The role of sawdust Ca-biochar on the phosphate adsorption: an optimization through a 2^3 experimental design

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Abstract

Phosphorus is a vital element for sustaining life on Earth, yet its scarcity is approaching. Its release -direct and indirect- into aquatic environments contributes to eutrophication, a growing environmental concern. Developing materials capable of recovering phosphate from these environments is crucial for ensuring food and water security. This study explores using sawdust, an abundant industrial waste in Brazil, to produce calcium-modified biochar for phosphate adsorption. A 2^3 experimental design was used to optimize the sawdust modification, the variables were time, concentration, and mass and the biomass pyrolysis was carried in a tubular furnace at 450 ºC. The phosphate adsorption exceeded 87 % in four experiments, with time and concentration being the most significant variables. The mathematical model that described the response could explain 99% ($R^2_{adj} = 0.9975$) of the variation in phosphate removal, showing no lack of fit and presenting a significant regression of 99% (R-sqr = 0.9996). Additionally, a comparison between biochar produced in a tubular furnace and a continuous flow furnace revealed similar phosphate adsorption efficiency, demonstrating the process's viability for large-scale production. Characterizations using FTIR and Raman spectroscopy confirmed the presence of functional groups and the structural integrity of the biochar, indicating its effectiveness as an adsorbent. The study concludes that calcium-modified pine sawdust biochar is a promising solution for phosphate recovery, contributing to the mitigation of eutrophication and environmental sustainability.

Keywords: calcium; biomass; pine; phosphorus; eutrophication;

1. Introduction

Pine sawdust, an abundant industrial byproduct in the Paraná region of Brazil, is particularly significant. Pine plantations are concentrated in southern Brazil, with Paraná being the leading producer, accounting for nearly 42% of the 1.6 million hectares of pine forests nationwide. In the wood-processing industry, pine waste generation is substantial, with 50 tons of waste for every 100 tons of cellulose produced. 67% of this waste is sawdust, presenting significant management and disposal challenges. With 620,000 tons of sawdust generated annually in Brazil, there is an urgent need to transform them into valuable bioproducts.[1] Biochar, a carbon-rich material produced through the pyrolysis of biomass in oxygen-limited or oxygen-free environments, stands out for its low production costs and the affordability of its precursor materials, being an amorphous, stable, and great adsorbent. Modifying biochar with magnesium, calcium, aluminum, or lanthanum salts/oxides etc., enhances its properties

and increases its affinity for phosphate, optimizing its performance.[2]

Phosphorus (P), particularly in the form of orthophosphates, is a major pollutant contributing to the eutrophication of water bodies. The eutrophication is caused by the artificial enrichment of nutrients, leading to the degradation of aquatic environments. This issue is exacerbated by the discharge of P in treated and untreated sewage, along with the widespread use of phosphorus-based chemical fertilizers in agriculture. These fertilizers are crucial for meeting the global food production demand, but the excessive exploitation of phosphate rock deposits has led to concerns about their imminent depletion. The potential scarcity of phosphorus could severely jeopardize global food security. Biochar presents a promising solution for recovering phosphate species from eutrophic waters. This approach not only facilitates the removal and recovery of phosphate from eutrophic aquatic environments but also contributes to restoring a key element for humanity.[3][4]

Understanding the synergy between modification parameters and phosphate adsorption

is essential for optimizing phosphorus recovery. Thus, this study focused on the production of sawdust calcium-modified biochars, and its development in a pilot-scale furnace, aiming to create a material capable of efficiently removing phosphate from eutrophic environments.

2. Methodology

The biomass of Pine sawdust was grounded in a knife mill and sieved (28 mesh). A modification with calcium ($CaCl_2.2H_2O$) was conducted with a 2^3 experimental design. The process variables were: modification time (t), concentration of the modification solution (c), and biomass mass (m). Eight experiments were conducted to optimize the variable values. The lower and upper levels of each variable were, respectively, t: 1 and 2 hours, c: 0.5 and 1.0 mol L^{-1}, and m: 5 and 10 g.

After, the samples were filtered and the pyrolysis were carried out in a tubular furnace with 450 °C of temperature, 5 °C min^{-1} as the heating rate and no residence time. For adsorption, the biochars were added to a KH_2PO4 10 mg L^{-1} solution and kept stirring for 24 hours. The solution was filtered and the final phosphate concentrations were determined using blue molybdenum method, which is based on a reaction of ammonium molybdate, tartrate of antimony and potassium, sulfuric acid, and ascorbic acid. The solutions were analyzed using a UV spectrophotometer at 880 nm. The dependent variable was the percentage removal of phosphate. Statistical significance was tested (95% confidence level).

Two conditions (of the total eight) were chosen to be pyrolyzed in the continuous flow furnace for comparison with the samples made in the tubular furnace. For the pilot-scale furnace, the conditions were: temperature = 450 °C, feeding flow = 1 rpm, N_2 flow rate = 4 L min^{-1}, furnace rotation = 8 rpm, inclination = 6 cm. The final samples were BSCa1T, BSCa2T, BSCa1F and BSCa2F, where B = biochar, S = sawdust, Ca = calcium, 1 or 2 = modification time, and T or F = tubular or continuous flow furnace. The biochars were characterized with Fourier Transform Infrared (FTIR) and Raman spectroscopy. The phosphate adsorption and isotherms were tested. For the adsorption isotherms, Langmuir and Freundlich models were studied at the concentrations of 1, 5, 10, 25, 50, 100, 200, 300, and 500 mg L^{-1}.

3. Results and discussion

3.1 Modification with 2^3 experimental design

For the biomass modification, a 2^3 experimental design was developed and Table 1 shows the response in terms of phosphate removal for the biochars modified with calcium.

Table 1. Percentage of phosphate removal under a 2^3 experimental design

| Samples | Variables | | | Percentage of removal (%) |
	t (h)	c (mol L^{-1})	m (g)	
1	1	0.5	5	31
2	2	0.5	5	28
3	1	1.0	5	**87**
4	2	1.0	5	**93**
5	1	0.5	10	13
6	2	0.5	10	**87**
7	1	1.0	10	18
8	2	1.0	10	**97**

Four out of the eight experiments achieved a phosphate removal higher than 87%. The time, the concentration, the interaction between time and mass, and the interaction between concentration and mass were statistically significant (95 % of significance level) for phosphate removal. A mathematical model was adjusted (Equation 1), and its fit was evaluated using ANOVA. In this model, X_1 = time, X_2 = concentration, and X_3 = mass.

Removal (%) = 56.67 + 3031.9X_1 + 2276.8X_2 + 2789.3X_1X_3 - 1388.6X_2X_3 (Equation 1)

The mathematical model that describes the response can explain 99% (R^2_{adj} = 0.9975) of the variation in phosphate removal, showing no lack of fit and presenting a significant regression of 99% (R-sqr = 0.9996). Time (X_1) stood out among the other variables as having the greatest effect, with a p-value of 0.021. Therefore, the longer the time, the greater the removal efficiency. Concentration (X_2) was the other independent variable that stood out, with a p-value of 0.024, indicating that the higher the concentration of the modification, the greater the efficiency of phosphorus removal.

Figure 1 presents the response surface plots, correlating the variables with the percentage of phosphate removal.
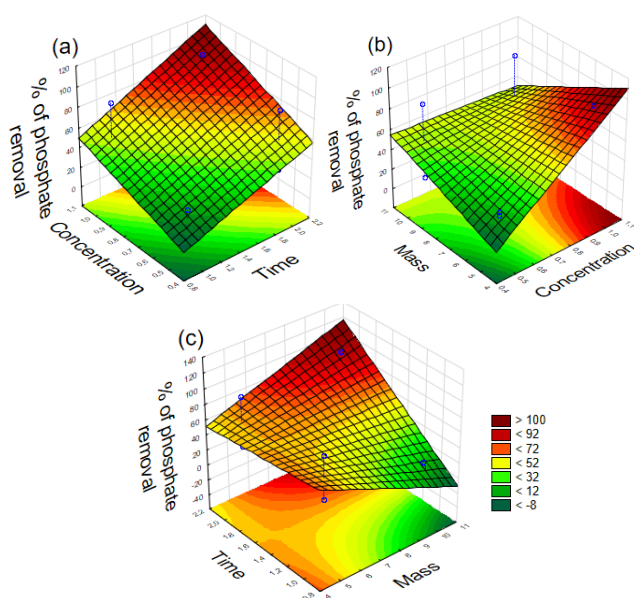

Fig 1. Response surface plots of the independent variables correlated to the dependent variable

According to Figure 1a, the m was fixed at its average value (7.5 g), and the variables c and t were analyzed. It was observed that phosphate removal is intensified as both concentration and time increase. In Figure 1b, the t was fixed at its average value (3 hours), and the variables m and m were correlated. It was noted that phosphate removal is intensified as concentration increases. It is important to note that although biomass mass is not significant on its own, the interaction between mass and concentration has a significant effect. This means that the lower the mass and the higher the concentration, the greater the phosphate removal, which is also observable in the plot. In Figure 1c, the c was fixed at its average value (0.75 mol L^{-1}), and the variables t and m were correlated. It was observed that removal is enhanced with longer time and higher biomass mass, as the interaction between them is significant, even though biomass mass alone is not a significant effect.

3.2 Comparison between tubular furnace and continuous flow furnace and biochars characterization

The conditions of samples 3 and 4 were chosen to be pyrolyzed in the pilot-scale furnace for a

comparison of phosphate adsorption between furnaces. The percentages of phosphate removal for the samples were 87 % for BSCa1T and 75 % for BSCa1F, and 93 % for BSCa2T and 91 % for BSCa2F. As seen in the experimental design, the modification time was the variable with most statistical significance, and the samples with longer modification exhibited similar adsorption rates between furnaces, highlighting the material's suitability for large-scale production and the importance of the experimental design.

As for the characterizations, in FTIR the results had a similarity of functional groups among the materials, even between furnaces. The band 1300-1000 cm^{-1} can be attributed to C-O-C stretching vibrations referring to lignocellulosic material in the biomass, with less presence in the biochars related to the pyrolysis. In 1650-1750 cm^{-1}, the band is associated to the stretching vibrations of C=O, related to the partial oxidation of organic matter. The region of 2900-2990 cm^{-1} can be assigned to stretching vibrations of aliphatic structures, which only appears in the sawdust spectrum, meaning a pyrolysis decomposition of aliphatic C-H bonds. The band at 3350-3700 cm^{-1} is related to the stretching vibrations of O-H groups, which are common in biomasses due to glucose molecules and phenolic functionalities. The functional groups can interact with phosphate, and it is noted that most of the bands remain in the biochars even after the pyrolysis process, making it ideal for adsorbent materials.[5]

In Raman, the structural order was studied. All the samples had the defect band D, related to the disorder in the planes of carbon atoms, the graphite band G, related to the E$_{2g}$ vibrational modes and the 2D band, related to the structural transformation. The ratio between the area of the D (I$_D$) and G (I$_G$) bands determines the structural defects in the biochar, and when lower the ratio, less defects, and greater the similarity to the graphite structure.[6] The I$_D$/I$_G$ ratio for the samples were 2.62 for BSCa1T, and 2.01 for BSCa1F, and 2.35 for BSCa2T and 2.01 for BSCa2F. Even in a tubular furnace, where the conditions had more control than the pilot-scale, the samples had more defects, showing the applicability of the material for a large-scale production.

The adsorption capacity of the biochars was assessed through an equilibrium study, which illustrates how the adsorbate molecules distribute between the liquid and solid phases once the

adsorption process reaches equilibrium. In Table 2 the isotherms parameters for Langmuir and Freundlich models are presented.

Table 2. Isotherm parameters for Langmuir and Freundlich models

Biochars	Langmuir			Freundlich	
	q_{max} (mg g^{-1})	R^2	R_L	1/n	R^2
BSCa1T	5546	0.98	0.62	0.94	0.99
BSCa1F	10,000	0.99	0.59	0.99	0.99
BSCa2T	506	0.99	0.58	0.84	0.99
BSCa2F	818	0.98	0.54	0.83	0.98

Table 1 reveals that the R^2 values for both the Langmuir and Freundlich isotherms were similar (0.99 and 0.98), suggesting simultaneous adsorption mechanisms with no predominance mechanism. The Langmuir model is more suitable for describing adsorption on homogeneous surfaces and maximum adsorption capacity, while the Freundlich model is better for heterogeneous surfaces and capturing the variability in adsorption site affinity. To determine the most appropriate model for the samples, additional parameters like the 1/n value in the Freundlich isotherm should be considered. A 1/n value below 1 indicates a tendency towards the Langmuir isotherm, while a value above 1 suggests cooperative adsorption.[7] No sample had a value above 1, suggesting a preference for the Langmuir model.

Other additional parameter that can be evaluated is the dimensionless equilibrium parameter (R_L) that provides further insight into the Langmuir model's suitability. When the R_L is higher than 1, it indicates an unfavorable fit; when the R_L is equal to 1, indicates a linear fit; when the R_L is between 0 and 1, it suggests a favorable fit; and when the R_L is 0, the fit is irreversible.[7] For all samples, RL values were between 0 and 1, indicating a favorable alignment with the Langmuir isotherm. The maximum adsorption capacities of the samples ranged from 506 to 10,000 mg g^{-1}.

These findings suggest the biochars fit both the Freundlich model, which accounts for varying adsorption energies, and the Langmuir model, which represents monolayer adsorption. However, there was a tendency towards the Langmuir model when considering the R_L and 1/n parameters. The adsorption mechanisms occur simultaneously, enhancing the understanding of the biochars' adsorption capacity, the affinity of the adsorption sites, and the surface heterogeneity of the materials.

Therefore, the significance of employing experimental designs is evident in optimizing the biochar production for phosphate adsorption. This approach yields more satisfactory results and ensures a comprehensive study of the various parameters that may influence the process, which are essential for refining the experiment. Additionally, the comparison between biochar produced in a tubular furnace and a continuous flow furnace revealed similar phosphate adsorption efficiency, demonstrating the process's viability for large-scale production.

Acknowledgements

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