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I CONGRESSO BRASILEIRO DE BIOTECNOLOGIA INDUSTRIAL
XXIV SINAFERM • XV SHEB • XV ENZITEC FLORIANÓPOLIS • 2024
Creating connections between biotechnology and industrial sustainability
August 25 to 28, 2024
Costão do Santinho Resort, Florianópolis, SC, Brazil
BIOPRODUCTS ENGINEERING

VALORIZATION OF LIGNOCELLULOSIC BIOMASS FOR THE PRODUCTION OF AN ADDITIVE WITH BIOACTIVE COMPOUNDS

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ABSTRACT

This study aimed to utilize lignocellulosic biomass (bagasse from sweet sorghum) as a source of cellulose for the production of a food additive through the adsorption process, incorporating bioactive compounds (anthocyanins) extracted from grape peels to immobilize these compounds. The extract with the highest concentration of anthocyanins (475 mg. L^{-1}) was obtained using ethanol (50% v.v^{-1}) as the solvent. Regarding the kinetic study, it was observed that the adsorption process to produce the additive reached equilibrium within 30 minutes. The experimental kinetics data exhibited a superior fit when modeled using the pseudo-second-order approach. Based on the adsorption isotherm results at a temperature of 25°C, a maximum adsorptive capacity of approximately 0.8 mg. g-1 was attained. Subsequent application of empirical models revealed that the Langmuir model proved most suitable for analyzing the equilibrium.

Keywords: Lignocellulosic biomass. Circular economy. Antioxidant properties. Adsorption. Sustainability.

1 INTRODUCTION

Anthocyanins are natural pigments found in various fruits and vegetables, known for their antioxidant properties that contribute to the prevention of diseases such as diabetes and cardiovascular diseases.[1] However, their application as natural colorants is challenging due to their instability in the face of temperature variations, pH, light, and the presence of oxygen. Adsorption, a separation process widely used in various industries, emerges as a viable solution to prevent the degradation of anthocyanins under these adverse conditions. This process involves the interaction between a solid substance and a liquid, where liquid particles are retained on the surface of the solid. Lignocellulosic materials, composed of cellulose, hemicellulose, and lignin, are renewable and low-cost sources, making them applicable in various industrial sectors, including adsorptive processes.[2] Sweet sorghum, a lignocellulosic biomass, is particularly adaptable to different climates and is structurally composed of stalk, leaves, bagasse, and grain, with bagasse being a rich source of cellulose, approximately 37%.[3] Cellulose, a glucose polymer, is used in the production of various commercial products and can be employed in adsorption processes, acting as an adsorbent.[4,5] Thus, this study aimed to stabilize the bioactive properties of an alcoholic extract from grape skins through the adsorption process on microcrystalline cellulose obtained from sweet sorghum bagasse. The result is an additive with antioxidant properties that can be applied in various industries.

2 MATERIAL & METHODS

Figure 1 summarizes the methodology employed to obtain the additive from cellulose derived from sweet sorghum bagasse and the anthocyanin-rich extract from grape skins.

Figure 1 Flowchart of the adsorption process methodology

In the process of obtaining microcrystalline cellulose (the adsorbent), fresh sweet sorghum bagasse underwent a physicochemical treatment following the methodology outlined by Neto et al.[6] To extract the anthocyanin-rich compound (the adsorbate), grape skins were sanitized using a 2.5% sodium hypochlorite solution and then rinsed with running water. Afterward, they were dried in a circulating oven at 55°C until reaching a constant weight and then ground using a knife mill. The extract was obtained from the grape skin powder using two solvents, water, and ethanol (50% v/v), through a maceration process lasting 15 minutes. For the adsorption study, kinetic tests were conducted using 0.4 g of adsorbent and 10 mL of adsorbate, diluted in a pH 2.0 buffer solution (HCl/KCl), to attain initial concentrations of 33 and 111 mg. L-1. The mixture was placed in an Erlenmeyer flask on a shaker table with an agitation speed of 150 rpm at 25 °C. The total anthocyanin content was determined by removing samples at intervals of 5, 10, 20, 30, 40, and 60 minutes, followed by filtration and analysis using a T80 + UV/VIS spectrophotometer from PG Instruments Ltd., at a wavelength of 535 nm. Additionally, an equilibrium study was conducted by constructing an adsorption isotherm at a temperature of 25°C. The experimental conditions mirrored those of the kinetic study, except for the use of the optimal time determined in the previous step. Furthermore, the initial concentrations of adsorbates were varied within a predetermined range of low and high concentrations to achieve the region of maximum affinity and adsorbent site saturation.

For mechanism analysis, the data obtained in the kinetic study were fitted to two models: pseudo-first order and pseudo-second order, and the adsorption isotherm to Langmuir and Freundlich models. Table 1 shows the equations used.

Table 1 Kinetic models and adsorption isotherm equations

	Pseudo-First Order	Pseudo-Second Order	Langmuir	Freundilich
Eq	$q_{ta} = q_{ea} - (qe_a - q_{0a})exp(-k_{1a}t)$	$q_{ta} = q_{ea} + \frac{q_{0a} - q_{ea}}{k_{2a}t(q_{ea} - q_{0a}) + 1}$	$q_e = q_{e,max}\left(\frac{K_L\ C_e}{1+\ K_L\ C_e}\right)$	$q_e = K_F.(C_e)^{\frac{1}{n}}$
N°	(1)	(2)	(3)	(4)

Ce - concentration of total phenolic compounds in solution; qe - concentration of phenolic compounds adsorbed onto microcrystalline cellulose solid phase at equilibrium; qt - concentration of phenolic compounds adsorbed onto microcrystalline cellulose solid phase at time; k1 - kinetic constant for the pseudo-first-order model; k2 - kinetic constant for the pseudo-second-order model; kF - Freundlich constant; and kL - Langmuir constant.

3 RESULTS & DISCUSSION

The cellulose obtained through physicochemical treatment exhibited a mass yield of approximately 32%. This yield was calculated based on the fresh sweet sorghum bagasse and the final mass of obtained cellulose, a similar yield to that reported by Neto et al.[6] Regarding the anthocyanin-rich extract, the most effective solvent for extracting these compounds was ethanol (50% v/v), resulting in an anthocyanin concentration of 475 mg. L-1. Figure 2 depicts the adsorptive capacity of anthocyanins on microcrystalline cellulose over time at initial concentrations of 33 and 111 mg. L-1. Table 2 presents the parameters obtained and adjusted to the pseudo-first order and pseudo-second-order kinetic models.

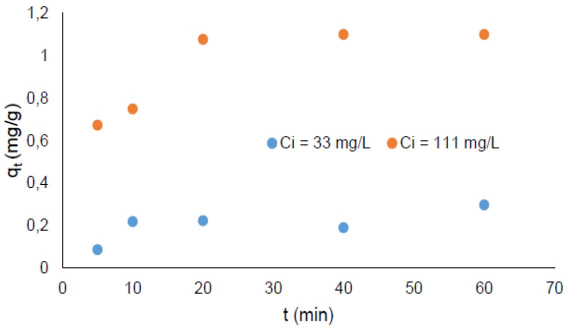

Figure 2 Adsorption Kinetics.

Table 2 Parameters of the kinetic models

Model	Ci = 33 mg.L^{-1}	Ci = 111 mg.L^{-1}
Pseudo-First Order		
q_e (mg.g^{-1})	0,2463	1,0648
k_1 (min^{-1})	0,1282	0,1614
SSE	0,0082	0,2255
R^2	0,9257	0,8881
Pseudo-Second Order		
q_e (mg.g^{-1})	0,2910	1,2066
k_{2_2} (g.mg^{-1}.min^{-1})	0,4802	0,1735
SSE	0,0082	0,2027
R^2	0,9256	0,9000

It was observed in Figure 2 that in the time interval from 0 to 10 minutes, there was an increase in adsorption capacity, and from 20 minutes onwards, the adsorption process reached equilibrium. The values obtained and adjusted to the kinetic models are presented in Table 2. Upon reviewing the results, it is evident that the coefficient of determination (R^2) for the pseudo-first-order model ranged from 0.8881 to 0.9257, and for the pseudo-second-order model, it ranged from 0.900 to 0.926. The SSE (Sum of Squares Error) ranged from 0.0082 to 0.2255 and from 0.0082 to 0.2027, respectively, for these concentrations and models. Based on these results, it is concluded that the model that best fits the experimental data was the pseudo-second order. Thus, it is inferred that the adsorption rate of grape skin anthocyanins on microcrystalline cellulose is directly proportional to the square of the number of active sites on the adsorbent surface. Adsorption is a chemical involving electron exchanges between adsorbent and adsorbate, covering the entire adsorption time range.[7] Figure 3 presents the curves obtained from the Langmuir and

Freundlich models adjusted to the experimental data regarding concentration, while Table 3 shows the parameters obtained for each model.

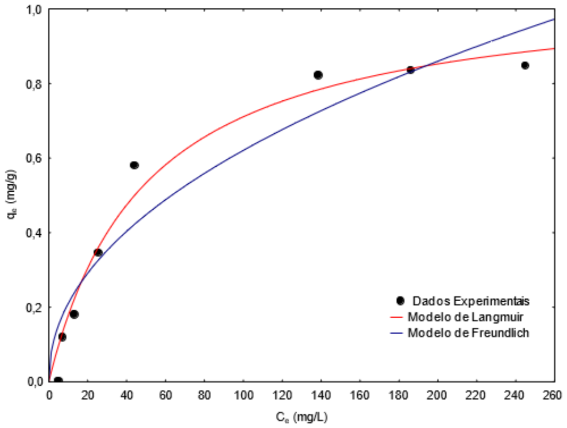

Figure 3 Curves of the Langmuir and Freundlich models

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Table 3 Parameters of the Langmuir and Freundlich models

Model	T = 25°C
Langmuir	
q_L (mg.g^{-1})	1,0679
K_L (L.mg^{-1})	0,0200
R_L	0,3247
SSE	0,0204
R²	0,9879
Freundlich	
K_F (L.mg^{-1})	0,0714
1/n	2,1276
SSE	0,0738
R²	0,9557

Figure 3 demonstrates that at the equilibrium concentration of 140 mg. L^{-1}, the maximum adsorptive capacity (0.8 mg. g^{-1}) is attained under the studied conditions. Regarding the data presented in Table 3, analyzing the parameters R² and SSE, the Langmuir model, which best suited the experimental data, exhibited values of 0.988 and 0.020, respectively. Thus, adsorption occurs in a monolayer; each site is occupied by only one molecule; the adsorbate activity is proportional to its concentration on the surface; there is energetic homogeneity of the sites; and there is no interaction between the adsorbed molecules.[8]

4 CONCLUSION

This study explored the use of cellulose derived from lignocellulosic biomass as an adsorbent in the process of adsorption with the aim of immobilizing anthocyanins present in grape peels in this biomass. It was observed that the adsorption process reached equilibrium in 30 minutes and a maximum adsorption capacity of around 0.8 mg/g. Therefore, it is possible to conclude that the cellulose obtained from sweet sorghum bagasse demonstrated to be effective in the adsorption of bioactive compounds present in grape peel for the synthesis of an additive with potential future applications in several industrial areas, to possibly avoid degradation of these compounds when exposed to temperature, light, humidity and oxygen.

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ACKNOWLEDGEMENTS

The Federal Rural University of Semi-Arid for providing the necessary means for the development of this study.