



Effective Phosphate Removal from Water by Electrochemically Mediated Precipitation with Coffee Grounds Biocarbon Obtained by Non-Thermal Plasma Method

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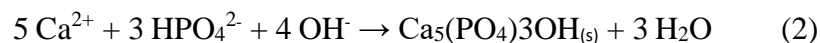
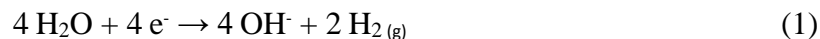
Abstract. This study investigates the use of biocarbon electrodes, produced from coffee grounds through plasma pyrolysis, in the electrochemically mediated precipitation process for phosphorus removal in a flow reactor. The structural and electrochemical properties of biocarbon were analyzed using X-ray powder diffraction (XRD), Raman spectroscopy, and cyclic voltammetry. The results show that biocarbon consists of both graphene oxide and lignocellulose with surface OH groups that facilitate the breakdown of water, a key step in the electrochemically mediated precipitation process for phosphorus removal. The addition of graphite to the biocarbon paste was found to be necessary to obtain a response from the biocarbon in cyclic voltammetry. The Gr₇₅BC₂₅ electrode achieved higher phosphorus removal rates than other tested electrodes, particularly at low flows, due to the functional groups present in biocarbon enhancing the breakdown of water. However, electrodes with a greater amount of biocarbon exhibit lower rates of phosphorus removal and higher consumption of electrical power, which can be attributed to their higher electrical resistivity. Thus, to optimize its use, it is important to balance the benefits of increased phosphorus removal rates with the trade-off of increased energy consumption and decreased phosphorus removal at higher levels of biocarbon. The results suggest that biocarbon produced from coffee grounds by plasma pyrolysis has the potential to be used as an effective electrode material for electrochemically mediated precipitation processes.

Keywords. *Non-Thermal Plasma Synthesis; Biocarbon, Phosphate Removal, Water Treatment, Green Electrochemistry.*

Introduction. Phosphorus plays a pivotal role in the development of plants, animals, and industrial manufacturing (1). However, due to its overexploitation, especially in agriculture, global reserves of phosphate are predicted to be depleted within the next 50-100 years (2). The excessive release of phosphates in wastewater can lead to environmental problems such as eutrophication, which can cause public health concerns and damage aquatic ecosystems. The concept of smart cities has been endorsed as an effective approach to enhancing urban sustainability by improving citizens quality of life while also reducing the environmental impact of urbanization. Thus, the

elimination of phosphates from wastewater is a crucial challenge in the context of smart cities, as it can assist in mitigating water pollution and safeguarding public health (3).

To prevent water bodies from this undesirable phenomenon and pave the way for phosphorus recovery (2), various technologies are available to manage phosphorus pollution. These technologies can be categorized into chemical methods (4, 5), biological methods (6), and physical methods (7). Recently, there has been increasing attention on the use of electrochemical technologies for wastewater treatment (8-10). Electrochemically mediated precipitation has emerged as a promising approach for removing and recovering P from wastewater streams. The process involves elevating the pH at the electrode surface, with phosphate ions not directly involved in the electrochemical reactions. At the cathode, water molecules are broken down into H₂ and OH⁻, resulting in an increase in local pH. Cations, such as Ca²⁺, migrate towards and accumulate near the cathode through electric migration, triggering the formation and precipitation of P minerals, such as calcium phosphate, in response to the pH increase. This pH rise also increases the saturation index, while the high local pH near the electrode reduces the solubility of P minerals (Ca-P), further promoting the precipitation of P minerals as expressed in equations 1-2 (11).



Electrochemically mediated precipitation is a promising strategy for removing and recovering P from waste streams, although it can be demanding on the electrodes. To make the process more cost-effective and environmentally friendly, easily replaceable materials should be used. Carbonaceous materials-based electrodes are an attractive option due to their excellent electrical conductivity and low cost (12). Additionally, functional groups can be added or doped onto these electrodes to enhance water electrolysis. Biocarbon, which is produced from biomass residue, is a type of carbonaceous material that retains functional groups like OH, making it an excellent candidate for water breakdown (12, 13). Biocarbon is also environmentally responsible and porous. Therefore, this study investigates the use of biocarbon electrodes in the electrochemically mediated precipitation process for phosphorus removal in a flow reactor.

Materials and Methods. The biocarbon synthesis was carried out using the De Souza method (14), which involves a non-thermal plasma generator coupled to a reaction vessel to produce an arc. In this reactor, a certain amount of coffee grounds was exposed to a 60kV arc with a flow of N₂(g) between two 316L steel electrodes per 4 hours.

The material obtained was characterized using scanning electron microscopy (SEM) Jeol JSM-6701F. X-ray diffraction (XRD) patterns of the materials was measured using a Miniflex II diffractometer, with a Cu K α radiation source of 0.15406 Å, set at a 2 θ range of 2–90°, and a scan

speed of 2 min^{-1} . The Raman spectra were collected using a Horiba Scientific MacroRam Raman spectroscopy equipment with a 785nm laser, and the infrared spectra were performed on a Nicolett® 6700 with an ATR Miracle (Pike) accessory and a diamond/ZnSe crystal and an MCT detector.

Assays for phosphate removal were carried out in a flow electrochemical reactor (see figure 1) featuring a carbon paste working electrode with a surface area of 2.8 cm^2 . The electrode was constructed by mixing carbon (graphite (Gr) powder - 150 mesh and biocarbon (BC), in appropriated proportions) and mineral oil in a 70:30 weight-to-weight ratio. This mixture was used to fill the support cavity (15). The Ag/AgCl electrode was used as a reference, and a stainless steel ring was used as a counter electrode. A different flow of a 0.5 mol L^{-1} aqueous KCl solution was used, with the addition of 100 mg L^{-1} phosphoric acid (Aldrich) and 1 g L^{-1} CaCO_3 and KCl.

Effluents for each flow was collected after 30 min in a unique passage on reactor and the phosphate as measured by Murphy and Riley (16) utilising the antimony-molybdate as a complexant in a UV/Vis spectrometer Kasvi K37=UVVis with analytical curve of $\text{Area} = 0.00264 + 0.0002663 \cdot [\text{P}]$ with $r^2 = 0.914$.

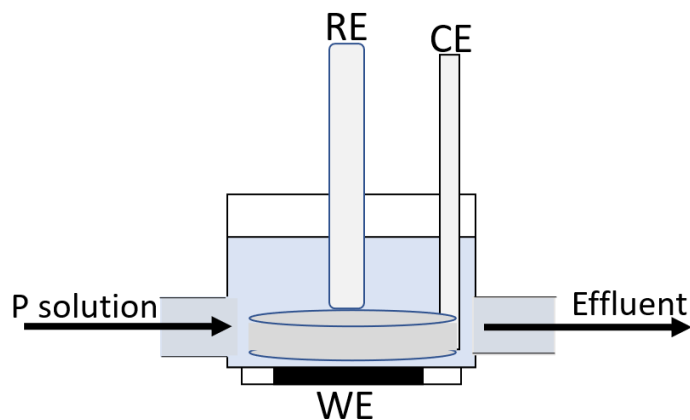


Figure 1. schematic flow electrochemical reactor for phosphorus removal, WE - working electrode, RE - reference electrode, CE - counter electrode.

Results and Discussion. SEM images of the prepared biocarbon from coffee grounds are shown in Figure 2. The topographic images were obtained at different magnifications (500-10,000x) and are characteristic of biocarbons. The observed morphology pattern shows a presence of irregular channels, remnant of the fibrous cellulosic biomass. This is consistent with the dehydration during plasma pyrolysis (17).

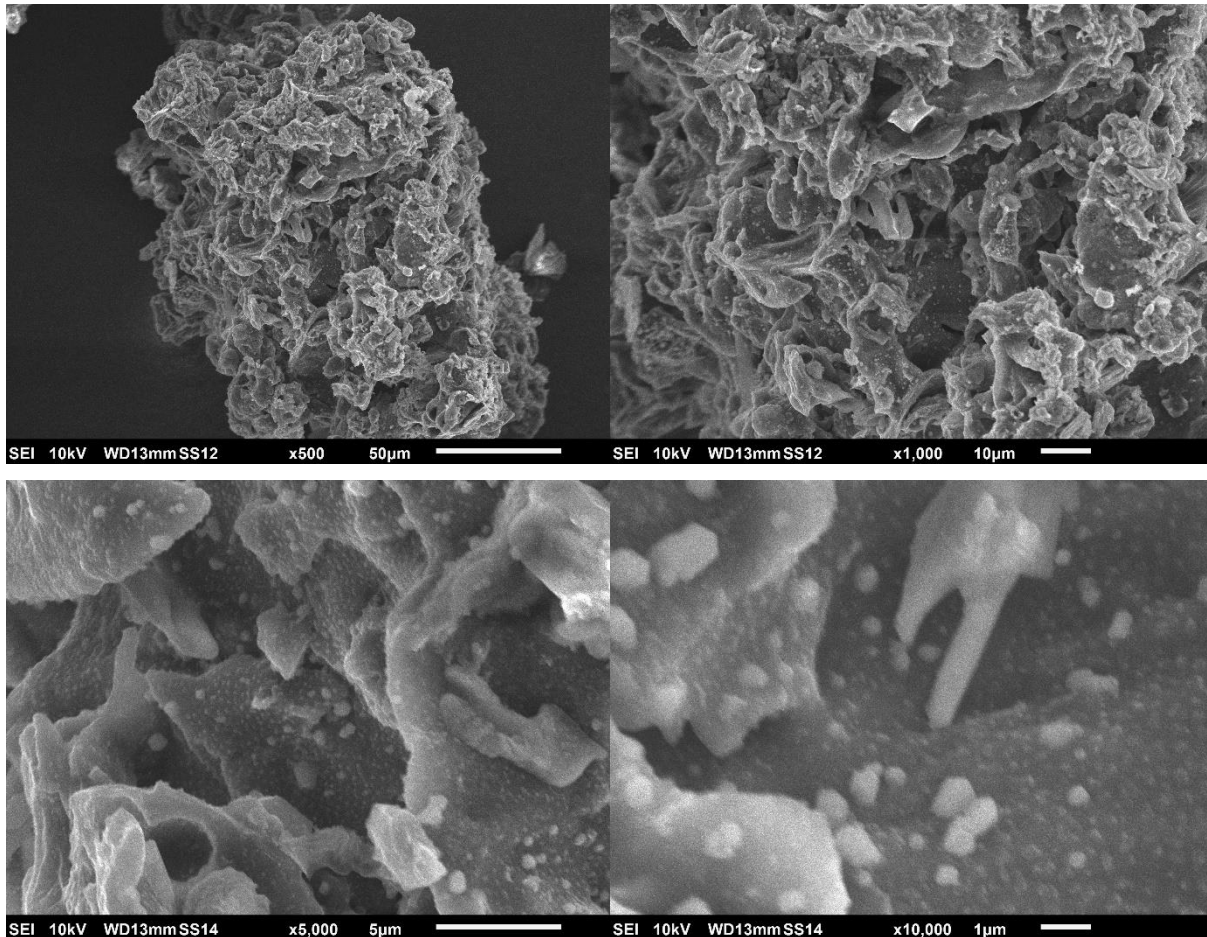


Figure 2. SEM micrograph biocarbon prepared by cold plasma with different magnifications.

X-ray powder diffraction (XRD) was utilized to analyze the structural characteristics of the biocarbon, as depicted in Figure 3a. The XRD pattern exhibits two primary peaks. Specifically, a peak appears at $2\theta = 11^\circ$, which corresponds to the (002) diffraction plane of GO, and the broad peak at $2\theta \sim 23.2^\circ$ can be attributed to the convolution of the (002) and (100) diffraction plane of carbon and graphene, respectively (18). The wide peak observed at $2\theta = 24.6^\circ$ suggests that the structure has a decreased level of crystallinity. According to the data, this structure has 41% amorphousness, and the partially disordered configuration displays d-spacing at 0.358 nm graphene layers.

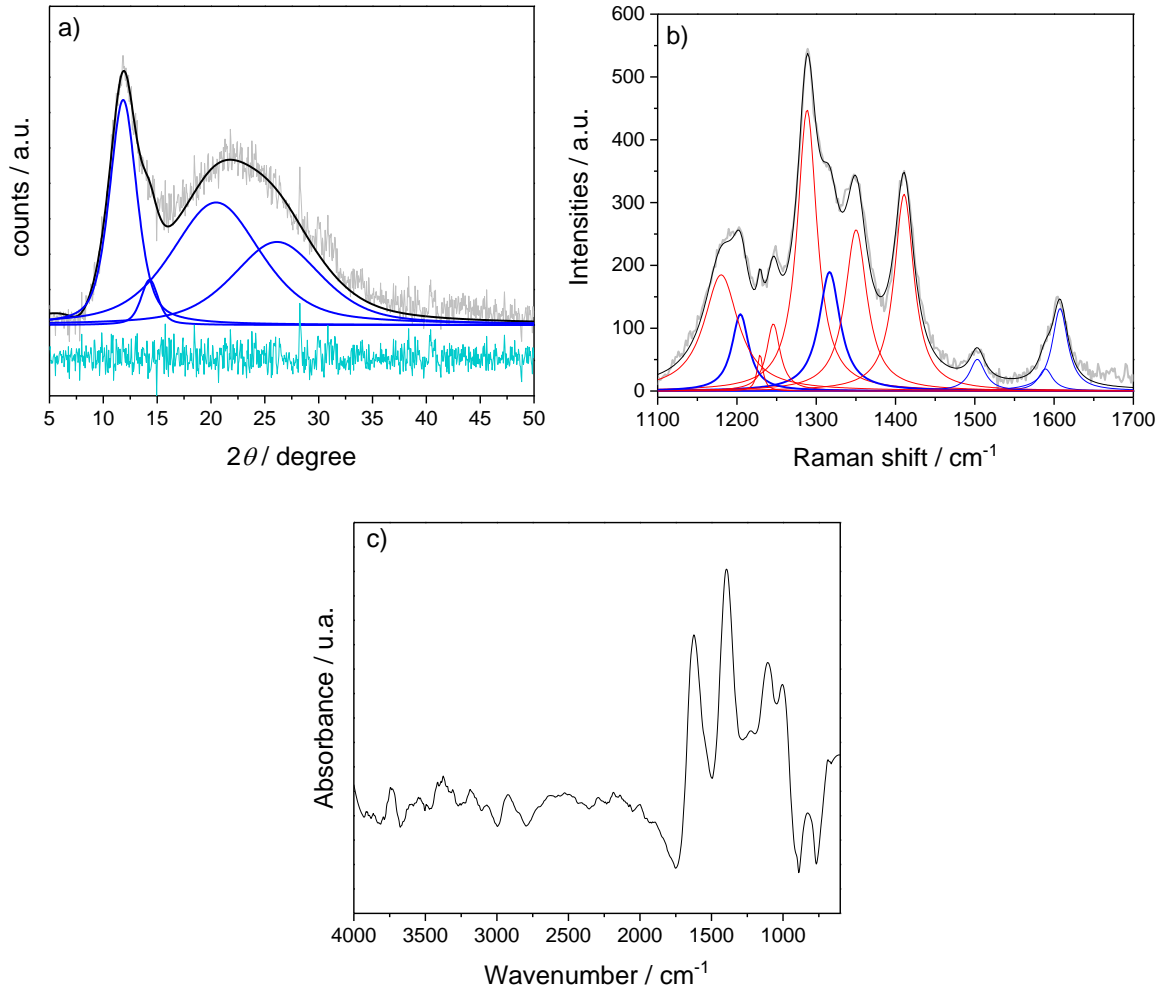


Figure 3. a) X-ray powder diffraction pattern of the nanoflakes graphene with to the deconvolution of the peak corresponding to (002) plane diffraction. b) Raman Spectrum of the nanoflakes graphene with the D, G and 2D band and the deconvolution of the D1, D2, D3, D4 and G bands in the lower frequency regions. c) ATR-FTIR spectrum of biocarbon

The Raman spectroscopy analysis (Figure 3b) provides information about GO and graphene produced using carbon from coffee grounds. The analysis reveals the presence of carbon bands at approximately 1322, 1623, 1495, 1196, and 1587 cm^{-1} , which correspond to D1, D2, D3, D4, and G bands, respectively (19). According to the literature, the intensity ratio of the D-band to G-band (I_D/I_G) is a parameter used to characterize the degree of disorder in graphene (20), and in this case, the ratio was characteristic of graphene.

Other bands are also evident in the spectrum, referring to functional groups and other species from the coffee grounds biomass, which was not converted into graphene or graphene oxide. Analysis of the ATR-FTIR spectrum (figure 3c) shows the existence of bands at 3403 cm^{-1} confirmed the -OH stretching vibration; the peaks at 1619 cm^{-1} (C-C skeleton vibration), and 1233 cm^{-1} (C-O) (18), at 1103 cm^{-1} are ascribed to the stretching vibration of C-O (21). The presence of hydrocarbons in biocarbon is indicated by the bands at $2800\text{--}2980\text{ cm}^{-1}$ (C-H aliphatic stretching) and 1375 cm^{-1} (C-H aliphatic bending) (22), as well as the band at 1101 cm^{-1} , which corresponds to symmetric C-O stretching (C-O-C in lignocelluloses) (23). These bands confirm the persistence of hydrocarbons in the biocarbon.

Cyclic voltammetry was performed in a 0.5 M KCl medium to analyze the electrochemical properties of biocarbon (BC) (as shown in Figure 4). It was noted that the addition of graphite (Gr) to the carbon paste was necessary to obtain a response from the biocarbon. From the voltammetric profiles, it was observed that the specific area decreased with an increase in the amount of graphite, indicating the high capacitance of the BC (24).

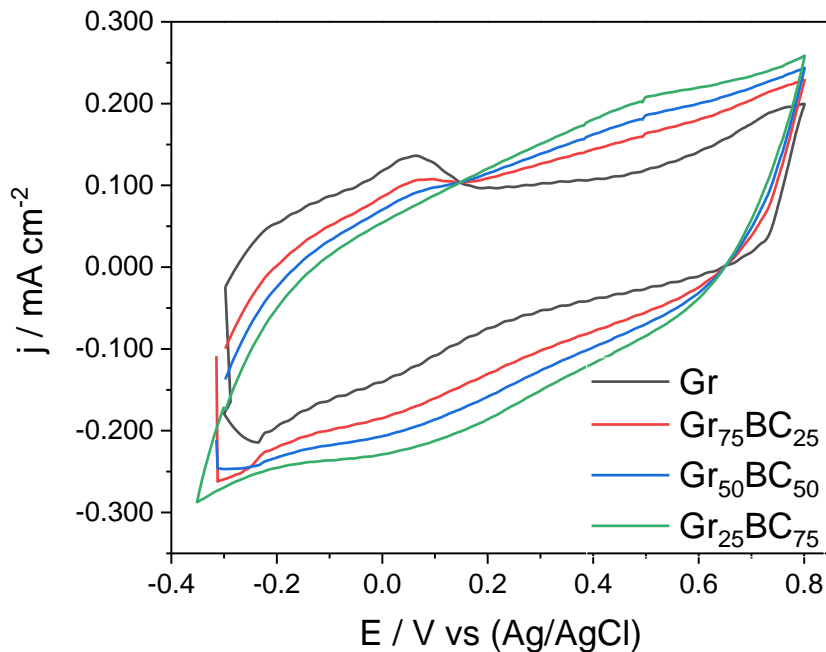


Figure 4. Cyclic voltammetry of carbon paste electrodes containing graphite (Gr) and biocarbon (BC) in a 0.5 mol L^{-1} KCl aqueous solution, with a scan rate of $\nu = 50\text{ mV s}^{-1}$.

Figure 5 displays the results of phosphorus removal by electrochemically mediated precipitation and energy consumption, showing that the Gr₇₅BC₂₅ electrode achieved higher removal rates than the other tested electrodes, particularly at low flows (0.1 and 0.5 mL min⁻¹). This suggests that the functional groups present in biocarbon may enhance the breakdown of water, a key step in this type of reaction.

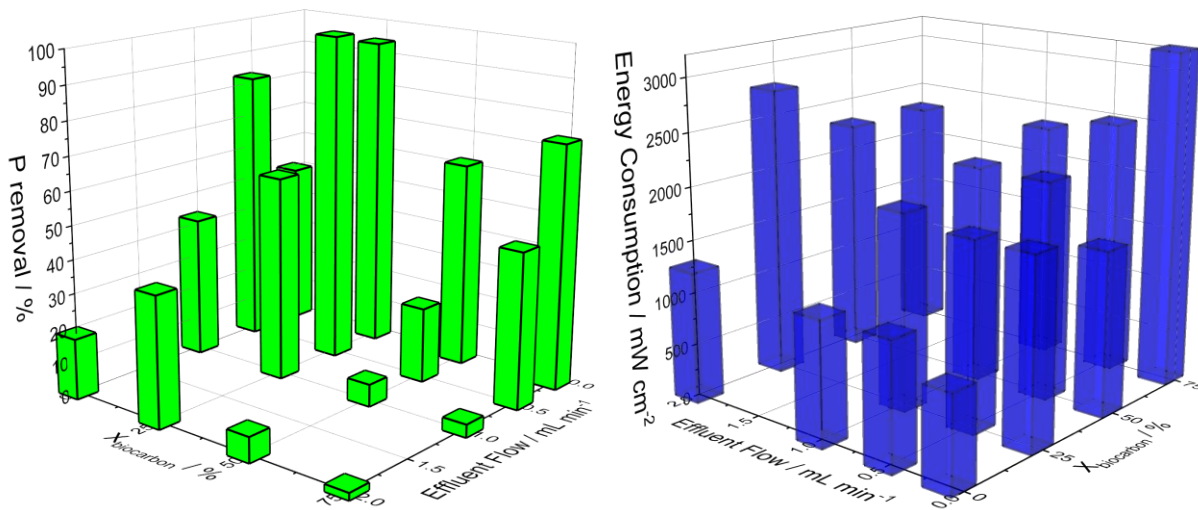


Figure 5. Removal of P and Energy consumption as a function of amount of BC in Gr and flow in a density current of 1 mA cm⁻².

This result is in agreement with the results found in the literature with more noble electrodes in batch reactor (25). However, electrodes with a greater amount of biocarbon exhibit lower rates of phosphorus removal and higher consumption of electrical power, which can be attributed to their higher electrical resistivity, as observed in cyclic voltammetry. This may result in the dissipation of the extra energy consumed in the form of heat or the oxidation of partially oxidized material from the electrode itself.

Conclusion. The biocarbon obtained from coffee grounds by plasma pyrolysis is composed of both graphene oxide and lignocellulose, with surface OH groups that facilitate the breakdown of water, a key step in the electrochemically mediated precipitation process for phosphorus removal. However, using large quantities of biocarbon increases energy consumption and decreases phosphorus removal, as this could be attributed to the higher electrical resistivity of the electrode and/or the oxidation of incompletely oxidized biomass remnants. Therefore, the results suggest that biocarbon produced from coffee grounds by plasma pyrolysis has the potential to be used as an effective electrode material for electrochemically mediated precipitation processes.

However, in order to optimize its use (25% biocarbon and 75% graphite), it is important to balance the benefits of increased phosphorus removal rates with the trade-off of increased energy consumption and decreased phosphorus removal at higher levels of biocarbon.

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