Valorization of baru waste (*Dipteryx alata* vog.) for the synthesis of porous materials with potential for application in Advanced Oxidative Processes

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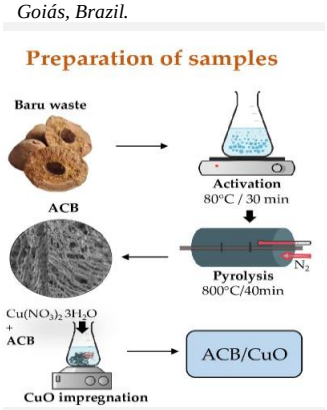

Currently there is a growing interest in the development of efficient and sustainable processes to carry out the decontamination of pollutants in the gaseous and aqueous phases. In this context, advanced oxidation processes by adsorption with activated carbon are one of the most promising alternatives. The objective of this work is to use baru (*Dipteryx alata* Vog) waste for recovery through the preparation of activated carbons that can be used to eliminate contaminants. Samples were prepared and characterized by N_2 adsorption-desorption at -196°C, scanning electron microscopy (SEM) and thermogravimetric (TGA). All the adsorbents presented values of BET surface area (S_{BET}) between 291 and 886 $m^2\ g^{-1}$ and a total pore volume between 0.16 and 0.46 $cm^3\ g^{-1}$. Based on its chemical composition and textural characteristics (high degree of surface development and porosity), samples prepared from baru provide high quality ACs with good adsorption capacity for organic pollutants, which will be carried out later.

Introduction

Activated carbons (ACs) have been used over the years in a wide range of environmental applications. Greater surface area and total pore volume, along with surface chemical groups, have given ACs a more versatile application for eliminating pollutants in both gas and aqueous phases [1].

Although the nature of porous adsorbent materials is quite diverse and variable, the use of AC in advanced oxidative processes by adsorption to remove organic pollutants has shown promising results [2–4].

Advanced Oxidative Processes constitute a class of technologies, which are mainly based on the in situ generation of hydroxyl radicals. AOPs are capable of removing organic pollutants non-selectively, regardless of their chemical nature [5]. In this context, this study aimed to bring a new use to wasted baru biomass, making sustainable use of baru (*Dipteryx alata* Vog.) shells in the synthesis of activated carbons and impregnated with copper oxides with the potential to be applied in Oxidative Processes Advanced.

Material and Methods

The biomass precursor (baru waste) was ground and sieved with a particle size of 2 mm. Activated carbons were prepared from the precursor material according to the methodology described by other authors [7]. First, the sample was impregnated with phosphoric acid (H_3PO_4, 85%) at an impregnation ratio of 1:2 (raw material:acid). Then, the mixture was heated up to 80°C and kept under mechanical stirring for 30 minutes. The resulting material was filtered and dried in an oven at 110°C for 15 hours. After this step, the impregnated material was carbonized in a tubular oven (FT 1200, Sanchis, Porto Alegre, Brazil) under the following conditions: temperature of 800°C for 40 minutes; heating rate of 20°C min-1 under nitrogen flow or in air (160 $cm^3\ min^{-1}$). After that, the carbonized sample was washed with distilled water until the pH was close to neutral. Finally, the activated carbon (ACB) gener-ated from baru waste was oven-dried at 50°C. In addition to these samples, non-activated baru carbon (CB) was also obtained. The process is the same as the preparation of ACB but in the absence of H3PO4 as activating agent. Surface modification of activated carbon with copper oxide (CuO) was performed by a simple wet impregnation method described elsewhere [6]. Different complementary techniques were used to characterize the samples. Morphology and chemical composition of carbons were determined by scanning electron microscopy (SEM). Nitrogen adsorption and desorption isotherms of AC samples were obtained in a Micrometrics ASAP instrument (Gemini V2380) at -196°C. Thermogravimetric analyses (TGA) of the samples were performed on a NET-ZSCH thermobalance ST409PC.

Results and Discussion

The carbonization processes were simulated on a thermobalance. The carbonization of baru shell follows a process analogous to that of other materials. The TG-DTG results (Figure 1) show the typical behavior of the decomposition of lignocellulosic materials, with two significant stages between 210 and 800 ºC, corresponding to the decomposition of hemicellulose and cellulose, respectively. The biochar yield is 22% in good agreement with the results obtained experimentally in the oven. The morphology of the ACs observed by SEM (not showed) also resembles that of ACs prepared from other biomass residues, particles that show large channels associated with the precursor structure. Textural features of carbonaceous materials were analyzed by nitrogen adsorption and desorption at -196°C and results are compiled in Figure 2 and Table 1. As it was expected, the CB sample, which did not undergo any activation step, presented a low surface area and reduced pore

volume, denoting that the chemical activation process is the main contributing factor in the development of microporosity and mesoporosity. Loading the activated carbon surface with CuO has a significant effect on micropore volume (0.30 cm^3 g^{-1}). Thus, comparing to activated carbon (ACB), the total pore volume, surface area and average width of micropores decreased. It seems that the loaded CuO particles blocked part of the micropore structure, having less effect on the mesopores.

Results found in the present work are comparable and even superior to other activated carbons generated from fruit wastes. For example, activated carbons from palm kernel shell activated in a nitrogen and air atmosphere showed a S_{BET} value of 457 m^2 g^{-1} [8]; while activated carbon based on lemon peel produced a S_{BET} value around 500 m^2 g^{-1} [9] and activated carbon derived from mangosteen peel generated S_{BET} values between 460 – 1039 m^2 g^{-1} [10]. Such textural characteristics are important in adsorption processes, since the application of mesoporous and microporous materials in these processes tends to increase the speed of pollutant degradation.

Table 1. Textural characteristics of adsorbent materials.

Samples	S_{BET} [m^2 g^{-1}]	V_T [cm^3 g^{-1}]	V_{micro} [cm^3 g^{-1}]	L_0 [nm]
CB	291	0.16	0.11	4.35
ACB	886	0.46	0.37	1.72
ACB/CuO	628	0.34	0.30	1.37

S_{BET}: BET surface área; V_T: total pore volume; V_{micro}: micropore volume; V_{meso}: mesopore volume; L_0: mean micropore width.

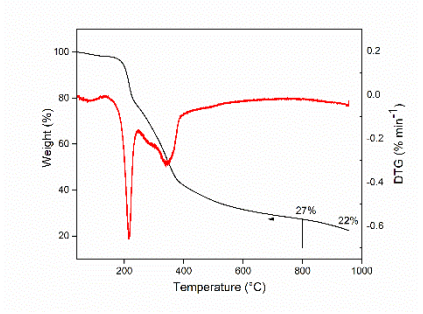

Figure 1. TGA and DTG curves of baru waste.

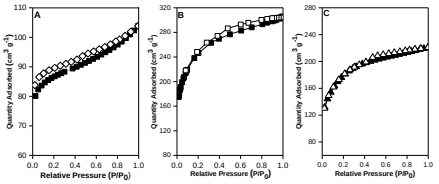

Figure 2. N_2 isotherms at -196°C: (A) non-activated baru carbon (CB), (B) baru activated carbon (ACB) and (C) baru activated carbon impregnated with copper oxide.

Conclusions

Baru waste has the potential to be used as a low-cost precursor in the generation of activated carbons, as it has significant levels of lignin, cellulose and hemicellulose, low ash content, leading to a considerable carbonization yield, even in high temperature conditions. Furthermore, it was possible to prepare carbonaceous materials and make surface modifications through the insertion of copper species improving the textural properties with greater development of porosity in the micro and mesopore regions. Based on these data, ACB and ACB/CuO samples can be excellent adsorbents for different adsorbates in aqueous solutions, which will be carried out later.

Acknowledgments

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