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CINÉTICA DE SECAGEM DE RESÍDUOS DE CAMU-CAMU (*Myrciaria dubia*) E CARACTERIZAÇÃO DOS EXTRATOS

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Tese apresentada ao programa de pós- graduação em Ciência de Alimentos da Universidade Estadual de Maringá, como parte dos requisitos para obtenção do título de doutor em Ciência de Alimentos

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Tese apresentada à Universidade Estadual de Maringá, como parte das exigências do Programa de Pós-graduação em Ciência de Alimentos, para obtenção do grau de Doutor em Ciência de Alimentos.

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BIOGRAFIA

Luciana Alves da Silva, nascida na cidade de Camapuã no estado do Mato Grosso do Sul em 26 de novembro de 1990. Filha de Claudinéia Alves de Queiroz e Gildo da Silva, neta do pernambucado Severino Inácio da Silva, da sergipana Maria Zenillda dos Santos, do bahiano Benvindo Alves de Queiroz e da paulista Alzira Maria de Alencar.

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Dedico

A minha mãe,

Meus avós Bil e Maria,

Minhas amigas Suelen, Hanna, Stefani, Lais e Carla,

Que me apoiram e incentivaram nessa trajetória e sonho.

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APRESENTAÇÃO

Esta tese está apresentada na forma de DOIS artigos científicos:

1. Luciana Alves da Silva, Monica Regina da Silva Scapim, Ana Paula Stafussa, Grasiele Scaramal Madrona.
Drying effects on Camu-camu residue: An approach of mathematical modeling, thermodynamic properties, and color evaluation in order to obtain a natural food dye.
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2. Luciana Alves da Silva, Monica Regina da Silva Scapim, Ana Paula Stafussa, Ana Caroline Raimundini Aranha, Rafael Oliveira Defendi, Oscar de Oliveira Santos Júnior Oliveira Santos, Grasiele Scaramal Madrona.
Modelagem da extração de componentes bioativos de cascas de camu-camu em diferentes colorações (verde e avermelhada) e identificação usando UPLC-MS/MS
Submetido a revista: Chemical Engineering Research And DesignQualis
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RESUMO

INTRODUÇÃO

Myrciaria dubia McVaugh é o nome científico do Camu-camu, uma fruta nativa da América do Sul, encontrada principalmente na região amazônica. Muitas empresas processadoras de frutas utilizam o camu-camu como matéria-prima na produção de sucos, concentrados e geleias. No entanto, o resíduo industrial da fruta (por exemplo, casca, sementes e polpa residual) ainda é descartado. Considerando a perecibilidade dos resíduos frescos, a secagem é um dos processos tecnológicos mais viáveis para a indústria alimentícia. Definida como uma técnica de redução de umidade, a secagem é baseada em um procedimento simultâneo de transferência de calor e massa entre o material e o ar quente, adequado para a obtenção de pós corantes naturais. A modelagem das curvas de secagem permite conhecer os índices físicos e termodinâmicos relevantes para o processo de transferência de calor e massa da amostra. Essas informações podem ajudar a melhorar o desempenho de análises futuras. O processo de secagem aqui estudado para o bagaço de camu-camu é uma opção no caso de obtenção de corante natural. Esta tecnologia é de fácil acesso e pode ser utilizada em pequenas ou grandes escalas de produção. Assim, é importante destacar que este estudo está focado na obtenção de um corante alimentar natural por meio da secagem do resíduo de camu-camu, que apresenta considerando potencial nutricional melhorando o seu aproveitamento e beneficiando a sociedade e meio ambiente.

OBJETIVOS

A primeira parte do trabalho objetivou verificar qual o melhor modelo matemático que se enquadra na secagem dos resíduos de Camu-camu e o efeito de diferentes temperaturas, calcular o coeficiente de difusão efetivo e a energia de ativação dos resíduos, e avaliar a mudança de cor nos resíduos de camu-camu após o processo de secagem para obtenção de corante natural. A segunda parte do estudo tem como objetivo avaliar a influência do tempo e temperatura de secagem de cascas de Camu-camu e na preservação de seus compostos bioativos, verificar qual o melhor modelo matemático se enquadra para a extração de compostos das cascas do fruto com diferentes colorações, e por fim, avaliar o efeito da secagem por convecção de ar quente no material vegetal.

MATERIAIS E MÉTODOS

Na primeira parte do trabalho utilizou-se os frutos maduros (descartando os frutos verdes ou muito maduros), os selecionados foram processados inteiros em equipamento industrial e na sequência prensado para separação da parte sólida e líquida. O material vegetal sólido foi colocado dentro de um secador de laboratório de bancada em bandejas de aço inoxidável e desidratados nas temperaturas de 60, 80, 100 e 120 ºC com fluxo de ar constante de 1 m/s. A cada intervalo de 15 minutos, uma amostra era retirada do secador, deixada para descanso em secador para estabilidade da temperatura a 25 ºC, após era moída em liquidificador industrial e transferida para embalagem plástica

laminada e armazenada a 5 ºC para análise de cor. Para descrever a cinética e modelagem de extração de compostos bioativos, da segunda parte da pesquisa, foram separadas e utilizadas somente as cascas de Camu-camu em coloração verde e avermelhada. A cor das cascas foi analisada a fim de obter uma padronização das amostras com colorímetro portátil. O material vegetal passou pelo processo de secagem por convecção forçada com ar quente a na temperatura de 60 ºC. Após a secagem, as amostras foram moídas em moedor industrial. As cascas passaram pelo processo de extração assistida por ultrassom (UAE) na temperatura de 50 ºC durante os tempos de 1h, 6h, 12h e 24h com solventes ecológicos, água e mistura água-etanol (50:50 v/v). As análises realizadas nas amostras das cascas foram de DPPH, FRAP e UPLC-MS/MS. Os modelos escolhidos para a verificação do perfil de extração dos compostos bioativos presentes nas cascas foram Modelos de Difusão Parabólica, Lei de potência, Modelo hiperbólico e Pseudo-segunda Ordem. Os dados de secagem da primeira e segunda parte passaram pela análise de regressão não linear pelo Método Gauss-Newton. Utilizou também para a modelagem cálculos do coeficiente de determinação (R^2, decimal), teste de Qui-quadrado (x^2, decimal) e raiz quadrada do erro médio (RMSE, decimal). Empregou o método de análise de variância (ANOVA) seguida pelo teste de Tukey com intervalo de confiança de 95% para a diferença de cor total analisada (primeira parte), assim como, para o rendimento dos extratos obtidos pelo método DPPH e FRAP (segunda parte).

RESULTADOS E DISCUSSÕES

Para a modelagem da cinética de secagem do resíduo de fruto de Camu-camu, nas quatro temperaturas de secagem o R^2 ficou acima de 98%. Analisando cada coeficiente de determinação que atingiram R^2 acima de 99%, tem-se na temperatura de 60 ºC os modelos de Difusão Aproximada, Midilli e Page, para 80 ºC os modelos de Midilli e Valcam, em 100 ºC temos Midilli, Page e Valcam e em 120 ºC os modelos de Midilli e Page. Além de avaliar o coeficiente de determinação (R^2) que se manteve >0,90, o RMSE e X^2 também foram analisados. Com isso o Modelo de Midilli apresentou os melhores resultados, sendo indicado o modelo de melhor ajuste para os dados do experimento com resíduo de Camu-camu. A energia de ativação calculada nesse estudo foi de 10,82 kJ mol^{-1} e coeficiente da difusão efetiva D0=0,0012 (m^2 s^{-1}). Para a entalpia específica (ΔH) observa que ela diminuiu à medida que a temperatura utilizada nos experimentos de cinética de secagem aumentou, já a entropia específica (ΔS) e a energia livre de Gibbs tiveram um comportamento inverso ao da entalpia, com valores crescentes com o aumento da temperatura. Em relação aos parâmetros de cor, onde o vermelho predomina quando o fruto de Camu-camu está maduro, o resíduo seco não apresentou muita diferença nos valores de ângulo de tonalidade quando comparado ao resíduo fresco, ficando entre 0,74 e 1,15. Na segunda fase da pesquisa, com o uso das cascas de Camu-camu, as cascas de coloração avermelhada *in natura* frescas apresentaram uma atividade antioxidante para DPPH de 42,78±1,70 mmolTrolox /g e 72,53±0,34 mmolTrolox/g e FRAP de 62,33±0,63 mmolTrolox /g e 88,96±0,60 mmolTrolox /g, sendo as condições de extração com etanol/água (v/v) e água pura, respectivamente. Para as cascas de coloração verde *in natura* os valores calculados foram de 89,45±0,65 mmolTrolox /g e

90,57±0,06 mmolTrolox /g (DPPH) e 105,07± mmolTrolox /g e 106,29± mmolTrolox /g (FRAP) para extração com etanol/água (v/v) e água, respectivamente. Com relação ao rendimento de extração os maiores rendimentos foram registrados nos tempos de 12 e 24h nos extratos com etanol/água 50/50 (v/v) tanto para a casca verde quanto avermelhada. Os modelos matemáticos Hiperbólico e Pseudo-segunda Ordem melhor se ajustaram aos dados experimentais com menores valores de χ^2, MSE, RMSE e NRMSE, além de valores mais próximos de 1 de EF. Os extratos passaram por UPLC-MS/MS e nove compostos foram identificados nas cascas, onde se destaca cyanidina 3-o-glucoside, delphinidina, quercetina, myricetina, rutina, ácidos gálico, clorogênico. p-coumarico e ellagico. Portanto, as cascas de Camu-camu em coloração verde e avermelhada possuem potencial antioxidante mesmo após o processo de secagem, com destaque para as extrações durante 12 horas com água-etanol (50:50 v/v). A modelagem matemática dos resíduos de Camu-camu mostrou que a temperatura de secagem influencia no tempo de secagem e, posteriormente, na perda de umidade da amostra. O modelo Midilli apresentou os ajustes matemáticos mais satisfatórios aos dados experimentais obtido e as constantes de secagem k do modelo variaram ligeiramente entre as temperaturas de secagem. Em relação à cor, notou-se que em temperaturas mais baixas (60 e 80°C) as amostras ficaram mais vermelhas e não apresentaram grandes variações de cor (ΔE). Assim, levando em consideração o tempo de perda de massa de água e os parâmetros colorimétricos, a temperatura de 80°C é altamente recomendada para secagem de resíduos de Camu-camu e posteriormente sua utilização como corante natural. Já na modelagem cinética de extratos de Camu-camu utilizando somente as cascas de cor verde e avermelhada, houve destaque para a utilização do solvente etanol/água 50/50 (v/v) e nos tempos de extração12 e 24h, esses parâmetros favoreceram a extração (em média 38% maiores que no tempo de 1 hora), sendo indicado o tempo de 12 h por ser o menor e assim mais econômico. O modelo cinético Hiperbólico e Pseudo-segunda apresentaram os melhores ajustes, sendo possível, a partir dos dois modelos, a realização de outros estudos em outras faixas de secagem e tempo de extração, promovendo assim novas estratégias de utilização de modelos em aplicação industrial.

CONCLUSÃO

Analisando todos os resultados obtidos, é possível concluir que a pesquisa corrobora sobre a relevância de estudo do fruto de Camu-camu e da secagem de seus resíduos que muitas das vezes são descartados. Contudo, ainda há uma necessidade de estudos mais aprofundados da utilização de subprodutos industriais, como fonte de compostos nutritivos.

PALAVRAS-CHAVE: Modelagem matemática, Cinética de extração, Camu-camu (*Myrciaria dubia*), Secagem de resíduos, Antioxidantes.

GENERAL ABSTRACT

INTRODUCTION

Myrciaria dubia McVaugh is the scientific name of Camu-camu, a native fruit from South America, mainly found in the Amazon region. Many fruit processing companies use camu-camu as a raw material in the production of juices, concentrates, and jellies. However, the industrial pomace of the fruit (e.g., peel, seeds, and residual pulp) are still discarded. Considering the perishability of fresh pomaces, drying is one of the most feasible technological processes for the food industry. Defined as a moisture reduction technique, drying is based on a simultaneous procedure of heat and mass transfer between the material and the hot air which is suitable for the obtention of natural dye powders. The modeling of drying curves provides knowledge regarding the physical and thermodynamic indices relevant to the heat and mass transfer process of the sample. This information might help to improve the performance of future analyses. The drying process studied here for camu-camu pomace is an option in the case of natural dye obtention. This technology is easily accessible and can be used on small or large production scales. Thus, it is important to highlight that this study is focused on obtaining a natural food dye by drying camu-camu pomace, which presents considering nutritional potential, improving its use and benefiting society and the environment.

AIMS

The first part of the study aimed to verify the best mathematical model that fits the drying of Camu-camu residues and the effect of different temperatures, calculate the effective diffusion coefficient and the activation energy of the residues, and evaluate the color change in camu-camu residues after the drying process to obtain natural dye. The second part of the study aims to evaluate the influence of drying time and temperature of Camu-camu peels and the preservation of its bioactive compounds, to verify which mathematical model is best suited for the extraction of compounds from the fruit peels with different characteristics. stains, and finally, to evaluate the effect of drying by convection of hot air on the plant material.

MATERIALS AND METHODS

In the first part of the work, the ripe fruits were used (discarding the green or very ripe fruits), the selected ones were processed whole in industrial equipment and then pressed to separate the solid and liquid parts. The solid plant material was placed inside a laboratory bench dryer on stainless steel trays and dehydrated at temperatures of 60, 80, 100 and 120 ºC with a constant air flow of 1 m/s. At each 15-minute interval, a sample was removed from the dryer, left to rest in a dryer for temperature stability at 25 °C, then ground in an industrial blender and transferred to laminated plastic packaging and stored at 5 °C for color analysis. To describe the kinetics and modeling of extraction of bioactive compounds, in the second part of the research, only the green and reddish Camu-camu peel were separated and used. The color of the peels was analyzed in order to obtain a standardization of the samples with a portable colorimeter. The plant material went through the forced convection drying process with hot

air at a temperature of 60 ºC. After drying, the samples were ground in an industrial grinder. The peels underwent the ultrasound-assisted extraction process (UAE) at a temperature of 50 °C for 1h, 6h, 12h and 24h with ecological solvents, water and a water-ethanol mixture (50:50 v/v). The analyzes performed on the peel samples were DPPH, FRAP and UPLC-MS/MS. The models chosen to verify the extraction profile of the bioactive compounds present in the shells were Parabolic Diffusion Models, Power Law, Hyperbolic Model and Pseudo-second Order. The drying data of the first and second parts underwent non-linear regression analysis by the Gauss-Newton Method. Also used for modeling calculations of the coefficient of determination (R^2, decimal), chi-square test (x^2, decimal) and square root of the mean error (RMSE, decimal). The analysis of variance method (ANOVA) was used, followed by Tukey's test with a 95% confidence interval for the total color difference analyzed (first part), as well as for the yield of extracts obtained by the DPPH and FRAP method (second part).

RESULTS AND DISCUSSION

For modeling the drying kinetics of Camu-camu fruit residue, at the four drying temperatures the R^2 was above 98%. Analyzing each determination coefficient that reached R^2 above 99%, at 60 ºC we have the Approximate Diffusion, Midilli and Page models, at 80 ºC the Midilli and Valcam models, at 100 ºC we have Midilli, Page and Valcam and at 120 ºC the Midilli and Page models. In addition to evaluating the coefficient of determination (R^2) that remained >0.90, the RMSE and X^2 were also analyzed. Thus, the Midilli Model presented the best results, indicating the best fit model for the data from the experiment with Camu-camu residue. The activation energy calculated in this study was 10.82 kJ mol-1 and the effective diffusion coefficient D0=0.0012 (m^2 s^{-1}). For the specific enthalpy (ΔH) it was observed that it decreased as the temperature used in the drying kinetics experiments increased, whereas the specific entropy (ΔS) and the Gibbs free energy had an inverse behavior to the enthalpy, with increasing values with the temperature rise. Regarding the color parameters, where red predominates when the Camu-camu fruit is ripe, the dry residue did not show much difference in shade angle values when compared to the fresh residue, ranging from 0.74 to 1.15. In the second phase of the research, with the use of Camu-camu peels, the fresh in natura reddish peels showed an antioxidant activity for DPPH of 42.78±1.70 mmolTrolox /g and 72.53±0.34 mmolTrolox/ g and FRAP of 62.33±0.63 mmolTrolox /g and 88.96±0.60 mmolTrolox /g, being the extraction conditions with ethanol/water (v/v) and pure water, respectively. For the green colored shells in natura the calculated values were 89.45±0.65 mmolTrolox /g and 90.57±0.06 mmolTrolox /g (DPPH) and 105.07± mmolTrolox /g and 106.29± mmolTrolox / g (FRAP) for extraction with ethanol/water (v/v) and water, respectively. Regarding the extraction yield, the highest yields were recorded at 12 and 24 h in extracts with 50/50 (v/v) ethanol/water for both green and reddish bark. The Hyperbolic and Pseudo-Second Order mathematical models better fit the experimental data with lower values of χ^2, MSE, RMSE and NRMSE, in addition to values closer to 1 of EF. The extracts underwent UPLC-MS/MS and nine compounds were identified in the peels, where cyanidin 3-o-glucoside, delphinidin, quercetin, myricetin, rutin, gallic acid, chlorogenic acid stand out. p-coumaric and ellagic acid. Therefore, Camu-camu peels in green

and reddish color have antioxidant potential even after the drying process, with emphasis on extractions for 12 hours with water-ethanol (50:50 v/v). Mathematical modeling of Camu-camu residues showed that the drying temperature influences the drying time and, subsequently, the sample's moisture loss. The Midilli model presented the most satisfactory mathematical adjustments to the experimental data obtained and the drying constants k of themodel varied slightly between drying temperatures. Regarding color, it was noted that at lower temperatures (60 and 80°C) the samples were redder and did not show large color variations (ΔE). Thus, taking into account the time of loss of water mass and the colorimetric parameters, the temperature of 80°C ishighly recommended for drying Camu-camu residues and subsequently using them as a natural dye. In the kinetic modeling of Camu-camu extracts using onlythe green and reddish husks, the use of 50/50 (v/v) ethanol/water solvent was highlighted, and at 12 and 24h extraction times, these parameters favored extraction (on average 38% longer than in the time of 1 hour), with the time of 12 hours being indicated because it is the shortest and therefore the most economical. The Hyperbolic and Pseudo-second kinetic models presented the best adjustments, making it possible, from the two models, to carry out further studies in other drying ranges and extraction time, thus promoting new strategies for using models in industrial application.

CONCLUSION

Analyzing all the results obtained, it is possible to conclude that the research corroborates the relevance of studying the fruit of Camu-camu and its residuesthat are often discarded. However, there is still a need for further studies on theuse of industrial by-products as a source of nutritional compounds.

KEYWORDS: Mathematical modeling, Drying kinetics, Camu-camu (*Myrciaria dubia*), Waste drying, Antioxidants.

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ORIGINAL ARTICLE

Drying effects on Camu-camu residue: An approach of mathematical modeling, thermodynamic properties, and color evaluation in order to obtain a natural food dye

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Abstract

The present study evaluated the drying of camu-camu pomace (reducing waste generation), and a mathematical model is proposed for drying at four different temperatures (60, 80, 100, and 120°C), and 1 m/s airflow. The thin-layer model that best fitted the experimental data was by Midilli, compared to ten other models. The evaluation method used the coefficient of determination (R^2), RMSE (root mean square), and X^2 (Chi-square), wherein the coefficient of determination remained >0.90. The activation energy calculated in the present study was 10.82 kJ mol^{-1}, and effective diffusion coefficient D0 = 0.0012 (m^2 s^{-1}). Considering colorimetric parameters and the time of water mass loss, the temperature of 80°C is appropriate to produce a good powder. Thus, the drying of camu-camu pomace is an alternative to obtain a natural (red-purple) food dye.

Novelty impact statement: To our knowledge, the present study is a pioneer on the grounds that it presents the mathematical modeling data of the residue at high temperature, and also the obtention of camu-camu powder as natural dye. Considering the perishability of fresh residues, drying is one of the most feasible technological processes for the food industry, also to obtain natural dyes, highlighting to the natural powders. The modeling of drying curves provides an understanding as regards the physical and thermodynamic indices relevant to the heat and mass transfer process of the sample. So, this information is very important and might help to improve the performance of future analyses.

1 | INTRODUCTION

Myrciaria dubia McVaugh is the scientific name of camu-camu, a native fruit from South America, mainly found in the Amazon region. The camu-camu is scientifically known for its high rates of ascorbic acid, phenolic compounds, antioxidants, and antimicrobial activity (Fracassetti et al., 2013; Fujita et al., 2013; Kaneshima et al., 2016; Rodrigues et al., 2020). Camu-camu presents a reddish color when ripe, due to the concentration of anthocyanins, a sour and juicy pulp, with an average diameter of 2.5 cm, being able to be consumed in its natural form (Zanatta et al., 2005).

Many fruit processing companies use camu-camu as a raw material in the production of juices, concentrates, and jellies. However, the industrial pomace of the fruit (e.g., peel, seeds, and residual pulp) are still discarded. Therefore, to add value to the camu-camu industrial pomaces, studies have been developed aiming to re-purpose this by-product and incorporate it into food (Azevêdo et al., 2014; Conceição et al., 2020; Fidelis et al., 2020; Rodrigues et al., 2020),

since seed and peel yield ranges from 38% to 40% of the total fruit weight (Rodrigues et al., 2001).

Considering the perishability of fresh pomaces, drying is one of the most feasible technological processes for the food industry. Defined as a moisture reduction technique, drying is based on a simultaneous procedure of heat and mass transfer between the material and the hot air (Silva et al., 2021) which is suitable for the obtention of natural dye powders.

In recent years, the use of natural dyes has been growing due to the advantages of the use natural products, mainly focusing on consumers who have allergies or intolerances to synthetic dyes. However, according to Antigo et al. (2020), natural dyes have some disadvantages compared to artificial ones. Costs are usually higher, and depending on the specific dye, they exhibit lower stability under processing and storage conditions.

The modeling of drying curves provides knowledge regarding the physical and thermodynamic indices relevant to the heat and mass transfer process of the sample. This information might help to improve the performance of future analyses. The generated data enables the assessment of the product characteristics, allowing comparisons with similar materials, such as grains, fruits, vegetables, among others. According to Midilli et al. (2002), mathematical models are used to estimate the products' ideal drying time, in which the drying curves are obtained, and it is possible to describe the physical characteristics of the materials.

Various types of processing can be used to reduce the moisture in foods. The drying process studied here for camu-camu pomace is an option in the case of natural dye obtention. This technology is easily accessible and can be used on small or large production scales. Thus, it is important to highlight that this study is focused on obtaining a natural food dye by drying camu-camu pomace, which is considered a waste.

To our knowledge, the present study is a pioneer on the grounds that it presents mathematical modeling data of the pomace at high temperature, and obtention of camu-camu powder as natural dye. Thus, this study aimed to (1) verify which mathematical model best fits the drying process and evaluate the effect of drying by convection at different temperatures; (2) calculate the pomaces effective diffusion coefficient and activation energy; and (3) evaluate effects of temperature on the color of camu-camu pomaces to obtain a natural dye.

2 | MATERIALS AND METHODS

2.1 | Plant material

Fruits were acquired from the camu-camu trees of the Amazon Forest (Vitória do Xingu, Brazil—latitude: 02°52′48″ S; Longitude: 52°00′36″ W), and kept frozen during transport until the analysis. The fruits were selected according to their ripening stage, in which unripe or very ripe (soft) fruits were discarded. After selection, the fruits were washed, sanitized (100 ppm of sodium hypochlorite), and processed in an industrial grinder (Model Jl Colombo, 700 W) for 2 min at 10°C (±1°C). Afterward, they were pressed to separate the solid and liquid parts. The solid plant material was immediately packed in polyethylene packages and stored at −18°C in the dark until drying kinetics. The initial moisture content (Wi) was determined by the AOAC method (1990). The pomace was also analyzed by pH, moisture, lipids, protein, and ash according to AOAC International (2016). Carbohydrates were calculated by difference and °Brix was measured using a refractometer (HI 96801 Hanna). All analyses were performed in triplicate.

2.2 | Experimental drying technique

The plant material was thawed at 7°C and evenly distributed with layers of 10 ± 1 mm in thickness on stainless steel trays of 100 × 100 mm and 0.35 three-mesh opening. The trays were placed inside a benchtop laboratory dryer (Solab brand, model SL-102). The drying method used was forced convection with hot air at a constant airflow of 1 m/s. Knowing the initial moisture content of the sample (Wi), the camu-camu pomace was dehydrated using mass balance in the temperatures of 60, 80, 100, and 120°C, with an initial mass of 35 ± 1 g, and assuming constant dry matter along the kinetics (Equation 1), a semi-analytical electronic scale (Model RS232-MogiGlass), with a resolution of 0.001 g, was used. On average, the samples lost 71 ± 1% of their initial weight at each drying temperature. Every 15-min interval, a sample was removed from the dryer and placed in a vacuum desiccator until reaching 25°C. Subsequently, the samples were ground in an industrial blender (Metvisa, model Lar 1.5) for 60 ± 10 s, being transferred to laminated plastic packaging and stored at 5°C for color analysis. The samples were identified according to the drying temperature and time.

$$W_t = \frac{m_t \cdot 1 + W_i}{m_i} - 1 \quad (1)$$

where wt is the water content (g water/g dry matter), mt is the product mass (g) (both at each time t), and Wi and mi are the initial values, respectively.

2.3 | Mathematical models and calculations

To study the temperature influence and describe the drying curves of the camu-camu pomace dehydration, mathematical model adjustments were used. Regarding the moisture data obtained in the kinetics study, the moisture ratio (MR) was calculated using Equation 2, where the water content of the product is represented by a dry basis (bs) (M) (g water / g dry matter or dry solids (bs), the water content equilibrium of the product (bs) (Mi) (g water / g bs) and the initial water content of the product (bs) (Mo) (g water / g bs). The parameters used to adjust the curves were R^2 (coefficient of determination), RMSE (root mean square error), and X^2 (chi-square).

$$MR = \frac{M - M_i}{M_0 - M_i} \quad (2)$$

TABLE 1 Mathematical models used in the drying kinetics of camu-camu residue

Equation	Model name	Mathematical expression	References
(3)	Difussion Approach	$MR = a\exp(-kt) + (1\text{-}a)\exp(-kbt)$	Akpinar (2006)
(4)	Two Term	$MR = a\exp(-k_1t) + b\exp(-k_2t)$	Sharaf-Eldeen et al. (1980)
(5)	Henderson e Pabis	$MR = a\exp(-kt)$	Henderson (1974)
(6)	Logaritmic	$MR = a\exp(-kt) + c$	Kingsly et al. (2007)
(7)	Midilli	$MR = a\exp(-kt^n) + bt$	Midilli et al. (2002)
(8)	Newton	$MR = \exp(-kt)$	Lewis (1921)
(9)	Page	$MR = \exp(-kt^n)$	Page (1949)
(10)	Thompson	$MR = \exp(-a\text{-}(a^2 + 4bt)^{0,5}/(2b))$	Thompson et al. (1968)
(11)	Valcam	$MR = a + bt + ct^{1,5} + dt^2$	Madamba et al. (1996)
(12)	Verma	$MR = a\exp(-k_1t)) + (1\text{-}a)\exp(-k_2t)$	Verma et al. (1985)

Notes: t: drying time (min); k, k_0, k_1: drying constants (h^{-1}); a, b, c, n: model coefficients.

For the present study, the thin-layer mathematical models most cited in the literature were selected (Azeez et al., 2017; Junqueira et al., 2017; Méndez-Lagunas et al., 2017; Tavone et al., 2021), so Table 1 shows the models and their corresponding equations.

Moisture transport mechanisms can be mathematically modeled during drying according to the Fick's second diffusion law and the Activation Energy (Ea), which show the behavior of the effective diffusion coefficient (Def in $m^2\ s^{-1}$). Regarding the temperatures used in the drying kinetics, they were calculated using the Arrhenius equation. The expression coefficients were linearized using the logarithm described in Equations 13 and 14.

$$MR = \frac{(Mx - Mxo)}{(Mxi - Mxo)} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \exp\left[(2n+1)^2 \pi^2 Di \frac{t}{4L^2}\right] \quad (13)$$

$$D_{ef} = D_o \exp\frac{-Ea}{RT} \quad (14)$$

from the pre-exponential factor; E the activation energy (KJ mol^{-1}); R means the universal gas constant (8.134 kJ$mol^{-1}K^{-1}$); and Tab is the absolute temperature (K).

Activation energy (Ea) was calculated using the Arrhenius curve plotted in ln k opposing the inverse of the absolute temperature (1/T). Regarding the calculations, it is important to emphasize that the coefficients in Equation 4 were linearized using the logarithm, as described in Equation 15 (Fiorentini et al., 2015).

$$L_n D_{ef} = -\frac{Ea}{R}\frac{1}{T_{ab}} + L_n D_o \quad (15)$$

The thermodynamic properties associated with the drying process were determined according to the method proposed by Jideani and Mpotokwana (2009). Equations 16, 17, and 18 were used to calculate the specific enthalpy, specific entropy, and Gibbs free energy, respectively.

$$\Delta H = E_a - RT_a \quad (16)$$

$$\Delta S = R\left[\ln D_0 - \ln\frac{K_B}{h_p} - \ln T_a\right] \quad (17)$$

$$\Delta G = \Delta H - T_a \Delta S \quad (18)$$

where ΔH is the specific enthalpy (J mol^{-1}); ΔS is the specific entropy (J mol^{-1} K^{-1}); ΔG is the Gibbs free energy (J mol^{-1}); KB is the Boltzmann constant ($1.38 \times 10{-}23\ J K^{-1}$); and hp is Planck's constant ($6.626 \times 10{-}34\ m^2$ Js).

2.4 | Determination of CIE-LAB color of camu-camu pomace

The color of each sample collected during the drying kinetics study was analyzed using a portable Minolta CR400 colorimeter, with an integrating sphere and a 3° viewing angle (illumination d/3 and illuminant D65). The sample was uniformly placed in a 90 × 15 mm petri dish. Each analysis was performed in triplicate. The color was determined according to the CIE-LAB system (L^* represents the luminosity—from dark (0) to light (100); the coordinate a^* represents green (−) and red (+); and the coordinate b^* represents blue (−) and yellow (+)). The total color difference (ΔE) was assessed using Equation (9) (Obón et al., 2009), where L^*0, a^*0, and b^*0 are the sample color values at time zero; and L^*1, a^*1, and b^*1 are the sample color values at time t, where high values of ΔE indicate large color changes compared to the control. In addition to the color difference, the chroma (C^*) and hue (H^*) were calculated using Equations 19–21.

$$\Delta E = \sqrt{(L_1^* - L_0^*)^2 + (a_1^* - a_0^*)^2 + (b_1^* - b_0^*)^2} \quad (19)$$

$$C^* = \sqrt{(a^{*2} + b^{*2})} \quad (20)$$

$$H^* = \tan^{-1}\frac{b^*}{a^*} \quad (21)$$

2.5 | Statistical analysis

The models' accuracy to fit the drying curves experimental data was evaluated by calculating the coefficient of determination

(R^2, decimal), Chi-square test (x^2, decimal), and root mean square error (RMSE, decimal). The models' constants were statistically calculated using adjustments from the non-linear regression analysis by the Gauss-Newton method, using the Statistica 8.0 software. Drying kinetics data were expressed as mean ± standard deviation for each treatment, and the total color difference was analyzed using the analysis of variance method (ANOVA), followed by Tukey's test with a 95% confidence interval.

3 | RESULTS AND DISCUSSION

3.1 | Pomace characterization, determination of curves, and drying modeling

In natura pomace at the beginning of the process presented pH of 3.15, 7.5 ºBrix, and around 69.30 humidity, 0.91 protein, 0.59 lipids, 9.36 ash, and 19.84 carbohydrates in g/ 100 g. Rodrigues et al. (2020) evaluating the same variety of camu-camu fruit in nature observed a pH = 3.24, moisture content of approximately 84.00, and 0.21 ash, protein content was 0.81, and lipids 0.25 and carbohydrates of 14.94 g/100 g on wet basis. Figure 1 shows the moisture decline rate on a wet basis (b.u.) at the temperatures of 60, 80, 100, and 120°C during the drying kinetics of camu-camu pomace. The fresh pomace sample exhibited a b.u. average of 69.30 g of water/100 g of dry material. At the beginning of the drying process, a sharp drop in the b.u. percentage was observed at 80, 100, and 120°C up to 60 min, when the moisture stabilization process began.

When comparing the drying curves at 120 and 60°C, it is notable that with an increase in temperature, the humidity drops dramatically to stability and is halved ($p < .05$). The drying effect may be related to the diffusion of internal moisture in the sample. In the case of camu-camu pomace, once it is a mixed by-product consisting of pulp, seeds, and peel, the internal resistance in water transfer tends to be greater at low temperatures.

Regarding the drying rate over time (Figure 2), it is possible to analyze that in the first 20 min, the drying speed intensifies at the four temperatures assessed. For the temperatures of 120, 100, and 80°C, the drying rate reached its peak at 0.076, 0.061, and 0.074 kg water/kg dry solids dm. min, respectively. As already mentioned, the moisture content tends to reduce over time, in which at higher temperatures, the reduction rate occurs faster and more abruptly, corroborating with the evidences found in the literature (Aral & Bese, 2016; Darvishi et al., 2014).

Regarding the mathematical adjustments, Table 2 shows the calculated values of the coefficient of determination (R^2, decimal), Chi-square test (X^2, decimal), and the square root of the mean error (RMSE, decimal) for each model. It was observed that the R^2 was above 98% at the four temperatures used. According to Madamba et al. (1996), to obtain a satisfactory result in relation to drying kinetics, the R^2 values must be greater than 95%.

In a separate analysis of each coefficient of determination which the R^2 was above 99%, the Approximate Diffusion, Midilli and Page models reached this value at 60°C, the Midilli and Valcam models achieved this value at 80°C, Midilli, Page, and Valcam models reached this coefficient at 100°C, and the Midilli and Page models achieved this value at 120°C. In addition to meeting a significant percentage of the coefficient of determination (R^2 close to 1), the Midilli model presented the lowest values of X^2 and RMSE (close to 0) at most of the drying temperatures. Tavone and colleagues (Tavone et al., 2021) emphasize that the model suitability is related to higher values of R^2 and low values of the estimated mean error (RMSE).

Thus, based on the results, the Midilli model was significantly adjusted to the drying kinetics of the camu-camu pomace. Literature presented some studies about the model for drying kinetics; for example, Azeez et al. (2017) in their study with dried tomato slices at temperatures of 50, 60, and 70°C determined that the Page model was the most adequate to describe the sample drying. Aral and Bese (2016) evaluated the convective drying of hawthorn fruits and recommended the Midilli model in their study. The same recommendation was made by Motevali et al. (2016), who evaluated the drying of chamomile, and Tavone et al. (2021), who assessed effects of drying on calabura bark.

At 90 min of drying kinetics, the percentage wet base of the samples was >10. The comparison between the data collected during

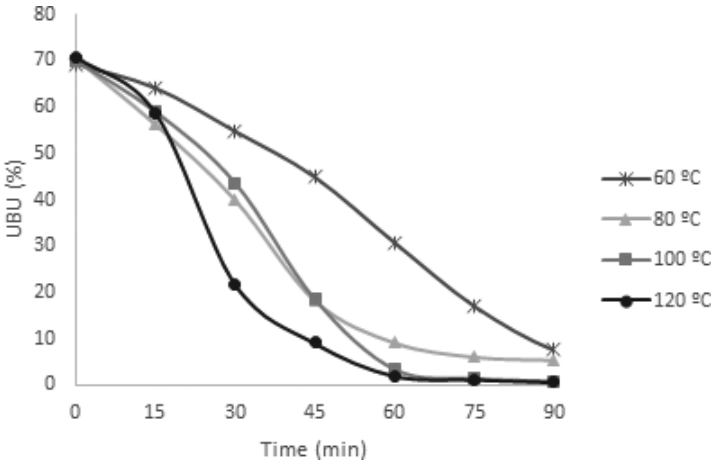

FIGURE 1 Moisture on a wet basis (b.u.) as a function of drying time of the camu-camu pomace at different temperatures (60, 80, 100, and 120°C)

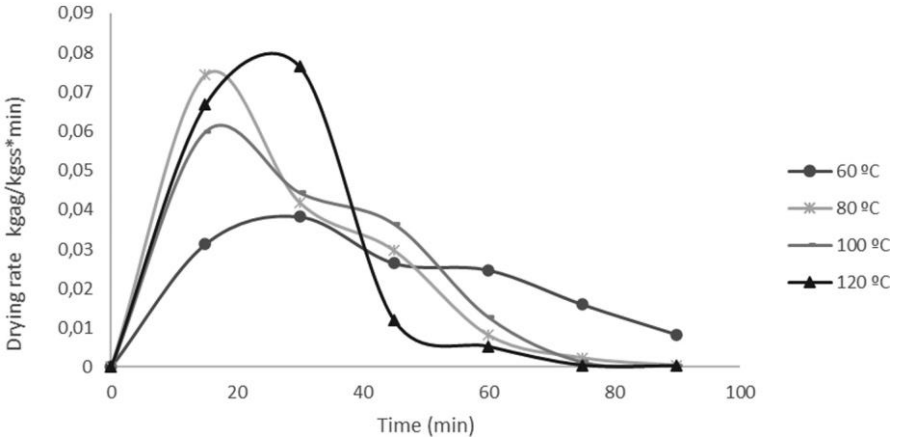

FIGURE 2 Drying rate as a function of drying time of the camu-camu pomace at different temperatures (60, 80, 100, and 120°C)

TABLE 2 Mathematical models used to describe the drying process of camu-camu residue. Coefficients of determination (R^2, decimal), chi-square test (X^2, decimal), and root mean error square (RMSE, decimal)

	Drying temperatures (°C)											
	60			80			100			120		
Model name	R^2	χ^2	RMSE	R^2	χ^2	RMSE	R^2	χ^2	RMSE	R^2	χ^2	RMSE
Difussion Approach	0.999	0.0002	0.0171	0.998	0.0003	0.0183	0.998	0.0008	0.0290	0.983	0.0076	0.0869
Two Term	0.989	0.0037	0.0615	0.997	0.0006	0.0250	0.990	0.0056	0.0751	0.984	0.0097	0.0985
Henderson e Pabis	0.989	0.0029	0.0543	0.997	0.0005	0.0220	0.990	0.0034	0.0582	0.984	0.0058	0.0763
Logaritmic	0.994	0.0018	0.0428	0.997	0.0005	0.0229	0.995	0.0021	0.0463	0.986	0.0062	0.0787
Midilli	0.999	0.0001	0.0127	0.999	0.0002	0.0128	0.999	0.0007	0.0273	0.999	0.0003	0.0171
Newton	0.987	0.0031	0.0565	0.997	0.0004	0.0212	0.989	0.0030	0.0548	0.983	0.0050	0.0710
Page	0.999	0.0001	0.0117	0.998	0.0003	0.0174	0.999	0.0005	0.0224	0.999	0.0002	0.0152
Thompson	0.993	0.0018	0.0424	0.998	0.0004	0.0199	0.995	0.0017	0.0417	0.987	0.0047	0.0687
Valcam	0.997	0.0007	0.0276	0.999	0.0003	0.0165	0.999	0.0007	0.0260	0.989	0.0066	0.0811
Verma	0.994	0.0017	0.0419	0.997	0.0006	0.0237	0.989	0.0045	0.0671	0.983	0.0076	0.0869

the kinetics and the data predicted by the Midilli model is shown in Figure 3. It is possible to observe a substantial alignment between the values collected and those estimated by the mathematical model at the four drying temperatures (60, 80, 100, and 120°C).

Considering the Midilli model as the one that best fitted the experimental data, the drying rate constants and the coefficients of the model equation are shown in Table 3. The constant k is related to the effective diffusion and characterizes the implication of the temperatures used on the sample (Jorge et al., 2021). A constant k variation was observed on the drying temperatures. At 120°C, the constant presented its lowest value (k = 0.0025). This result may be associated with a sudden reduction of sample moisture, due to the higher temperature (120°C) and shorter time.

It is worth mentioning once again that in this study, the sample used has a mixed origin, (i.e., it is characterized by the presence of camu-camu peel, seeds, and pulp). The presence of different plant matrices in the sample probably means that the results of constant k did not have empirical constancy (i.e., a linear reduction of sample moisture with an increase in temperature used in the drying process). Homogeneous samples tend to present continuously increasing

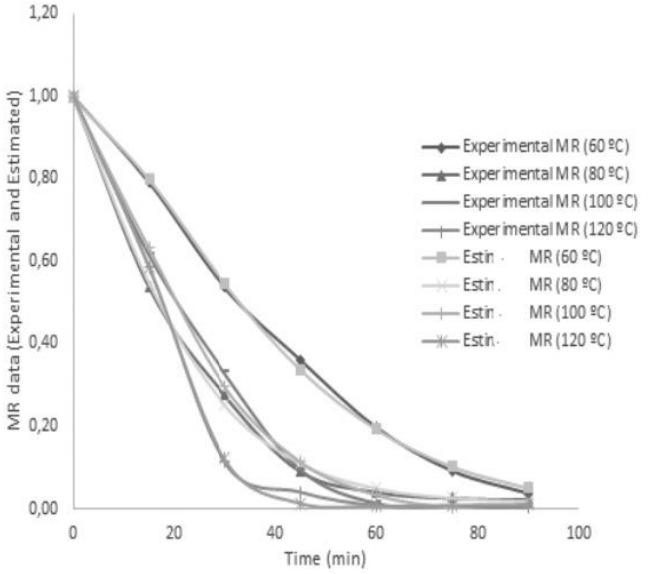

FIGURE 3 Experimental data of moisture ratio (MR) versus estimated data by the Midilli model on drying kinetics of camu-camu pomace

TABLE 3 Constant k and Midilli model parameters adjusted for the drying of camu-camu residue

Temperature (°C)	Midilli parameters				Midilli equation $y = a\exp(-kt^n) + bt$
	a	k	n	b	
60	0.99567	0.00440	1.44455	−0.00004	$y = 0.99567 * \exp - 0.00440 * x^{1.44455} + - 0.4^{-4} * x$
80	0.99852	0.023545	1.1989	0.000148	$y = 0.99852 * \exp - 0.023545 * x^{1.1989} + 1.48^{-4} * x$
100	0.99624	0.010147	1.401491	−0.00014	$y = 0.99624 * \exp - 0.010147 * x^{1.401491} + - 1.4^{-4} * x$
120	1.00066	0.0025	1.984744	0.000124	$y = 1.00066 * \exp - 0.0025 * x^{1.984744} + 1.24^{-4} * x$

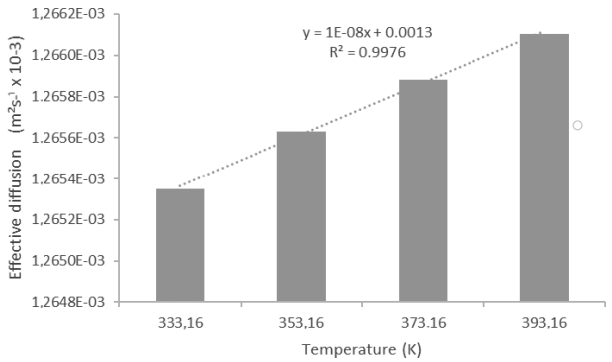

FIGURE 4 Effective diffusion coefficient of dried camu-camu pomace

k values with an increase in temperature (Jorge et al., 2021; Lima et al., 2021; Tavone et al., 2021).

The variation of effective diffusion coefficients occurred in the sixth decimal place, with an increase in Def according to an increase in the drying air temperature (e.g., 60, 80, 100, and 120°C). According to Azeez et al. (2017), it is possible to calculate the values for the constant k drying with the graphical plot of ln (MR) as a function of time (t in min). The transfer of internal mass from the sample to its exterior is associated to the drying temperature, which means that the higher the temperature used in the kinetics, the higher the effective diffusion rate (Figure 4).

Thus, after plotting the Arrhenius graph, the following equation was obtained: (22) $y = -1301.4x - 6.6685$ with $R^2 = 0.9209$ (consider Equation 22 analogous to Equation 23). Therefore, $D0 = 0.0012$ (m^2 s^{-1}), and activation energy of 10.82 kJ mol^{-1} values was found. According to Perea-Flores et al. (2012), the activation energy (Ea) is a barrier that must be broken so that the effective diffusion procedure can occur with the undergoing drying sample. The Ea value found in this study for camu-camu pomace dried at four different temperatures is relatively lower than those estimated by Zogzas and Maroulis (2007)) who stipulated a variation that ranges from 12.7 to 110.0 kJ mol^{-1} for agricultural products. This small difference can probably be related to the nature of the material used, and/or to the amount of moisture present at the beginning of the drying process (Corrêa et al., 2007).

Analyzing the thermodynamic properties (Table 4), it can be seen that the specific enthalpy (ΔH) decreased as the temperature in the drying kinetics experiments increased, confirming that at higher temperatures, less energy will be spent during the drying process. On the other hand, the specific entropy (ΔS) and Gibbs free energy had a reverse behavior to that of enthalpy, with values increasing as the temperatures increased. The small entropy changes from −0.3013 to −0.3026 and is related to the low variation of the temperatures used (10°C), and the negative values are usually related to the changes in the structure of the material. Positive enthalpy values may indicate that there was an endothermic heat transfer process.

TABLE 4 Thermodynamic properties of camu-camu residue: Specific enthalpy (ΔH), specific entropy (ΔS), and Gibbs free energy (ΔG)

Thermodynamic properties			
Temperature (°C)	ΔH (kJ Mol^{-1})	ΔS (kJ Mol^{-1} K^{-1})	ΔG (kJ Mol^{-1})
60	8.0499	−0.3013	108.4215
80	7.8837	−0.3018	114.4519
100	7.7174	−0.3022	120.4916
120	7.5511	−0.3026	126.5403

3.2 | Camu-camu pomace color during kinetics

Color is one of the sensory parameters with the greatest impact on consumers. Color change in samples subjected to drying can occur due to the degradation of bioactive compounds. The total color difference (ΔE) was used in this study to compare the dried samples with the fresh pomace (control).

The comparison between the samples dried at the four temperatures investigated (60, 80, 100 and 120°C) and the control sample was carried out (Table 5). The closer the sample ΔE is to zero, the most similar the color is to the control. According to Adekunte et al. (2010), the analytical color using ΔE can be classified as "very different" ($\Delta E > 3$), "different" ($1.5 < \Delta E < 3$), and "with little difference" ($1.5 < \Delta E$). Considering this classification, pomaces dried at 100°C and 120°C had a drastic change in color in the final drying.

Comparing the fresh pomace (25°C) with the one at 90 min (end of drying), the color chroma (C^*) of the sample dried at 120°C showed an opaquer result, being significantly different ($p < .05$) from the other samples. When the hue angle of the fresh camu-camu

TABLE 5 Color parameters for drying camu-camu residue in the initial and final times

Time (min)	Temperatura (°C)	*L**	*a**	*b**	ΔE	*C**	*H**
0	25	46.38^{a}	15.46^{b}	22.26^{a}	0.00^{a}	8.55^{ab}	0.79^{b}
90	60	47.59^{a}	18.30^{a}	18.05^{ab}	5.15^{b}	8.38^{b}	0.80^{b}
	80	47.64^{a}	17.00^{a}	18.02^{ab}	4.64^{b}	8.31^{b}	0.86^{c}
	100	43.81^{b}	15.74^{b}	19.08^{ab}	4.41^{b}	7.66^{c}	0.99^{a}
	120	40.71^{b}	11.34^{c}	14.56^{b}	8.80^{c}	8.55^{ab}	0.79^{b}

Notes: Results expressed as mean ± standard deviation (triplicate). ^{abc}Means with the same lowercase letters in the same time block are not significantly different (Tukey test. $p < .05$). *L**. brightness/darkness; *a**. greenness/redness; *b**. yellowness/blueness; ΔE. total color difference; *C**. Chroma; *H**. hue angle.

pomace is analyzed, it has a value close to 1. According to Zia and Alibas (2021), the angle has as reference the redness of the sample, that is, when the values are close to zero, they tend to have a change of color to a red-purpura color, while values that reach up to 30 tend to reach a red-orange color. Considering the natural color of camu-camu, in which red predominates when the fruit is ripe, it is noted that the dried pomace did not show much difference in hue angle values compared to the fresh pomace staying between 0.74 and 1.15.

Drying conducted at 60 and 80°C (Figure S1) produced darker samples (higher L value), showing more intense red coloration (*a**). Regarding the parameter *b**, the sample dried at 120°C showed less tendency to yellow when compared to the other temperatures analyzed ($p < .05$). Thus, the obtained powder can be used as a natural dye by the food industry being a healthy option when compared to artificial colorings, and finally, according to Santos et al. (2022) from the pulp to the peel, camu-camu is a raw material with wide perspectives.

4 | CONCLUSION

This is the first study that performed mathematical and kinetic modeling of degradation of bioactive compounds in camu-camu pomaces at four drying temperatures (60, 80, 100, and 120°C). The mathematical modeling showed that the drying temperature influences the drying time, and subsequently loss of moisture in the sample. The Midilli model presented the most satisfactory mathematical adjustments to the experimental data obtained. The drying constants k of the Midilli model varied slightly among the drying temperatures.

The best drying time was at 80°C. Regarding color, it was noted that at lower temperatures (60 and 80°C) the samples became redder and did not present great variations in color (Δ*E*). Thus, taking into consideration the time of water mass loss and the colorimetric parameters, the temperature of 80°C is highly recommended.

Finally, the drying of camu-camu pomace is a viable alternative with great potential for obtaining an interesting food ingredient, considering that currently the plant material is discarded by the food industry. However, as future work, it is important to evaluate the application of this dye and its stability when applied to the products.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

DATA AVAILABILITY STATEMENT

The data used to support the findings of this study are available within the article.

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Artigo 2

Modeling the extraction of bioactive components of green and red camu-camu peel and identification using UPLC-MS/MS

Highlights

- Extraction modeling analysis is essential for future applications of Camu-camu peel in food industries.
- Drying camu-camu peel at 60 ºC is an excellent alternative for bioactive compound concentration and by-product storage.
- The best models to describe extraction kinetics were Hyperbolic and Pseudo-second order.
- Nine compounds were identified in green and red peel after drying.
- Drying process increased the quantification of myricetin and ellagic acid.
- Green and red Camu-camu peels are important sources of phenolic compounds.

Abstract

The use of kinetic modeling data for the extraction of bioactive compounds is essential for food industries. This work aimed to investigate which mathematical model is best adjusted for extraction of bioactive compounds from camu-camu peel and to evaluate the effect of drying by hot air convection (60 ºC). Four mathematical models (parabolic diffusion, power law, hyperbolic and pseudo-second order) were applied to adjust the extraction conditions. To describe the kinetics and data modeling the peels went through ultrasound-assisted extraction (UAE) for 1h, 6h, 12h and 24h with water and water-ethanol (50:50 v/v) as solvents. The hyperbolic and pseudo-second order mathematical models were best adjusted to the experimental data with lower values of χ^2, MSE, RMSE and NRMSE, in addition to values closer to 1 of EF. The extracts went through UPLC-MS/MS and nine compounds were identified in the peels: cyanidin 3-o-glucoside, delphinidin, quercetin, myricetin, rutin, gallic acid, chlorogenic acid p-coumaric and ellagic acid. Therefore, dried camu-camu peels still have antioxidant potential, especially when extracted for 12 hours with water-ethanol (50:50 v/v) as solvent.

Keywords: Hyperbolic model; Power law model; Quantification of bioactives; UPLC-MS/MS; Ultrasound-assisted extraction; Camu-camu peel.

Introduction

The commercialization of whole and fresh fruits in locations far from the harvest region is still a challenge for industries. To mitigate fruit loss the pulping processing is a viable alternative, however, during the process, peel and seeds are discarded being considered industrial waste. Like many other fruits, Camu-camu is a raw material in the production of juices and frozen pulps and its peel, seeds and residual pulp is discarded.

Camu-camu is a fruit native to Brazil and is being studied by several research groups due to its great functional capacity for health benefits, such as low glycemic properties, hypertension, antimicrobials and cell rejuvenation, containing many antioxidants and ascorbic acid – vitamin C (Altenhofen et al., 2005; Fracassetti et al., 2013; Fujita et al., 2015). Camu-camu (*Myrciaria dubia*) is part of the *myrtaceae* family found natively in the Amazon rainforest. Camu-camu fruits vary from green to red, depending on maturation stage, with approximately 2.5 cm in diameter, the fruits are composed of pulp and about 40% seeds and peel (Araújo Padilha et al., 2018).

It is known that peels and seed extracts have certain properties of tannins, such as C-glycosidic ellagitannins (Kaneshima et al., 2016), cytotoxic effect against cancerous cell lines (Azevedo et al., 2018; Carmo et al., 2019), anti-hyperglycemic, anti-proliferating and anti-inflammatory action (Fidelis et al., 2020b). These factors, plus the search for foods with high antioxidant capacity by pharmaceutical and food companies, caused camu-camu residues to be seen as an economic potential (Conceição et al., 2020; Fidelis et al., 2020a).

The drying conservation method is an excellent option for these residues (peel and seeds) until they are reinserted in industries as food additives. Moreover, since it is a material seen with low potential value, traditional methods, such as cold conservation, are not well evaluated for storage of these products, due to electric consumption. Drying vegetable matrices brings several benefits in conservation and storage, because the material needs smaller spaces and packaging. Studies have proven that bioactive compounds and primary characteristics, such as fruit color, can be preserved and even enhanced when the correct method, time and drying temperature are employed (Silva et al., 2022; Araújo Padilha et al., 2018; Méndez-lagunas et al., 2017; Santos et al., 2019; Zielinska and Michalska, 2016).

In addition to considering the use of so-called industrial waste, another point that should be taken into account, for an ecological approach are the types of solvents used during the extraction process. The use of water as an extraction solvent is associated to its non-toxicity and reduction of environmental impacts (Silva et al., 2022.; Siqueira et al., 2021), when compared to other chemicals for extraction, such as organic solvents (methanol), that can bring negative effects to human health and environment (Li et al., 2006). The extraction solvent in synergy with the extraction method tends to offer excellent results. Ultrasound-assisted extraction (UAE) is reported as a method that provides higher yield in extraction due to its efficiency in increasing mass transfer of plant material to the medium (Espada-Bellido et al., 2017; Görgüç et al., 2020; Meregalli et al., 2020).

The use of kinetic models to understand the solid-liquid extraction profile is well disseminated among studies (Colosimo et al., 2022; Natolino and Porto, 2020). Mathematical models help in the identification of extraction method, with binomial time and temperature, and solvent type that results in the best conditions for extraction of bioactive compounds (Raimundini-Aranha et al., 2021).

Therefore, this study evaluates the influence of drying time and temperature on the dehydration of Camu-camu peel and on the preservation of bioactive compounds. To date, no study has been found on mathematical modeling of the concentration of bioactive compounds in dried camu-camu peel at different stages of fruit maturation. This study considered the potential of camu-camu bioactive compounds and the importance of using by-products for society, given the environmental impact that industrial waste has on the environment. Thus, the study aims to verify which is the best mathematical model for the extraction of camu-camu compounds, and to evaluate the effect of drying by convection of hot air on plant material.

Material and methodology

The reagents used were the radical 2,2-diphenyl-1-picrilhydrazil (DPPH•), 2,4,6-Tris(2-pyridil)-s- triazine (TPTZ), 6-hydroxy-2,5,7,8- tetramethylcromano-2-carboxylic acid (Trolox) obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The HPLC grade mobile phase (methanol) was acquired from J. T. Baker (Edo. of Mexico, Mexico). Ultrapure water was obtained from a Milli-Q ultrapure water purification system (Millipore, USA). Formic acid, used in the

mobile phase, was acquired from Sigma-Aldrich (Saint Louis, USA).

Plant material

Camu-camu (*Myrciaria dubia*) fruits acquired directly from the grower located in the city of Registro/SP, Brazil (latitude: 24º29'15"S; Longitude: 47º50'37") were transported refrigerated in thermal boxes at 10 ºC to the campus of the State University of Maringá in the city of Maringá/PR, Brazil (latitude: 23° 25'31 "S; Longitude: 51° 56'19" W). Fruit selection was done by peel color: green and red, being separated into two lots and sanitized with running water. The fruits went through the peeling process and the material (green and red peel) separately packed in polyethylene bags and stored at -18 ºC in the dark until drying. The initial peel moisture content was ±70%, determined using the AOAC method (1990). Peel color was analyzed to obtain sample standardization. The portable colorimeter Minolta ® CR400, with integration sphere and viewing angle of 3º, (illuminating d/3 and illuminating D65) was used, the peel was placed in a petri dish and the analysis performed with a repetition of ten times for each lot (green and red peel). The color was determined with the CIELAB - L* system representing the luminosity - from dark (0) to light (100), coordinate a* representing green (-) and red (+) and coordinate b*- representing blue (-) and yellow (+). Thus, the samples were standardized according to the following coloration: L*38.11, a*28.32 and b*22.29 mean values obtained for the red peel, and values of L*59.38, a*3.23 and b*32.44 for the green peel.

Drying

The plant material was thawed until reaching a temperature of 1 ºC where it went through forced convection drying with hot air at a constant speed of 1 m/s (sbench top laboratory, Solab brand, model SL-102) at 60 ºC. The dehydration temperature of camu-camu peels was chosen after laboratory tests and previous studies by our research group [11] and according to other literature [10].

After drying, the samples were ground in an industrial grinder (Model Jl Colombo, 700 Watts) and to reduce loss of photosensitive compounds, transferred separately to laminated plastic bags and stored at 5 ºC until extraction. The samples were identified according to peel color and two samples were obtained, named: 60Green and 60Red.

Extract preparation

The extraction of the bioactive compounds of camu-camu peel was performed in an ultrasonic bath in indirect contact (Model USC - 1400) with ultrasonic frequency of 40 KHz and ultrasonic power of 135 watts RMS. Taking into account the use of ecologically correct solvents for food application, water extraction and hydroalcoholic mixture were used in the proportion of 1g of solids to 100 mL of solvent (proportion of sample mass and solvent was performed according to Chagas et al. (2021)). Peel and solvents were placed in a Becker and immersed in the ultrasonic equipment where the extraction test began. After preliminary tests, the extraction conditions were defined: temperature of 50 ºC ± 2 and times of 1, 6, 12 and 24 h. The extracts obtained were filtered with filter paper. The extractions were performed in triplicate, without light. The extracts obtained were placed in an amber vial and stored under refrigeration between 5 ± 1 ºC until use.

Antioxidant activity

DPPH method (2.2 diffiphenyl-1-picril-hydrazil): The method of measuring antioxidant activity using free radical DPPH consists of the use of a volume of 150 µL of extract mixed in 2850 µL of working solution (DPPH diluted in methanol until absorbance of 1.1 nm at 515 nm in the spectrum). The sample was kept in the absence of light and the absorbance measurement was performed after 1 h of incubation. Methanol was used as blank, and the reading performed at 515 nm. The antioxidant inhibition activity in camu-camu samples was calculated using Eq (1) (Thaipong et al., 2006).

$$\%\ \text{radical inhibition} = \frac{(Absorbance\ negative\ control - Absorbance\ sample\ )}{Absorbance\ negative\ control} x\ 100 \qquad (1)$$

The results were calculated using the standard Trolox curve and expressed in mg Trolox/g of sample. The extract was diluted to a concentration of 0.5 mg/mL so that the DPPH values were within the standard curve ($y = 0.1101x + 3.8612/R^2 = 0.9979$).

Iron Reduction Power (FRAP): The method of ferric reduction in extracts was applied following Benzie & Strain (1996) with modifications. In summary, the FRAP reagent was prepared using the combination of acetate buffer 0.3 M/TPTZ

10 nM/ ferric chloride 20 nM in the ratio 10:1:1 (v:v:v). TPTZ 10 nM solution was prepared with 2,4,6-tris(2-pyridil)-s-triazine in 40 mmol hydrochloric acid. An aliquot of 90 µL of extract was mixed in 270 µL of distilled water and 2.7 mL of FRAP reagent in test tubes, homogenized and left at 37 ºC. FRAP reagent was used as blank in absorbance reading at 595 nm. Sample absorbance reading was performed after 30 min of incubation and the results expressed in mg Trolox/g of sample. For this FRAP analysis, camu-camu peel extracts were diluted to a concentration of 0.5 mg/mL (curve $y = 0.0016x - 0.0368$/ $R^2 = 0.9901$).

Bioactive compound analysis by UPLC-MS/MS

The phenolic compounds of the sample extracts were identified and quantified using a Waters ACQUITY UPLC® H-Class (Miliford, MA, USA) system coupled to a Xevo TQD triple-quadrupole mass spectrometer equipped with an electrospray ionization source (ESI) Z spray™ (Waters, Milford, MA, USA). For chromatographic separation of phenolic compounds, 5.0 µL of the final solution was injected into an Acquity UPLC® BEH C18 column (50 × 2.1 mm (i.d.), particle size of 1.7 µm) (Waters, Milford, MA, USA) that was maintained at 40 ± 1°C. The mobile phases were acidified in water with 0.1% formic acid (solvent A) and methanol (solvent B) at a flow rate of 0.300 mL min^{-1}.

The ESI source was operated in positive and negative ion mode using the following MS/MS parameters: 3.0 kV in positive ion mode and -2.5 kV in negative ion mode for capillary voltage, extractor voltage of 3.0 V, source temperature of 150 °C and 550 °C for the dissolvation gas. For the quantification of the extract [ethanol: water (50:50, v/v)], analytical curves were constructed at six concentration levels in triplicate. The results were expressed in milligrams per gram of sample (mg g^{-1}). The linear dynamic range and the calculation of the detection limit (LOD) and quantification limit (LOQ) were performed according to Gong et al. (2012).

$LOQ = 10 \times (Sa/b)$

$LOD = 3.3 \times (Sa/b)$

where Sa corresponds to the standard deviation of the linear coefficient and b corresponds to the slope of the analytical curve obtained by linear regression.

Kinetic models used to describe the concentration of bioactive compounds during camu-camu drying

To verify the extraction profile of the bioactive compounds present in camu-camu peel after the assays, four different mathematical models were adjusted: parabolic diffusion, power law, hyperbolic and pseudo-second order.

Parabolic diffusion model

For extracts from plant matrices, the parabolic diffusion model described by Equation 2 is commonly used:

$$Y = Y_0 + Y_1 t^{1/2} \quad (2)$$

Being: Y the extraction yield, Y_0 the initial yield and Y_1 the diffusion coefficient obtained during the extraction process. This model is used to describe extraction processes consisting of two stages, the first of which corresponds to washing, in which the compounds present on the surface of the solid material are transferred to the solvent, followed by the diffusion of the extracted bioactive compounds (Natolino and Porto, 2020; Rostami et al., 2017).

Power law model

The power law model can be described by Equation 3:

$$Y = Bt^n \quad (3)$$

B corresponds to the constant associated to extraction rate, incorporating the characteristics of the active transporter agent, t is the extraction time and n is the difusional exponent. When plant matrices are extracted, the value of n is less than 1. This model is usually used for solid-liquid extraction processes (Kashaninejad et al., 2017; Patil and Akamanchi, 2017; Rostami et al., 2017; Xie et al., 2020).

Hyperbolic model

The hyperbolic model (also called the Peleg model) is determined by Equation 4:

$$Y = \frac{k_1 t}{1 + k_2 t} \quad (4)$$

Where k_1 corresponds to the extraction rate initially in min-1, and the ratio k_1/k_2 is related to the maximum extraction yield (Y), this ratio being called a Peleg constant (Lee and Kim, 2019; Raimundini Aranha et al., 2021). This model is the result of a second-order velocity law, which was applied for the modeling of protopine extraction from *Fumaria officinalis* (Rakotondramasy-rabesiaka et al., 2007). At the beginning of the extraction, the order of the reaction is considered first-order, and then decreases to zero order in the last phase of the process.

Pseudo-second order model

The pseudo second order model can also be applied to antioxidant extraction rate data, as described by Equation 5 (Agu et al., 2018; Qu et al., 2010):

$$\frac{dq}{dt} = k(C_s - q)^2 \quad (5)$$

K is the constant of the second-order extraction rate, in L $^{g-1}$ min-1, C_s is the equilibrium concentration value of total phenolic compounds present in the liquid extract (g $^{L-1}$) and q is the extraction yield.

Considering the boundary conditions t=0 and q=0, it is possible to perform the integration and to obtain Equation 6 (Agu et al., 2018; Qu et al., 2010):

$$q = \frac{-C_s^2 kt}{1 + C_s kt} \quad (6)$$

Statistical analysis

For the verification of the best mathematical model for the extraction kinetics of the bioactive compounds of camu-camu peel, the reduced chi-square (χ^2), mean squared error (MSE), root-mean-square error (RMSE), normalized root-mean-square error (NRMSE) and modeling efficiency (EF) tests were used, represented by Equations 7 to 11, respectively.

$$\chi^2 = \frac{\sum(y_{exp} - y_{cal})^2}{N_0 - N_c} \quad (7)$$

$$MSE = \frac{\sum(y - y_{cal})^2}{N_0} \quad (8)$$

$$RMSE = \left(\frac{\sum(y_{exp}-y_{cal})^2}{N_0}\right)^{1/2} \quad (9)$$

$$NRMSE = \frac{RMSE}{y_{max}-y_{min}} \quad (10)$$

$$EF = \frac{\sum(y_{exp}-\bar{y}_{exp})^2-\sum(y_{cal}-y_{exp})^2}{\sum(y_{exp}-\bar{y}_{exp})^2} \quad (11)$$

Where N_c corresponds to the number of constants in the model, N_0 the number of observations, is $\bar{y}_{exp}$ the average value of the experimental data, y_{max} and y_{min} are the values corresponding to the maximum and minimum yield, respectively. The best adjustments occur when the values of χ^2, MSE, RMSE and NRMS areequal to 0, or as close as possible. For EF, the closer to 1, the better the fit (Horn & Engstrom, 1979, Meisami-Asl et al., 2010).

All experiments were carried out in triplicate and the results were calculated by Matlab R217b (Mathworks, Inc, USA).

Results and discussion

1 Behavior of antioxidant activity in drying kinetics

The drying process of the plant material before extraction of antioxidant compounds is interesting, since there is a greater ease of bioactive release at the time of extraction (Ahmad-Qasem et al., 2013). In addition, the drying process in plant matrices is associated with food preservation since the quantification of free water in the cell is reduced thus decreasing microbiological reactions.

Fresh Camu-camu red peels presented antioxidant activity for DPPH of 42.78±1.70 mmolTrolox /g and 72.53±0.34 mmolTrolox/g and FRAP of 62.33±0.63 mmolTrolox/g and 88.96±0.60 mmolTrolox/g, in the extraction conditions with ethanol/water (v/v) and pure water, respectively. For fresh green peels the calculated values were 89.45±0.65 mmolTrolox/g and 90.57±0.06 mmolTrolox/g (DPPH) and 105.07± mmolTrolox/g and 106.29± mmolTrolox/g (FRAP) for ethanol/water extraction (v/v) and water, respectively. The results observed in this study for DPPH of green peel are above those presented in the work of Rodrigues et al (2020) who analyzed whole fresh fruits of Camu-camu.

When comparing the results obtained for DPPH with the values presented by Azevêdo et al. (2014) for fresh Camu-camu residue (100 g of residue consists of 65.6 g of seeds and 34.4 g of peel), our values are approximately twice lower (in our case only peel was used), this result can be explained due to the high concentration of antioxidant compounds present in Camu-camu seeds (Araújo et al., 2019; Fidelis et al., 2020b). For the antioxidant activity by iron reduction (FRAP) the highest values found were for green peels, which were higher than those presented by Fujita et al., (2013) with Camu-Camu pulp (values between 30-40 mmolTrolox/g in dried fruits at 60 ºC without maltodextrin concentration). Regarding peel extraction yield (Table 1), the best results in general are in ethanol/ water 50/50 (v/v) in the two methods used (DPPH and FRAP). According to Raimundini-Aranha et al. (2021) the quantification of water in the solvent generates a medium with greater polarity thus facilitating the extraction of compounds and increasing yield.

Table 1 - Yield of extracts obtained by DPPH and FRAP method for camu-camu peel.

GREEN PEEL				
			y Trolox (mmol Trolox $^{g-1}$ sample)	
Solvents	**Proportion (v/v)**	**Time (hours)**	**DPPH**	**FRAP**
Ethanol/Water	50/50	1	1.67E-01 ± 3.00E-04^{d}	2.39E-01 ± 1.76E-03^{d}
Water	-	1	1.51E-01 ± 3.00E-04^{and}	2.20E-01 ± 2.36E-03^{d}
Ethanol/Water	50/50	6	1.89E-01 ± 5.40E-03^{b,c}	3.06E-01 ± 2.66E-03^{b,c}
Water	-	6	1.79E-01 ± 9.22E-04^{c,d}	2.52E-01 ± 1.15E-03^{C,D}
Ethanol/Water	50/50	12	2.57E-01 ± 9.00E-04to	3.87E-01 ± 2.63E-03to
Water	-	12	1.96E-01 ± 2.16E-03^{b}	2.49E-01 ± 2.38E-03^{d}
Ethanol/Water	50/50	24	2.69E-01 ± 1.31E-03to	3.91E-01 ± 2.46E-03^{a,b}
Water	-	24	1.77E-01 ± 1.89E-03^{c,d}	2.34E-01 ± 3.04E-04^{d}
RED PEEL				
			y Trolox (mmol Trolox $^{g-1}$ sample)	
Solvents	**Proportion (v/v)**	**Time (hours)**	**DPPH**	**FRAP**
Ethanol/Water	50/50	1	1.62E-01 ± 2.39E-03^{f}	2.12E-01 ± 4.74E-03^{c,d}
Water	-	1	1.56E-01 ± 1.82E-03^{g}	1.78E-01 ± 3.86E-03^{and}
Ethanol/Water	50/50	6	2.19E-01 ± 2.10E-03^{c}	2.52E-01 ± 5.97E-03^{b}
Water	-	6	1.59E-01 ± 6.08E-04^{and}	2.15E-01 ± 5.47E-03^{c,d}
Ethanol/Water	50/50	12	2.35E-01 ± 1.20E-03^{b}	2.89E-01 ± 3.51E-04to
Water	-	12	1.90E-01 ± 6.08E-04^{and}	2.04E-01 ± 5.44E-03^{d}
Ethanol/Water	50/50	24	2.47E-01 ± 4.81E-03to	2.95E-01 ± 3.51E-04to
Water	-	24	1.98E-01 ± 3.04E-04^{d}	2.21E-01 ± 8.08E-03^{c}

Results expressed with mean±standard deviation (triplicate). ^{abcd} means with the same lowercase

letters are not significantly different (Tukey test, p <0.05).

For extraction, there is a diversity of options, not necessarily existing an ideal method because each sample has a distinct composition, and a given solvent can be suitable in one case and not in another. Extraction parameters such as solvent polarity, pH, temperature, number of extraction steps, solvent volume and particle size of samples are the factors explored by several authors working with Camu-camu (Chagas et al., 2021; Azevêdo et al., 2014; Fidelis et al., 2020; Kaneshima et al., 2016).

In addition, extraction time also considerably affects the recovery of bioactive compounds. According to research by Naczk and Shahidi (2004) the extraction period can vary from 1 minute to 24 hours and long extraction periods may increase the possibility of phenolic oxidation requiring researchers to use reducing agents to the solvent. Thus, for both green and red peel, the highest yields were recorded at 12 and 24h in ethanol/water 50/50 (v/v) extraction. The interval between 1 and 6h presented the lowest yields, not being favorable to antioxidant extraction of camu-camu peels. In the study of Siqueira et al. (2022), the authors investigate the best extraction conditions in blackberry bagasse, longer extraction times also favored the extraction of anthocyanins, the authors point out that the positive effect on extraction yield is related to mass transfer and its dependence over time. Silva et al., (2022) showed that extraction with higher time and temperature variation was efficient to extract phenolic compounds from *Muntingia calabura* peels.

2 Modeling

The adjustment of the kinetic models for extraction of bioactive compounds was used to minimize the objective function, according to Equation 13.

$$\Phi = \sum(y_{cal} - y_{exp})^2 \quad (13)$$

The coefficients obtained for each mathematical model of extraction kinetics are presented in Table 2 and statistical analyses varying the solvent, method used (DPPH or FRAP) and extract condition (drying temperature and green/red peel) are presented in Table 3.

To evaluate the quality of the adjustments, the lowest values d and χ^2, MSE, RMSE and NRMSE were used as a comparison criterion, thus, it was verified that for both camu-camu peel the two best models that adjusted to the extraction kinetic data were the Hyperbolic and Pseudo-second order, with the lowest statistical values and results closer to 1 of EF. These models present good adjustments for samples that have desired bioactive compounds dissolving rapidly in the solvent, and then a slow diffusion step occurs. In addition, they are widely used models for solid-liquid chemical extractions (Cheung et al., 2013; Raimundini Aranha et al., 2021).

On the other hand, it was verified that the parabolic diffusion and power law models did not present good adjustments for the kinetics of extraction of bioactive compounds from camu-camu peel. This occurs for extractions that present predominance in the washing mechanism, instead of diffusion (Agu et al., 2018; Chinedu and Ijeoma, 2019).

Table 2 - Coefficient obtained for each mathematical model for the DPPH methodology and FRAP drying temperature of 60°C.

DPPH							
Solvent EtOH/H_2O 50/50 (v/v), green peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	7.11E-02	6.00E-03	-	-	-	-	-
Power Law	-	-	8.00E-03	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	6.70E-03	2.60E-02	-
Pseudo Second Order	-	-	-	-	-	-	7.63E-02
Solvent Water, green peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	7.94E-02	3.60E-03	-	-	-	-	-
Power Law	-	-	5.90E-03	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	1.32E-02	7.01E-02	-
Pseudo Second Order	-	-	-	-	-	-	2.70E-01
Solvent EtOH/H2O 50/50 (v/v), red peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	2.82E-02	1.60E-03	-	-	-	-	-
Power Law	-	-	7.60E-03	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	7.60E-03	3.11E-02	-
Pseudo Second Order	-	-	-	-	-	-	1.25E-01
Solvent Water, red peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	7.62E-02	4.00E-03	-	-	-	-	-
Power Law	-	-	6.30E-03	5.00E-01	-	-	-

Hyperbolic	-	-	-	-	1.22E-02	6.17E-02	-
Pseudo Second Order	-	-	-	-	-	-	3.05E-01
FRAP							
Solvent EtOH/H_2O 50/50 (v/v), green peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	1.04E-01	9.00E-03	-	-	-	-	-
Power Law	-	-	1.19E-02	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	9.20E-03	2.37E-02	-
Pseudo Second Order	-	-	-	-	-	-	5.91E-02
Solvent Water, green peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	1.14E-01	4.50E-03	-	-	-	-	-
Power Law	-	-	8.00E-03	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	3.55E-02	1.44E-01	-
Pseudo Second Order	-	-	-	-	-	-	4.51E-01
Solvent EtOH/H_2O 50/50 (v/v), red peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	9.33E-02	6.50E-03	-	-	-	-	-
Power Law	-	-	9.10E-03	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	1.22E-02	4.41E-02	-
Pseudo Second Order	-	-	-	-	-	-	1.31E-01
Solvent Water, red peel							
Model	**Y0**	**Y1**	**B**	**n**	**K1**	**K2**	**K**
Parabolic Diffusion	8.82E-02	4.40E-03	-	-	-	-	-
Power Law	-	-	7.00E-03	5.00E-01	-	-	-
Hyperbolic	-	-	-	-	1.62E-02	7.45E-02	-
Pseudo Second Order	-	-	-	-	-	-	3.02E-01

Being: Y the extraction yield, Y0 the initial yield, Y1 the diffusion coefficient obtained during the extraction process, Constant B related to the extraction rate, k1 initial extraction rate, K is the constant of the second order extraction rate.

The coefficients are well correlated to the data adjustments of the models. As observed in the results of our experiment, the Parabolic Diffusion model presented the coefficient of y_0 greater than y_1 in all DPPH adjustments, being $7.11E^{-02} > 6.00E^{-03}$ and 2.82E-02 >1.60E-03 for the ethanolic solvent and, $7.94E^{-02} > 3.60E^{-03}$ and $7.62E^{-02} > 4.00E^{-03}$ for the aqueous solvent, for both green and red peel, respectively. This phenomenon is repeated in other results for iron reduction analysis (FRAP). According to Cheung et al., (2013) the Parabolic Diffusion model presents an initial stage for yield (y_0) and a slow stage (y_1) for increasing the yield of $t^{1/2}$.

For the power law model constant B, which incorporates the characteristics of the particle-active substance system, its maximum point was in the extraction of

green peel (1.19E^{-02}, FRAP) and its minimum point with red peel (9.10E^{-03}, FRAP) both with ethanolic solvent. While, the diffusion coefficient n, presented for all results values below 1 as expected for most plant materials. The results of this study can be compared with others reported in the literature, for example, Kashaninejad et al., (2020) reported values lower than 0.2 for the diffusion coefficient in the extraction curves of phenolic compounds for pure water and ethanol/water solvents.

Table 3 - Statistical analyses for each mathematical model for DPPH and FRAP methodology, drying temperature of 60°C.

DPPH					
Solvent EtOH/H2O 50/50 (v/v), green peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	2.10E-03	1.30E-03	3.55E-02	1.44E-01	8.38E-01
Power Law	4.00E-03	3.20E-03	5.65E-02	2.29E-01	5.91E-01
Hyperbolic	1.00E-03	6.00E-04	2.45E-02	9.92E-02	9.23E-01
Pseudo Second Order	1.10E-03	6.51E-04	2.55E-02	1.03E-01	9.17E-01
Solvent Water, green peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	2.70E-03	1.60E-03	4.02E-02	2.32E-01	5.90E-01
Power Law	4.90E-03	3.90E-03	6.28E-02	3.63E-01	1.35E-04
Hyperbolic	2.48E-04	1.49E-04	1.22E-02	7.04E-02	9.62E-01
Pseudo Second Order	2.93E-04	1.76E-04	1.33E-02	7.66E-02	9.55E-01
Solvent EtOH/H2O 50/50 (v/v), red peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	3.10E-03	1.80E-03	4.29E-02	1.82E-01	7.57E-01
Power Law	4.80E-03	3.80E-03	6.18E-02	2.62E-01	4.94E-01
Hyperbolic	6.71E-05	4.03E-05	6.30E-03	2.69E-02	9.95E-01
Pseudo Second Order	6.74E-05	4.04E-05	6.40E-03	2.69E-02	9.95E-01
Solvent Water, red peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	2.70E-03	1.60E-03	4.01E-02	2.23E-01	6.48E-01
Power Law	4.70E-03	3.80E-03	6.14E-02	3.41E-01	1.75E-01
Hyperbolic	1.17E-04	6.99E-05	8.40E-03	4.65E-02	9.85E-01
Pseudo Second Order	1.17E-04	7.01E-05	8.40E-03	4.65E-02	9.85E-01
FRAP					
Solvent EtOH/H2O 50/50 (v/v), green peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	5.30E-03	3.20E-03	5.65E-02	1.55E-01	8.23E-01
Power Law	9.30E-03	7.40E-03	8.61E-02	2.36E-01	5.89E-01
Hyperbolic	1.10E-03	6.32E-04	2.51E-02	6.89E-02	9.65E-01

Pseudo Second Order	1.10E-03	6.34E-04	2.52E-02	6.90E-02	9.65E-01
Solvent Water, green peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	6.10E-03	3.70E-03	6.04E-02	2.68E-01	5.02E-01
Power Law	1.05E-02	8.40E-03	9.15E-02	4.05E-01	1.41E-01
Hyperbolic	3.23E-04	1.94E-04	1.39E-02	6.16E-02	9.74E-01
Pseudo Second Order	3.42E-04	2.05E-04	1.43E-02	6.35E-02	9.72E-01
Solvent EtOH/H2O 50/50 (v/v), red peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	4.80E-03	2.90E-03	5.37E-02	1.92E-01	7.28E-01
Power Law	7.70E-03	6.20E-03	7.87E-02	2.82E-01	4.16E-01
Hyperbolic	2.79E-04	1.67E-04	1.29E-02	4.63E-02	9.84E-01
Pseudo Second Order	2.92E-04	1.75E-04	1.32E-02	4.74E-02	9.84E-01
Solvent Water, red peel					
Model	**χ^2**	**Mse**	**RMSE**	**NRMSE**	**Ef**
Parabolic Diffusion	3.50E-03	2.10E-03	4.57E-02	2.30E-01	6.23E-01
Power Law	6.20E-03	5.00E-03	7.05E-02	3.55E-01	1.02E-01
Hyperbolic	2.11E-04	1.27E-04	1.13E-02	5.66E-02	9.77E-01
Pseudo Second Order	2.19E-04	1.31E-04	1.15E-02	5.76E-02	9.76E-01

Being: reduced chi-square χ^2, quadratic mean MSE , mean square root RMSE , NRMSE normal quadratic mean error and EF square root error**.**

Figures 1 and 2 present the graphs of the mathematical adjustments for the kinetic models of extraction that best fit the green and red peel according to the type of solvent and analysis used.

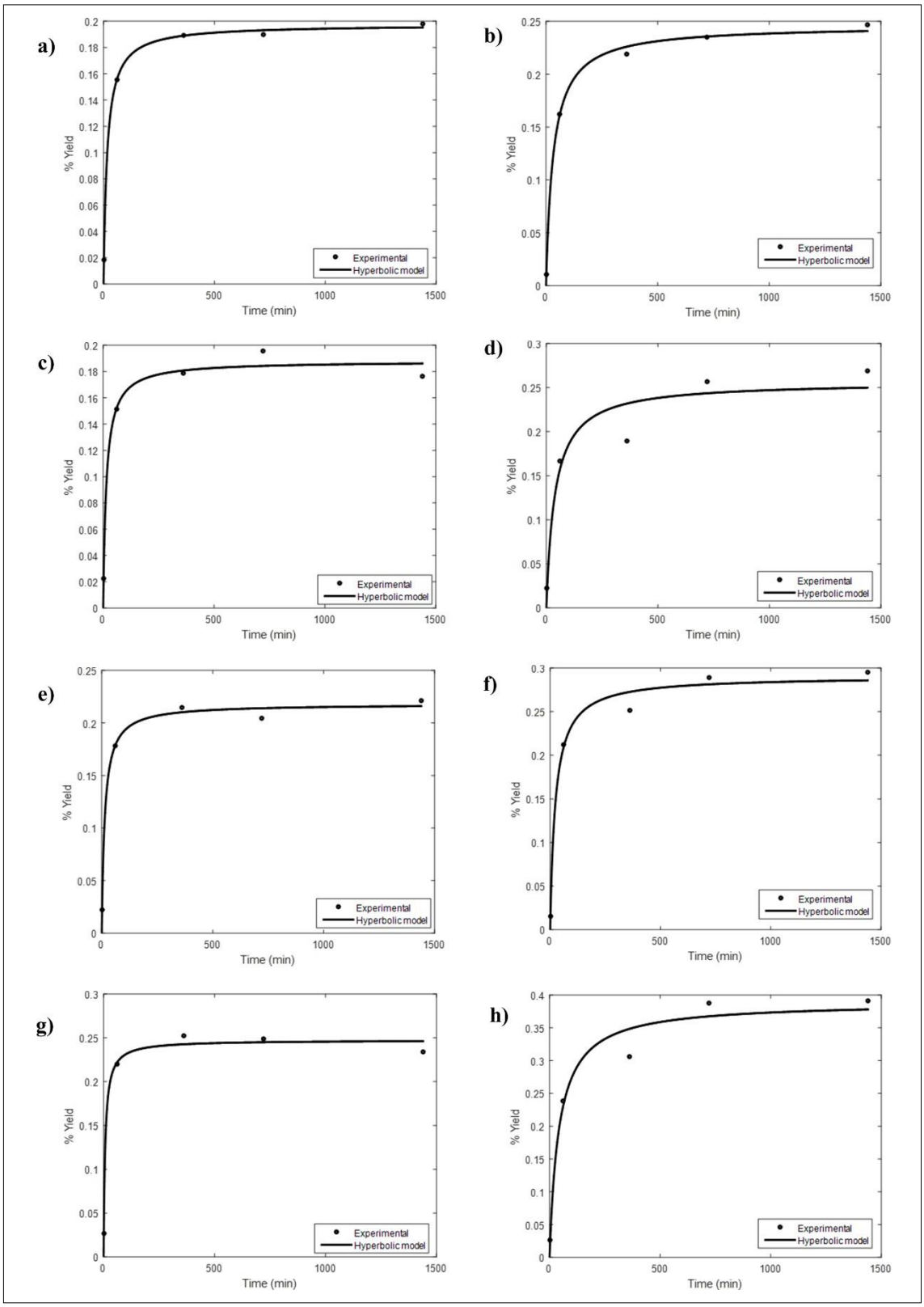

Figure 1. Mathematical adjustments for the kinetic model of Hyperbolic extraction, for DPPH analysis mature peel solvent water (a), mature peel solvent 50% ethanol (v/v) (b), green peel solvent water (c), green peel solvent 50% ethanol (v/v) (d), FRAP analysis with mature peel solvent water (e), mature peel solvent ethanol 50% (v/v) (f), green peel solvent water (g) and green peel solvent ethanol 50% (v/v) (h).

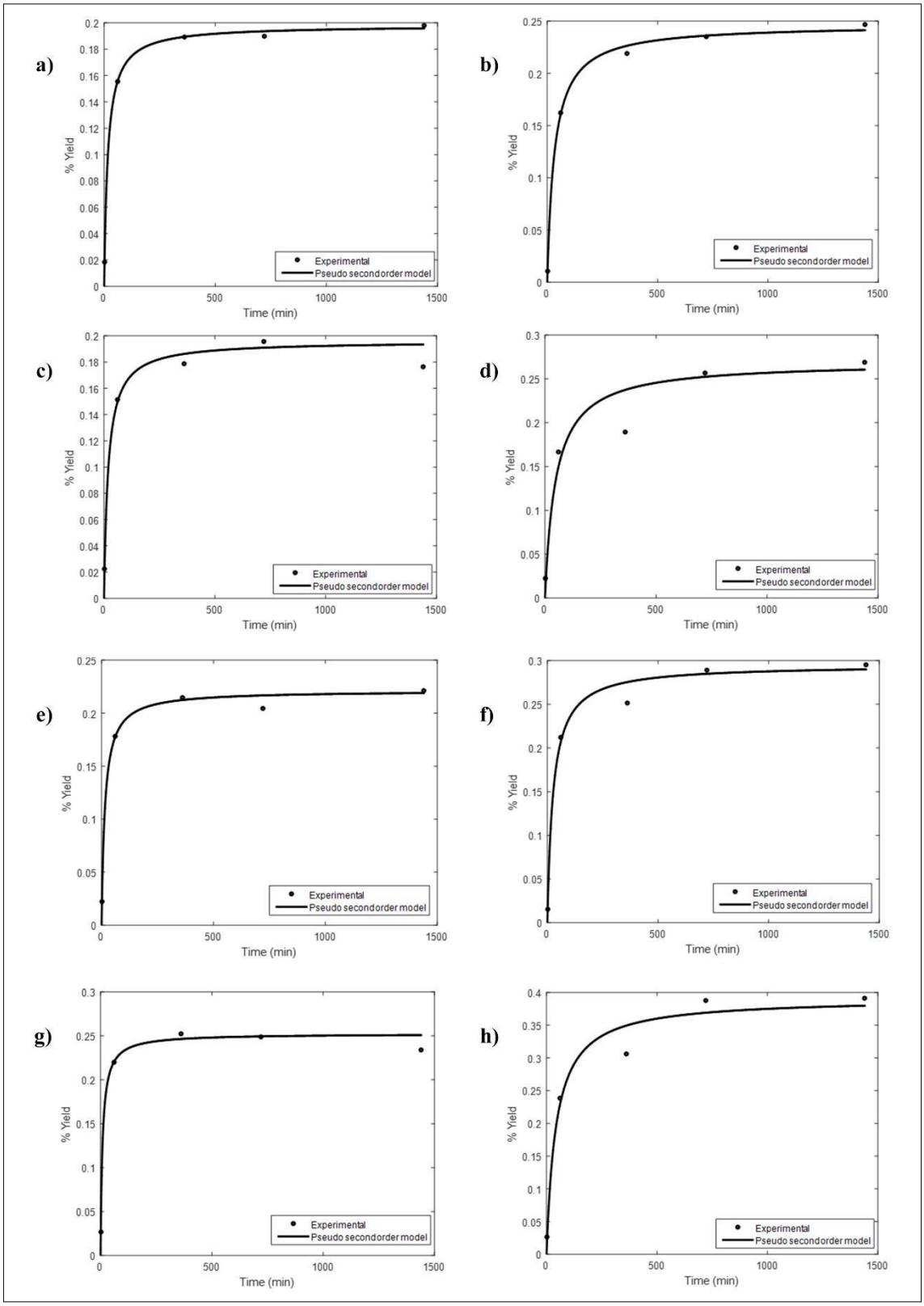

Figure 2. Mathematical adjustments for the kinetic model of Pseudo Second Order extraction, for DPPH analysis mature peel solvent water (a), mature peel solvent 50% ethanol (v/v) (b), green peel solvent water (c), green peel solvent 50% ethanol (v/v) (d), FRAP analysis with mature peel solvent water (e), mature peel solvent ethanol 50% (v/v) (f), green peel solvent water (g) and green peel solvent ethanol 50% (v/v) (h).

3 UPLC-MS analysis of bioactive compounds of different camu-camu peel colors

The data obtained with fresh and dried, green and red camu-camu peel are shown in Table 4 and 5. The identification of the compounds occurred using the comparison of the spectra found with those of the literature and public database (Degtyarenko et al., 2008; Kim et al., 2016). The presence of nine bioactive compounds, classified as anthocyanins, flavonoids, phenolic acids and ellagic acid, was identified.

Compounds 3, 4 and 5 with mass $[M]^-$ (m/z) 301.1, $[M]^-$ (m/z) 317.05 and $[M]^-$ (m/z) 609.15 were identified as quercetin ($C_{15}H_{10}O_7$), myrcetin ($C_{15}H_{10}O_8$) and rutin ($C_{27}H_{30}O_{16}$), respectively, belonging to flavonoids (Table 8). These compounds have already been identified by other researchers in Camu-camu fruits (Bataglion et al., 2015; Araújo Padilha et al., 2018; Fidelis et al., 2020a). Flavonoids are compounds present in several fruits besides Camu-camu, such as lemons, oranges, grapefruits, and act positively on human health, reducing risk of physiological and degenerative diseases (Aadil et al., 2013).

Within the class of anthocyanins, cyanidin-3-O-glucoside $[M]^+$ (m/z) 449.2 and delphinidin $[M]^+$ (m/z) 303.15 were identified, both in positive mode, and these compounds have been previously reported in Camu-camu (Conceição et al., 2020; Fujita et al., 2015; Zanatta et al., 2005). Anthocyanins are heat treatment sensitive compounds and can be easily degraded, however, in this study, it is possible to verify that the drying temperature employed (60 ºC) was effective in retaining anthocyanins in the sample.

Phenolic acids were the group of compounds detected in Camu-camu peel extracts in negative mode with [M]- (m/z) 169.02 for gallic acid, [M]- (m/z) 353.12 for chlorogenic acid and [M]- (m/z) 163.0 for p-coumaric acid. Bataglion et al., (2015) in their studies detected in Camu-Camu pulp values of gallic acid (7.39 ± 0.46) and p-Coumaric acid (5.13 ± 0.61) however chlorogenic acid was not detected in their studies. However, Rodrigues et al., (2020b) were able to detect concentrations of gallic, chlorogenic and p-Coumaric acid in Camu-Camu fruits (pulp, peel and seed residues) using UHPLC-Q-TOF-MS/MS. The maximum values found for p-coumaric acid were 0.150±0.00 and 97.298±0.179 for gallic acid, both values in samples submitted to concentration by reverse osmosis. The

compound ellagic acid ($C_{14}H_6O_8$) showed a predominant ion in the mass [M]- (m/z) 301.05.

The quantification of compounds identified in this study is similar to that of other studies that identified the presence of phenolic compounds in pulp, peel, and seed of camu-camu residue (Azevêdo et al., 2014; Rodrigues et al., 2020b). Chagas et al, (2021) when analyzing camu-camu powder at three distinct temperatures (50, 60 and 70 ºC) identified eleven flavonoids, flavones, and anthocyanins.

Table 9 shows the quantification of phenolic compounds in green and red camu-camu peel. Is noted that the standard curves presented a correlation coefficient value (R^2) greater than 0.99, in addition the table presents the minimum limit values of detection and quantification of each product (LOQ and LOD). According to the analytical methods used, quantification by UPLC-MS/MS determined that the recovery of Cyanidin 3-glucoside was 3±0.00 mg/100g, 108±0.09 mg/100g, 3±0.01 mg/100g and 2±0.00 mg/100g and for Delphinidin was 18±0.05 mg/100g, 72±0.09 mg/100g, 33±0.03 mg/100g and 20±00mg/100g , in green and red fresh peel and green and red dry peel, respectively.

Compared to the literature, this study presented a lower quantification of bioactive compounds which may be related to the type of material used, in this case, only green and red Camu-camu peel were evaluated. In addition, regarding fruit growing conditions, in this study the fruits came from the southwestern region of Brazil, not from the northeast region where the fruit is native. This could have influenced the concentration of photochemical molecules and similar variations were also reported by Neves et al. (2015) and Fujita et al. (2015).

Conclusion

Camu-camu peel currently considered a waste from pulp production, has potential application in foods. Considering the interest in adding value to by-products, the drying process and kinetic modeling of Camu-camu extracts are interesting both for green and red fruits. Best results were obtained with ethanol/water 50/50 (v/v) as solvent and extraction times of 12 and 24h that favored extraction, on average 38% higher than 1 hour.

The Hyperbolic and Pseudo-second kinetic model presented the best adjustments for the extraction of compounds in both green and red peel. It is

noteworthy that from the two models, it is possible to carry out other studies in other drying ranges and extraction times, thus promoting new strategies for the use of models in industrial application.

In addition, the use of the UPLC-MS/MS method resulted in the determination of nine bioactive compound types (anthocyanins, flavonoids, phenolic acids and ellagic acid) in dry camu-camu peels. Therefore, our research not only corroborates the relevance of studying camu-camu, but also the need for in-depth studies for the use of industrial by-products such as peel as a source of nutritive compounds.

Table 4: Bioactive compounds identified by UPLC-MS/MS in fresh green and red Camu-camu peels.

	Compound	Molecular Formula	TR (min)	[M-H] $^{-}$ (m/z)	[M] $^{+}$ (m/z)	Fragments (m/z)
Anthocyanins						
	1 cyanidin 3-O-glucoside	$C_{21}H_{21}The_{11}$	3.14		449.2	287.1; 213.0
	2 Delphinidin	$C_{15}H11\ O_{7}$	4.22		303.15	229.15; 257.05; 153.0
Flavonoids						
	3 Quercetin	$C_{15}H_{10}O_{7}$	4.82	301.1		151.0; 179.0; 121.0
	4 Myricetin	$C_{15}H_{10}O_{8}$	4.46	317.05		179.0; 151.0
	5 Rutin	$C_{27}H_{30}O_{16}$	4.20	609.15		300.05; 271.05
Phenolic acids						
	6 Gallic acid	$C_{7}H_{6}The_{5}$	0.72	169.02		124.95; 78.95
	7 Chlorogenic acid	$C_{16}H_{18}The_{9}$	2.56	353.12		191.0; 85.0
	8 p-coumaric	$C_{9}H_{8}The_{3}$	3.50	163.0		93.0; 119.0
Ellagic Acid Derivatives						
	9 Ellagic acid	$C_{14}H_{6}The_{8}$	4.77	301.05		229.0; 283.5

Note: All results were made in triplicate; TR retention time; [M-H]-: deprotonated molecule (negative mode); [M]+: protonated molecule (positive mode).

Table 5: Content of phenolic compounds in camu-camu peel.

	Fresh		Peel (mg/100g dry weight) 60 ºC		Analytical curve parameters			
Compound	**Green**	**Red**	**Green**	**Red**	**Equation**	**R^2**	**LOQ (ug/g)**	**LOD (ug/g**
3-glucoside Cyanidin	3±0.00	108±0.09	3±0.01	2±0.00	31223.5x – 17.729	0.9941	0.01	0.005
Delphinidin	18±0.05	72±0.09	33±0.03	20±0.02	1830.87x - 13.7043	0.9990	0.03	0.009
Chlorogenic acid	<LOD	<LOD	<LOD	<LOD	7307.82x - 64.8727	0.9984	0.30	0.090
Quercetin	<LOD	<LOQ	2±0.00	<LOQ	28899.9x – 126.996	0.9991	0.01	0.003
Myricetin	<LOQ	<LOD	11±0.01	6±0.00	25287.6x - 60.7504	0.9992	0.01	0.005
Gallic acid	2±0.0	2±0.0	3±0.00	<LOQ	31112.9x - 601,086	0.9991	0.03	0.010

Rutin	<LOD	<LOD	<LOD	<LOD	30944.9x - 17.8356	0.9947	0.01	0.006
p-coumaric	<LOD	<LOD	<LOD	<LOD	45863.1x + 76.4219	0.9984	0.02	0.008
Ellagic Acid	<LOD	<LOD	16±0.02	<LOQ	2939.44x + 167.14	0.9951	0.05	0.016

Note: limit of detection (LOD) and limit of quantitation (LOQ)

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