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EFFECTS OF NON-THERMAL PLASMA ON GUARANA RESIDUE: PRELIMINARY STUDY ON BIOMASS MODIFICATION

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ABSTRACT

Enhancing production chains by valorizing waste from lignocellulosic biomass highlights green chemistry role in sustainable development and environmental waste management. This study aimed to characterize guarana (*Paullinia cupana*) residues and conduct a preliminary investigation on the use of non-thermal plasma (NTP) as a pretreatment. The results demonstrated that NTP treatment significantly increased the cellulose content from 38.0% ± 1.2 to 55.2% ± 0.9. Hemicellulose content remained practically constant, with a slight increase from 24.9% ± 1.5 to 27.4% ± 0.5. The lignin fractions (insoluble, soluble, and total) did not show variations, indicating that NTP treatment does not affect lignin for the conditions tested in this study. The extractive content decreased substantially from 12.4% ± 1.2 to 4.4% ± 0.03. These findings suggest that NTP can affect the guarana residue composition which might be applied for subsequent biochemical processing, highlighting its potential for sustainable and eco-friendly industrial applications. Further research is needed to optimize treatment conditions and assess economic feasibility on an industrial scale.

Keywords: Guarana residue. Non-thermal plasma. Biomass valorization. Lignocellulosic biomass. Biorefinery.

1 INTRODUCTION

The valorization of production chains involves adding value to waste or lignocellulosic biomass, underscoring the significance of green chemistry to enable sustainable development, mitigate environmental damage, and manage the residues across several industrial processes.[1] Guarana (*Paullinia cupana*) is considered a crucial plant biomass in the state of Amazonas, ranking as the second-largest national producer in 2022.[2] Indigenous to the Amazon region and historically utilized by local tribes, guarana is cultivated across several municipalities, notably Maués, Presidente Figueiredo, and Urucará.[3] Residues from guarana processing primarily consist of lignocellulosic biomass, comprising cellulose, hemicellulose, and lignin in varying proportions. Notably, the economic significance of guarana seeds is evident, extensively employed in the production of energy drinks, particularly within the soft drink industry. Moreover, its application has expanded to other sectors such as cosmetics and pharmaceuticals, attributable to its nutritional and medicinal attributes, including high caffeine content and the presence of bioactive compounds.[4] Nonetheless, substantial waste is generated during processing, encompassing residual peel, pulp, and seeds, which are presently underutilized, predominantly for organic fertilizer production.[5,6]

From lignocellulosic materials, fermentable sugars can be derived. Thus, pretreatment assumes paramount importance, enhancing cellulose breakdown efficiency and crystallinity while dismantling the complex structure of lignocellulosic biomass. Various pre-treatment methods are available, encompassing acid [7,8], alkali [9,10], enzymatic [11], steam explosion [12,13], ozone [14,15] and plasma[16] techniques. Each method harbors distinct advantages and drawbacks, with selection contingent upon the specific characteristics of the lignocellulosic biomass and the conversion process objectives. In this regard, the utilization of non-thermal plasma (NTP) [17,18] as a pre-treatment technique for lignocellulosic materials has garnered attention, capable of reducing lignin content and enhancing the value of products derived from its constituents. Predominantly, these methods find application in lignocellulosic ethanol production, bio-oil production, cellulose, and paper manufacturing, paper pulp bleaching, and chemical product synthesis[7-16]. In this sense, the present study aims to characterize guarana residue while proposing a preliminary investigation into the application of NTP. Leveraging low-cost and innovative treatment technologies will facilitate the production of high-value biomolecules, fostering income generation, local economic development, and environmental preservation.

2 MATERIAL & METHODS

Guarana (*Paullinia Cupana*) was acquired from the municipality of Urucará - AM. Guarana residue was obtained after extraction of the seeds (roasted and ground) using a 50% hydroethanolic solution, with a seed ratio of 1:3 (w/w), mechanically agitated for 24 hours at 25°C in the dark [19]. For compositional analysis of guarana residue, NREL analytical methods for standard biomass analysis were employed. Extractives were estimated through sequential extraction using a cellulose cartridge in a Soxhlet system with water and ethanol [20]. Ash content was determined by calcination of dried samples in a muffle furnace at 575°C for 4 h [21]. Subsequently, a 300 mg portion of guarana residue was hydrolyzed with 72% (v/v) H_2SO_4 for 1 h at 30°C, followed by autoclaving at 120°C for 1 h and filtration. Insoluble acid lignin content was determined using the retained residue, while soluble lignin content was determined by spectrophotometry at 280 nm using the permeated liquid. Structural sugars in the hydrolyzed liquor were quantified via HPLC using a Biorad HPX 87H column and refractive index detector, with 0.005 M H_2SO_4 as the mobile phase at a flow rate of 0.6 mL/min, using monomeric sugars as reference standards [22].

Finally, the residue underwent NTP pretreatment conducted in a dielectric barrier discharge reactor, using a liquid-to-solid ratio of 20 ($Kg_{Water}/Kg_{Biomass}$) for 1 h. The reaction was initially conducted at 25°C. Characterization of the pre-treated biomass was performed according to NREL methods as described above.

3 RESULTS & DISCUSSION

Understanding the chemical composition of guarana residue is crucial for choosing potential applications and optimizing its utilization in various industries. Differences in chemical composition can significantly impact the effectiveness of guarana residue in different applications, making it important to compare current findings with existing literature. Table 1 presents a comparison between the chemical composition of guarana residue obtained in this study and the values reported in the literature.

Table 1 Comparison of the composition of guarana residue with literature values

Component	Oliveira Júnior *et al*. (2022) [23] (%)	This study (%)
Cellulose	19.16 ± 1.07	38.00 ± 1.18
Hemicellulose	32.83 ± 1.03	24.97 ± 1.52
Lignin	6.06 ± 0.31	3.49 ± 0.85
Ash	7.37 ± 0.42	4.65 ± 1.03

The data in Table 1 reveal differences between experimental results and literature values. The cellulose content found in this study was 38.0% ± 1.9, whereas the literature reports 19.2% ± 1.1. Hemicellulose content was 24.97% ± 1.5 compared to 32.8% ± 1.03 found by Oliveira Júnior *et al*. (2022) [23]. Similarly, the lignin content obtained was 3.5% ± 0.8, whereas the literature reports 6.1% ± 0.3. These differences in the chemical composition of guarana residue can be attributed to variations in extraction and processing methods, as well as specific cultivation conditions and intrinsic characteristics of the guarana plants used in each study.

After, the NTP pretreatment was used to evaluate changes in guarana composition. Table 2 summarizes the chemical composition of the guarana residue before and after NTP treatment, highlighting the average percentages and standard deviations of the analyzed samples.

Table 2 Composition of the residue before and after NTP pretreatment

Component	Before (%)	After (%)
Cellulose	38.00 ± 1.18	55.24 ± 0.90
Hemicellulose	24.97 ± 1.52	27.43 ± 0.49
Insoluble Lignin	3.49 ± 0.85	3.12 ± 0.31
Soluble Lignin	1.16 ± 0.19	1.64 ± 0.08
Total Lignin	4.65 ± 1.03	4.76 ± 0.22
Extractives	12.37 ± 1.24	4.39 ± 0.03
Ash	1.75 ± 0.02	0.36 ± 0.04

The results presented in Table 2 indicate chemical composition changes in guarana residue after NTP pre-treatment. The cellulose content substantially increased from 38.0% ± 1.2 to 55.2% ± 0.9. This increase suggests that NTP treatment is effective in concentrating the cellulose fraction, possibly due to the removal of other components. Hemicellulose remained practically constant, showing a slight increase from 24.97% ± 1.5 to 27.4% ± 0.5. Insoluble lignin content remained relatively constant, changing slightly from 3.5% ± 0.8 to 3.1% ± 0.3, while soluble lignin content did not show variation, changing from 1.2% ± 0.2 to 1.6% ± 0.1. These minor changes suggest that NTP treatment does not significantly affect the lignin fractions for the conditions tested in this study. Total lignin also showed minimal variation, changing from 4.7% ± 1.0 to 4.8% ± 0.2.

The relative stability of hemicellulose and total lignin contents suggests that NTP selectively affects certain biomass components, possibly due to differences in chemical structures and plasma reactivity. These findings highlight the potential of NTP pretreatment to enhance the production of sugars or other added-value products from guarana residue, as the increased cellulose content could lead to higher yields in subsequent processes.

4 CONCLUSION

The NTP pretreatment has modified the chemical composition of guarana seed waste under the investigated conditions in this study. An increase in cellulose content occurred, which can be mainly attributed to the removal of extractives, and a reduction in ash contents, while total lignin and hemicellulose remained relatively constant. These changes suggest that NTP may enhance biomass preparation for bioconversion processes.However, it is essential to consider that the cellulose increase and extractives reduction, although promising, require a deeper understanding of the mechanisms involved in NTP treatment. Therefore, further experiments are needed to optimize treatment conditions, assess result consistency across different biomass batches, and explore the economic viability and sustainability of this process on an industrial scale. Additionally, investigating plasma interaction with specific components could provide valuable insights for customizing treatment according to specific industrial needs.

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