Adsorption of phosphate on iron-coated sand granules as a robust end-of-pipe purification strategy in the horticulture sector

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Highlights:

- Low-cost iron-coated sand (ICS) sorbent was successfully applied to remove phosphate from greenhouse effluent
- The adsorption capacity of ICS was enhanced by introducing intermediate resting periods
- The design and operating management of the pilot filter bed needs optimization to extend the service time until breakthrough
- Possibilities for phosphate recovery are offered by developing an efficient desorption

Keywords: Iron coated sand; phosphate; adsorption; greenhouse effluent

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ABSTRACT

Nutrient enrichment in water bodies, and its detrimental consequences, are a well known and worldwide environmental problem. Agricultural activities are identified as an important source of diffuse losses of phosphate and nitrate because of the leaching out fertilizers from agricultural fields. This study encompasses the implementation of an end-of-pipe treatment by capturing phosphate from greenhouse effluent, using granular iron-coated sand (ICS) in an adsorption process. ICS is evaluated as a low-cost by-product because of its adsorption capacity and kinetics. The Langmuir isotherm was suitable for describing the adsorption thermodynamics. The adsorption capacity at an equilibrium concentration C_e of 25 mg $\text{PO}_4\text{-P/L}$ ranged between 1.85 and 3.07 mg $\text{PO}_4\text{-P/g}$ sorbent. Furthermore, both the pseudo-second-order model ($R^2 = 0.9823$) and the Elovich model ($R^2 = 0.9803$) showed a good fit with the kinetic data over the time range investigated, indicating that chemisorption is the rate-limiting step controlling the adsorption process. Higher adsorption capacities were observed at lower initial pH. Continuous bench-scale column experiments were performed to verify the adsorption potential of a filter bed under flow-through conditions, and the experimental data were fit to the Bohart-Adams model. Additionally, a discontinuous feeding regime of the column, resulting in intermediate resting periods, was introduced and showed an enhanced adsorption efficiency over a longer period. Finally, a pilot-scale experiment showed the potential of the ICS for the removal of phosphate from greenhouse effluent. The adsorption process, moreover, enables the recovery of phosphate via efficient desorption.

1 Introduction

The agricultural use of fertilizers has been a significant source of nitrate and phosphate pollution in Europe. In the horticultural sector, good farming practices for fertigation and measures to limit these losses were already implemented (Thompson et al., 2018). For example, irrigation water, so-called “drain water” is collected and reused. Nevertheless, drain water is still discharged when ballast materials accumulate, the drain buffer overflows, or the disease pressure and risks of growth inhibition or crop damage increase (Berckmoes et al., 2013). Nutrient losses not only originate from drain water that is no longer reusable for crop irrigation but also cleaning water of the irrigation system and nutrient-rich rinsing water of sand filters are considered as greenhouse effluent. The effluent of horticulture activities typically contains high concentrations of both nitrate and phosphate. Park et al. (2009, 2008) determined nitrate and phosphate concentrations of 325 mg $\text{NO}_3\text{-N/L}$ and 29.4 mg $\text{PO}_4\text{-P/L}$, respectively. Gagnon et al. (2010) assumed an average nutrient content of 225 mg $\text{NO}_3\text{-N/L}$ and 57 mg $\text{PO}_4\text{-P/L}$. Compared to drainage water originating from tile-drained agricultural fields, containing concentrations up to 5 mg $\text{PO}_4\text{-P/L}$ and 28.3 mg $\text{NO}_3\text{-N/L}$ (Saadat et al., 2018; Vandermoere et al., 2018), the nutrient concentrations in greenhouse effluent are significantly higher. The annual effluent volume produced by a greenhouse highly depends on the irrigation/fertigation process and the technologies used to improve the quality of the water being introduced into the fertigation system (Thompson et al., 2018). Values between two to several hundred cubic metres of water per ha of greenhouse surface are reported (Berckmoes et al., 2013). In a study on the environmental impact of these high concentrations, an annual emission of 1300 tons of N and 200 tons of P from soilless cultivation, i.e., crop cultivation using different growth substrates other than soil and or aerated nutrient solutions, in the Netherlands was estimated (Beerling et al., 2014).

In most cases, effluents are emitted to surface waters without further purification, leading to a correlation between the presence of greenhouses in a specific region and exceedances of nitrate and phosphate standards in surface water (Morin et al., 2017; Thompson et al., 2018). Consequentially, the

71 discharge of nutrient-rich effluent results in eutrophication of the surface water close to the
72 greenhouses.

73 In the framework of the FERTINNOWA project, a survey on the irrigation and fertigation management
74 of farms in the main EU horticultural production countries was performed (Lechevallier et al., 2018).
75 On the question “is the drain water treated before discharge?”, 67% of the respondents with soilless
76 crops was willing to answer, and 95% of them did not treat the drain water before discharging it.
77 Despite efforts done on limiting and optimizing the use of fertilizers the desired impact of lowering
78 effluent concentrations is not obtained, necessitating end-of-pipe treatments to improve the quality
79 of greenhouse effluent to an acceptable range.

80 Because of their complexity and limited efficiency, combined with the typical low water volumes to be
81 processed in horticulture, purification systems based on biological phosphate removal are not
82 applicable in practice. Small-scale applications most frequently employ metal salt dosing to precipitate
83 ortho-phosphate, followed by removing the formed precipitate via sedimentation. A significant
84 drawback of this physicochemical treatment technique is the sensitivity metal salt dosage towards
85 influent $\text{PO}_4\text{-P}$ concentration, which leads in many cases to overdosage of the metal salt or requires an
86 expensive online total phosphate measuring device (Moelants et al., 2011).

87 Adsorption processes, on the other hand, enable a fast phosphate immobilization and require less
88 post-processing (Groenenberg et al., 2013). In recent years, several low-cost and readily available
89 sorbents have been examined for phosphate removal (see Table S-1). Mezenner and Bensmaili (2009)
90 investigated waste iron hydroxide-eggshells formed during the deferrization of industrial wastewater
91 and identified that calcium present in the eggshells enhanced phosphate removal. The adsorption
92 kinetics were found to fit best with the pseudo-second-order model, suggesting chemisorption is the
93 primary sorption mechanism. The mechanism of chemisorption was also observed by Lalley et al.
94 (2016) when using (modified) Bayoxide sorbents for the removal of phosphate from lake water. The
95 potential of industrial waste iron oxide tailings for phosphate removal from wastewater was

investigated by Zeng et al. (2004). The strong bond between phosphate ions and iron oxide in the tailings was demonstrated resulting in a difficult desorption. Another iron-based sorbent material, i.e., granular ferric hydroxide, showed an adsorption capacity in the range of 10 to 12 mg PO₄-P/g sorbent at initial concentrations of 1 mg PO₄-P/L and varying the solid to liquid ratio from 1/50 to 1/1.25 (Sperlich et al., 2010). A higher adsorption capacity of 20 mg PO₄-P/g sorbent was observed by Agyei et al. (2002) and Moelants et al. (2011) for the slag by-product of pig iron manufacturing in a blast furnace and iron coated sand (ICS), respectively. Agyei et al. (2002) obtained the adsorption capacity by performing a breakthrough experiment ($C_0 = 130$ mg PO₄-P/L; 5 g sorbent; contact time = 16 min) while batch experiments ($C_0 = 0-2200$ mg PO₄-P/L; solid to liquid ratio = 1/2) were performed by Moelants et al. (2011). By blending the slag with ordinary Portland cement, Agyei et al. (2002) successfully increased the adsorption capacity up to 27 mg PO₄-P/g sorbent. To date, extensive research is performed to develop materials for the efficient and cost-effective removal of phosphate, as proven by the review of Liu et al. (2018). However, only marginal attention has been paid on the functional performance of sorbents in a real-scale context.

The main goal of this study is to demonstrate the applicability of iron coated sand (ICS) as a low-cost phosphate sorption material to treat nutrient-rich greenhouse effluent. The ICS granules are derived from rapid sand filters used for the deferrization in the production of drinking water from groundwater. During the quick sand filtration process, the granule is formed through the adsorption of Fe(II) onto the sand core, and in the presence of oxygen the adsorbed Fe(II) is in situ oxidized to Fe(III). In this way, a deposition of Fe(III) compounds occurs onto the sand core, which steadily grows to a full-grown granule with a diameter of a few millimeters. The granule diameter will thus increase with time, resulting in an increasing height of the sand bed. Periodically, part of the granules has to be removed from the sand bed and are discharged as solid material (Van Beek et al., 2016).

Both batch experiments and small-scale column tests will be carried out to identify the adsorption equilibria and kinetics, and the maximum adsorption capacity of the sorbent. The experimental results

will further be used to calculate breakthrough times of ICS adsorption filters and to assess the feasibility of ICS as a sorbent at relevant scale. The results will be validated by a 160 day pilot scale adsorption column experiment, using 60 kg sorbent and processing 200 L real greenhouse effluent per day. During this test particular attention will be paid to the management of the phosphate filter.

2 Materials and Methods

2.1 Sorbent material

ICS granules are a by-product originating from the deferrization of ground water during drinking water production (Van Beek et al., 2016). The ICS granules used in this study were obtained from the drinking water production facilities of PIDPA (a drinking water company in Flanders - Belgium) in Balen, Grobbendonk, Herentals and Mol. Before use, all ICS samples were pre-dried for 48 h at 40 °C. The iron content of the ICS granules is determined by a complete destruction of the granule by Aqua Regia combined with an ICP analysis. A value of 590.7 ± 8.7 mg Fe/g sorbent was obtained. SEM-EDX (TESCAN VEGA 3 LMU) analyses of the ICS granules showed only the presence of Fe and Si as main elements (see Figure S-1). Also Oxygen and phosphorus were observed but only in low concentrations. Other metals, possibly interfering the phosphate adsorption, were not detected. The thickness of the iron coating is determined as 676 ± 373 μm . Based on a sieve analysis experiment, the particle size distribution (PSD) was determined by the drinking water company. The D10, D50 and D90 percentiles for all ICS samples are included in

Table 1, as well as the uniformity coefficient (U_c) and the saturated hydraulic conductivity (K_{sat}), which are calculated according to Equation 1 and Equation 2, respectively. U_c corresponds to the degree of uniformity in the granular material and K_{sat} expresses the maximum water discharge of a (porous) medium at a given hydraulic gradient (Canga et al., 2014). Also, the initial phosphate concentration in the granules as a result of phosphate adsorption from the groundwater and both bulk and material density of the granules are included in Table 1. When the ICS material is packed in an adsorption column, a bed porosity of 51.5 % must be taken into account. This porosity was determined using the widely accepted water displacement method (Bear, 1972).

$$U_c = \frac{D_{60}}{D_{10}} \quad \text{Equation 1}$$

$$\log(K_{sat}) = 4.66 + 0.63 \times \log(D_{20}) + 0.94 \times \log(D_{50}) \quad \text{Equation 2}$$

Table 1: Physical properties of the ICS granules obtained from the different drinking water production facilities

Location	D10 (mm)	D50 (mm)	D90 (mm)	$U_c^{(1)}$	$K_{sat}^{(2)}$ (cm/d)	Initial PO ₄ -P conc. in granules (mg PO ₄ -P/g sorbent)	Bulk density (g/cm ³)	Material density (g/cm ³)	Porosity (%)
Balen ⁽³⁾	2.937	3.990	4.894	1.44	10.26	1.84	1.246	2.492	50%
Balen ⁽⁴⁾	0.584	2.334	3.376	4.32	9.77	/	1.294	2.441	53%
Grobbendonk	0.332	0.481	0.595	1.53	8.83	3.03	0.860	1.194	72%
Herentals	1.310	1.878	2.952	1.58	9.73	13.91	1.002	1.789	58%
Mol	2.173	2.870	3.467	1.39	10.05	3.03	1.017	1.753	53%

⁽¹⁾Calculated according to equation 1 (Canga et al., 2014)

⁽²⁾Calculated according to equation 2 (Canga et al., 2014)

⁽²⁾ First shipment

⁽³⁾ Second shipment

2.2 Adsorption Isotherms and capacity

Batch experiments were all performed at a constant temperature (20 °C) under continuous stirring by a horizontal shaker at 100 movements per min at a pH ranging between 6.5 and 7.2. 10 g of pre-dried ICS was brought in contact with 100 mL of an synthetic phosphate solution (solid to liquid ratio = 1/10) for 24 h, whereafter the residual phosphate concentration in the liquid was determined, using the ascorbic acid method as described in the Supplementary Information. The synthetic phosphate solution was produced by dissolving K₂HPO₄ in tap water to obtain different initial phosphate concentrations ranging from 10 to 3000 mg PO₄-P/L. The resulting initial phosphate over sorbent mass ratio (X₀/M) varied between 0.25 and 28.5 mg PO₄-P/g sorbent. Tap water was used to prepare the solution to mimic the calcium concentration of the greenhouse effluent, i.e., approximately 60 mg

Ca/L. The total phosphate concentration in the tap water was about 11 $\mu\text{g P/L}$ (Pidpa, 2019), which is negligible compared to the phosphate added to the synthetic solution. For investigating the effect of pH on the phosphate adsorption, the initial pH of phosphate solutions containing 1440 mg $\text{PO}_4\text{-P/L}$ was varied by using a 1 M HCl and 1M NaOH solution. The initial phosphate over sorbent mass ratio (X_0/M) and the solid to liquid ratio in these experiments were kept constant at 14.4 mg $\text{PO}_4\text{-P/g}$ sorbent and 1/10, respectively. The isotherms were obtained by fitting the Langmuir and Freundlich equation to the experimental data, as described in detail in Text S-2 of the Supplementary Information.

2.3 Adsorption kinetics

Batch kinetic experiments were conducted according to the description in section 2.2. In this case, a solid to liquid ratio of 1/20 was attained by bringing 5 g of pre-dried ICS in contact with 100 mL of the synthetic phosphate solution, containing 25 mg $\text{PO}_4\text{-P/L}$ ($X_0/M = 0.5 \text{ mg PO}_4\text{-P/g sorbent}$). At fixed times, i.e., 5 min, 15 min, 30 min, 60 min and 24 h, samples were taken of the liquid phase. The samples were filtered with a 0.45 μm filter before phosphate analysis using a Metrohm 833 Basic ion chromatography system (the full analytical procedure is described in the Supplementary Information). Kinetic models were derived by fitting the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion model to these data, as described in detail in Text S-2 of the Supplementary Information.

2.4 Lab-scale column experiments

Continuous lab-scale column tests were performed to determine the adsorption capacity and rate. Information provided by column tests is essential to predict the breakthrough time and to design and scale up adsorption filter systems.

An synthetic phosphate solution was produced by dissolving K_2HPO_4 in tap water to obtain a concentration of 25 mg $\text{PO}_4\text{-P/L}$, similar to greenhouse effluent. Each column was filled with a predetermined mass of pre-dried ICS granules (195.23 g) until a filter bed depth of 14 cm was obtained.

A pore volume, i.e., the empty space between the ICS granules, of 77 cm³ was determined, resulting in a bed porosity of 51.5 %. The diameter of the column was 3.7 cm, resulting in a diameter to height ratio equal to 0.26. Each column was equipped with a water jacket to keep the temperature constant at 20 °C during the experiment. The synthetic phosphate solution was fed to the columns in an up-flow manner via a peristaltic pump with adjustable flow rate. Flow rates were chosen to result in an upflow velocity of approximately 62 cm/d (low flow rate) and 667 cm/d (high flow rate), resulting in an actual contact time of 16 min and 168 min, respectively. One part of the greenhouses are equipped with a buffer tank that is large enough to absorb fluctuations in flow and are able to generate a constant effluent flow throughout the year. The low flow rate chosen represents this situation. On the other hand, when no buffer tank is present, the drain water has to be treated immediately when it is discharged, resulting in fluctuating flow rates, which can be as high to cause the high upflow velocity selected in the experiments.

At the high flow rate, samples were taken daily while the sampling frequency at the low flow rate was three times a week. The samples were filtered with a 0.45 µm filter before phosphate analysis using a Metrohm 833 Basic ion chromatography system (the full analytical procedure is described in the Supplementary Information). The breakthrough curves were obtained by fitting the Bohart-Adams model to these data, as detailedly described in Text S-2 of the Supplementary Information.

2.5 Long-term pilot-scale column experiment

The obtained lab-scale results were validated via a long-term pilot-scale experiment, during which real greenhouse effluent was used. The pilot installation consisted of two separate columns, operated in upflow mode, meaning that the ICS granules were continuously submerged, and arranged in series. Each column had a height of 53 cm and a diameter of 30 cm. Both reactors were filled with ICS granules until a filter bed depth of 22.6 cm in each reactor was obtained, corresponding to a total mass of 60 kg pre-dried ICS granules. An inert supporting material, i.e., glass wool, was used at the bottom and top of each column to retain the ICS granules in the columns and to guarantee an even distribution of

the influent over the columns avoiding short-circuiting, a reduced flow velocity or an increased pressure drop. To prevent clogging of the filter, the system was periodically aerated with a low-pressure air blower. The greenhouse effluent was fed to the adsorption system four times a day for 15 min with 50 L. This scheme resulted in a total flow rate of 200 L/d and an upflow velocity of 283 cm/d. Taking into account the volume of the columns, each day the water in the column was replaced four times.

Daily samples were taken of both influent and effluent. The samples were filtered with a 0.45 μm filter before phosphate analysis using a Metrohm 833 Basic ion chromatography system (the full analytical procedure is described in the Supplementary Information). The concentrations of Mg, Ca, K, Na, B, Cu, Fe, Mn and Zn in the influent and effluent samples were also determined using ICP-OES.

2.6 Chemical analysis

All methods of analysis used are described in detail in the Supplementary Information (Text S-1).

2.7 Data analysis

The methodology used to model the experimental data is described in the Supplementary Information (Text S-2).

3 Results and discussion

3.1 Phosphate sorption isotherms

Langmuir and Freundlich isotherms of all ICS materials were established to estimate the maximum $\text{PO}_4\text{-P}$ sorption capacity ($q_{e,\text{max}}$), the Langmuir constant (b), the Freundlich distribution coefficient (K_f) and the Freundlich correction factor (n). As an example, the fitting of both Langmuir and Freundlich isotherms to the experimental data of the ICS granules from the facility in Balen is shown in Figure S-2. Both isotherms described the phosphate adsorption on ICS granules well, resulting in high R^2 , i.e., between 0.9340 and 0.9929. In general, the R^2 of the Langmuir correlation are higher compared to the

Freundlich isotherm. Therefore, only the Langmuir constants from the different ICS samples (originating from deferrization at different locations) are summarized in Table 2, together with the corresponding correlation coefficients R^2 . Moelants et al. (2011) and Vandermoere et al. (2018) also used the Langmuir model to describe the phosphate adsorption isotherm of ICS granules. A $q_{e,max}$ around 20 mg PO_4 -P/g sorbent was obtained for most of the ICS samples, which corresponds realistically with actual adsorption capacity of this type of sorbent. However, different results are obtained for the ICS granules of Grobbendonk, with $q_{e,max} = 43$ mg PO_4 -P/L and $b = 0.0018$ L/mg. Referring to

Table 1, also the particle size distribution deviates from the other samples. For example, the D90 of the Grobbendonk material was 0.595 mm while for the other locations, it ranged between 2.952 mm and 4.894 mm. Most probably, there is indeed a correlation between sorbent size and maximum adsorption capacity, as was already confirmed by Liu et al. (2018). Additionally, a smaller particle size indicates that the granules took up less iron during the deferrization process. The granules will, therefore, show less tendency to adsorb phosphate, which is translated in the lower b parameter (Saadi et al., 2015). By determining the separation factor R_L , it was clear that the phosphate adsorption was favourable ($0 < R_L < 1$) (Desta, 2013). To combine the effect of both $q_{e,max}$ and b , the q_e values at a C_e of 25 mg PO_4 -P/L were calculated and are in the same order of magnitude, in accordance with Moelants et al. (2011).

Table 2: Overview of the results of the evaluation of the established Langmuir and Freundlich isotherms of the ICS granules from the different deferrization sites ($C_0 = 10 - 3000$ mg PO_4 -P/L; solid to liquid ratio = 1/10).

Location	Langmuir				
	$q_{e,max}$	b	R^2	$q_e (C_e=25\text{mg/L})$	R_L ($C_0=25\text{mg/L}$)
	$\left[\frac{\text{mg } PO_4 - P}{\text{g sorbent}} \right]$	$\left[\frac{\text{L}}{\text{mg}} \right]$		$\left[\frac{\text{mg } PO_4 - P}{\text{g sorbent}} \right]$	
Balen (first shipment)	20.0	0.0058	0.9706	2.54	0.87
Balen (second shipment)	26.0	0.0054	0.9813	3.07	0.88
Grobbendonk	43.0	0.0018	0.9929	1.85	0.96

Herentals	20.8	0.0052	0.9884	2.41	0.88
Mol	19.2	0.0043	0.9909	1.86	0.90

3.2 Phosphate sorption kinetics

Different kinetic models, i.e., the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion model, were applied to the obtained kinetic data and the pseudo-second-order model showed the best results, as depicted in Figure S-3. The excellent fitting to the obtained kinetic data was expected since this model is applicable for most liquid adsorption systems, especially when C_0 is not excessively high (Tan and Hameed, 2017). Additionally, Li et al. (2016) concluded that for phosphate adsorption by metal (hydr)oxides, the kinetic data are usually better represented by the pseudo-second-order model. Nevertheless, this model represents a flexible formula combining many different controlling mechanisms (Tan and Hameed, 2017), and it does not allow to determine the rate-controlling mechanism, although Li et al. (2016) suggested chemisorption as the primary mechanism. The process of chemisorption is well described by the Elovich model (Tan and Hameed, 2017; Tran et al., 2017). The correlation coefficient for this model fit, i.e., 0.9803, was almost as high as for the pseudo-second-order model, i.e., 0.9823, indicating that chemisorption is the rate-limiting step that controls this adsorption process. Phosphate adsorption by similar ICS granules was investigated by Moelants et al. (2011) and Vandermoere et al. (2018). In both studies, the adsorption kinetics were investigated, but the mechanism behind was not identified. Vandermoere et al. (2018) did mention the strong hydrolyzing power of iron-rich materials to form chemical bonds with phosphate.

3.3 Effect of pH on adsorption capacity

The influence of initial pH on the adsorption capacity q_e is depicted in Figure 1. In initial pH range between pH 1 and pH 5, higher adsorption capacities were observed, with a maximum value of 12.1 mg PO_4 -P/g sorbent at initial pH 2. At initial pH 6 or higher, the adsorption capacity drops significantly

from 9.8 mg PO₄-P/g sorbent at initial pH 6 to 2.2 mg PO₄-P/g sorbent at initial pH 13. Considering the pK_a values, the presence of specific phosphate species (H₃PO₄, H₂PO₄⁻, HPO₄²⁻ & PO₄³⁻) are determined by the initial pH of the solution. According to Li et al. (2016), a strong competition between phosphate species and deprotonated hydroxyl groups occurs at higher pH, causing strong repulsions between both ions and resulting in a decreased adsorption capacity. Indeed, the pH has a significant effect on the characteristics of surface sorbent particles. Siwek et al. (2019) referred to the pH_{pzc} (point of zero charge) to conclude that the surface of goethite, a simple iron oxide mineral, is positively charged at pH values lower than 8.2, favouring the adsorption of phosphate ions. In this study, the pH_{pzc}, i.e., 8.7 (where the final pH is equal to the initial pH), is approximately similar as the one reported in the study of Siwek et al. (2019). However, Tran et al. (2017) mentioned the critical role of pK_a values and refer to the isoelectric point to point out the electrostatic interactions. This may explain that q_e decreases even at pH values lower than pH_{pzc}. The high pH dependency of the adsorption process offers opportunities for phosphate recovery by changing the pH to high values once the adsorption columns are saturated and hence release the adsorbed phosphate to a concentrated stream that can be easily recovered.

Figure 1: Effect of initial pH on adsorption capacity of PO₄-P on the iron granules (C₀ = 1440 mg PO₄-P/L; solid to liquid ratio = 1/20)

3.4 Adsorption column experiments

Figure 2 (a) and (b) show two typical breakthrough curves obtained by adding a solution of approximately 25 mg PO₄-P/L to an adsorption column filled with ICS granules at an actual contact time of 16 min and 168 min, respectively. The mathematical model of Bohart-Adams (see equation S-11) was fit to the experimental data by modifying the sorption capacity of the bed at equilibrium (N_0) and the Bohart-Adams rate constant (k_{BA}). The results, as well as the experimental conditions and column characteristics, are summarized in Table S-2 (Supplementary Information). The effluent concentration follows the typical sigmoidal evolution of a breakthrough curve. As expected, the time before the effluent concentration starts to increase differs for both flow velocities. Within a certain time range, the amount of phosphate entering the column is lower at the low velocity, and consequently, less phosphate needs to be adsorbed. This effect is also visible by comparing the Bohart-Adams rate constants. k_{BA} at the low velocity, i.e., 0.0034 L/(mg.d) is almost 5 times lower than the constant obtained at 16 min contact time, i.e., 0.0167 L/(mg.d). Furthermore, the low velocity allows the adsorbed phosphate to migrate inside the iron shell of the ICS granule, resulting in a higher take up represented by the N_0 -values. This conclusion is confirmed by comparing the total amount of adsorbed phosphate, i.e., 9.62 mg PO₄-P/g sorbent and 8.76 mg PO₄-P/g sorbent at 186 min and 16 min contact time, respectively. These adsorption capacities are significantly higher than those obtained in the batch experiments (see Table 2), highlighting the benefits of column adsorption experiments under flow-through conditions. The continuous flow experiments produce results under conditions comparable to those of real adsorption columns and show that the adsorption capacities obtained in the batch experiments are an underestimation. Finally, when considering a breakthrough concentration C_b of 2.5 mg PO₄-P/L, the breakthrough time t_b can be determined for a contact time of 16 min and 186 min, i.e., 7 days and 186 days, respectively. This breakthrough concentration approaches a phosphate concentration that meets the regulations for disposal on grassland for this specific situation.

Figure 2: Adsorption column experiments on lab-scale ($C_0 = 25$ mg $\text{PO}_4\text{-P/L}$; Pore volume = 77 mL; 195.23 g ICS granules) at 62 cm/d (a) and 667 cm/d (b), corresponding with an actual contact time of 16 min and 168 min, respectively

Based on the former conclusions, intermediate rest periods were introduced while performing the column experiments. In this strategy, the column was only fed 8 h per day and left to rest for 16h per day. By applying this feed scheme, the phosphate is allowed to migrate into the iron shell of the ICS granules (towards the iron-silicon border), even at high flow rates, and therefore the adsorption capacity is increased. Enabling a comparison with the continuous flow experiment, the evolution of the effluent concentrations are shown in relation to the treated volume of phosphate-rich influent, as depicted in Figure 3. The phosphate concentration of the effluent was significantly lower compared to the continuous flow experiments. Only a maximum concentration of approximately 1.1 mg $\text{PO}_4\text{-P/L}$ was observed, instead of more than 10 mg $\text{PO}_4\text{-P/L}$ in the continuous flow experiment. After a volume of 36 L passed through the adsorption columns, a limited increase in effluent phosphate concentration was followed by a decrease because of the resting periods. Thus, the resting periods cause a significant improvement of the adsorption efficiency, opening the possibility to reach a higher adsorption capacity of the ICS granules. The mechanism of phosphate migration into the iron shell still needs further investigation. While investigating the heterogeneous phosphate adsorption on iron oxyhydroxides and soil, a distinction is often made between fast, instantaneous adsorption and slow fixation (Warrinnier

et al., 2018). The mechanisms explaining the slow sorption reactions, i.e., nano-pore diffusion and slow surface precipitation, are maybe also useable to describe the effect of the intermediate resting periods, showing the need for a full in-depth study to confirm this hypothesis.

Figure 3: The effect of intermediate rest periods on the breakthrough curve of the high flow experiment (rest period of 16 h/d)

Finally, a pilot-scale experiment treating real greenhouse effluent was performed for more than 160 days. The results of this long-term experiment are shown in Figure 4. Since real greenhouse effluent was treated, the influent phosphate concentration of the adsorption column fluctuates between 1.6 mg PO₄-P/L and 35.3 mg PO₄-P/L. By using the previously obtained Bohart-Adams model constants at a high flow rate, the breakthrough time t_b was estimated assuming an influent concentration C_0 of 25 mg PO₄-P/L and a breakthrough concentration C_b of 2.5 mg PO₄-P/L (disposal on grassland). The Bohart-Adams model constants at a high flow rate were used because the pilot adsorption column processed an average flow rate of 200 L/d at a flow velocity through the bed of 283 cm/d. Since the flow rate and flow velocity were much higher compared to the conditions at lab scale, intermediate resting periods were introduced to enhance the adsorption process. The service time of the bed until breakthrough (t_b) was estimated at approximately 53 days. The first time that the threshold value was exceeded was after 88 days. During the first 30 days the influent concentration was remarkably low, i.e., an average

concentration of 1.85 mg PO₄-P/L. Afterwards, the influent concentration increased towards values as expected, i.e., 25 mg PO₄-P/L. The phosphate take-up by the ICS granules was much lower as considered in the calculations of t_b . In the periode between day 30 and day 87, the effluent concentration only increased slightly towards a maximum of 1.81 mg PO₄-P/L. After day 88, the effluent concentration fluctuate around $C_b = 2.5$ mg PO₄-P/L, exceeding this value on day 100, 104, 105, 114, 116, 117, 131, 137. From day 139 until the end of the experiment, the effluent concentration slowly increased until a maximum value of 6.03 mg PO₄-P/L. The removal efficiency of phosphate during the first 100 days ranged between 70% and 100%, as in the last 60 days the efficiency decreased towards a range between 50% and 96%.

Considering the discharge limit to surface water specific for this situation, i.e., 0.1 mg PO₄-P/L, the effluent concentration was unfortunately only below the discharge limit for 30 days, whereas a breakthrough time of 45 days was calculated. Possibly, the design of the adsorption column as well as the operating conditions are not suitable to reach these low concentrations. In the column experiments at lab-scale, the width to height ratio of the column was in the range of 0.26, while a ratio of 0.42 was applied for the pilot experiment. The lower breakthrough concentration increases the Mass Transfer Zone (MTZ), which in turn will reach the breakthrough zone much sooner. The ideal width to height zone can be determined by calculating the MTZ from similar column experiments. However, because of the intermediate rest periods, this was not possible in this study. Secondly, a batch volume of 50 L greenhouse effluent was pumped through the column within 15 min, resulting in high flow velocity through the filter bed. Improvements on both design and operating management are needed. Lowering the width to height ratio will certainly increase the removal efficiency of the column. Also lowering the high velocity of the water through the column will have a positive effect.

Nevertheless, this long term experiment clearly illustrated the potential of the ICS granules to remove phosphate from greenhouse effluent. In Table S-2, a general overview of the influent and effluent quality, excluding phosphate content, is given. No significant difference between influent and effluent

content is observed. More specific, iron (or other metals) leaching from the ICS granules was a big concern but was not observed.

Figure 4: Adsorption column experiments at pilot scale on real drainage water (intermediate rest periods of 4 times 5.75 h/d, at 200 L/day, actual contact time = 122 min & Z = 45.2 cm)

3.5 Prospects for P-recovery

The phosphate removal potential by the ICS granules is clearly illustrated in this study. From a circular economy perspective, the recovery of both granules and phosphorus further needs to be considered because they impact the sustainability of the treatment process. Piol et al. (2019) identified desorption as a promising technique since it (i) regenerates the adsorbent making it reusable for multiple adsorption/desorption cycles, and (ii) it isolates the adsorbate making it possible to recover. Different desorption reagents, such as inorganic and organic acids, chelating agents and alkaline solutions, have already been proposed in the literature (Dox et al., 2019; Luyckx et al., 2020; Zhao et al., 2010). In this case, the reusability of the granules is as essential and their particular composition necessitates a good choice of desorption agent. Indeed, when using acidic solutions, the iron shell around the sand core will dissolve leading to the destruction of the granules. Additionally, both adsorption and desorption are balancing processes until an equilibrium is reached, meaning that the results depicted in Figure 1

show the pH influence on the desorption process as well. An alkaline environment showed low phosphate adsorption, indicating stronger desorption under these conditions. Because of the strong bond of phosphate and ICS granules, a strong base, such as NaOH, is considered to be more appropriate. A preliminary experiment using 100 mL 1 M NaOH solution and 5 g fully saturated ICS granules from the lab column experiment at low velocity (9.62 mg PO₄-P/g sorbent) showed that 7.35 mg PO₄-P/g sorbent can be recovered. So, approximately 76% of the adsorbed phosphate can be recovered by the desorption step. Once desorbed, the phosphate can be recovered by precipitation or used directly with irrigation water as fertilizer (Loganathan et al., 2014). However, further use of this solution requires a pH adjustment to meet the requirements of irrigation water or the ideal conditions for precipitation. Moreover, other elements, such as iron, leaching during the desorption step will also determine the quality of the solution. These parameters should be considered in further investigations.

4 Conclusions

To avoid the disposal of greenhouse effluent without proper treatment, ICS granules were investigated as a low-cost sorbent to remove phosphate by adsorption. The adsorption capacity at a C_e of 25 mg PO₄-P/L of all locations ranges between 1.85 and 3.07 mg PO₄-P/g sorbent. The kinetics are well described by both the pseudo-second-order (R² = 0.9823) and Elovich model (R² = 0.9803), suggesting chemisorption as the primary mechanism. The initial pH influences the presence of specific phosphate species and changes the strength of the electrostatic attraction at higher pH, resulting in a reduced adsorption capacity. The Bohart-Adams model was used to fit the breakthrough curves of the bench-scale experiments under flow-through conditions. The results are useful to scale up the adsorption columns and to verify the adsorption potential. A significant improvement of the adsorption efficiency was obtained by implementing intermediate resting periods, allowing phosphate to migrate into the granules. Finally, a pilot-scale experiment during more than 160 days was performed and showed removal efficiencies between 50% and 100% while iron leaching from the ICS granules was not observed. The discharge limit was already exceeded after 30 days. Despite the need for improvements

on both design and operating management, the potential of the ICS granules to remove phosphate from greenhouse effluent is demonstrated.

Credit author statement

Nico Lambert: Investigation, Methodology, Roles/writing – original draft. Pieter Van Aken: Investigation, Roles/writing – original draft. Rob Van den Broeck: Funding acquisition, Writing – review & editing. Raf Dewil: Funding acquisition, Supervision, Writing – review & editing.

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