Phosphorus recovery from sewage with a sustainable and low-cost treatment system

Vitor Tonzar Chaves, Dione Mari Morita, Iara Regina Soares Chao and Ronan Cleber Contrera

ABSTRACT

This study proposes a technology conceived based on an integrative approach that aims to promote phosphorus recovery and to recycle ferric water treatment sludge (FWTS), using it as a phosphorus adsorbent which may be applied as a soil ameliorant after reaching saturation. The assessed pilot plant operated with a daily influent flow of 360 litres and presented a removal efficiency of 94.4% ± 3.2% for COD and of 91.2% ± 7.8% for suspended solids. It also presented promising results for phosphorus removal. The maximum efficiency of dissolved reactive phosphorus removal was 95% on the first day and it decreased until reaching adsorbent saturation. The estimated breakthrough time was one year in the condition in which the filling medium of a second constructed wetland was only FWTS. In this situation, the effluent phosphorus concentration was 0.2 mg·L⁻¹. The authors concluded that the application of FWTS in a constructed wetland bed is an interesting alternative.

Batch adsorption experiments were run using phosphorus stock solution. Langmuir and Freundlich adsorption isotherm models were obtained for different initial pH values. The maximum adsorption capacity decreased as the initial pH was increased; values ranged from 4.76 mg P·g⁻¹ (pH = 3.9) to 1.44 mg P·g⁻¹ (pH = 9.0).

Key words | constructed wetland, ferric sludge, phosphorus recovery, sustainable sewage treatment, water treatment sludge

INTRODUCTION

Population growth is forecast to rise in the world and this growth imposes a heavy demand for fertilizers (Alexandratos & Bruinsma 2012). Since the 1950s, mass agricultural production has been supported by mineral/synthetic fertilization; however, this practice has resulted in eutrophication of water bodies and decline of the organic matter content in agricultural soils (Galloway et al. 2003; Intergovernmental Technical Panel on Soils 2015). Moreover, phosphorus reserves are limited, and scientists predict they will last at most 400 years (Van Kaunwenbergh 2003; Calvo et al. 2017).

Tropical soils comprise one-third of the superficial soils in the world, with 75% of the global population living on them (van Wambeke 2010; Calvo et al. 2017). Tropical soils comprise one-third of the superficial soils in the world, with 75% of the global population living on them (van Wambeke 2003). In the urban areas of tropical cities, water treatment sludge (WTS) is usually discharged directly into rivers or publicly owned treatment works (POTWs). Although the discharge into POTWs is reported as an alternative in the literature (Marguti et al. 2018), the sludge generated in the wastewater treatment processes has its potential methane generation reduced by up to 21% due to the presence of aluminum and iron (Smith & Carliell-Marquet 2009). Another usual destination for WTS is sanitary landfills, but the sludge has high plasticity, low shear strength and low permeability to water. As a result, if the sludge is not properly dried, it causes structural problems for the landfill. A solids content of 25%–30% and shear stress greater than 25 kPa have been recommended for this destination (O’Kelly 2016).

The use of WTS as a phosphorus adsorbent has been recently studied in the lab and at pilot scale (Babatunde et al. 2009; Ahmad et al. 2016; Jung et al. 2016). After reaching saturation, WTS can be applied as a soil ameliorant in agriculture (Dassanayake et al. 2015). Some authors diverge about this topic; for example, Walsh et al. (2008) concluded that the aluminum from alum or ferric WTS could bind to...
phosphorus and reduce its availability to plants. However, in the case of tropical soils, this would not be a problem because alum or ferric WTS has similar mineralogical composition to these soils, including low pH (Tartari et al. 2011; Hegazy et al. 2012a, 2012b; Victoria 2012).

Constructed wetlands are known to be efficient and resilient technologies (Nivala et al. 2012), but traditional filling materials such as sand and gravel have low phosphorus removal efficiency (Farahbakshazad & Morrison 2005; Arias & Brix 2005). The application of WTS as a constructed wetland filling material is an interesting alternative to promote low-cost technologies capable of recovering phosphorus from sewage (Park 2009; Babatunde et al. 2010; Zhao et al. 2011).

Thus, the goal of this research was to propose a treatment system that can remove organic matter and suspended solids and promote phosphorus recovery from sewage. This system must also have low cost and simple operation and maintenance, which is a necessity in many areas in tropical countries. It uses WTS as phosphorus adsorbent, which can also afterward be applied as soil ameliorant.

**METHODS**

**Pilot plant**

**Pilot plant design**

A daily influent flow of 360 L day⁻¹ was considered for the pilot plant design. To control influent flow, a pump Nietzsche, model NM021BY, was used.

The proposed technology was composed of four reactors:

(i) upflow septic tank: a commercial 1,000 L water tank;
(ii) decanter: a 500 L water tank. This reactor was conceived to retain suspended solids that were released from the upflow septic tank and to prevent clogging in the subsequently constructed wetland;
(iii) upflow constructed wetland: a 1,000 L water tank with a mean internal diameter of 1.35 m, filled with gravel of effective diameter (d₅₀) of 7.85 mm, d₆₀ of 11.3 mm, a coefficient of uniformity of 1.44 and porosity of 0.45. Typical wetland species were planted: *Canna x generalis*, *Coix lacryma-jobi*, *Dioscorea* spp, and *Zingiber officinale*.

These first three stages had already been monitored for 300 days before the fourth-stage installation. The system was not capable of removing phosphorus from sewage. For this reason, it was decided to evaluate, initially at a laboratory scale, the possibility of ferric water treatment sludge (FWTS) removing phosphorus. The methods used for this evaluation are described in the section ‘Laboratory experiments’. Once the possibility of phosphorus removal was verified, tests were performed in a wetland, described below, to observe the behavior of FWTS as an adsorbent with real sewage.

(iv) Constructed wetland partially filled with FWTS: this used a 1,000 L tank with a mean internal diameter of 1.35 m, filled with gravel and a 2 mm layer of FWTS (3.17 kg, dry mass) at the top, covered with a gravel layer of 5 mm. The small quantity of FTWS introduced was intentional to provide information about the exhaustion time in the short run. Ten seedlings of ginger (*Zingiber officinale*) taken from a natural wetland in the university campus were planted. The hydraulic loading rate was 0.27 m³ m⁻² d⁻¹.

**Pilot-plant monitoring**

The pilot plant was monitored for 83 days. During this period, 18 samples were taken to determine the concentrations of COD, suspended solids, total phosphorus (TP) and dissolved reactive phosphorus (DRP) in the influent and effluent.

All concentrations were determined following the standard methods (SM) described by APHA, AWWA, WEF (2012) and listed in Table 1.

**Determination of breakthrough time when the wetland filling medium is only FWTS**

\[
\text{Removed mass (g)} = \left(\frac{(C_{i(j+1)} - C_{e(i+1)}) + (C_{ij} - C_{ej})}{2}\right)t_{i(j+1)} \times 0.36
\]

\[\text{Eq. 1}\]

The breakthrough time \(t_{ba}\) when the wetland-filling medium is only FWTS was calculated using the following procedure:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>SM 5220-D</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>SM 2540-D</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>SM 4500-P B4 and SM 4500-P E</td>
</tr>
<tr>
<td>DAP</td>
<td>SM 4500-P B1 and SM 4500-P E</td>
</tr>
</tbody>
</table>
(a) Determination of the maximum solid phase concentration of phosphorus \((q_e)\):

\[q_e = \frac{C_i t_{ep} Q}{m_{FWTSp}} \quad (2)\]

where

- \(C_i\) = influent phosphorus concentration (mg L\(^{-1}\))
- \(Q\) = flow (L d\(^{-1}\))
- \(t_{ep}\) = exhaustion time when the wetland was partially filled with FWTS (d)
- \(m_{FWTSp}\) = dry mass of FWTS used in the experiment with wetland partially filled with FWTS (g).

(b) Determination of the fraction of FWTS adsorption capacity left unused \((f)\):

Total adsorption capacity of FWTS = \(t_{ep}Q.C_i\) \quad (3)

Phosphorus mass removed before breakthrough = \(t_{bp}Q.C_i\) \quad (4)

\[f = \frac{C_iQ.t_{ep} - C_iQ.t_{bp}}{C_iQ.t_{ep}} = \frac{t_{ep} - t_{bp}}{t_{ep}} \quad (5)\]

where \(t_{bp}\) = breakthrough time when the wetland was partially filled with FWTS (d).

(c) Determination of breakthrough time when the wetland filling medium is only FWTS \((t_{bt})\):

\[t_{bt} = \frac{m_{FWTSI}(1-f)}{C_iQ/q_e} \quad (6)\]

By substituting \(q_e\) (Equation (2)) into Equation (6), \(t_{bt}\) can be determined:

\[t_{bt} = \frac{m_{FWTSI}(1-f).t_{ep}}{m_{FWTSp}} \quad (7)\]

where

- \(m_{FWTSI}\) = mass of FWTS when the wetland was partially filled with FWTS (g)
- \(m_{FWTSp}\) = mass of FWTS when the wetland was only FWTS (g).

**Laboratory experiments**

**FTWS characterization**

The dewatered FWTS collected initially had a solids content of approximately 20% and the amount of time that the FWTS remained in the decanter (age) was 93 days. Then, the FWTS was left for 3 weeks in a sheltered environment to drain additional water and a representative sample was taken for analysis using the quartering procedure. The FWTS selected was grounded and sieved to provide an adsorbent with a diameter smaller than 2 mm, which was used for scanning electron microscopy (SEM) analysis, for the energy dispersive X-ray (EDS) analysis, the isotherms experiments, and, afterward, for porosity and bulk density determination. Finally, the FWTS was applied as a constructed wetland filling material.

Surface morphology and microstructure were examined using SEM with a Thermo Fisher Scientific model Quanta 650FEG. The SEM was further combined with EDS to determine the composition and relative distribution of elements on the FWTS surface. The equipment used was Bruker’s Quantax EDS with Esprit 1.9 software. For these procedures, the samples were placed on carbon double-sided tapes and recovered with platinum. The work routine comprised the collection of secondary electron and back-scattered images. These analyses were performed at the Technological Characterization Laboratory of the Department of Mining and Petroleum Engineering of the Polytechnic School, University of São Paulo. The FWTS zeta potential was measured using a Malvern Zetasizer, Model Nano Series ZS. Six different pH values were compared. For each pH, an FWTS solution containing 5 mg PO\(_4\)-P L\(^{-1}\) was also prepared.

The FWTS porosity was determined from the amount of water needed to saturate a known volume of FWTS samples \((n = 5)\). The bulk density was determined from the volume of water displaced by a known mass of FWTS samples \((n = 5)\). The FWTS applied was taken from the previously quartered sample, to allow comparison between the results obtained in batch adsorption experiments and the pilot plant.

To characterize its ferric mass weight, a triplicate of a representative sample of FWTS was taken. The digestion method applied was SM 3030 F and the characterization procedure was conducted with an atomic absorption spectrometer, Varian model 214 FS, following SM 3111 B (APHA, AWWA, WEF 2012).
Batch adsorption experiments

The batch adsorption experiments were performed using a stock solution of 5 mg P·L⁻¹ prepared by dissolving KH₂PO₄ in deionized water. For adjusting pH, a 0.01 M NaOH solution was used. Four batches were carried out, each at a different initial pH (3.9, 6.0, 6.9 and 9.0). All the batches were performed in duplicate with six Duran flasks filled with 100 mL of stock solution and FWTS concentrations ranging from 0.1 to 10.0 g·L⁻¹. The sludge concentrations applied were approximately 0.1, 1.0, 2.0, 5.0, 8.0 and 10.0 g·L⁻¹. They were mixed for 24 hours in a rotary shaker, Etica 109.1, 220 V, at 180 rpm and the average ambient temperature was 25 °C. The 24 h period was adopted based on the procedures standardized by the United States Environmental Protection Agency – USEPA (1992) and the Organization for Economic Cooperation and Development – OECD (2000). Besides that, most studies on the adsorption of phosphorus by WTS concluded that the equilibrium time was less than 24 hours (Razali et al. 2007; Babatunde et al. 2009; Gao et al. 2015).

Duplicate samples were collected at the end of each batch and filtered through a 0.45 μm membrane. The phosphate concentrations were determined according to APHA, AWWA, WEF (2012).

To precisely determine the FWTS solids content, a triplicate sample from the sieved adsorbent was withdrawn before each batch was performed. These samples were dried to constant weight in an oven at 140 °C and were placed for 2 hours in a suitably sealed desiccator for cooling. All the sludge concentrations presented herein refer to dry mass content.

pH and zeta potential influence on the FWTS adsorption capacity

The same sludge dry mass of 0.1 g and 100 mL of the same stock solution (5 mg P·L⁻¹) was dosed in eight Duran flasks. The pH was the only variable. They were mixed for 24 hours in a rotary shaker, Etica model 109.1, 220 V, 180 rpm, and the average ambient temperature was 25 °C. All the samples collected were filtered and the filtrates were analyzed to determine the phosphorus concentrations. This batch was repeated twice to validate the results.

RESULTS AND DISCUSSION

Pilot-plant results

COD and suspended solids removal

The proposed technology presented a removal efficiency of 94.4% ± 3.2% for COD and of 91.2% ± 7.8% for suspended solids. Figures 1(a) and 1(b) show overall COD and suspended solids removals, respectively, during the operation time of the pilot plant. Influent concentration presented considerable oscillations, but effluent concentration was stable, which suggests that the assessed treatment system is resilient in terms of organic matter removal.

Phosphorus removal

The FWTS had a bulk density of 1.50 ± 0.13 g·cm⁻³ and a porosity of 42% ± 3%, similar to typically constructed
wetland filling materials (Babatunde et al. 2009; Kadlec & Wallace 2009). The influent and effluent TP and DRP were monitored for 83 days. The results are shown in Figure 2. A rapid decrease in DRP removal efficiency was observed, which may be associated with the low availability of adsorbent surface, due to the small quantity of FWTS applied (3.17 kg, dry mass).

The first sample presented a removal efficiency of 95%. The samples collected on the second and fifth days, respectively, presented 72% and 60%. After 20 days of operation, reported DRP removal efficiencies were below 25%. After 60 days of operation, the DRP removal efficiencies were below 10%, indicating the FWTS was nearing exhaustion. Hence, the removal efficiency decreased as the active sites available for adsorption were reduced. A possible reason for the rapid initial decrease is inorganic complex formation.

The TP removal efficiency also shows a decreasing trend, but it presents more oscillations through the monitored period. Non-soluble forms of phosphorus are found as organic matter and its removal mechanisms depend on other processes, such as filtration, physical trapping, and sedimentation in the bed.

The results indicate that in the first 5 days of operation when a considerable number of active sites were still available, the adsorption of DRP was the main removal mechanism. The difference between TP and DRP is explained by the physical and filtering process, responsible for organic phosphorus removal. After the 20th day of operation, a lower contribution of the physical process was verified. This may be explained by the limitation of physical removal mechanisms due to the gravel’s effective diameter size of 7.85 mm and porosity of 0.45, which are not effective for retaining small particulate organic matter.

Determination of breakthrough time when the wetland filling medium is only FWTS

If the filling medium of the wetland is only FWTS, the mass of adsorbent can be calculated by Equation (8):

\[
m_{\text{FWTS}} = V_{\text{WFM}} \cdot d_{\text{FWTS}} = 850 \times 1.37 = 1,164.5 \text{ kg} \quad (8)
\]

where

- \( V_{\text{WFM}} \) – volume of wetland filling medium = 850 L
- \( d_{\text{FWTS}} \) – sludge bulk density = 1.50 ± 0.13 kg L\(^{-1}\) (considering the worst case: 1.37 kg L\(^{-1}\)).

Considering \( t_{\text{ep}} = 61 \) days and \( t_{\text{bp}} = 1 \) day (see Figure 2), \( f = 0.984 \) by Equation (5). As \( m_{\text{FWTSp}} = 3.17 \) kg, \( t_{\text{ma}} = 367 \) days or approximately 1 year (Equation (7)). After reaching this time, the adsorbent needs to be replaced. The old phosphorus-adsorbed sludge can be disposed on forests, plant nurseries, public parks, golf courses, lawns, home gardens, agriculture, and pastures. This kind of practice allows the assimilation of the applied waste without adversely affecting the soil quality and may even improve the soil’s physical properties such as aggregation, moisture-holding capacity and water permeability (Ahmad et al. 2016). This proposal is inserted into the circular economy framework, which seeks a transition to a resource-efficient future (Iacovidou et al. 2017).

Laboratory experiments results

Ferric sludge characterization

Figure 3 shows a very porous sludge with a predominance of iron (Fe) on the surface. This element and aluminum are expected because the sludge originates from a WTP that
uses ferric chloride as the coagulant. The predominance of reactive iron on the surface is associated with the high affinity for phosphorus adsorption (Babatunde et al. 2009; Babatunde et al. 2010; Song et al. 2011). Calcium comes from the alkali used to correct the pH and Si from clay, one of the main impurities of the water.

The ferric WTS mass content was determined as $273.1 \pm 17.4 \text{ mg g}^{-1}$.

### Batch adsorption experiments

**Isotherms.** The results of batch adsorption experiments were evaluated using the Langmuir and Freundlich equations. The coefficients obtained are presented in Table 2.

A maximum adsorption capacity ($Q_0$) of 4.76 mg P·g$^{-1}$ was obtained for pH 3.9, approximately three times the value obtained for pH 9.0. Babatunde et al. (2009) found similar behavior in their study of phosphate adsorption on aluminum sludge. Song et al. (2011) found a decrease in FWTS phosphate maximum adsorption capacity for pH above 5.5. However, they obtained an increase in the adsorption capacity between pH 3.0 and 5.5. For pH = 5.5, the maximum adsorption capacity was 25.5 mg P·g$^{-1}$.

**Freundlich's coefficient $K_f$ decreased as the pH increased from 3.9 to 9.0 (see Table 2). This coefficient is related to the affinity of FWTS for phosphate. Hence, the higher $K_f$ value obtained at lower pH suggests that, under acidic conditions, the phosphate-binding forces in the FWTS are stronger. The value of $n$, which is higher than 1 in all the cases, also indicates that the adsorption of P can be described as favorable.

FWTS presented lower adsorption capacity compared with values reported in the literature for aluminum and ferric sludge, which may be associated with the FWTS age and the application of polymers to the dewatering process of sludge in the WTP. Age is an important variable for comparing different sludge adsorption capacities. The morphology of WTS structure changes through time because ionic intensity reduces and the fresh amorphous precipitates turn into crystalline solids, which have less active sites. As a result, ferric and aluminum sludge lose adsorption capacity (Sims & Ellis 1983; Galarneau & Gehr 1997). Babatunde et al. (2009) and Song et al. (2011) do not describe if there were polymers applied to the sludge or specify its age.

**pH and FWTS’s zeta potential influence on the phosphorus adsorption capacity.** The results concerning the influence of pH and the FWTS's zeta potential on the phosphorus adsorption capacity are shown in Figure 4.

The adsorption capacity decreased with the increase in pH from 3.9 to 9.0, being favored under acidic conditions. At low pH, phosphate adsorption is facilitated by electrostatic and chemical attraction onto the FWTS. However, when the pH rises, the surface charge changes and becomes more negative, which is associated with the higher negative values of zeta potential (see Figure 4). This phenomenon tends to raise repulsive forces.

---

**Table 2** | Adsorption isotherm model equations and corresponding parameters at different pH values at 25°C

<table>
<thead>
<tr>
<th>Model equation</th>
<th>Parameters (units)</th>
<th>pH</th>
<th>3.9</th>
<th>6.0</th>
<th>6.9</th>
<th>9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q_0$ (mg P·g$^{-1}$)</td>
<td>4.76</td>
<td>2.32</td>
<td>1.49</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b$ (L mg$^{-1}$)</td>
<td>0.49</td>
<td>1.42</td>
<td>2.79</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.978</td>
<td>0.994</td>
<td>0.927</td>
<td>0.977</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$ (L g$^{-1}$)</td>
<td>1.661</td>
<td>1.153</td>
<td>0.900</td>
<td>0.942</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.46</td>
<td>0.41</td>
<td>0.36</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.995</td>
<td>0.996</td>
<td>0.948</td>
<td>0.985</td>
<td></td>
</tr>
</tbody>
</table>

---

**Figure 3** | FWTS surface image using (a) SEM and (b) SEM-EDX qualitative assessment of elemental distribution.
Figure 4 also shows that the pH increased for initial pH values of 3, 4, 5 and 6. For an initial pH of 7, 8, 9 and 10, a decreased final pH was observed. This decrease can be explained by the dissolution of the FWTS in the phosphate solution:

\[
\text{Fe(OH}_3\text{)}_{\text{solid}} + \text{H}_2\text{O} \rightleftharpoons (\text{FeOH}_4^-) + \text{H}^+
\]  

(9)

However, when the phosphate removal occurs at the initial pH of 3, 4, 5 and 6, there is an increase of pH because the phosphate reacts with the FWTS superficial ions according to the following reaction (Stumm 1992), releasing OH⁻:

\[
\text{X-O-H} + \text{HPO}_4^{2-} \rightleftharpoons \text{X-O-PO}_4^- + 2\text{OH}^-
\]  

(10)

CONCLUSIONS

Low-cost sanitation technologies are necessary to achieve sustainability in underdeveloped and developing countries. Thus, this study proposed a sewage treatment system that can be applied to many different contexts of cities from tropical countries. As it requires little maintenance and simple operation, it can be used as a decentralized alternative, but can also be upscaled and used as a centralized solution for e.g. villages or small settlements. It is a sustainable alternative that may promote the use of WTS as a low-cost adsorbent for phosphorus recovery. This proposal is inserted into the circular economy framework that seeks a transition to a resource-efficient future.

In the current study, the technology was designed for a daily influent flow of 360 L day⁻¹ and consisted of an upflow septic tank, a decanter, a constructed wetland filled with gravel and a constructed wetland filled with FWTS. The proposed technology presented a removal efficiency of 94.4% ± 3.2% for COD and of 91.2% ± 7.8% for suspended solids. The efficiency of DRP removal for this system was 95% and decreased until reaching adsorbent exhaustion. The estimated breakthrough time was one year when the wetland filling material was only FWTS.

Batch adsorption experiments showed that phosphate removal was influenced by sludge dosage and favored in acidic conditions. The Langmuir and Freundlich models were able to satisfactorily represent adsorption equilibrium. The adsorption capacity ranged from 1.44 mg P·g⁻¹ (pH = 9) to 4.76 mg P·g⁻¹ (pH = 3.9).

The authors also reinforce that studies assessing WTS adsorption capacity should always present the sludge age, a concern not expressed in other recent studies published in the literature.

ACKNOWLEDGEMENTS

We thank the National Council for Scientific and Technological Development (CNPq) for the financial support.
(process 133676/2016-1) and Sabesp for contributing to this research and providing the sludge.

REFERENCES


APHA, AWWA and WEF 2012 Standard Methods for the Examination of Water and Wastewater, 23rd edn. APHA, AWWA and WEF, Washington, DC, USA.


Van Kaubenbergh, S. J. 2010 *World Phosphate Rock Reserves and Resources*. International Fertilizer Development Center (IFDC), Muscle Shoals, AL, USA.


First received 21 January 2019; accepted in revised form 15 September 2019. Available online 28 September 2019