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SUSTAINABLE POTENTIAL OF CANTALOUPE MELON PEEL: SEQUENTIAL ACID/ORGANOSOLV PRE-TREATMENT METHOD

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ABSTRACT

This study proposes a scheme for fractionation and valorization of the potential of cantaloupe melon peel, a significant byproduct of the Brazilian agricultural industry. The methodological process consisted of fractionation through a sequential method of diluted acid pre-treatment/acid organosolv. In the first step, acid pre-treatment was optimized under conditions of 110°C, 0.5% sulfuric acid, and 45 minutes of reaction, resulting in a sugar release efficiency of 144%. Subsequently, the solid fraction obtained under these optimized conditions was delignified by the acid organosolv method, resulting in delignification and sugar efficiency rates, relative to the raw material, of 22.5% and 244%, respectively, achieved at 180°C. The results obtained indicate the promising feasibility of this approach for the utilization of cantaloupe melon peel waste, as it not only contributes to reducing the disposal of this waste in the agro-industrial process but also provides an alternative for the economical and sustainable production of bioethanol.

Keywords: Agricultural sustainability. Cucumis melo var. cantalupensis. Lignocellulosic residues. Biofuels.

1 INTRODUCTION

In Brazilian agriculture, melon production takes center stage, particularly in the Northeast region, where more than 90% of the national output is concentrated. Rio Grande do Norte alone contributes 58.23% of this total, as per SEBRAE.¹ The substantial fruit production generates a significant amount of waste, posing environmental and economic challenges that could be more effectively addressed. Melon consists of lignocellulosic biomass, predominantly composed of cellulose, hemicellulose, and lignin, giving it a high potential for generating value-added products. Among the various promising applications, the production of biofuels, such as bioethanol, stands out. This conversion of waste would not only reduce dependence on fossil fuels but also help mitigate the environmental impacts associated with the production and use of these fuels.

In the production of bioethanol, it is necessary to fractionate the lignocellulosic material, reducing the crystallinity of its complex structure, removing part of the lignin and hemicellulose, increasing the material's porosity, and enabling the obtainment of fermentable sugars. Various chemical, physical, and biological methods can be employed for sugar transformation. In the study conducted by Ashokkumar et al.,² pre-treatment with diluted sulfuric acid at 160°C is highlighted as an essential step in the delignification process of lignocellulosic biomass. Additionally, Pals et al.³ emphasize the importance of organosolv pre-treatment to remove lignin and hemicellulose, resulting in a residue rich in cellulose that can be hydrolyzed more easily.

Hence, this study aims to utilize the Box-Behnken method for diluted acid pre-treatment, examining the interplay between crucial parameters to enhance the liberation of fermentable sugars from the material. Moreover, it intends to assess the impact of the sequential organosolv method on the efficacy of this process. The study's objective is to ascertain the viability of Cantaloupe melon peels (Cucumis melo var. cantalupensis) as a residue for sustainable biofuel production. Consequently, it is anticipated to foster the progression of more sustainable and responsible agricultural practices.

2 MATERIAL & METHODS

The material characterization involved lignocellulosic analyses, performed in triplicate, covering extractives, lignin, holocellulose, alpha-cellulose, and hemicellulose. These analyses strictly followed the guidelines established by TAPPI standards, as cited by Morais et al.,⁴ for both the raw material and the samples subjected to acid and acid organosolv treatments. An acid pre-treatment was performed on the melon peel using a Box-Behnken experimental design. The independent variables included temperature (110, 130, and 150°C), sulfuric acid concentration (0.5, 1, and 1.5%), and time (30, 45, and 60 minutes), while the ratio of dry mass to acid volume was kept constant at 1/12 (w. v⁻¹). Subsequently, using the most efficient experimental condition obtained in this pre-treatment, two organosolv treatments were conducted, with temperature variations between 150°C and 180°C. In these treatments, the concentration of ethanol solvent (50%), sulfuric acid (1%), treatment duration (30 minutes), and the ratio of dry mass to volume (1/12 w. v⁻¹) were maintained constant.

3 RESULTS & DISCUSSION

The data regarding the physicochemical characterization of Cantaloupe melon peel in its natural state and after treatments with diluted acid and acid organosolv are presented in Table 1.

TREATMENT	(TE%)	(TL%)	(THO%)	(TA%)	(THE%)
Raw natural material	7,20 ± 2,1	8,04 ± 2,1	52,99 ± 2,35	27,87 ± 2,47	25,11 ± 0,12
Organosolv/ acid pretreatment	5,72 ± 0,11	$6,88 \pm 0,96$	53,96 ± 0,25	37,77 ± 1,58	$15,24 \pm 1,33$

Table 1 Characterization of Cantaloupe Melon Peels

TE%: Extractives Content; TL%: Lignin Content; THO%: Holocellulose Content; TA%: α-Cellulose Content; THO%: Hemicellulose Content

Comparing the data presented in Table 1 with the literature reveals notable differences. While Gómez-García⁵ recorded a lignin content in raw natural material melon peels (Cucumis melo var. inodorus) of approximately 26.46%, this study obtained a considerably lower value, reaching only 8.20%. However, the results for alpha-cellulose are more similar: Gómez-García⁵ found 27.68%, while this study obtained 27.87%. These differences can be attributed to the variety of melons analyzed. Furthermore, the material studied here shows promising traits, such as its low lignin content, which facilitates biofuel production, and its high alphacellulose content, suggesting the potential for producing fermentable sugars. Melon peels have a complex chemical composition, including cellulose, lignin, and hemicellulose, requiring pre-treatment steps to obtain fermentable sugars. The acid organosolv pretreatment method, widely used, selectively removes lignin and hemicellulose from the biomass, improving enzymatic digestibility. The acid organosolv pre-treatment method is widely employed to selectively remove and depolymerize lignin and hemicellulose from the biomass, as highlighted by Carvalheiro et al.⁶ As evidenced in the study by Cardoza et al.,⁷ this technique improved the enzymatic digestibility of grapevine shoots by partially removing lignin, resulting in a higher cellulose conversion rate. Additionally, the results obtained in this work show a solubilization in the lignin content (TL) and hemicellulose content (THE) of 14.4% and 39.3%, respectively. In the study conducted by Pazzaglia et al.,8 they used wood bark residues, where applying the acid organosolv method, they managed to solubilize about 33% of TL and 61.2% of THE at 160°C for 15 min using a solution of 2% w/w H₂SO₄ and 0.8% w/w ethanol concentration. However, in a study conducted by Agnihotr et al.⁹ using spruce wood (Picea abies), a delignification of approximately 65% at 235°C was observed. Despite significant differences in solubilized contents, it is essential to emphasize that these are distinct materials, each with its peculiar structures. Figure 1 illustrates the solid and liquid fractions of the natural raw material after sequential acid/organosolv pre-treatment, showing the resulting powder and liquor.



Figure 1 Raw natural material and after sequential acid/organosolv pretreatment

The optimal conditions for the sequential treatment, resulting in the highest sugar release efficiency, were achieved by employing the following parameters: for the first step of diluted acid pre-treatment, a temperature of 110° C, sulfuric acid concentration of 0.5%, and a reaction time of 45 minutes. For the second step using the acid organosolv method, favorable conditions included a temperature of 180°C, ethanol solvent concentration of 50%, sulfuric acid concentration of 1%, reaction time of 30 minutes, and a dry mass to volume ratio of $1/12 \text{ w. v}^{-1}$. The concentrations of reducing sugars (RS) and the efficiency obtained at the end of each step are presented in Table 2.

Table 2 Reducing :	sugars concentration
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Condition	RS concentration (g/L)	
Raw natural material	0,63	
Acid pretreatment	1,54	
Organosolv acid	2,17	

In terms of the number of sugars generated after applying this sequential treatment to the raw material, as shown in Table 2, there is a notable increase in the concentration of reducing sugars of approximately 244% compared to the raw material. In a similar study, Cardoza et al.⁷ employed this sequential strategy under comparable conditions, using vine shoots, and effectively fractionated this biomass through sequential acid-organosolv pretreatment, recovering over 80% of the sugars present for ethanol conversion. Consistent with these results, Carvalheiro et al.⁶ demonstrated that pretreatment application to the material using diluted H_2SO_4 resulted in a significant improvement in sugar production from lignocellulosic biomass, facilitating hemicellulose solubilization and lignin structure breakdown, exposing cellulose and making it more accessible for subsequent processing.

4 CONCLUSION

The results have shown that cantaloupe melon peel represents a promising renewable source with the potential to produce various value-added products, particularly the biofuels investigated in this study. This finding not only promotes environmental, economic, and social benefits but also highlights the effectiveness of a sequential method of diluted acid pre-treatment/acid organosolv in lignin and hemicellulose solubilization and fermentable sugar production, underscoring the favorable properties of the material for biofuel generation. These confirmations have significant implications for sustainable development, providing valuable insights for practical applications. It is worth noting that this study has some limitations, such as equipment constraints; therefore, future research should focus on exploring properties not addressed in this study.

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