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From waste to resource: a comparison of batch and continuous flow pyrolysis of orange bagasse biochars for phosphate adsorption

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Abstract

The orange production in Brazil is among the most significant in the world, and the by-product orange bagasse is a critical agro-industrial waste, which can be converted into biochar through pyrolysis to address environmental challenges and effectively adsorb phosphate. This pollutant causes eutrophication in aquatic environments. For this reason, biochar has a great contribution to both waste management and environmental remediation. Thus, this study investigates the conversion of orange bagasse modified with zinc into biochar for phosphate adsorption, using two different pyrolysis methods: batch and continuous flow. The materials were characterized by Fourier Transform Infrared (FTIR) and Raman spectroscopy, to demonstrate the surface functional groups and the graphitization level. Adsorption tests revealed high phosphate removal efficiencies (99-100 %), and across various pH levels, explaining how phosphate speciation behaves as a function of pH and its interaction with the surface chemistry of biochar. The adsorption isotherms were analyzed using Langmuir and Freundlich models, and both models fitted the data well, with a tendency toward Langmuir for most samples, suggesting the predominance of homogeneous surface adsorption. The findings underscore the potential of zinc-modified orange bagasse biochar as an effective adsorbent for phosphate removal, offering a sustainable solution for managing agro-industrial waste and mitigating eutrophication in aquatic environments.

Keywords: biomass; sorption; phosphorus; eutrophication;

1. Introduction

Brazil's orange production is one of the most significant in the world, positioning the country as one of the largest producers and exporters of the fruit. In the first half of 2024, the planted orange area was 570 hectares, with a production exceeding 15 million tons.[1] A substantial portion of the harvested oranges is directed to the juice industry, where the process generates solid waste, comprising nearly 50% of the fruit. This waste includes the peel, internal tissues (pulp), and seeds, resulting in an abundant amount of residue.[2] These by-products are not adequately managed, posing an environmental challenge due to their accumulation and the pollution caused by improper waste disposal. However, they have the potential for reuse, as they can be converted into value-added products.[3]

Through thermochemical processes such as pyrolysis, it is possible to convert agro-industrial waste into carbonaceous products like biochar. The thermal decomposition process, carried out in an atmosphere with limited or no oxygen, can be performed in either batch or continuous flow furnaces, each with its own characteristics. Batch furnaces operate in cycles, allowing for precise control of process conditions, whereas continuous flow furnaces offer constant, large-scale production, making them more suitable for extensive operations. The conditions of the pyrolysis process, including heating rate, temperature, residence time, and type of furnace, directly influence the physical and chemical properties of the produced biochar.[3] Typically, biochar is an amorphous, stable, porous material with properties such as adsorptive active sites, stability, removal efficiency, and low environmental impact, making it a promising adsorbent for the remediation of inorganic contaminants in water, such as phosphate.[4]

Eutrophication is a global problem caused by the excessive growth of organic matter, such as algae, due to the enrichment of phosphorous (P) and/or nitrogen (N) in aquatic environments. The discharge of P in treated and untreated sewage is one of the main causes of it, making P a pollutant in these environments. Biochar has demonstrated effectiveness in the remediation of eutrophicated environments due to its high adsorption capacity for orthophosphates, which are primarily found in the bioavailable species H_2PO^{4-} and HPO_4^{2-}.[5]

Biochar adsorbs phosphate through mechanisms of chemisorption and physisorption, reducing its availability in water and mitigating the negative effects of eutrophication. Additionally, phosphate-saturated biochar can be reused as a fertilizer, promoting a sustainable nutrient cycle. [4-5] Therefore, converting orange waste into biochar not only aids in waste management but also offers an innovative solution for the restoration of eutrophicated aquatic ecosystems.

In this context, the present study investigated the use of zinc-modified orange bagasse to produce biochar, employing two different pyrolysis processes, batch process and continuous flow process, and evaluated the performance of the produced materials in phosphate adsorption.

2. Methodology

The orange bagasse was grounded in a knife mill and sieved. The modification with zinc was conducted with a 1.0 mol L^{-1} $ZnCl_2$ solution, stirred for 1 and 2 hours. Afterward, it was filtered, and dried at 100 ºC for 24 hours. The batch pyrolysis was caried out in a laboratory-scale tubular furnace, and the continuous flow pyrolysis was conducted in a pilot-scale furnace. The established parameters were a temperature of 450 °C and no residence time. For the tubular furnace, the heating rate was 5 °C min^{-1}. For the pilot-scale furnace, the N_2 flow rate was 4 L min^{-1}, rotation of 8 rpm, inclination of 6 cm and feeding flow of 1 rpm. The samples were ORZn1T, ORZn2T, ORZn1F and ORZn2F, where OR = orange residue, Zn = zinc, 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.

For adsorption, a stock solution (KH_2PO_4 10 mg L^{-1}) was prepared, and 0.1 g of each biochar was added to 50 mL of the solution and continuously stirred for 24 hours. The solution was then filtered, and the residual phosphate concentrations were measured using blue molybdenum method. This method involves a reagent composed of antimony potassium tartrate, sulfuric acid, ammonium molybdate, and ascorbic acid into the samples. They were analyzed using a UV spectrophotometer at 880 nm. A pH adsorption study was conducted with pH values of 2, 4, 6, 7, 8, 10 to verify its effects on the phosphate adsorption. 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

In Figure 1, the FTIR spectra of OR (orange residue), ORZn1T, ORZn2T, ORZn1F and ORZn2F are presented.

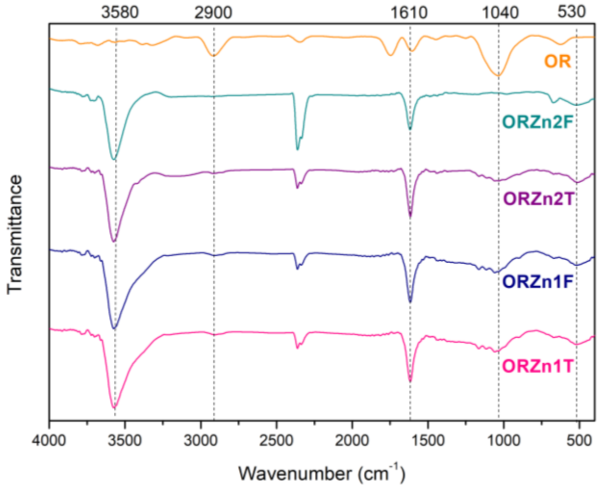

Fig 1. FTIR spectra of OR samples

The results show a considerable similarity of functional groups among the materials, even with different furnaces. This indicates that none of the pyrolysis processes result in the complete elimination of surface functional groups.

The band at 3350-3700 cm^{-1} corresponds to the stretching vibrations of O-H groups. Hydroxyl groups are commonly present in biomasses, derived from glucose molecules in numerous positions in cellulose and hemicellulose, as well as in phenolic functionalities in lignin. The band in the region of 2900-2990 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of CH_2 and CH_3, of aliphatic structures. This band is observed in the orange bagasse, and it practically disappeared in the biochar spectra, indicating the decomposition of aliphatic C-H bonds by the pyrolysis process.[6]

In 1650-1750 cm^{-1}, the bands correspond to C=O stretching vibrations. These groups may be related to carboxylic acids, esters, ketones, and aldehydes, indicating the partial oxidation of organic matter during pyrolysis. The band between 1300-1000 cm^{-1}, notably present in the biomass spectra, can be attributed to C-O-C stretching vibrations of polysaccharide compounds present in cellulose, hemicellulose, and lignin. Its presence in some biochars is of low intensity, referring to the lower amount of lignocellulosic material after pyrolysis.[7]

Overall, it is noted that most of the bands representing the functional groups of the biomass remain in the biochars, regardless the type of furnace used. The functional groups interact with phosphate, making it ideal for them to remain in the adsorbent materials.

In Raman, the structural similarities between the biochars and the graphite structure were analyzed, studying the structural order. It is observed the defect band, D (1300-1400 cm^{-1}), that depicts the disorder in the planes of the carbon atoms; the graphite band, G (1500-1600 cm^{-1}), representing the E_{2g} vibrational modes; and the structural transformation band, 2D (2500-3000 cm^{-1}). The ratio between the area of the D and G bands (I_D/I_G) determines the structural defects present in the sample, lower the ratio, fewer the number of defects, and greater the similarity to the graphite structure.[3-8] The I_D/I_G ratio for the samples were 1.58 for ORZn1T and 3.36 for ORZn1F, and 1.60 for ORZn2T and 1.63 for ORZn2F. As expected, both batch samples have less defects, because the furnace allows a precise control of process conditions, but as it is possible to observe in sample ORZn2 (1.60 to the tubular and 1.62 to the continuous flow process), the difference between the processes is trivial, showing a formation of fewer defects in the structure.

For the phosphate adsorption, the rates were 99-100 % for all samples. These values indicate that the samples produced in the continuous flow furnace exhibited adsorption rates similar to those produced in the tubular furnace, highlighting the material's suitability for large-scale production.

To better understand how adsorption behaves under different conditions, a pH study was conducted to assess its influence in the medium. In Figure 2, the percentage of phosphate removal at different pH levels (2, 4, 6, 7, 8, 10) for all produced biochars (ORZn1T, ORZn2T, ORZn1F, ORZn2F) can be observed.

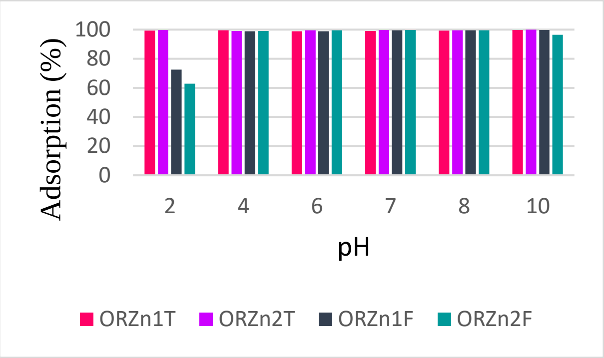

Fig. 2. Percentage of adsorption on pH 2, 4, 6, 7, 8, 10 for the OR samples

The pH of the medium is a crucial factor affecting the efficiency of phosphate adsorption by biochars, primarily due to changes in phosphate speciation at different pH levels. In acidic solutions (pH $\leq$ 2), phosphate predominantly exists as phosphoric acid (H_3PO_4), which is neutral and interacts weakly, resulting in low adsorption efficiency. As the pH increases to a range between 2 and 7, phosphate mainly exists as the dihydrogen phosphate ion ($H_2PO_4^-$), which is better adsorbed due to its negative charge and the positively charged biochar surfaces, particularly when modified with Zn.[9]

In the pH range of 7 to 12, phosphate primarily exists as the hydrogen phosphate ion (HPO_4^{2-}). Although HPO_4^{2-} can still be adsorbed, the efficiency is lower compared to $H_2PO_4^-$, as the biochar surface tends to deprotonate and acquire a negative charge at higher pH levels. In very alkaline conditions (pH > 12), phosphate predominantly exists as the phosphate ion (PO_4^{3-}), which is less effectively adsorbed due to strong electrostatic repulsion between the negatively charged ions. However, in the samples, the alkaline pH did not significantly affect adsorption, likely due to the modification with Zn on the biochar surfaces.[9]

Overall, the optimal pH for phosphate adsorption by biochars is typically neutral to slightly acidic, where $H_2PO_4^-$ is maximized, and the biochar surface remains positively charged, facilitating electrostatic attraction. Notably, there was little difference in phosphate removal efficiency across different pH levels between biochars produced in tubular and continuous flow furnaces. Understanding phosphate speciation as a function of pH and its interaction with the surface chemistry of biochar is essential for optimizing phosphate removal from aqueous solutions.

The adsorption capacity of the biochars was evaluated through an equilibrium study. This study demonstrates how the molecules available for adsorption distribute between the liquid and solid phases when the adsorption process reaches a state of equilibrium. In Table 1 the isotherms parameters for Langmuir and Freundlich models are presented.

Table 1. Isotherm parameters for Langmuir and Freundlich models

	Langmuir			Freundlich	
Biochars	q_{max} (mg g^{-1})	R²	R_L	1/n	R²
ORZn1T	1856	0.98	0.46	0.90	0.98
ORZn1F	10000	0.97	0.53	1.15	0.97
ORZn2T	1021	0.99	0.45	0.87	0.99
ORZn2F	10000	0.98	0.53	0.99	0.98

Based on the analysis of the data in Table 1, it was observed that the fit of the models, according to the R² values, for both the Langmuir and Freundlich isotherms were the same, suggesting the possibility of simultaneous adsorption mechanisms. To further evaluate the most suitable model for the samples, additional parameters such as the 1/n value in the Freundlich isotherm can be considered. When this value is below 1, there is a tendency toward the Langmuir isotherm, while a value above 1 indicates a tendency toward cooperative adsorption.[10] The only sample with a 1/n parameter above 1 was ORZn1F, indicating a preference for the Freundlich isotherm and cooperative adsorption.

The dimensionless equilibrium parameter (R_L) expresses the preference for the Langmuir model. $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favorable and $R_L = 0$ is irreversible.[10] For all samples, the RL value fell between 0 and 1, indicating a favorable fit for the Langmuir isotherm. The maximum adsorption capacity of the samples ranged from 1021 to 10000 mg g^{-1}. All samples demonstrated the possibility of simultaneous adsorption mechanisms occurring on their surfaces. The Langmuir model is more appropriate for homogeneous surfaces and for describing maximum adsorption capacity, while the Freundlich model is better suited for heterogeneous surfaces and capturing the variability in adsorption site affinity.[10]

Understanding the Langmuir and Freundlich isotherms is crucial for characterizing phosphate adsorption on biochars. Applying these models aids in optimizing the use of biochars as adsorbents, thereby enhancing the efficiency of phosphate adsorption. Therefore, the materials offer a sustainable solution for managing agro-industrial waste and mitigating eutrophication in aquatic environments.

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