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Iron oxide coated sand (IOS): Scale-up analysis and full-scale application for phosphorus removal from goat farm wastewater

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ABSTRACT

Effective eutrophication control, especially for decentralized wastewater treatment, has received increasing attention in recent years. In view of this, iron oxide coated sand (IOS) granules, a recycled waste product from the drinking water industry, was investigated for phosphorus removal from goat farm wastewater, both at laboratory-scale and at full-scale. Brunauer-Emmett-Teller adsorption revealed a high specific surface area (249 m^2/g) of the IOS. Fourier Transform Infrared Spectroscopy and X-ray Diffraction demonstrated that Fe(III) compounds are the main functional component and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy showed that Fe and O elements covered more than 84% of the surface of the IOS. The IOS granules showed good phosphorus adsorption capacity over a wide pH range during laboratory-scale batch tests. Moreover, the phosphorus adsorption was very fast and the residual phosphorus concentration dropped below 0.02 mg/L within an hour at a dosage of 20 g/L. After adsorption, the exhausted IOS could be regenerated by using 0.5 M KOH, and more than 80% adsorption capacity remained. Laboratory-scale column tests with real wastewater originating from a goat farm were run and Bed Depth Service Time and Bohart-Adams models were applied in view of scale-up. Based on this, a full-scale IOS based fixed bed reactor was designed, built and tested at a goat farm. A TP removal efficiency of 99% with a 0.87 m³ IOS fixed bed reactor (fed at 2.2 m³/d) was obtained. The TP concentration in the effluent remained below 0.3 mg/L for nearly 400 days, achieving long term TP removal. This study demonstrates that IOS based treatment is an ecological and environmentally friendly method, suitable for full-scale (decentralized) wastewater treatment.

1. Introduction

In urban areas, wastewater is typically collected through sewers and treated in centralized wastewater treatment plants (WWTPs) in order to meet strict discharge limits. However, rural wastewater treatment systems are often not as performant as urban systems because they are usually organized and financed on a decentral level [1]. Recently, phosphorus discharge from decentralized systems has been shown to have a greater environmental impact than previously believed [2]. For example, in the UK, more than 70% of phosphorus in surface water is attributed to decentralized wastewater effluent and agriculture run-off [3]. Also in Flanders (Belgium), about one third of all P released to

surface waters originates from decentralized discharge. Therefore, controlling P release should be more focused on decentralized and small scale applications which should be sustainable and reliable and require minimal operating expertise and maintenance [3,4].

Today Constructed wetlands (CWs) are one of the most widely used wastewater treatment technologies in decentralization practice [5], but CWs generally have unsatisfactory low efficiency for phosphorus removal [6]. An additional effluent polishing step based on adsorption is therefore often suggested to improve phosphorus removal [7]. Different types of natural and synthetic adsorbents were assessed on laboratory and field-scale [8–10]. Zeolite is a commonly used low-cost natural substrate and showed up to 2.15 mg P/g adsorption capacity [11].

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Received 6 September 2021; Received in revised form 22 November 2021; Accepted 25 November 2021 Available online 6 December 2021 1383-5866/© 2021 Elsevier B.V. All rights reserved. lava rock filter could remove 58% of TP from household greywater [12]. Activated carbon is a promising and relatively mature (synthetic) adsorbent already used at full-scale [13,14]. Ion exchange resin as a relatively expensive adsorbent showed nearly 98% removal efficiency in inorganic phosphorus [15]. In a preliminary step of this research, these potential adsorbents were compared in a laboratory test (**Table S1**). Some of these adsorbents showed good phosphorus removal efficiency but they are not the appropriate choice in decentralized systems. On the other hand, some novel but not yet industrialized synthetic adsorbents including hydroxide nano-composites [16], lanthanum loaded biochar [17], Fe-Zeolite-A [8], humic acid coated magnetite nanoparticles [18] and modified iron oxide-based sorbents [19] demonstrated good performance at laboratory-scale, but their complicated preparation makes them unsuitable for decentralized application.

Previous research showed that materials with a high content of metal elements have good phosphorus removal performance both in synthetic wastewater and real wastewater [20,21]. Compared to Al, Zr, La and other metals for P-control, iron is environmentally friendly, costeffective and easily available [22]. Iron based materials including iron oxides, iron salts and zero-valent iron have been widely used in wastewater treatment [23–25]. However, these synthetic materials are still costly for long term operation. In that sense, iron oxide granules are interesting as these granules are a waste residue from drinking water companies when iron needs to be removed from groundwater. During treatment, the Fe(II) present in groundwater, which is generally anaerobic, is oxidized to Fe(III) when brought in contact with air and the Fe (III) compounds precipitate on the sand to form IOS (iron oxide coated sand). These iron oxide pellets are periodically removed when saturated with iron. An estimated 10⁶ tons of IOS (with an average diameter of 2 mm) are produced worldwide annually which constitutes a huge cost for drinking water companies [26]. A first research on IOS investigated the maximum phosphorus sorption capacity in a batch test with high P concentrations (11,000 mg P/L) and demonstrated the potential decentralized application through modelling [27]. Then IOS was applied to reduce phosphorus losses from drained agricultural fields in short term experiments (70% P removal efficiency, 10 weeks) [28]. Recently, a long term pilot test (180 days) and preliminary regeneration of IOS was investigated as a step towards full-scale engineering [29]. Therefore, a full-scale decentralized demonstration of IOS would be useful to further prove its usefulness.

The main goal of this study is therefore to demonstrate the applicability of IOS in a long term full-scale setting for decentral use. IOS was used in a fixed bed reactor as a polishing step after CWs, treating household wastewater and goat farm wastewater for more than one year. The influence of time, dosage and pH on P adsorption and regeneration of IOS were also fully investigated. In addition, properties of the IOS and adsorption mechanisms were elucidated using Brunauer-Emmett-Teller adsorption (BET), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS). Finally, based on laboratory-scale adsorption tests and characterizations, Bed Depth Service Time (BDST) and Bohart–Adams models were applied for scale-up and design of the fixed bed reactor.

2. Materials and methods

2.1. Adsorbent materials

IOS (2–5 mm) in this study was obtained from the Provincial and Intercommunal Drinking Water Company of the Province of Antwerp (PIDPA, Belgium)[28,29]. The bulk density of the IOS was calculated by measuring the volume occupied by demi water in a filled column with a certain mass of IOS [28].

2.2. IOS physicochemical properties

To establish the phosphorus adsorption mechanism of IOS, BET, SEM-EDS, FTIR and XRD techniques were applied to analyze the IOS characteristics before and after adsorption. IOS was collected before (further referred to as pristine) and after (further referred to as used) the isotherm studies at pH 7 (see below). IOS was rinsed three times by demineralized water and dried at 60 °C. Specific surface area, micropore volume, and micropore size were measured using nitrogen Brunauer Emmett Teller (BET) isotherms on an Autosorb iQ instrument (Quantachrome, USA) [17]. FTIR spectra were recorded at room temperature using a CCR-1 FTIR Spectrometer (Thermo-Nicolet, USA) over the range 400–4000 cm⁻¹ [7]. XRD data were collected using an X-ray diffraction diffractometer in reflection (Empyrean, Netherland) over the range 10-90°. The surface morphology and microstructure were examined using SEM analysis (Carl Zeiss AG Merlin, Germany) to visualize inner porosity, surface properties, and the potential environment for biofilm bacterial attachment and growth. The SEM was further equipped with EDS to determine the composition and relative distribution of elements particularly on the surface of IOS [8].

2.3. Batch experiments

2.3.1. Phosphate adsorption kinetics

Phosphate adsorption kinetics of IOS were determined using 50 ml of P solution (using KH₂PO₄, 30 mg P/L, which is similar to the P concentration in the wastewater from the goat farm) at four different adsorbent doses (5, 10, 20 and 50 g/L). Sampling was performed at different time intervals (0.25, 0.5, 1, 2, 8, 24, 48 and 96 h). Solution pH was not adjusted but remained around 9 during the adsorption kinetics experiments. The used Erlenmeyer flasks were covered with parafilm and shaken on a rotational shaker at 150 rpm. Samples were filtered immediately after collection with a 0.45 μ m Macherey-Nagel syringe filter, in order to minimize additional P sorption.

Pseudo first-order (Eq. (1)) [30] and pseudo second-order (Eq. (2)) models [31] were used to determine adsorption kinetics.

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{1}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$
(2)

Where q_e and q_t are the adsorbed P amount (mg/g) at equilibrium (q_e , mg/g) and a predetermined time (t, hour), respectively. k_1 and k_2 are the rate constants for the pseudo first-order (min⁻¹) and pseudo second-order model (g/mg min) respectively. In addition, the Weber-Morris intraparticle diffusion (Eq. (3)) was used to further explore the mass transfer mechanisms in adsorption reaction kinetic model fitting [21].

$$q_t = k_i t^{1/2} + C_i (3)$$

Where k_i (mg/g min) is the intra-particle diffusion rate constant and C_i (mg/g) is a constant which gives an indication of the thickness of the boundary layer.

2.3.2. Phosphate adsorption isotherms at different pH

To determine the influence of pH on IOS adsorption, adsorption experiments were carried out at different pH values (2, 4, 7, 9, 12) and dosage (1, 3, 5, 8, 10, 12, 15 g/L) using 50 ml P solutions (30 mg P/L). The solution pH was adjusted by 0.1 M HCl or 0.1 M NaOH. The samples were shaken on a rotational shaker at 150 rpm and samples were taken for analysis after 96 h [19].

Furthermore, the P adsorption isotherms at different pH were obtained by model fitting. Such model fitting can reveal the adsorption mechanism. Langmuir and Freundlich isotherm models [21] were used to explore P adsorption behavior and are presented in Eq. (4) and Eq. (5) respectively.

$$q_{\rm e} = \frac{q_{\rm max} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{4}$$

$$q_{\rm e} = K_{\rm F} C_e^{1/n} \tag{5}$$

where q_e is the amount of phosphorus adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration, K_L and K_F are the Langmuir (L/mg) and Freundlich (mg/g)/(mg/L)ⁿ constants, respectively, and q_{max} (mg/g) denotes the predicted maximum adsorption capacity.

2.3.3. IOS regeneration and reusability test

Regeneration and reusability tests were performed to extend the lifetime of IOS during application. The exhausted IOS from the column tests (see below) was used in regeneration experiments [32]. Elution is the most studied approach to recover adsorbates and regenerate adsorbents [33]. NaOH and KOH were selected for the regeneration test, and five different base concentrations (0.01, 0.05, 0.1, 0.5 and 1 M) were used as desorption solution. The regeneration experiments were conducted as batch experiments. A high solid to liquid ratio (5 g/L), 24 h regeneration time and shaking on a rotational shaker at 150 rpm was applied for all tests.

Recovery efficiency, which is the proportion of desorption to adsorption was calculated by Eq. (6)

$$R_e = \frac{C_R V_R}{(C_0 - C_1) V_1} 100\%$$
(6)

Where C_R , C_0 and C_I are the phosphorus concentration of the desorption solution, the initial and final phosphorus concentration during adsorption respectively. V_I and V_R are the volumes of the solution during adsorption and desorption respectively.

As a result of the regeneration experiments, 0.5 M KOH was selected for further reusability experiments. The reuse experiments were performed with effluent of the goat farm (containing 27.6 mg P/L) at a 1 g/L solid (IOS) to liquid ratio. Samples were shaken at 150 rpm. Each cycle consisted of 96 h of adsorption and 24 h of desorption and 6 consecutive adsorption/desorption cycles were performed.

All the laboratory-scale experiments were conducted at room temperature (20 $^{\circ}$ C).

2.4. Column experiment

Continuous laboratory-scale column tests aimed at obtaining the IOS adsorption capacity from real wastewater [34] and were performed with a glass column (diameter 11 mm) packed with 40 cm of IOS (final volume 40 ml, mass 49.2 g). The information derived from column experiments is essential to predict the substrate saturation time and aids scaleup of the system. Three columns were continuously fed in an up-flow mode by goat farm unfiltered effluent (containing 27.6 mg P/L) using peristaltic pumps at hydraulic loads of 60 ml/h (which is the equivalent of 1.5 bed volume BV/h), 20 ml/h (0.5 BV/h) and 12 ml/h (0.3 BV/h) until P breakthrough (defined as residual P concentration beyond 2.5 mg/L). Exhausted IOS was collected from the 1.5 BV/h column after 1400 BV for regeneration experiments.

In order to design and optimize a column adsorption process for scale-up, prediction of the breakthrough curve is required [35]. BDST and Bohart – Adams mathematical models were applied to describe experimental breakthrough curves and predict the breakthrough curves for the full-scale application.

The BDST model (Eq. (7)) is defined based on the linear relationship between bed height (H) and service time (t) of a column [36]. The BDST model assumes that the adsorption rate is controlled by the surface reaction [37].

$$t = \frac{N_0 H}{C_0 u} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right)$$
(7)

where: *t* is the service time at breakthrough (h); N_0 the dynamic bed capacity (mg/L); H the column bed height (cm); *u* the HLR (cm/h); C_0 and C_t are the influent and the effluent concentration of the adsorbate (mg/L), respectively; and K_a is the adsorption rate constant (L mg⁻¹h⁻¹).

The Bohart – Adams model (Eq. (8)) assumes that external mass transfer controls the adsorption and that the equilibrium is not instantaneous [38,39]. This model is widely used to predict the initial part (C_t / C_0 <0.5) of the breakthrough curve [35].

$$\ln\left(\frac{C_t}{C_0}\right) = k_b C_0 t - k_b N_1\left(\frac{H}{u}\right) \tag{8}$$

where: K_b is the Bohart – Adams kinetic constant (L mg⁻¹h⁻¹); N_1 is the saturation concentration (mg/L); C_0 and C_t are the influent and effluent adsorbate concentration (mg/L); u is the HLR (cm/h); and H is the adsorbent height in the column (cm).

2.5. Full-scale decentralized application

A small-scale goat farm for goat milk production located in a rural area near Ghent (Lochristi, Belgium) was used as site for a case study. This goat farm produces about $2.2 \text{ m}^3/\text{d}$ wastewater consisting of a mix of domestic wastewater (5 IE), husbandry wastewater and cleaning water from the milking installation. The Flemish environmental legislation stipulates that such wastewater must be treated. There are many similar small farms in Flanders (the northern part of Belgium) and many of them also require low cost and efficient decentralized wastewater treatment systems. For this goat farm, an integrated CW system was designed to meet the required discharge limits (VLAREM II: Article 5BIS.19.8.4.5.6, Table 2). A schematic overview of the integrated CW system is shown in Fig. 1.

The primary treatment consists of two septic tanks (volume: 2 m³ each) in series, after which the wastewater is collected in a pump well. From this pump well, the wastewater is intermittently pumped to two parallel vertical-flow CWs (NITs) for COD removal and nitrification. The effluent of both parallel vertical-flow CWs is then recirculated back to the pump well, where it is mixed with the effluent from the septic tanks. Effluent recirculation has been found to enhance system performance concerning nitrogen removal. The mixed effluent of NIT CWs and the septic tanks effluent is pumped to a third horizontal subsurface-flow CW (DENIT) for denitrification (Fig. 1). All three CWs have the same size (LxWxH: 5.7 m \times 2.0 m \times 1.0 m). Both NIT CWs were filled with lava rock (12-18 mm diameter), and the DENIT CW was filled with sand (1 mm diameter). The IOS fixed bed reactor (LxWxH: 113 cm \times 96 cm \times 80 cm, 0.87 m³) contained 1067 kg IOS substrate. As such, influent flow rate is 2.5 BV/day and the hydraulic load rate (HLR) is 8.5 cm/h. The system was monitored from September 2019 to October 2020.

2.6. Water sample analysis

COD, ammonium, nitrate, nitrite, total nitrogen (TN), ortho-phosphate and total phosphorus (TP) were measured spectrophotometrically according to standard methods [40] using HACH test kits and a DR 6000 VIS Spectrophotometer [41]. COD, TN, TP, TSS were analyzed unfiltered, whereas the other parameters analyzed using 0.45 µm filtered samples. In particular, COD was measured according to ISO 15705:2002. Ammonium, nitrate, nitrite, phosphate were analyzed according to ISO 159231. TN was measured according to ISO 5663 and EN 25663. TP was measured by ISO 11,885 [42]. TSS was determined according to Standard Methods [40]. Metal elements were analyzed by inductively coupled plasma optical emission spectrophotometry (ICP-OES, Agilent 7000 series ICP OES, USA) according to standard methods [43]. The absorbance at a specific wavelength (254 nm) was measured with a UV-VIS spectrophotometer (HACH DR 6000 VIS) using 1 cm quartz cuvettes. The dissolved oxygen (DO), temperature and pH were measured on site using a portable meter with a temperature readout



Fig. 1. Schematic overview of the goat farm wastewater treatment system (CW: constructed wetland, NIT: nitrifying CW, DENIT: denitrifying CW, IOS: IOS fixed bed).

(HQ30d, HACH, US, probe LDO10103 for DO and temperature, probe IntelliCalTM PHC101 for pH).

3. Results and discussion

3.1. Physicochemical properties of IOS

The physicochemical parameters of pristine IOS and used IOS are summarized in Table 1. The BET analysis revealed that IOS has a higher specific surface area ($249 \text{ m}^2/\text{g}$) and bulk density (1.23 g/cm^3) than many other phosphorus removal substrates [44]. SEM-EDS showed that Fe covered nearly half (47%) of the IOS surface. There is a correlation between phosphorus adsorption and the specific surface of the iron oxides [45]. Pore volume and average pore size of IOS decreased after phosphorus removal, but this did not affect IOS micropore properties.

Furthermore, the phosphorus content of IOS increased from 1.8% to 4.5% after adsorption, while the Fe content remained nearly the same. IOS showed high phosphorus adsorption capacity and low Fe loss (0.2%) which indicates the potential for high reusability. Adsorption hardly affects the Si content (from 2.6% to 2.3%), which means that the sand core of IOS is stable during the adsorption. Ca can also contribute to phosphorus removal but the content of Ca in IOS is low (0.6%), and most Ca is lost during the adsorption. The high specific area, bulk density and iron content of IOS make it a promising material for phosphorus

Table 1

Physicochemical characteristics of IOS before and after adsorption.

Physicochemical characteristics	Pristine IOS	Used IOS*
Physical properties		
Bulk density (g/cm ³)	1.23	1.23
Specific Surface (m^2/g)	249	184
Pore volume (cm^3/g)	0.19	0.13
Average pore size (nm)	3.1	2.8
Micropore volume (cm ³ /g)	0.023	0.022
Micropore area (m^2/g)	48.2	48.2
Element properties (weight ratio %)		
C	10.6	12.8
0	37.4	33.5
Si	2.6	2.3
Р	1.8	4.5
Са	0.6	0.1
Fe	47.0	46.8

*Used IOS represents the IOS adsorbent after P isotherm adsorption (96 h) at P concentration of 30 mg P/L with a dosage of 5 g/L at pH 7.

immobilization.

SEM micrographs (Fig. 2) of both samples showed an irregular microstructure. The surface of IOS did not change significantly after adsorption. The pristine IOS showed the highest EDS peaks for oxygen, which indicates the abundance of oxide forms such as $Fe(OH)_3$ and SiO_2 . As the second-highest peak was from Fe, it can be concluded that Fe (OH)₃ can be considered part of the Fe(III) compounds that adsorb P in IOS, which is in line with the amorphous nature of the sample (XRD analysis, see below), the large surface area (BET analysis, see Table 1) and a previous study [28].

FT-IR spectra were used to characterize the functional groups on the pristine and used IOS. Fig. 3a shows that the structure of IOS before and after P adsorption is almost the same. In the region of $400-1000 \text{ cm}^{-1}$, the bands can be assigned to stretching of Si-O of the sands grains that are used as backbones for the IOS [8]. The small wavenumber shift may be caused by P bonding onto the IOS. The C = O stretching at 1634 cm⁻ along with –OH stretching at 3332 cm⁻¹ corresponds to the carboxylate anion, indicating that Fe(III) might form a complex with the carboxylate group [46]. The existence of –OH stretching also showed that hydrous ferric oxides Fe(OH)3 might be part of Fe(III) compounds in IOS. The hydroxyl groups attached to Fe³⁺ compensate for the negative charge of the molecular structure [47,48]. The appearance of another strong bond at 1398 cm^{-1} can be assigned to the scissoring of the $-\text{CH}_2$ group [18]. The XRD spectrum (Fig. 3b) indicates a small difference between pristine IOS and used IOS regarding the amorphous nature of IOS. For some iron oxyhydroxides including Fe(OH)₃ and lepidocrocite (γ -FeOOH), the same amorphous structure and morphology (red color) as for the IOS is observed. Such iron oxyhydroxides can remove P via the formation of Fe (III)-phosphate species [49,50].

3.2. Phosphorus adsorption characteristics

3.2.1. Effect of time and dosage

The contact time is one of the essential parameters in adsorption processes. A kinetic study can determine the contact time required to achieve optimal conditions. As shown in Fig. 4a and Fig S1, rapid adsorption is observed within the first 24 h. As the dosage increases, the number of adsorption sites in the IOS will increase [17], and as a result the removal efficiency of phosphorus will also increase. When the IOS dosage was higher than 20 g/L, the removal efficiency was more than 99.9% and the residual P concentration dropped below 0.02 mg/L after one hour.

The effect of contact time on the amount of phosphorus adsorbed by



Fig. 2. SEM micrographs of (a) pristine IOS and (b) used IOS (used IOS represents the IOS adsorbent after P isotherm adsorption at P concentration of 30 mg P/L with a dosage of 5 g/L at pH 7).



Fig. 3. Adsorbent characterization results of the pristine and used IOS form: (a) FT-IR spectra and (b) XRD spectra. Used IOS represents the IOS adsorbent after P adsorption at P concentration of 30 mg P/L with a dosage of 5 g/L at pH 7.



Fig. 4. Batch adsorption experimental results at different IOS dosages compared to: (a) adsorption kinetics model fit and (b) Weber-Morris (WB) intraparticle diffusion model fits.

IOS was observed at a dosage in the range of 10 to 50 g/L. The measurements were used to fit the different kinetic models that can help to identify the reaction/mass-transfer mechanisms. By comparing the R² values, it can be concluded that the pseudo-second-order model fitted the data better than the pseudo-first-order model (Table 2). The rate constant (K_2) is typically used to describe how fast the adsorption equilibrium is achieved [51]. The K_2 values as determined by the pseudo-second-order model are 0.05, 0.2, 3.9 and 474 g mg⁻¹ min⁻¹ at 5, 10, 20 and 50 g/L respectively. The values of K_2 and h (initial adsorption rate) are proportional to the value of IOS dosage, which means the adsorption rate increases with increasing IOS dosage. In addition, the removal of P by IOS likely occurs through the combination of multilayer adsorption and precipitation [52]. Precipitation through sharing or exchange of electrons takes place between phosphate and the functional groups of IOS [53,54]. The good fit of the pseudo-second-order model indeed suggests that diffusion and subsequent reactions will occur after the surface sites are occupied [55].

The results from the Weber-Morris fit also confirmed that film diffusion and intraparticle diffusion were involved in the overall adsorption process and the latter is not a rate-limiting step (Fig. 4b). The

Table 2

Kinetic model parameters corresponding to P adsorption from 30 mg P/L solutions by means of 96 h batch test at different IOS dosage.

Parameters		IOS dosage (g/L)			
		5	10	20	50
Pseudo-first order	$q_{e,cal} (mg/g)$ $k_1 (min^{-1})$ R^2	3.4 0.15 0.92	2.4 0.44 0.89	1.6 3.26 0.98	0.6 7.8 0.99
Pseudo-second order	$q_{e,cal} (mg/g)$ $k_2 (g/mg$ min) $h (mg/g min)$ R^2	3.8 0.05 0.74 0.96	2.6 0.2 1.42 0.95	1.6 3.9 9.94 0.94	0.6 474.4 182.4 0.99
Weber-Morris intraparticle diffusion model	$k_{i1} (mg/g)$ $min^{1/2}$ $C_1 (mg/g)$ R^2 $k_1 (mg/g)$	1,4 0.27 0.99	0.45 0.49 0.98		
	$\kappa_{i2} (mg/g)$ min ^{1/2}) $C_2 (mg/g)$ R^2	0,67 0.19 0.99	0.14 1.5 0.93		

film diffusion process was very fast asthe equilibrium was reached in less than 30 mins and 60 mins at dosages of 20 g/L and 50 g/L respectively, when intraparticle diffusion no longer dominates due to low phosphate concentration [18,54]. IOS showed high P sorption affinity by reaching equilibrium in a few minutes even when influent concentrations were below 5.0 mg/L [28]. At lower dosages (5 g/L and 10 g/L) a significant amount of P was adsorbed on the IOS surface within 8 h. As such the adsorbent exhibits a good performance either in high or low P concentration but requires more time to reach equilibrium as the initial P concentration increases.

3.2.2. Effect of pH

Adsorption experiments were also conducted at different pH values and the results are presented in Fig. 5. Lower pH had a positive influence on P removal. Maximum adsorption capacities of 21.8, 10.2, 6.7 and 4.7 mg P/g at pH 2, pH 4, pH 7 and pH 9 were obtained by sorption isotherm model fitting, respectively (Table 3). IOS demonstrated a high adsorption capacity in acid wastewater, even at pH 2 where some iron might be dissolved, so IOS could be used for specific wastewater streams [56]. At higher pH (greater than12), no P adsorption was noticed. The competition between deprotonated hydroxyl groups and phosphate would increase with an increasing pH and this as a consequence would reduce the



Fig. 5. Freundlich isotherm fitted to the experimental batch tests at different pH values.

adsorption capacity [57]. Furthermore, iron-based material is typically positively charged at low pH values, favouring the adsorption of phosphate ions [22].

Data on pH is lacking in previous research [27,28] and that might be the reason for different adsorption capacities as 10.5 mg P/g IOS and 20 mg P/g IOS were mentioned in previous research [27,28]. Nevertheless, the results presented here are in the same order of magnitude.

The values of the Freundlich and Langmuir constants and the correlation coefficients at different pH are presented in Table 3. The R² of the Freundlich isotherm is higher than the one of the Langmuir isotherm. It can therefore be concluded that in this study the Freundlich isotherm model explains the adsorption process better. This agrees with other P adsorption research [58]. The Freundlich equation, although empirical, implies that the affinity for adsorption decreases exponentially with increasing saturation, which may be closer to reality than the assumption of constant binding energy inherent to the Langmuir equation [11]. Although the Freundlich K_F values give a measure of relative P adsorption capacity, these values are not directly related to the P adsorption maxima estimated by the Langmuir equation (an increase in Freundlich K_F value does not correspond to an increase in adsorption maxima Table 3). This kind of situation may come from the precipitation of phosphate with freely available Fe^{3+} of IOS [11]. Precipitation also contributes to P removal in the adsorption process.

3.3. Column test and prediction of saturation time of IOS

The performance of IOS was further evaluated using the goat farm CW effluent in a laboratory-scale column. Fig S2 shows that the breakthrough curve of the 1.5, 0.5, and 0.3 BV/h reached the breakthrough point (2.5 mg/L) at 111, 280 and 450 BV respectively. Hence, with the flow rate decreasing from 1.5 BV/h to 0.3 BV/h, the breakthrough point was postponed significantly (111 BV to 450 BV). The breakthrough curve rose rapidly after the breakthrough point and stabilized. It is worth noting that the IOS is not saturated in the stabilized period because the C/C₀ was still below 1.0. This situation means that intraparticle diffusion dominated after the initial rapid increase caused by film diffusion (Fig. 4b), and that the inner part of the adsorbent plays an increasingly important role over time. IOS showed a higher phosphorus adsorption capacity (13.84 mg P/g) in the column test than measured in batch (kinetic and isotherm) tests, because of the longer contact time (1400BV/40 days). A similar situation has occurred in a previous study [29], which highlights the benefits of column adsorption experiments. Based on the above, a fixed bed column with lower HLR (8.5 cm/h) and high bed height (80 cm) was selected for the full-scale test.

Based on the laboratory-scale column test results, the breakthrough time of the full-scale IOS granular reactor was predicted using calculation and model fitting approaches. The calculation is based on the assumption that the entire IOS substrate would be saturated with phosphorus at the end of its functional lifetime (Yuan et al., 2020). The average operational values used in this calculation are as follows: flow rate of 2.2 m³/d (8.5 cm/h), an influent concentration of 27.6 mg P/L, an effluent concentration of 2.5 mg P/L (discharge limit), an IOS

Table 3

Parameters corresponding to P adsorption isotherms of IOS from 30 mg P/L synthetic solution by means of batch tests at different pH.

Parameters		рН				
Isotherm model		pH 2	pH 4	pH 7	pH 9	
Freundlich	$K_F (mg/g)/ (mg/L)^n$	4.02	4.6	3.88	3.11	
	1/n	0.51	0.31	0.25	0.17	
	R^2	0.99	0.97	0.92	0.9	
Langmuir	q_{max} (mg/g)	21.81	10.21	6.71	4.68	
	K_L (L/mg)	0.16	1.15	4.91	6.19	
	R^2	0.92	0.75	0.66	0.74	

phosphorus adsorption capacity of 13.84 mg/g (as obtained in the column test), an IOS bulk density of 1.23 g/cm³ and a volume of 0.87 m^3 . Based on these values, the IOS phosphorus saturation time is predicted to be about 292 days.

The Bohart – Adams and BDST adsorption model have been successfully employed to fit the experimental data in order to describe the breakthrough curve (Fig S2). The R^2 values are 0.83–0.96 and 0.75–0.92 for the BDST and Bohart – Adams models, respectively (Table 4), and the model parameters can thus be considered suitable for scaling up to field experiments [59]. The saturation time from the BDST model and the Bohart – Adams model were 169–233 days and 262–319 days respectively. This is in line with the value calculated above (292 days), and in any case the results show that at field-scale the IOS can be used from six months to a year at least.

3.4. Demonstration of IOS integrated at full-scale

The performance of the CWs at the goat farm was monitored for two years (Sept 2017 - Sept 2019) prior to full-scale IOS testing and the results are shown in Table 5. The CWs showed high removal efficiency of TSS (71%), COD (93%), ammonium nitrogen (96%), nitrate (57%) and TN (74%). The pH remained between 6.5 and 7.5. However, the *ortho*phosphate (33%) and TP (32%) removal was insufficient. The average effluent TP concentration is 25.5 mg P/L, which is about one order of magnitude above the discharge limit (2.5 mg P/L) imposed by the Flemish Government. This insufficient phosphorus removal is a common problem in CWs [42,60]. Especially in decentralized wastewater treatment, additional polishing steps must be economically feasible and easy to operate. To meet these requirements, a fixed bed IOS reactor was designed and integrated into the system as discussed above.

The performance of the integrated system was examined for one year (Sept 2019-Oct 2020). For organic matter and nitrogen removal efficiency, the performance of the CWs and the IOS is illustrated in Fig. 6. The CWs continued to show a high COD removal efficiency throughout the whole monitoring period, with COD effluent concentrations remaining below 50 mg/L. IOS contributes to 33% COD removal from the effluent of CW and UV₂₅₄ results show that the IOS granular reactor also removes part of the UV₂₅₄. As such, some of the remaining dissolved organic matter is removed by the IOS. Only little nitrogen removal is observed by the IOS.

As shown in Fig. 7, the TP removal efficiency of the CWs was lower than 40% and variable. The TP removal efficiency of the integrated system can reach 99% when applying the IOS and over the full experimental period an effluent TP concentration of less than 0.3 mg/L was obtained. The IOS reactor performed well for 400 days/1000 BV (and even better than the predicted 292 days) and demonstrated its potential for long-term decentralized wastewater treatment. Due to Covid-19

Table 4

Parameters of the BDST and Bohart–Adams models derived from the column test results, and prediction of field-scale performance based on those models (assuming influent C_0 27.6 mg P/L).

Models	H (cm)	V (cm/ h)	$K (L mg^{-1}h^{-1})$	Ν	R ²	$t_{2,5}$ at field scale (H = 80 cm and V = 8.5 cm/h)
BDST	40	60	0.00027	15,706	0.83	233 d
		20	0.00013	16,436	0.86	169 d
		12	0.000098	16,688	0.94	198 d
Bohart–Adams	40	60	0.00015	24,944	0.75	319 d
		20	0.000079	23,417	0.83	276 d
		12	0.000062	23,328	0.92	262 d

K is the adsorption rate constant $(L \text{ mg}^{-1}\text{h}^{-1})$; *N* is the dynamic bed capacity (mg L⁻¹); *C*₀ is the influent adsorbate concentration (mg L⁻¹); *V* is the HLR (cm h⁻¹); and *H* is the adsorbent height in the column (cm), t_{2.5} is the field scale predicted breakthrough time based on models (adsorbate concentration is 2.5 mg/L).

Table 5

Influent and effluent wastewater characteristics of the CW system at the goat farm, prior to adding the IOS polishing step and comparison with the Flemish discharge limits (average \pm standard deviation, n = 12).

Parameters	Influent	Effluent	Flemish discharge limit	Removal efficiency
pH	6.9 ± 0.4	7.5 ± 0.3	6.5–9	
Conductivity	1805 ± 240	1610 ± 165		\
	μS/cm	µS/cm		
Dissolved	0.5 ± 0.15	9.2 ± 1.1	Λ	Λ
oxygen	mg/L	mg/L		
Suspended	101 ± 31	29 ± 6.8	60	71 %
solids	mg/L	mg/L		
UV254	1.1 ± 0.39	$\textbf{0.4} \pm \textbf{0.14}$	\	Λ
	cm^{-1}	cm^{-1}		
COD	768 ± 317	54 ± 37	125	93 %
	mg/L	mg/L		
Phosphate	$\textbf{24.7} \pm \textbf{8.2}$	16.6 ± 5.6	Λ	33 %
	mg P/L	mg P/L		
TP	$\textbf{37.5} \pm \textbf{10.1}$	$\textbf{25.5} \pm \textbf{8.8}$	2.5	32 %
	mg P/L	mg P/L		
Ammonium	33.4 ± 15.9	1.4 ± 1.2	\	96 %
	mg N/L	mg N/L		
Nitrite	0.3 ± 0.22	0.3 ± 0.1	\	\
	mg N/L	mg N/L		
Nitrate	16.1 ± 12.2	6.6 ± 5.1	\	\
	mg N/L	mg N/L		
TN	49.1 ± 18	13.0 ± 8	15	74 %
	mg N/L	mg N/L		



Fig. 6. Average effluent organic matter and nitrogen concentration of CWs and IOS in goat farm wastewater treatment system for 400 days (Sept 2019-Oct 2020).

restrictions, there was no sampling during the middle 150 days of the demonstration but the goat farm worked as usual and there is no reason to suspect a different behavior of the integrated system during this period. Moreover, the application of IOS is also interesting from an economical point of view as it is a waste product of the drinking water industry. As such this material can be obtained at a low cost and the drinking water company can reduce its waste disposal costs. This successful demonstration of IOS for phosphorus removal during decentralized treatment contributes to the sustainability of such systems in terms of the reuse of waste as substrate and high phosphorus removal efficiency.

In comparison to different substrates [61–63], the IOS has the potential to become a relevant substrate to be used in constructed wetlands system for decentralized wastewater treatment.



Fig. 7. Removal efficiency for TP in CWs (before IOS) and IOS in goat farm wastewater treatment system for 400 days (Sept 2019- Oct 2020). Gap between days 160–280 due to lack of samples because of Covid-19 restrictions.

3.5. IOS regeneration and reusability test for 5 cycles

Reusability of adsorbents plays an important role in actual engineering because of the economic implications. As shown in Fig. 8, when saturated IOS is transferred to strong alkaline conditions, phosphorus was released from the IOS to the liquid. Desorption performance with 0.01 M - 1 M NaOH and KOH after 24 h was assessed. The phosphorus recovery efficiency increased with increasing concentration of NaOH and KOH and KOH showed the best performance. It is worth noting that the phosphorus released from used IOS at 1 M KOH is higher than the IOS adsorption capacity (13.84 mg P/g IOS in the column test). This result discloses that the extra phosphorus comes from the pristine IOS, which is also confirmed by the SEM-EDS results. The extra phosphorus might have come from the ground water and be adsorbed during the formation of IOS [64]. Therefore, the phosphorus recovery efficiency was higher than 100%. The phosphorus in the IOS is as such prone to efficient desorption (using 0.5-1 M KOH), indicating its potential to consequentially serve as potential phosphorus fertilizer through e.g. struvite precipitation (using external NH₄⁺ and Mg²⁺ sources and at pH 8) [21,33,65].

An economical relevant adsorbent is expected to show good adsorption capacity even after several adsorption and desorption cycles. Fig. 8b shows the adsorption and desorption capacity of IOS using 0.5 M KOH desorption solution during 6 cycles. It is worth noting that the adsorption capacity of IOS increased in the first three cycles, and it reached 22.5 mg P/g at the third cycle. The adsorption capacity increased in the second and third cycle because of the P release from the pristine IOS. Then the adsorption capacity decreased from the third cycle onwards. The potential application of IOS as a renewable adsorbent was demonstrated by the high adsorption capacity which remained about 80% of that of pristine IOS after 6 cycles. This is promising as IOS has a lower material and regeneration cost than other synthetic materials [66] and also a higher adsorption capacity and reusability than natural materials [67].

4. Conclusion

In this work, different characterization methods (including FTIR, XRD, SEM-EDS and BET) were used to study the properties of IOS (a waste product from the drinking water industry) as a substrate for phosphorus removal in view of decentralized wastewater treatment. The IOS surface was covered by Fe (47%) and O (37%) and offers sufficient area $(249 \text{ m}^2/\text{g})$ for adsorption. Fe(III) compounds are the main components of IOS. In a laboratory-scale column test with the effluent of a goat farm, a high phosphorus adsorption capacity of 13.8 mg P/g was obtained. Batch tests indicate that several parameters including IOS dosage, pH and adsorption time have an important influence on phosphorus adsorption by IOS. Phosphorus adsorption capacity by IOS increased with lower solution pH. In the goat farm field test, a pilot-scale fixed bed IOS filter was designed and integrated into the existing decentralized wastewater treatment system. This IOS granular filter showed 99% TP removal efficiency and the TP concentration in the effluent remained less than 0.3 mg/L during the whole monitoring period (400 days). In a regeneration and reusability test, KOH gave better results than NaOH, and nearly 80% adsorption capacity remains after six adsorption/desorption cycles.

In summary, an IOS (re)use opportunity is demonstrated in view of enhanced phosphorus removal for decentralized applications.

CRediT authorship contribution statement

Rui Zhang: Conceptualization, Methodology, Formal analysis, Validation, Writing – original draft, Data curation. Lutian Wang: Software. Fida Hussain Lakho: Investigation, Resources. Xuetong Yang: Writing – review & editing. Veerle Depuydt: Project administration, Funding acquisition. Wouter Igodt: Project administration, Funding acquisition. Hong Quan Le: Supervision, Writing – review & editing. Diederik P.L. Rousseau Rousseau:: Supervision, Writing – review & editing. Stijn Van Hulle: Supervision, Writing – review & editing, Project administration, Funding acquisition.



Fig. 8. Phosphorus recovery of IOS at (a) different concentrations of desorption agents and (b) adsorption/recovery efficiency of 0.5 M KOH determined by a reusability test (line is the reminded adsorption capacity % in each cycle).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2021.120213.

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