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Evaluation of the Use of Fly Ash as a Low Cost Technology for Phosphorus Removal in Wastewater Treatment

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ABSTRACT

"Pozzolan" is a slag from the burning of coal in power plants which has the potential to assist as a low-cost adsorbent for wastewater treatment. The excess of Phosphorus (P) in the environment can promote chemical pollution and harm ecosystems, especially water. It is therefore necessary to implement inexpensive techniques and processes for the efficient treatment of water and wastewater. In this context, this study evaluated the use of the pozzolanic fly ash material for P removal from wastewater for the development of low-cost treatment technologies for environmental restoration and remediation of water resources. The treatment systems were developed in batch configuration. The removal tests from a synthetic sample with a known concentration of P reached a maximum of 30% removal in concentration, even varying the pH and performing different treatments of the pozzolanic material. This low removal efficiency of Phosphorus led to a comparative test between different lots of pozzolan in order to verify if the results obtained were characteristic of the material itself or of the lot obtained. Also the P adsorption isotherms were constructed with the two lots achieving adsorption capacities from 0.87 mg g^{-1} to 74 mg g^{-1}. This difference indicates that the low P removal efficiency in the preliminary tests is due to the characteristics of the substrate of the first lot. Tests on a real effluent using the pozzolan from the second sample lot indicated a 99% efficiency of P removal, with an initial concentration of Phosphorus in the effluent of 5.5 mg L^{-1}.

Keywords: adsorption, effluents, pozzolan, tertiary treatment.

Avaliação do uso de cinzas volantes como tecnologia de baixo custo para remoção de fósforo no tratamento de águas residuárias

RESUMO

A Pozolana é uma escória da queima de carvão em usinas de energia termoelétrica que tem o potencial de servir como adsorvente de baixo custo para tratamento de águas residuárias. O excesso de fósforo (P) no ambiente pode promover a poluição química e prejudicar os ecossistemas por acelerar a eutrofização. Neste contexto, este estudo avaliou o uso do material de cinzas volantes (pozolanas) para remoção de P de águas residuárias visando o desenvolvimento de tecnologias de tratamento de baixo custo para restauração ambiental e remediação de recursos hídricos. Para tanto, os sistemas de tratamento foram desenvolvidos em configuração de batelada. Os testes de remoção de uma amostra sintética com concentração conhecida de P atingiram um máximo de 30%, mesmo variando o pH e realizando diferentes tratamentos do material pozolânico. Esta baixa eficiência de remoção de fósforo levou a um teste comparativo entre diferentes lotes de pozolana, a fim de verificar se os resultados obtidos eram característicos do material em si ou do lote utilizado. Isotermas de adsorção de P foram construídas com os dois lotes de pozolana alcançando capacidades de adsorção de 0,87 mg g^{-1} a 74 mg g^{-1}. Essa diferença indica que a eficiência de remoção de P baixa nos testes preliminares deve-se às características do substrato do primeiro lote. Os testes com um efluente real utilizando a pozolana do segundo lote indicaram uma eficiência de 99% da remoção de P, com uma concentração inicial de fósforo no efluente de 5,5 mg L^{-1}.

Palavras-chave: adsorção, cinzas volantes, efluentes, pozolana, tratamento terciário.

1. INTRODUCTION

The ceramic industry, the burning of coal by thermoelectric power plants and various other manufacturing processes generate inorganic residues and wastes that may be environmental liabilities (Hansen et al., 2015). Among these are pozzolans, which naturally originate from volcanic rocks rich in non-crystalline silica as a result of weathering processes. In Brazil, a widely used pozzolanic material is fly ash, derived mainly from the burning of coal in thermoelectric power plants (Yamamoto et al., 1997; Cunha et al., 2011). Thus, fly ash is a residue predicted to increase significantly in the coming years. Only a small percentage of fly ash is used in concrete production, road base construction, soil amendment and zeolite synthesis; the large majority is still discharged into ash ponds, lagoons or landfills (Imbabi et al., 2012). In recent years, other possible applications to pozzolans have been proposed, including wastewater treatment (Hermassi et al., 2017).

In terms of chemical composition, fly ash consists of more than 70% silicon, aluminum and iron oxides (SiO_2 + Al_2O_3 + Fe_2O_3). Natural pozzolans consist of materials rich in silica and alumina and artificial pozzolans consist of baked clay between 600°C and 900°C. Pozzolans are inert but can react with certain chemical species in the presence of water, producing a binder material. The reactivity of the pozzolan material, known as the pozzolanic activity, can be measured using pozzolanicity activity: a chemical process that measures the reaction rate of pozzolan with Ca^{2+} ions in the presence of water. This reaction rate is dependent on intrinsic characteristics of the pozzolan, such as specific surface area, chemical composition and active phase content (Zeng et al., 2012).

Many studies have shown that pozzolanic material can act as an adsorption substrate for phosphate, heavy metals and organic pollutants, indicating a potential application as a low cost adsorbent for wastewater treatment (Ahmaruzzaman, 2010; Blissett and Rowson, 2012; Yao et al., 2015). Hermassi et al. (2017) provided an understanding of Phosphorus removal by fly ash and described that the adsorption kinetics occurs as a diffusion-based process of phosphate ions on fly ash particles. Besides that, agronomical assay of recovering phosphate release confirmed the possibility of using this material as fertilizer, even in calcareous soils. Kandel et al. (2017) used a mixture of 5% (in weight) of fly ash with sand in Bioretention cells (BRCs) filter media and verified that the BRCs containing fly ash showed significant phosphorus concentration and mass reduction in the BRCs effluent, about 85% removal of P due to adsorption.

The chemical element Phosphorus (P) is an essential nutrient that controls plant growth. In water bodies, when present in excess, it enhances the growing of aquatic micro- and macrophytes and may lead to deoxygenation of the water column, a process known as eutrophication. Phosphate ions (PO_4^{3-}) are discharged into the aquatic environment by rock leaching, in agricultural, domestic and industrial effluent discharge or run-off (Conley et al., 2009; Shortle and Horan, 2017). Considered an environmental pollutant of major concern, Phosphorus removal or significant reduction from effluents is of crucial importance for watershed protection. Thus, various nutrient removal technologies, based on physical, chemical and biological methods, have been implemented in water treatment systems (Oleszkiewicz and Barnard, 2006; Wilfert et al., 2015). Among them, adsorption is one of the most-used techniques due to its economic viability and ease of implementation. The application of low-cost and commercially available materials as substrates for adsorption has been widely investigated in recent years (Lu et al., 2009; Loganathan et al., 2014). The main advantage of pozzolan substrates compared to synthetic materials for adsorption is its abundance and low cost since they often have no commercial value.

The physical adsorption of P occurs due to the Van der Waals' forces, or potential difference of the attraction forces, resulting in physical binding of the molecules to the adsorbent through a weak interaction. In a chemical adsorption, there is a rearrangement between the electrons of the molecules and the solid, and consequently a change in the shape of the orbitals; it is a strong interaction and virtually irreversible (Loganathan et al., 2014; Ramasahayam et al., 2014; Huang et al., 2017).

Considering the increase in fly ash generation due to growth in coal combustion for energy supply and the possibility of reusing this material as a nutrient in soils, this study investigated the application of fly ash pozzolans for the removal of Phosphorus from synthetic solutions and domestic wastewater samples (treated at secondary or tertiary levels) and evaluated the potential of the material for wastewater polishing as a low-cost alternative with the likelihood of reusing the residue generated after adsorption for agricultural purposes, offering a more sustainable approach for the tertiary wastewater treatment process.

2. MATERIALS AND METHODS

2.1. Reagents and equipment

All reagents used were of analytical grade or better. Potassium phosphate monobasic powder (KH_2PO_4) was purchased from Proquimios Comércio e Indústria Ltda (Brazil), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) from Sigma-Aldrich (USA), ascorbic acid ($C_6H_8O_6$) from Synth (Brazil), antimony potassium tartrate solution ($K(SbO)C_4H_4O_6$) and sodium hydroxide (NaOH) from Vetec (Brazil) and ammonium molybdate solution ($(NH4)_6Mo_7O_{24}$) and glacial acetic acid ($C_3H_4O_2$) from Êxodo Científica (Brazil).

The total Phosphorus determinations were made using a UV-Vis spectrophotometer (Nova®, Model UV-1800), using glass cuvettes with a 10 mm light path; pH and turbidity of the synthetics samples were measured using a pH Meter (Nova Instruments®, Model NI PHM) and a turbidimeter (PoliControl®, Model AP2000 iR).

The samples were stirred on an orbital shaker (Solab Científica®, Model SL-180 / DT) and under centrifugation (Solab Científica®, Model SL-700) prior to spectrophotometric determination. Calcination and digestion to characterize the pozzolanic material were carried out, respectively, in a muffle (Magnu's Oven Industry and Trade Ltda®) and digester block (Marconi®, Model MA4004).

The pH, turbidity and electrical conductivity measurements of natural effluent were carried out with a multiparameter probe (Hanna®, Model HI 9829) and the color measurement by colorimeter (Policontrol®, Mmodel AquaColor Color IP67), whilst Chemical Oxygen Demand (COD) was determined by the Standard 5220 D method (APHA et al., 2012b) using a digester block (Marconi®, Model MA-4004).

2.2. Substrate characterization

The pozzolanic material was donated by the Votorantim Company at Cubatão – SP (Brazil). According to the Chemical Products Safety Data Sheet provided by Votorantim Cimentos (2009), this pozzolan is acquired from calcined clay in a temperatures range of 700°C to 1000°C. Two lots of samples of the pozzolanic material were used in the present work, which were given away in different periods (first sample in September 2014 and the second in March 2015).

The major chemical composition of the fly ash samples (concentrations of Al, Ca, Fe, Mg, and Si) was measured after a sodium peroxide fusion by inductively-coupled plasma-optical-emission spectrometry (ICP-OES; Varian, Model S700) (Ahmaruzzaman, 2010). The organic matter content of each pozzolan sample was gravimetrically determined by the calcination method performed in a muffle at 600°C for 20 minutes, using 1.0 g of the dry substrate in an oven for 2 hours at 105°C and comparing with the mass after calcination.

2.3. Phosphorus Spectrophotometric determination

The methodology for the quantification of total Phosphorus was based on Standard Methods for the Examination of Water and Wastewater – (4500-P E) Phosphorus – Ascorbic Acid Method. The orthophosphate anion (derived from the aqueous solution of potassium phosphate diacid - KH_2PO_4) reacts with antimony and potassium tartrate, ammonium molybdate and ascorbic acid forming a blue complex of molybdenum. The color intensity is proportional to the orthophosphate concentration and can be quantified by UV-Vis spectrophotometry at a wavelength of 880 nm (APHA et al., 2012a).

2.4. Calibration curve

The method for constructing a calibration curve was adapted from APHA et al. (2012a). To create the calibration curve of the Phosphorus standard solution, Absorbance *vs.* Concentration graph was made using ortophosphate concentrations of 0.00, 0.05, 0.10, 0.20, 0.35, 0.50 mg L^{-1} and the absorbance values obtained in the spectrophotometer were subtracted from the absorbance value of the blank.

2.5. Phosphorus removal test with solutions

The procedure of P removal tests followed the following sequence (Figure 1).

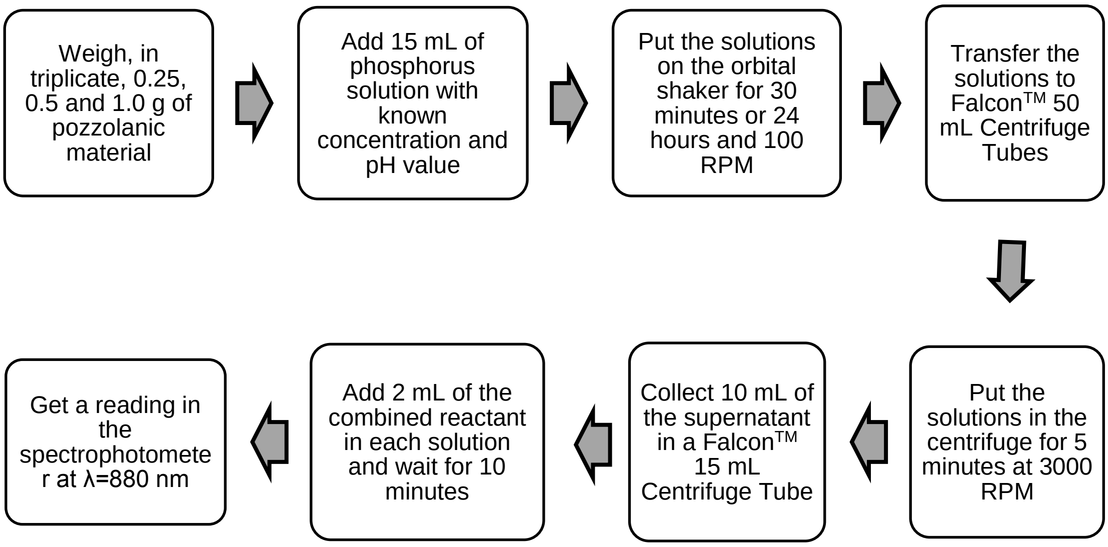

Figure 1. Flowchart of the Phosphorus removal test.

The test was performed in triplicate with an orthophosphate standard (2.5 mg L^{-1}) and a solution of lower concentration (0.5 mg L^{-1}), both at four pH values: natural, 6, 7 and 8 adjusted with 0.5% NaOH solution (w/v). The Phosphorus concentrations in the samples with pozzolanic material were compared with a control sample (P solution without pozzolan). The stirring time was fixed at 30 minutes.

2.6. Phosphorus removal test with pozzolan treated with different processes

Tests were performed using pozzolan treated by various processes to check for enhancement on Phosphorus adsorption on the material's surface. The first lot of pozzolan was evaluated in different forms: i) natural (raw); ii) washed with water; iii) calcined; iv) washed with NaOH; v) washed with CH_3COOH and vi) washed with HCl.

The natural pozzolan material was dried in an oven at 100°C for 24 hours. The pozzolan washed in water was prepared by adding 10 g of the material to 1.0 L of deionized water, kept under magnetic stirring for 24 hours. The calcination was carried out by placing a quantity of the material in the muffle at 600°C for 20 minutes in order to eliminate any organic matter and volatile compounds present on its surface. To wash the material in NaOH solution, 10 g of material was kept under stirring in a NaOH solution (0.15 mol L^{-1}) for 24 hours. The acid washes were similar to NaOH, however, for CH_3COOH 6 mL was added to in 1.0 L of deionized water to obtain a concentration of 0.1 mol L^{-1} and, for the HCl, 60 mL was added to 1.0 L of deionized water to obtain a concentration of 0.72 mol L^{-1}.

With the processed materials, a P removal test was performed as described in Figure 1 using a 0.5 mg L^{-1} Phosphorus solution with a natural pH (around pH=7) and 0.5 g of mass of each treated substrate. The tests were performed for 24 hours.

2.7. Phosphorus removal tests using different samples of pozzolan

The low removal efficiency of orthophosphate achieved with the first lot of pozzolan prompted a comparative test between different samples of the material. The process occurred as shown in the flowchart of Figure 1: 0.5 g of each pozzolan was used and 15 mL of the P solutions at concentration of 0.10, 0.25, 0.50, 1.00, 2.50 and 5.00 mg L^{-1}. The stirring time was 24 hours.

From the initial (C_i, in mg L^{-1}) and final (C_e, in mg L^{-1}) concentrations, volume of Phosphorus solutions (V, in L) and mass of pozzolan used (M, in g), it was possible to obtain the adsorption capacity (Q_e, in mg g^{-1}) by Equation 1:

$$Qe = \frac{(C_i - C_e) \times V}{1000 \times M} \tag{1}$$

2.8. Adsorption isotherms

Isotherms were created with the two samples of pozzolan to verify the maximum adsorption capacity of each material and to perform a comparative analysis between them in terms of chemical and physical structure.

The adsorption isotherms were performed with a procedure analogous to that shown in the flowchart of Figure 1: six tests were done with the following P concentrations (according to adsorption capacity of each one): 0.1; 0.25; 0.5; 1.0; 2.5 and 5.0 mg L^{-1} for the material of the first lot and 5.0; 10.0; 20.0; 50.0; 80.0 and 100.0 mg L^{-1} for the second sample of pozzolan. In each assay 0.5 g of the pozzolanic material was weighed and the system was stirred for 24 hours. After reading the samples in the spectrophotometer, the adsorption capacity was calculated for the construction of the isotherms according to the Langmuir (Equation 2) and Freundlich (Equation 3) Models.

$$Q_e = \frac{Q_m \times K_L \times C_e}{1 + K_L \times C_e} \tag{2}$$

$$Q_e = K_F . C_e^{1/n} \quad (3)$$

Where:

Q_e = Adsorption capacity (mg g^{-1});
Q_m = Maximum adsorption capacity (mg g^{-1});
C_e = Final concentration of adsorbate (mg L^{-1});
K_L = Langmuir constant (L mg^{-1});
K_F = Freundlich constant (mg g^{-1});
n = Constant related to the adsorption intensity.

2.9. Phosphorus removal test with wastewater effluents

Phosphorus removal tests were conducted with sanitary effluents treated at tertiary level by an MBR system (Membrane Bio Reactor) located at the International Reference Center for Water Reuse (CIRRA) at the University of São Paulo (USP, Brazil) (Subtil et al., 2013). To characterize this effluent, pH, turbidity, color, electrical conductivity, chemical oxygen demand (COD) and the concentration of P were evaluated.

The Phosphorus removal test with wastewater effluent was made considering the scenario in which the higher removal percentages were obtained in the tests with the synthetic phosphorus samples. Thus, the experiment was carried out with the pozzolan from the second lot, in triplicate, stirred for 30 minutes at a 100 RPM.

The amount of pozzolan used was defined by considering the ratio of the higher Phosphorus adsorption capacity for the P content of the raw effluent. The ratio substrate/solution was 1 g L^{-1}.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the pozzolans

The content of main chemical components and of organic matter (in weight) of both pozzolan samples are shown in Table 1.

Table 1. Organic matter and main chemical composition (w/w) of the two samples of the pozzolan.

Sample	Organic matter (%)	Al (%)	Ca (%)	Fe (%)	Mg (%)	Si (%)
Pozzolan first lot	<1	<1	1.9	<1	<1	93.1
Pozzolan second lot	18.3	<1	1.2	<1	<1	80.0

The silicon originated from clays (kaolinite, montmorillonite, illite), oxides (quartz) and other silicates (chlorite) and at room temperature is a solid. The high silicon content in the sample is consistent with the information given by Votorantim, which provides a range from 20 to 95% of SiO_2 in the composition of the pozzolan.

Fisher et al. (1978), Kutchko and Kim (2006) and Piispanen et al. (2009) performed scanning electron microscopy on fly ashes from different conditions and verified the forms that the material particle can acquire. Spherical particles make up most of fly ash which are vitreous and transparent indicating the complete melting of the silicate minerals. These spheres may be hollow (cenosphere), solid or filled with other smaller spheres, amorphous particles or crystals (plerospheres).

The coloring of the pozzolan may vary from brown, gray or black (depending on the amount of unburnt carbon present). When silicone or aluminum materials are thermally synthesized jointly with water and calcium hydroxide, they form a white-colored complex (Yamamoto et al., 1997; Ahmaruzzaman, 2010). The surface area of the pozzolan particles depends on their shape. Solid particles can have a surface area of approximately 3.0 $m^2\ g^{-1}$ (Van Jaarsveld et al., 2002; Guo et al., 2010) and pleosphere have a very large surface area due to their filling by other spheres or crystals and can reach almost 200 $m^2\ g^{-1}$ (Mall et al., 2005; Srivastava et al., 2006; Ahmaruzzaman, 2010).

3.2. Calibration curve

After obtaining each standard absorbance values, it was possible to plot a graph of absorbance vs. phosphorus concentration. The linear equation obtained by the graph was: Abs = 0.7208conc + 0.001, with R^2 = 0.9999.

3.3. Phosphorus removal using pozzolan treated by different processing strategies

These essays were realized with the pozzolanic material from the first lot. Phosphorus concentration of 2.5 mg L^{-1} showed less than 6% removal in P concentration, even varying the pH (natural, 6, 7 and 8) and amount of pozzolan (0.25 to 1.0 g) (Table 2, entries 1 to 12). Pozzolanic material has a certain ability to remove Phosphorus under conditions in which there are higher substrate amounts (0.5 to 1.0 g) and lower concentration of solution (0.5 mg L^{-1}), with a maximum removal of about 35% (Table 2, entries 17 to 24). Studies indicate that the fly ash can provide 99% P removal capacity when operated within optimal conditions (Ugurlu & Salman, 1998; Wang, 2012; Huang et al., 2017).

The test with the pozzolan treated by different processes showed that beneficiation by washing in water is the most effective of the six procedures performed (Table 2). However, Ahmaruzzaman (2010) and Wang (2012) state that acid-modified fly ash is very effective in the removal of Phosphorus in contaminated wastewater.

Table 2. Phosphorus removal efficiency at variation of substrate amounts, Phosphorus concentration and pH.

Entry	Amount of pozzolan (g)	Phosphorus concentration (mg L^{-1})	pH	P removal (%)
1	0.25	2.5	Natural	2.33
2	0.25	2.5	6	6.05
3	0.25	2.5	7	1.58
4	0.25	2.5	8	4.27
5	0.50	2.5	Natural	3.03
6	0.50	2.5	6	2.03
7	0.50	2.5	7	0.82
8	0.50	2.5	8	0.86
9	1.00	2.5	Natural	3.59
10	1.00	2.5	6	2.41
11	1.00	2.5	7	1.63
12	1.00	2.5	8	3.76
13	0.25	0.5	Natural	4.28
14	0.25	0.5	6	3.57
15	0.25	0.5	7	2.89
16	0.25	0.5	8	0.11
17	0.50	0.5	Natural	24.54
18	0.50	0.5	6	21.93
19	0.50	0.5	7	19.60
20	0.50	0.5	8	20.36
21	1.00	0.5	Natural	35.44
22	1.00	0.5	6	32.68
23	1.00	0.5	7	18.84
24	1.00	0.5	8	23.56

3.4. Comparative test using different samples of pozzolan

The Figure 2 shows the P removal by the two samples of pozzolan. Note that the material from the first lot reached a maximum removal of 12% in concentration. On the other hand, the material from the second sample, even without any processing of the pozzolan, exceeded 90% removal for the same Phosphorus concentrations from the synthetic solution. This indicates that, although it is the same material, the samples have physical-chemical differences that may influence the adsorption process.

Knowing that organic matter, calcium, magnesium and aluminum elements are mainly responsible for adsorbing Phosphorus on the substrate surface (Ahmaruzzaman, 2010; Blisset and Rowson, 2012; Yao et al., 2015), it is noted that the 93% of the silicon content in the sample (Table 1) indicates that the remaining reduced 7% were composed of some elements capable of adsorbing Phosphorus, as well as the presence of greater amount of residual organic matter in the sample from Lot 2, justifying the reduced potential for adsorption of the pozzolan of the first sample. This fact indicates that there is a wide variety of organic groups, such as carboxylic acids, phenols and amines which can retain Phosphorus by complexation, ion exchange and microprecipitation with the surface of the adsorbent (Ahmaruzzaman, 2010).

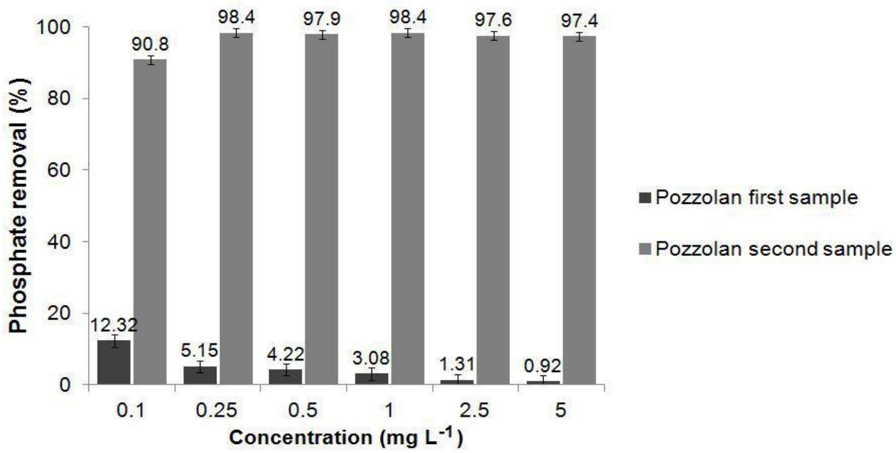

Figure 2. Phosphorus removal using different samples of pozzolan and varying the concentrations of the synthetic sample solution.

3.5. Adsorption isotherms

From Equation 1, the adsorption capacity obtained for the pozzolan first sample was 0.87 mg g^{-1}, and for the second sample was 74 mg g^{-1}. The difference in the adsorption capacities between both samples indicates that the low Phosphorus removal in the preliminary tests is due to the characteristics of the substrate. The features of the pozzolans are related to the type of material from which the ashes were derived, possibly with different percentages of silica, alumina, calcium, iron oxide, magnesium oxide and carbon in its composition, being the oxides of calcium, aluminum and iron responsible for adsorbing Phosphorus on the substrate surface (Ahmaruzzaman, 2010). Those elements, depending on the amount present in the composition of the pozzolan, may increase or reduce its P adsorption capacity.

By comparing the values between R^2 curves of the isotherm of the Langmuir and Freundlich's models (Figure 3) for the two samples of substrate, it is noted that the regression of the Langmuir's model presented a higher correlation among the data. Thus, it can be supposed that both sample materials are governed by the Langmuir's model, i.e., they present adsorption behavior as a monolayer in which the surface of the adsorbent has a fixed number of active sites and each site is equivalent in energy, with no interaction between the adsorbent species (Cunha et al., 2011; Loganathan et al., 2014).

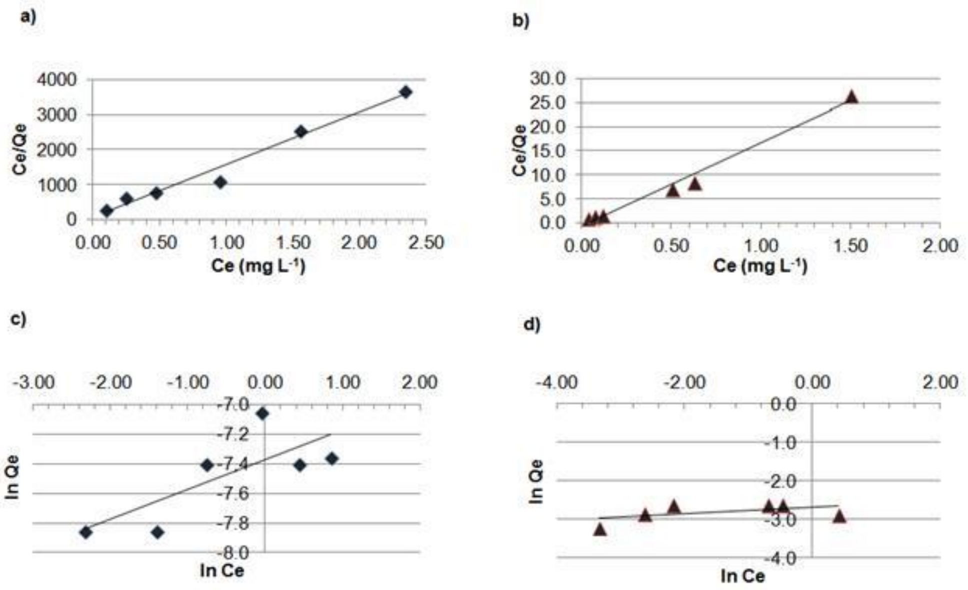

Figure 3. Isotherms linearized models for both pozzolan samples: (a) Langmuir's model for pozzolan first sample. (b) Langmuir's model for pozzolan second sample. (c) Freundlich's model for pozzolan first sample. (d) Freundlich's model for pozzolan second sample.

The substrates present in their chemical structures a wide variety of organic groups, such as carboxylic acids, phenols and amines which can retain adsorbates by complexation, ion exchange and microprecipitation with the surface of the adsorbent. Considering the adsorption mechanism, substrates with more organic active sites can retain the orthophosphate by hydrophobic interaction and Van der Waals forces (Dabrowski, 2001). The main advantage of many of these substrates compared to the synthetic materials is its abundance and low cost since they often have no commercial value, as well as that this material can also be an environmental liability not easily reusable. Other substrates have been tested for P removal by adsorption, also achieving satisfactory results for orthophosphate adsorption capacity (mg g^{-1}), such as: aluminum and its oxides (5 mg g^{-1}), iron and its oxides (70.9 mg g^{-1}), mussel shell (6.9 mg g^{-1}), ceramic biomaterials (13.6 mg g^{-1}) and red mud (113.9 mg g^{-1}) (Karageorgiu et al., 2007; Chen et al., 2013; Guaya et al., 2015).

3.6. Phosphorus removal test from sanitary effluent

The characterization of the sanitary effluent treated at tertiary level is shown in Table 3.

The test carried out in triplicate showed that the pozzolan of the second lot showed a high mean percentage of P removal, higher than 99%, with the sanitary effluent, indicating that the removal effectiveness when the matrix sample is complex and the competitiveness among active sites of the adsorption material could significantly decrease removal efficiency.

Table 3. Characterization of the sanitary effluent treated at tertiary level.

Parameter	Sanitary Effluent
pH	7.6
Turbity (NTU)	9.8
Color (uC)	65.9
Electrical conductivity (µS cm^{-1})	1320
COD (mg L^{-1})	40.3
Orthophosphate (mg L^{-1})	5.5

3.7. Advantages of the use of pozzolan in the adsorption process

The conventional techniques available today for Phosphorus removal are chemical precipitation, biological activated sludge and ion exchange resins. These techniques achieve satisfactory results for P removal; however, they are expensive and difficult to implement. Thus, adsorption can be considered a more useful and economic technique, which can also allow the regeneration of the adsorbents or their later use in the chain, for example, in civil works (Ahmaruzzaman, 2010; Huang et al., 2017).

The waste generated by the production of the ceramic industry, the burning of mineral coal by thermoelectric plants, rock crushing to make concrete or the operation of several other industries constitute an important environmental liability and a serious difficulty faced by the industries that generate this waste. These residues may exhibit some natural pozzolanic activity or may become pozzolanic after suitable heat treatment (Cunha et al., 2011; Wang, 2012).

Pozzolan also contains several essential elements, including macronutrients (P, K, Ca, Mg), micronutrients (Fe, Mn and B) and some beneficial elements (Si, Na) for plant growth (Yamamoto et al., 1997; Ahmaruzzaman, 2010). Thus, after the P removal process, it is possible that the adsorbent could be applied in agriculture or in composting processes, which is a sustainable alternative when considering nutrient cycling.

Moreover, due to its cementitious properties, pozzolanic material is widely used as an additive for cement production (Shi and Day, 2001; Bondar et al., 2011). This use can still be contemplated after the use of the material as adsorbent in the P removal process, because its resistive properties are not lost (Shehata et al.,1999; Hemalatha and Ramaswamy, 2017).

4. CONCLUSION

Difficulties in raising the adsorption potential of the first sample of pozzolan and its subsequent characterization showed that pozzolanic material presents a huge heterogeneity, not only related to the origin of the production process, but also related to the period of collection of the study material (about six months had passed between the acquisition of the first and the second samples of pozzolan, supplied by the same company).

Comparative tests and the material characterization of both pozzolan samples showed high silicon content (93%) in the first sample, which justifies the maximum efficiency of only 30% in removal tests of Phosphorus synthetic samples, even with the processing of the material. The construction of adsorption isotherms indicated that both pozzolans are governed by the Langmuir's model (monolayer) and also showed that the maximum adsorption capacity of the pozzolan from the second sample is 85 times higher than the material of the first sample.

The batch tests showed that the pozzolan from the second sample has high efficiency even with higher concentrations of phosphorus solutions. Furthermore, that substrate showed a 99% efficiency of P removal from the sanitary effluent from MBR treatment system whose initial P concentration was 5.5 mg L^{-1}.

Although the P removal is efficient in a batch system, its application in large-scale systems becomes limiting because of the variability of the pozzolanic material. Thus, it would be necessary to perform a characterization of the substrate from each sample to be used in the process in order to verify the percentage of silica that makes up the material.

Among numbers of removing techniques, adsorption considered economical, because it allows the regeneration of the adsorbents and an application of low-cost materials in the treatment of effluents. Pozzolanic material is a waste generated by the outputs of several industries, representing an important environmental liability. It can be therefore uses as low-cost adsorbent in the phosphorous removal process for wastewater treatment.

After the adsorption process, the pozzolan adsorbent can be applied in agriculture or in composting processes because this material also contains several essential elements for plant growth. On the other hand, the cementitious properties of pozzolan are not lost after the Phosphorous removal process, so that it can still be disposed as an additive for cement production and civil works.

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