Phosphorus recovery from wastewater using TechPhos® and its potential application as fertilizer

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Phosphorus (P) is an important nutrient and many essential biomolecule have this element in their composition (Wilfert et al., 2015; Wilson, 2017). The P cycle is regulated by geology. The main sources of P, *i.e.* phosphate rocks, are mainly explored for fertilizer production. However, P demands for food production in agriculture are raising due to population growth. In this scenario, the depletion of P mineral sources threatens human subsistence (Cordell et al., 2009). Some studies claim that the current sources of P will be depleted in 50 to 100 years (Cordell et al., 2009; Melia et al., 2017). Therefore, recovering P from sustainable and abundant sources such as domestic wastewater is an approach to overcoming the food scarcity scenario. Research in this field has gained considerable attention from the global scientific community in the last decade (Cieślik & Konieczka, 2017; Pantano et al., 2016; Y. Wang et al., 2015).

In this context, this works proposes the use of a modified clay, TechPhos®, for removing and recovering P from real domestic wastewater by adsorption/desorption cycles. Additionally, this study aimed to evaluate potential applications of P-enriched sewage sludge as an alternative fertilizer and to investigate adsorption/desorption mechanisms of P on TechPhos® sites.

Several batch adsorption tests were carried out to investigate the behavior of TechPhos® in synthetic P solutions and real domestic wastewater. P in the samples was quantified using the ascorbic acid method (4500-P E method – American Public Health Association (APHA, 2001)). A synthetic aqueous solution of P was used to obtain TechPhos® adsorption isotherms. The experimental data obtained at 25 °C was analyzed using four common isotherm models: Langmuir, Freundlich, Dubinin-Radushkevich, and Tempkin linearized models (Al-Ghouti & Da'ana, 2020; Gupta et al., 2020; J. Wang & Guo, 2020a). As a result, the determination coefficients (R^2) obtained were 0.9895, 0.8706, 0.6918, and 0.8817, respectively, for Langmuir, Freundlich, Dubinin-Radushkevich, and Tempkin models. Based on these coefficients, the experimental data were better explained by the Langmuir model and a maximum P adsorption capacity of 32.08 mg g^{-1} was estimated at pH 7. Kinetic monitoring of the process at an initial concentration of 5 mg P L^{-1} demonstrated that the system reached the equilibrium stage in approximately 30 min. Equilibrium constants for pseudo-first order, pseudo-second order (PSO), and Elovich models indicated a better correlation for PSO model ($R^2 = 0.997$).

The better correlation for PSO model and Langmuir isotherm model might be explained by P and TechPhos® properties. The PSO model best represents adsorption in which two sites are occupied per each molecule of the adsorbate (J. Wang & Guo, 2020b). The P molecules contained in the aqueous solutions used in the tests at pH 7 are mainly in the form of dihydrogen orthophosphate ($H_2PO_4^-$) and monohydrogen orthophosphate (HPO_4^{2-}) (Wu et al., 2020). Some studies propose P-O-Fe bond formation on iron-based adsorbents (Wilfert et al., 2015; Wu et al., 2020) as TechPhos®. However, ions with two charges, such as HPO_4^{2-}, can form two oxygen-iron bonds per each HPO_4^{2-} molecule adsorbed (Wu et al., 2020), which explains the better correlation of the PSO model. As the process of P removal is regulated by the formation of a chemical bond O-Fe, this also corroborates with the Langmuir model best fit, because this model assumes monolayer formation mediated by chemisorption (J. Wang & Guo, 2020a). Multilayer adsorption might also occur by hydrogen bonding interaction of phosphate ions. Thus, obtained linear correlation coeficients are congruent with expectations and previous studies of P adsorption.

Studies in real wastewater effluent were conducted in a Wastewater Treatment Plant (WWTP) located in the city of São Carlos, SP, Brazil. A dosage of 0.22 g L^{-1} of TechPhos® was applied in an effluent containing 3.7 mg P L^{-1}. The adsorbent was kept in contact with the effluent for 1 h at 25 °C, 1.02 MPa, and pH 7. As a result, an adsorption capacity (q) of 10.8 mg g^{-1} and a P removal efficiency of 65.4 % were obtained. Using a synthetic aqueous P solution, an adsorption capacity of 8.47 mg g^{-1} was obtained, which is lower than the value of 10.8 mg g^{-1} found when the adsorbent was applied in the real wastewater effluent. It must be considered that the real effluent contains fine suspended sludge particles, which also contain P. TechPhos® attracts these particles promoting a flocculation phenomenon that enhances the P removal process, increasing its retention capacity. In addition, the flocculation promoted byTechPhos® also decreases the turbidity of the effluent.

After adsorption treatment on WTP effluent, 0.37 g of sewage sludge (dry basis) was produced per liter of treated wastewater with TechPhos®. Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD); Scanning

Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS) were performed on TechPhos®; TechPhos®satured with P, named as TP; sewage sludge containing TechPhos® after P adsorption, named as ST; sludge generated from conventional effluent treatment from WTP, names as SC.

FTIR results indicated the presence of organic groups at SC and ST spectra, which were absent in TechPhos® and TP spectra. All groups presented some sharp -OH stretching peaks from inorganic -OH, as well as silica peaks in 794 cm^{-1} (Si-O-Si). The presence of montmorillonite (M) and quartz (Q) was confirmed by XRD in all samples containing TechPhos®, with signals at $2\theta = 19.8°$ (M), 26.7° (Q), 35.0° (M), and 62.0° (M). These results are in accordance with previous literature (Barrientos-Velazquez et al., 2022; Cuevas et al., 2022; Yu et al., 2022). Morphology obtained by SEM exhibited smooth surfaces, with pores covering samples. EDS, performed alongside SEM, indicated the presence, in ascending order, of calcium, magnesium, chlorine, iron, aluminum, silicon, oxygen, and carbon. From XRD, a crystalline pattern was found for TechPhos® and TP, respectively, and a more amorphous profile was found for SC and ST due to the presence of organic matter in the samples.

The phytotoxicity of SC and ST was evaluated by germination index essays. The germination index (GI), the radicle elongation (RE), and the hypocotyl elongation (HE) were determined on seeds of *Lactuca sativa* (Brasil, 2009; Meier et al., 2020). Results were presented as mean and standard deviation from five replicates. Each replicate represented a group composed of a Petri dish with 20 seeds of *L. sativa*. GI, RE, and HE were expressed in percentage, in which a negative percentage indicates a decrease in the parameter compared to the negative control (NC). Similarly, a positive percentage represents an increase in the parameter when compared to the NC (Bagur-González et al., 2011). In general, all parameters of ST were positive, or, when negative, ranged between 0 and -25 %, which can be considered low toxicity. ST presented less toxicity than SC. The release of nutrient P in the ST group, present in greater quantity due to the existence of TechPhos®, minimized the possible deleterious effects caused by toxic organic compounds present in the sewage sludge. Thus, ST did not affect the seeds in the same proportion observed in the SC group.

To predict the P release potential in real applications of ST or SC in the soil, desorption tests were carried out according to Hedley method (Hou et al., 2018; Y. Wang et al., 2015). In this method, the P reversibly bounded to calcium, aluminum, and iron is extracted from the samples by hydroxide ions. As a result, SC and ST samples desorbed respectively 1.74 ± 0.06 mg P g^{-1} and 2.05 ± 0.08 mg g^{-1} in NaOH extraction.

Therefore, results found in this work revealed that TechPhos® is a suitable material for sustainable P recovery due to its properties on adsorption/desorption of P from domestic wastewater, with a maximum P adsorption capacity of 32 mg g^{-1}, as well as flocculation properties that enhance the overall quality of the treated effluent.Multiple P adsorption mechanisms occurring in TechPhos® resulted in an efficient P removal and recovery from the domestic effluent studied in this work. In addition, the incorporation of enriched P TechPhos® into the recovered sludge decreased its toxicity, allowing its subsequent use as an alternative fertilizer. Overall, the material might be a sustainable recovery method adding value to sewage sludge and decreasing mining extraction dependency on P obtention for fertilizer production.

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