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Articles

Filter packed with Al-sludge waste for phosphorus removal as a polishing system in a wastewater treatment plant

Filtro empacado con residuos de lodos de Al para la eliminación de fósforo como sistema de pulimento en una planta de tratamiento de aguas residuales

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Abstract

Recently, using residual aluminum sludge (Al-sludge) from drinking water treatment plants for phosphorus removal has been assessed and it has shown to be highly efficient. However, most of the studies have been conducted using synthetic water. Only a few works have applied this method to real wastewater (WW), and none of them have been tested in continuous mode, as a polishing step, in a pilot-scale, decentralized wastewater treatment plant (WWTP).

This paper aimed to evaluate the performance of an immersed filter packed with a bed of residual Al-sludge as a polishing system for Phosphorous removal, in a pilot-scale, decentralized WWTP.

The study determined at laboratory-scale the capacity for phosphorus removal through batch and continuous tests using both synthetic and real wastewater and evaluated the effect of retention time. Based on the results, an Al-sludge immersed filter (Al-sludge Filter) at pilot-scale was constructed, implemented, and evaluated as a polishing step for the effluent of a decentralized-WWTP.

The results showed that during continuous testing with real WW, the phosphorus removal capacity was 2.55 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$ per gram of Al sludge using a retention time of 120 min. The Al-sludge filter as a polishing system presented an average removal efficiency of 94 ± 8 % and an effluent concentration of under 0.50 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$ during the first

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20 operational days. For the next 17 days, the system removed 85 ± 9 % on average, showing an effluent concentration of under 1.0 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$. From operational day 32 onwards, the removal efficiency was 63.6 ± 10.7 %, with an average effluent concentration of 2.20 ± 0.39 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$.

Keywords: Wastewater polishing treatment, phosphorus removal, decentralized WWTP, Al-sludge filtration, biofiltration system, wastes reuse, filtration over wood chips, residual Al-sludge reuse.

Resumen

Recientemente se ha evaluado el uso de lodos residuales de aluminio (lodos-Al) de plantas de tratamiento de agua potable para la eliminación de fósforo y ha demostrado ser altamente eficiente. Sin embargo, la mayoría de los estudios se han realizado utilizando agua sintética. Solo unos pocos trabajos han aplicado este método a aguas residuales (AR) reales y ninguno de ellos ha sido probado en modo continuo, como paso de pulido, en una planta de tratamiento de aguas residuales (PTAR) descentralizada a escala piloto.

Este trabajo tuvo como objetivo evaluar el desempeño de un filtro sumergido empacado con un lecho de lodos residuales de Al como sistema de pulido para la eliminación de fósforo en una PTAR descentralizada a escala piloto.

El estudio determinó a escala de laboratorio la capacidad de eliminación de fósforo mediante pruebas discontinuas y continuas, utilizando aguas residuales tanto sintéticas como reales, y se evaluó el efecto del tiempo de retención. Con base en los resultados, se construyó, implementó y evaluó un filtro sumergido de lodos de Al (filtro lodos-Al) a escala piloto como paso de pulido para el efluente de una PTAR descentralizada.

Los resultados mostraron que durante las pruebas continuas con AR real, la capacidad de eliminación de fósforo fue de 2.55 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$ por gramo de lodo-Al utilizando un tiempo de retención de 120 min. El filtro de lodos Al como sistema de pulido presentó una eficiencia de remoción promedio de 94 ± 8 % y una concentración de efluente inferior a 0.50 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$ durante los primeros 20 días operativos. Durante los siguientes 17 días, el sistema eliminó 85 ± 9 % en promedio, mostrando una concentración de efluente inferior a 1.0 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$. A partir del día operativo 32, la eficiencia de remoción fue de 63.6 ± 10.7 %, con una concentración promedio de efluente de 2.20 ± 0.39 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$.

Palabras clave: tratamiento de pulimento de agua residual, remoción de fósforo, PTAR descentralizada, filtración en lodos de Al, sistema de biofiltración, reúso de residuos, filtración sobre astillas de madera, reutilización de lodos residuales de Al.

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Introduction

Phosphorus contained in wastewater is one of the main causes of primary producers' growth (phytoplankton, benthic algae, macrophytes), which leads to eutrophication of surface water bodies such as rivers, lakes, and dams (De-Bashan & Bashan, 2004). Currently, conventional treatment methods for phosphorus removal include biological treatments such as enhanced biological phosphorus removal and physicochemical precipitation treatments with metal salts like iron, aluminum, and calcium (De-Bashan & Bashan, 2004). Although these technologies are efficient in removing Phosphorus, their application can be limited in many countries because they require complex and expensive operations, which is especially acute in rural areas where there is a demand for inexpensive and easy-to-operate decentralized systems. In this regard, alternatives such as constructed wetlands (CW) and biofilters over organic beds (BFOB) are viable options for decentralized wastewater systems (DWWTS) in rural areas. DWWTS are wastewater treatment plants (WWTP) that treat small volumes of WW in the same place where they are generated, making it unnecessary to send them from a city pipe system to a WWTP. However, it is well known that traditionally these systems have low phosphorus removal efficiencies (Vohla, Kõiv, Bavor, Chazarenc, & Mander, 2011; Garzón-Zuñiga, González-Zurita, & García-Barrios, 2016). For a couple of decades, several materials have been tested which physicochemical properties provide high phosphorus sorption capacity (mg P-PO_4^{3-}·l^{-1} g material) and their use has been recommended as a substrate in CW to prolong and improve phosphorus removal treatment capacity in those systems (Herrmann, Jourak, Hedström, Lundström, & Viklander, 2013; Doherty, Zhao, Zhao, & Wang, 2015). Examples of these materials include: a) natural materials such as sands (Arias & Brix, 2005), wollastonite (Hedström, 2006), and shell sand (Ádám, Krogstad, Vråle, Søvik, & Jenssen, 2007); b) commercial products to remove Phosphorus, e.g. Filtralite P™ (Herrmann *et al*., 2013); and c) industrial wastes as furnace slag (Gustafsson, Renman, Renman, & Poll, 2008). To solve this problem, another option could be to install a polishing system focusing on phosphorus removal after decentralized wastewater treatment systems, which is the focus of this work.

On the other hand, the possibility of reusing waste materials as adsorbent materials is very interesting and has gained popularity in recent years. In particular, the case of aluminum sludge (Al-sludge), which is a waste from the process of coagulation with aluminum sulfate in drinking water treatment plants. This waste has been studied at laboratory scale using synthetic phosphorus solutions at different concentrations, prepared with tap and distilled water. Then, its capacity for removing phosphorus has been well documented (Muisa, Nhapi, Ruziwa, & Manyuchi, 2020) using synthetic wastewater (Babatunde, Zhao, Burke, Morris, & Hanrahan, 2009; Babatunde & Zhao, 2009a) and real municipal wastewater effluents (Maher, Neethling, Murthy, & Pagilla, 2015; Maqbool, Khan, & Asghar, 2016), showing different capacities for phosphorus removal, ranging from 1 to 30 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$. These capacities are influenced by the characteristics of the Al-sludge and the operational conditions applied during the treatment. However, it has been reported that by applying optimized doses of Al-sludge, a maximum phosphorus removal efficiency of 83 and 88 % from real wastewater was achieved for two kinds of sludge studied in batch mode and operated at laboratory scale (Maqbool *et al*., 2016). However, this promising technological option to remove phosphorus with Al-sludge waste has not been studied as a polishing system in a pilot-scale treatment process under real operating conditions. Therefore, the objective of this research was to assess the efficiency of phosphorus removal of an immersed filter, packed with residual Al-sludge as a polishing system in a pilot-scale decentralized WWTP.

The study includes: 1) Determining the residual sludge's ability to remove $P\text{-}PO_4^{3-}$ from synthetic wastewater at laboratory scale in a batch test; 2) Validating the $P\text{-}PO_4^{3-}$ removal capacity of the Al-sludge using real wastewater and in a continuous system; 3) Assessing the effect of the empty bed contact time (EBCT) on the removal efficiency in a continuous system, and finally, 4) Implementing and assessing a submerged filter packed with Al-sludge for phosphorus removal as polishing of a decentralized-WWTP at the pilot scale.

Materials and methods

Al-sludge filter material (Al-SFM)

Al-sludge waste from the drinking water treatment plant (DWTP) "Los Berros" of the Cutzamala purification system in the State of Mexico, Mexico, was used to produce the Al-sludge filter material (Al-SFM) used for packing the polishing system. In this facility, there is a huge amount of accumulated old sludge that can be reused. Even though it is known that sludge age diminishes waste's phosphorus adsorption capacity (Yang, Zhao, & Kearney, 2008), this waste was selected for this research to assess the possibility of reuse.

Once the Al-sludge was obtained, it was air-dried for seven days. The dry sludge was then sieved on a 6.35 mm open mesh and then in a 2 mm one (standard ASTM number ¼ sieves and 10, respectively) to avoid dust and particles that are either too large or too small. The sludge particles obtained had a diameter between 2.1 and 6.2 mm and were used as packing material.

Al-SFM characterization

The elemental composition of the adsorbent Al-SFM was determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

The size distribution was determined using sieving techniques to calculate the effective size or d10 (the diameter of the particle corresponding to a percentage finer than 10 % of the sample), and the uniformity coefficient or UC (the ratio of the particle which is finer than 60 % of the sample or d60 and the d10), according to method D 2862 (ASTM, 1997). Porosity was determined by the amount of water required to saturate a known volume of the material, and bulk density was determined by measuring the volume of water displaced by a known mass of the material (APHA, 2005). The specific surface area was determined using the methylene blue dye method by adsorption isotherms (Därr & Ludwig, 1973).

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Al-sludge phosphorus removal capacity in batch test

The phosphorus adsorption capacity of the Al-SFM was first determined in laboratory batch experiments under controlled conditions (synthetic water). Adsorption isotherms were carried out using three initial phosphorus concentrations (5, 10, and 20 mg $P\text{-}PO_4^{3-}\cdot l$ solutions), which correspond to a range of values commonly found in domestic and municipal rural wastewater. Six defined masses of dry Al-SFM (1, 2, 3, 4, 5, and 6 g) were added to a 500-ml solution of a known initial phosphorus concentration. Then, the solutions with the Al-SFM were stirred at 100 rpm (to improve the contact between phosphorus and the Al-SFM) for 60 to 72 hours in a jar test device. The solutions were prepared using distilled water and KH_2PO_4. In each jar, the Al-SFM was placed on a plastic net to avoid fragmentation by the collision with the stirring blades. Each jar was stirred to equilibrium (a point at which both the speed of adsorption and desorption are equal). The pH was adjusted to 7 using NaOH and H_2SO_4 solutions because the effluent of the pilot scale-WWTP that would be treated (polished) in the Al-sludge filter at the last part of this research was neutral. The experiment was conducted at room temperature (24-25°C), and the phosphorus in the solution was measured as $P\text{-}PO_4^{3-}$ according to the Hach method 8048 (equivalent to US EPA Method 365.2 and Standard Method 4500-P E for wastewater). Three repetitions were performed, and subsequently, the average data were analyzed according to the models of Freundlich (Equation (1)) and Langmuir (Equation (2)) to determine the adsorption behavior:

$$logq = {}^{1}/_{n}\, logC_e + logK_F \quad (1)$$

$$ {}^{C_e}/_{q} = {}^{C_e}/_{q_m} + {}^{1}/_{bq_m} \quad (2)$$

Where:

q = (adsorption capacity) is the equilibrium capacity (mg g^{-1} media)

$1/n$ = adsorption density

C_e = equilibrium concentration (mg l^{-1})

K_F = Freundlich constant (mg g^{-1} media)

q_m = maximum adsorption capacity (mg g^{-1} media)

b = affinity constant (l mg^{-1})

Al-sludge phosphorus removal capacity in continuous test: Effect of contact time

A system of three immersed filters packed with the Al-SFM (described in sections 2.1 and 2.2) was designed. The effluent flow rate of the pilot-scale WWTP (described below) used to assess the filter as a polishing system was used as a starting point to design a column with an empty bed contact time (EBCT) of 40 min. This is, the time it takes for a fluid to pass through the column, if it were empty. Each filter consisted of a column of acrylic with an internal diameter of 10 cm and a height of 40 cm, with a working volume of 3.14 l. The three filters were connected in series to test the effect of three different EBCTs (40, 80, and 120 min)

(Figure 1). The filters were operated with a hydraulic surface load (HSL) of 10.8 $m^3 \cdot m^2 \cdot d^{-1}$, corresponding to a flow rate of 83.5 $l \cdot d^{-1}$. To carry out these experiments, a series of batches of real treated water from the pilot decentralized-WWTP were used. The decision to use such a high HSL and short retention times (EBCT) was to evaluate Al-sludge filters under conditions that represent a normal operation of the pilot decentralized-WWTP. The phosphorus concentration of this water during this experimental period was 11.0 ± 0.8 mg $P\text{-}PO_4^{3-}$ l^{-1}. The pH of the influent was not adjusted. It remained at 7.3 ± 0.2 during this experimental period. The phosphorus removal was measured until the brake point concentration was attainted in the 3 EBCTs studied. The brake points concentration or target concentrations were 2 and 5 mg/l because 2 mg/l is the maximal P concentration permissible to discharge treated urban wastewater in natural water bodies in United States (USEPA, 2012) and 5 mg/l of P is the maximal discharge concentration permitted by Mexican regulations to discharge in water bodies to preserve aquatic life (Semarnat, 1996).

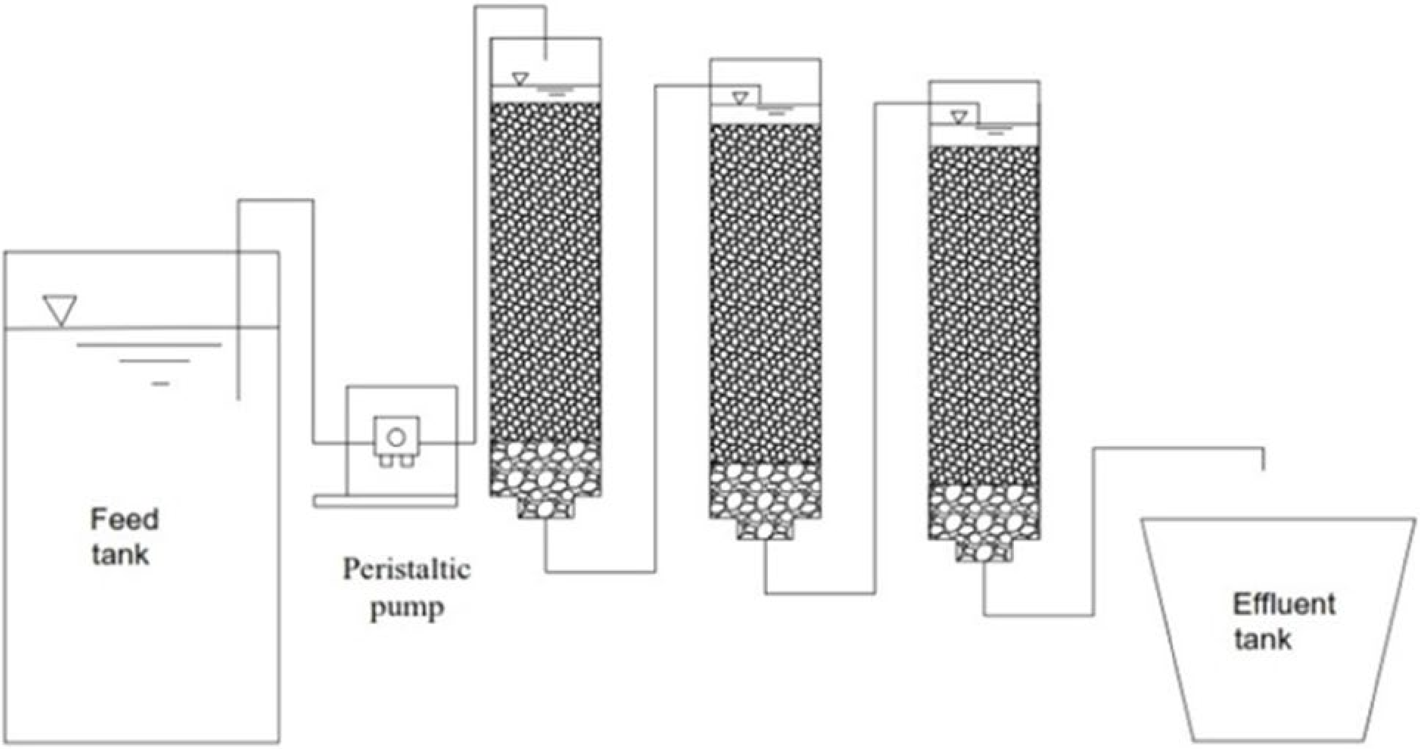

Figure 1. Schematic of columns connected in series.

The phosphorus concentration of the influent and effluent of each column was used to determine the removal efficiency evolution obtained for the Al-sludge filter under three different EBCTs. These results were used then to determine the P-removal capacity of the Al-sludge in a filter operated continuously, according to Equation (3):

$$q = \sum_{i=1}^{n} {(C_{in} - C_{ef})}/{m} \qquad (3)$$

Where:

q = adsorption capacity (mg g^{-1} media)

C_{in} = initial concentration at the column (mg l^{-1})

C_{ef} = concentration at the effluent of the column (mg l^{-1})

m = mass of material (g)

n = number of samples

Al-sludge filter performance as polishing system under real conditions

In this part of the study, an Al-sludge filter was implemented as the last process in a decentralized WWTP (pilot scale) in operation for 2 years, to improve phosphate removal efficiency.

Description of the pilot scale decentralized WWTP

The decentralized WWTP is a biological pilot-scale facility constituted by a septic tank (ST), a biofilter over an organic bed (BFOB) packed with wood chips, and a horizontal sub-superficial constructed wetland (CW) packed with gravel and ornamental plants, that treats 1.28 m^3d^{-1} of domestic WW. This system was described (each treatment process) and its performance discussed, evaluated, and presented in a previous publication (Garzón-Zúñiga *et al*., 2016). The pilot decentralized-WWTP was fed with a typical influent WW (Table 1) and presented excellent removal efficiencies of COD (83 %), $N\text{-}NH_4^+$ (82 %), and FC (99.999 %), but with low phosphorus removal efficiency (19.5 % $P\text{-}PO_4^{3-}$).

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Table 1. Wastewater characterization.

Parameter	
COD (mg/l)	401 ± 129
BOD (mg/l)	143 ± 26
CF (NMP 100 ml)	7.57 E+06 ± 8.35E+06
NH_4^+-N (mg/l)	29.5 ± 6.1
PO4-P (mg/l)	6.7 ± 1.9
pH	7.2 ± 0.4
Oil and grasse (mg/l)	36.2 ± 25.8
SST (mg/l)	139 ± 62

After two years of continuous operation of this decentralized-WWTP, an immersed filter packed with the filtering material elaborated with Al-sludge as mentioned before was implemented and its performance in terms of phosphorus removal was evaluated for more than 60 days.

Description of the Al-sludge immersed filtering module (Al-sludge filter)

The Al-sludge filter was designed to work with an EBCT of 120 min. Taking into account that the effluent flow of the decentralized-WWTP is 1.28 m^3d^{-1}, the diameter of the filter was 0.40 m and height of the filter bed was 0.85 m, which is equivalent to a volume of 0.1068 m^3 filter bed. Therefore, the Al-sludge filter was constructed in an acrylic column with an internal diameter of 0.40 m, a height of 1.35 m, and was packed with 72 kg of Al-sludge FM as mentioned in section 2.1 (equivalent to a filter bed height of 0.85 m). The Al-sludge Filter was placed after the CW process (Figure 2). All information about the description and performance of the decentralized WWTP (from the influent to the septic tank until the CW effluent) was previously described in Garzón-Zúñiga *et al*. (2016).

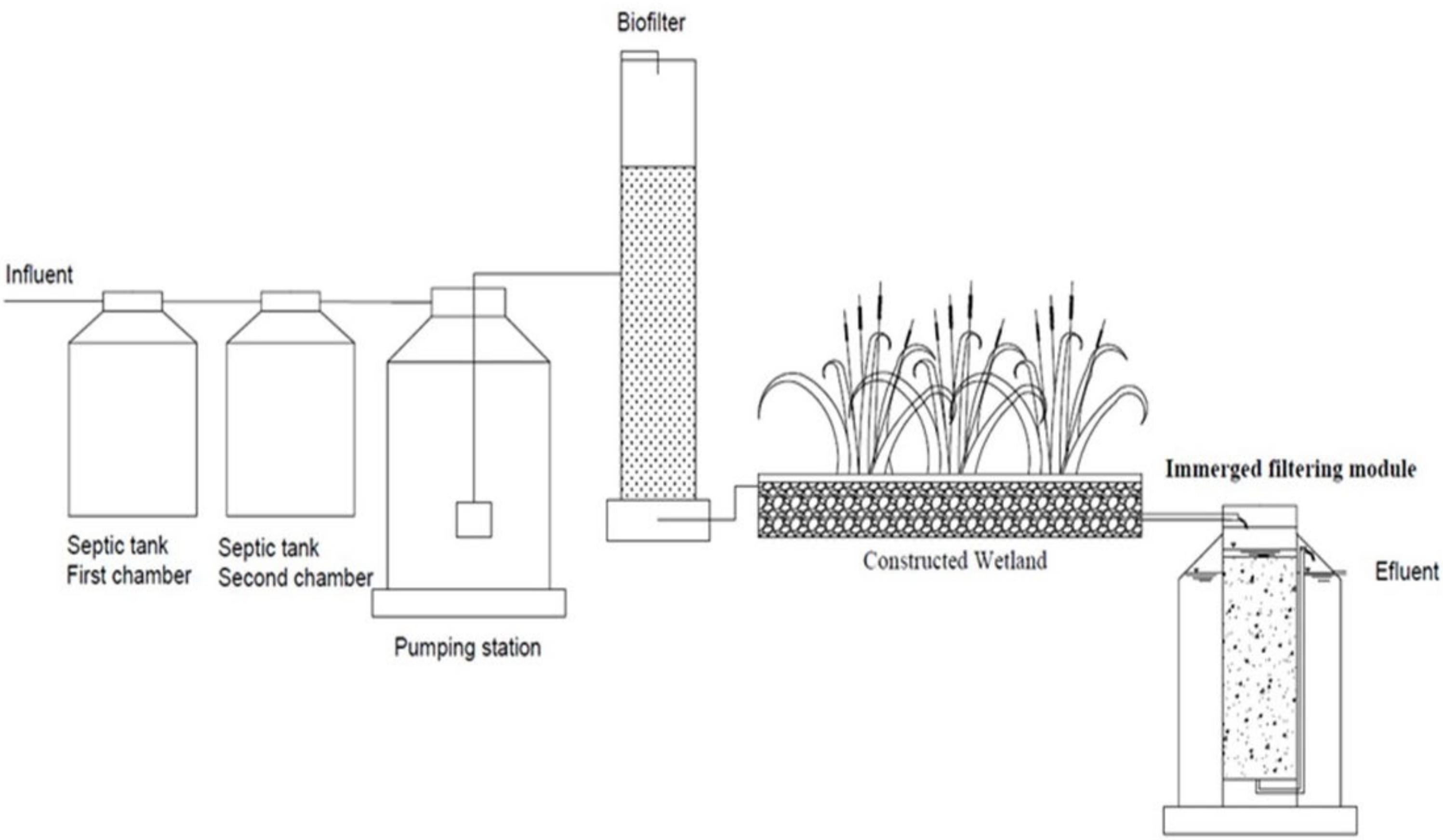

Figure 2. Schematic representation of the decentralized-wastewater treatment plant (decentralized-WWTP) and the immersed filtering module for polishing the effluent (Al-sludge filter).

Immerged filtering module (Al-sludge Filter) assessment as polishing system at pilot scale

The pilot scale Al-sludge Filter packed with Al-SFM was fed by means of gravity with the effluent from the CW stage at an average HSL of 10.8 m^3 m^2 d^{-1} and an EBCT of 120 min. The coupled system was operated for 60 days. A daily monitoring of the $P\text{-}PO_4^{3-}$ concentration in the influent and effluent of the Al-sludge Filter was followed during 60 operational days. Additionally, a weekly sampling of the exit of each treatment process, composing all treatment systems: ST, BFOB, CW, and Al-sludge Filter was taken. These samples were analyzed for $N\text{-}NH_4^+$ concentrations according to the Nessler Method, using a HACH DR2900 spectrophotometer and to the Hach Method 8048 for $P\text{-}PO_4^{3-}$ concentrations; to evaluate the nutrient removal behavior of the coupled treatment system.

Results and discussion

Al-sludge filter material (Al-SFM) characterization

The results showed that the Al-sludge filter material (Al-sludge FM) obtained could be considered a good filter media with low clogging risk. A proper material to be used, for example in a CW, shall have an effective size (d_{10}) between 0.20 and 1.2 mm, a d_{60} between 0.5 and 8 mm, and a uniformity coefficient ($UC = d_{60}/d_{10}$) lower than 4 (UN-HABITAT, 2008). According to the Grain-Size analysis, the Al-sludge FM elaborated has a d_{10} = 2.1 mm, a d_{60} = 3.2 mm, and a UC = 1.5. Therefore, it is considered a good filtering material.

Regarding the specific surface area (SSA), a value of 7.04 $m^2 \cdot g^{-1}$ was obtained which does not necessarily indicate whether the material will perform well or not. Table 2 shows the adsorption capacities and the SSA for different adsorbent materials. There is no evident correlation between these two properties. For example, Al-Sludge assessed by Babatunde and Zhao (2009a) has an SSA very similar to the Al-Sludge assessed by Maqbool *et al*. (2016). Nevertheless, the latter has a 20 times lower P-binding capacity. This is because the adsorption capacity is also related to the initial phosphorus concentration, the pH used in each test, the grain size, and other variables. However, it is recommendable to check these values to be able to compare them with those from other materials.

Table 2. Comparison of the adsorption capacity and the specific surface area with other filtering-adsorbent materials.

Material	***q* (mg $P\text{-}PO_4^{3-} \cdot g^{-1}$)**	**SSA ($m^2 \cdot g^{-1}$)**	**Grain size (mm)**	**Reference**
Al-modified Bentonite Clay	12.2	NR	0.063- 0.425	El-Sergany and Shanableh (2012)
Al-sludge	4.86	39.41	Nd	Maqbool *et al*. (2016)
Al-sludge	1.58	42.76	Nd	Maqbool *et al*. (2016)
Al-sludge	31.9	41.4	0.5-1.80	Babatunde and Zhao (2009a)
Wollanstonite	0.85	NR	<0.355	Hedström (2006)
Zeolita	0.46	31.4	4.2-12.2	Drizo, Frost, Grace and Smith (1999)
Al-sludge	2.55	7.04	3.2	**Present study**

Nd: Non-determined.

It also should be noted that the elemental composition of the Al-sludge will vary depending on several factors such as the source of the water to be treated, the coagulant dose, and the operating parameters of the Drinking-WTP. As expected, the old sludge used in the current study has a lower aluminum concentration than those from other Al-sludges of different drinking-WTP (Table 3). aluminum is the main component that plays a very important role in the P-removal through the ligand exchange to form an intra-sphere complex (Babatunde *et al*., 2009). Therefore, it is expected that the rich aluminum materials will effectively remove phosphorus (Babatunde *et al*., 2009). However, there is not a direct correlation between the amount of aluminum and the adsorption capacity. Table 3 shows the composition and the adsorption capacities of different Al-sludges determined in batch experiments. The Al-sludge FM of the current study has an adsorption capacity lower than other Al-sludge studied. However, taking into account the ratio between the aluminum content of each material and the amount of phosphorus adsorbed (μmol P/mol Al^{3+}); the sludge of this study appears more competitive (Table 3). That is an example of why the aluminum content does not directly determine the adsorption capacity.

Table 3. Elemental composition of different Al-sludge.

Parameter	Units	This study	References				
			Dong, Ju, Hong and Jong (2005)	**Babatunde *et al.* (2009)**	**Zhao, Babatunde, Zhao, and Li (2009)**	**Maqbool *et al.* (2016)**	**Maqbool *et al.* (2016)**
Aluminum content (as Al_2O_3)	$mg \cdot g^{-1}$	18.652	458-463	80.603	555.36	108	174.6
Iron content (as Fe_2O_3)	$mg \cdot g^{-1}$	2.534	11.9-12.3	4.770	90.01	17.31	14.70
Calcium content (as CaO)	$mg \cdot g^{-1}$	0.414	11.6-11.7	Nd	Nd	214.0	240.0
Adsorption capacity (q)	mg $P\text{-}PO_4^{3-}g^{-1}$	2.55	3.5	23	25	1.58	4.86
Aluminum performance	µmol P/mol Al^{3+}	224.92	12.50	469.45	74.06	24.07	45.79

Nd: Non-determined.

Determination of adsorption capacity in batch test

The average adsorption values were analyzed according to the linear forms of Langmuir and Freundlich equations. As can be seen in Figure 3a and Figure 3b, the data fit well in both models. Nevertheless, the Langmuir model shows a better linear relationship (all correlation coefficients are above 0.9) indicating monolayer adsorption on the surfaces when the initial concentration of phosphorus is between 5 and 20 mg $P\text{-}PO_4^{3-}$ l^{-1}, which is in accordance with most studies using sludge

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containing aluminum (Babatunde & Zhao, 2009b; Maqbool *et al*., 2016; Takashima, Nakamura, Takano, & Ikemoto, 2015; Yang *et al*., 2008). As an example, Figure 3c shows how the experimental data fits better the Langmuir model.

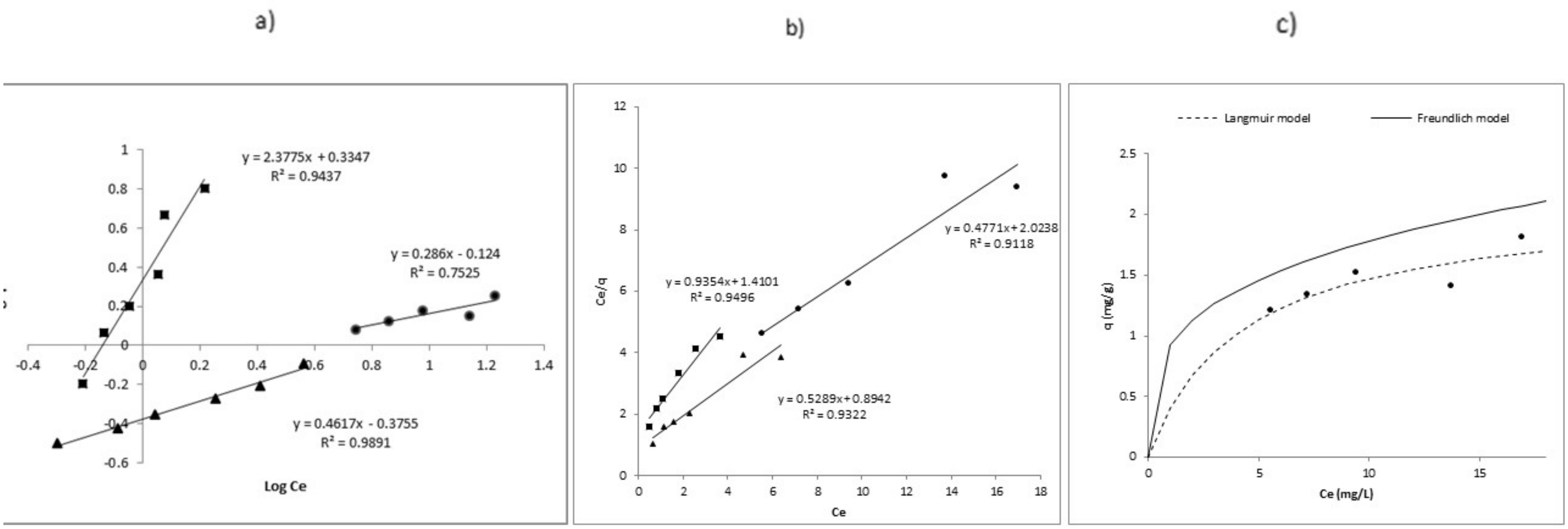

Figure 3. Adsorption behavior in batch experiments at different initial concentrations (▲) 5 mg·l^{-1}, (■) 10 mg·l^{-1}, (●) 20 mg l^{-1}): **a)** Freundlich linearization plot; **b)** Langmuir linearization plot; **c)** experimental data adjustment to Langmuir and Freundlich models.

Adsorption model parameters were calculated and are shown in Table 4. As it was expected, the adsorption behavior of Al-sludge FM depends strongly on the initial concentration of phosphorus in water. This means that the higher the initial concentration, the higher the adsorption capacity of the material, which can lead to an overestimation of the adsorption capacity of the material, as it has been demonstrated by Babatunde and Zhao (2009b), when they used an initial concentration of 360 mg/l and obtained an adsorption capacity of 31.9 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$ (Table 2). On the other hand, when they used an initial concentration of 5 mg/l, the adsorption capacity was between 0.5 and 0.99 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$. In this study, a maximum adsorption capacity (q_m) of 1.069, 1.891, and 2.0951 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$ was found for initial concentrations of 5, 10, and 20 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$, respectively, in batch test.

Table 4. Constant parameters of the Adsorption model onto Al-SFM.

C_0 (mg l^{-1})	Langmuir			Freundlich	K_F (mg g^{-1})	R^2
	q_m (mg g^{-1})	b (l mg^{-1})	R^2	$1/n$		
5	1.069	0.663	0.949	0.462	0.421	0.989
10	1.891	0.592	0.932	2.378	2.161	0.944
20	2.095	0.236	0.912	0.286	0.752	0.753

Effect of the EBCT on the P-PO4-3 removal in continuous test at laboratory scale

Phosphorus removal efficiency

The effluent phosphorus concentration data of the three columns connected in series to evaluate three different EBCTs (40, 80, and 120 min) were plotted as a function of time (Figure 4a). The performance of the three columns in terms of phosphorus removal efficiency was as follows: In all cases, the initial phosphorus removal efficiency was 100 %, which progressively decreased until reaching an equilibrium that was achieved at different times (8, 18, and 28 days, respectively). These results are in agreement with Muisa *et al*. (2020), who reported that phosphorus adsorption by aluminum sludge is biphasic, consisting of a rapid initial phase followed by a slow phase. The rapid initial phase is related to phosphorus adsorption onto the exterior, easily accessing sites such as macropores, as well as on-surface functional groups in a ligand exchange mechanism. Whereas the slow phase is related to the intra-particle diffusion mechanism into meso and micropores, precipitation, and chemical reactions. The removal efficiencies achieved at equilibrium were: 18.2 ± 4.5 % for the EBCT column of 40 min; 34.5 ± 2.7 % for the EBCT column of 80 min, and 49.1 ± 1.8 % for the EBCT column of 120 min. The behavior observed regarding the increase in removal efficiency by increasing the EBCT agrees with that reported by Maher *et al*. (2015), who found out that the effect of retention time is more significant than the age of the sludge. However, the maximum efficiency achieved (49.1 ± 1.8 %) is lower than that reported by the same authors, close to 90 %, but is higher than the removal efficiency reported by traditional technologies such as a *Cyperus alternifolius* planted CW that removed 48.1 % of PO_4^{3-} (Alayu & Leta, 2021).

a) b)

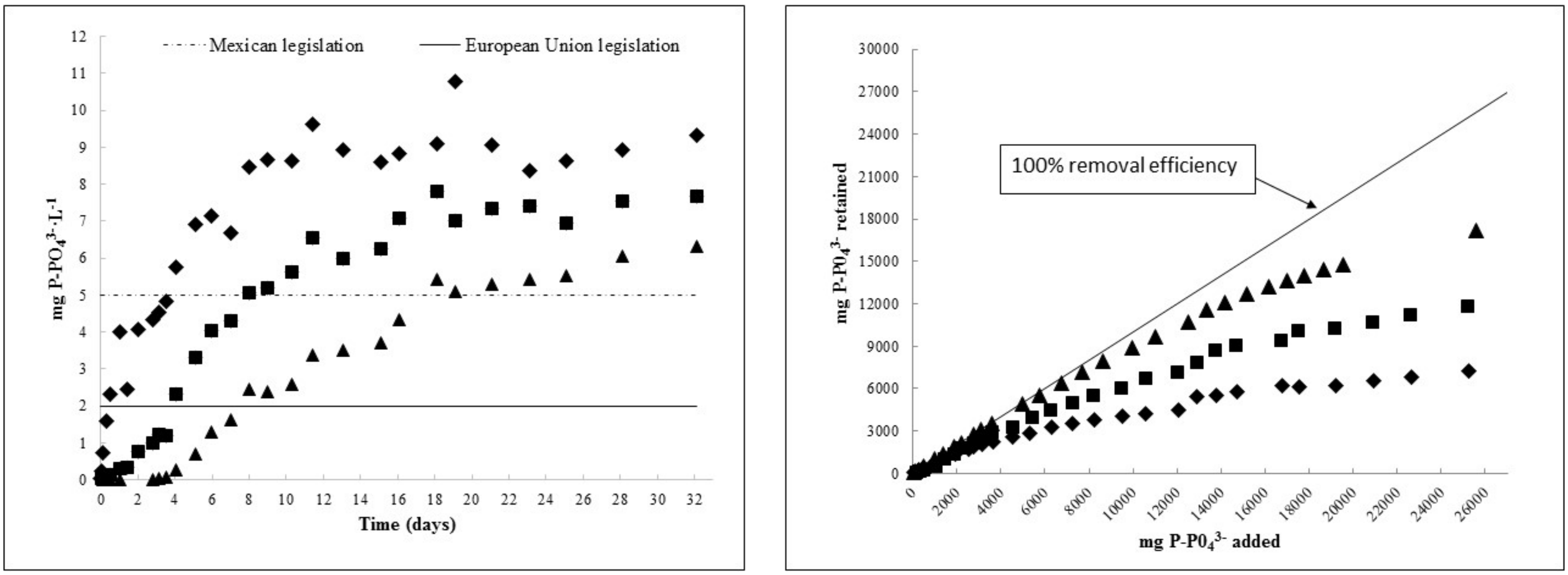

Figure 4. a) P effluent concentration in columns. Solid and dashed lines represent the maximal phosphorus concentrations for different regulations; b) P removed as a function of P added to the column. EBCTs of (♦) 40 min, (■) 80 min, (▲) 120 min.

Phosphorus removal capacity

In order to estimate the phosphorus removal capacity of the Al-sludge in continuous tests, the data of the phosphorus mass added to the columns *vs*. the phosphorus mass retained in the columns (Figure 4b) was also plotted. The P-removal capacity of the three columns connected in series (EBCT = 120 min) was calculated in 1.298 mg P-PO$_4^{3-}$·g^{-1} when the breakpoint was 2 mg P-PO$_4^{3-}$·l^{-1}; and 2.509 mg P-PO$_4^{3-}$·g^{-1} when the breakpoint was 5 mg P-PO$_4^{3-}$·l^{-1}. This P-removal capacity was obtained using the phosphorus concentration in the real effluent of the decentralized-WWTP (11.03 ± 0.86 mg $P\text{-}PO_4^{3-} \cdot l^{-1}$). It should be noted that our study was performed with an HSL significantly higher and EBCT shorter, compared to those found in other studies (Table 5). It means that the results obtained in this study, despite being good, can still be better if a lower HSL and a higher EBCT are used to operate the filter. About the braking points, 2.0 mg P l^{-1} is the European regulation to discharge urban treated wastewater (EU, 2014), and 5.0 mg P l^{-1} is the stricter limit concentration for the Mexican regulation (NOM-001-SEMARNAT-1996 type C for protection of aquatic life, which applies to rivers and natural or artificial water reservoirs for public urban use). In 2022 a new regulation was published, in which the concentration limit to discharge in rivers changed and can be between 15 and 21 mg P l^{-1}, depending on if it is an average value or a punctual one. However, this new regulation is not applicable yet.

Table 5. Experimental conditions and removal efficiencies of phosphorus reported for different adsorbent materials in columns systems.

Adsorbent material filter	Grain size (mm)	Initial phosphorus concentration (mg P-$PO_4^{3-}$$l^{-1}$)	Hydraulic surface load (HSL) ($m^3 \cdot m^{-2} \cdot d^{-1}$)	Phosphorus loading rate (g P$\cdot m^{-2} \cdot d^{-1}$)	Empty bed contact time (EBCT) (h)	Removal efficiency (%)	Reference
Al-sludge	0.60-2.36	0.048-0.159	0.45-0.91	0.022-0.145	3-6	88-92	Takashima *et al*. (2015)
Al-sludge	< 2.0	18.1-346.1	12.24	31-592	3	92	Zhao *et al*. (2009)
Al-sludge	0.5-1.8	32.9-220	1.70	56-373	No data	-	Babatunde *et al*. (2009)
Al-sludge	**2.1-3.2**	**11.0**	**10.80**	**127**	**2**	**94**	**This study**
Apatite mineral	2.5-10	30.0	0.09	2.7	36	-	De-Bashan and Bashan (2004)
Electric arc furnace	0.6-3.2	20.0	0.17	3.3	12-24	100	Drizo, Forget, Chapuis and Comeau (2006)
Al-sludge and shellsand	0.6-1.3	10.0-27.0	0.13	1.3-3.5	24	99.4	Park (2009)
Wollastonite	No data	0.1-9.8	0.66	0.1-6.5	40	80-96	Brooks, Rozenwald, Goehring, Lion and Steenhuis (2000)
Filtralite P®	0.5-4	10.0	0.29	2.9	84	91	Ádám *et al*. (2007)
Shellsand	3-7	10.0	0.32	3.2	91	92	Ádám *et al*. (2007)

The P-removal capacity of the Al-sludge FM is higher than the one obtained in batch tests, if the entire experimental period (32 operational days) is considered. In that case, the P-removal capacity was 4.25, 3.75, and 3.31 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$ for columns with an EBCT of 40, 80, and 120 min, respectively and it should be noted that the saturation was not achieved in any of the columns. However, these removal capacities were obtained after the breaking point of 1.0 mg when the concentration of phosphorus in the effluent was equal to 5.6 ± 0.5 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$, so they were not appropriate to define the dimensions of the filter for the next experimental period. According to Drizo, Comeau, Forget and Chapuis (2002), this kind of results can be used to estimate the time in which a full-scale treatment system will deliver an effluent with quality to comply with the regulations. To this respect, Dong, Ju, Hong and Jong (2005) used columns with different amounts of adsorbed material (oyster shells) to extrapolate the saturation time of bigger columns, which could be applied in this case.

Therefore, by applying this technique, the time of work of a column with a certain amount of Al-sludge FM required for the polishing prototype in a field test can be estimated. The filter proposed had an EBCT of 2 h (120 min) and worked with an HSL established by the biological-WWTS, 10.8 $m^3\cdot m^{-2}\cdot d^{-1}$.

Al-sludge filter test as a polishing system for a decentralized-WWTP

Phosphorus removal in the Al-sludge immersed filtering module (Al-sludge IFM)

Figure 5a shows the phosphorus removal performance of the Al-sludge immersed filter module installed at the end of the decentralized-WWTP. During the first 34 days, the average P concentrations in the effluent of the decentralized WWTP was 3.08±0.89 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$. This concentration is lower than the one expected for a typical effluent of domestic and municipal WWTP in developing countries (like Mexico), but similar to the effluent P concentration of treated WW in countries like Canada (Garzón-Zúñiga, Buelna & Moeller-Chávez, 2012). Working the Al-sludge Filter module under these conditions, the P concentration in the effluent remained under 1.0 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$ during 37 days with an average effluent of 0.52 ± 0.35 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$. During the first 20 days, the removal efficiency was in average 94 ± 8 % and the effluent average concentration value was equal to 0.29 ± 0.2 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$ complying with strict regulations of discharge for example, European Union regulations (EU, 2014). Then, for the next 17 days the system removed in average 85 ± 9 %, showing an effluent concentration under 1.0 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$, equal to 0.78 ± 0.3 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$ complying with less strict regulations for example, American regulation (USEPA, 2012). Then from operational day 32 onwards, the effluent of the decentralized-WWTP presented higher phosphorus concentrations equal to 5.6 ± 0.6 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$, which are typical P concentrations in treated wastewaters in developing countries.

Tecnología y ciencias del agua, ISSN 2007-2422, 15(6), 311-353. DOI: 10.24850/j-tyca-2024-06-07

Under these conditions, the Al-sludge Filter module reduced the concentration at an average value of 2.20 ± 0.39 mg P-$PO_4^{3-}l^{-1}$ (Figure 5), which represents a phosphate removal efficiency of 63.6 ± 10.7 %, being this removal efficiency enough to comply with less strict removal regulations, for example the Mexican regulation (Semarnat, 1996; Semarnat, 2022). At the end of the experimental period (day 62), the Al-sludge Filter module continued removing phosphorus with an efficiency equal to 45.5 ± 5.5 %. These results proved that it is possible to implement a filter packed with Al-sludge waste for phosphorus removal as polishing system for a decentralized WWTP, and that the filter must be dimensioning according with the concentration limit set by the regulations of each country. The highest phosphorus removal efficiencies reached in this study (85 ± 9 %) are comparable to those reported by Maqbool *et al*. (2016) (83 and 88 %) who evaluated two kinds of Al-sludge to treat real MWW in batch tests at laboratory scale. They are quite like the removal efficiency reported by Doherty *et al*. (2015), who reports a phosphorus removal efficiency between 85-86 % in a CW packed with Al-sludge treating pig slurry.

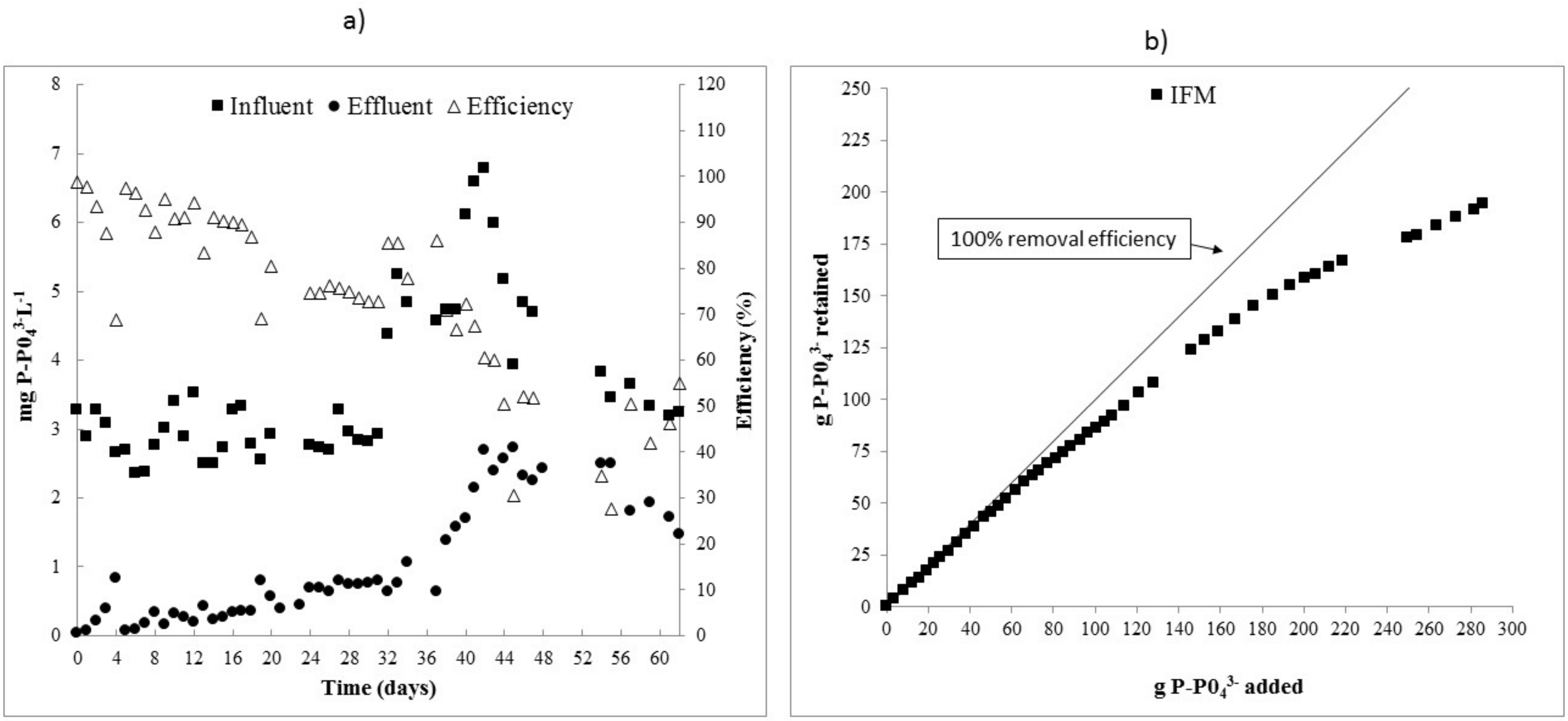

Figure 5. a) Concentration of phosphorus entering and leaving the IMF; b) P removed as a function of P added to the Al-sludge Filter module.

The P-removal capacity of the Al-sludge Filter module was calculated in the same way as the laboratory scale columns. The P-removal capacity found until day 32 was 1.50 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$, with an influent concentration of 3.08 ± 0.89 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$, and at the end of the test (day 62), the removal capacity was calculated at 2.69 mg $P\text{-}PO_4^{3-}\cdot g^{-1}$, with an influent concentration of over 5 mg $PO_4^{3-}\cdot l^{-1}$, which means that a mass of 194.12 g $P\text{-}PO_4^{3-}$ was retained in the Al-sludge Filter module, from the total $P\text{-}PO_4^{3-}$ mass introduced (286.13 g) into the Filter. The Al-sludge Filter module was operated with phosphorus loadings between 20 and 70 g $P\text{-}PO_4^{3-}\cdot m^{-2}\cdot d^{-1}$ and an average value between day 1 and 32 of

36.53 g $P\text{-}PO_4^{3-}\cdot m^{-2}\cdot d^{-1}$. From day 34 to 62, the average value was 47.26 g $P\text{-}PO_4^{3-}\cdot m^{-2}\cdot d^{-1}$. The phosphorus load applied and the HSLs were similar to those reported in other studies at laboratory scale with aluminum sludge but much higher than what has been reported for other adsorbent materials (Table 4). Therefore, the phosphorus removal capacity can be improved by decreasing the HSL applied. However, the decision to use such a high HSL and short retention times (EBCT) was to evaluate the Al-sludge Filter module under conditions that represent a normal operation of the decentralized-WWTP. This condition has not been reported in similar studies. At the end of the experimental period (62 days), a biological film grew on the top part of the Al-sludge Filter module generating operational problems due to clogging.

Phosphorus removal efficiency in the decentralized pilot-WWTP coupled to the Al-sludge immersed Filter module (IFM)

Figure 6 shows the average phosphorus concentration for each process of the decentralized-WWTP (ST, BFOB, and CW) plus the polishing filter (Al-sludge filter module). The values presented are the average obtained during the first 32 days of operation. The influent wastewater concentration was 5.0 ± 1.6 mg l^{-1}. From which 4 % was removed in the ST, while an additional 16 % and 22.4 % were removed in the BFOB and the CW, respectively. In both cases, it can be explained mostly by assimilation mechanisms of bacterial and plant for their growth, since as it is discussed and proved in a document previously published (Garzón-Zúñiga *et al.*, 2016) after few months of continuous operation of the BFOB and CW, the adsorption mechanism do not play anymore a major role in phosphorus removal due to saturation of the packing filter material.

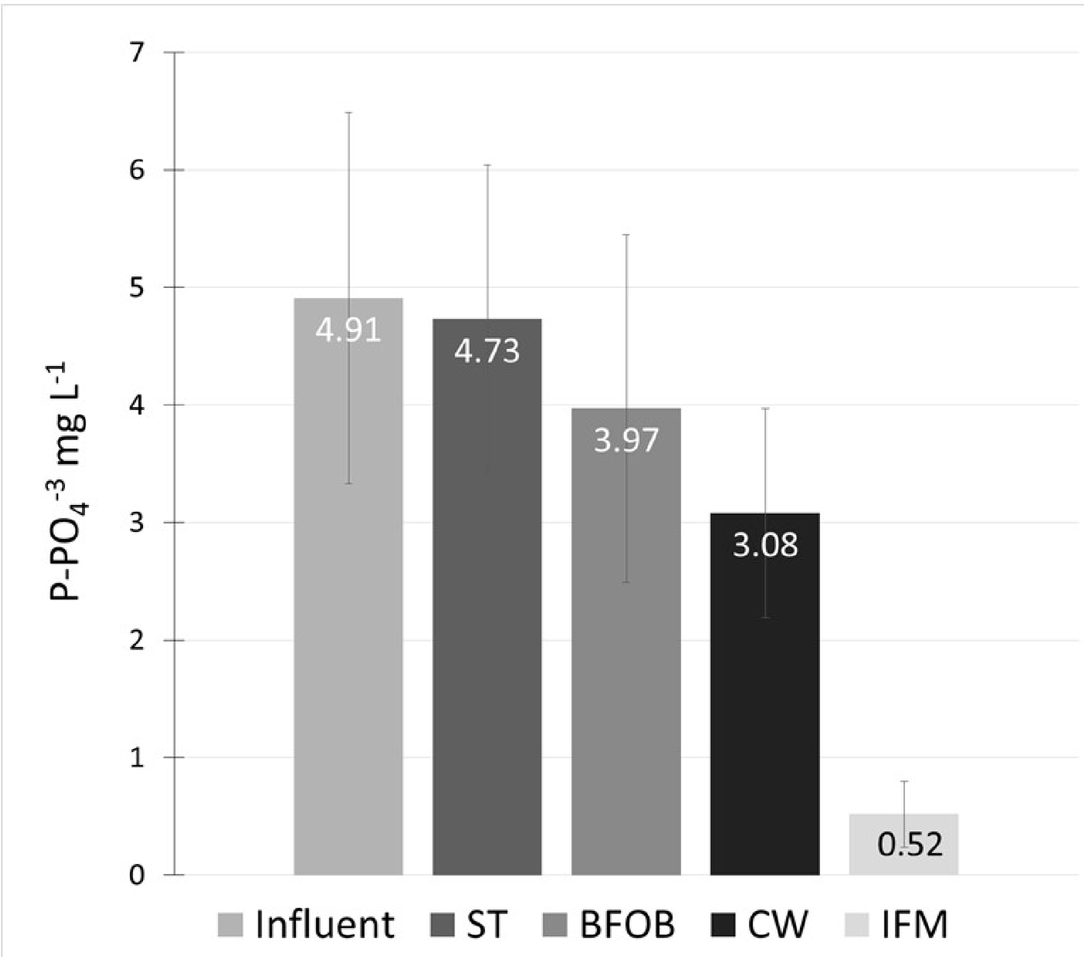

Figure 6. Phosphorus concentrations in the influent and effluent of each treatment process of the decentralized WWTP plus the polishing immersed filter module.

Tecnología y ciencias del agua, ISSN 2007-2422, 15(6), 311-353. DOI: 10.24850/j-tyca-2024-06-07

Under these conditions, the CW effluent presented an average concentration of 3.08 ± 0.8 mg $P\text{-}PO_4^{-3}$ l^{-1}. Feeding this effluent in the Al-sludge Filter module, it performed an additional removal efficiency of 83.1 %. Therefore, the global removal efficiency (pilot-WWTP plus AL-sludge filter) was equal to 89.4 % and the final effluent concentration was equal to 0.52 ± 0.28 mg $P\text{-}PO_4^{-3}$ l^{-1}. There is no report about an Al-sludge polishing system for phosphorus removal operating in continuous mode, so the removal efficiency reached cannot be compared. However, the removal efficiency agrees with that reported in batch tests at laboratory scale by Doherty *et al*. (2015) (85-86 %) and Maqbool *et al*. (2016) (83-88 %).

If an IFM is installed to remove Phosphorus, an estimation of its lifetime is desired. This calculation was made by the management of wastewater for a four-person household in rural zone. Considering that: a) the removal capacity of the IFM (2.69 mg $P\text{-}PO4^{-3}\cdot g^{-1}$); b) considering a P contribution per person of 2.3 g $P\text{-}PO4^{-3}$ d^{-1} (839.5 g $P\text{-}PO4^{3-}$ $year^{-1}$) (Drizo *et al*., 1999); c) the removal efficiency of the biological-WWTS presented in Figure 6b. For this phosphorus mass, the theoretical lifetime of the filter was calculated as follows: For an IFM with a sectional area of 1.2 m^2 and a depth of 1.0 m, packed with Al-SFM (1 394 kg) like the one used in this study, it is estimated that such a system would provide an effluent with a concentration under 2.0 mg $P\text{-}PO4^{-3}\cdot l^{-1}$ for 490 days (1.3 years), and by this time the system would had adsorbed 3.750 kg $P\text{-}PO4^{-3}$.

Once the filter material becomes saturated, it would be replaced by a new Al-sludge to continue operating and the saturated material could be used as a soil improver, having carried out a previous study to ensure that aluminum is not released into the environment. Another option would be that the saturated Al-sludge could be processed to extract the captured Phosphorus.

Al-sludge Filter effluent characterization

Table 6 shows the characterization of the influent and effluent of the Al-sludge filter. It can be observed that, except for NH_4^+-N, the concentrations of all the parameters remain almost unchanged, as is the case of COD, BOD, or their concentration decreased, as is the case of fecal coliforms (FC), alkalinity, turbidity, color, and Phosphorus. The latter being the one that presented the greatest removal of 83 %.

Table 6. Influent and effluent IFM wastewater characterization.

Parameter	IFM influent	IFM effluent	Removal efficiency (%)
COD (mg l^{-1})	51.0 ± 14.1	49.5 ± 7.2	3
BOD (mg l^{-1})	16.0	15.8	7
FC (NMP 100 ml)	7.9 E 03	5.2 E 02	1 U log
NH_4^+-N (mg l^{-1})	4.0 ± 1.9	4.8 ± 1.7	-
PO4-P (mg l^{-1})	3.1 ± 1.0	0.52 ± 0.1	**83**
Color	160 ± 86.8	142.5 ± 89.9	11
Turbidity	11.9 ± 10.1	4.5 ± 3.1	62
pH	6.6 ± 0.3	7.0 ± 0.2	-
Alkalinity (mg l^{-1})	170.9 ± 67.8	135.3 ± 17.4	21
Aluminum (mg l^{-1})		0.0144 ± 0.0100	N.d.

Nd: Non-determined.

On the other hand, it is well known that aluminum causes toxicity in aquatic environments and affects a wide diversity of fish, algae, and invertebrate species (George *et al*., 1995; Mortula, Bard, Walsh, & Gagnon, 2008). It should be noted that the toxic effects of aluminum are associated with soluble aluminum (Al_3^+), which is biologically available in soils and acidic waters (pH < 5.5) but is biologically inactive under conditions of a pH between 5.5 and 8.4 (Zhao, Babatunde, Hu, Kumar, & Zhao, 2011).

Figure 7 shows the monitoring that was done to the IFM effluent with respect to pH and aluminum concentration. The pH always presented values greater than 6.0 and the Al_3^+ concentration was always less than 0.04 with an average value of 0.014 ± 0.010 mg/l.

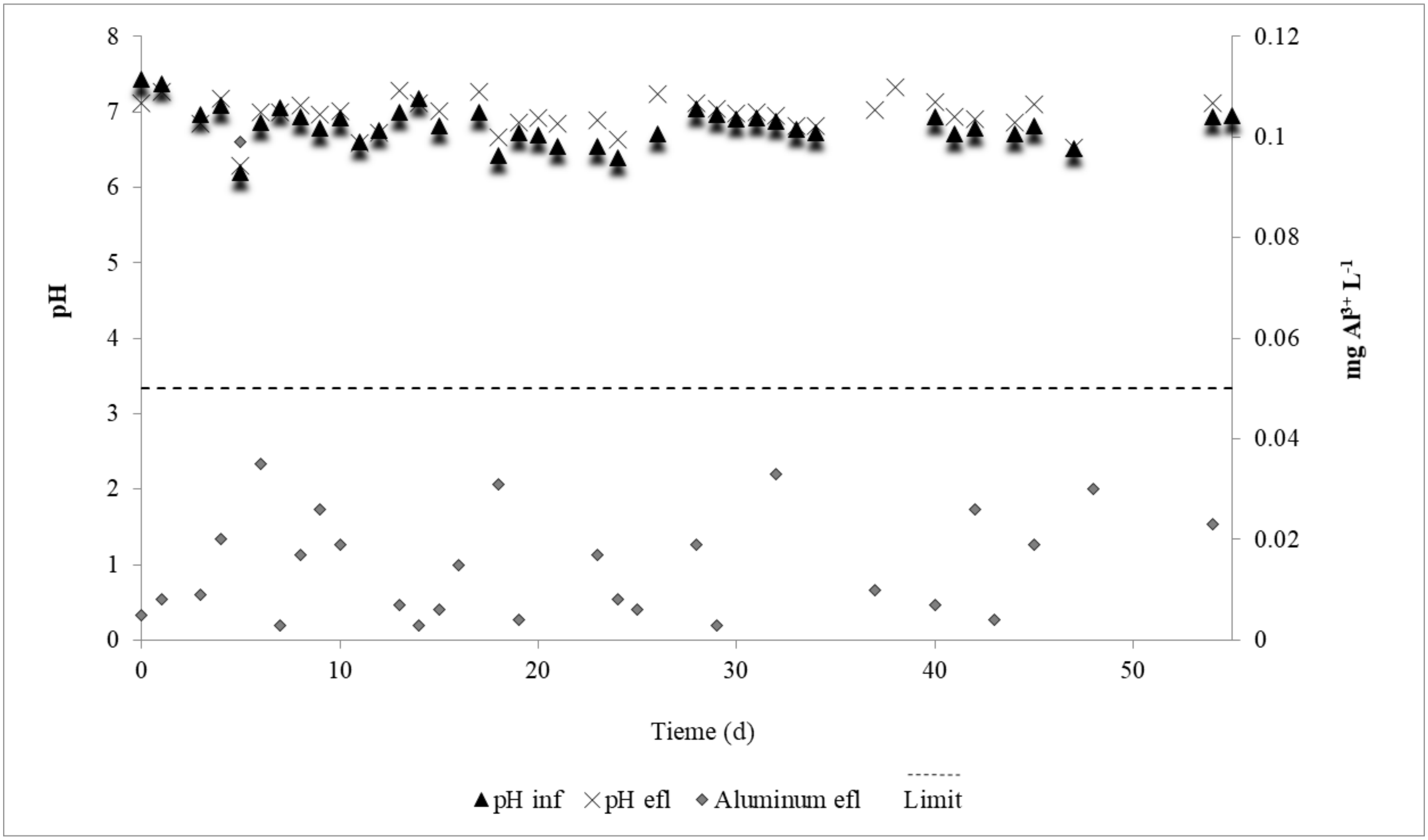

Figure 7. Values of pH and aluminum in the IFM evaluated as polishing for phosphorus in a pilot scale decentralized WWTP.

Although there was a release of aluminum in the IFM effluent, the levels found were very low since, according to the Ecological Criteria for Water Quality (CECA, 1989) CE-CCA-001/89, a body of water for the protection of aquatic life should not exceed 0.2 mg $Al_3^{+} \cdot l^{-1}$ in marine or coastal waters, and 0.05 mg $Al_3^{+} \cdot l^{-1}$ for fresh water and the IFM effluent always remained below 0.04 mg $Al_3^{+} \cdot l^{-1}$. Therefore, the aluminum released does not represent an imminent risk to the environment or human health.

Conclusions

Al-sludge waste from the drinking water treatment plant "Los Berros" of the Cutzamala system in the State of Mexico, Mexico was successfully used as packing material for a filter treating the effluent of a pilot decentralized-WWTP to enhance the phosphorus removal.

The evaluation of the Al-SFM at laboratory scale in a continuous system using real wastewater showed an adsorption capacity of 2.509 mg $P\text{-}PO_4^{3-} \cdot g^{-1}$. This by applying an initial concentration of 11.03 ± 0.86 mg $P\text{-}PO_4^{3-} \cdot l^{-1}$, an EBCT of 120 min, and a breaking point of 5 mg $P\text{-}PO_4^{3-} \cdot l^{-1}$.

However, when the Al-SFM was evaluated in a phosphorus removal polishing filter (Al-sludge Filter) for a pilot-scale decentralized WWTP, the adsorption capacity was 2.69 mg $P\text{-}PO_4^{3-} \cdot g^{-1}$ or 1.86 kg $P\text{-}PO_4^{3-} \cdot m^{-3}$, with an EBCT of 120 min, but after the breaking point of 5 mg $P\text{-}PO_4^{3-} \cdot l^{-1}$. without reaching saturation of the material after 62 days of continuous operation.

Operating a pilot scale Al-sludge filtration module as a polishing system of a pilot-WWTP presented a phosphorus removal efficiency of 83 ± 3 %. The entire system (pilot WWTP plus Al-sludge Filter) showed a removal efficiency 89.4 ± 5.7 % of $P\text{-}PO_4^{3-}$, and the effluent concentration was 0.54 ± 0.24 mg $P\text{-}PO_4^{3-}\cdot l^{-1}$, proving that the Al-sludge Filter could achieve high phosphorus removal efficiency in a continuous system as a polishing system for a pilot scale WWTP.

The filter packed with Al-sludge can be designed to comply with different maximum allowable discharge values for Phosphorus, according to recent stricter regulations of different countries such as the European Union (0.5 mg/l), USA (1.0 mg/l), or Mexico. (5.0 mg/l).

These results demonstrated that this process could be a real option to remove phosphorus from WW.

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