SPENT COFFEE GROUND BIOCHAR: OBTAINING AND USE IN HYDROLYSATE DEXTOXIFICATION

Letícia V. Moreno[1], Mariana de O. Bérgamo[1], Sâmilla G. de Almeida[1] & Kelly J. Dussán[1,2,3]

[1]*Department of Engineering, Physics and Mathematics, São Paulo State University (UNESP)/Institute of Chemistry, Araraquara, Brazil.*
[2]*Bioenergy Research Institute (IPBEN), São Paulo State University (Unesp), Araraquara, São Paulo, Brazil.*
[3]*Center for Monitoring and Research of the Quality of Fuels, Biofuels, Crude Oil, and Derivatives - CEMPEQC, Institute of Chemistry (UNESP), Araraquara, São Paulo, Brazil.*
** email address: leticia.v.moreno@unesp.br*

ABSTRACT

Biochar has a wide range of applications, including soil remediation agent, fuel for energy production and greenhouse gas reduction. Additionally, it can be utilized in emerging fields, such as an adsorbent used in the removal of various pollutants from effluents due to its low cost and process simplicity, as an activator in advanced oxidation processes, or even for energy storage as a supercapacitor. These high-value applications stem from the chemical composition and physicochemical characteristics of biochar that primarily consists of carbon, but it also contains significant amounts of oxygen, minerals, and small quantities of nitrogen and sulfur. The textural properties of biochar, including its high specific surface area and microporosity, make it an ideal compound for removing contaminants through physical adsorption processes. In this context, this work aims to produce biochar from spent coffee grounds and evaluate its adsorptive capacities for phenolic compounds in the hemicellulosic sugarcane bagasse and straw hydrolysates obtained in pretreatment acid stage.

Keywords: Waste Valorization. Biomass. Toxic Removal. Hydrolysate.

1 INTRODUCTION

According to the United Nations (UN), Brazil has a significant amount of food loss and waste, with quantities ranging from 23 million tons in 2021 to 82.1 million tons in 2019[1].These wastes are a direct source of lignocellulosic materials, requiring effective management strategies that convert waste into biomass to produce bioproducts. Biomass typically contains about 10-30% lignin, 15-35% hemicellulose and 30-50% cellulose. Environmental and agro-industrial changes have urged research and development of sustainable technologies using biotechnology and chemical engineering techniques.[2] Examples of lignocellulosic biomass include rice husks, animal manure, coffee, and sugarcane residues that are relevant for studies. Coffee waste consists of pulp, hulls, and grounds, while sugarcane waste includes bagasse and straw. These materials are used in the production of fuels, paper, bioplastics, and fertilizers, helping to reduce of greenhouse gas emissions.[3,4] Sugarcane residues facilitate the decomposition of organic matter, creating an environment conducive to microbial activity, enabling nutrient recycling, aiding in composting processes, and producing biofertilizers, ethanol, and other products. However, these phenolic-containing residues degrade hydrolyzed lignin and inhibit the growth and microbial activity necessary to produce these bioproducts. This requires investment in methods to remove these compounds, such as physicochemical extraction methods, resin treatment, oxidation, or through adsorbents such as biochar, which can effectively remove phenolic compounds due to its large surface area. [5,6,7] Biochar, a portmanteau of "biomass" and "charcoal," is a carbonaceous material produced by the thermal conversion of biomass through processes such as gasification, carbonization, torrefaction, or pyrolysis. It has multiple applications, including soil remediation, fuel, and greenhouse gas mitigation, and it is also effective as an adsorbent for pollutant removal.[8,9,10] While activated carbon biochar is commonly used to adsorb phenolic compounds, biochar derived from other organic materials, such as coffee grounds, can also be used. Therefore, the production of biochar from spent coffee grounds is a viable alternative for adsorbing phenolic compounds from sugarcane hydrolysates. This approach mitigates the negative impact of phenolic compounds on the microorganisms necessary for bioproduct production in a fermentative process.

2 MATERIAL & METHODS

Preparation of the sugarcane hydrolysate.

The production of sugarcane bagasse and straw hydrolysate was carried out in a pilot-scale reactor at the National Laboratory for BioRenewables, located at the National Center for Energy and Materials Research (CNPEM), on January 29, 2019. The conditions used for the mixture of sugarcane bagasse and straw were a solid-liquid ratio of 1:10, a temperature of 140°C, a sulfuric acid concentration of 0.5% (w/v), and a reaction time of 15 minutes. The resulting liquid was concentrated 2.5 times using a rotary evaporator, and aliquots of the concentrated hydrolysate were then used in detoxification tests.

Preparation of the carbonaceous material.

Biochar was produced by the pyrolysis process using the FORTELAB® FRO1100 rotary oven. Angle and temperature settings were varied: E1 (400°C, 6.7°), E2 (600°C, 6.7°), E3 (400°C, 2.1°), E4 (600°C, 2.1°), and E5 (500°C, 4.4°). These biochar samples were then used to determine their performance in adsorbing phenolic compounds.

Adsorption process.

To detoxify the concentrated hydrolysate, the pH was raised to 7 with CaO, followed by filtration. The remaining filtrate was treated with H_3PO_4 to pH 2.5 and filtered with a vacuum pump. Adsorption experiments were performed in 5 mL amber glass vials by adding 1% (w/v) biochar and 4 mL filtrate hydrolysate. These samples were placed on a shaker at 60°C for 30 minutes with agitation at 100 rpm. After agitation, the samples were filtered through Millipore® Swinnex filters with filter paper to remove the biochar. The filtrate was subjected to HPLC analysis on an Agilent® Zorbax Eclipse Plus C18 column at a flow rate of 0.8 mL/min and a temperature of 30°C with an eluent of acetonitrile (1:8) and 1% acetic acid to determine the phenolic compounds (5-HMF, furfural, syringaldehyde, ferulic acid, and benzoic acid) in the samples. All experiments were run in duplicate.

Determination of total phenols.

The concentration of total phenols was determined by adding 1 mL aliquots of the hydrolysate samples into test tubes and adjusting the pH to 12 using a 6M sodium hydroxide (NaOH) solution. Subsequently, the samples were diluted in a 250 mL volumetric flask, and their absorbance was measured at 280 nm using a spectrophotometer. The concentration of total phenols was calculated using Equations 1 and 2.

$$Total\ phenol\ (g/L) = 0.04187 \times \left(A - A_{dp}\right) - 0.0003279 \quad (1)$$

$$A_{dp} = (C_F \times \varepsilon_F - C_{HMF} \times \varepsilon_{HMF}) \quad (2)$$

Where, A_{dp} is the absorbance of sugar decomposition products (furfural and 5-HMF) at 280 nm; C_F and C_{HMF} are the concentrations of furfural and 5-HMF (g/L), determined by HPLC, ε_F and ε_{HMF} are the molar absorptivities of furfural and 5-HMF (146.85 and 114.00 L/g.cm, respectively).

ICUMSA coloration.

The hydrolysate's color was determined using the International Commission for Uniform Methods of Sugar Analysis (ICUMSA) method adjusted for the sugarcane bagasse and straw hydrolysate (Equation 3).

$$ICUMSA\ color\ (IU) = \frac{A_{420} \times 100}{\rho \times °Brix} \quad (3)$$

Where, °Brix represents the amount of soluble solids in the concentrated sample; A420 is the absorbance determined in a spectrophotometer at 420 nm using deionized water as reference; and ρ is the density of the sample.

3 RESULTS & DISCUSSION

Analysis of phenolic compounds.

These phenolic compounds are related to the extracted lignin present in the biomass. In Table 1, a significant reduction in phenolic compounds can be observed when comparing the concentrated hydrolysate and the detoxified hydrolysate (after adsorption by the carbonaceous material). When comparing the E3 and E5 samples with the concentrated hydrolysate, 25% of 5-HMF was removed, and the E3 sample removed 12% and 25% of furfural and syringaldehyde, respectively.

Table 1 Phenolic concentrations in the samples.

Sample	5-HMF (mg/L)	Furfural (mg/L)	Syringaldehyde (mg/L)	Ferulic Acid (mg/L)	Benzoic Acid (mg/L)
E1	780.7 ± 115.62	76.2 ± 17.67	115.4 ± 7.43	0.86 ± 0.300	532.4 ± 73.15
E2	832.4 ± 110.68	86.9 ± 15.97	125.8 ± 1.86	1.59 ± 1.281	503.0 ± 40.81
E3	772.4 ± 130.07	78.5 ± 15.78	113.3 ± 0.91	1.59 ± 0.768	504.5 ± 19.97
E4	786.6 ± 12.00	99.3 ± 0.24	126.0 ± 4.07	1.49 ± 1.174	567.7 ± 13.84
E5	771.3 ± 136.08	82.5 ± 18.76	113.9 ± 4.60	0.90 ± 0.101	510.0 ± 1.55
Concentrated hydrolysate	1028.7	89.3	150.2	n.d.	n.d.

Figure 1 shows the total phenols removed after detoxification of concentrated hydrolysate using different biochars (E1 to E5). The better condition was the sample E3 which presented a 42% of removal of total phenols. This biomaterial used as adsorbent was synthesized at 400°C with a reactor angle of 2.1°. The low inclination angle allows a longer residence time in the tubular furnace, ensuring the completion of the pyrolysis process and potentially resulting in a larger surface area for the adsorption process. Further analysis is required to confirm these results.

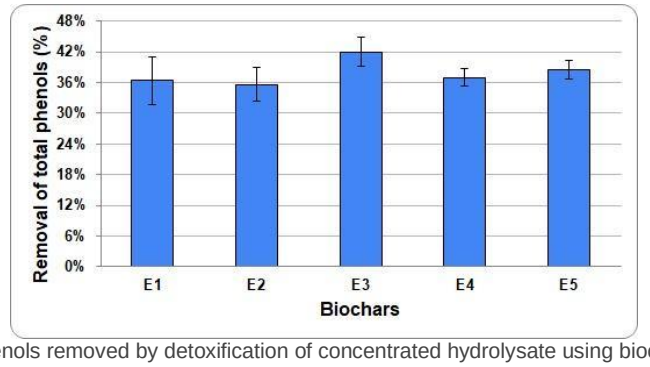

Figure 1 Total phenols removed by detoxification of concentrated hydrolysate using biochar as adsorbent.

ICUMSA Coloration Analysis

The ICUMSA test is used to evaluate differences in coloration based on the amount of phenolics still present in the concentrated hydrolysate. In this study, the ICUMSA test was used to quantify the color in the concentrated hydrolysate (Table 2). The ICUMSA test values indicate that darker solutions correspond to higher concentrations of phenolic compounds. Therefore, the concentrated hydrolysate had the highest ICUMSA (423 IU). In contrast, the biochar-treated hydrolysate with the highest phenol adsorption capacity shows a lighter color with an ICUMSA value of 197 IU (E3), confirming a reduction in phenol concentration.

Table 2 ICUMSA coloration and visual reference.

Sample	ICUMSA color (IU)	Visual Reference
E1	194	
E2	220	
E3	197	
E4	214	
E5	228	
Concentrated hydrolysate	423	

4 CONCLUSION

Based on the total phenol concentrations and ICUMSA analysis, it is evident that the biochar produced from spent coffee grounds at 400°C with a reactor angle of 2.1° showed superior performance in adsorbing phenolic compounds from concentrated hydrolysates of sugarcane bagasse and straw. Further studies should be conducted to determine the initial sugar content of the concentrated hydrolysate and after contact with the carbonaceous material. However, the results indicate a promising potential for removing phenols and thereby improving the environment for the microorganisms necessary to produce bioproducts such as ethanol or xylitol. The impact of this research is significant because it not only provides an effective solution for managing agricultural waste, but also improves the sustainability of bioproducts production processes. By improving the efficiency of microbial fermentation, this approach can help reduce the overall carbon footprint and advance the development of green technologies.

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ACKNOWLEDGEMENTS

The authors grateful to the Research Foundation of São Paulo (FAPESP): grant number #2022/03000-0 and # 2023/03650-8 for financial support of the current study.