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 saturating. The assessed pilot plant operated with a daily influent flow of 360 liters 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 second constructed wetland was only FWTS. In this situation, the influent phosphorus concentration is 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

The 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 resulted in eutrophication of water bodies and decline of the organic matter content in agricultural soils (Galloway et al. 2003; Intergovernmental Technical Panel of Soils 2015). Moreover, phosphorus reserves are limited, and scientists predict they will last at most 400 years (Van Kaunwenbergh 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 Wambke 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 POTW is reported as an alternative in the literature (Marguti et al. 2018), the sludge generated on 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 are 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 to the landfill. The 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 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 of many areas in tropical countries. It uses WTS as phosphorus adsorbent, which also can 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 ($d_{10}$) of 7.85 mm, $d_{60}$ 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 in a laboratory scale, the possibility of a ferric water treatment sludge (FWTS) removing phosphorus. The methods used for this evaluation are described in section ‘laboratory experiments’. Once the possibility of phosphorus removal was verified, tests were performed in a wetland, described bellow, to observe the behavior of FWTS as an adsorbent with real sewage.

 (iv) Constructed wetland partially filled with FWTS: It was 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 m\(^3\) m\(^{-2}\) d\(^{-1}\).

 Pilot plant monitoring

 The pilot plant was monitored along 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 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

 \[
 Removed mass (g) = \frac{(C_{ij}(t) - C_{ef}(t+1)) + (C_{ef} - C_{ij})}{2} t_{ij(t)} \times 0.36 
 \]

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

 Table 1 | Methods used to determine the concentrations of COD, suspended solids and phosphorus

<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 ($q_e$):

$$q_e = \frac{C_i \cdot t_{ep} \cdot Q}{m_{FWTS}} \quad (1)$$

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)
- $m_{FWTS}$ – 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 ($f$):

$$\text{Total Adsorption Capacity of FWTS} = t_{ep} \cdot Q \cdot C_i \quad (2)$$

$$\text{Phosphorus mass removed before breakthrough} = t_{bp} \cdot Q \cdot C_i$$

$$f = \frac{C_i \cdot Q \cdot t_{ep} - C_i \cdot t_{bp}}{C_i \cdot Q \cdot t_{ep}} = \frac{t_{ep} - t_{bp}}{t_{ep}} \quad (3)$$

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 ($t_{bt}$)

$$t_{bt} = \frac{m_{FWTS} \cdot (1 - f)}{C_i \cdot Q / q_e} \quad (4)$$

By substituting $q_e$ (Equation (1)) into Equation (4), $t_{bt}$ can be determined:

$$t_{bt} = \frac{m_{FWTS} \cdot (1 - f) \cdot t_{ep}}{m_{FWTS}} \quad (5)$$

where
- $m_{FWTS}$ – mass of FWTS when the wetland was partially filled with FWTS (g)
- $m_{FWTS}$ – mass of FWTS when the wetland medium was only FWTS (g)

**Laboratory experiments**

**The 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 of 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 backscattered 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, a 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 FWTS samples ($n = 3$). The bulk density was determined from the volume of water displaced by a known mass of FWTS sample ($n = 5$). The FWTS applied was taken from the previously quartered sample, to allow comparison between the results obtained in batch adsorption experiments and 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 KH\(_2\)PO\(_4\) 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 6 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 of 25 °C. The 24 h period was adopted based on the procedures standardized by United States Environmental Protection Agency – USEPA (1992) and Organization for Economic Cooperation and Development – OECD (2000). Besides that, the most of researches who studied the adsorption of phosphorus by WTS concluded that the equilibrium time was lower 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.

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 small 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 sample collected on the second and fifth day, 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 is nearing exhaustion. Hence, the removal efficiency decreased as the active sites available for adsorption were reduced. The possible reason for rapid initial decrease is the inorganic complex formation.

The TP removal efficiency also shows a decreasing trend, but it presents more oscillations along 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 five 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 twentieth 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 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 media of wetland is only FWTS, the mass of adsorbent can be calculated by Equation (6):

\[
m_{FWTS} = V_{WFM} \cdot d_{FWTS} = 850 \cdot 1.37 = 1,164.5 \text{ kg}
\]

where: \(V_{WFM}\) = Volume of wetland filling medium = 850 L

\(d_{FWTS}\) = sludge bulk density = 1.50 ± 0.13 kg·L\(^{-1}\) (consider the worst case: 1.37 kg·L\(^{-1}\))

Considering \(t_{sp} = 61\) days and \(t_{bp} = 1\) day (see Figure 2), \(f = 0.984\) by Equation (3). As \(m_{FWTSp} = 3.17\) kg, \(t_{ml} = 567\) days or approximately one year (Equation (5)). 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 soil 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 the predominance of iron (Fe) on the surface. This element and aluminum are expected because the sludge is originated 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 & Zhao 2010; Song et al. 2011). Calcium comes from alkali used to correct pH and Si from clay, one of the main impurities of the water.

The ferric WTS mass content was determined as 273.1 ± 17.4 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_o) 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 about the phosphate adsorption on aluminum sludge. Song et al. (2011) found a decrease of 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.

<table>
<thead>
<tr>
<th>Model Equation</th>
<th>Parameters (units)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Q_o (mg·g⁻¹)</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>b (L·mg⁻¹)</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.978</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Kf (L·g⁻¹)</td>
<td>1.661</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Freundlich’s coefficient Kf decreased as the pH increased from 3.9 to 9.0 (see Table 2). This coefficient is related to the affinity of FWTS to phosphate. Hence, the higher Kf value obtained in 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 to 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 WTP. Age is an important variable for comparing different sludge adsorption capacities. The morphology of the WTS structure changes along 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 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 5). This phenomenon tends to raise repulsive forces.
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 FWTS dissolution in the phosphate solution.

\[
\text{Fe(OH}_3\text{)}_{\text{solid}} + \text{H}_2\text{O(FeOH}_4\text{)}^- + \text{H}^+ \quad (3)
\]

However, when the phosphate removal occurs in 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 \( \text{OH}^- \).

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.

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


