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SEWAGE PHOSPHORUS REMOVAL USING HEN EGGSHELLS THROUGH DIFFERENT CONTACT SYSTEMS

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Agro-industrial solid waste
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ABSTRACT

Hen eggshell is a waste with high phosphorus (P) removal capacity from synthetic solutions. However, there is a lack of knowledge about how to use this material on P removal from real wastewater. The present study proposed to evaluate two types of system for P removal from wastewater using eggshells. On the first system, eggshells grinded, sieved in 0.425 mm, and contained in coffee filters, were fixed to baffles using calico cloth bags. On the second, the eggshells in the same conditions were attached to vertical wooden rods and distributed at different heights. For both systems, P concentration was daily monitored for four weeks, with and without medium acidification and hydraulic retention time of one day. The baffles system was more efficient, reaching a maximum removal of 15.93% in wastewater with pH 4.73. P removals did not differ significantly over the weeks; however, there is a tendency to vary the efficiencies according to the change in pH. The baffled tank, for presenting higher performance in P removal, is the most suitable for use in a domestic wastewater treatment system.

Palavras-chave:
Resíduos sólidos agroindustriais
Dureza
Precipitação
Sorção
Tratamento de águas residuárias

REMOÇÃO DE FÓSFORO DE ESGOTO COM CASCA DE OVO DE GALINHA ATRAVÉS DE DIFERENTES SISTEMAS DE CONTATO

RESUMO

A casca de ovo de galinha é um resíduo que apresenta alta capacidade de remoção de fósforo (P) em soluções sintéticas. Entretanto, há um desconhecimento sobre o seu uso na remoção de P em águas residuárias. O presente estudo teve como proposta avaliar dois tipos de sistema para remoção de P do esgoto sanitário usando cascas de ovo. No primeiro sistema, cascas trituradas, peneiradas em malha de 0,425 mm e contidas em filtros de café, foram presas a chicanas utilizando bolsas de tecido Morim. No segundo, as cascas nas mesmas condições foram afixadas a hastes verticais de madeira e distribuídas em diferentes alturas. Em ambos os sistemas as concentrações de P foram monitoradas por quatro semanas, com e sem acidificação do meio e um tempo de detenção hidráulica de um dia. O sistema de chicanas foi mais eficiente, alcançando uma remoção máxima de 15,93% em pH 4,73. As remoções de P não diferiram significativamente ao longo das semanas, no entanto, há uma tendência de variação das eficiências de acordo com a mudança de pH. O tanque chicaneado, por ter apresentado maior desempenho na remoção de fósforo, é o mais indicado para utilização em um sistema de tratamento de esgoto doméstico.

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INTRODUCTION

Phosphorus is a chemical element present in all living organisms on Earth and has been well-studied in many aspects. While there are reports of its scarcity for soil fertilization in some regions, the release into water bodies may cause severe environmental impacts, such as eutrophication (VON SPERLING, 2014; IWANIEC *et al.,* 2016).

The biological wastewater treatment has low efficiency on P removal which needs some alternatives such as the use of plants, algae, and chemical precipitation for increasing its potential (RAMASAHAYAM *et al*., 2014; SUKACOVÁ *et al.,* 2015; QUAN *et al*., 2016; KASPRZYK; GAJEWSKA, 2019). Some studies used a reactive medium, which provides P removal through precipitation, and this solid can return to the soil as an alternative fertilizer (QUAN *et al*., 2016). For instance, Romar-Gasalla *et al*. (2016) used oyster shells, a waste rich in calcium carbonate, for P removal. Vohla *et al*. (2011) correlated the calcium and calcium oxide content in the residue to P retention.

Hen eggshell is an agro-industrial waste rich in calcium carbonates, which makes it a candidate residue for the formation of insoluble P salts, which facilitates its removal (MEDEIROS; ALVES, 2014; OLIVEIRA *et al*., 2015). The use of eggshell as sorbent became necessary because of their soil conditioning potential, the ease of purchase (MAGALHÃES *et al*., 2011; YIN *et al.,* 2017), and the possibility of providing P to the environment.

Fia and Ribeiro (2017) observed a great potential of the hen eggshell in removing P. However, more significant removals occurred in the first millimeters of the mass of the material added into the filters. The calcium present in the shell may have reacted chemically with P, generating precipitates, blocking the wastewater entry, and consequently, the reaction with other layers of reactive material. Therefore, to increase the P removal efficiency, the eggshells need to be located in a system with a thin layer and larger surface before the contact with the wastewater. In addition, most of the experiments with reactive filters involves conditions of batch balance tests, and evaluations in environments simulating Wastewater Treatment Plants (WWTP) are needed (KARCZMARCZYK; BUS, 2017).

Baffles are devices used to approximate the piston flow, reducing the preferential paths and the formation of dead zones (VON SPERLING, 2013), increasing contact with the reactive medium (TEE *et al*., 2012). Moreover, it may enhance contact among particles, such as in flocculation (LEE, 2017). In this way, the insertion of barriers, like baffles or vertical rods containing sorbents may increase the efficiency of contaminant removal in wastewater treatment tanks.

Another factor that has been identified as influential in the P removal from wastewater is the pH (GUO *et al*., 2017). In acidic medium, there may be a predominance of positive charges, favoring higher phosphate adsorption (YANG *et al.,* 2006; YIN *et al.,* 2011; FIA; RIBEIRO, 2017). On the other hand, the precipitation of P salts in reactors occurs at higher pH values (ANGELA *et al.,* 2011; YAN *et al.,* 2014a; YAO *et al.,* 2017) and the addition of alkaline materials such as eggshells could raise the pH of the solution (LIM; ARIS, 2014).

Thus, the objective of this study was to evaluate the removal of available phosphorus (orthophosphates) from sanitary sewage with secondary treatment (after submerged aerated filters), through two different contact forms with grinded hen eggshells: arranged in baffles and vertical wooden rods inserted in contact tanks.

MATERIAL AND METHODS

Study area and experimental apparatus

The study was conducted at the Wastewater Treatment Plant of the Federal University of Lavras (WWTP-UFLA). WWTP-UFLA consists of a system composed of thick and thin grids, Parshall flume, UASB (Upflow Anaerobic Sludge

Blanket) reactors, SAFs (Submerged Aerated Filters), sand filters, chlorination tank, and UV lamps contact tank. The latter two were inactive during the experimental period.

For the prototype scale evaluation, the treated wastewater was captured in the UV lamps contact tank and manually redirected for two 200 L plastic containers, with daily renewal. Each of the containers was connected by a tube to a tank that composes the system, where the flow was manually regulated with the aid of a register installed on each tube.

The system was composed of two 45 L (useful volume) glass tanks, fed with 30 mL.min^{-1} (43.2 L.d^{-1}) sewage flow, providing a hydraulic retention time (HRT) of around 1.0 d in each unit, assessed in parallel.

To calculate the reactive material mass to be added to the systems, a concentration of 10 mg.L^{-1} of P in sanitary sewage was considered, which is the range typically found for this type of wastewater (VON SPERLING, 2014); and P retention capacity of 20.4 mg for each gram of eggshell (FIA; RIBEIRO, 2017). Based on this information, and considering other wastewater pollutants, such as nitrogen and heavy metals, 180 g of hen eggshells were used per tank. In the calculation of the amount of residue to be used, the useful volume of the reactor (45 L) was used, since the HRT design of 1.0 d was considered. In practice, the amount of wastewater in contact with the eggshell was lower, since the system operated with 43.2 L daily. Further substantial projects must work with the adequate flow of the tanks so that there is no underestimation or overestimation of the amount of waste.

The eggshells were collected in a local poultry house (chicken aviary), cleaned in running water, dried in an oven, grinded and homogenized, and sieved in a 0.425 mm mesh. After, the eggshells were attached to the devices for contact with the wastewater as described below.

To evaluate P removal capacity by contact with the eggshells, these were differently arranged in the two systems. In the first tank (Figure 1a), baffles were installed in the transversal direction, with 0.25 m in width, 0.25 m of useful height and 5 mm in thickness, 9 cm apart from each other and the walls, totaling six structures. These baffles have opposite dispositions to form a labyrinth and force the passage of the liquid through the added structures (PARVIZI *et al.*, 2016). According to von Sperling (2013), the calculation of the $\left(\frac{L}{B}\right)$ ratio (length and width) equivalent $\left(\frac{L}{B}\right)$ in a tank with partitions (baffles) parallel to the B width is given by Equation 1.

$$\left(\frac{L}{B}\right)' = \frac{B}{L}(n+1)^2 \quad (1)$$

where,

L = tank length (m);
B = tank width (or breadth) (m) and
n = number of baffles.

To add the reactive material to the baffles tank, 12 calico cloth bags of 0.25 m height were made, and each one was divided into three horizontal compartments, enabling a height variation of the eggshells of approximately 7 cm. These compartments were filled with size 103 coffee filters containing 5 g of grinded hen eggshells each, resulting in 180 g in the entire tank (6 baffles = 12 faces).

On the second tank (Figure 1b), a polystyrene cover was placed where vertical wooden rods (“barbecue sticks” type) with a 0.30 m height were affixed. There were 20 rods with 9 g of eggshell each. Again, it was divided into three different heights of approximately 7 cm and affixed in each rod three size 103 coffee filters with 3 g each, completing the 180 g in the tank, the same amount of the baffles tank.

Both tanks were covered with opaque adhesive paper (“contact paper”) to prevent incoming sunlight, which may promote the growth of algae and other organism and could interfere with the results.

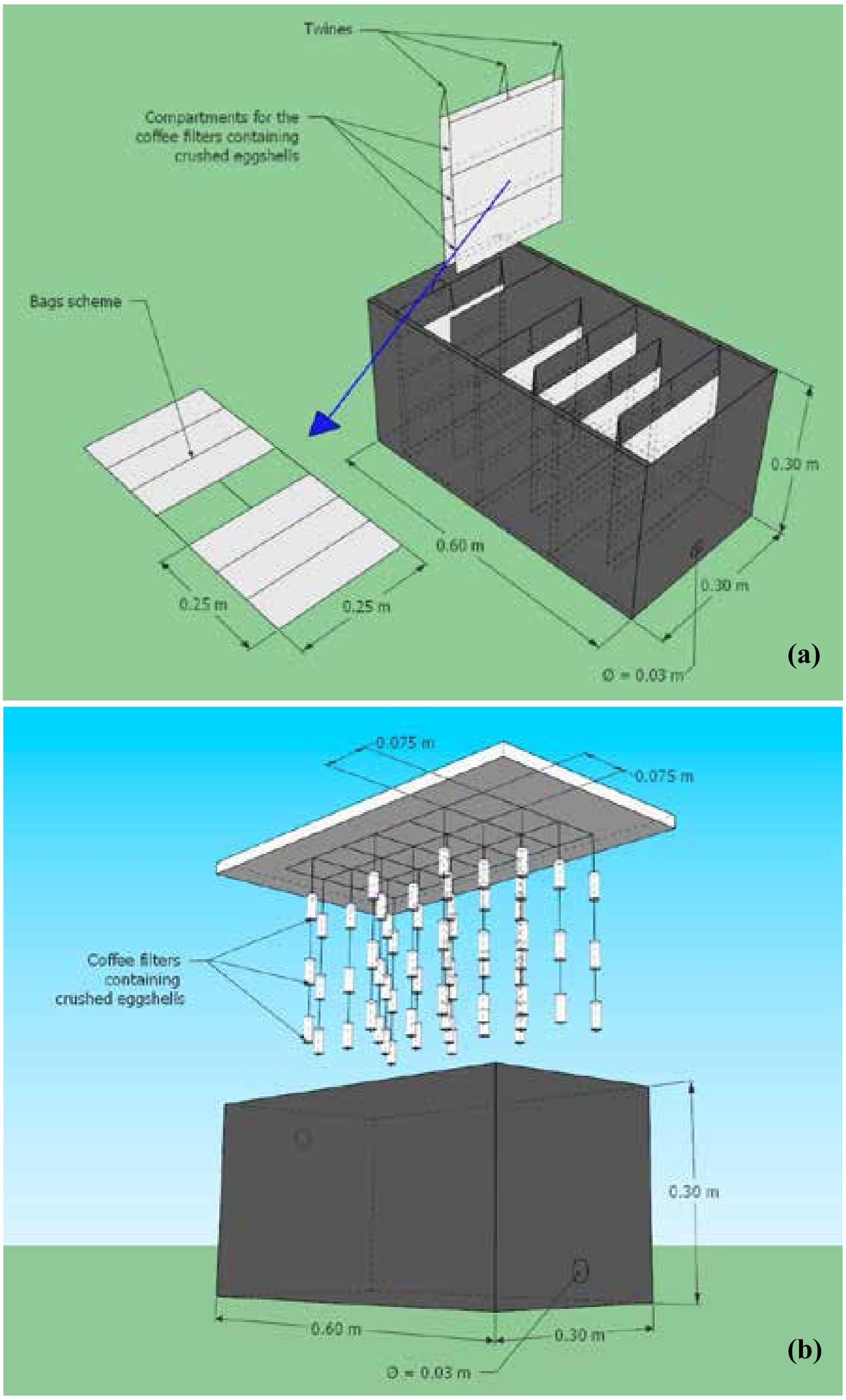

Figure 1. Layout of the systems used in the experiment made with software *SketchUp Make* (version 16.1.1450): (a) Baffles tank; (b) Vertical wooden rods tank

Monitoring

P removal efficiencies were monitored from June 4 to 8, June 11 to 15, July 11 to 15, and July 16 to 20, 2018, with daily determination of influent and effluent available P (orthophosphates) concentrations to the systems, with triplicate analysis. As the eggshell quantities were calculated for complete influent P adsorption for five days, after the first week the sorption/precipitation material was renewed. This practice was carried out for four weeks (20 samplings), determining the orthophosphate concentration using the colorimetric method described in Apha *et al.* (2012) and Matos (2015).

Concurrently, the sample hardness, which expresses the concentration of multivalent cations (such as Ca^{2+} and Mg^{2+}) in solution, which may increase in the liquid by the eggshell presence, known to be rich in calcium (SOARES *et al.,* 2015), was quantified by titrimetric method (MATOS, 2015). Leaching and solubilization of eggshell inorganic components may increase sewage pH and electrical conductivity (EC), thus pH and EC meters were used, following the recommendations according to Matos (2015).

In the fourth week (or last testing week), concentrated sulfuric acid solution (≈ 18 $mol.L^{-1}$) was added on the first day to reduce the liquid influent pH in the system, in a proportion of 20 mL of acid for each 200 L container. This proportion provided a reduction in the sewage pH to values around 3.0-3.5 in laboratory tests, a favorable range for increasing sorption as discussed by Yin *et al*. (2011). On the remaining days, the pH followed the wastewater inlet and outlet dynamics (and liquid renewal in the systems), without acid addition.

Statistical analyses

For the comparison of the influent sewage orthophosphate concentration of the units among the four weeks (compared week by week), the *Mann-Whitney* test was used, a non-parametric statistical test for two independent data, with a significance level of 5.0%. Thus, the sewage characteristics were compared (input or influent to the systems during weeks 1 to 4). This procedure allowed the choice of a statistical test to compare the grinded eggshells layout effect on the available P (P_{av}) removal. If the sewage characteristics that fed the units were different, the test to be employed would be *Mann-Whitney*, otherwise, with no significant difference, the choice would be *Wilcoxon* (non-parametric test for paired data), comparing the two systems efficiency in the same week. Furthermore, the sewage passage through the tanks may change their characteristics (pH, EC, and hardness), so the comparison of these input and output data for each week were performed through the *Mann-Whitney* test. Finally, the *Kruskal-Wallis* test was employed to compare influent concentrations and orthophosphate removal efficiencies over the four weeks (comparing for each treatment separately – baffles or rods).

Analyses were performed with the software *Statistica 10.0* (STATSOFT, 2010), always taking into account the 5% significance level.

RESULTS AND DISCUSSION

Orthophosphate removal

Sewage from universities has characteristics that may differ from the typical composition mentioned for domestic wastewater in cities, due to the possible contribution of laboratories and university hospitals. Campos *et al.* (2020), for example, characterized the raw sewage from WWTP-UFLA and found chemical oxygen demand (COD) concentrations, total solids (TS), volatile solids (VS), total nitrogen Kjeldahl (TNK) and alkalinity of 847, 986, 550, 154 and 528 $mg.L^{-1}$, respectively. For comparison purposes, typical values for domestic sewage are, in the same order, 600, 1100, 620, 45 and 200 $mg.L^{-1}$, indicating composition with a high presence of ions, therefore reflecting high concentrations of nitrogen and alkalinity, and COD, which could suffer interference from some reduced ions (AQUINO *et al*., 2006), above what is commonly found.

However, the concentrations found for P after the secondary treatment were within the range found in raw sewage, which is 4 to 15 $mg.L^{-1}$ (VON SPERLING, 2014). The average value was 9.92 ± 0.32 $mg.L^{-1}$ (average ± standard deviation), with a median of 9.75 $mg.L^{-1}$ (Table 1), with a significant difference by *Kruskal-Wallis* test at the level of 5% significance among the four weeks (analysis presented in Table 1). Since a high efficiency of UASB reactors (PINTO *et al*., 2014) and biofilters (GALINDO *et al.,* 2016) is not expected, post-treatment evaluation is needed.

Contrary to expectations, the installed systems did not provide high P removal efficiencies. Efficiencies were even negative on the first day of monitoring and increased on the remaining days of the week, with the performance decreasing on the fifth day of the first week. This comparison is numerical since it is not possible to statistically compare the efficiencies per day as there was only a single tank per treatment.

Regarding the efficiencies per week (taking into account the median values), a non-significant difference was observed even in the fourth week (with acidification), indicating that the contact time between the wastewater and the residue may have been short to allow the observation of a significant effect of the acidification. As a comparison, Oliveira *et al.* (2015) kept a solution of P and oyster shells in contact for 72 hours with agitation. According to Torit and Phihusut (2019), the contact time is of great importance for precipitation and allow the connection of P with the active sites of the residue. Even if the test time is measured in minutes, the contact in isothermal tests is higher than that provided by the flow inside reactors. Furthermore, in this study, the acid addition was performed only on the first day of the fourth week and was not continuous throughout the week, and the P influent concentrations were statistically different over the weeks, interfering in the efficiency analysis.

According to Dias *et al.* (2017), the importance of baffles is to reduce preferential paths, therefore forcing wastewater to follow a predetermined path in the reactor in which they were installed. Thus, better hydrodynamic conditions are expected with increasing $\left(\frac{L}{B}\right)$ ratio of the units. The tanks were manufactured with $\left(\frac{L}{B}\right)$ = 2.0, but the equivalent

Table 1. Concentration of orthophosphate (P_{av}) and removal efficiency (Eff) from samples collected over the evaluation period

Day	Sample		1st week		2nd week		3rd week		4th week	
			P_{av}	Eff	P_{av}	Eff	P_{av}	Eff	P_{av}	Eff
			mg.L^{-1}	(%)	mg.L^{-1}	(%)	mg.L^{-1}	(%)	mg.L^{-1}	(%)
1	Baffles	Inlet	9.71	-	9.38	-	10.55	-	10.55	-
	Rods	Inlet	10.01	-	9.46	-	10.12	-	10.12	-
	Baffles	Outlet	9.73	-0.16	10.17	-8.34	10.53	0.24	10.53	-2.72
	Rods	Outlet	10.12	-1.15	9.68	-2.35	10.32	-2.01	10.32	-1.22
2	Baffles	Inlet	9.36	-	9.23	-	10.88	-	10.88	-
	Rods	Inlet	9.75	-	9.25	-	11.06	-	11.06	-
	Baffles	Outlet	9.29	0.74	9.19	0.50	10.66	2.11	10.66	3.16
	Rods	Outlet	9.68	0.71	9.22	0.25	10.96	0.92	10.96	1.06
3	Baffles	Inlet	10.27	-	9.27	-	10.20	-	10.20	-
	Rods	Inlet	9.91	-	9.39	-	10.38	-	10.38	-
	Baffles	Outlet	9.36	8.88	9.11	1.74	9.20	9.75	9.20	12.50
	Rods	Outlet	9.66	2.55	8.99	4.25	10.04	3.19	10.04	5.08
4	Baffles	Inlet	9.36	-	9.43	-	10.68	-	10.68	-
	Rods	Inlet	9.11	-	9.75	-	10.50	-	10.50	-
	Baffles	Outlet	8.42	10.08	9.01	4.47	9.43	11.69	9.43	15.93
	Rods	Outlet	8.82	3.20	9.55	2.12	10.07	4.13	10.07	4.19
5	Baffles	Inlet	9.09	-	9.43	-	10.99	-	10.99	-
	Rods	Inlet	9.18	-	9.43	-	11.17	-	11.17	-
	Baffles	Outlet	8.30	8.61	8.30	12.04	9.92	9.74	9.92	9.16
	Rods	Outlet	9.09	1.00	9.17	2.76	10.99	1.60	10.99	3.28
MED	Baffles	Inlet	9.36B	-	9.38B	-	10.68A	-	10.30AB	-
	Rods	Inlet	9.75B	-	9.43B	-	10.50A	-	10.09AB	-
	Baffles	Outlet	9.29	8.61A*	9.11	1.74A	9.92	9.74A	9.38	9.16A
	Rods	Outlet	9.66	1.00A	9.22	2.12A	10.32	1.60A	9.76	3.28A

MED = Median week values for each treatment; * = significant difference by the *Wilcoxon* or *Mann-Whitney* test (P_{av} removal efficiencies, comparing both systems). Efficiencies followed by the same upper letter (A or B) did not differ significantly by the *Kruskal-Wallis* test (comparing influent concentrations or removal efficiencies separately for each tank).

ratio with the presence of baffles is 24.5/1, calculated from Equation 1. This may be a factor that explains why the baffles tank presented higher performance, except for the second week that presented atypical results (Table 1). Despite the fact the efficiencies in the third and fourth weeks did not differ significantly, the difference in orthophosphate removal superiority of the baffles tank is remarkable. The *Wilcoxon* test was chosen because the influent characteristics did not differ (for all monitored variables) in the baffles tank and the vertical wooden rods tank.

Values obtained for the treatments were less than those found in the literature for secondary/tertiary treatments. Costa *et al*. (2015), for example, they reached 69% removal of total P from sanitary sewage (UASB reactor effluent) in horizontal subsurface-flow constructed wetlands (HSSF-CW), filled with blast furnace slag. Combining a pond system with algae and constructed wetlands (CWs), Zhimiao *et al*. (2016) achieved the same P removal efficiency (69%) by treating synthetic wastewater (with higher P concentration; greater than 50.0 mg.L^{-1} orthophosphates). In vertical CWs, filled with sand and bio-carbon as medium support, Rozari *et al.* (2016) increased the system available phosphate removal capacity up to 91%.

Regarding the sorption/precipitation tests with reactive mediums, Oliveira *et al*. (2015) used calcinated eggshells and obtained P removal efficiencies greater than 80%. Thermal or chemical treatment increases the sorption capacity of the material, as demonstrated by Yan *et al*. (2014a). Yin *et al.* (2017) enriched a clay mineral (attapulgite) with calcium and performed thermal treatment, which resulted in an effluent with 90% of P removed.

Several studies have evaluated the removal capacity of the reactive medium using batch tests, in which P remains longer in contact with the substrate. However, the results demonstrated that in regular operating conditions, part of the sorption/precipitation potential of the material employed is impaired. For comparison purposes, it was calculated the P removal capacity of each gram of the residue employed in each week (Figure 2), using as reference, the value found by Fia and Ribeiro (2017). This study suggested the need for increasing the exposure area of the residue with the wastewater in treatment.

Once again, P removal capacity was less than expected, being observed by how much each gram was able to sorb/precipitate at the end of the five days of each week (P accumulated charge removed / shell mass employed). In the fourth week, the baffles tank showed better performance, including the same unit in the second week, probably due to the acidic solution added to the influent liquid. As sewage characteristics did not vary from one week to another, the operation conditions may have influenced the result.

Ramasahayam *et al*. (2014), in their compilation,

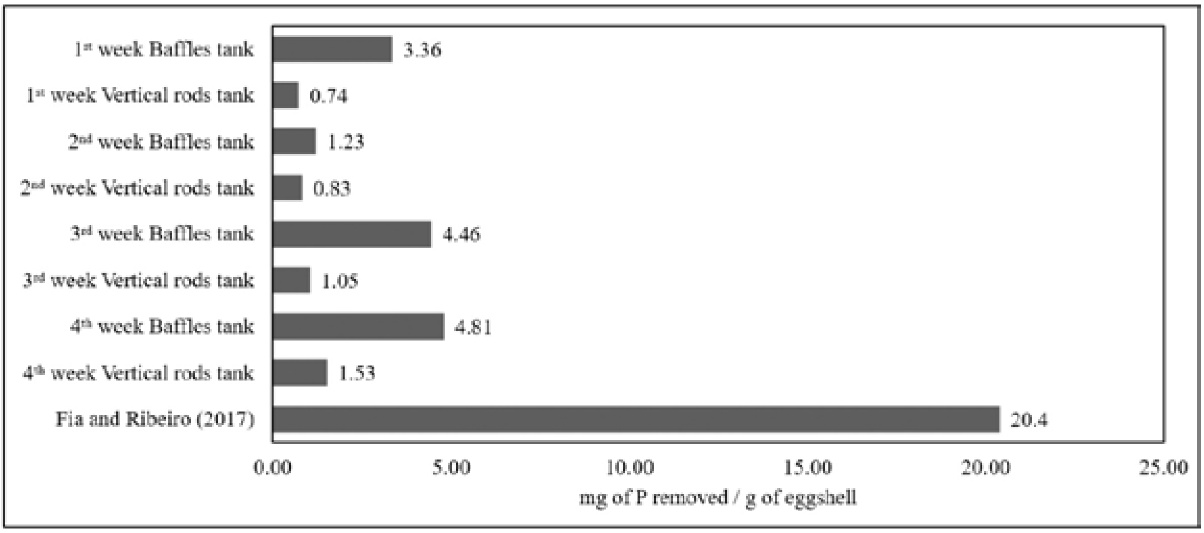

Figure 2. Phosphorus removal capacity by the grinded eggshell (mg of P per g of grinded eggshell) and comparison with the value used as a reference

presented the sorption capacity of some materials such as wood impregnated with iron oxide (43.70 $mg.g^{-1}$); nanomagnetite treated with iron hydroxide (49.3 $mg.g^{-1}$), goethite (7.92 $mg.g^{-1}$), iron oxide (0.22 $mg.g^{-1}$), kaolin (0.08 $mg.g^{-1}$), and modified lignin (8.90 $mg.g^{-1}$), and in some materials, the values were even lower than in the present study. Nevertheless, most of the mentioned materials had a higher removal capacity than the treatments evaluated in this study. Yan *et al*. (2014b) reported values of 139.00 mg per gram of an alkaline residue from the chemical industry (sodium carbonate plant). Panagiotou *et al*. (2018) observed sorption capacities ranging from 8.00 to 32.00 $mg.g^{-1}$, using calcined eggshell at different temperatures. Guo *et al*. (2017) were able to increase the eggshell removal capacity from 0.26 $mg.g^{-1}$, lower than in this study (Figure 2), to 6.23 $mg.g^{-1}$, performing heat treatment and incorporating aluminum in the residue, demonstrating that modifications in the residue are recommended in order to increase the performance of the baffles and the vertical wooden rods tanks.

Some other factors may also influence the sorption or precipitation capacity of the reactive material, such as the particle size. Panagiotou *et al*. (2018) observed a better performance for 1-2 mm particles with the sorption capacity of larger particles, considering a larger particle size than the one used in this study (< 0.425 mm). The pH can influence the presence of positive and negative charges in the residue, also resulting in different P removal capacities. Yan *et al*. (2014b) obtained better results at pH 5.5. According to Oliveira *et al*. (2015), calcined eggshells are not influenced by pH in their performance, but in the fresh residues, this physical-chemical variable seems to imply an increase or decrease in P removal capacity. Fia and Ribeiro (2017) reached the value in Figure 2 using a synthetic P solution with pH 5.5, a condition that the authors found to be the most conducive to P sorption. Numerically, the best results observed in the last week are mainly due to the addition of concentrated sulfuric acid and pH reduction, but, as previously discussed, there was no significant difference in weekly medians. In addition to the contact time, the fluctuations in efficiencies over the days (Table 1), which may be linked to the change in pH, did not allow a significant difference in efficiency after the acidification.

For Maroneze *et al*. (2014), P removal efficiencies of about 90% are usually achieved in plug flow units, filled with residues, which are also easy to be operated. Therefore, other conditions that may have reduced efficiency should be investigated. The hydrodynamic conditions and the significant variations in the flow (manually controlled) may have caused a change in the HRT, reducing contact of P with the grinded eggshell.

Li *et al*. (2018) collected information from different authors about the functioning of polishing ponds, among them, regarding the installation conditions of the baffles. According to the authors, there should be a maximum of six baffles, with a minimum spacing of 1/7 of the length. Besides, the maximum length of baffles should not exceed 90% of the length or width, depending on the structural arrangement (baffles parallel to length or width). All these requirements have been satisfied in the baffles tank, so the influence of other factors such as flow regulation and influence on HRT is suspected.

Regarding the vertical rods tank, it is believed that the cover movement in times of higher wind incidence, and the presence of preferential paths under the rods, may have caused a reduction in their performance.

Although the eggshells were distributed in smaller quantities, the formation of the precipitate (calcium phosphate) may have hindered the wastewater entry into the compartments containing the eggshells, as observed by Fia and Ribeiro (2017), influencing the yield of both systems, despite the unclear trend in P removal over the days. Furthermore, the eggshell losses through the coffee filter pores or eventual damage to the filter tissue (observed during the experiment), would imply in a decreased amount of reactive material, which would explain the results obtained. Thus, the low contact time plus the precipitation of salts on the material surface and the possible loss of the sorbent may explain the low values of the results.

pH, EC, and hardness

The pH values (Table 2) fluctuate close to the lower limit of the typical range (6.7 to 8.0), while the EC can be considered high since values from 480 μS.cm^{-1} were found (VON SPERLING, 2014; MATOS; MATOS, 2017), reinforcing the discussion about the presence of ions in university sewers. Regarding hardness, as it is a poorly monitored variable in the sewer, there is no typical range. Using the study of Bonfim *et al*. (2016) (200 mg.L^{-1} of $CaCO_3$) when monitoring a WWTP in Recife, it was found that the hardness values in the WWTP-UFLA are low.

After discussing the factors that led to the low performance of systems containing grinded eggshells in different arrangements, their influence on the sewage characteristics will now be considered, with the pH, EC, and hardness data shown in Table 2.

Due to the presence of carbonates such as calcium and magnesium (MEDEIROS; ALVES, 2014) and the potential use as a soil improver (LO MONACO *et al*., 2015), it was expected that the passage through the tanks would increase the pH of sewage, and the ion concentration (measured by EC), and hardness (due to the presence of Ca^{2+} and Mg^{2+}). However, only hardness showed a significant difference between the first and last weeks for both treatments, and between the second

Table 2. Values of potential of hydrogen (pH), electrical conductivity (EC), and hardness from samples collected over the evaluation period

Day	Sample		1st week			2nd week			3rd week			4th week		
			pH	EC	Hardness	pH	EC	Hardness	pH	EC	Hardness	pH	EC	Hardness
			-	μS.cm^{-1}	mg.L^{-1}	-	μS.cm^{-1}	mg.L^{-1}	-	μS.cm^{-1}	mg.L^{-1}	-	μS.cm^{-1}	mg.L^{-1}
1	Baffles	Inlet	6.52	1022	34	6.81	943	39	6.67	968	34	2.62	2410	36
	Rods	Inlet	6.42	1034	47	6.80	991	28	6.61	979	47	2.63	2470	36
	Baffles	Outlet	6.91	1012	57	6.74	943	52	6.89	948	57	5.21	1410	54
	Rods	Outlet	6.79	1059	41	6.58	960	47	6.77	953	41	5.76	1525	79
2	Baffles	Inlet	6.82	884	41	6.69	892	37	6.55	952	41	2.62	2120	43
	Rods	Inlet	6.83	871	46	6.61	890	41	6.52	973	46	2.58	2360	43
	Baffles	Outlet	6.87	877	56	6.88	850	54	6.85	959	56	3.65	1601	94
	Rods	Outlet	6.80	883	47	6.80	866	39	6.83	977	47	3.44	1675	88
3	Baffles	Inlet	6.90	674	34	6.75	1014	36	6.68	859	34	3.19	1547	39
	Rods	Inlet	6.54	708	35	6.80	1024	35	6.64	861	35	3.18	1531	42
	Baffles	Outlet	6.62	693	45	6.87	943	49	7.00	899	45	5.57	1398	86
	Rods	Outlet	6.72	747	50	6.93	997	46	6.97	911	50	4.26	1505	74
4	Baffles	Inlet	6.64	885	33	6.73	930	38	6.52	920	33	4.73	1513	33
	Rods	Inlet	6.70	925	42	6.83	965	40	6.56	961	42	4.84	1522	40
	Baffles	Outlet	6.58	812	50	6.77	868	53	6.87	924	50	6.16	1395	64
	Rods	Outlet	6.70	851	40	6.80	910	43	6.87	927	40	6.22	1432	55
5	Baffles	Inlet	6.62	845	35	7.14	1010	34	6.47	870	35	5.79	1415	36
	Rods	Inlet	6.64	861	36	7.11	1031	36	6.54	890	36	6.45	1382	33
	Baffles	Outlet	6.62	812	51	7.12	952	48	6.88	884	51	6.34	1420	63
	Rods	Outlet	6.66	868	47	7.11	1025	43	6.86	933	47	6.68	1478	50
MED	Baffles	Inlet	6.64	862	34	6.62	958	37	6.55	920	34	3.19	1547	36
	Rods	Inlet	6.64	880	42	6.70	980	36	6.56	961	42	3.18	1531	40
	Baffles	Outlet	6.62	841	51*	6.63	911	52*	6.88*	924	51*	5.57	1410	64*
	Rods	Outlet	6.72	882	47	6.59	952	43	6.86*	933	47	5.76	1505	74*

Hardness = mg.L^{-1} of $CaCO_3$; MED = Median week values for each treatment (tanks with baffles or vertical wooden rods); * = significant difference by *Mann-Whitney* test comparing the input and output data of the hardness, pH, and EC variables).

and third weeks, comparing the inlet and outlet of the baffles tank, as it can be seen in Table 2. Thus, the contribution of calcium and magnesium ions was not sufficient to increase the pH (basic cations) and EC. The same observations were reported by Galindo *et al.* (2016), using seashells as a filling medium for biological filters.

It can be seen from daily EC, pH, and hardness data that at the beginning (first day), there was an increase in the presence of ions, raising the pH and hardness, therefore indicating that some chemical elements (present in eggshells) may be available in the sewage. This fact would explain the negative P removal efficiencies provided at the beginning of each week of the experiment. Karczmarczyk and Renman (2011) and Torit and Phihusut (2019) cited that P retention in the support medium tends to decrease over time due to the saturation of the adsorption complex. Using oyster shells in filters, Magri *et al*. (2013) observed an increase in the presence of calcium carbonates and alkalinity in the medium, reinforcing the hypothesis of a possible material loss during the operation of the systems.

The removal of P increased and oscillated on the last day of monitoring. Then it cannot be said that there was a saturation of the exchange sites and precipitation capacity. Probably in the non-calcined eggshell, the last mechanism is more important in the P removal, forming calcium phosphate, which can be used in agriculture, a critical issue nowadays, given the size of available macronutrient reserves (PANTANO *et al*., 2016). In these five days of each week, the EC increased, although not resulting in a significant difference (compared to the median weeks), as well as hardness, reinforcing the calcium and magnesium contribution from the eggshell.

With the reduction in the pH in the fourth week, the orthophosphate removal efficiency of the systems increased (Figure 3). It can be seen in Table 2 that after the EC increase on the first day of the fourth week, there was a gradual reduction in conductivity values over the week. This occurred due to the increased pH value caused by the constant feeding with wastewater, which returned the pH conditions of the system close to neutrality. In the last week of monitoring, with the pH reduction, there was higher solubilization and availability of eggshell cations, resulting in significantly higher hardness at the outlet of the two systems, which had only been observed in the reactor with baffles.

It was observed in the fourth week fluctuations in the removal of P according to the pH variation. By analyzing Tables 1 and 2, it can be seen that the highest efficiencies were observed at pH between 3.00 and 5.00, corroborating Yin *et al*. (2011).

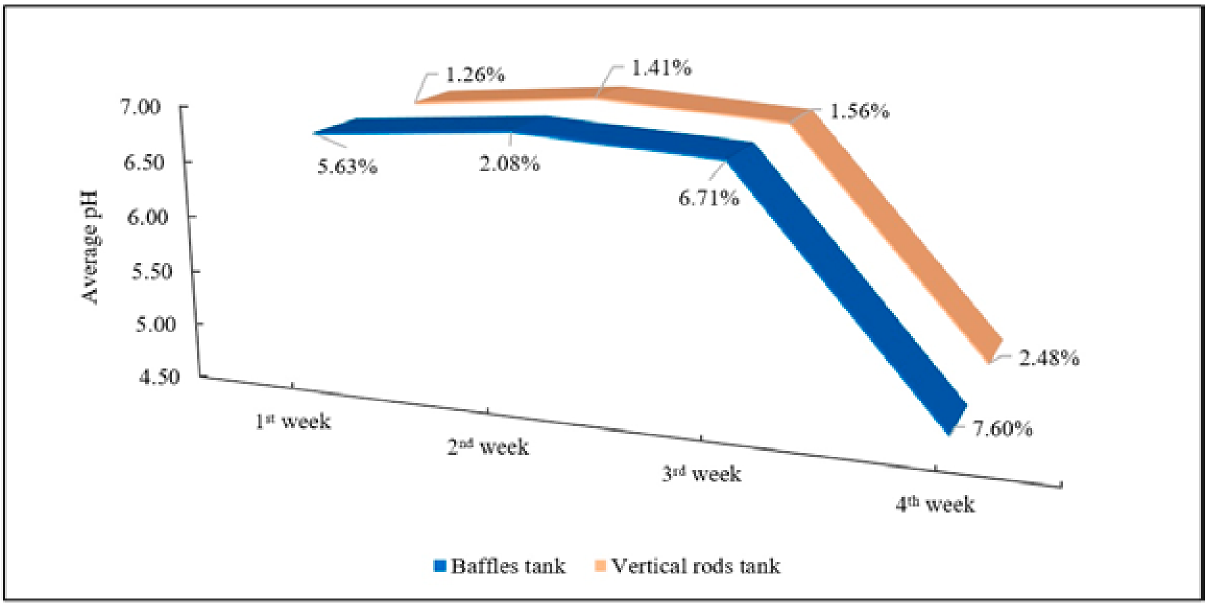

Figure 3. Influence of pH on the average orthophosphate removal efficiency (%) for the baffles tank and the vertical rods tank during the four weeks of testing

CONCLUSIONS

- The unit containing eggshells attached to baffles provide a better performance than vertical wooden rods tank, with maximum efficiency of 15.93% of phosphorus removal in pH 4.73 from the sanitary sewage;
- The maximum sorption capacity was 4.81 mg of P per gram of grinded hen eggshells in baffled tanks with pH 4.73;
- The efficiencies of each tank did not differ significantly over the weeks. However, there was a change in the efficiency of removing orthophosphates according to pH variation;
- Operating conditions did not allow the eggshells to influence the sewage characteristics (after passage through a submerged aerated biological filter), resulting in a significant increase in hardness only.

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