

Phosphorus retention capacity in red ferralitic soil

M. M. Pérez, J. Bossens, E. Rosa and F. M. G. Tack

ABSTRACT

In this study the main physical–chemical characteristics of red ferralitic soil to use as substrate in subsurface wetlands was determined. The P-removal was evaluated in a short-term isotherm batch experiment and in a column percolation experiment. The acid characteristic and high content of iron minerals in the red ferralitic soil facilitated the phosphorus removal. Also the sorption isotherms at two different temperatures were obtained. The results showed that the sorption capacity increases with an increase in solution temperature from 25 to 35 °C. The experimental data were fitted to Langmuir and Freundlich models, having a better fit to the Freundlich isotherms. The maximum P-sorption capacities estimated using the Langmuir isotherm were 0.96 and 1.13 g/kg at 25 and 35 °C respectively. Moreover a column experiment was carried out at two different flows. Sequential extractions of the phosphorus-saturated soil indicated that phosphorus is mainly bound with iron or aluminum minerals. The results have demonstrated a good potential for red ferralitic soil for phosphorus removal from urban wastewater.

Key words | phosphorus removal, sorption isotherms, subsurface wetlands

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INTRODUCTION

Subsurface-flow constructed wetlands have gained in popularity as an efficient and economical treatment alternative. Wastewater treatment is achieved in a constructed wetland through an integrated combination of biological, physical and chemical interactions between plants, substrate and microorganisms (De Feo 2007). Due to the minimum requirement for their operation and management, constructed wetlands are promoted as low-cost technology for the treatment of both municipal and industrial wastewater.

Generally, subsurface wetlands present a good performance in the removal of main pollutants. However, phosphorus removal has not been effective, removal efficiencies of 20–30%, being obtained. Hence it is important to consider the complexity of phosphorus removal mechanisms in the design of these treatment systems (Kadlec & Knight 1996).

Phosphorus removal in wetlands may take place due to plant uptake, accretions of wetland soils, microbial immobilization, retention by the substrate and precipitation in the water column. Among these factors, the substrate may play the greatest role and could be the factor most amenable to control (Ayoub *et al.* 2001; Brix *et al.* 2001). Consequently, it is important to select those substrates presenting the highest phosphate adsorption capacity, which depends mainly

on the specific physical–chemical properties of these materials, including pH, redox potential, dissolved ions and minerals content (Vohla *et al.* 2011).

The ability of substrate for phosphorus retention is attributed to content of iron, aluminum, and calcium because the phosphorus is removed by sorption and precipitation processes (Vohla *et al.* 2011; Klimeski *et al.* 2012). In substrates with high iron and aluminum contents, at pH lower than 6, precipitation processes are favoured, whereas at higher pH values the physical adsorption processes are favoured (Zhu *et al.* 2003). The most oxidized conditions also tend to favour phosphorus removal in subsurface wetlands. Phosphorus sorption efficiencies of many substrates have been examined including gravel, dolomite, furnace slag, fly ash, shale, limestone, and sand. Many studies have been carried out with natural products (Arias *et al.* 2001; Sikdar 2007; Gustafsson *et al.* 2008), and other studies have been based on man-made products and industrial by-products (Zhu *et al.* 2003; Xu *et al.* 2006; Adam *et al.* 2007; Gustafsson *et al.* 2008).

In previous studies, phosphorus removal using different substrates and sediments proved to be an endothermic process, and higher temperature was preferred for the removal of phosphorus (Huang *et al.* 2011; Jin *et al.* 2005; Mezenner

& Bensmalli 2009; Herrmann *et al.* 2014). The adsorption of phosphorus may involve not only physical but also chemical sorption processes, and the particular processes that take place depend on the composition of the substrate used.

Pérez *et al.* (2009) evaluated several substrates in vertical subsurface wetlands at laboratory level and obtained good results for phosphorus removal with the use of red ferralitic soil as substrate. This soil has an elevated minerals composition so it can be an attractive substrate to use in subsurface wetlands and is naturally available in different regions of Cuba.

The present work aimed to evaluate the P-removal capacities at two temperature of red ferralitic soil for use as substrate in subsurface wetlands and to identify the main phosphorus removal mechanisms.

MATERIALS AND METHODS

Red ferralitic soil characterization

The soil used in this study was obtained in Mata, Cifuéntes, Villa Clara, in the central region of Cuba. P-removal properties of this soil were evaluated and hence its applicability for use as subsurface constructed wetlands substrate. The porosity was determined using the standard soil science procedure based on estimations of bulk density and particle density (Klute 1986). The following physical–chemical soil parameters were determined according to Van Ranst *et al.* (2005): pH-KCl, pH-H₂O and electrical conductivity (EC) by electrometric methods, organic matter was determined by gravimetric method and total carbonate by volumetric method. The total phosphorus was measured according to the colorimetric method of Sheel (Van Ranst *et al.* 2005). Total nitrogen and ammonium nitrogen were determined by the Kjeldahl method. Cation exchange capacity (CEC) was determined according to the continuous extraction methods and finally the metals were analysed by plasma optical emission spectroscopy.

Kinetic experiment

A kinetic experiment was carried out by contacting 5 g of red ferralitic soil, placed in a 200 mL Erlenmeyer flask, with 150 mL of standard solution of KH₂PO₄ with a concentration of 8 mg P/L. This concentration is in the order of that in typical urban wastewaters. To minimize splashing and evaporation, all Erlenmeyer flasks were covered with plastic

film. Measurement was performed at different times (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 h). The solutions were continuously agitated using a magnetic stirrer (Heidolph MR Hei-Tec, Germany) with temperature control. Initial pH of solution was adjusted to the required value (pH 7) with diluted NaOH solutions. Duplicate analyses were conducted for each experiment. Samples were filtered using Whatman polyamide membrane filters (0.45 µm) in order to obtain a clear solution for phosphorus determination. The phosphorus concentration was determined according to *Standard Methods (APHA 2000)* using the ammonium molybdate method. All procedures described above were repeated for two different temperatures (25 and 35 °C) and with urban wastewater, whose properties are shown in Table 1.

The experimental data for phosphorus removal were fitted to the different kinetic models. The integrated form of the rate expression for zero order and second order are given by Equations (1) and (2)

$$C_{in} - C_{out} = -kt \quad (1)$$

$$kt = \frac{1}{C_{out}} - \frac{1}{C_{in}} \quad (2)$$

where k is a reaction rate constant (mg L⁻¹ d⁻¹), C_{in} is an influent concentration (mg/L) and C_{out} effluent concentration (mg/L).

First order degradation represents the basic kinetic model for these systems; it is expressed by Equation (3).

$$\ln \frac{C_{out}}{C_{in}} = -kt \quad (3)$$

where k is a reaction rate constant (d⁻¹).

Table 1 | Averages and standard deviations of main chemical–physical characteristics in three urban wastewater samples

Parameter	Values
pH	7.2 ± 0.01
Electrical conductivity (µS/cm)	669 ± 12
Total nitrogen (mg/L)	15.7 ± 2.6
Nitrogen – NH ₄ ⁺ (mg/L)	9.5 ± 0.9
Total phosphorus (mg/L)	7.7 ± 0.1
Chemical oxygen demand (mg/L)	108.4 ± 8.8
Total suspended solids (mg/L)	18.3 ± 3.3
Dissolved oxygen (mg/L)	0.8 ± 0.1

Equation (4) represents the Monod model (Metcalf and Eddy, Inc. 2003).

$$kt = K \ln \frac{C_{in}}{C_{out}} + (C_{in} - C_{out}) \quad (4)$$

where k is a reaction rate constant ($\text{mg L}^{-1} \text{d}^{-1}$) and K is a damping factor (mg/L).

Sorption isotherm experiments

Equilibrium experiments were performed with the red ferralitic soil to determine sorption isotherms. Five grams of soil was placed in a 200 mL Erlenmeyer flask and 150 mL of standard solution of KH_2PO_4 , to give eight levels of phosphorus (0, 2.5, 5, 10, 20, 40, 80 and 120 mgP/L), were then added. The Erlenmeyer flasks were sealed and were continuously agitated in a magnetic stirrer (Heidolph MR Hei-Tec, Germany) with temperature control, at two different temperatures (25 and 35 °C), for 8 h. Blanks containing no soil were always included in the experiments. The samples were filtered using Whatman polyamide membrane filters (0.45 μm) and the concentration of P in the filtrate was measured according to *Standard Methods* (APHA 2000) using the ammonium molybdate method. The amount of phosphorus removed from solution by the soil was calculated from the decrease in P concentration in the solution. The apparent P-sorption capacity of the soil was estimated using the linear form of the Langmuir equation

$$\frac{C_e}{q} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}} \times b \quad (5)$$

where C_e is concentration of P in solution at equilibrium (mg/L); q is mass of P adsorbed to the soil (g/kg); q_{\max} is apparent P-sorption capacity (g/kg); b is a constant related to the binding strength of P.

The Freundlich isotherm was derived empirically and refers to a sorption model where the affinity term decreases exponentially as the sorption amount increases. It also incorporates the heterogeneity of the surface and the distribution of adsorption sites and their energies. It is possible to determine the constants in the following Freundlich isotherm by log-transforming the equation

$$\ln q = \frac{1}{n} \ln C_e + \ln k \quad (6)$$

where C_e is concentration of P in solution at equilibrium

(mg/L); q is mass of P adsorbed to the soil (g/kg); n , Freundlich intensity parameter, which changes according to heterogenic grade; k is Freundlich capacity factor (L/g), related to affinity between solvent and solvate.

To determine the best fit of the collected isotherm data, both the Langmuir and Freundlich isotherm models were fitted to each of the experimental data sets. For the Langmuir model, this was accomplished by plotting C_e/q versus C_e and then fitting a linear regression line to the data using Excel software. The appropriateness of the Langmuir isotherm was assessed by determining the R^2 values (coefficient of determination) of the linear regression lines. Similarly, for the Freundlich model, $\ln(q)$ was plotted against $\ln C_e$ and a linear regression line was fitted. As described previously, it was possible to determine the effectiveness of the model based on the correlation coefficient (R^2) value of the modelled results.

Column experiment

Two experimental columns (diameter 40 mm) were packed with 200 g of red ferralitic soil. Water spiked with KH_2PO_4 to a P concentration of 8 mg/L (pH adjusted to 7.2 with NaOH) was supplied continuously at two different flows, 0.03 and 0.06 L/h, using a feeding tank. The two flow rates correspond to a nominal retention time of 4.5 and 2.3 h, respectively. The effluent from each column was collected at different times (0.5, 1, 2, 3, 4, 6, 8, 32, 56, 80, 104, 128, 152, 176 and 200 h respectively). The P concentration was analyzed as described above. Furthermore, pH and electrical conductivity were measured.

Sequential extraction

After approximately 8 days of continuous loading, the column experiment was concluded. In order to elucidate the main binding of the phosphorus in the soil and the main mineral that intervenes in the phosphorus adsorption, a sequential extraction scheme was performed on the soil used in the columns, following a protocol of Hieltjes and Lijklema (1980). The fractionation scheme included: (1) two consecutive extractions in 1 mol/L NH_4Cl at pH 7 (denoted adsorbed-P), (2) two consecutive extractions in 0.1 mol/L NaOH followed by extraction in 1 mol/L NaCl (denoted Fe + Al-P), (3) extraction in 0.5 mol/L HCl (denoted Ca + Mg-P), and (4) analysis of the remaining P in the soil after ignition at 550 °C and extraction in boiling 1 mol/L HCl (denoted residual-P). Analyses were performed in duplicate for each column.

Statistical analysis

One-way analysis of variance with 95% as the significance criterion was performed using Statgraphics centurion software XV.II to determine if significant differences exist between the phosphorus concentration at two temperatures in the kinetic and sorption experiment and between the wastewater and standard solution in the kinetic experiment.

RESULTS AND DISCUSSION

Characteristics of the red ferralitic soil

The acid characteristic and high iron content of red ferralitic soil make it suitable for use as substrates in subsurface constructed wetlands systems. The main phosphorus removal mechanisms take place by means of the reactions of the minerals contained in the soil with phosphorus presented in the wastewater. When the soil has acid characteristic, the minerals that have more influence in phosphorus removal are iron and aluminum. The main chemical-physical characteristics of this soil are presented in Tables 2 and 3.

Kinetic model of phosphorus removal

Figure 1 shows the kinetic behaviour of phosphorus removal with red ferralitic soil. The maximum phosphorus adsorption was obtained at 3.5 h in all the cases. Also it is

Table 2 | Chemical-physical characteristic of red ferralitic soil samples and standard deviation of two samples analyzed

Parameter	Values
Particle density (g/cm ³)	2.22 ± 0.07
Bulk density (g/cm ³)	1.03 ± 0.01
Porosity (%)	54
pH-KCl	5.74 ± 0.03
pH-H ₂ O	6.81 ± 0.02
Electrical conductivity (μS/cm)	131 ± 3
Total nitrogen (mg/kg soil)	4130 ± 20
N-NH ₄ ⁺ (mg/kg soil)	16.94 ± 0.11
Total phosphorus (mg/kg soil)	1650 ± 32
Organic matter (%)	12.3 ± 0.5
Total carbonate (%)	0.63 ± 0.32
CEC (meq/100 g soil)	18.1 ± 0.9

Table 3 | Metal content of red ferralitic soil and standard deviations of two samples analyzed

Metals (mg/kg soil)	Values
Cd	10.3 ± 0.1
Cd available	0.925 ± 0.004
Cr	341 ± 14
Cr available	0.076 ± 0.001
Fe	1228800 ± 1742
Fe available	3.46 ± 0.03
Mn	7429 ± 200
Mn available	72.45 ± 0.38
Ni	519 ± 25
Ni available	1.39 ± 0.08
Pb	59 ± 8
Pb available	0
Zn	486 ± 34
Zn available	1.71 ± 0.19
Al	63172 ± 915
Al available	2.32 ± 0.09

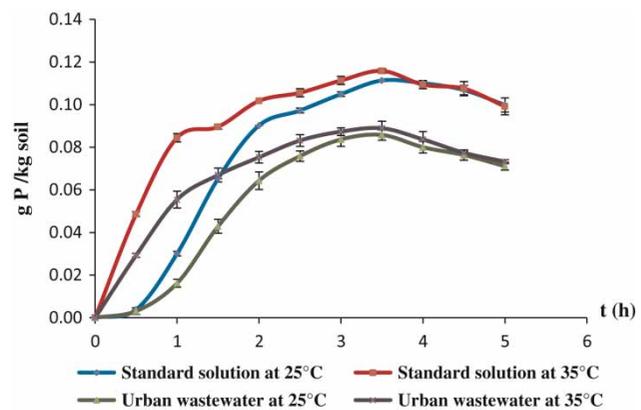


Figure 1 | Kinetics of phosphorus retention in red ferralitic soil.

observed that at 35 °C the adsorption began faster than at 25 °C.

Table 4 shows the line equation and the correlation coefficient for the four models studied. In all cases the experiment data fit to the second order model. According to what is reported in the literature, phosphorus removal does not follow a first order model, which is suitable for biological removal. The main removal mechanisms in the phosphorus retention are chemical adsorption and precipitation with the soil minerals (Kadlec & Knight 1996; Zhang et al. 2014). The range of second order constants obtained for the phosphorus removal in all the cases

Table 4 | Kinetic models describing kinetics of phosphorus sorption on the red ferralitic soil and determination coefficient

	Standard solution of KH_2PO_4		Urban wastewater	
	25 °C	35 °C	25 °C	35 °C
Zero order $C_{\text{out}} - C_{\text{in}} = kt$	$y = 1.80x - 0.009$ $R^2 = 0.90$	$y = 0.97x + 2.76$ $R^2 = 0.84$	$y = 1.48x - 0.37$ $R^2 = 0.93$	$y = 0.92x + 1.55$ $R^2 = 0.87$
First order $\ln \frac{C_{\text{out}}}{C_{\text{in}}} = -kt$	$y = -0.41x + 0.13$ $R^2 = 0.96$	$y = -0.29x - 0.37$ $R^2 = 0.93$	$y = -0.29x + 0.12$ $R^2 = 0.96$	$y = -0.21x - 0.19$ $R^2 = 0.93$
Second order $\frac{1}{C_{\text{out}}} = kt + \frac{1}{C_{\text{in}}}$	$y = 0.10x + 0.07$ $R^2 = 0.99$	$y = 0.09x + 0.16$ $R^2 = 0.98$	$y = 0.06x + 0.09$ $R^2 = 0.98$	$y = 0.05x + 0.15$ $R^2 = 0.97$
Monod $\frac{1}{t \ln(C_{\text{out}}/C_{\text{in}})} = \frac{k}{K} + \frac{1}{K} \left(\frac{C_{\text{out}} - C_{\text{in}}}{t} \right)$	$y = 0.19x - 0.02$ $R^2 = 0.88$	$y = 0.12x + 0.18$ $R^2 = 0.95$	$y = 0.18x - 0.02$ $R^2 = 0.95$	$y = 0.11x + 0.11$ $R^2 = 0.95$

(Table 5) is greater than for other substrates, due to the high contents of iron minerals in the red ferralitic soil. Sikdar (2007) reported second order constant values ranging of $0.031\text{--}0.31(\text{mg/L})^{-1} \text{d}^{-1}$ for gravel.

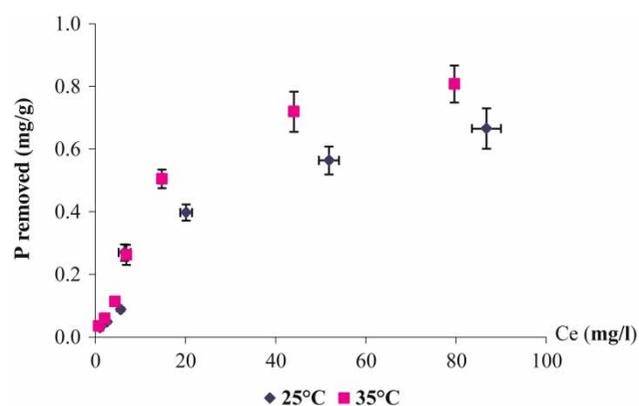
There are significant differences between the phosphorus retention in the standard solution and urban wastewater at two temperatures ($p < 0.05$). Urban wastewater contains relatively high contents of other anions which may compete with the phosphate for the adsorption sites, and hence the efficiency of the adsorption may be reduced. However, there are no significant differences between phosphorus retention ($p < 0.05$) at the two temperatures studied; there are only significant differences between the two temperatures for the standard solution in the first hour of the reaction ($p < 0.05$).

Sorption isotherm experiments

Figure 2 shows the adsorption isotherm; an increase of the adsorption is observed at 35 °C, principally for the more concentrated solutions. This result agrees with Shilton *et al.* (2006), Huang *et al.* (2011), Mezenner and Bensmaili (2009), Jin *et al.* (2005) and Herrmann *et al.* (2014) about the temperature influence in the phosphorus adsorption. Statistically significant differences were observed between the phosphorus adsorption at these temperatures ($p < 0.05$). Several authors agree that retention of phosphorus in substrates and sediments occurs through endothermic

Table 5 | Second order kinetic constant of phosphorus removal with red ferralitic soil

Standard solution		Urban wastewater	
25 °C	35 °C	25 °C	35 °C
2.47 ± 0.12 $\text{mg L}^{-1} \text{d}^{-1}$	2.18 ± 0.13 $\text{mg L}^{-1} \text{d}^{-1}$	1.44 ± 0.04 $\text{mg L}^{-1} \text{d}^{-1}$	1.18 ± 0.01 $\text{mg L}^{-1} \text{d}^{-1}$

**Figure 2** | Relation between equilibrium solution P and adsorbed P for red ferralitic soil at two temperatures.

reactions; thus the extent of adsorption increases with increasing temperature. This increase of temperature can increase the kinetic energy of adsorbent particles. Consequently, the collision frequency between adsorbent and adsorbate increases. Also, the adsorption increase may be due to the dimensions of the pores, which increase at high temperatures. The greater the size of the particle pores, the smaller is the contribution of intraparticle diffusion resistance.

Statistical fit of the two models described previously was compared by using data of adsorption isotherms. The Langmuir and Freundlich models commonly are fit by transforming the data and performing a linear regression. The increase of adsorption with the increase of temperature was corroborated.

The regression equations for the Langmuir and Freundlich isotherm models and the resulting model parameters are listed in Table 6. The experimental results demonstrated that they fit better to the Freundlich model than the Langmuir model based on the R^2 values. Both models are better at higher temperature. Del Bubba *et al.* (2003) and

Table 6 | Freundlich and Langmuir adsorption constants and correlation coefficients for red ferralitic soil

Langmuir	T (°C)	Regression equation	R ²	b (L/mg)	q _{max} (g/kg)
	25	y = 1.0899x + 38.125	0.86	0.03	0.96
	35	y = 0.8878x + 24.974	0.93	0.04	1.13
Freundlich	T (°C)	Regression equation	R ²	k (L/g)	1/n
	25	y = 0.1847x - 0.5104	0.90	0.60	0.185
	35	y = 0.1834x - 0.4286	0.94	0.65	0.183

Sikdar (2007) also found that the Freundlich isotherm model fitted the data better than the Langmuir isotherm model.

The red ferralitic soil has Langmuir adsorption capacities (0.96–1.13 g/kg) superior to different natural media tested with low mineral content. Drizo *et al.* (1999) observed in a study of several media that the best medium was fly ash (0.86 g/kg) followed by shale (0.65 g/kg) and Sikdar (2007) reported 0.0207 g/kg for gravel. Arias *et al.* (2001) carried out a study with different sand of Dinamarca and obtained a maximum adsorption capacity of 0.27–3.94 g/kg; the best adsorption was obtained with the sands that present

higher minerals content. Similar results were obtained by Li *et al.* (2013) for sludge samples of China (0.15–4.16 g/kg).

Other studies carried out with substrates that have high content of calcium iron or aluminum presented better results. Adam *et al.* (2007) reported for shellsand (9.6 g/kg) and Filtralite P® (2.5 g/kg); Xu *et al.* (2006) observed that furnace slag (8.89 g/kg) was the best amongst all the media tested followed by fly ash (8.81 g/kg). However, some industrial byproducts had an extremely high phosphorus adsorption capacity, e.g. 444 g/kg for blast furnace slag (Sakadevan & Bavor 1997). Furthermore, light expanded clay aggregates (produced by LECA) tested by Reddy *et al.* (1999) had highly variable phosphorus adsorption capacities (0.037–2.9 g/kg), depending on the soil of origin. The good results obtained allow the use of red ferralitic soil to improve the phosphorus removal in wastewater, considering that this soil is available in the natural form in different regions of Cuba.

Column experiment

The adsorption column was operated for approximately 8 days and the results obtained from this study are shown in Table 7. A decrease in the phosphate removal rate was observed during the last period of operation for two columns. This decrease in P removal was quicker in the

Table 7 | Phosphorus sorption in the column with red ferralitic soil at flow rate of 0.03 L/h and 0.06 L/h

Time (h)	0.03 L/h				0.06 L/h			
	pH	EC (µS/cm)	C (mg P/L)	Removal (%)	pH	EC (µS/cm)	C (mg P/L)	Removal (%)
0	7.2	90	7.81		7.2	90	7.96	
0.5	6.5	90	4.62	40.8	6.8	80	4.97	37.6
1.0	6.6	80	1.51	80.6	6.9	80	2.78	65.1
2.0	6.8	80	0.94	88.0	6.9	70	2.32	70.9
3.0	6.8	70	1.01	87.0	6.8	70	2.36	70.4
4.0	6.8	70	0.94	88.0	6.9	80	2.15	73.0
6.0	6.8	70	0.94	88.0	7.0	80	1.97	75.2
8.0	6.8	70	0.98	87.5	7.1	90	1.97	75.2
32.0	6.9	70	1.00	87.3	7.1	90	2.13	73.3
56.0	6.8	70	1.21	84.5	7.0	90	3.32	58.3
80.0	6.9	80	2.38	69.6	7.1	90	4.14	48.0
104.0	6.9	80	3.43	56.0	7.1	90	4.36	45.3
128.0	7.0	80	3.65	53.3	7.1	90	4.55	42.9
152.0	7.0	80	3.84	50.9	7.1	90	4.93	38.1
176.0	7.0	80	3.95	49.4	7.1	90	4.93	38.1
200.0	7.0	90	3.95	49.4	7.1	90	4.93	38.1

column with a higher flow, about 49 and 38% at 200 h for 0.03 and 0.06 L/h respectively. Figure 3 shows the break point at two flows. As expected, the breaking point in the column that operates at higher flow occurred (32 h) in less time than for the lower flow column (56 h). The column that operated at higher flow reaches saturation quicker, and less phosphorus removal is obtained. The mass balance in both columns obtained phosphorus retention of 0.7 g/kg.

Sequential extraction

It was *a priori* assumed that the phosphorus bond to Fe and Al would be the main P removed, because of the low pH and high Fe content of red ferralitic soil. The results from the sequential extraction of red ferralitic soil used in the experimental columns justified this hypothesis since the phosphorus bond to Fe and Al contributed 95% of the total P removal. The result strongly suggests that the phosphorus removal in the columns occurs by chemical adsorption or precipitation processes in the red ferralitic soil, forming strong Fe–P bonds. Lyngsie et al. (2014) also obtained the formation of strong Fe–P bonds with Fe oxide-based CFH-12 substrate. Table 8 show the phosphorus extracted in each fraction. The physical adsorption was insignificant in all the cases; this experiment corroborated the previous results about the increase of adsorption with the increase of temperature. The total phosphorus extracted

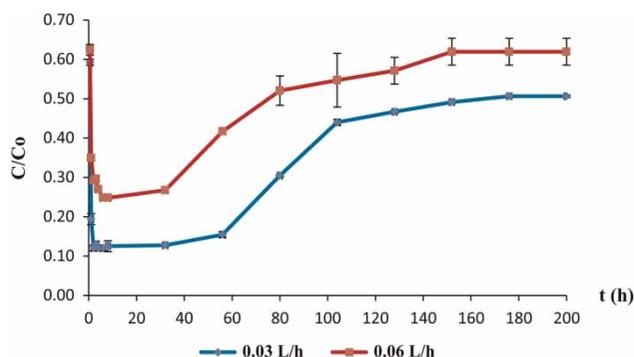


Figure 3 | Phosphorus adsorption in experimental columns.

Table 8 | Fractionation of P in the red ferralitic soil of the columns after the experiment (mg P/kg soil)

Soil	Loosely bound P	Al + Fe-P	Mg + Ca-P	Residual-P	Total
Column 1	0.7 ± 0.1	649 ± 18	16 ± 2	21 ± 10	687
Column 2	0.7 ± 0.1	659 ± 45	12 ± 4	14 ± 1	686

in both columns was similar to that achieved in the mass balance of the columns (0.7 g/kg), but it was smaller than the maximum capacity adsorption obtained for the Langmuir model (0.96–1.13 g/kg).

CONCLUSIONS

The kinetic modelling studies showed that the removal of phosphorus mainly occurred by chemical process. The increase of temperature resulted in a corresponding increase in the phosphorus removal. Consequently, the chemical absorption and precipitation are dominant phosphorus removal mechanisms in red ferralitic soil. In addition, the results show a better fit to the Freundlich model. The red ferralitic soil has high a phosphorus sorption capacity (0.96–1.13 g/kg) in comparison to other natural substrates used for phosphorus removal in wastewater. The main binding of phosphorus in the soil was with iron or aluminum minerals, confirming what has previously been discussed. The total phosphorus extraction in the soil in the columns was 0.7 g/kg. The red ferralitic soil may be a good option to increase the phosphorus sorption in wastewater treatment, mainly in countries where it is naturally available.

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REFERENCES

- Adam, K., Krogstad, T., Vrale, L., Sovik, A. K. & Jenssen, P. D. 2007 Phosphorus retention in the filter materials shellsand and Filtralite P (R) – batch and column experiment with synthetic P solution and secondary wastewater. *Ecological Engineering* **29**, 200–208.
- APHA 2000 *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.
- Arias, C., Del Bubba, M. & Brix, H. 2001 Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. *Water Research* **35** (5), 1159–1168.
- Ayoub, G., Koopman, B. & Pandya, N. 2001 Iron and aluminum hydroxyl (oxide) coated filter media for low-concentration phosphorus removal. *Water Environment Research* **73**, 478–485.
- Brix, H., Arias, C. A. & Del Bubba, M. 2001 Media selection for sustainable phosphorus removal in subsurface flow

- constructed wetlands. *Water Science and Technology* **44** (11–12), 47–54.
- De Feo, G. 2007 Performance of vegetated and non-vegetated vertical flow reed beds in the treatment of diluted leachate. *Journal of Environmental Science and Health*, **42** (7), 1013–1020.
- Del Bubba, M., Arias, C. A. & Brix, H. 2003 Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Research* **37** (14), 3390–3400.
- Drizo, A., Frost, C. A., Grace, J. & Smith, K. A. 1999 Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research* **33** (17), 3595–3602.
- Gustafsson, J. P., Renman, A., Renman, G. & Poll, K. 2008 Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment. *Water Research* **42**, 189–197.
- Herrmann, I., Nordqvist, K., Hedström, A. & Viklander, M. 2014 Effect of temperature on the performance of laboratory-scale phosphorus-removing filter beds in on-site wastewater treatment. *Chemosphere* **117**, 360–366.
- Hieltjes, A. H. M. & Lijklema, L. 1980 Fractionation of inorganic phosphates in calcareous sediments. *Journal Environmental Quality* **9**, 405–407.
- Huang, L. D., Fu, L. L., Jin, C. W., Gielen, G., Lin, X. Y., Wang, H. L. & Zhang, Y. S. 2011 Effect of temperature on phosphorus sorption to sediments from shallow eutrophic lakes. *Ecological Engineering* **37**, 1515–1522.
- Jin, X., Wang, S., Pang, Y., Zhao, H. & Zhou, X. 2005 The adsorption of phosphate on different trophic lake sediments. *Colloids and Surfaces A: Physicochemical Engineering Aspects* **254**, 241–248.
- Kadlec, R. H. & Knight, L. 1996 *Treatment Wetlands*, Lewis Publishers, Boca Raton, FL, USA.
- Klimeski, A., Chardon, W. J., Turtola, E. & Uusitalo, R. 2012 Potential and limitations of phosphate retention media on water protection: A process-based review of laboratory and field-scale tests. *Agricultural and Food Science* **21**, 206–223.
- Klute, A. 1986 *Methods of Soil Analysis. Part I: Physical and Mineralogical Methods*, 2nd edn. American Society of Agronomy, Madison, WI, USA.
- Li, Z., Jiang, N., Wu, F. & Zhou, Z. 2013 Experimental investigation of phosphorus adsorption capacity of the waterworks sludges from five cities in China. *Ecological Engineering* **53**, 165–172.
- Lyngsie, G., Penn, C. J., Hansen, C. B. & Borggaard, K. 2014 Phosphate sorption by three potential filter materials as assessed by isothermal titration calorimetry. *Journal of Environmental Management* **143**, 1–214.
- Metcalfe and Eddy, Inc. 2003 *Wastewater Engineering: Treatment and Reuse*, 4th edn. McGraw Hill, New York.
- Mezener, N. Y. & Bensmaili, A. 2009 Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chemical Engineering Journal* **147**, 87–96.
- Pérez, M. M., Rosa, E., Martínez, P., López, M. E., González, Y. & Monteagudo, M. 2009 Evaluación de la eficiencia de diferentes sustratos de filtros de suelo plantados en la depuración de aguas residuales domésticas (Evaluation of efficiency of planted soil filter substrates in domestic wastewater depuration). *CENIC Ciencias Biológicas* **40**, 99–103.
- Reddy, K. R., Kadlec, R. H., Flaig, E. & Gale, P. M. 1999 Phosphorus retention in streams and wetlands: a review. *Environmental Science Technology* **29** (1), 83–146.
- Sakadevan, K. & Bavor, H. J. 1997 Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. *Water Research* **32** (2), 393–399.
- Shilton, A. N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R. G. & Bilby, S. C. 2006 Phosphorus removal by an active slag filter: a decade a full scale experience. *Water Research* **40** (1), 113–118.
- Sikdar, A. 2007 *Quantification of complex phosphorus removal reactions occurring within wetlands filtration treatment systems*. DPhil thesis, Department of Civil Engineering, Queen's University, Kingston, Ontario, Canada.
- Van Ranst, E., Verloo, M., Demeyer, A. & Pauwels, J. M. 2005 *Manual for the Soil Chemistry and Fertility Laboratory: Analytical Methods for Soil and Plants, Equipment, and Management of Consumables*. International Training Centre for Post-Graduate Soil Scientists, University of Ghent, Ghent, Belgium.
- Vohla, C., Kõiv, M., Bavor, J. H., Chazarenc, F. & Mander, Ü. 2011 Filter materials for phosphorus removal from wastewater in treatment wetlands – a review. *Ecological Engineering* **37**, 70–89.
- Xu, D., Xu, J., Wu, J. & Muhammad, A. 2006 Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere* **63**, 344–352.
- Zhang, Y., He, F., Xia, S., Kong, L., Xu, D. & Wu, Z. 2014 Adsorption of sediment phosphorus by porous ceramic filter media coated with nano-titanium dioxide film. *Ecological Engineering* **64**, 186–192.
- Zhu, T., Mæhlum, T., Jenssen, P. D. & Krogstad, T. 2003 Phosphorus sorption characteristics of light-weight aggregate. *Water Science and Technology* **48**, 93–100.

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