Removing phosphorus with Ca-Fe oxide granules – a possible wetlands filter material

Egle Saaremäe, Martin Liira, Morten Poolakese and Toomas Tamm

ABSTRACT

Phosphorus (P) is one of the nutrients causing eutrophication in many of our waterways. In the present study, we investigated Sachtofer PR Ca-Fe oxide granules as a potential P sorption material (PSM) for constructed wetlands. We found the P sorption with various experiments as follows: the 24 h batch experiment with the highest initial concentration of 50 mgP L^{-1} yielded 0.48 mgP g^{-1} P removal per mass unit, the kinetic P removal batch experiment of 600 h duration yielded 1.25 mgP g^{-1}, the maximum phosphorus adsorption capacity estimated from the Langmuir equation yielded 23.78 mgP g^{-1}, and the long term flow-through experiment with drainage ditch water yielded indicative saturated sorption of 1.4 mgP g^{-1}. Flow-through experiments revealed that phosphate removal was rapid and the efficiency was 10–70%, depending on the retention time and age of granules. Possible weaknesses of this material for sorption filter systems were found to include the loss of mass caused by the rapid dissolution of gypsum, increased sulfate and calcium concentrations in the water, and rapidly changing hydraulic conductivity. Considering hydraulic and chemical properties, further pilot experiments are necessary to develop technical solutions for optimal use of Ca-Fe oxide granules in sorption filter systems at constructed wetlands.

Key words | Ca-Fe oxide granules, constructed wetland, flow-through structure, phosphorus

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INTRODUCTION

A number of studies have revealed that reductions in the inputs of plant nutrients, mainly nitrogen (N) and phosphorus (P), are required for significant improvements of water quality in the Baltic Sea (e.g. Wulff *et al.* 2007; Conley *et al.* 2009). The largest contributors of nutrient loading to the Baltic Sea are diffuse loading from agriculture and municipal wastewater treatment plants, which account for over 90% of both N and P loading (HELCOM 2009). The European Water Framework Directive (2000/60/EEC) classifies the ecological status of water bodies as 'high', 'good' or 'poor' and aims to achieve 'good' status in all water bodies by the year 2015. Although the Estonian and EU regulations continue to improve Estonian wastewater quality, an enhanced effect would be achieved through a comprehensive approach targeting not only urban but also rural areas. Therefore, additional measures should be taken to lessen the diffuse nutrient loadings and ensure compliance

with the Water Framework Directive (Pachel *et al.* 2012). The reduction of nutrients from diffuse sources such as drained agricultural land is difficult to achieve, therefore eutrophication abatement measures such as constructed wetlands have been studied (e.g. Koskiaho *et al.* 2003). The potential of constructed wetlands to remove P is limited compared with their ability to remove N. In agricultural drainage waters, one possible solution is to use specific P removal structures and methods, e.g. constructed filters, in combination with suitable sorbents to sequester dissolved P from ditch flow (Penn *et al.* 2007, 2012). This enhancement is mainly due to adsorption and precipitation reactions with calcium (Ca), aluminum (Al) and iron (Fe) substrates (Gerrites 1993). Thus, the capacity and longevity of constructed wetlands are highly dependent on the nature of the materials used in their construction (Seo *et al.* 2005). The sorption of phosphorus is also controlled by other factors like redox

potential, pH, concentration of P in water and hydraulic retention time (Reddy *et al.* 1998).

Researchers have searched for efficient and long lasting filter materials addressing theoretical and practical aspects of P sorption capacity. For example, shellsand and Filtralite P were studied in Norway (Roseth 2000; Ádám *et al.* 2006; Herrmann *et al.* 2012); wollastone, serpentinite and electric arc furnace steel slag were tested in the USA (Brooks *et al.* 2000; Drizo *et al.* 2006); steel slag was investigated in New Zealand (McDowell *et al.* 2007; Pratt & Shilton 2009) and in the USA (Penn & McGrath 2011); zeolites were tested in Australia (Sakadevan & Bavor 1998); fly ash and bentonite were studied in China (Xu *et al.* 2006), and oil shale ash was tested in Estonia (Liira *et al.* 2009; Kõiv *et al.* 2010).

Ca-Fe oxide granules (Sachtofer PR, Pori, Finland), a co-product of titanium oxide production, was studied in laboratory experiments by Uusitalo *et al.* (2012) as a new potential phosphorus sorbing material (PSM). P retention was studied in flow-through columns with a vacuum extractor and the phosphate retention capacity was found to be 6–7 mg g^{-1}; in batch tests with 1 mg L^{-1} P solution, the phosphorus retention revealed 85% efficiency with 5 min contact time (Uusitalo *et al.* 2012).

Thus, the important criteria in selecting and comparing PSMs are P sorption capacity and sorption kinetics. Batch experiments are relatively easy and inexpensive methods to estimate the P sorption capacity of materials; such experiments are therefore commonly used as the criterion for material selection (Cucarella & Renman 2009). Several studies have used adsorption isotherms to test the retention of PSMs (Sakadevan & Bavor 1998; Drizo *et al.* 2002; Pratt & Shilton 2009). Batch tests provide preliminary rough estimations of the capacity of a PSM to retain P (Sakadevan & Bavor 1998), whereas small scale flow-through structures in laboratory conditions provide preliminary information for the design of on-site P removal structures and can be used to predict the lifetime of the materials (Drizo *et al.* 2002; Penn & McGrath 2011).

The aims of this research were: firstly, to study the P sorption properties of Ca-Fe oxide granules in standard batch isotherm experiments; and, secondly, to carry out flow-through column experiments to investigate the effects of retention time and P removal efficiency in different P concentrations. The latter experiment was conducted in field conditions using actual ditch water.

MATERIALS AND METHODS

Materials

In this study, Ca-Fe oxide granules (Sachtofer PR, Pori, Finland), which are co-products of titanium dioxide pigment and ferrous sulphate production, were tested for the sorption of phosphorus. The granules are made by mixing acidic ferrous sulphate, calcium oxide and water in a granulator. The material was supplied by the plant of Sachtleben Pigments Oy in Pori, Finland. According to the production certificate (Sachtofer 2011), the bulk density of the granules is 1.5 kg dm^{-3} and the pH is ranged 8–10.

The mineralogical composition of the Ca-Fe oxide granules was analyzed in this study by means of powder X-ray diffraction. The samples were ground with an agate mortar and pestle to the maximum particle size of about 5 μm; unoriented preparations were made. The powdered preparations were measured on a Bruker D8 diffractometer using Ni-filtered CuKα radiation over 2–70° 2θ region, with a scan step of 0.02° 2θ and a count time of 2 s per step. The semi-quantitative mineral composition was found by full-profile Rietveld analysis using the Siroquant^{TM} code (Taylor 1991). The chemical composition of the material was determined using X-ray fluorescence (XRF) spectroscopy analysis.

Batch experiments

All the batch experiments were carried out in sealed glass containers at room temperature (22 °C) using artificial phosphorus solution made by dissolving potassium dihydrogen phosphate (KH_2PO_4) in distilled water. The initial ratio of P solution to mass of material was 25:1, which corresponds to 500 mL of the P solution and 20 g of material. The batch experiments lasted for 24 h and were continuously shaken with 50 rpm to guarantee sufficient contact between solution and media, while preventing break-up of the material (Drizo *et al.* 2002; Cucarella & Renman 2009).

In the batch test, six different P concentrations were used ranging from 0.05 to 1 mgP L^{-1} in order to simulate the expected P concentration in natural stream. Also, to estimate maximum removal efficiency in equilibrium conditions, a batch test with a P concentration of 50 mgP L^{-1} was used. The initial unreacted material was used in the experiments without any kind of pre-treatment (e.g. sieving) in order to simulate the probable situation in real systems. As stated by Drizo *et al.* (1999), in a batch experiment, the material should be used in the same form as is expected to be used in field conditions.

The kinetic absorption experiment was conducted for a total period of 600 h, using an initial P concentration of 50 mgP L^{-1}. During the experiment, six sub-samples from the P solution were taken.

The phosphorus concentration in solutions of batch experiments was measured with a Hach Lange spectrometer DR/2400 according to method 8190 (PhosVer®3) accepted by the US EPA (United States Environmental Protection Agency) for the reporting of wastewater analyses. Test results are measured at 890 nm wavelength, and the results obtained are in mgP L^{-1}. The water samples were filtrated with 0.45 μm syringe filters *in situ* before measurements. After the experiment, all the water samples were measured with the ion chromatograph Dionex-1000 to identify possible dissolved ion complexes. The same equipment was also used for analyzing the chemical composition of the ditch water.

Data on P removal and equilibrium P concentration obtained from the experiment were fitted with the Langmuir and Freundlich isotherm equations. In particular, the Langmuir equation is broadly used in this field, because it has the advantage to give an estimate of the maximum P removal capacity. The mathematical expression for the Langmuir equation is (Olsen & Watanabe 1957):

$$q_e = (QbC_e)/(1 + bC_e) \tag{1}$$

where C_e is the equilibrium adsorbate concentration (mg L^{-1}), q_e the mass of adsorbate per mass unit of adsorbent at equilibrium (mg g^{-1}), Q the maximum mass adsorbed at saturation conditions per mass unit of adsorbent (mg g^{-1}), b the empirical constant with units of inverse of concentration. The Langmuir equation allows one to estimate the

maximum adsorption, Q, and the constant, b, which represents the inverse of the adsorbate at one-half saturation and therefore gives a measure of the affinity of the adsorbate for the adsorbent. The Freundlich equation in the form of (Barrow 1983) is:

$$q_e = K_F C_e^{1/n} \tag{2}$$

where q_e and C_e have the same meaning as in the Langmuir equation, and K_F and n are constants, whereas the index $1/n$ is adsorption intensity and K_F can be related to the surface energy of the adsorbent.

The Langmuir equation is valid for single-layer adsorption and assumes maximum adsorption corresponding to a saturated monolayer of adsorbate molecules on the surface of the adsorbents, where the energy of adsorption is considered to be constant and the Freundlich equation often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction, and it also incorporates the heterogeneous surface energy in which the energy term b in the previous Langmuir equation varies as a function of surface coverage due to the heat of adsorption (Barrer 1978).

Flow-through experiments

Short term flow-through experiments with drainage ditch water were conducted at the Rahinge ditch in southern Estonia to reveal the effect of retention time and variable P concentration on removal efficiency. One flow-through column was left in the ditch for several days to get an indicative value for P sorption capacity.

The catchment of Rahinge ditch covers an area of 7 km^2. The water quality of Rahinge ditch was monitored for one year. The total phosphorus and phosphate concentration ranged from 0.08 to 1.2 mg L^{-1} and 0.08 to 1.03 mgP L^{-1}, respectively, indicating a significant level of pollution and corresponding to 'poor' ecological status classification. The full chemical analysis of ditch water also revealed a high concentration of nitrates, i.e. 19.92 mg L^{-1}, and other chemical compounds (in mg L^{-1}): sodium – 14.43; potassium – 3.66; magnesium – 30.99; calcium – 347.10; fluoride

– 0.26; chloride – 26.76; sulfate – 70.61 in spring conditions. Thus, it is an appropriate site to implement active measures to reach 'good' ecological status. In fact, assessing the monitoring results together with the national database of stream water quality, we found that potential problems may exist in smaller bodies of water near large farms and areas of very intensive farming, whereas water quality can usually be observed to improve in areas with larger streams and rivers.

The flow-through column was constructed from PVC tube with an inside diameter of 10.4 cm. Three kilograms of granules were placed into the column, forming an initial granule depth of 31 cm. The ditch water was pumped up to the top of the column, and the effluent flow rate was regulated with a valve to achieve variable retention time.

The retention time was based on measured effluent flow using the following equation:

$$T = \frac{\pi r^2 h \varphi}{Q_{ave}} \tag{3}$$

where T is the retention time (min), Q_{ave} is the average measured flow rate (L s^{-1}), r is the radius of the column (cm), h is the height of the granules in the column (cm), φ is the porosity of the granules.

Before the measurements started, the column was run for approximately 15 min to flush away the dust fraction of the Ca-Fe oxide granules. The flow rates were measured using the volumetric method and were first varied from high flow to low flow rates. Next, flow rates were varied from low to high, to achieve variable flow rates in the column experiments. To receive the removal efficiency in different influent P concentrations the experiment was conducted three times throughout the summer season in 2012. On the experiment dates, the P concentrations of the ditch water were 0.2, 0.47 and 1.03 mgP L^{-1}, respectively. Effluent and influent water samples were analyzed for soluble reactive phosphate using the ascorbic acid method.

To study the long term possible decrease of the hydraulic conductivity through the layer of granules, a laboratory flow-through column was constructed, where 1 kg of granules was placed into the column, forming an initial filter layer of 24 cm, which was gravity-fed continuously from the top with a constant head of 6.5 cm. The experiment lasted for 22 days. The hydraulic conductivity was determined in this experiment by Darcy's law with the constant head method:

$$K_S = \frac{Q \, dl}{A \, t \, dh} \tag{4}$$

where A is cross-sectional area of permeameter (cm), Q is volume of discharge (dm^3), l is length of specimen (cm), h is hydraulic head difference across length l, in cm of water, t is the time for discharge (s).

RESULTS AND DISCUSSION

Characterization

The chemical composition of granules shows Ca and Fe content of approximately 19 and 10%, respectively (Table 1). The content of S is about 12%. The concentration of other compounds in the Ca-Fe oxide granules is presented in Table 1.

The mineralogical composition of the granules (Table 2) is dominated by gypsum ($CaSO_4 \cdot 2H_2O$), which accounts for more than 90% of the granule mass. Minor amounts of iron oxides (magnetite – Fe_3O_4, maghemite – Fe_2O_3) and also some traces of anhydrite ($CaSO_4$) and calcite ($CaCO_3$) are present.

Table 1 | Chemical composition of initial Ca-Fe oxide granules in mass percentages (mass %)

Compounds	Ca-Fe oxide granules (%)	Compounds	Ca-Fe oxide granules (%)
Na$_2$O	0.505	CaO	26.81
MgO	1.85	TiO$_2$	4.40
Al$_2$O3	0.99	V$_2$O$_5$	0.42
SiO$_2$	0.84	Cr$_2$O$_3$	0.17
P$_2$O$_5$	0.017	MnO	0.56
SO$_3$	31.68	Fe$_2$O$_3$	13.95
Cl	0.025	NiO	0.014
K$_2$O	0.133	ZnO	0.03
		Balance[a]	17.59

[a]Corresponds to elements lighter than F.

Table 2 │ Mineralogical composition of initial Ca-Fe oxide granules

Phase	Weight%	Error of fit
Gypsum ($CaSO_4 \cdot 2H_2O$)	91.3	0.8
Calcite ($CaCO_3$)	2.3	0.7
Magnetite (Fe_3O_4)	1.8	0.2
Maghemite (Fe_2O_3)	3.1	0.2
Anhydrite ($CaSO_4$)	0.7	0.3

Batch experiments

The results of the P removal experiments are shown in Figure 1 and Table 3. The results reveal that the phosphorus removal was between 0.0013 to 0.4763 $mgP\,g^{-1}$ (corresponding to removal efficiency ranging between 38 and
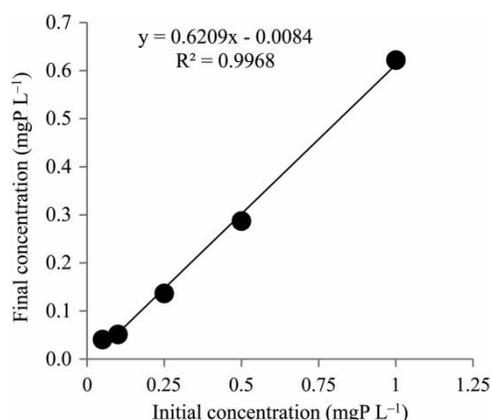

Figure 1 │ Phosphorus removal with different initial concentration in batch experiments. The data are fitted with an illustrative linear trendline (the result with initial concentration 50 $mgP\,L^{-1}$ is excluded from this figure to permit a better overview).

Table 3 │ Phosphorus removal with different initial concentration in batch experiments

Initial concentration $mgP\,L^{-1}$	Final concentration $mgP\,L^{-1}$	P removal %	P removal $mgP\,g^{-1}$
0.05	0.04	20	0.0003
0.1	0.05	50	0.0013
0.25	0.14	44	0.0028
0.5	0.29	42	0.0053
1	0.62	38	0.0095
50	30.95	38	0.4763

50%) in the batch experiments with initial concentrations higher than 0.1 $mgP\,L^{-1}$. In experiments with the lowest initial concentration, 0.05 $mgP\,L^{-1}$, removal was found to be 0.0003 $mgP\,g^{-1}$ (20% removal efficiency). Removal efficiency below 50% is considered to be insufficient for efficient removal of the P in real systems (Liira *et al.* 2009). In the given experimental conditions, a P sorption value of 0.48 $mgP\,g^{-1}$ was achieved with an initial concentration of 50 $mgP\,L^{-1}$ after 24 hours. However, Figure 1 reveals that different initial P loadings (between 0.05 and 1 $mgP\,L^{-1}$) do not affect the overall removal efficiency ($R^2 = 0.9968$) and the slope of the linear trendline remains the same even if the highest P concentration (50 $mgP\,L^{-1}$) would be included. This indicates that 24 h was not sufficient to reach maximum P sorption capacity. It can be noted that such a high concentration is not representative of natural drainage ditches.

The kinetic P removal experiment results are shown in Figure 2. The kinetic P removal experiment was conducted for a period of 600 hours. By the end of the experiment, practically all of the P from the initial solution (50 $mg\,L^{-1}$) was removed which corresponds to the final adsorption up to 1.25 $mgP\,g^{-1}$. Moreover, removal efficiency of 98% was achieved after 216 hours, indicating that in the given batch experiment conditions, the removal of the P from the solution takes more than 24 hours. These results obtained for P removal differ from those of Uusitalo *et al.* (2012), who found that sorption reactions proceed rapidly when applying agitation at 120 rpm with initial concentrations of 1 and
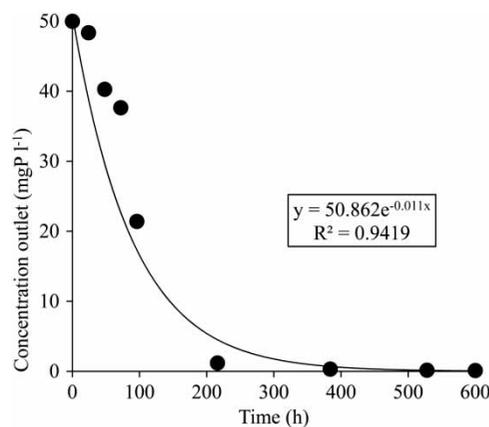

Figure 2 │ The kinetic P removal experiment of duration 600 h. The data are fitted with an illustrative exponential trendline.

10 mgP L^{-1}. Oguz (2004) reported that the diffusion of phosphate ions from the solution to the surface of adsorbent and into the pores improves with increased agitation rate.

The experimental data on P removal and equilibrium P concentration were fitted with the Langmuir and Freundlich isotherm equations (Table 4). The equilibrium data in the P removal batch experiments suggest that the adsorption mechanism determines the P binding in the material and therefore can be considered as a main mechanism for P removal with Ca-Fe oxide granules. Using both the Langmuir and Freundlich equations, good correlation is observed ($R^2 > 0.98$). However, the theoretical maximum P adsorption capacity estimated from the Langmuir equation ($Q = 23.78 \text{ mgP g}^{-1}$) is much higher than the maximum removal per mass unit measured in batch experiments. Several earlier authors (Barrow 1978; Arias *et al.* 2001; Drizo *et al.* 2002) have indicated that the Langmuir model tends to overestimate the maximum adsorption capacity.

Interestingly, after the batch experiment, only 16 g of material were collected compared to the 20 g of material at the beginning of the experiment, which corresponds to 20% of mass loss. In the as-received state, 90% of Ca-Fe oxide granules have particle size greater than 1 mm

(Uusitalo *et al.* 2012), but visual observation after the batch experiment showed breakdown of most of the granules, resulting in large numbers of small Ca-Fe oxide particles. Some of these newly created small particles could still be sorbing P, but at the same time being very volatile and capable of passing through 0.45 μm syringe filters, thus leading to higher P concentrations in the measured samples.

After the batch experiment, all the water samples were measured to identify possible dissolved ion complexes. The results show (Table 5) increased concentrations in major cation complexes such as calcium and sodium. The most significant increase was in sulfate concentration, where a maximum concentration of 1020 mg L^{-1} was achieved. The increase in sulfate and calcium concentrations indicates the rapid dissolution of gypsum ($CaSO_4 \cdot 2H_2O$).

Sulfate occurs naturally in all waters and is difficult to remove by treatment. It is possible that use of Ca-Fe oxide granules for P removal in large quantities and/or in large areas may lead to elevated concentrations of the sulfate, which has potential for ecological impact to the surroundings and could be taken into account when designing real scale constructed wetlands.

Flow-through column experiment

Flow-through experiments of several hours duration were conducted at the Rahinge ditch, on an as-needed basis, determined by the water quality monitoring data. When considerable changes in water quality were noted, the experimental column was set up and the flow-through columns were gravity fed with pumped stream water. The experiment was performed using varying flow rates, first diminishing from maximum to minimum, and thereafter increasing again to the maximum. Due to technical reasons

Table 4 │ Fitting of the Langmuir and Freundlich equations for phosphorus adsorption by Ca-Fe oxide granules

Equation	Parameter	Ca-Fe oxide granule
Langmuir	R^2	0.989
	Q	23.78
	b	1.08
Freundlich	R^2	0.997
	K_F	0.02
	N	1.07

Table 5 │ Major ion complexes dissolved from Ca-Fe oxide granules after batch test with different P initial concentrations. Results are shown in mg L^{-1} (n.a. – below detection limit)

P initial (mgP L^{-1})	Fluoride	Bromide	Nitrate	Sulfate	Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
0.05	0.02	0.03	0.24	890.7	0.03	126.12	n.a.	23.5	16.33	180.82
0.1	0.04	0.31	0.35	820.28	0.04	124.75	n.a.	23.85	17.61	156.93
0.25	0.09	n.a.	0.43	947.74	0.03	134.76	n.a.	26.07	21.83	195.81
0.5	0.05	n.a.	0.35	1020.67	0.03	146.89	n.a.	27.8	21.07	197.24
1	n.a.	n.a.	0.26	912.9	0.02	130.04	0.22	26.23	20.63	169.59
50	0.02	n.a.	1.11	971.73	0.06	144.1	1.43	93.19	21.57	182.39

it was not possible to repeat exact flow rates. Figure 3 describes the general tendency that the removal efficiency was slightly lower at the end of the experiment with high flow rate, revealing that the P sorption properties slightly changed during the experiment.

In the flow-through experiments, it was observed that fresh Ca-Fe oxide granules (used only for a relatively short time) resulted in good retention efficiency and quite rapid P retention with ditch water, where retention time of less than 2 min was sufficient for removal of over 50% of the phosphate with all tested concentrations naturally occurring at the drainage ditch water: 0.2, 0.47, 1.03 mgP L^{-1} (Figure 4). The selected concentrations represent the typical values at Rahinge ditch water. The rapid retention can be
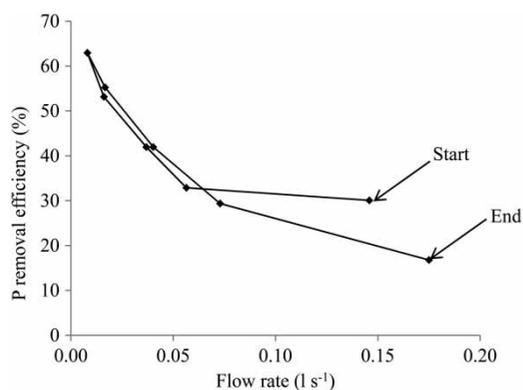
explained by sorption mechanism kinetics. Sorption is described as a two step process in which a rapid initial adsorption by ligand exchange with surface OH groups is followed by a slower diffusion through pores (Parfitt 1989). For example, Luengo *et al.* (2006) found that the rapid first stage of phosphate adsorption on goethite takes place over a few minutes. In our work, the results followed a similar removal trend. We found that P removal efficiency increased with longer retention time, but the increase was highly non-linear (Figure 4). It was found that the inflow P concentrations did not reveal a significant impact on P removal efficiency at tested P concentrations. In the case of high P inlet initial concentrations, calcium ions resulting from gypsum dissolution may induce phosphate precipitation, as suggested by Bastin *et al.* (1999) in the P removal experiment with the synthetic iron oxide – gypsum compound 'OX compound' (composition: gypsum ($CaSO_4 \cdot 2H_2O$); ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$)).

The removal efficiency of Ca-Fe oxide granules is found to diminish when the available adsorption sites become filled. When we used Ca-Fe oxide granules which had already been exposed to 600 liters of ditch water, the retention efficiency was lower compared with fresh granules, particularly at longer retention times (Figure 5).

One column was left in the ditch for several days to get an indicative value for sorption capacity in field conditions. The influent and effluent concentrations were measured on
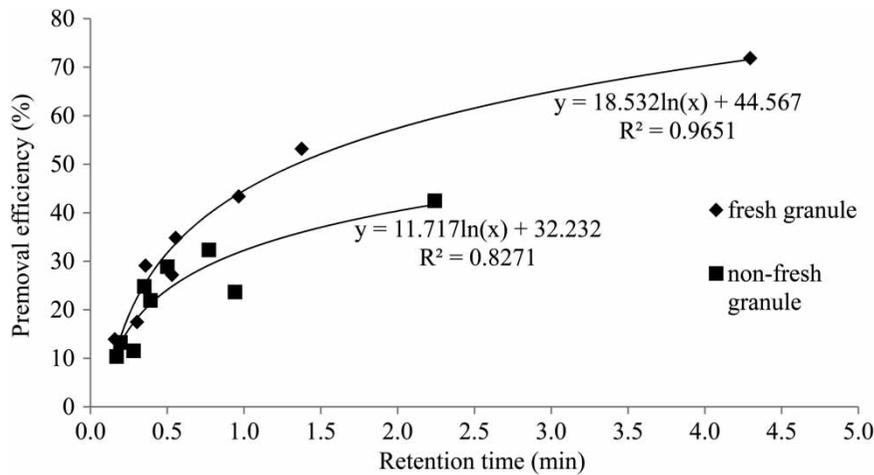

Figure 3 | Smpling scheme of the flow-through experiment (0.47 mgP L^{-1}).
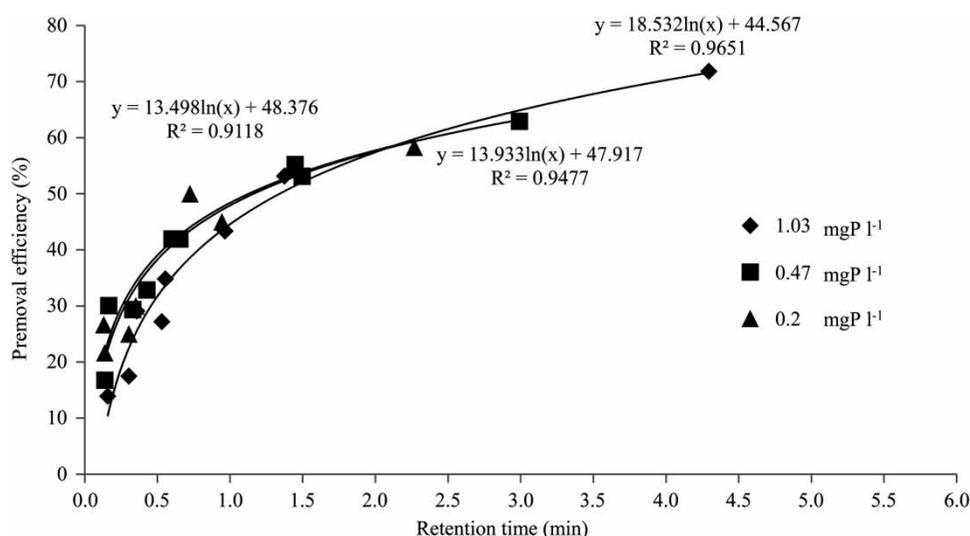
Figure 4 | Relationship between P removal efficiency (%) and retention time (min).

Figure 5 | Relationship between P removal efficiency (%) and retention time (min) of the fresh and non-fresh granules in P solution 1.03 and 1.13 mgP L^{-1}, respectively.

the first, fifth and seventh day. The influent concentrations were highly variable during the experiment (from 0.95 to 2 mgP L^{-1}). On the seventh day, the influent and effluent concentrations were similar, implying that the granules could no longer efficiently remove P. The amount of P retained by the granules was 1.4 mgP g^{-1} after 7 days, determining with XRF spectroscopy analysis. It should be emphasized that in this experiment we exposed the granules to relatively high P concentration.

We found that P removal results between batch and column experiments varied in our study. These results are not directly comparable due to the differences in chemical composition of solution (distilled water vs natural water), material to solution ratio, agitation, differences in effluent concentrations and contact time. The results from column experiments are in good correlation with previous studies conducted by Uusitalo et al. (2012), where granules showed similar rapid P retention. Batch tests are widely used to make a first estimate of the P retention of the material (Cucarella & Renman 2009; Klimeski et al. 2012), however results are often found to be noncomparable and misleading (Drizo et al. 2002). The discrepancies between laboratory and field results have been reported, in some cases it was found that batch experiments underestimated the adsorption capacity (Pratt & Shilton 2009), but overestimated in other cases (Arias et al. 2001; Drizo et al. 2002; Ádám et al. 2006). Pratt & Shilton (2009) reported similar findings when comparing the P adsorption capacity in laboratory scale batch tests and field scale experiments on melter

slag. The results showed an inconsistency of two orders of magnitude between the laboratory and field results. The observed increase in P removal in field scale experiments was due to the weathering effect, which generated new adsorption sites.

In our study, the Langmuir model poorly predicted the performance of pilot-scale P removal efficiency, which is in accordance with Penn & McGrath (2011).

Long term flow-through column experiment

The effects of long term structural stability of Ca-Fe oxide granules and granulometric fractional changes on hydraulic conductivity were tested in the long term flow-through experiment.

It was found that the hydraulic conductivity diminished significantly over time, due to the break down of the Ca-Fe oxide granules (Figure 6). The most rapid change occurred during the first 24 hours, when hydraulic conductivity decreased from 1.87 to 0.23 m d^{-1}. The final hydraulic conductivity value of 0.003 m d^{-1} after 528 experimental hours was more similar to clay soils rather than granulated media. This result is inconsistent with the aim of the filter materials to have steady properties during the lifetime of the filter system. The large decrease in the hydraulic conductivity of granules was due to gradual loss of their granulometric structure. Also, the 20% mass loss in batch tests suggests changes in the original structure of granules, i.e. further
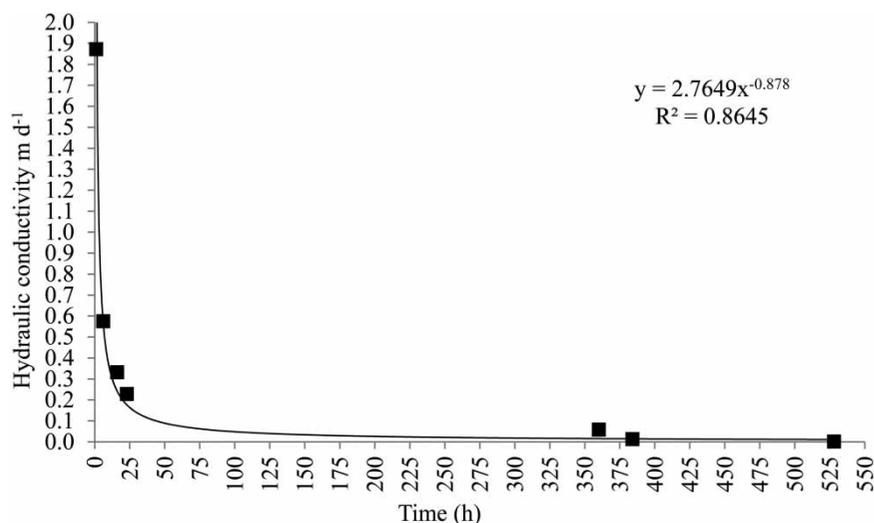
$$y = 2.7649x^{-0.878}$$
$$R^2 = 0.8645$$

Figure 6 | Hydraulic conductivity measured in the column experiment over 22 days.

developments are needed to improve the stability of the granules.

A key consideration in the design of appropriate filter systems to be used in constructed wetlands is achieving the ideal balance between maximum P sorption and hydraulic conductivity. Low hydraulic conductivity limits the treatment of large amounts of runoff water, resulting in retention times and reduced treatment efficiencies (Penn & McGrath 2011) and may cause clogging in the filter material (Chardon *et al.* 2012).

CONCLUSION

The potential of constructed wetlands to remove phosphorus can be enhanced with filter systems using PSMs. For this study, Sachtofer PR Ca-Fe oxide granules were selected due to their possible practical potential. Ca-Fe oxide granules are not a thoroughly studied PSM, and at the time of our experiments, only one published study was available. Therefore, we investigated the behavior of Ca-Fe oxide granules under various conditions.

Experiments were carried out based on different designs and scales, performed at laboratory and field sites. The short term flow-through column experiments revealed that Ca-Fe oxide granules bound P rapidly in a few minutes. Our batch experiments underestimated P sorption capacity and may not be a suitable method for the estimation of P removal efficiency in this type of material. It was found that the Langmuir equation overestimated the sorption capacity for these materials ($23.78 \, mgP \, g^{-1}$). The flow-through approach is analogous to real scale systems and was found to be the most reliable method to design the P removal structures. After 7 days the field experiment revealed a sorption capacity of $1.4 \, mgP \, g^{-1}$. Both retention time and the age (i.e. saturation) of the granules had an important impact on the Ca-Fe oxide granules filters. Within certain limits, we found that Ca-Fe oxide granules were effective in removing soluble P from the water.

However, we also found some concerns for the use of this particular material. Under certain conditions, one concern was the loss of mass caused by the rapid dissolution of gypsum, and increased sulfate and calcium concentrations in the water, indicating the rapid dissolution of gypsum. Secondly, during the downward flow-through column experiment, hydraulic conductivity diminished rapidly (particularly in the first 24 h); this may also limit the usage of Ca-Fe oxide granules in some cases.

Considering the hydraulic aspects (i.e. hydraulic conductivity, flow rate and retention time) together with the chemical properties of sorption material, we determined that further pilot scale experiments are necessary to develop new technical solutions.

In conclusion, the Sachtofer Ca-Fe oxide granules could be used as a PSM in constructed wetlands under some specific conditions, while taking into account hydraulic aspects (i.e. changes in hydraulic conductivity, flow rate and retention time) together with the chemical properties of the granules. Further studies are needed to assess the prospects for implementing this material in real-scale constructed wetlands.

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