluent from HTW, the load of phosphates from HTW effluent can reach 10 kg/year. Achieved sorption capacity of Phoslock<sup>®</sup> during the performed study was equal to 2.09 mg/g, which gives almost 5 tons of Phoslock<sup>®</sup> for removing 10 kg of phosphates per year.

According to Mackay et al. (2014), the price of Phoslock<sup>®</sup> can be assumed 2750€/ton, which brings to a total cost of annual maintenance for additional treatment filter close to 14,000€. Cost per 1 kg PO<sub>4</sub><sup>3-</sup>-P removed from effluent is very high and equal almost 1,400€, while treatment of the 1 m<sup>3</sup> of the effluent may reach 6€.

Due to this calculations, the unitary price of phosphates removal by Phoslock<sup>®</sup> may still appear as a major restriction for its application on the real scale in wastewater treatment plants.

Implementation of filter unit may bring necessity to collect exhausted material and replace with new one. Possibilities of recyclability of waste material, as a slow P-releasing fertilizer or ability of reusing, need further investigation and will be a subject of future studies.

## Conclusions

Carried out research confirmed high sorption capacity of LMB - Phoslock<sup>®</sup> for removal of phosphorous compounds from wastewater both synthetic and effluent from biological WWTP working in treatment wetland technology. 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). But still sorption capacity for very high concentration of PO<sub>4</sub><sup>3-</sup>-P in wastewater reaching even 90 mg/L was up to 95% for synthetic wastewater. Langmuir adsorption model has shown relatively good matching of isotherm in graphical analysis at the level of correlation coefficient equal to 0.81. Better results were obtained for kinetic studies where correlation coefficient was close to 1.0 both for synthetic and effluent from WWTP. Application of LMB caused not only a rapid decrease of PO<sub>4</sub><sup>3-</sup>-P concentration, but also no other meaningful influence on the water solution was discovered. Investigated LMB caused slight increasing of the conductivity and pH of the solution. Also, color and turbidity were subjected to fluctuations but in final due both properties were raising along with contact time. Since no relation between amount of absorbed phosphorus compounds and time of mixing was revealed contact time could be optimized to achieve required color and turbidity in final effluent.

Possibilities of implementation of post treatment Phoslock<sup>®</sup> filter in large scale is the aim of further investigation and still need careful attention. Potential costs of such treatment could be equal 6€ per 1m<sup>3</sup> of the effluent. Probabilistic approaches or data analytic approaches also suggested in "computational intelligence approach for estimation of wilting point in green infrastructure" can be looked into.

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## References

- Barry M.J., Meehan B.J., (2000). The acute and chronic toxicity of lanthanum to *Daphnia carinata*, *Chemosphere* 41, 1669–1674.
- Bus, A. Z., Karczmarczyk, A. A. (2015). Kinetic and sorption equilibrium studies on phosphorus removal from natural swimming ponds by selected reactive materials, *Fresenius Environmental Bulletin* 24(9), 2736–2741.
- Copetti, D., Finsterle, K., Marziali, L., Stefani, F., Tartari, G., Douglas, G., Reitzel K., Spears, B.M., Winfield, I.J., Crosa, G., D'Haese, P., Yesseri, S., Lürling, M. (2015). Eutrophication management in surface waters using lanthanum modified bentonite : A review, 1–13. <https://doi.org/10.1016/j.watres.2015.11.056>

Cucarella, V., Renman, G. (2009) Phosphorus Sorption Capacity of Filter Materials Used for On-Site Wastewater Treatment Determined in Batch Experiments - A Comparative Study. *J. Environ. Qual.* 38, 381-392.

Douglas, G.B., Adeney, J.A., Robb, M., (1999). A novel technique for reducing bioavailable phosphorus in water and sediments. *Int. Assoc. Water Qual. Conf. Diffuse Pollut.* 517-523.

Douglas G.B., Adeney, J.A, Zappia LR (2000) Sediment Remediation Project: 1998/9 Laboratory Trial Report. CSIRO Land and Water. Report No. 6/00 2000 CSIRO.

Douglas, G. B., Lurling, M., & Spears, B. M. (2016). Assessment of changes in potential nutrient limitation in an impounded river after application of lanthanum-modified bentonite. *Water Research*, 1–8. <https://doi.org/10.1016/j.watres.2016.02.005>

Del Bubba, M., Arias, C. A., Brix, H. (2003). Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Research*, 37(14), 3390–3400. [https://doi.org/10.1016/S0043-1354\(03\)00231-8](https://doi.org/10.1016/S0043-1354(03)00231-8)

Drizo, A., Frost, C.A., Grace, J., Smith, K.A., (1999). Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Wat. Res.* 33, 3595–3602.

Drizo, A., Forget, C., Chapuis, R.P., Comeau, Y., (2002). Phosphorus removal by EAF steel slag—A parameter for the estimation of the longevity of constructed wetland systems. *Environ. Sci. Technol.* 36, 4642–4648.

Gajewska, M., Kasprzyk, M. 2017. Preliminary results from application Phoslock® to remove phosphorus compounds from wastewater. *Journal of Ecological Engineering*, 18(4), 82–89. <https://doi.org/10.12911/22998993/74275>

Gajewska, M., Obarska-Pempkowiak H., 2011. Efficiency of pollutant removal by five multistage constructed wetlands in a temperate climate. *Environmental Protection Engineering*, vol. 37, no. 3, 27-36.

Gajewska M., Kopeć Ł, Obarska-Pempkowiak H. (2011). Operation of small wastewater treatment facilities in a scattered settlement, *Annual Set of Environment Protection*, Tom 13 (Tom 1) 207-225.

Haghseresht, F., Wang, S., Do D.D., A novel lanthanum-modified bentonite, Phoslock®, for phosphate removal from wastewaters, *Applied Clay Science* 2009, 46, 369-375.

HELCOM Recommendation 28E/5. Adopted 15 November 2007. Municipal wastewater treatment

HELCOM Recommendation 28E/6. Adopted 15 November 2007. On-site wastewater treatment of single family homes, small businesses and settlements up to 300 Person Equivalents (P.E.).

Ho, Y.S., Chiang, C.C., (2001). Sorption studies of acid dye by mixed sorbents. *Adsorption* 7, 139–147.

Kadlec R.H., Wallace S., (2009) *Treatment Wetlands*, Second Edition CRC Press Taylor & Francis Group, Boca Raton, London, New York.

Limousin, G., Gaudet, J.P., Charlet, L., Sznknect, S., Barthea, V., Krimissa, M. (2007). Sorption isotherms : A review on physical bases, modeling and measurement, *Applied Geochemistry* 22, 249–275. <https://doi.org/10.1016/j.apgeochem.2006.09.010>

Liu, X., Zhang, L. (2015). Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies. *Powder Technology*, 277, 112–119. <https://doi.org/10.1016/j.powtec.2015.02.055>

Mackay, E., Maberly, S., Pan, G., Reitzel, K., Bruere, A., Corker, N., Douglas, G., Egemose, S., Hamilton, D., Hatton-Ellis, T., Huser, B., Li, W., Meis, S., Moss, B., Lüring, M., Phillips, G., Yasseri, S., Spears, B., (2014). Geoengineering in lakes: welcome attraction or fatal distraction? *Inland Waters* 4, 349–356. <https://doi:10.5268/IW-4.4.769>

Martin M.L., Hickey C.W., (2004). Determination of HSNO Ecotoxic Thresholds for Granular Phoslock™, Phase 1: Acute Toxicity, National Institute of Water and Atmospheric Research Ltd. Report prepared for Primaxa Ltd., Hamilton, New Zealand.

Nastawny, M., Jucherski, A. Walczowski, A., Józwiakowski, K., Pytka, A., Gizińska-Górna, M., Marzec, M., Gajewska, M., Marczuk, A., Zarajczyk, J. (2015) Preliminary evaluation of selected mineral adsorbents used to

remove phosphorus from domestic wastewater. *Przemysł Chemiczny*, 10(94), 1000–1004. <https://doi.org/10.15199/62.2015.10.XX>

Obarska-Pempkowiak, H., Gajewska, M., Wojciechowska, E., Pempkowiak, J. (2015) *Treatment Wetlands for Environmental Pollution Control*, Springer International Publishing.

PWS Media Center Blogs, 2018. Phoslock Water Solution Blogs (05 March 2018).

<http://blog.phoslock.com.au/using-constructed-wetlands-to-clean-polluted-water/> (accessed 6 July 2018).

Ross, G., Haghseresht, F., Cloete, T. E. (2008). The effect of pH and anoxia on the performance of Phoslock<sup>®</sup>, a phosphorus binding clay. *Harmful Algae*, 7(4), 545–550. <https://doi.org/10.1016/j.hal.2007.12.007>

Van Oosterhout, F., Lüring, M., (2013). The effect of phosphorus binding clay (Phoslock<sup>®</sup>) in mitigating cyanobacterial nuisance: a laboratory study on the effects on water quality variables and plankton, *Hydrobiologia* 2013, 710, 265–277.

Vymazal, J. (2011) *Constructed wetlands for wastewater treatment: five decades of experience*. *Environ. Sci. Technol.* 45, 61–69.

Xu, Z., Cai, J., Pan, B. (2013). Mathematically modeling fixed-bed adsorption in aqueous systems, *Journal of Zhejiang University-SCIENCE A, Applied Physics & Engineering*, 14(3), 155–176. <https://doi.org/10.1631/jzus.A1300029>

Zamparas, M., Gavriil, G., Coutelieris, F. A., & Zacharias, I. (2015). A theoretical and experimental study on the P-adsorption capacity of Phoslock<sup>TM</sup>. *Applied Surface Science*, 335, 147–152. <https://doi.org/10.1016/j.apsusc.2015.02.042>

