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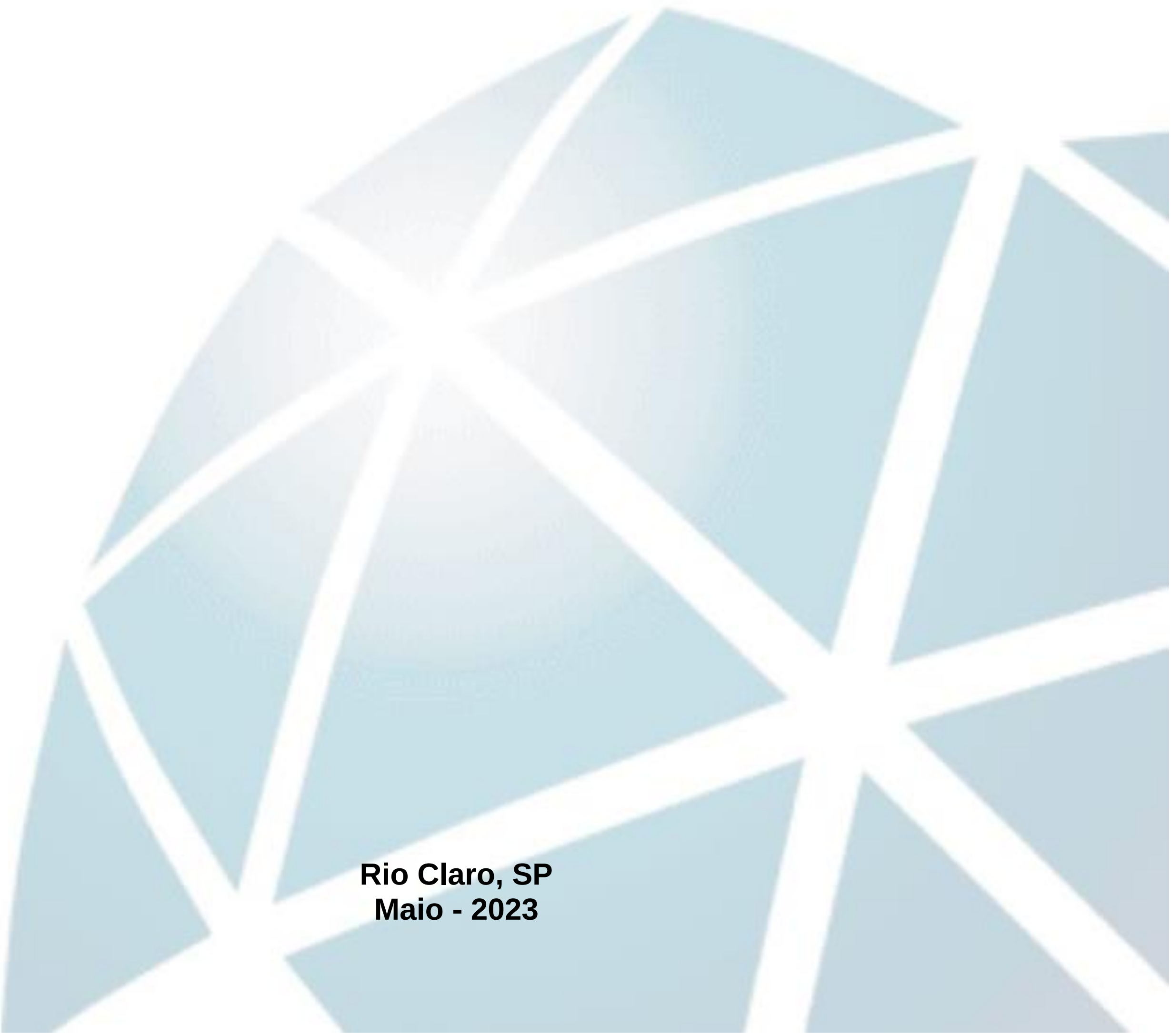
“JÚLIO DE MESQUITA FILHO”
INSTITUTO DE PESQUISA EM BIOENERGIA

IPBEN
Instituto de Pesquisa
em Bioenergia

PROGRAMA INTEGRADO (UNESP, USP E UNICAMP) DE PÓS-GRADUAÇÃO EM BIOENERGIA

ORGANOSOLV PRETREATMENT ASSESSMENT ON FRUIT WASTE TO OBTAIN PLATFORM CHEMICALS AND BIOPLASTICS

HERNÁN DARÍO ZAMORA ZAMORA



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Tese apresentada ao Instituto de Pesquisa em Bioenergia de Rio Claro, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Doutor em Ciências.

Orientador: Prof. Dr. Michel Brienzo

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AUTOR: HERNÁN DARÍO ZAMORA ZAMORA

ORIENTADOR: MICHEL BRIENZO

Aprovado como parte das exigências para obtenção do Título de Doutor em Bioenergia, área: Bioenergia pela Comissão Examinadora:

Prof. Dr. MICHEL BRIENZO (Participaçao Virtual) M.Brienzo
Laboratorio de Caracterizacao de Biomassa / Instituto de Pesquisa em Bioenergia UNESP Rio Claro

PROFESSOR ADJUNTO DANIEL PASQUINI (Participaçao Virtual)
Instituto de Química / UNIVERSIDADE FEDERAL DE UBERLÂNDIA

Prof. Dr. JESÚS DAVID CORAL MEDINA (Participaçao Virtual)
Departamento de Engenharia / Universidade Cooperativa de Colômbia

Profa. Dra. VILÁSIA GUIMARÃES MARTINS (Participaçao Virtual)
Escola de Química e Alimentos / Universidade Federal do Rio Grande (FURG)

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To God for the opportunity to live.

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RESUMO

Esta pesquisa consistiu em duas fases principais, a primeira relacionada com avaliar os efeitos de um pré-tratamento organossolve etanólico catalisado por álcali (OHEOP) na composição e estrutura lignocelulósica (LC) do pseudocaule de bananeira e da torta de semente de goiaba, e na obtenção de uma fração rica em celulose (CL), hemiceluloses (HC) e lignina (LG). E, a segunda fase relacionada com a produção e caracterização de bioplásticos com base em quitosana (Ch) e adição de HC e LG extraídos de pseudocaule de bananeira e da torta de semente de goiaba. Na primeira fase, a avaliação do OHEOP foi realizada por meio de um planejamento composto central 2^3. Os fatores do planejamento foram a concentração do álcali (OHC) em relação à massa do resíduo, temperatura (T), e concentração da solução aquosa de etanol (EC), e as variáveis de resposta foram o rendimento mássico de HC extraídas (HCy), o rendimento mássico de LG extraída (LGy) e a conversão de celulose (CLX). Além disso, o OHEOP envolveu caracterizações químicas dos resíduos pré-tratados e não tratados, e hidrólise enzimática (Cellic® CTec2). As HC e LG extraídas foram analisadas por espectroscopia de infravermelho com transformada de Fourier (FTIR), comparando-as com produtos comerciais. Com um nível de confiança de 95%, a T foi o fator com maior influência nas variáveis de resposta. Para o pseudocaule de bananeira, 78% correspondeu ao máximo HCy (a 170 ºC, EC de 30%, e OHC de 60%), 35.2% para LGy (a 170 ºC, EC de 30%, e OHC de 10%) e 96.6% para CLX (a 120 ºC, EC de 70%, e OHC de 60%). E, no caso da torta de semente de goiaba, 97.3% foi o mais alto HCy (a 170 ºC, EC de 30%, e OHC de 60%), 45.0% para LGy (a 170 ºC, EC de 30%, e OHC de 60%), e 50.3% para CLX (a 170 ºC, EC de 30%, e OHC de 60%). Na segunda fase, bioplásticos foram produzidos pelo método casting, apresentando uma estrutura homogênea, flexível, e sem rachaduras, e tendo a intensidade da cor aumentando proporcionalmente com a massa de HC e LG adicionadas. Os bioplásticos com adição de 10, 5, e 25% de HC apresentaram maior teor de umidade (22.3%), solubilidade em água (22.4%), e opacidade (1.95 mm^{-1}), respetivamente. A adição de 10% de LG no bioplástico resultou nas maiores percentagens de umidade (19.4%) e opacidade (4.75%). A adição de HC e LG melhorou a resistência à tração e o módulo de Young, enquanto o inchamento dos bioplásticos reduziu. A análise termogravimétrica revelou que a degradação dos bioplásticos ocorreu em quatro etapas diferentes; a primeira de evaporação de água e ácido acético, a segunda de degradação de glicerina, a terceira de despolimerização de HC, Ch e LG, e a última correspondente à etapa de carbonização. De acordo com os resultados o OHEOP permitiu extrair HC e LG semelhantes aos encontrados comercialmente, e estes componentes como aditivos na produção de bioplásticos contribuíram com a melhoria em algumas propriedades, com potencial para aplicação na indústria de alimentos ou na medicina.

Palavras-chaves: Pré-tratamento; Organossolve; Hemiceluloses; Lignina; Bioplásticos.

ABSTRACT

This research consisted of two main phases, the first one related to assess effects of an ethanolic organosolv pretreatment catalyzed by alkali (OHEOP) on the lignocellulosic (LC) composition and structure of banana pseudostem and guava seed cake, and on the obtaining of a rich fraction in cellulose (CL), hemicelluloses (HC) and lignin (LG). And the second one linked to produce and characterize bioplastics based on chitosan (Ch) and addition of HC and LG extracted from banana pseudostem and guava seed cake. In the first phase, the OHEOP evaluation was performed through a central composite design 2^3. The factors were the alkali concentration (OHC) in relation to the waste mass, temperature (T), and concentration of the ethanolic aqueous solution (EC), and the response variables were the mass yield of extracted HC (HCy), the mass yield of extracted LG (LGy), and the cellulose conversion (CLX). Additionally, the OHEOP involved chemical characterizations of the pretreated and untreated wastes, and enzymatic hydrolysis (Cellic® CTec2). The extracted HC and LG were analyzed by Fourier-transform infrared (FTIR) spectroscopy, comparing them with commercial products. With a confidence level of 95%, T was the factor with the greatest influence on the response variables. For banana pseudostem, 78% corresponded to the maximum HCy (at 170 ºC, EC of 30%, and OHC of 60%), 35.2% for LGy (at 170 ºC, EC of 30%, and OHC of 10%) and 96.6% for CLX (at 120 ºC, EC of 70%, and OHC of 60%). And, in the case of guava seed cake, 97.3% was the highest HCy (at 170 ºC, EC of 30%, and OHC of 60%), 45.0% for LGy (at 170 ºC, EC of 30%, and OHC of 60%), and 50.3% for CLX (at 170 ºC, EC of 30%, and OHC of 60%). In the second phase, bioplastics were produced by the casting method, presenting a homogeneous, flexible, and without cracks structure, and having the color intensity increasing proportionally with the mass of added HC and LG. Bioplastics with the addition of 10, 5, and 25% of HC had the highest moisture content (22.3%), water solubility (22.4%), and opacity (1.95 mm^{-1}), respectively. The addition of 10% of LG in the bioplastic resulted in the highest percentages of moisture (19.4%) and opacity (4.75 mm^{-1}). The addition of HC and LG improved tensile strength and Young's modulus, while swelling was reduced. The thermogravimetric analysis (TGA) revealed that the bioplastics degradation occurred in four different stages; the first of water and acetic acid evaporation, the second of glycerin degradation, the third of HC, Ch, and LG depolymerization, and the last one corresponding to the carbonization stage. According to the results, the OHEOP allowed to extract HC and LG similar to the commercial ones, and these components as additives in the production of bioplastics contributed to improve some properties, with potential for application in the food or medical industry.

Keywords: Pretreatment; Organosolv; Hemicelluloses; Lignin; Bioplastics

ABBREVIATIONS

1G	First generation
2G	Second generation
ADH	Alcohol dehydrogenase
AI	L-arabinose isomerase
AR	Arabinose
AR(XR)	Aldose reductase
ATP	Adenosine 5′-triphosphate
BRF	Biorefinery
BS	Biomass
Ch	Chitosan
CL	Cellulose
CLX	Cellulose conversion/Glycose yield
D-XY	D-xylose
DNA	Deoxyribonucleic acid
EC	Ethanol concentration
EDTA	Ethylenediamine tetraacetic acid
FTIR	Fourier Transform Infrared
GSH	Glutathione
HC	Hemicelluloses
HCy	Mass yield of extracted hemicelluloses
HDPE	High density polyethylene
L-AR	L-arabinose
LAD	L-arabitol-4-dehydrogenase
LC	Lignocellulosic
LCH	Lignocellulosic hydrolysate
LG	Lignin
LGy	Mass yield of extracted lignin
LXR(ALX)	L-xylulose reductase
MFS	Major facilitator superfamily
OHC	Alkali concentration
OHEOP	Alkali ethanolic organosolv pretreatment
PB	Pretreated biomass

PDC	Pyruvate decarboxylase
PP	Polypropylene
PPP	Pentose-phosphate pathway
QTL	Quantitative trait loci
R5PE	L-Ribulose-5-P-4-epimerase
RK	L-Ribulokinase
RNA	Ribonucleic acid
ROS	Reactive oxygen species
SEM	Scanning electronic microscopy
SNPs	Single nucleotide polymorphisms
T	Temperature
TCA	Tricarboxylic acid
TFs	Transcription factors
VB	Vegetal biomass
XDH	D-xylulose reductase
XI	Xylose isomerase
XK	Xylulokinase
XR	Xylose reductase
XDH	Xylitol dehydrogenase
XY	Xylose

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GENERAL INTRODUCTION

Currently, it is no longer a secret that lignocellulosic (LC) biomass is being considered as a strong and potential option to substitute fossil resources, since the last ones, despite being used to obtain different types of products (fuels, plastics, clothing, chemicals, and so on) have been commonly pointed out for causing negative alterations to natural ecosystems and adverse effects on human health. When LC biomass comes from vegetal waste, this is regarded as a better alternative, due to it does not interfere with crops destined for human food, shows wide availability, is relatively low cost, represents the key for the bioeconomy development, and can be harnessed in a similar route than oil through refinery scheme (SHIMIZU *et al.*, 2020). The generation of biomass-based products (also called bioproducts) using a refinery scheme is known as biorefinery, which effectively uses biomass for the combined development of several categories of products such as biofuels, biopolymers, biomaterials, carboxylic acids, pharmaceuticals, sweeteners, and platform chemicals (FLÓREZ; LÓPEZ; LOZANO, 2018).

The biggest challenges of a biorefinery are related to achieve high conversion yields through technologies with suitable cost-effective, which means, low cost, low production time, low energy consumption, cheap raw materials, high value-added bioproducts, and environmentally friendly processes (CORAL; MAGALHAES, 2020). Much research experiences involving biorefinery have been completed using diverse LC wastes come from sugarcane (straw and bagasse), rice (spent grounds, husk, and straw), corn (cob and leaves), coffee (pulp and husk), fruit (peel, seeds, and vegetal plant byproducts), etc. In every case, LC material was conditioned through pretreatment processes in order to generate a loose biomass allowing better accessibility to its main constituents (CL, HC, and LG) (MANKAR *et al.*, 2021). Thus, the generation of bioproducts via biorefinery depends on pretreatment performance and use related to what constituent(s) is(are) desired for preservation, solubilization, or even breaking down (ZAMORA *et al.*, 2021). Organosolv pretreatment is a promissory process with great versatility among the pretreatments used in a biorefinery since it can take several configurations and thus obtain CL-rich, HC, and LG individual solid fractions as a result of the LC biomass deconstruction (PURKAIT; HALDAR, 2021; VAIDYA *et al.*, 2022).

In the whole world exist many types of LC waste and its vast generation should be harnessed. Among them, fruit wastes are LC materials that have provoked great interest in research and industries (MANHONGO *et al.*, 2022; TSEGAYE; JAISWAL; JAISWAL, 2021). In 2020, banana was the most produced fruit in the world with 119.83 million tons, followed by watermelon, apple, grape, orange, and guava with 101.62, 86.44, 78.03, 75.46, and 54.83 million tons, respectively (SHAHBANDEH, 2022a). It is estimated that 1 ton of harvested banana generates 3 tons of pseudostem (CHANG *et al.*, 2014; SOUZA *et al.*, 2014). Brazil stands out in the fruit world production being the third global producer, which leads to great amounts of waste generated from fruits (SHAHBANDEH, 2022b). In 2020, were produced around 6.64 million tons of banana (IBGE, 2022), which supposes an estimated generation of 19.9 million tons/year of pseudostem, becoming a potential LC source to obtain diverse bioproducts using a biorefinery scheme. On the other hand, fruit wastes are also generated in industries, such as the guava industry, which is stood out for its economic importance in various regions worldwide, owing to the high agricultural yield of the fruit and the permanent demand for its products that are industrially obtained (ANGULO-LÓPEZ *et al.*, 2021). During the industrial process of pulp extraction from guava, seeds (mostly) and peel are generated as byproducts (commonly called as guava seed) (BIBWE *et al.*, 2022). Despite being commonly discarded, guava seed is a LC waste that contains approximately 13% of oil, which can be extracted in order to valorize the waste (ANGULO-LÓPEZ *et al.*, 2021). From the extraction process, the cake is another waste generated, which likely will have a similar composition of cellulose, HC, and LG to the guava seed (PEREIRA *et al.*, 2022).

The research interest to extract/recover CL-rich fractions, HC and LG from banana pseudostem and guava seed cake is because those molecules are considered as platform chemicals (also named intermediate products) or direct feedstock to obtain biofuels and bioplastics. For instance, from the CL-rich (pretreated material) fraction can be obtained fermentable sugars, which are the base to obtain 2nd generation bioethanol (THANGAVELU; AHMED; ANI, 2016). On the other hand, cellulosic fibers can be used as reinforcing elements in polymeric matrices and are considered highly promising fillers in composite preparation such as particleboards (MONTEIRO *et al.*, 2016; XIE *et al.*, 2016). Additionally, holocellulose, xylan, and cellulose extracted from sugarcane bagasse have been used as additives in starch-based bioplastics, which are considered alternatives to substitute common plastics and thus avoid environmental issues (ABE *et al.*, 2022). LG upgrading and valorization processes are significantly less-developed than those related to HC and CL, however, LG has been used as additive in polymeric films too, but based on chitosan (Ch) (ROSOVA *et al.*, 2021).

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GENERAL CONCLUSIONS

Raw banana pseudostem and guava seed cake were chemically characterized, thereby, it was found that their compositions fit to a similar lignocellulosic biomasses that have been considered as potential sources to obtain different types of bioproducts from its main components (cellulose, hemicelluloses and lignin).

With the alkali organosolv pretreatment was possible to fraction each fruit waste (banana pseudostem and guava seed cake) in three solid fractions (cellulose-rich, hemicelluloses, and lignin). The ethanol addition (to the spent liquor) and the solvent evaporation (after hemicelluloses extraction), allowed hemicelluloses and lignin precipitations, respectively, and its subsequent extractions with significative yields. Digestibility (enzymatic hydrolysis) of each pretreated biomass confirmed that the alkali organosolv pretreatment greatly contributed to obtain materials with loose lignocellulosic structure. Thus, the alkali organosolv pretreatment ratified that it can be used as fractionation strategy of lignocellulosic biomass when a biorefinery scheme is applied.

To the pretreated biomass from every configuration of alkali organosolv pretreatment was determined the lignocellulosic composition, which had direct relation with the mass yields of extracted hemicelluloses and lignin. High yields of extracted hemicelluloses and lignin matched with low hemicelluloses and lignin contents, respectively, in each pretreated biomass.

FTIR spectroscopy used to analyze the hemicelluloses and lignin extracted from banana pseudostem and guava seed cake, allowed to conclude that those macromolecules showed great correspondence with the commercial ones.

Two types of bioplastics were successfully produced using the mass proportions established for hemicelluloses and lignin. The hemicelluloses and lignin affected the color, opacity, moisture content, solubility, swelling, tensile and thermal properties of the obtained bioplastics. The bioplastics with the highest contents of hemicelluloses and lignin had a less distribution in color, and showed the maximum opacities. Hemicelluloses and lignin additions improved the tensile strength and Young's modulus properties. Besides that, the addition of hemicelluloses decreased the temperature at which the bioplastics lost mass during the thermal degradation analysis. Conversely, the same analysis showed that the lignin incorporation raised the temperature at which the bioplastics had their maximum mass losses. Overall, the study suggests that these bioplastics could be used in food or medicine packaging, where light and water control are important factors.