Adsorption of Phosphorus on Activated Charcoal enriched with Zero-Valent Iron Nanoparticles

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Abstract

The focus of the research is to evaluate the phosphorus adsorption potential of activated carbon modified with different activating agents (NaOH, $ZnCl_2$ and $Al_2(SO_4)_3$). This research was developed in two stages. In the first, the precursor material was activated with different parameters, such as chemical agent, temperature and burning time. At this stage, the coals were characterized regarding their yield, pH, moisture content, ash content and methylene blue adsorption. The best adsorbents from this stage were sent to the second stage, where they were better characterized using SEM and XRD techniques. They were enriched with zero-valent iron nanoparticles and tested through equilibrium and kinetic adsorption tests with applications of the respective models. The activated carbons CA-ZN-300-4, CA-ZN-300-2 and CA-NA-250-3 were those that achieved methylene blue removal greater than 90%. The porous structure of carbons activated with zinc chloride showed better developed pores when compared to carbon activated with NaOH. Activated carbons enriched with zero-valent iron nanoparticles demonstrated a significant increase in adsorption capacity. CA-ZN-300-2 had an average increase of 4,815.5% in adsorption capacity, and CA-ZN-300-4 had an average increase of 5,5% over unenriched coals and 3,631% for CA -NA-250-3. The Sips and Freundlich models were the ones that best fit the experimental data. The pseudo-first order model fitted the coals better. The diffractograms of activated carbons indicated the presence of highly disordered graphite and patterns of amorphous solids, with peaks compatible with zinc and iron oxides in the case of adsorbents activated with ZnCl2. The activated carbons with zinc chloride presented pHPCZ of 4.75 and 5.30, while the activated carbon with sodium hydroxide presented a pHPCZ of 8.42. This biochar remove, on average, 94.63% of phosphorus present in real wastewater.

Keywords: Adsorption; diclofenac; emerging contaminants; magnetic graphene oxide.

1. Introduction

The consumerist model and population growth have led to increased pressure on the environment, whether for the exploitation of raw materials for production processes, or for the release of domestic and/or industrial effluents, which have caused environmental degradation and pollution. [1, 2].

Dyes, metals and nutrients such as phosphorus are considered potential pollutants. They contribute to the pollution of rivers and lakes, affecting underwater fauna and flora [3, 4].

Among the pollutants in the aquatic environment, phosphorus stands out. Phosphorus is present in sanitary sewage and industrial effluents, and its main impact on the environment is eutrophication. Eutrophication is a global problem that causes a series of impacts such as a decrease in dissolved oxygen in water, excessive growth of surface aquatic plants, as well as algae, putting aquatic life and water quality at risk [5,6].

Water treatment techniques, based on coagulation processes, followed by separation by flotation or sedimentation, are highly efficient in removing particulate matter. However, for the removal of color, nutrients and dissolved organic compounds, adsorption processes using activated carbon are more effective in the post-treatment of these effluents. [7, 8]. Activated carbon can be used in the process of removing pollutants, nutrients, specific molecules, as well as natural organic matter. The adsorption capacity of charcoal is dependent on its surface area, pore distribution and the existence of functional groups on the surface of the adsorbent material, as well as the operational conditions of the process. [9, 10].

Interest in using biomass as a precursor for activated carbon has grown, as they are low-cost, renewable materials with high availability, such as taperebá, grasses, bamboo, coffee, açaí, coconut shells, banana peels, among many others. The production of Tabeperá (*Spondias mombin L.*) in six municipalities in the State of Paraíba alone was approximately 700 tons in 2006, while in Pará, a production around 200 tons was recorded in Curionópolis and 280 tons in Tomé-Açu [11,12].

This work addresses the application of agricultural waste in the removal of phosphorus from effluents from Sewage Treatment Plants (STP). The research combined two innovative technologies: the activation and production of taperebá charcoal and the application of zero-valent iron nanoparticles.

2. Methodology

2.1 Biochar production

For the production of the adsorbent material, the seed of the species (stone) *Spondias mombin L* was used as raw material. The material was collected in fruit pulp processing and manufacturing industries in the municipality of Tomé-Açú (Pará, Brazil).

Seeking a change in the precursor material, opening the fibers further and altering the functional groups, a pre-pyrolysis activation (with ZnCl2, NaOH and $(Al_2(SO_4)_3(14\text{-}18).H_20)$ was chosen. Therefore, the samples were initially activated in natura. They were then washed with deionized water, dried in an oven at 150 ºC for 3 hours, and stored in closed containers. After the activations, the material underwent pyrolysis in porcelain crucibles, in a muffle furnace at different temperatures (400ºC, 350ºC, 300ºC, 250ºC and 200ºC) for different periods (2, 3, and 4 hours).

The second stage was the synthesis of zero-valent iron nanoparticles (Nanoscale Zero Valente Iron - nZVI) for coal enrichment; followed by characterization of the new coal and adsorption tests

2.3 Characterization

were the following characterizations: pH of biochars following the methodology of Medeiros (2008); moisture content according to standard 2867 (ASTM, 2017); ash content following standard D2866 (ASTM, 2018); microporosity was determined with the ANOVA 1000e from Quantachrome Autosorb-iQ Instrument, adjusting equations such as BET, Langmuir or BJH through N_2 adsorption-desorption isotherms [13,14].

2.4 Adsorption test

After selecting the biochars that obtained the best results in the adsorption of methylene blue, the phosphorus adsorption test was carried out. For these tests, samples of treated sewage were used from the Sewage Treatment Station (ETE) of the Federal University of Western Pará (UFOPA) on the Rondon campus, called ETE Rondon, in the municipality of Santarém-PA.

The tests were carried out in columns. This were designed to operate with a hydraulic detention time of 20 minutes. The choice of detention time was based on an analysis of the balance between removal efficiency and operational viability. The determinations of Alkalinity, Total Phosphorus, pH, COD and NTK were carried out following methods set out in the SMEWW (APHA, 2023). TOC determination was carried out using the potassium dichromate method (SCHUMACHER, 2002)

Table 1 – Column parameters

Parameters	**CA-ZN-300-4**
Column diameter (cm)	1,00
Bed length (cm)	25,00
Mass of adsorbent (g)	13,32
Operating flow ($mL.min^{-1}$)	1,00

3. Results

Fig 1 shows the point of zero charge pH (pH_{PZC}), where it can be observed that the material has a pH_{PZC} of 8,3. When the pH of the medium is lower than the pH_{PZC}, the surface is positively charged.

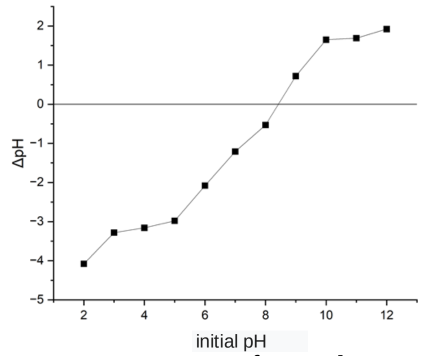

Fig. 1. Point of zero charge pH

The diffractogram obtained (Fig. 2) did not show diffraction peaks characteristic of crystalline structures, indicating a pattern of amorphous solids. It also presented peaks at positions 18.15º, 24.85º and 38.77º, the latter being compatible with Zinc and Iron Oxide standards, which may have been formed with Iron from the composition of Spondias mombin L., and Zinc from chemical activator. The peak at position 30.40º indicates the presence of Potassium Chloride (KCl), which can be formed through the potassium present in the composition of Spondias mombin L. with residues of Zinc Chloride used in the chemical activation process.

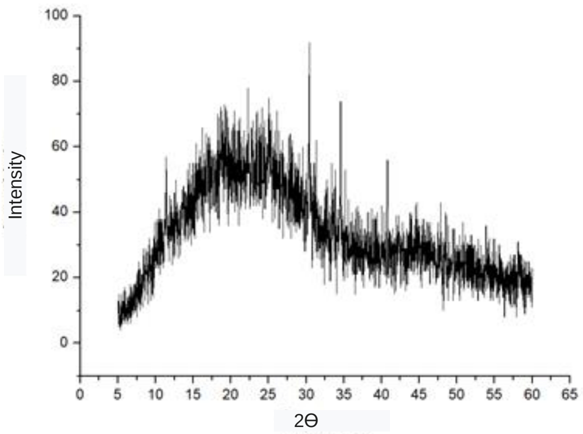

Figure 2 - X-ray diffraction diagram of biochar

Phosphorus was the parameter that showed the greatest reduction (Fig. 3). In the first test, the total phosphorus concentration reduced from 4.83 mg/L to 0.34 mg/L, representing a reduction of 92.96%. In the first repetition, total phosphorus decreased to 0.28 mg/L, a reduction of 94.20%, and in the last repetition, the concentration reached 0.16 mg/L, representing a reduction of 96.69% in relation to to the initial value. These results suggest that the adsorbent maintained its high phosphorus removal capacity throughout the repetitions, without being significantly influenced by the increase in COD and the decrease in alkalinity.

The COT presented its highest value in the first replication, even higher than the value before passing through the column. This is due to the interference of iron in the method used for determination. The method used, proposed by Teixeira et al. (2017) and Schumacher (2002), consists of the oxidation of organic carbon in the sample using potassium dichromate in an acidic medium, followed by the quantification of the remaining dichromate to calculate the amount that reacted, thus allowing the TOC concentration to be determined. Despite iron leaching in the first test, the material continued to be active in subsequent tests.

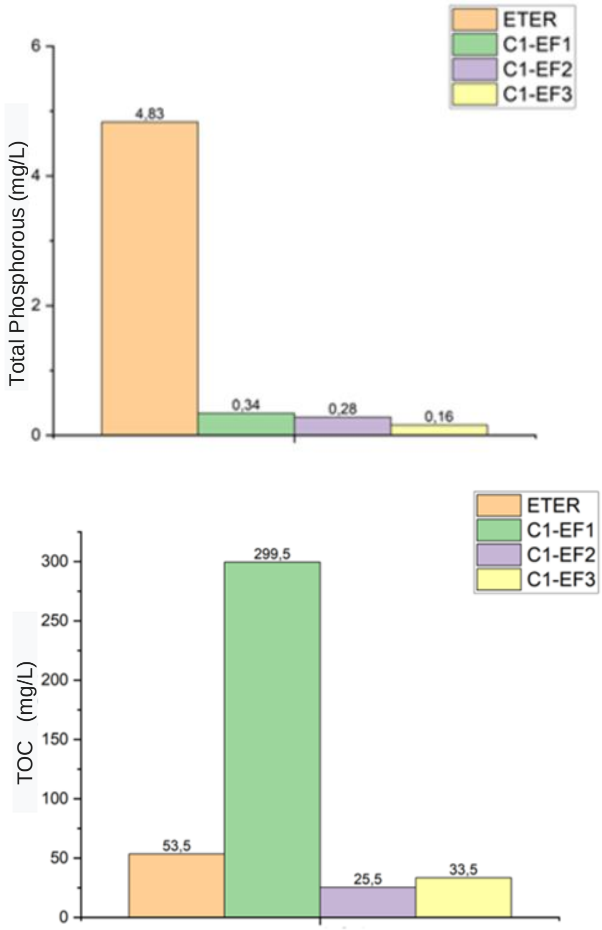

Fig. 3. Behavior of Total Phosphorus and TOC before and after the CA-ZN-300-4 adsorption column.

Among the adsorbents tested, CA-ZN-300-4 demonstrated high effectiveness in removing phosphorus, achieving the best removal average of 94.63%. This material demonstrated a continuous tendency to reduce remaining phosphorus concentrations until the end of the tests, which prevents a clear identification of the break point. This behavior indicates it has a high capacity for phosphorus removal, exceeding the tested conditions.

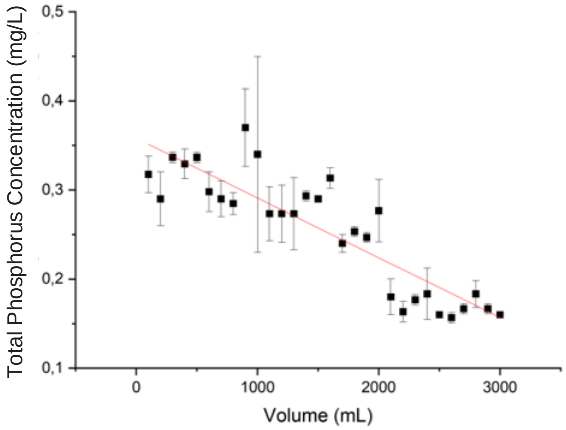

Fig. 4 - Concentration of phosphorus remaining after passing through the columns per volume of treated effluent

4. Conclusion

Column tests were carried out with real effluent, aiming to test the material in conditions closer to operational ones. These trials confirmed that CA-ZN-300-4 was the most efficient. This biochar managed to remove, on average, 94.63% of phosphorus, while CA-ZN-300-2 removed 92.46% and CA-NA-250-3 removed 71.87%. LIU et al. (2021), and AI et al. (2022) achieved phosphorus removals of 84.4% to 99.21%, however with synthetic solutions that do not portray the complexity of a real sewage treatment plant effluent. Therefore, the results obtained with the adsorbents in this research stand out for using real effluent, and offering contributions to the treatment of effluents. They objectively demonstrate the robustness and applicability of activated carbons in real scenarios, reinforcing their potential for practical and effective use in sewage treatment plants, especially in regions affected by eutrophication.

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