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Phosphorus reactive materials for permeable reactive barrier filling – lifespan estimations

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ABSTRACT

Phosphorus (P) losses to the water bodies are considered as one of the main culprits in eutrophication process and gradual deterioration of water quality. The agricultural environment is the main nonpoint P source to surface water which is difficult to limit. Permeable reactive barriers (PRB) are one of the methods to limit P outflow from agricultural areas. The aim of the study was to assess the sorption properties and the lifespan of two different reactive materials (RMs) that may be used as a filling of permeable reactive barriers preventing water environment against P contamination. Two different P RMs: autoclaved aerated concrete (AAC) and Polonite® (POL) were used in the tests. Both tested RMs are characterised by better fit to pseudo-second-kinetic model. Calculated by Langmuir isotherm model, the maximum sorption capacity equalled to 81.13 and 95.70 mg P–PO_4 g^{-1} for AAC and POL, respectively. Based on these values, the lifespan of PRBs were calculated for variable hydraulic gradient (0.005–0.020) and P–PO_4 concentrations (0.1–5.0 mg L^{-1}). The lifespan of AAC ranged from 1 to 5 y for the highest tested concentration (5.0 mg L^{-1}) regarding to hydraulic gradient. In case of POL, the values are higher and ranged from 4 to 15 y depending on the hydraulic gradient and P–PO_4 concentrations.

Keywords: Agricultural areas; Diffuse pollution; Groundwater remediation; Surface and subsurface runoff

1. Introduction

Phosphorus (P) is a mineral nutrient, essential for plant growth and also necessary for modern agriculture production. Phosphorus (P) is one of the essential plant nutrients, needed for plant growth and ensuring appropriate level of agriculture crop production. On the other hand, an excess of P in the water causes its fertilization and degradation, widely known as eutrophication process. However, the surplus of P is regarded as a main factor causing eutrophication process of water bodies. In consequence, eutrophication may lead to a drastic decrease of dissolved oxygen in the absence of sunlight and, subsequently, to depopulation of aquatic species, creating "dead zones" [1–3]. Generally, farming is characterized by intensive cereal and vegetable production, which demands intensive use of fertilizers and consequently causes high risk of P losses [4]. P-saturation is reached in the soil, high levels of phosphate could leach to deeper layers of the soil and groundwater as it has been reported before in some parts of Northwestern Europe and range from 0.1 to 3.3 mg/L [5] and even higher [6]. For these reasons, agricultural environment is the main diffuse P sources to surface water which is both difficult to limit and remove [7].

The need to control eutrophication in water bodies coming from agricultural areas is a reason to apply permeable reactive barriers (PRB) filling with reactive material (RM) dedicated to P removal. The groundwater cleanup

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attempts have been started since the earnest 1980s and PRBs are called as a passive treatment system [8,9]. The concept of the technology is defined as an emplacement of RM in the subsurface structure designed to intercept a contaminated plume, provide a flow path through the RM, and transform the contaminants into environmentally acceptable forms to attain remediation concentration goals downstream of the barrier [10]. The PBR technology is also defined as a low-cost treatment technology [11,12].

Reactive materials dedicate to remove P should be based on metals oxides or hydroxides have been the most successful ones for the uptake of different oxyanions from water. Different metals (Al, Ca, Ce, Fe, La, Mg, Zn, and Zr) have been used as natural RMs or to synthesize those materials. However, the most popular are Ca and Mg due to their high availability, low cost, and low toxicity [1]. The possible mechanisms of phosphate adsorption on metal (oxy-) hydroxides can be reduced to two main P sorption mechanism: iron (Fe)/aluminium (Al) based PSMs that remove P by ligand exchange reactions, and calcium (Ca)/magnesium (Mg) based PSMs that work by precipitating Ca and Mg phosphate minerals [13].

One of the most challenging issue in designing PRBs is a RM lifespan estimation. Time of working PRB depend on such parameters as: site hydrology and water quality characteristics, distributing the water entering the PRB bed, the particle size of used RM and a sufficiently long contact time [8,13].

The novelty of this study is an attempt to estimate working time of phosphorus PRB. To our knowledge, despite the fact that PRB are popular methods of limiting the displacement of pollutants in the ground [5,14,15], there were not so many attempts to calculate and estimate their lifespan in relation to phosphorous. It should be remembered that PRB is a kind of permanent interference with the environment and for this reason their working time should be estimated because as every such action like the RM exchange is difficult and costly [15].

The aim of the study was to assess the sorption properties and lifespan of two different reactive materials that may be used as a filling of PRB preventing water environment against phosphorus contamination.

2. Materials and methods

2.1. Reactive materials

Two different P reactive materials: autoclaved aerated concrete (AAC) and Polonite® (POL) were used in the tests. AAC is a lightweight popular material used in civil engineering made of quartz sand, lime, or cement and water as a binding agent. POL is manufactured opoka rock, which is a calcium silicate sedimentary rock, heated at temperature of 900°C. Main properties of tested materials are set in Table 1. Scanning electron microphotograph (SEM) of tested reactive materials are presented in Fig. 1. Determination of bulk density and porosity were carried out in accordance with PN-EN 1097-3:2000 [16] and PN-EN 1936:2010 [17] standards. Filtration coefficient was determined by Witt apparatus. The value of the coefficient was calculated from the equalization:

$$k = 144\frac{Q \cdot L}{\Delta h \cdot F} \tag{1}$$

where k is the filtration coefficient (m d^{-1}), Q is the water volume V (cm^3) infiltrating through the sample over time t (min), L is the sample height (cm), Δh is the difference in water levels in the cylinder and in the tank (mm), and F is the sample cross-sectional area (cm^2).

Table 1
Main chemical composition with physical properties of AAC and POL

Parameter	Unit	Reactive material	
		AAC	POL
SiO_2	%	57.0	55.1
CaO	%	25.0	23.9
Al_2O_3	%	2.0	5.7
Fe_2O_3	%	1.0	2.1
Hydraulic conductivity	m d^{-1}	573	530
Bulk density	g cm^{-3}	0.35	0.78
Porosity	%	83.75	38.00

2.2. Adsorption kinetic models

Different concentration of the artificial P solution prepared using KH_2PO_4, were used in kinetics tests. The triplicate samples of material were mixed in Erlenmeyer glass flasks, each contained 1.0 g of material and 100 mL of P solutions. The kinetic tests were performed at various contact times (5–6,900 min) and at a constant average solution concentration of 4.877 mg P–PO_4 dm^{-3}.

Kinetic models are generally used to understand sorbent – sorbate interactions. Two most popular models, namely pseudo-first-order (PFO) and pseudo-second-order (PSO) were applied in the present study to describe the experimental data. The PFO and PSO models are expressed by formulas [18]:

$$\log\left(q_e - q_t\right) = \log q_e - k_t \tag{2}$$

$$\frac{1}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \tag{3}$$

where q_t (mg g^{-1}) represents the amount adsorbed at any time t, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are rates of sorption of the PFO and PSO, and q_e is the amount adsorbed at equilibrium (mg g^{-1}).

The parameters of both kinetic models were obtained by Solver (Microsoft Excel).

2.3. Sorption capacity

A phosphorus sorption batch test was performed mixing of 1 g of the RM (triplicate) with 100 mL of P-solution in increasing concentrations from 1 to 1,000 mg L^{-1}. P-sorption was calculated based on the difference of load

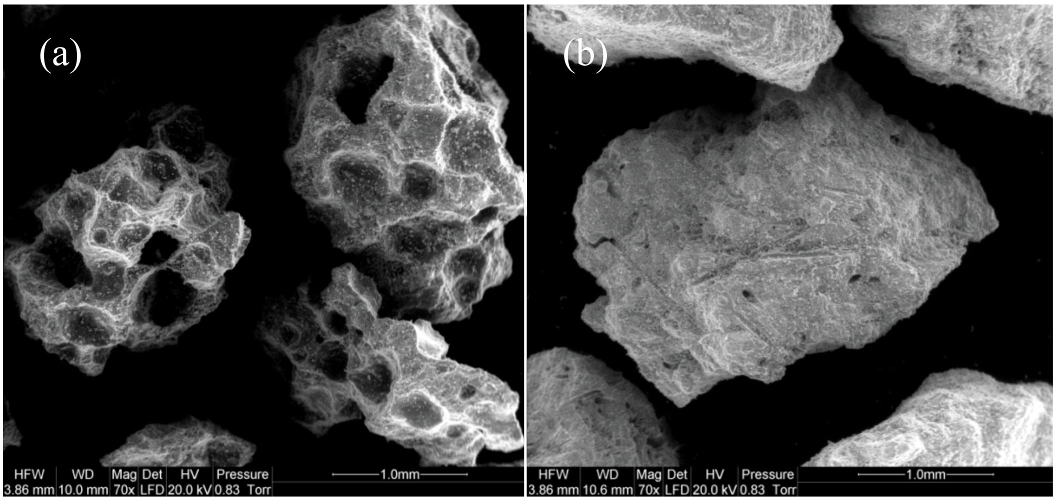

Fig. 1. Scanning electron microscopy (SEM) micrographs of AAC (a) and POL (b).

of P added and obtained in a filtered sample. Description of the sorption process between solid phase and solution was made based on mathematical equations given by Langmuir [Eq. (2)] and Freundlich [Eq. (3)] [19].

$$\frac{1}{q_s} = \frac{1}{C_s} \cdot \frac{1}{K_L} + \frac{a_L}{K_L} \tag{4}$$

where K_L is the constant parameter reflects the solute absorptivity (L g^{-1}), a_L is the constant parameter related to the energy of adsorption (L mg^{-1}), q_s is the sorption (mg g^{-1}), C_s is the solute concentration at equilibrium (mg L^{-1}). Parameters K_L and a_L are Langmuir constants, whereas K_L/a_L ratio is defined as adsorption capacity.

$$\log q_s = b_F \cdot \log C_s + \log a_F \tag{5}$$

where a_F is the constant which express the adsorbent capacity (g L^{-1}), b_F is the heterogeneity factor (–), q_s is the sorption (mg g^{-1}), and C_s is the solute concentration at equilibrium (mg L^{-1}).

2.4. Lifespan estimation

The lifespan estimation of phosphorus permeable reactive barrier (LS_PRB) was made according to Darcy flow and [20] methodology.

- The flow rate through the PRB (q) is calculated based on Darcy flow:

$$q = k \cdot i \tag{6}$$

where k is the filtration coefficient of RM (m s^{-1}) and i is the hydraulic gradient (–).

- The P–PO$_4$ mass flowing through PRB:

$$M_P = q \cdot C \cdot A \tag{7}$$

where q is the water flow (m s^{-1}), C is the P–PO$_4$ concentration in groundwater (g m^{-3}), A is the cross-sectional area of PRB (m^2); defined as: ($l \cdot d$) where l is PRB length (m) and d is PRB depth (m).

- Mass of RM filling the PRB (M_RM):

$$M_\text{RM} = V \cdot \rho_\text{RM} \tag{8}$$

where V is the PRB volume (m^3) and ρ_RM is the bulk density (g m^{-3}).

- The PRB lifespan:

$$\text{LS}_\text{PRB} = \frac{S_\text{max} \cdot M_\text{RM}}{M_P} \tag{9}$$

where S_max is the maximum sorption capacity of RM (g g^{-1}), M_RM is the mass of RM filling the PRB (g), M_P is the P–PO$_4$ mass flowing through PRB (g s^{-1}).

The calculations were made for barrier volume of 1 m^3. The P–PO$_4$ groundwater concentrations ranged from 0.1 to 5.0 mg L^{-1} and correspond to the real concentrations [6,21,22].

3. Results and discussion

3.1. Determination of the sorption capacity

The kinetic study of P–PO$_4$ adsorption was studied using the PFO and PSO kinetic model. Fig. 2 shows the kinetic plots vs. contact time (min) for P–PO$_4$ with experimental data. The more rapid P–PO$_4$ removal is seen with POL than AAC. After 5 min of contact time 31% and 15% of P–PO$_4$, respectively, was removed from the solution. However, any of the tested RMs removed 100% of P–PO$_4$ after 6,900 min. The best results equal 95% and 90% for AAC and POL, respectively. The equilibrium was reached the fastest with AAC (300 min). In contrary, POL needed

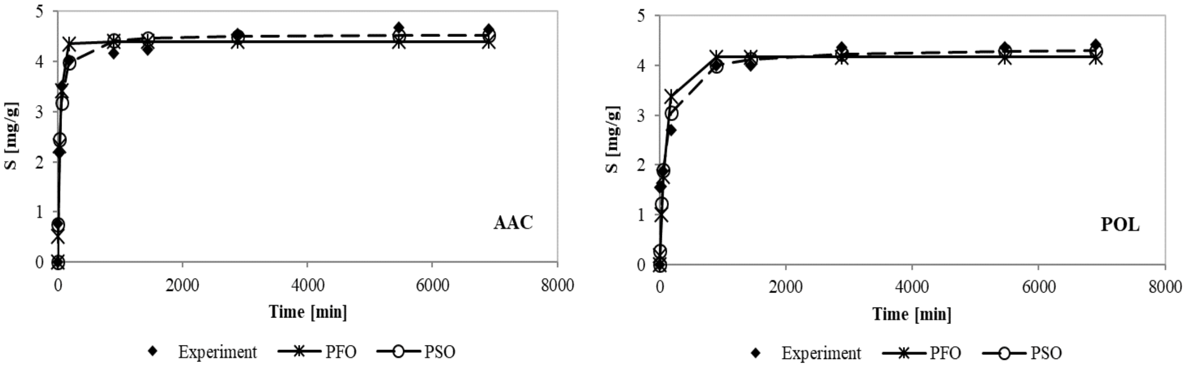

Fig. 2. Effect of contact time of the experimental data and results of PFO and PSO for tested RM.

more than two times more time (720 min). This statement is confirmed by the *k* value (Table 2) which is higher for AAC than POL. The obtained parameters of PFO and PSO are set out in Table 2. Based on the calculations (Table 2), removal of phosphates onto tested RMs follows the PSO kinetic models.

The PFO model is defined as the irreversible sorption of the solid/liquid systems whereas PSO model is based on the assumption that chemical sorption is one of the factors controlling the sorption kinetics and the rate expression can be seen [20,23,24]. The examined RMs better fit to PSO model (Table 2) that suggest that chemisorption is the dominant rate-limiting step. Riahi et al. [24] speculated that the adsorption of phosphate species can be reasonably presumed to occur in following steps: transfer of phosphate from the aqueous solution to the sites on the P-BMM and chemical complexation or ion exchange at the active sites and precipitation on the P-BMM surface. It is observed that the process of phosphate uptake onto tested RMs appears to occur over three stages which confirmed [25]: 1st stage – a first sharper reaction stage which is clearly seen during the first minute of contact time; 2nd stage – a low reaction stage at 60–300 min, and 3rd stage – at equilibrium with strong and stable adsorption (Fig. 2).

The relationship between the equilibrium concentration and the P amount adsorbed at the surface of RMs can be revealed by adsorption isotherms. The raw data of tested RMs behavior obtained from sorption capacity tests is shown at Fig. 3 with the exponential functions fitting to the data.

A linear plots of specific adsorption against equilibrium concentration (C_s^{-1} vs. q_s^{-1}) and ($\log C_s$ vs. $\log q_s$) indicate that phosphate adsorption on both AAC and POL obey the Langmuir isotherm model stated by higher fitting R^2 (Table 3). Better fit to Langmuir isotherm model indicate that in case of rested RMs adsorption is limited to one monolayer, all surface sites are equivalent and adsorption to one site is independent of adjacent sites occupancy condition [26]. Also, better fit to Langmuir model confirms that the chemisorption is a dominant adsorption process [27] that is also comfirmed by better fit to the PSO kinetic model. This adsorption mechanism was also confirmed by Kang et al. [28] and Bus and Karczmarczyk [29] for AAC and POL, respectively. The Langmuir and Freundlich constants determined from the slope and intercept of the plots are presented in Table 3. The K_L and k_F constants provide the sorption properties of tested materials. The higher values obtained, the better sorption properties of tested material. K_L in Langmuir isotherm indicate the binging energy of P with tested materials [27]. For POL, the value is 96 times higher than for AAC (Table 2) that imply there existed a stronger adsorption force between P and, in case of tested materials, Ca [27]. The a_L constant represents the affinity between P and RM [29]. The k_F in Freundlich isotherm is usually used to evaluate adsorption capability of P with RM [26]. In case of tested RMs, the k_F value is 11 times higher for POL than AAC. The b_F constant reveals adsorption sites with low energetically heterogeneity of RM [30].

The maximum adsorption capacity calculated by the Langmuir isotherm model defined as $S_{\max}$ equaled 81.13 and 95.70 mg P–PO_4 g^{-1} for AAC and POL, respectively. Considering the constants obtained for both isotherm models (Table 3), better sorption properties were noted for POL what is also confirmed by $S_{\max}$ value.

3.2. Lifespan estimation

The main parameters influencing PRB lifespan according to presented methodology are filtration coefficient (*k*) of RM, maximum sorption capacity of RM ($S_{\max}$), hydraulic

Table 2
Calculated parameters of the pseudo first and pseudo-second-kinetic order

RM	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (min^{-1})	q_e (mg g^{-1})	R^2 (%)	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2 (%)
AAC	0.025	4.404	88.99	0.039	4.544	99.18
POL	0.009	4.171	94.87	0.013	4.348	95.78

Table 3
Langmuir and Freundlich isotherm parameters for tested RMs

	Langmuir isotherm parameters			Freundlich isotherm parameters		
RRM	K_L	a_L	R^2	k_F	b_F	R^2
AAC	0.6166	0.0076	0.9998	0.6075	0.2886	0.9388
POL	42.808	0.4473	0.9841	0.8347	3.2522	0.9281

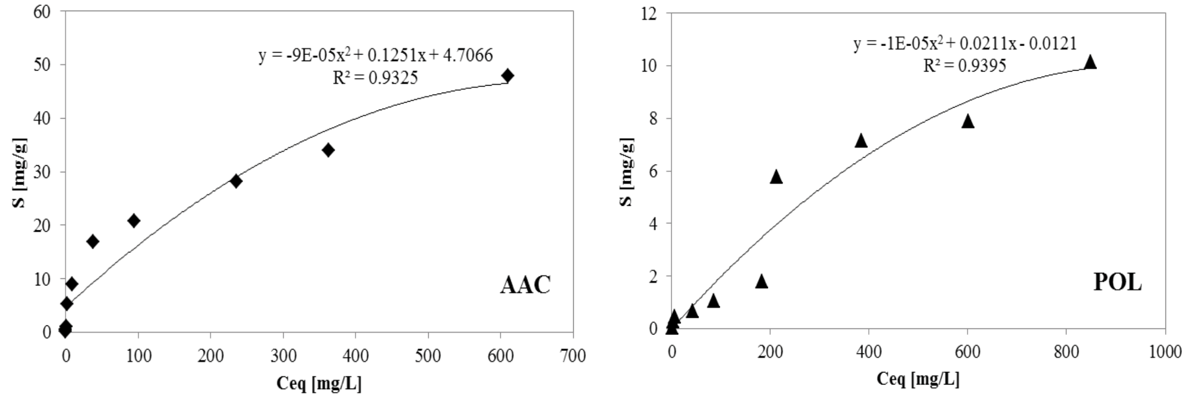

Fig. 3. Experimental data of AAC and POL isotherms.

gradient (*i*), and P–PO_4 concentration (*C*) in subsurface flow. Knowledge of *k* parameter of RM used in water treatment technologies such as PRB plays an important role for optimizing the retention of P–PO_4. This parameter and also chemical properties of RM determine the hydraulic capacity, which affect the treatment performance of the PRB system [31]. Maximum sorption capacity informs of the RM ability to sorb contamination. Assumed hydraulic gradient <0.005–0.02> means that PRB of 1 m width has a slope of 0.5%–2.0%. Also, the concentration of P–PO_4 in groundwater affect on PRB lifespan: the higher the value the shorter PRB lifespan.

The lifespan of tested RM with different scenarios of P–PO_4 concentrations in subsurface flow (0.1–5.0 mg L^{-1}) and hydraulic gradient (0.005–0.020) are presented in Fig. 4. For P–PO_4 groundwater concentration = 1.0 mg L^{-1}, the lifespan of POL PRB ranged from 77 to 19 y for hydraulic gradient of 0.005 and 0.020, respectively. In case of AAC PRB, the lifespan ranged from 27 to 7 y. Whereas, for maximum considered subsurface flow concentration = 5.0 mg L^{-1}, the lifespan ranged from 15 to 4 y and from 5 to 1 y for hydraulic gradient of 0.005 and 0.020, for POL and AAC PRBs, respectively. Also during previous study [21], both of tested RMs did not saturated during 90 d of column experiment with soil leaching that confirms the observations.

In case of tested RMs, the most affecting factor of the lifespan is bulk density. For tested materials, the difference between the bulk density differs over two times and also finds confirmation in the materials porosity (Table 1). Other factors such as: hydraulic conductivity (573 and 530 m d^{-1} for AAC and POL, respectively) and maximum sorption capacity (81.13 and 95.70 mg P–PO_4 g^{-1} for AAC and POL, respectively) are on similar level and do not affect the time of PRB lifespan. Thakur et al. [15] analyzing the factors influencing the lifespan of PRBs, lists the Darcie variables as a critical factors that must be taken into account. They recommend the leakage rates of groundwater less than 0.3 m d^{-1} for more favorable sorption condition. Thus, in case of tested RMs, the finer fraction of the material is recommended. Jóźwiakowski et al. [32] found out that for carbonate-siliceous rock the higher sorption properties were observed for finer fraction of material. It also influence on contact time of groundwater with RM that based on kinetic studies should be more than 300 min. On the other hand, it should be remembered that using finer fraction may lead to clogging the barrier.

Comparing our results with those obtained by McKey [19], a discrepancy between the estimated lifespan is seen. By the tested "worse-case scenario" (*C* = 10 mg P L^{-1}; *i* = 0.02) barrier filled with Manatee and Punta Gorda Al wastewater residuals (Al-WTRs) exhausted after around 34 and 120 y, respectively. However, this observation was not confirmed by monitoring of pilot scale or full scale PRB systems [4,12].

The limestone-based barrier placed at Zarzęcin, Poland was constructed to limit the transfer of P pollution from groundwater and storm water, which directly flows into the near reservoir. The barrier dimensions are: 1.5 m deep, 1.5 m wide, and 10 m long. It was filled with limestone of grain size 5–8 cm. The monitoring of work efficiency lasted 3.5 y. The average P–PO_4 removal during analyzed period was 12.4%. However, the highest removal (58.1%) was recorded in the first year of the operation. In the second year, there was no P–PO_4 reduction noted and even an increase in P–PO_4 concentration was observed (–6.5%). This may have been indicator of barrier saturation and the lowest P–PO_4 concentration noted during the observed period. On the other hand, in third and fourth year of operation, the barrier effectiveness increased to the level of 13.8% and 15.7%,

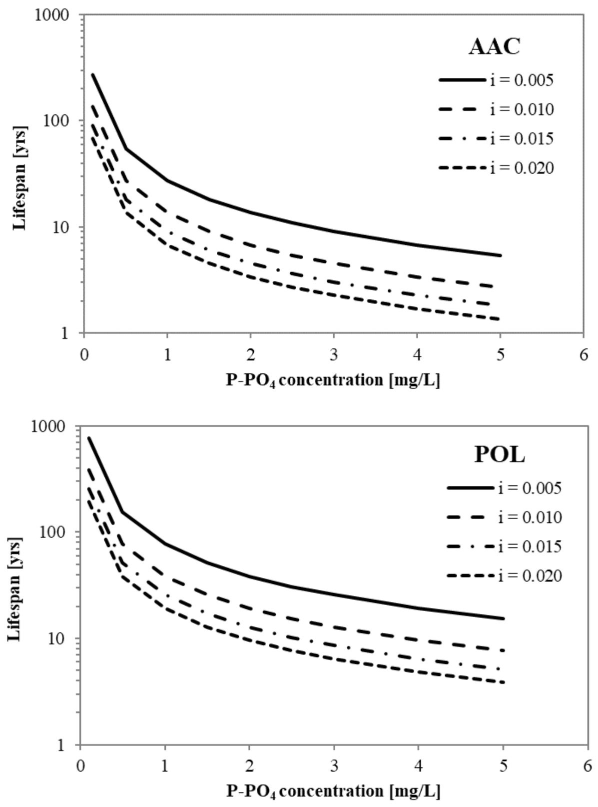

Fig. 4. Estimated lifespan for 1.0 m^3 volume of permeable reactive barrier for two tested RMs.

respectively that may be related to higher concentration than in second year [12]. Also, Kirkkala et al. [4] monitored full-scale PRB systems. One of them, filled with Fosfilt was placed in Imponoja, Finaland. The filtration area is: 10 × 20 m (volume 240 m^3) and retention time of 33 h. However, the filter stopped working for around 1.5 y and the probable reasons were: firstly, the percolation of water through the filter rapidly, secondly, clogging due to fine size of suspended solids, and thirdly, downward infiltration was restricted. What is more, after filter renovation it worked of a year and then percolation declined again. The second barrier was filled with lime, located in Mylly, Finland with filtration area of 5 × 15 m (volume 113 m^3) and retention time of 16 h. This barrier worked of 3.5 y and recorded the overall P–PO$_4$ reduction of 45%.

Considering the pilot scale and full scale PRB implementations, the results obtained by Miller et al. [20] seems to be overestimated. What is more, the presented results of P–PO$_4$ removal and lifespan efficiency, showed that the P retention at *in situ* conditions is sharply limited.

4. Conclusion

PRB filling by appropriately selected reactive materials seems to be a good way to limit P transport from agricultural areas to water bodies. The lifespan of barriers depends on sorption capacity of RMs and barrier water flow properties. In case of tested PRB RMs, the main factor that influence on lifespan is bulk density. For this reason, the lifespan of POL PRB is around 5 times longer than for AAC PRB. Generally, further studies should be performed based on obtained results for determination of optimum design condition of PRBs towards performance of in *in-situ* remediation applications.

References

[1] H. Bacelo, A.M. Pintor, S.C. Santos, R.A. Boaventura, C.M. Botelho, Performance and prospects of different adsorbents for phosphorus uptake and recovery from water, Chem. Eng. Technol., 381 (2020) 122566 (1–18), doi: 10.1016/j.cej.2019.122566.

[2] J. Łożyńska, A. Bańkowska-Sobczak, Z. Popek, J.A. Dunalska, Selection of P-reactive materials for treatment of hypolimnetic water withdrawn from eutrophic lakes, Ecohydrol. Hydrobiol., 20 (2020) 276–288.

[3] M. Kasprzyk, M. Gajewska, Phosphorus removal by application of natural and semi-natural materials for possible recovery according to assumptions of circular economy and closed circuit of P, Sci. Total Environ., 650 (2019) 249–256.

[4] T. Kirkkala, A.-M. Ventelä, M. Tarvainen, Fosfilt filters in an agricultural catchment: a long-term field-scale, Agric. Food Sci., 21 (2012) 237–246.

[5] O. Eljamal, I.P. Thompson, I. Maamoun, T. Shubair, K. Eljamal, K. Lueangwattanapong, Y. Sugihara, Investigating the design parameters for a permeable reactive barrier consisting of nanoscale zero-valent iron and bimetallic iron/copper for phosphate removal, J. Mol. Liq., 299 (2020) 112144, doi: 10.1016/j.molliq.2019.112144.

[6] D. Verheyen, N. Van Gaelen, B. Ronchi, O. Batelaan, E. Struyf, G. Govers, R. Merckx, J. Diels, Dissolved phosphorus transport from soil to surface water in catchments with different land use, Ambio, 44 (2015) 228–240.

[7] EC 2020, Commission Recommendation for Poland's CAP Strategic Plan. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52020SC0389 (accessed April 17, 2021).

[8] R. Thiruvenkatachari, S. Vigneswaran, R. Naidu, Permeable reactive barrier for groundwater remediation, J. Ind. Eng. Chem., 14 (2008) 145–156.

[9] A.H.A. Faisal, Z.T. Abd Ali, Groundwater protection from lead contamination using granular dead anaerobic sludge biosorbent as permeable reactive barrier, Desal. Water Treat., 57 (2016) 3891–3903.

[10] USEPA, Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA/600/R-98/125, United States Environmental Protection Agency, Washington, DC, 1998.

[11] S.J. Liu, Z.Y. Zhao, J. Li, J. Wang, Y. Qi, An anaerobic two-layer permeable reactive biobarrier for the remediation of nitrate-contaminated groundwater, Water Res., 47 (2013) 5977–5985.

[12] W. Frątczak, D. Michalska-Hejduk, M. Zalewski, K. Izydorczyk, Effective phosphorous reduction by a riparian plant buffer zone enhanced with a limestone-based barrier, Ecol. Eng., 130 (2019) 94–100.

[13] C. Penn, I. Chagas, A. Klimeski, G. Lyngsie, A review of phosphorus removal structures: how to assess and compare their performance, Water, 9 (2017) 583 (1–22), doi: 10.3390/w9080583.

[14] A. Safonov, N. Popova, N. Andrushenko, K. Boldyrev, N. Yushin, I. Zinicovscaia, Investigation of materials for reactive permeable barrier in removing cadmium and chromium(VI) from aquifer near a solid domestic waste landfill, Environ. Sci. Pollut. Res., 28 (2021) 4645–4659.

[15] A.K. Thakur, M. Vithanage, D. Das, M. Kumar, A review on design, material selection, mechanism, and modeling of permeable reactive materials for community-scale groundwater treatment, Environ. Technol. Innovation, 19 (2020) 100917 (1–20), doi: 10.1016/j.eti.2020.100917.

[16] PN-EN 1097-3:2000 Tests for Mechanical and Physical Properties of Aggregates. Determination of Loose Bulk Density and Voids (in Polish).

[17] PN-EN 1936:2010 Equivalent to EN 1936:2006 Natural Stone Test Methods. Determination of Real Density and Apparent Density, and of Total and Open Porosity (in Polish).

[18] Y.S. Ho, D. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[19] G. McKey, Use of Adsorbents for the Removal of Pollutants from Wastewater, CRC Press Inc., Tokyo, 1996.

[20] M.L. Miller, J.H. Bhadha, G.A. O'Connor, J.W. Jawitz, J. Mitchell, Aluminum water treatment residuals as permeable reactive barrier sorbents to reduce phosphorus losses, Chemosphere, 83 (2011) 978–983.

[21] A. Bus, A. Karczmarczyk, A. Baryła, Permeable reactive barriers for preventing water bodies from a phosphorus-polluted agricultural runoff-column experiment, Water, 11 (2019) 432 (1–13), doi: 10.3390/w11030432.

[22] A. Jamieson, C.A. Madramootoo, P. Enright, Phosphorus losses in surface and subsurface runoff from a snowmelt event on an agricultural field in Quebec, Can. Biosyst. Eng., 45 (2003) 1.1–1.7.

[23] A. Mittal, R. Singh, S. Chakma, G. Goel, Permeable reactive barrier technology for the remediation of groundwater contaminated with nitrate and phosphate resulted from pit-toilet leachate, J. Water Process Eng., 37 (2020) 101471, doi: 10.1016/j.jwpe.2020.101471.

[24] K. Riahi, S. Chaabane, B.B. Thayer, A kinetic modeling study of phosphate adsorption onto *Phoenix dactylifera* L. date palm fibers in batch mode, J. Saudi Chem. Soc., 21 (2013) 143–152.

[25] Y. Zhang, H. Li, Y. Zhang, F. Song, X. Cao, X. Lyu, Y. Zhang, C.J. Crittenden, Statistical optimization and batch studies on adsorption of phosphate using Al-eggshell, Adsorpt. Sci. Technol., 36 (2018) 999–1017.

[26] S.J. Allen, G. McKay, K.Y.H. Khader, Equilibrium adsorption isotherms for basic dyes onto lignite, J. Chem. Technol. Biotechnol., 45 (1989) 291–302.

[27] Z. Guo, J. Li, Z. Guo, Q. Guo, B. Zhu, Phosphorus removal from aqueous solution in parent and aluminum-modified eggshells: thermodynamics and kinetics, adsorption mechanism, and diffusion process, Environ. Sci. Pollut. Res., 24 (2017) 14525–14536.

[28] K. Kang, C.G. Lee, J.W. Choi, S.G. Hong, S.J. Park, Application of thermally treated crushed concrete granules for the removal of phosphate: a cheap adsorbent with high adsorption capacity, Water Air Soil Pollut., 228 (2017) 1–16.

[29] A. Bus, A. Karczmarczyk, Kinetic studies on removing phosphate from synthetic solution and river water by reactive material in a form of suspended reactive filters, Desal. Water Treat., 136 (2018) 237–244.

[30] N.Y. Mezenner, A. Bensmaili, Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste, Chem. Eng. J., 147 (2009) 87–96.

[31] E. Canga, B.V. Iversen, C. Kjaergaard, A simplified transfer function for estimating saturated hydraulic conductivity of porous drainage filters, Water Air Soil Pollut., 225 (2014) 1794 (1–13), doi: 10.1007/s11270-013-1794-8.

[32] K. Jóźwiakowski, M. Gajewska, A. Pytka, M. Marzec, M. Gizińska, A. Jucherski, A. Walczowski, M. Nastawny, A. Kamińska, S. Baran, Influence of the particle size of carbonate-siliceous rock on the efficiency of phosphorous removal from domestic wastewater, Ecol. Eng., 98 (2017) 290–296.