Application of TechPhos® in wastewater treatment for phosphorus removal: a study on toxicity and potential phosphorus release from generated sewage sludge

Alessandro Lamarca Urzedo[1], Gabriela Tuono Martins Xavier[1], Renan da Silva Nunes[1], Luana dos Santos Andrade[1], Pedro Sérgio Fadini[2], Wagner Alves Carvalho[1]

[1]Center for Natural and Human Sciences (CCNH), Federal University of ABC (UFABC), Santo André, SP, 09210-580, Brazil;
[2]Chemistry Department (DQ), Federal University of São Carlos (UFSCar), São Carlos, SP, 13565-905, Brazil.
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Presenting author email: a.lamarca@ufabc.edu.br

Introduction

Phosphorus (P) is a vital nutrient, crucially found in numerous essential biomolecules (Wilfert et al., 2015). Governed by geology, phosphate rocks play an important role in the P cycle and they are the primary source of P. Fertilizer production is phosphate rock dependent. However, increasing demands for food production, driven by population growth, coupled with the depletion of phosphorus mineral reserves, pose a risk to food production and threaten global food security (Cordell et al., 2009). Projections suggest that P sources might be depleted within 50 to 100 years (Cordell et al., 2009). Hence, attention has shifted to extracting P from sustainable and abundant sources like domestic wastewater (Wilfert et al., 2015), offering a potential solution to alleviate food scarcity.

This study utilized a modified clay (TechPhos®) to adsorb P from wastewater while exploring potential applications of P-enriched sewage sludge as fertilizer and delving into the mechanisms of P adsorption-desorption on TechPhos® sites.

Materials & Methods

P quantification employed the ascorbic acid method (APHA, 2001). Adsorption kinetics and isotherm studies were performed to investigate equilibrium time and adsorption behavior by correlation with several mathematical models. Kinetics and isotherm studies were conducted at 25 °C and pH 7.

P removal was tested in real effluent from two different wastewater treatment plants (WWTP) under the following conditions: 25 °C, 1.02 MPa, and wastewater pH value was 7.0. The first WWTP was located in São Carlos municipality, in São Paulo state, Brazil, and initial concentration of P was 3.7 mg P L^{-1} and TechPhos® was applied at a concentration of 0.2 g L^{-1}. The second WWTP was located at Itatiba city in São Paulo state, Brazil, with initial P concentration 4.6 mg P L^{-1}, and TechPhos® was applied at a concentration of 4 g L^{-1}.

TechPhos® that had no contact with P solution will be referred to as TB; TechPhos® after aqueous P solution contact will be referred to as TP; sludge generated from TB treatment at São Carlos' WWTP and Itatiba's WWTP will be referred to as ST1 and ST2, respectively, while control sludge from conventional treatments at São Carlos' WWTP and Itatiba's WWTP will be referred to as SC1 and SC2 respectively. Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD); and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS) were used to characterize TB; TP; ST1; ST2; SC1, and SC2. X-Ray Photoelectron Spectroscopy (XPS) was used to characterize TB and TP.

For potential applications as biofertilizer it was used phytotoxicity assays and the Olsen extractor method for P release. Phytotoxicity of SC and ST was evaluated with determination of germination index (GI); radicle elongation (RE) and hypocotyl elongation (HE) on seeds of *Lactuca sativa* (Brasil, 2009) after 5 days germination. P release potential in real applications of ST1, SC1, ST2, and SC2 in the soil, desorption tests were carried out using the Olsen extractor ($NaHCO_3$ 0.5 mol L^{-1} at pH 8.5) (Li et al., 2016).

Results & Discussion

Adsorption kinetics studies revealed similar correlations coefficients (R^2), with $R^2 > 0.96$ for Pseudo-First Order (PFO), Pseudo-Second Order (PSO), and Elovich (ELV). The equilibrium time obtained was 30 min. Adsorption isotherm was tested for Langmuir ($R^2 = 0.9895$), Freundlich ($R^2 = 0.8706$), Dubinin-Radushkevich (0.6918), and Tempkin ($R^2 = 0.8817$) models. Maximum adsorption capacity determined by Langmuir model was 32.1 mg g^{-1}.

Solution P exists mainly as $H_2PO_4^-$ at pH 7. P-O-Fe bonds form on iron adsorbents (Wilfert et al., 2015), supporting the PSO model, which assumes adsorption with two sites occupied by a single molecule adsorbed (Nethaji et al., 2013). This also agrees with single-layer models like Langmuir (Wang & Guo, 2020) expected for chemical reaction related adsorption.

Studies using real wastewater at São Carlos' WWTP obtained an adsorption capacity (q) of 10.8 mg g^{-1} and a P removal (R %) of 65.4 %. At Itatiba's WTTP the R % was 96.1 % and q obtained was 1.1 mg P g^{-1}. The difference in methodology is related to sludge generation. In order to favor the transfer of a greater amount of P

from the effluent to the sewage sludge, aiming at its application as a biofertilizer, the concentration of TechPhos® was increased to 4 g L^{-1} at Itatiba's WWTP. It was observed that suspended solid particles are also attracted by TechPhos®, promoting a flocculation process, which is observed by differences in turbidity in wastewater before and after treatment with TechPhos®, benefitting wastewater treatment applications using this material.

The yield of sewage sludge (YSS) is expressed in g of dry sewage sludge generated per litter of wastewater treated (g L^{-1}). At São Carlos' WWTP and Itatiba's WWTP the YSS was 0.37 g L^{-1} and 4.05 g L^{-1} respectively. FTIR analyses indicated the presence of organic groups at SC1, ST1, SC2, and ST2 spectra, which were absent in TB and TP spectra. All groups presented silica peaks in 794 cm^{-1} (Si-O-Si). The presence of montmorillonite (M) and quartz (Q) were confirmed by DRX in samples TB, TP, ST1, and ST2. These results are in accordance with the American Mineralogist Crystal Structure Database. The morphology obtained by SEM exhibited smooth surfaces, with some pores on samples. EDS indicated the presence, in ascending order, of calcium, magnesium, chlorine, iron, aluminum, silicon, oxygen, and carbon for SC1, ST1, SC2. XPS analysis of iron at TB sample presented binding energies of 708.7 and 711.9 for Fe^{2+} (3/2) and Fe^{3+} (3/2) which were attributed to FeOOH and FeO (Yamashita & Hayes, 2008). Peak areas revealed that approximately 34.2% of the iron was in the Fe^{3+} state, while 65.8% was in the Fe^{2+} state. The TP spectra of XPS presented no significant differences except an decrease in the peaks, for example Fe^{3+} (3/2) = 710.9 eV, probably due to bonding with phosphate ions.

Seed germination with ST1 presented ≤ 25% decrease on parameters IG, RE, HE compared to negative control. Contrastingly, SC1 group displayed significant reduction (25-50%) in these parameters. The higher levels of P in TechPhos® in the ST group likely released more phosphorus (P), mitigating the deleterious effects of toxins in the sludge, which might explain the reduced negative impact on seeds treated with ST1 compared to those treated with SC1. Further testing is ongoing for ST2, SC2. Soil analysis through the Olsen method indicated similar P availability across all groups, with P release about 2 mg P g^{-1}. This suggests potential for plant nutrient uptake if treated sludge is used.

Conclusion

TechPhos® demonstrates remarkable potential as a sustainable phosphorus (P) recovery solution, offering a multifaceted approach to P management. TechPhos® exhibits a high P adsorption capacity, reaching up to 32 mg g-1, and can effectively release P when needed, enabling both P removal and recovery. Moreover, this adsorbent demonstrated flocculation properties, facilitating the separation of P from water and contributing to efficient wastewater treatment. TechPhos® offers a sustainable alternative to conventional P management practices, promoting resource recovery and minimizing environmental impact. By facilitating P recovery from wastewater and sludge, TechPhos® can help reduce reliance on non-renewable mineral P fertilizers, contributing to a more sustainable agricultural sector.

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