UNIVERSIDADE FEDERAL DA PARAÍBA
CENTRO DE TECNOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E TECNOLOGIA DE ALIMENTOS

MARCONY EDSON DA SILVA JÚNIOR

EXTRAÇÃO DE COMPOSTOS FENÓLICOS DE FARINHA DE RESÍDUO DE CIRIGUELA POR DIFERENTES MÉTODOS E SUA ESTABILIDADE UTILIZANDO MICROENCAPSULAÇÃO POR ATOMIZAÇÃO

JOÃO PESSOA
2022

MARCONY EDSON DA SILVA JÚNIOR

EXTRAÇÃO DE COMPOSTOS FENÓLICOS DE FARINHA DE RESÍDUO DE CIRIGUELA POR DIFERENTES MÉTODOS E SUA ESTABILIDADE UTILIZANDO MICROENCAPSULAÇÃO POR ATOMIZAÇÃO

JOÃO PESSOA

2022

MARCONY EDSON DA SILVA JÚNIOR

EXTRAÇÃO DE COMPOSTOS FENÓLICOS DE FARINHA DE RESÍDUO DE CIRIGUELA POR DIFERENTES MÉTODOS E SUA ESTABILIDADE UTILIZANDO MICROENCAPSULAÇÃO

Tese apresentada ao Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, Centro de Tecnologia, da Universidade Federal da Paraíba, em cumprimento aos requisitos para obtenção do título de Doutor em Ciência e Tecnologia de Alimentos.

ORIENTADORA: Profª Drª Maria Inês Sucupira Maciel

JOÃO PESSOA

2022

Catalogação na publicação
Seção de Catalogação e Classificação

S586e Silva Júnior, Marcony Edson da.
Extração de compostos fenólicos de farinha de resíduo de ciriguela por diferentes métodos e sua estabilidade utilizando microencapsulação por atomização / Marcony Edson da Silva Júnior. - João Pessoa, 2022.
184 f. : il.

Orientação: Maria Inês Sucupira Maciel.
Tese (Doutorado) - UFPB/CT.

1. Antioxidantes. 2. Compostos bioativos. 3. Ultrassom. 4. Micro-ondas. 5. Microencapsulação. 6. Atomização. 7. Liofilização. 8. Spondias purpúrea L. I. Maciel, Maria Inês Sucupira. II. Título.

UFPB/BC CDU 678.048(043)

Elaborado por RUSTON SAMMEVILLE ALEXANDRE MARQUES DA SILVA- CRB-15/0386

MARCONY EDSON DA SILVA JÚNIOR

EXTRAÇÃO DE COMPOSTOS FENÓLICOS DE FARINHA DE RESÍDUO DE CIRIGUELA POR DIFERENTES MÉTODOS E SUA ESTABILIDADE UTILIZANDO MICROENCAPSULAÇÃO

Esta tese foi julgada para obtenção do título de Doutor em Ciência e Tecnologia de Alimentos e aprovada em 27/09/2022 pelo Programa de Pós-Graduação em Ciência e Tecnologia de Alimento em sua forma final.

BANCA EXAMINADORA:

Maria Inês Sucupira Maciel

Profa. Dra. Maria Inês Sucupira Maciel (Orientadora)
Universidade Federal da Paraíba (Membro Interno)

Prof. Dr. Flávio Luiz Honorato da Silva
Universidade Federal da Paraíba (Membro Interno)

Maria Elieidy Gomes de Oliveira

Profa. Dra. Maria Elieidy Gomes de Oliveira
Universidade Federal da Paraíba (Membro Externo)

Renata V. Tonon

Profa. Dra. Renata Valeriano Tonon
EMBRAPA - Rio de Janeiro (Membro Externo)

Attilio Converti

Prof. Dr. Attilio Converti
Universidade de Genova - Itália (Membro Externo)

A minha família, amigos e amigas,

com muito amor e carinho...

AGRADECIMENTOS

A Deus, por todas as bênçãos recebidas e que permitiram todo meu crescimento até então e continuarão a iluminar os caminhos a serem trilhados por mim na busca do aperfeiçoamento constante tanto profissional como espiritual.

Aos meus pais, Josefa Clara de Melo e Marcony Edson da Silva, pelo incentivo, confiança, apoio, conselhos, educação, carinho e amor. Sem dúvidas, vocês são as pessoas mais importantes na minha vida. E fizeram-me compreender o real valor do conhecimento e o grande prazer de estudar. Também agradeço às minhas avós Eulália Mariano e Josefa Clara, e ao meu avô Teodoro Antônio (*in memorian*) que lembrarei sempre das suas palavras, gestos e ensinamentos. E a toda minha família pelo carinho.

Às minhas amigas Ana Cristina, Nathália Barbosa, Priscilla Marinho e Jaqueline Ferreira, obrigada a todas pela amizade sincera, pelo carinho e por toda ajuda durante as análises.

Ao meu amigo Luiz Júnior, obrigado por todo apoio, incentivo, compreensão, companhia, e torcida nessa etapa difícil da minha vida. Que sempre esteve me auxiliando com os gráficos e planilhas no Excel. Sou eternamente grato por toda sua ajuda.

À professora Maria Inês Sucupira Maciel, muito obrigada pela sua orientação desde a iniciação científica, passando pelo mestrado e agora no doutorado. Com certeza, esse período foi um dos mais valiosos para minha formação acadêmica. Grato pela confiança no meu potencial, ensinamentos e conselhos que me permitiram um crescimento ímpar e a conquista de mais uma etapa.

Ao professor Flávio Luiz, muito obrigado por sempre está disponível em tirar minhas dúvidas das análises estatísticas. Por todos os encontros virtuais durante a pandemia, para me auxiliar com o Statistic.

Também agradeço a Vitória Rollim (PIBIC), que me acompanhou durante a jornada dos 4 anos do meu doutorado, e esteve presente em todas as etapas da pesquisa. Obrigado pela amizade, paciência e companheirismo no laboratório.

À banca examinadora por todas as contribuições e por terem aceitado participar.

Ao CENAPESQ, por disponibilizar o extrator de micro-ondas, liofilizador e o MEV.

Ao CETENE, pela realização das análises físicas do extrato em pó.

Por fim, agradeço a CAPES pelo apoio financeiro, a Universidade Federal Rural de Pernambuco (UFRPE), a Universidade Federal de Pernambuco (UFPE) e a Universidade Federal de Campina Grande (UFCG), por terem disponibilizado os laboratórios para realização da pesquisa. E a Universidade Federal da Paraíba (UFPB) pela oportunidade de obter o título de Doutor em Ciência e Tecnologia de Alimentos.

RESUMO

Nas últimas décadas, problemas econômicos e ambientais têm provocado crescentes preocupações com o grande volume de subprodutos gerados pelas indústrias alimentícias. Destes, destaca-se o resíduo da ciriguela (*Spondias purpurea* L.), que contém compostos bioativos com propriedades antioxidantes. Sendo assim, este trabalho teve como objetivo otimizar o processo de extração dos compostos fenólicos da farinha de resíduo de ciriguela (FRC) utilizando extração assistida por ultrassom (EAU) e comparar em relação ao teor de compostos fenólicos (TCF), aos extratos obtidos por extração convencional e extração assistida por micro-ondas. Em seguida foi realizada a otimização da microencapsulação por atomização do extrato de FRC obtido por EAU e produção do extrato microencapsulado por liofilização (controle). Caracterização física, determinação do perfil fenólico por HPLC, digestão gastrointestinal *in vitro*, e análise de estabilidade por 90 dias em duas temperaturas (7 e 25 ºC) foram realizadas com os extratos microencapsulados da FRC. A condição ótima da EAU dos compostos fenólicos do extrato de FRC foi obtida usando amplitude ultrassônica de 100% e tempo de 15 min. O processo de extração afetou TCF e a atividade antioxidante por DPPH e FRAP, quanto maior a amplitude ultrassônica e maior tempo, maior foi o TCF e atividade antioxidante. O TCF dos extratos atomizados variaram de 190.45 a 454.66 mg equivalentes de ácido gálico (EAG/g), tendo maior influencia pela formulação de agentes encapsulantes. A eficiência de encapsulamento (EE) dos extratos atomizados variou de 76.83% a 99.84%. A condição otimizada da microencapsulação por atomização do extrato de compostos fenólicos de FRC foi obtida utilizando temperatura de 150 ºC, vazão de alimentação de 0.80 L/h e 100% de goma arábica como agente encapsulante. A umidade, solubilidade e higroscopicidade dos extratos atomizados e liofilizados não apresentaram diferença significativa. Para EE e TCF houve diferença significativa ($p<0.05$), o extrato atomizado apresentou maior EE e o extrato liofilizado maior TCF. No extrato atomizado de FRC, a rutina (82.69 µg g^{-1}) foi o composto encontrado em maior quantidade. Enquanto catequina (93.94 µg g^{-1}) foi predominante no extrato de FRC liofilizado. Ao analisar a digestão gastrointestinal simulada dos extratos, observou-se que maiores valores de compostos fenólicos foram encontrados após a fase gástrica, e os menores valores na última fase. A rutina foi o composto que apresentou maior teor após a digestão dos extratos atomizado (68.74 µg g^{-1}) e liofilizado (93.98 µg g^{-1}). O microscópio eletrônico de varredura (MEV) revelou que as microcápsulas atomizadas apresentaram formato esférico e superficie lisa, com menos deformações do que as microcápsulas liofilizadas com extensas rugas e superfície mais dentada. As microcápsulas atomizadas e liofilizadas, independente da temperatura (7 ou 25 °C), mantiveram seu TCF quase inalterados por 90 dias de armazenamento. O extrato de compostos fenólicos atomizado de FRC apresentou elevado TCF, propriedade antioxidante e potencial mercadológico, visando à utilização do extrato como ingrediente no enriquecimento de alimentos e na produção de novos ingredientes alimentícios, cosméticos ou farmacêuticos.

Palavras-chaves: Compostos bioativos; antioxidantes; ultrassom; micro-ondas; microencapsulação; atomização, liofilização; *Spondias purpúrea* L.

ABSTRACT

In recent decades, economic and environmental problems have caused growing concerns about the large volume of by-products generated by the food industries. Of these, the ciriguela residue (*Spondias purpurea* L.) stands out, which contains bioactive compounds with antioxidant properties. Therefore, this study aimed to optimize the process of extracting phenolic compounds from ciriguela residue flour (CRF) using ultrasound-assisted extraction (UAE) and compare, in relation to the content of phenolic compounds (TPC), to the extracts obtained by conventional extraction and microwave-assisted extraction. Then, the optimization of microencapsulation was performed by spray-drying the CRF extract obtained by EAU and production of the microencapsulated extract by freeze-drying (control). Physical characterization, determination of the phenolic profile by HPLC, in vitro gastrointestinal digestion, and stability analysis for 90 days at two temperatures (7 and 25 ºC) were performed with the microencapsulated extracts of CRF. The optimal condition of the EAU of the phenolic compounds of the CRF extract was obtained using an ultrasonic amplitude of 100% and a time of 15 min. The extraction process affected TPC and antioxidant activity by DPPH and FRAP, the greater the ultrasonic amplitude and the longer the time, the greater the TPC and antioxidant activity. The TPC of the spray-dried extracts ranged from 190.45 to 454.66 mg equivalent of gallic acid (GAE/g), having greater influence on the formulation of encapsulating agents. The encapsulation efficiency (EE) of the spray-dried extracts ranged from 76.83% to 99.84%. The optimized condition of microencapsulation by atomization of the extract of CRF phenolic compounds was obtained using a temperature of 150 ºC, a feed rate of 0.80 L/h and 100% gum arabic as an encapsulating agent. Moisture, solubility and hygroscopicity of the spray-dried and freeze-dried extracts did not show any significant difference. For EE and TPC there was a significant difference ($p<0.05$), the spray-dried extract showed higher EE and the freeze-dried extract higher TPC. In the spray-dried extract of FRC, rutin (82.69 µg g^{-1}) was the compound found in greater quantity. While catechin (93.94 µg g^{-1}) was predominant in the freeze-dried CRF extract. When analyzing the simulated gastrointestinal digestion of the extracts, it was observed that higher values of phenolic compounds were found after the gastric phase, and the lowest values in the last phase. Rutin was the compound that presented the highest content after digestion of the spray-dried (68.74 µg g^{-1}) and freeze-dried (93.98 µg g^{-1}) extracts. The scanning electron microscope (SEM) revealed that the spray-dried microcapsules had a spherical shape and smooth surface, with less deformation than the freeze-dried microcapsules with extensive wrinkles and a more serrated surface. The spray-dried and freeze-dried microcapsules, regardless of temperature (7 or 25 °C), maintained their TPC almost unchanged for 90 days of storage. The spray-dried extract of CRF showed high TPC, antioxidant property and marketing potential, aiming to use the extract as an ingredient in food enrichment and in the production of new food, cosmetic or pharmaceutical ingredients.

Keywords: Bioactive antioxidant compounds; ultrasound; microwave; atomization; freeze-drying; *Spondias purpurea L.*

LISTA DE ILUSTRAÇÕES

ARTIGO I

ARTIGO II

ARTIGO III

LISTA DE QUADROS E TABELAS

ARTIGO I

ARTIGO II

ARTIGO III

LISTA DE SIGLAS E ABREVIAÇÕES

DPPH 1,1-diphenyl-2-picrylhydrazyl

EAU Extração Assistida por Ultrassom

EAG Equivalente Ácido Gálico

EAM Extração Assitida por Micro-ondas

ECM Extração Convencional por Maceração

EE Eficiência de Encapsulação

FRC Farinha de Resíduo de Ciriguela

FRAP Poder Antioxidante de Redução do Ferro

GAE Equivalente a ácido gálico

HPLC Cromatografia Líquida de alta eficiência

IC_{50} 50% da atividade de eliminação do radical presente na solução de DPPH

MEV Microscópio eletrônico de varredura

TCP Teor de Compostos Fenólicos Totais

UA Amplitude Ultrassônica

SUMÁRIO

1. INTRODUÇÃO

Nas últimas décadas vem ocorrendo um aumento no consumo internacional de frutas tropicais, que são bastante apreciadas por causa da sua diversidade no aroma e sabor exótico (SCHIASSI et al., 2018). Este aumento é devido ao valor nutricional e funcional destas frutas e de como são importantes para a saúde humana (HABIBI; RAMEZANIAN, 2017). O Brasil é um país com características geográficas e climáticas favoráveis para a produção de frutas, e muitas dessas, ricas em compostos bioativos e importantes para a indústria de alimentos, são encontradas nos biomas brasileiros da Floresta Amazônica, Cerrado, Mata Atlântica e Caatinga (CAPPATO et al., 2018).

A região do semiárido, principalmente o bioma Caatinga apresenta uma imensa biodiversidade de frutas, destacando-se as do gênero *Spondias*, principalmente a ciriguela (*Spondias purpurea* L.) que é originária do México e América Central. Esta fruta é rica em metabólitos secundários, em particular compostos fenólicos, de interesse biológico (MALDONADO-ASTUDILLO et al., 2014). No processamento de frutas, cascas e sementes são os dois principais subprodutos (GOOT et al., 2016). A casca da ciriguela representa aproximadamente 45% do peso total da fruta (ALBUQUERQUE et al., 2016).

Diante do aumento no consumo de frutas, o processamento destas em produtos como sucos e bebidas apresentou elevado crescimento, possibilitando a obtenção de novas fontes funcionais e saudáveis (JEDDOU et al., 2017). O elevado crescimento das indústrias de polpas e sucos de frutas tem gerado grande volume de resíduos, que pode ser explorado para a extração de substâncias de alto valor agregado (BEN-OTHMAN; JÕUDU; BHAT, 2020; SALEEM; SAEED, 2020; KRINGEL et al., 2020).

A extração dos compostos de interesse pode ser realizada por métodos convencionais, utilizando maceração e/ou agitação com solventes e extração por soxhlet, que se fundamenta na captação dos compostos de interesse de um soluto ou matriz, associado ou não ao uso de calor. No entanto, métodos convencionais de extração requerem tempos longos para se alcançar a concentração máxima dos compostos de interesse, grande demanda de solvente e degradação térmica devido ao longo tempo de processo (CALDAS et al., 2018). Diante dessas desvantagens, buscam-se métodos mais sustentáveis, em que o consumo de solventes e o tempo de extração sejam minimizados e o rendimento de extração aumentado (PINTAC et al., 2018).

As tecnologias inovadoras ou não-convencionais que vêm sendo utilizadas são aplicação de campos elétricos pulsados, extração assistida por ultrassom, micro-ondas, alta pressão, fluido supercrítico e extração acelerada por solvente (PUTNIK et al., 2018). Destaca-se a extração assistida por ultrassom, que utiliza ondas mecânicas que apresentam frequências entre 20 e 100 kHz (DADAN et al., 2018), e a extração assistida por micro-ondas, que utiliza ondas eletromagnéticas para penetrar nos materiais e interagir com grupos polares, aumentado a extração dos compostos de interesse (CALDAS et al., 2018; ZHAO et al., 2019).

Os compostos bioativos, principalmente os fenólicos, sofrem degaradação facilmente durante a extração, processamento e armazenamento de alimentos, sendo altamente sensíveis a fatores como luz, pH, temperatura, presença de oxigênio e enzimas (RENARD, 2018). A microencapsulação pode ser uma alternativa para aumentar a estabilidade dos compostos bioativos e, consequentemente, a atividade antioxidante (REZENDE; NOGUEIRA; NARAIN, 2018; SANTOS et al., 2019). A microencapsulação é uma das técnicas mais importantes sendo utilizada para revestir ou selar materiais durante o processamento de alimentos e proteger compostos sensíveis de condições externas (PIECZYKOLAN; KUREK, 2019). Dentre os métodos de microencapsulação de compostos destacam-se a atomização e a liofilização. A atomização é um processo contínuo, simples e rápido no qual um líquido é transformado em um produto em pó após um período de secagem relativamente curto (SANTHALAKSHMY et al., 2015). A liofilização, por sua vez, é baseada na remoção da água por sublimação, desenvolvida para superar as perdas de compostos responsáveis pelos aromas e sabor nos alimentos e de compostos bioativos (RAMÍREZ; GIRALDO; ORREGO; 2015; HARNKARNSUJARIT et al., 2016).

Esses aspectos, juntamente com o crescente interesse global em tecnologias de extração emergentes, que visam à minimização dos impactos ambientais, justificam a utilização de subprodutos gerados nas indústrias de processamento de frutas. Uma alternativa para o aproveitamento tecnológico do resíduo da ciriguela é a sua utilização na produção de extratos microencapsulados de compostos fenólicos que possam ser aplicados como ingredientes funcionais em vários alimentos. Este trabalho teve como objetivos: i) otimizar o processo de extração assistida por ultrassom de compostos fenólicos do resíduo de ciriguela, ii) avaliar a estabilidade física e química do extrato microencapsulado por atomização e liofilização frente ao extrato líquido, e iii) determinar a bioacessibilidade dos compostos fenólicos do extrato microencapsulado.

2. REVISÃO DE LITERATURA

Para realização desta pesquisa científica, antes apresento o necessário a se conhecer sobre o tema e o objeto que serão investigados, a fim de iluminar o delineamento do problema, dos objetivos e da metodologia da pesquisa, assim como oferecer subsídios para a interpretação dos dados na etapa de resultados e discussão. Sendo assim, apresento esta revisão de literatura, que aborda as temáticas de produção e consumo de frutas, destacando dados da ciriguela, resíduos de frutas, compostos bioativos e atividade antioxidante, principais métodos de extração de compostos fenólicos e alguns estudos sobre extração de compostos bioativos. Além de destacar os metódos de microencapsulação mais utilizados na literatura (atomização e liofilização), e as principais pesquisas envolvendo microencapsulação de extratos de compostos bioativos.

2.1. Produção e consumo de frutas

A grande biodiversidade encontrada nos biomas da América do Sul, principalmente o território Brasileiro (como a Floresta Atlântica, Caatinga, Cerrado e a Floresta Amazônica), representa uma importante fonte de novas plantas para nutrição humana, sabores e materiais para a indústria de alimentos (INFANTE et al., 2016). O Brasil é o terceiro maior produtor mundial de frutas tropicais, ficando atrás apenas da China e da Índia, e dentro deste cenário, destaca-se a região Nordeste. A produção brasileira de frutas tropicais atingiu 602,65 mil toneladas em 2018, correspondendo a 2,52% de toda a produção mundial (BARROS et al., 2017; FAO, 2018), possui uma grande variedade de espécies de frutos subexploradas, nativas e exóticas, de grande potencial e interesse pela agroindústria, devido aos seus sabores e cores agradáveis, mas principalmente porque são consideradas fontes ricas em compostos bioativos (PAZ et al., 2015; CARVALHO et al., 2017; SCHIASSI et al., 2018).

Apesar do alto potencial nutricional e econômico, o Brasil apresenta um grande número de frutas nativas e exóticas que permanece inexplorado. Principalmente as frutas presentes no bioma Caatinga, que ocupa 11% do território Brasileiro. Sua vegetação está presente nos nove estados nordestinos e faz parte da cultura social, econômica e também da educação da região. O bioma enfrenta desafios em sua preservação e valorização. Esta região desde 1980 tem descoberto sua vocação de produzir frutas de excelente qualidade, à medida que os avanços das tecnologias de irrigação e de manejo permitiram superar a limitação do déficit hídrico (ANUÁRIO

BRASILEIRO DE FRUTICULTURA, 2017). Com isso a caracterização físico-química de frutos da Caatinga Brasileira e a quantificação de seus componentes são importantes para a compreensão de seu valor nutricional, a fim de melhorar a qualidade e agregar valor econômico ao produto final.

Nas últimas décadas vem ocorrendo um aumento no consumo internacional de frutas tropicais, que são bastante apreciadas por causa da sua diversidade no aroma, sabor e valor nutricional (HABIBI; RAMEZANIAN, 2017; ALBURQUERQUE et al., 2019). Os sucos de frutas, de modo geral, são uma boa fonte de compostos antioxidantes biologicamente ativos, particularmente ácido ascórbico e compostos fenólicos. O ácido ascórbico é conhecido por sua ação antioxidante e anti-inflamatório, enquanto que os compostos fenólicos são conhecidos por sua ação preventiva em alguns tipos de câncer, doenças cardiovasculares e neurológicas (BENJAMIN et al., 2015). O consumo de frutas tropicais tem aumentado devido ao reconhecimento do seu valor para a saúde humana, aliado a tendência dos consumidores em valorizar a ingestão destas frutas (BARROS et al., 2017; ALBURQUERQUE et al., 2019).

Pesquisas indicam que o consumo frequente de frutas está associado não só a manutenção de diversas atividades metabólicas do organismo, como também, a uma menor incidência de doenças degenerativas e prevenção de anomalias fisiológicas, tais como câncer, disfunções cardiovasculares, inflamações, arteriosclerose, diabetes, aceleração do envelhecimento, Parkinson e Alzheimer (HABIBI; RAMEZANIAN, 2017; LESJAK et al., 2018; ABREU et al., 2022). Os benefícios à saúde podem ser atribuídos à capacidade antioxidante dos fitoquímicos, tais como vitaminas, carotenoides, flavonoides e outros polifenóis, e do conteúdo destes compostos nas frutas e produtos derivados (SAMOTICHA; WOJDYLO; GOLIS, 2017; KANG et al., 2018). Essas frutas tropicais podem se tornar uma fonte inesgotável de recursos nutricionais, uma vez que é uma fonte potencial de compostos bioativos, desempenhando um papel essencial na prevenção de doenças.

Diante desse aumento no consumo de frutas, aliado ao elevado potencial antioxidante de sucos e derivados de frutas, as indústrias de alimentos são estimuladas a desenvolver novas fontes de ingredientes funcionais e saudáveis, além de novos produtos.

2.2. Ciriguela

Na região Nordeste do Brasil destaca-se o consumo da ciriguela. A cirigueleira (*Spondias purpurea* L.) pertence ao gênero *Spondias*, que compreende mais de 600 espécies, as quais se concentram nas regiões tropicais da África, Ásia e América Central (AUGUSTO; CRISTIANINI; IBARZ, 2012; BARROS et al., 2017). A ciriguela (Figura 1) apresenta período de colheita entre dezembro e março e alta perecibilidade. É conhecida por diversos nomes, que variam em função da região geográfica, como: mombim vermelho, siriguela, seriguela, ceriguela, ciriguela, jocote, joco, corona, ciruela, ciruela mexicana, jobillo, ameixa espanhol e cajá-vermelho (AUGUSTO; CRISTIANINI; IBARZ, 2012; BICAS et al., 2011; FURTADO et al., 2010).

A ciriguela é um fruto tipo drupa, de cor bem acentuada e atrativa, que dependendo do estado de maturação pode variar de verde a amarelo, laranja, vermelho e até violeta; possui formato ovoide e cerca de 3 a 5,5 cm de comprimento, pesando aproximadamente de 12 a 28 g, de sabor adocicado e ácido, devido à influência de variedade botânica e da fase de amadurecimento (ENGELS et al., 2012).

Figura 1. Frutos de ciriguela (*Spondias purpurea* L.)

Fonte: Google Imagens (2020).

A coloração dessa fruta pode variar também em função do processo de amadurecimento como resultado do metabolismo dos carotenoides e da clorofila, além disso, a intensidade luminosa e composição atmosférica durante o armazenamento são fatores chaves para determinar essa característica (MALDONADO-ASTUDILLO et al., 2014).

Este fruto apresenta epicarpo liso, que representa aproximadamente 14% do peso total da fruta; endocarpo lignificado, fibroso, não comestível, de coloração esbranquiçada representando aproximadamente 17% do peso total do fruto; e mesocarpo, de *flavor* agradável ao paladar, contribuindo com aproximadamente 69% do peso total do fruto (MALDONADO-ASTUDILLO et al., 2014; ENGELS et al., 2012; OMENA et al., 2012). Apresenta excelente qualidade sensorial sendo consumida fresca ou processada, e ótimas perspectivas comerciais graças ao uso de processamento pós-colheita, além de agregar valor ao produto final e facilitar a comercialização em regiões onde o clima não é favorável para o cultivo (DUTRA et al., 2017, TODISCO et al., 2014).

A ciriguela possui baixas quantidades de proteínas, gorduras e teor moderado de calorias, além de grandes quantidades de fibras e de vitamina C (Quadro 1). Ela também contém uma alta quantidade de minerais, entre eles o cálcio, potássio, manganês, magnésio, cobre, fósforo e zinco (TACO, 2011).

Quadro 1. Composição química da ciriguela.

Constituintes	Quantidade em 100 g de ciriguela in natura
Umidade (%)	78,7
Energia (kJ)	317,98
Proteína (g)	1,4
Lipídeos (g)	0,4
Carboidrato (g)	18,9
Fibra Alimentar (g)	3,9
Cinzas (g)	0,7
Vitamina C (mg)	27,0
Fósforo (mg)	49,0
Cálcio (mg)	27,0
Magnésio (mg)	18,0
Potássio (mg)	248,0

Fonte: Adaptada de TACO (2011).

Do ponto de vista fitoquímico, a ciriguela (polpa e casca) é rica em metabólitos secundários, em particular compostos fenólicos, de interesse biológico (MALDONADO-ASTUDILLO et al., 2014; SILVA et al., 2016). No processamento de frutas, casca e sementes são os dois principais subprodutos e os seus extratos contêm uma considerável quantidade de compostos bioativos (GOOT et al., 2016).

O crescimento e o processamento de frutas geram um grande volume de resíduos, que pode ser explorado para a produção de substâncias altamente valorizadas (BEN-OTHMAN; JÕUDU; BHAT, 2020). Esses subprodutos de diferentes indústrias de processamento de frutas são tradicionalmente descartados como resíduos e estão sendo reconhecidos como importantes fontes de compostos químicos valiosos (SEPÚLVEDA et al., 2018; SANTANA NETO et al., 2022).

2.3. Resíduos de frutas

Nos últimos anos, a elevada quantidade de resíduos industriais têm gerado problemas econômicos e ambientais, causando preocupações crescentes com a poluição (CALDAS et al., 2018). Nesse sentido, um dos desafios atuais é a reclassificação de resíduos como "co-produtos" ou "subprodutos" que podem ser reprocessados, visando reduzir seus impactos negativos, bem como obter materiais de valor agregado (SETTE et al., 2020). A valorização de resíduos e subprodutos pode contribuir para a geração mínima de resíduos ou atender ao amplamente popular "conceito de desperdício zero" visando às necessidades e demandas atuais do consumidor e da sociedade (BEN-OTHMAN; JÕUDU; BHAT, 2020).

Globalmente, uma grande quantidade de subprodutos agrícolas é gerada a cada ano pelas indústrias de processamento de alimentos, levando a um sério problema ambiental. Apenas uma fração destes resíduos são reciclados e reutilizados na produção de fertilizantes, fonte de combustível, ração animal etc. (BEN-OTHMAN; JÕUDU; BHAT, 2020; KASAPIDOU, SOSSIDOU; MITLIANGA, 2015). A exploração deste tipo de recurso permite reduzir a quantidade de desperdício de alimentos, diminuindo assim o impacto negativo no meio ambiente devido ao efeito fitotóxico do alto conteúdo de matéria orgânica (LAVELLI et al., 2017).

De acordo com a Organização das Nações Unidas para Alimentação e Agricultura (FAO), todos os anos, cerca de um terço (1,6 bilhões de toneladas) dos alimentos produzidos globalmente são perdidos ou desperdiçados. O desperdício de alimentos é definido pela FAO como "perdas de qualidade e quantidade de alimentos pelo processo da cadeia de suprimentos que ocorre na produção, pós-colheita, e estágios de processamento" (FAO, 2018; CORRADO et al., 2019; TSANG et al., 2019).

O desperdício de alimentos é produzido durante toda a cadeia produtiva dos alimentos. Excluindo as perdas de alimentos pela produção agrícola, até 42% delas são

produzidos pelos consumidores, 38% ocorrem durante o processamento de alimentos e 20% são distribuídos ao longo de toda a cadeia (FAO, 2018). Associado ao desperdício de alimentos estima-se que a população mundial aumentará para mais de 9,7 bilhões em 2050 (SALIM; SINGH; RAGHAVAN, 2017), reforçando a necessidade de políticas mundiais prioritárias para redução desse desperdício (VAN HERPEN et al., 2019).

Grandes quantidades de resíduos e subprodutos agro-alimentares são geradas no setor industrial agroalimentar. Em torno de 50% dos resíduos agrícolas, não apenas criam problemas de descarte seguro, mas também contribui para impactos ambientais negativos. De acordo com a estimativa da FAO, no mundo um terço de todos os alimentos produzidos são desperdiçados ou perdidos, entre os quais a maior parte são frutas, hortaliças e frutos do mar. Além disso, ainda de acordo com a FAO, para alcançar e garantir o sucesso das "Metas do Desenvolvimento Sustentável" é importante que sejam tomadas as medidas apropriadas para minimizar os resíduos gerados no setor agroalimentar (FAO, 2018).

Em relação aos componentes potencialmente comercializáveis presentes nos subprodutos alimentares, o objetivo é explorar aqueles de alto valor como proteínas, polissacarídeos, fibras, compostos aromatizantes e fitoquímicos como ingredientes nutricionais e farmacologicamente funcionais (HEERES, 2009; KRINGEL et al., 2020). No cenário global atual, a utilização sustentável de subprodutos agro-alimentares para gerar produtos de elevado valor agregado para possíveis aplicações em usos cosméticos, farmacêuticos ou industriais de alimentos podem proporcionar oportunidades consideráveis para obter renda adicional para o setor industrial. Além disso, a valorização efetiva de resíduos/subprodutos pode ajudar eficientemente a reduzir o estresse ambiental, diminuindo a poluição e impulsionando o crescimento econômico (SEPÚLVEDA et al., 2018; BEN-OTHMAN; JÕUDU; BHAT, 2020, SANTANA NETO et al., 2022).

Os subprodutos vêm sendo utilizados devido à presença de compostos bioativos, que possuem atividade antioxidante e antimicrobiana. Além disso, a valorização de subprodutos agroalimentares pode garantir a segurança alimentar regional e, assim, garantir a produção sustentável de alimentos (BHAT, 2017; BEN-OTHMAN; JÕUDU; BHAT, 2020; KRINGEL et al., 2020).

Do total de resíduos gerados, estima-se que 14,8% sejam provenientes de produção e processamento de frutas/hortaliças. Além disso, quase 50% dos desperdícios

familiares de alimentos também concernem às frutas e hortaliças (LAURENTIIS; CORRADO; SALA, 2018).

Os resíduos de frutas representam uma quantidade significativa de desperdício total de alimentos produzido em todo o mundo. Hoje, com a disponibilidade das tecnologias modernas, juntamente com os princípios da "Química Verde", novos conceitos foram estabelecidos, levando à utilização eficaz de resíduos e subprodutos do setor agroalimentar para a produção de produtos de valor agregado (BEN-OTHMAN; JÕUDU; BHAT, 2020). Contudo, sua valorização através da recuperação de componentes valiosos é limitada. Nesse sentido, a indústria e os pesquisadores têm trabalhado juntos para transformar resíduos de frutas em produtos de alto valor agregado (KRINGEL et al., 2020). A redução de resíduos de alimentos e sua valorização tornaram-se um tópico de interesse crescente de pesquisa nos últimos anos. Diante do exposto, muitos pesquisadores estão trabalhando na recuperação, bioconversão, reciclagem e utilização de compostos bioativos a partir de resíduos de frutas (CALDAS et al., 2018; GUANDALINI et al., 2019; ROY; LINGAMPETA, 2014; SHARAYEI et al., 2019; SETTE et al., 2020; ABREU et al., 2022; SANTANA NETO et al., 2022, TOLEDO-MERMA et al., 2022).

2.4. Compostos bioativos

Seguindo a tendência de maior preocupação com a saúde e foco na prevenção de doenças, tem-se observado um aumento no consumo de frutas no Brasil e em todo o mundo após a pandemia de COVID 2019. Com efeito, várias evidências científicas apontam efeitos benéficos à saúde de dietas ricas em frutas e hortaliças, que apresentam em sua composição vários compostos com potencial antioxidante, como vitaminas, carotenóides e compostos fenólicos.

Os vegetais produzem metabólitos primários e secundários. Os metabólitos primários são responsáveis pela fotossíntese, assimilação de nutrientes, crescimento, desenvolvimento e reprodução das plantas, enquanto os secundários têm a função de defender o organismo de certos predadores e atrair polinizadores, liberando odores e coloração atrativos. Os metabólitos secundários são destacados pelas suas atividades biológicas diversas, tais como, anticarcinogênica, antiviral, anti-inflamatória, redução do risco de doenças cardiovasculares e neurológicas, entre outras (COSTA et al., 2015;

NOREEN et al., 2017; AGUDELO et al., 2017), o que confere aos produtos naturais o reconhecimento como substâncias bioativas (ALI et al., 2010).

Essas biomoléculas foram identificadas em vários subprodutos agrícolas, como cascas de frutas. Esses compostos são sintetizados como mecanismo de proteção contra estressores (luz, secas, pragas, mudanças térmicas, entre outros) (BANERJEE et al., 2017) e desempenham um papel essencial na pigmentação e sabor (BARBA et al., 2016).

Dentre os metabólitos secundários, encontrados em vegetais, estão os compostos fenólicos, o ácido ascórbico e os carotenoides. Os compostos fenólicos, como ácidos fenólicos, flavonoides (incluindo as antocianinas), têm por característica ao menos um anel aromático e um grupamento hidroxila, substituindo um átomo de hidrogênio (ALI et al., 2010). Fatores genéticos determinam quais classes e subclasses desses compostos são sintetizadas pelos vegetais. Os extratos de compostos bioativos podem apresentar teores diferentes entre amostras de um mesmo vegetal, e o perfil dos compostos fenólicos pode ainda variar em função dos estágios de crescimento e maturação, fatores bióticos e abióticos, aos qual o vegetal foi submetido, além das metodologias analíticas de extração e determinação utilizadas (BUNIOWSKA et al., 2017; DUTRA et al., 2017).

Estudos confirmam que uma das principais causas por trás do envelhecimento prematuro e de doenças como câncer, cardiovasculares, neurodegenerativas (Alzheimer e Parkinson) ou diabetes reside no acúmulo excessivo no corpo humano de produtos derivados de reações de oxigênio e nitrogênio que podem causar condições de estresse oxidativo, danificando moléculas de DNA, paredes dos vasos sanguíneos, proteínas e lipídios. Por sua vez, essa clivagem de moléculas de DNA pode influenciar a regulação do crescimento celular, que resulta na formação de células cancerígenas e no desenvolvimento de doenças cardiovasculares (AGUDELO et al., 2017; AGUIAR; ESTEVINHO; SANTOS, 2016).

Uma solução possível para esse problema é o consumo de produtos que contêm compostos fenólicos, uma vez que livres, atuam como catadores de radicais. Produtos fenólicos e polifenólicos, sozinhos ou em combinação com vitaminas e carotenoides, vitamina E e vitamina C, atuam como antioxidantes que protegem os tecidos no corpo humano dos efeitos nocivos do estresse oxidativo. Os polifenóis são os antioxidantes mais comuns encontrados em dietas à base de frutas e vegetais (RAHMAN et al., 2022). Os compostos bioativos, também chamados de fitoquímicos, são estruturas orgânicas

obtidas de fonte vegetal, geralmente de baixo peso molecular, que buscam e neutralizam radicais livres, contribuindo na atuação de atividades benéficas ao organismo humano, como redução do risco de doenças coronarianas, atividade antioxidante, estimulação do sistema imunológico, redução da pressão sanguínea, regulação hormonal, entre outras (AGUDELO et al., 2017). Além destas funções, nas indústrias alimentícias, sua adição a alimentos pode aumentar o prazo de validade, retardando a peroxidação lipídica e o crescimento microbiano, bem como permitir a produção de alimentos funcionais ou mesmo para serem incorpororados em embalagens de alimentos (FIDELIS et al., 2015; RAHMAN et al., 2022).

Cascas de frutas e hortaliças são consideradas resíduos que devem ser usados para extrair diversos compostos (bioativos, agentes antimicrobianos e antioxidantes). Os principais elementos com propriedades bioativas nos vegetais são os compostos fenólicos ou polifenóis (maior grupo de compostos), os carotenoides e os glicosinolatos (RAMÍREZ; GIRALDO; ORREGO; 2015). Os polifenóis são os principais compostos bioativos presentes nas frutas e em seus subprodutos (BATAGLION et al., 2015). Vários estudos realizados com subprodutos de vegetais revelaram a presença de compostos fenólicos (CALDAS et al., 2018; CASSOL; RODRIGUES; NOREÑA, 2019; GUANDALINI et al., 2019; MILANI et al., 2020; SHARAYEI et al., 2019), e que estes compostos podem ser utilizados pelas indústrias alimentícias, e também para fins farmacológicos ou farmacêuticos (SALEEM; SAEED, 2020).

2.5. Compostos fenólicos

Os compostos fenólicos, que estão amplamente distribuídos no reino vegetal, englobam uma gama de compostos (aproximadamente 10.000 estruturas fenólicas), divididos em duas classes em função da estrutura química: flavonoides e não-flavonoides (TSAO, 2010). Também chamados de polifenóis, os compostos fenólicos são micronutrientes que apresentam inúmeros benefícios à saúde humana e seus efeitos protetores nos sistemas alimentares como compostos antioxidantes são bem conhecidos e têm sido extensivamente investigados (DUTRA et al., 2017; LUCAS-GONZÁLEZ et al., 2018; RAFIEE et al., 2017; SHAVANDI et al., 2018). Variações na estrutura química de compostos fenólicos em frutas, hortaliças e resíduos agroindustriais estão relacionadas a proporções diferentes de fenóis simples e complexos, como ácido

benzoico e cinâmico, cumarinas, taninos, ligninas, lignanas e flavonoides (AHMAD et al., 2016).

Os ácidos gálico, elágico, protocatecuico e 4-hidroxibenzoico são os ácidos benzoicos mais consumidos por humanos, enquanto os ácidos cafeico, ferúlico, sinápico e p-cumárico são os ácidos cinâmicos mais comuns. As dietas à base de vegetais são ricas em polifenóis, que fornecem nutrientes, além de contribuir para a prevenção de doenças crônicas (MINATEL et al, 2017; RAHMAN et al., 2022).

As propriedades antioxidantes dos compostos fenólicos têm atraído cada vez mais a atenção de pesquisadores e consumidores, devido os seus inúmeros benefícios à saúde humana (ALBAYRAK; ATASAGUN; AKSOY, 2017). Esses compostos podem prevenir a reatividade negativa de espécies reativas de oxigênio/nitrogênio indesejadas produzidas pelas atividades metabólicas do corpo. Devido aos seus potenciais benefícios para a saúde, os polifenóis e outros fenólicos dietéticos estão gerando muita atenção no mundo científico (RAHMAN et al., 2022).

Estes compostos apresentam destaque especial como antioxidantes, por atuarem como eficientes captadores de espécies reativas de oxigênio (EROs), além de reduzirem e quelarem íons férricos que catalisam a peroxidação lipídica (MALDONADO-ASTUDILLO et al., 2014) e outras importantes atividades biológicas, como anticarcinogênica, doenças cardiovasculares e neurológicas (COSTA et al., 2015), antiviral (NOREEN et al., 2017), antibiótica, antialergênica, anti-inflamatória e de proteção fotoquímica (AGUDELO et al., 2017). Além disso, os compostos fenólicos podem ter um papel importante na saúde humana, interagindo com a microbiota intestinal (OZDAL et al., 2016), ser usados pela indústria alimentícia como substituto de antioxidantes sintéticos (RAFIEE et al., 2017) e para a produção de alimentos funcionais e pela indústria farmacêutica como fármacos (ASSADPOUR et al., 2017; FARIDI ESFANJANI; ASSADPOUR; JAFARI, 2018). As propriedades biológicas de compostos fenólicos são diversas, embora os mecanismos específicos que exercem efeitos preventivos das doenças permaneçam desconhecidos (RAHMAN et al., 2022).

A biodisponibilidade e função dos compostos fenólicos, presentes em alimentos de origem vegetal, no corpo humano dependem de muitos fatores como bioacessibilidade, efeito da matriz alimentar, transportadores, estruturas moleculares e enzimas metabolizadoras (REIN et al., 2013). Dutra et al. (2017) realizaram a caracterização do perfil fenólico de ciriguela, umbu-cajá e mangaba, bem como a bioacessibilidade dos compostos fenólicos e a atividade antioxidante dos dialisados

após a exposição a condições gastrointestinais simuladas Os principais compostos fenólicos livres e conjugados detectados por Dutra et al. (2017) foram: ácido gentísico (762,73 mg.100 g^{-1}), ácido p-hidroxibenzoico (391,25 mg.100 g^{-1}), ácido p-cumárico (217,8 mg.100 g^{-1}), rutina (174,35 mg.100 g^{-1}), ácido vanílico (158,78 mg.100 g^{-1}), ácido protocatecuico (143,77 mg.100 g^{-1}), ácido sinápico (122,83 mg.100 g^{-1}), ácido salicílico (98,56 mg.100 g^{-1}), catequina (62,61 mg.100 g^{-1}) e quercetina (59,92 mg.100 g^{-1}), expressos em base seca. Apesar das diferenças nas quantidades de cada composto fenólico identificado, perfis fenólicos relativamente semelhantes foram observados nos frutos da ciriguela, umbu-cajá e mangaba. Fenólicos livres totais foram predominantes em frutas e polpas congeladas de umbu-cajá e mangaba, enquanto fenólicos conjugados totais o foram na ciriguela. O ácido gentísico (derivado do ácido benzoico) foi o principal composto detectado por cromatografia líquida de alta eficiência, dentre os fenólicos livres e conjugados de todas as frutas analisadas, bem como o ácido fenólico detectado na concentração mais alta nos frutos de mangaba e ciriguela.

Os principais compostos fenólicos relatados na literatura em cascas de ciriguela foram: ácido gálico, quercetina, rutina e kaempferol (ENGELS et al., 2012; SILVA et al., 2016), enquanto flavonóides de glicosídeos, como rutina, quercetina-3-galactosídeo, cianidina-3-glicosídeo, quercetina-o-rutinosídeo (ramnosil) ou kaempferol-o-rutinosídeo, ácido elágico e ácido 4-hidroxibenzóico, foram detectados após a digestão *in vitro* em subprodutos de quinoa e de caqui (PELLEGRINI et al., 2017; LUCAS-GONZÁLEZ et al., 2018;).

Apesar da identificação dos diversos compostos fenólicos em frutas e resíduos, sua bioacessibilidade no organismo humano, indicada pelas quantidades liberadas após digestão gastrointestinal que se torna disponível para absorção no cólon, deve ser considerada (BUNIOWSKA et al., 2017). Os compostos fenólicos podem ser transformados durante a digestão em compostos com menor bioacessibilidade, e consequentemente, sua bioatividade pode ser comprometida. Durante a digestão gástrica e intestinal, a matriz alimentar determina a estabilidade e afeta a proporção de compostos fenólicos que atingem o cólon intacto ou que serão potencialmente absorvidos (MOSELE et al., 2015).

Geralmente, os níveis de compostos fenólicos diminuem após exposição a condições gástricas simuladas de polpas e resíduos de frutas (BUNIOWSKA et al., 2017; DUTRA et al., 2017). No estudo de Dutra et al. (2017) a bioacessibilidade dos fenólicos variarou entre as frutas avaliadas. Os dialisados da polpa de ciriguela e umbu-

cajá apresentaram a maior capacidade de captura do radical 2,2′-difenil 2-picrilhidrazil ($DPPH^{\bullet}$), enquanto o dialisado da polpa de mangaba apresentou a maior capacidade redutora de ferro. As concentrações de compostos fenólicos liberados após a fase gástrica e a fase intestinal foram menores do que suas concentrações iniciais em todas as frutas analisadas no estudo.

Ainda no estudo de Dutra et al. (2017) foi observado que o ácido gálico, um dos compostos mais bioacessíveis identificados após a digestão *in vitro* em polpa de umbu-cajá, não foi detectado após a etapa gástrica para polpas de mangaba e ciriguela. Os resultados das frações do dialisado da ciriguela, obtido por meio de uma membrana celulósica semipermeável, mostraram que o conteúdo de fenólicos foi significativamente menor do que aquele encontrado na digestão gástrica e intestinal. Notadamente, a rutina, o principal flavonoide presente em ciriguela, apresentou bioacessibilidade de 17,56%.

A extração dos componentes bioativos deve ser economicamente viável de executar. Este objetivo pode ser alcançado por meio da separação dos compostos de interesse por ações individuais e/ou combinadas, por abordagens físicas e bioquímicas para fornecer uma variedade de componentes, de alto a baixo valor. Os diversos tipos de compostos apresentam rendimentos variáveis a diferentes condições de extração. Além disso, a recuperação ideal de fenólicos difere de um substrato para outro e depende do tipo de frutas, hortaliças e seus subprodutos (BAKIĆ et al., 2019). Além do rendimento dos extratos, a bioacessibilidade dos compostos presentes nos extratos é afetada pelos processos de maceração e/ou trituração aplicados durante a obtenção dos extratos, que podem tornar os ácidos fenólicos conjugados mais acessíveis para absorção no organismo humano, uma vez que o processo de extração causa a quebra do tecido celular dos constituintes (TOMAS et al., 2015).

Os compostos fenólicos se degradam facilmente, diminuindo sua eficácia, durante a extração, processamento e armazenamento de alimentos. São altamente sensíveis a fatores como luz, pH, temperatura, presença de oxigênio e enzimas, que podem induzir alterações de seus níveis ou a conversão em compostos secundários. Reações enzimáticas e não enzimáticas podem ativar a absorção e o metabolismo de fenólicos. Alterações moleculares podem ocorrer durante a produção de alimentos, e reações de conjugação também podem aumentar ou diminuir a biodisponibilidade dessas moléculas (MERCALI et al., 2013; MINATEL et al., 2017). Além disso, a biodisponibilidade e a função dos compostos fenólicos, presentes nos alimentos de

origem vegetal, no corpo humano dependem de fatores variados, como bioacessibilidade, efeito da matriz alimentar, transportadores, estruturas moleculares e enzimas metabolizadoras (REIN et al., 2013). E sua biodisponibilidade pode ser afetada no decorrer da digestão, a depender das condições do trato gastrointestinal dos humanos (RAMÍREZ; GIRALDO; ORREGO; 2015).

Os compostos bioativos podem ser recuperados dos resíduos usando métodos de extração adequados. Condições operacionais de extração, como o tipo de solvente, duração do processo e temperatura ótima, determinam o desempenho e a qualidade dos compostos obtidos (PINTAC et al., 2018).

2.6. Métodos de extração de compostos bioativos

Na recuperação de compostos bioativos de fontes naturais, a etapa de extração desempenha um papel importante. É o principal passo para a recuperação (isolamento e purificação) de preciosos compostos bioativos presentes em matrizes vegetais e pode ser descrito como um fenômeno de transporte de massa onde componentes presentes em uma matriz são transferidos para o solvente (LEE et al., 2011; PAL; JADEJA, 2019). A técnica de extração selecionada para cada processo deve ser versátil, fácil de usar, eficiente e econômica, além de extrair e preservar a maior fração dos compostos bioativos naturais contidos nos materiais vegetais (GULLÓN et al., 2017; HOHNOVÁ; ŠALPLACHTA; KARÁSEK, 2017).

As condições de extração são extremamente importantes, devido a seus efeitos na liberação de compostos da matriz para o meio. Indústrias alimentícias recuperam valiosos compostos bioativos de fontes naturais utilizando diferentes técnicas de extração (PAL; JADEJA, 2019). Para garantir a obtenção máxima de compostos fenólicos sem nenhuma degradação e/ou modificação, a seleção do método e os principais fatores que afetam a extração são essenciais (TRUJILLO-MAYOL et al., 2019).

A extração dos compostos fenólicos presente em resíduos de frutas, especialmente a ciriguela, pode aumentar o valor comercial da matéria-prima. A extração representa o ponto central para obter extratos de compostos bioativos de resíduos de frutas (GARCIA-CASTELLO et al., 2015). No entanto, a taxa de extração dos compostos fenólicos e a eficiência do processo de extração são influenciadas pelo método de extração, tipo de solvente, razão sólido/líquido (amostra/solvente), tempo de

extração, temperatura, pH, tamanho de partícula, potência, frequência entre outros (ESPADA-BELLIDO et al., 2017; CHEMAT et al., 2017a). Além das condições de extração, o conteúdo fenólico dos materiais vegetais é fortemente afetado por outros fatores, como antecedentes genéticos e/ou condições climáticas (BLASI et al., 2016; LOMBARDI et al., 2017). O processo de extração visa promover o rendimento máximo de compostos fenólicos não degradados, o que aumenta a atividade biológica dos extratos (ESPADA-BELLIDO et al., 2017).

Geralmente, um processo de extração consiste em duas etapas consecutivas: (1) mistura do material com o solvente; e (2) movimento de compostos solúveis da célula para o solvente, difusão e extração (HUANG et al., 2013). Vários materiais vegetais requerem condições e procedimentos de extração distintos para se obter recuperação ideal de compostos fenólicos, pois cada vegetal possui características específicas em termos de constituintes fenólicos (CHEMAT et al., 2017a; GULLÓN et al., 2017).

Métodos tradicionais

A extração dos compostos bioativos pode ser realizada por métodos convencionais, como maceração e/ou agitação sólido-líquido com solventes, destilação, compressão ou extração por *Soxhlet*, que se fundamenta na captação dos compostos de interesse de um soluto ou matriz, associado ou não ao uso de calor. No entanto, esses processos são demorados e podem causar degradação de compostos termolábeis (CHEMAT et al., 2017a).

As técnicas tradicionais de extração normalmente exigem uma longa maceração, que pode variar de 1 a 20 horas e utilizam quantidades relativamente grandes de solvente, o que pode afetar o rendimento (GOGOI et al., 2019). A extração deve ter boa reprodutibilidade e a razão sólido-líquido tem maiores valores usando tempos de extração mais altos (CALDAS et al., 2019; GOGOI et al., 2019). As técnicas de extração convencionais mais utilizadas são: *Soxhlet*, refluxo de calor, agitação, ebulição, lixiviação e destilação (GULLÓN et al., 2017). Esses métodos convencionais baseiam-se na maceração dos frutos ou resíduos em diferentes condições de pH, concentração de solvente e tempo, requerendo elevados tempos para se alcançar a concentração máxima do composto de interesse, grande demanda de solvente, solventes com alta pureza, baixa seletividade de extração e degradação térmica dos compostos termolábeis (ARES et al., 2015; DROSOU et al., 2015; CALDAS et al., 2018).

O processo convencional de extração sólido-líquido é amplamente utilizado para recuperar compostos intracelulares de matrizes, que normalmente envolve o contato íntimo entre matriz alimentar e solvente orgânico ou mistura de solventes com alta afinidade para os compostos-alvo. Este se baseia na transferência de massa do soluto da matriz sólida para a solução extratora envolvendo mecanismos diversos como a difusão, sorção e dessorção, dentre outros, até que se atinja o equilíbrio entre as fases (GULLÓN et al., 2017).

A extração por refluxo térmico é o método convencional de extração que envolve aquecimento, fervura e refluxo por um período de tempo. É amplamente utilizada devido à sua simplicidade e facilidade de operação. No entanto, além dos menores rendimentos de extração associados a essa técnica, também requer o uso de grandes volumes de solvente, que não é ecológico e pode afetar a saúde humana (GULLÓN et al., 2017).

A extração por *Soxhlet* é empregada como um processo em lote, mas pode ser convertida em um processo contínuo. É um procedimento que, em média ou grande escala, permite economias adicionais comparadas à extração sólido-líquido. As vantagens incluem a lavagem repetida da matriz com solvente fresco, a maior solubilização possível do analito devido ao uso de solvente quente e a possibilidade de aplicá-lo a muitas matrizes alimentares. Por outro lado, apresenta desvantagens similares à extração sólido-líquido tradicional e o risco de degradação de compostos sensíveis à temperatura (BARBA et al., 2016).

A escolha do tipo de solvente é um fator muito importante, pois pode determinar o sucesso de um processo de extração específico. Deve ser feita com cuidado, a fim de eliminar ou minimizar interferências matriciais enquanto os parâmetros experimentais (temperatura, tempo, pH, relação sólido/líquido, tamanho de partícula, agitação, polaridade do solvente) devem ser otimizados para obter extração quantitativa dos compostos de interesse (VIAPIANA; WESOLOWSKI, 2017). Os principais fatores utilizados na escolha do solvente são: estrutura e polaridade do composto-alvo, segurança ambiental, toxicidade humana e viabilidade financeira (GULLÓN et al., 2017).

Os solventes mais empregados na extração de compostos fenólicos são metanol, hexano, acetona, etanol, éter dietílico, isopropanol, água, acetato de etila ou soluções aquosas destes solventes, o que aumenta a eficiência da extração aumentando a área da superfície de contato entre o soluto (polifenóis extraíveis) e o solvente (AIRES;

CARVALHO; SAAVEDRA, 2017; BAKIĆ et al., 2019; CALDAS et al., 2018). Também foi relatado o acréscimo de ácido clorídrico ou hidróxido de sódio a misturas de água ou água/solvente orgânico para melhorar a extração de compostos fenólicos (AIRES; CARVALHO; SAAVEDRA, 2017; GULLÓN et al., 2017; BAKIĆ et al., 2019). Esses solventes apresentam uma polaridade próxima à polaridade dos compostos alvo, o que facilita os estágios de difusão. No entanto, alguns solventes orgânicos convencionais podem causar problemas ambientais e risco à saúde, embora às vezes apresentem um maior rendimento; este é um ponto a ser considerado na escolha do solvente, além do custo e viabilidade operacional para a total remoção do mesmo (BARBA et al., 2016).

Embora os métodos convencionais sejam bastante utilizados, a maioria desses tem algumas limitações, e para aumentar o rendimento da extração, esses métodos requerem frequentemente pré-tratamentos intensivos, bem como temperaturas de extração relativamente altas, longos tempos de extração, e grandes volumes de solventes orgânicos, que muitas vezes são potencialmente tóxicos e prejudiciais ao meio ambiente. Além disso, eles podem induzir a perda de compostos valiosos ou a co-extração de componentes indesejáveis, aumentando assim os custos de processamento (FRONTUTO et al., 2019; GARCIA-CASTELLO et al., 2015). Diante dessas desvantagens, buscam-se métodos mais sustentáveis, em que o consumo de solventes e o tempo de extração sejam minimizados e o rendimento de extração aumentado (BARBA et al., 2016).

Métodos não-convencionais

Também chamados de tecnologias emergentes podem oferecer eficiência de extração superior em termos de custo, rendimento, tempo de extração e/ou seletividade (PUTNIK et al., 2018). As tecnologias emergentes visando uma extração mais aprimorada e eficiente estão sendo exploradas, incluindo ultrassons (SHARAYEI et al., 2019; WEN et al., 2019), micro-ondas (CASSOL et al., 2019; JESUS et al., 2019), campos elétricos pulsados (PASHAZADEH et al., 2020; FRONTUTO et al., 2019), fluidos pressurizados e supercríticos (GARCIA-MENDOZA et al., 2017) e extração acelerada por solvente (CAI et al., 2016; NAYAK et al., 2015).

O uso dessas tecnologias permite aumentar as taxas de transferência de massa, a permeabilidade das células e a difusão secundária do metabólito. Essas técnicas levam a maiores rendimentos de extração e menos impurezas no extrato final, são realizadas a

temperatura ambiente, com preservação de estruturas termossensíveis, fazem uso de diferentes solventes não orgânicos, e se caracterizam por baixo consumo de energia, curto tempo de operação e efeito desprezável sobre a estrutura de compostos bioativos (MOREIRA et al., 2019).

Os estudos sobre a obtenção de extratos antioxidantes de vários resíduos de frutas com diferentes métodos de extração têm aumentado recentemente. Além disso, a otimização de processos para parâmetros de extração visando maximizar a obtenção de compostos fenólicos antioxidantes vem atraindo a atenção de vários pesquisadores (REZENDE; NOGUEIRA; NARAIN, 2017; NIPORNRAM et al., 2018; GUANDALINI et al., 2019; SHARAYEI et al., 2019; TRUJILLO-MAYOL et al., 2019; SETTE et al., 2020; ZULKIFLI et al., 2020).

A ineficiência das abordagens tradicionais promoveu o desenvolvimento de alternativas altamente eficientes e abordagens compactas (HOU et al., 2019). Extração assistida por ultrassom e por micro-ondas oferecem vantagens sobre as extrações de líquidos pressurizados, de fluidos subcríticos e supercríticos e por aceleração de solvente, devido ao seu custo razoável, fácil escalabilidade e alta versatilidade para extrair moléculas de diferentes polaridades (NAYAK et al., 2015; NIPORNRAM et al., 2018).

Em comparação com os métodos convencionais, as extrações não-convencionais visam evitar/minimizar o uso de solventes orgânicos, reduzir o tempo de processo, potencializar a penetração do solvente na matéria-prima, diminuir a temperatura de processamento, intensificar o processo de transferência de massa, aumentar os rendimentos e/ou reduzir consumo de energia. Além disso, apresentam boa reprodutibilidade e possibilidade de utilização de solventes alternativos mais econômicos e mais seguros para o ambiente e para a saúde (BARBA et al., 2016; CALDAS et al., 2018).

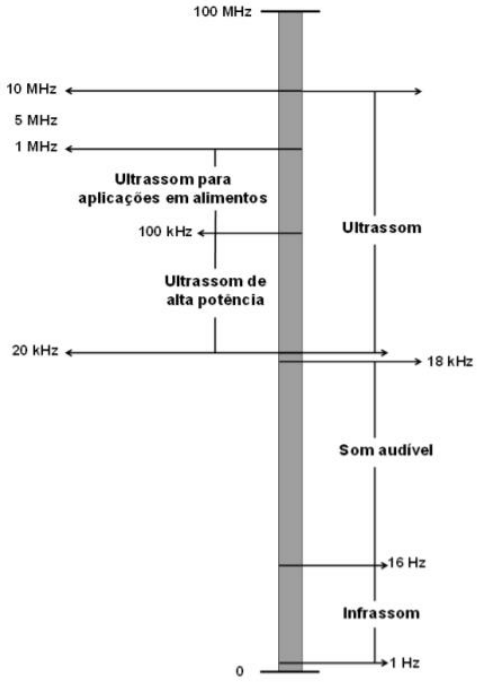
Sendo assim, a escolha de qual técnica deve ser usada para realizar a extração de um metabólito desejado de um vegetal específico tem que ser resultado de uma análise entre a eficiência e a reprodutibilidade da extração, facilidade de processo, juntamente com considerações de custo, tempo, segurança e grau de automação (CHEMAT et al., 2017a).

2.6.1. Extração assistida por ultrassom (EAU)

A extração assistida por ultrassom é um processo relativamente simples que representa uma ligeira modificação do método de extração convencional por agitação (CALDAS et al., 2018). EAU é considerada um processo verde, simples, barato e econômico, por utilizar energia acústica e solventes para melhorar a liberação e difusão de compostos-alvo de várias matrizes (GUANDALINI et al., 2019; ROMBAUT et al., 2014).

EAU utiliza ondas mecânicas que se dividem em elásticas e acústicas. As ondas mecânicas que se propagam em sólidos são chamadas de "elásticas", enquanto aquelas que se propagam em fluidos são denominadas "acústicas" (ENSMINGER; BOND, 2011). A frequência das ondas mecânicas varia de menos de 16 Hz a acima de 1 GHz e permite dividir "sons" em quatro grupos (Figura 2): infrassons (1 a 16 Hz), sons audíveis (16 a 20 kHz), ultrassons (20 kHz - 1 GHz) e hipersons (acima de 1 GHz) (CHEEKE, 2012).

Figura 2. Faixa de frequência das ondas sonoras.



Fonte: Adaptado de Cheng et al. (2015).

As diferentes aplicações dos ultrassons são baseadas na faixa de frequência utilizada e podem ser classificadas como de baixa potência/alta frequência (100 kHz a 10 MHz e potência inferior a 1 W/cm^2) e alta potência/baixa frequência (<16–100 kHz

de frequência e 10–1000 W/cm^2 de potência) (MOREIRA et al., 2019). Os ultrassons de baixa potência/alta frequência são utilizados para diagnóstico médico e monitoramento da qualidade dos alimentos, redução de íons metálicos e oxidação de poluentes orgânicos, enquanto os ultrassons de alta potência/baixa frequência são usados para induzir alterações químicas em materiais biológicos através da cavitação e uso de altas temperaturas (ASHOKKUMAR, 2015).

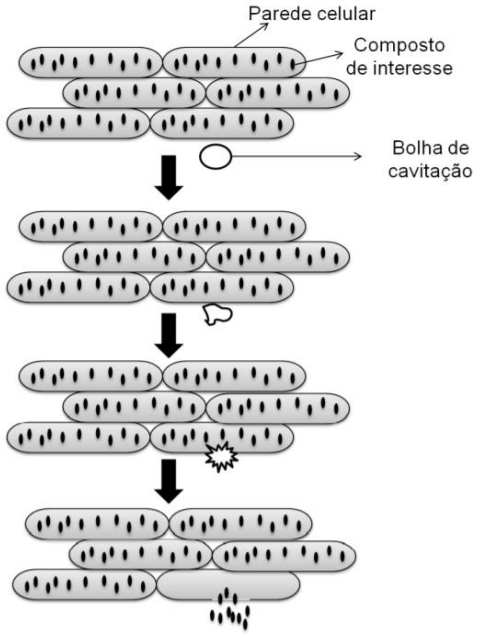
Os ultrassons podem ser gerados com o uso de métodos mecânicos (aero e hidrodinâmico), térmicos (descarga elétrica), ópticos (impulso de um laser de alta potência) ou elétricos e magnéticos reversíveis (piezoelétrico, eletrostrição, magnetostrição) (MUSIELAK; MIERZWA; KROEHNKE, 2016). Os ultrassons podem ser propagados através de um meio (gás, líquido ou sólido), criando compressão e expansão (DADAN et al., 2018).

Um dos fenômenos gerados pela propagação do ultrassom em meios líquidos é a cavitação (Figura 3), caracterizada pela produção de bolhas, seu crescimento e consequente colapso (ADETUNJI et al., 2017). As ondas ultrassônicas criam forças de cavitação, que ocorrem pela implosão de microbolhas que são formadas no meio líquido devido a oscilações de pressão (compressões e rarefações alternadas) causadas pela passagem das ondas acústicas no meio (DADAN et al., 2018; CHEMAT et al., 2017a). Este processo consiste na criação de uma forte vibração entre moléculas da amostra, levando à formação e ruptura de bolhas dentro da parede celular, danificando sua estrutura e facilitando a transferência de massa das partículas celulares para o solvente. O colapso das bolhas de cavitação e a temperatura altamente localizada levam à quebra das paredes celulares e liberação, por difusão, dos compostos das células no solvente de extração (MOREIRA et al., 2019). Durante o estágio inicial da cavitação, há inchaço da parede celular juntamente com aumento dos poros, o que incrementa a difusividade do solvente na matriz sólida. Com exposição adicional, a matriz celular entra em colapso e há máxima difusão do conteúdo interno no solvente, facilitando a extração de compostos fenólicos (AL-DHABI; PONMURUGAN; JEGANATHAN, 2017).

Sendo assim o ultrassom é também conhecido por acelerar a transferência de massa e calor durante os processos de extração, na medida em que seus efeitos de cavitação perturbam a parede celular, e, assim, liberam uma maior quantidade de compostos bioativos (ROSELLÓ-SOTO et al., 2015). De forma geral, o ultrassom induz uma maior penetração de solvente nos materiais celulares, melhorando a transferência

de massa e também rompe as paredes celulares biológicas, facilitando a liberação do conteúdo (WANG, 2008).

Figura 3. Processo de cavitação por ultrassom (colapso da bolha de cavitação e liberação do material vegetal da estrutura celular).



Fonte: Adaptado de Chemat et al. (2011).

A extração assistida por ultrassom não atua apenas com o mecanismo de cavitação sobre a matriz, mas também através de mecanismos independentes ou combinados como fragmentação, erosão, capilaridade, detexturização, sonoporação e tensão de cisalhamento (CHEMAT et al., 2017b).

Fragmentação: ocorre durante a aplicação de ultrassom em um meio líquido contendo uma matéria-prima sólida, causando a redução no tamanho das partículas pela ação do ultrassom, devido a colisões entre partículas e ondas de choque criadas a partir de bolhas de cavitação em colapso no líquido. Como consequência da fragmentação ocorre o aumento da área superficial do sólido, resultando em maior transferência de massa e aumento da taxa de extração e produção.

Erosão: mecanismo que, devido à implosão de bolhas de cavitação na superfície da matéria-prima, induz a erosão de estruturas de vegetais, auxiliando na liberação dos compostos de interesse no meio de extração.

Capilaridade: O efeito capilar ultrassônico refere-se ao aumento da profundidade e velocidade de penetração do líquido em canais e poros sob algumas condições de sonicação.

Detexturização: Em alguns casos, após a extração por ultrassom, uma destruição ou detexturação de estruturas de vegetais é observada. Pode-se supor que tal ruptura celular favoreça a acessibilidade ao solvente.

Sonoporação: efeito aplicado quando uma permeabilidade das membranas celulares é desejada. No campo da extração, a sonoporação pode ser reversível ou irreversível, o que resulta na liberação do conteúdo celular no meio extrativo. A sonoporação pode ser utilizada in vitro para a absorção celular em moléculas, por exemplo, em medicamentos, genes (sonoporação reversível) ou para destruição celular (sonoporação irreversível).

Tensão de cisalhamento: Durante a aplicação de ultrassom em uma mistura sólido-líquido, algumas forças de cisalhamento e turbulências são geradas no meio líquido resultando da evolução (oscilação e colapso) da bolha de cavitação dentro do fluido. No entanto, a combinação desses efeitos simultâneos na matéria-prima pode explicar o desempenho aprimorado de extrações assistidas por ultrassom (CHEMAT et al., 2017b).

A EAU é uma alternativa potencial a extração convencional de compostos fenólicos, e é amplamente aplicada, uma vez que reduz o uso de compostos tóxicos e requer temperaturas e períodos de tempo mais baixos. Além isso, apresenta alta reprodutibilidade, conferindo maior pureza ao produto final, eliminando o pós-tratamento das águas residuais e consumindo apenas uma fração da energia fóssil normalmente necessária para um método de extração convencional, como extração de Soxhlet, maceração ou destilação a vapor (REZENDE; NOGUEIRA; NARAIN; 2017; MARIĆ et al., 2018; VERRUCK; PRUDENCIO, 2018).

Na EAU é possível usar água como solvente, para reduzir o tempo de extração, reduzir o desperdício de solvente orgânico, aumentar o rendimento da extração e melhorar a qualidade dos extratos (TAO; ZHANG; SUN, 2014). Outras vantagens são a alta taxa de transferência de processamento, diminuição de ruído, extração de componentes lábeis ao calor, economia significativa em manutenção, menos energia necessária para o processamento, maior compatibilidade com o meio ambiente e menor custo. Além disso, essa tecnologia é altamente versátil, pois pode ser usada em muitos alimentos, na agricultura e na produção de produtos biotecnológicos, desde matérias-

primas a produtos finais. Também pode ser facilmente conectada com os dispositivos como parte do site da planta tecnológica ou como uma nova linha de produção (ROSELLÓ-SOTO et al., 2015; MOREIRA et al., 2019). Comparado a EAU à extração convencional, pode-se aumentar significativamente o rendimento de extração de compostos fenólicos (MANE et al., 2015).

O processo de EAU é afetado por vários fatores, como frequência, potência de sonicação, tempo e distribuição das ondas ultrassônicas (CHEMAT et al., 2017a). De uma forma geral pode-se afirmar que a cavitação é a força motriz da extração assistida por ultrassom que a uma temperatura específica por um determinado período são fatores que regem a eficiência da extração (CHEMAT et al., 2017b). A frequência do ultrassom pode ter grandes efeitos sobre o rendimento de extração e cinética, dependendo da natureza do material vegetal a ser extraído (CHEMAT et al., 2017a; VERRUCK; PRUDENCIO, 2018).

2.6.2. Extração assistida por micro-ondas (EAM)

A extração por microondas é um método de extração promissor com alta eficiência de extração, com potencial para reduzir a quantidade de solvente a ser usado e o tempo do processo. Também apresenta fácil controle, utiliza baixa temperatura e baixo consumo de energia, resultando em uma melhor separação e recuperação de compostos de interesse (KRISHMAN; RAJAN, 2016; ROMBAUT et al., 2014).

Micro-ondas são ondas eletromagnéticas que consistem em um campo elétrico e um campo magnético que oscilam perpendicularmente um ao outro em frequências que variam de 300 MHz a 300 GHz, sendo a de 2,45 GHz geralmente usada para equipamentos laboratoriais e 915 MHz para equipamentos industriais (VINATORU; MASON; CALINESCU, 2017; SUN et al., 2016). As ondas eletromagnéticas são responsáveis pelo rápido movimento de moléculas polares e da mobilidade iônica do meio sem alterar a amostra. Esta rotação das moléculas polares gera a absorção e dissipação de energia no meio, causando uma rápida migração de todos os compostos ativos da fase sólida para a fase solvente (SUN et al., 2016). A energia das micro-ondas atua diretamente nas moléculas por condução iônica e rotação dipolar e, portanto, apenas materiais polares podem ser aquecidos com base em sua constante dielétrica (CHEN et al., 2020).

O princípio da EAM é baseado no efeito direto do aquecimento das micro-ondas nas moléculas por condução iônica ou rotação dipolar, que causam fricção e colisão entre íons e dipolos, onde os dois mecanismos podem ocorrer simultaneamente (LIU et al., 2019; CHEN et al., 2020). Moléculas polares, como a água, possuem cargas parciais positivas e negativas em extremos opostos e giram à medida que a incidência de ondas eletromagnéticas produzidas pelas micro-ondas aumentam, numa tentativa de alinhar com o campo elétrico formado (BARBA et al., 2008). Como a irradiação por micro-ondas promove o processo de extração ou reação química através da rotação dipolar e da condução iônica, isso torna a EAM um dos métodos mais promissores (ZHAO et al., 2019). EAM aquece a matriz interna e externamente sem um gradiente térmico; sendo assim, as biomoléculas podem ser extraídas com eficiência e proteção (ROMERO-DIEZ et al., 2019).

Na extração assistida por micro-ondas, as ondas eletromagnéticas são utilizadas para penetrar nos materiais e interagir com grupos polares, gerando calor e promovendo assim o aquecimento do sólido e do solvente (ROUTRAY; ORSAT, 2012). O princípio fundamental do aquecimento volumétrico por micro-ondas é atribuído à fricção rápida da condução de partículas iônicas e rotação rápida do relaxamento dipolar dentro de um material dielétrico (SUN et al., 2016). O movimento do nível molecular e o atrito entre as moléculas fazem com que a energia das ondas eletromagnéticas seja transformada em energia térmica, aumentando a temperatura da matriz, e esse efeito leva a ruptura celular que facilita a extração dos compostos de interesse (ASPÉ; FERNÁNDEZ, 2011) e ao aumento da difusão de massas constantes dos solutos no solvente, reduzindo o tempo de extração e o consumo de solventes, além de permitir taxas de extração mais elevadas, melhores resultados, menores custos, técnicas automatizadas e maior preocupação com a prevenção da poluição (CALDAS et al., 2018; CVJETKO BUBALO et al., 2016).

A EAM é caracterizada pela ruptura da estrutura celular causada pelo volume penetrante de aquecimento por irradiação das micro-ondas. A capacidade de difusão dos componentes-alvo pode ser melhorada pelo incremento da temperatura do solvente sob aquecimento por micro-ondas. Sendo assim, a irradiação por micro-ondas induz a rápida elevação da temperatura do solvente para acelerar a difusão do compostos-alvo na matriz do vegetal. Como consequência, a penetração do solvente é favorecida, resultando na alteração ou na ruptura da estrutura celular, o que torna mais fácil a extração de compostos bioativos e sua dissolução em solvente (LIU et al., 2019). O aquecimento volumétrico por micro-ondas provoca elevação rápida da temperatura de

extratos para aumentar a pressão dentro das células do material vegetal. Quando a pressão dentro da célula excede a força de escoamento da parede celular, ocorre a ruptura das células vegetais e os compostos bioativos do material vegetal são facilmente liberados no solvente de extração (CHAN et al., 2016; SUN et al., 2016). Essas características de aquecimento permitem que a EAM seja utilizada na extração de compostos bioativos de produtos naturais (CASSOL; RODRIGUES; NOREÑA; 2019).

Comparado com os métodos tradicionais de extração por aquecimento, a EAM obviamente possui características superiores, como taxa de aquecimento rápido, controle eletrônico constante e preciso e aquecimento limpo (SADEGHI; HAKIMZADEH; KARIMIFAR, 2017), além de apresentar à redução do tempo de extração e da quantidade de solvente, obtenção de melhores rendimentos de compostos de interesse, alta reprodutibilidade, bem como o controle da temperatura e da pressão (COVA et al., 2019).

Porém, em comparação ao ultrassom, EAM apresenta elevado custo (CVJETKO BUBALO et al., 2016). EAM pode acelerar a transferência de energia e reduzir o gradiente térmico, o que torna o aquecimento mais eficiente e seletivo para certos materiais e, portanto, tem sido amplamente usada na indústria de alimentos (CASSOL; RODRIGUES; NOREÑA, 2019; VINATORU; MASON; CALINESCU, 2017; SUN et al., 2016; PÓŁTORAK et al., 2015; PU; SUN, 2016 e 2017).

2.6.3. Estudos sobre extração de compostos bioativos

Diversos estudos foram publicados utilizando extração assistida por ultrassom e micro-ondas de compostos bioativos de diferentes resíduos de frutas. Estudos de extração de compostos bioativos foram realizados utilizando EAU em casca de manga (GUANDALINI et al., 2019); casca de romã (SHARAYEI et al., 2019); cascas e sementes de manga *Haden* (manga rosa) (CASTANEDA-VALBUENA et al., 2021); subproduto do café (pele) (WEN et al., 2019); e subprodutos da sálvia (ZEKOVIĆ et al., 2017). Já com a técnica de extração de compostos bioativos assistida por micro-ondas foram encontrados os trabalhos realizados com casca de romã (KADERIDES et al., 2019); casca de manga (PAL; JADEJA, 2019); semente de uva (CHEN et al., 2020); casca de tomate (BAKIĆ et al., 2019); subprodutos de alcachofra (MENA-GARCÍA et al., 2020); casca de urucum (QUIROZ et al., 2019); hibisco (CASSOL; RODRIGUES;

NOREÑA, 2019); bambu (MILANI et al., 2020); e casca de *Albizia myriophylla* (MANGANG; CHAKRABORTY; DEKA, 2020).

Também foram publicados estudos que comparam diferentes métodos de extração de compostos bioativos. Pollini et al. (2021) estudaram a extração de compostos fenólicos do bagaço de maça por diferentes métodos de extração não convencionais (extração assistida por ultrassom, extração em ultraturrax, extração acelerada por solvente e extração em campo elétrico pulsado. Os autores concluíram que a EAU é o método mais eficiente na extração de compotos fenólicos do bagaço de maça. Marinelli et al. (2020) compararam três técnicas de extração (líquido pressurizado, ultrassom e fluido supercrítico) em termos de eficiência de extração de compostos bioativos de subprodutos de brócolis. Oroian, Dranca e Ursachi (2020) avaliaram a extração de compostos fenólicos de própolis, comparando três técnicas (maceração, micro-ondas e ultrassom). A eficiência da extração foi medida com base no rendimento de extração dos compostos fenólicos e a EAU teve um rendimento de extração superior à extração por maceração e por micro-ondas. Caldas et al. (2018) compararam a extração convencional e não-convencional (EAU e EAM) de compostos fenólicos do resíduo da uva. A EAU mostrou o melhor desempenho, resultando em um extrato com teor fenólico duas vezes superiores ao obtido por extração convencional (agitação mecânica), em um tempo muito menor (9 min). Rocchetti et al. (2019) estudaram a extração de polifenóis de folhas de *Moringa oleifera* utilizando extração por maceração, extração assistida por homogeneizador, extração rápida por sólido-líquido, EAU e EAM. A extração assistida por homogeneizador permitiu extrair as maiores quantidades de polifenóis das folhas de *Moringa oleífera*.

2.7. Microencapsulação

Devido à crescente demanda por compostos com propriedades antioxidantes, a investigação de novas fontes antioxidantes e a incorporação destes compostos em produtos da indústria alimentícia, farmacêutica e de cosméticos estão sendo estudados. No entanto, várias limitações têm sido associadas ao uso de extratos de compostos bioativos em produtos devido à sua instabilidade sob condições de alta temperatura e oxigênio durante os períodos de armazenamento, que é influenciada por solventes, pH, temperatura, oxigênio, luz e enzimas (ÇAM; IÇYER; ERDOGAN, 2014; RIBEIRO; ESTEVINHO; ROCHA, 2020). Assim, as técnicas de microencapsulação são um

processo alternativo para superar esses problemas, aumentando a estabilidade destes compostos e protegendo-os de efeitos adversos ambientais por incorporação de uma matriz protetora (LEE; CHANG, 2020).

A tecnologia da microencapsulação surgiu na década de 30, mas foi apenas em 1950 que ocorreu a primeira aplicação em larga escala deste procedimento (CARVALHO; ESTEVINHO; SANTOS, 2016). O termo microencapsulação é definido como um processo em que pequenas partículas sólidas, gotículas de líquidos ou compostos gasosos, geralmente definidos como ingredientes ativos (material de núcleo) são envolvidos, aprisionados por um revestimento ou incorporados em uma matriz homogênea ou heterogênea e as propriedades requeridas das cápsulas como proteção química e mecânica, liberação controlada, ou outras, podem ser atingidas manipulando-se a composição da matriz. Por outro lado, o material a ser revestido pode ser composto por sólidos, líquidos ou gases (GHARSALLAOUI et al., 2007; EZHILARASI et al., 2013).

Em alimentos, os estudos sobre microencapsulação se iniciaram na década de 1960, com óleos essenciais, visando evitar a perda de compostos voláteis, promovendo liberação controlada de aromas e reduzindo a oxidação (RÉ, 1998). A microencapsulação de diferentes componentes bioativos dos alimentos desempenha um papel crítico na proteção desses nutrientes contra condições desfavoráveis de processo e armazenamento (KATOUZIAN; JAFARI, 2016; JAFARI et al., 2017). Como os principais contribuintes para a baixa estabilidade dos fitoquímicos são ambientais (oxigênio, umidade, luz, pH, calor etc.), uma alternativa eficaz para melhorar a estabilidade é formar uma barreira entre fitoquímico e ambiente externo (LABUSCHAGNE, 2018). Esse desafio pode ser superado adicionando materiais de parede ao extrato para promover a formação de filme durante a microencapsulação para servir como barreira para proteger os materiais essenciais do ambiente durante o microencapsulamento e o armazenamento (MOSER et al., 2017; ZHANG et al., 2020). Além disso, o material de revestimento usado na microencapsulação mantém as várias características físico-químicas do composto protegido, incluindo suas propriedades de umidade e prazo de validade. Essas propriedades dependem da estrutura dos materiais de revestimento (NAWI; MUHAMAD; MARSIN, 2015).

A microencapsulação é uma alternativa de proteção aos compostos que se degradam facilmente devido a condições adversas e o intuito deste processo é aprisionar uma substância dentro de outro material (revestimento, escudo ou material de

suporte/parede), formando pequenas partículas, seladas, que podem liberar seu conteúdo a taxas controladas em condições específicas (CELLI *et al*., 2015; CARVALHO *et al*., 2016). O ingrediente a ser preso é chamado de “material ativo", "núcleo", "fase interna" ou "preenchimento", considerando que o material que forma a matriz é denominado "material de parede", "agente encapsulante ou carreador", "invólucro", "transportador" ou "membrana" (DAVIDOV-PARDO; MCCLEMENTS, 2015). A composição do agente carreador é o principal determinante das propriedades funcionais da microcápsula e de como ela pode ser utilizada para melhorar o desempenho de um determinado ingrediente (MORENO *et al*., 2016; EZHILARASI et *al*., 2013).

Vários tipos de materiais de parede estão sendo utilizados na microencapsulação de polifenóis, principalmente os que apresentam baixo custo, incluindo polissacarídeos (maltodextrina, goma arábica, amidos e xaropes de milho), lipídios (mono e diglicerídeos) e proteínas (caseína, proteína do soro de leite, gelatina e proteína de soja). De modo geral, são empregados biopolímeros naturais de diversas fontes, usados sozinhos ou em combinações (ESTEVEZ *et al*., 2019; FARRAG *et al*. 2018). Dependendo do polímero utilizado, a microencapsulação pode controlar modificações sensoriais e aumentar a taxa de solubilidade/dissolução do produto em pó. Um bom agente de encapsulamento deve ter propriedades emulsificantes e formadoras de filme, exibir baixa higroscopicidade, baixa viscosidade e alto conteúdo de sólidos, resistência ao trato gastrointestinal, ser biodegradável, não tóxico, de baixo custo, sem sabor, sem odor, solúvel em solventes aquosos e de qualidade alimentar (TAN *et al*., 2015).

A aplicação de diferentes materiais de parede influencia as características físico-químicas do pó, incluindo o teor de umidade, a atividade da água e a morfologia da superfície, devido à formação do filme pelos materiais de parede. Os grupos funcionais químicos presentes nos materiais de parede também podem interagir com os materiais encapsulados, funcionando como estabilizadores (MICHALSKA *et al*., 2018).

A maltodextrina é um material de parede amplamente utilizado na microencapsulação por atomização devido ao seu baixo custo, alta eficiência de microencapsulação, alta solubilidade, baixa viscosidade em alta concentração e proteção eficaz contra a oxidação (LABUSCHAGNE, 2018). Além disso, as maltodextrinas são caracterizadas por um sabor suave e suas soluções são incolores. A maltodextrina é classificada com base em valor equivalente à dextrose (DE), que representa o teor de redução de açúcar (ZHANG *et al*., 2020). A goma arábica também apresenta eficiência,

estabilidade e boas características de formação de filme, apesar de seu alto custo (FERNANDES *et al*., 2014).

Para os compostos bioativos, como os polifenólicos, a microencapsulação vem sendo largamente avaliada e testada devido aos ganhos efetivos com estabilidade, aumento da meia-vida, e redução dos sabores desagradáveis, quando comparado ao uso dos mesmos compostos na forma livre. A microencapsulação destaca-se por permitir um controle sofisticado de certas propriedades do produto e por ser uma tecnologia que envolve processos complexos que permitem incorporar a um material ativo novas propriedades funcionais e "inteligentes". A liberação ou atuação controlada/direcionada de ingredientes bioativos em produtos comerciais em um meio específico ou no corpo humano sob condições apropriadas, tornando mais eficaz o produto final do qual esse material fará parte (FARIDI ESFANJANI; ASSADPOUR; JAFARI, 2018). Dependendo da escolha do material de parede e de suas características, o composto é liberado do material de parede através de vários mecanismos, como inchaço, dissolução ou degradação. Dependendo da velocidade desses mecanismos, a liberação pode ocorrer durante períodos diferentes. A escolha do material da parede também deve ser compatível com os métodos convencionais de encapsulamento (LABUSCHAGNE, 2018).

A microencapsulação de ingredientes alimentares em materiais de revestimento pode ser realizada por diversas técnicas como atomização, coacervação, liofilização, aprisionamento em lipossomas, revestimento em leito fluidizado, revestimento por extrusão, cocristalização dentre outros (SANTHALAKSHMY *et al*., 2015).

2.7.1. Atomização

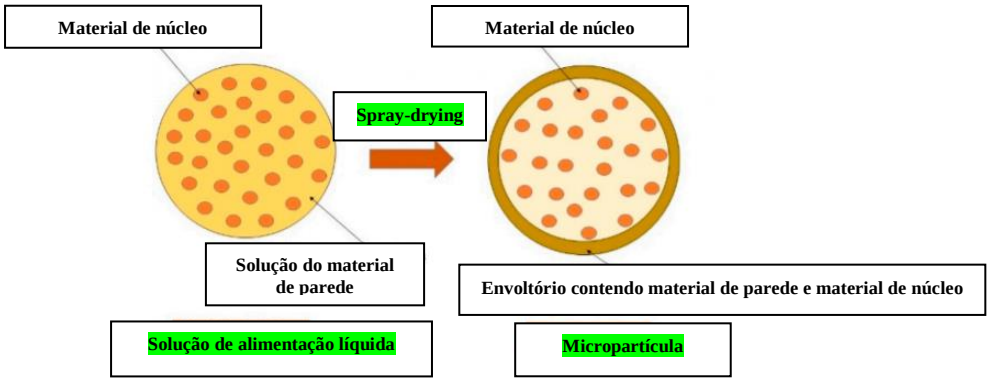
A atomização também chamada de spray drying, é uma das mais populares tecnologias de encapsulamento, por ser simples e econômica, podendo ser utilizada em ampla gama de nutracêuticos, probióticos, sabores, enzimas e peptídeos (SARABANDI *et al*., 2018). É uma técnica amplamente utilizada na indústria alimentícia para secar produtos de frutas, especialmente em formas de purê ou suco. A atomização é o método de encapsulamento mais popular usado para a estabilização e proteção de compostos biologicamente ativos de várias condições ambientais, como oxidação, luz, umidade, pH e temperatura (PUDZIUVELYTE *et al*., 2019; EROGLU; TONTUL; TOPUZ, 2018).

A atomização consiste na transformação de um produto no estado fluido para o estado sólido na forma de pó, numa operação contínua, em um tempo relativamente curto (FERRARI *et al*., 2012). Esse processo é realizado através da dispersão de gotículas do material dentro de uma câmara, na qual o material fluido entra em contato com o ar aquecido, na forma de nuvem ou *spray* (SANTHALAKSHMY *et al*., 2015). A técnica de microencapsulação por atomização é aplicada, devido ao seu custo relativamente baixo de instalação de equipamentos, alta produtividade e desidratação rápida (ZHANG *et al*., 2020).

A qualidade dos produtos obtidos por atomização depende das características do atomizador e da transferência de calor e massa entre o ar aquecido e as gotículas da câmara de secagem. Entre as vantagens da atomização destaca-se a alta relação entre a área de superfície e o volume das gotículas, resultando em menor tempo de exposição das partículas à temperatura de secagem. Além disso, o processo produz partículas muito pequenas, tornando o produto final bastante solúvel. Em relação às desvantagens, temos que os compostos, com baixo ponto de ebulição, responsáveis pelo sabor e aroma podem ser perdidos (PHISUT, 2012; SHISHIR & CHEN, 2017, ZHANG et al., 2020).

A principal vantagem da microencapsulação por atomização é a rápida formação (alguns segundos) das cápsulas/esferas (material de parede), que protegem o encapsulado (material do núcleo) (Figura 4) mesmo em temperatura elevada, permitindo assim poucas perdas e preservação; por esta razão, mesmo ingredientes sensíveis ao calor, como compostos fenólicos, podem ser encapsulados por atomização (DI BATTISTA *et al*., 2017; SHAMAEI *et al*., 2017).

Figura 4. Esquema mostrando a cápsula formada ao redor das partículas durante a secagem por atomização.



Fonte: Adptado de PUDZIUVELYTE et al. (2019).

Geralmente, duas grandes categorias relacionadas à morfologia das partículas existem: microcápsula e microesfera. A primeira é um reservatório onde o núcleo é cercado por uma camada externa, enquanto a segunda é considerada como um tipo de matriz onde o núcleo é homogeneamente integrado ao material da parede (AGUIAR; ESTEVINHO; SANTOS, 2016).

A microencapsulação apresenta inúmeras vantagens, incluindo prolongamento do prazo de validade, preservação do conteúdo de compostos fenólicos e redução no custo de embalagem (ZHANG *et al*., 2020). Além disso, a microencapsulação pode aumentar a vida de armazenamento de um composto volátil, diminuir a taxa de evaporação ou transferência do material ativo do núcleo para o meio (liberação controlada) e prevenir reações químicas com fatores externos. Também apresenta como benefícios para encapsulamento de ingredientes bioativos de alimentos: o controle do tamanho, forma e morfologia das partículas (forma amorfa/cristal, porosidade) e a melhoria e/ou modificação das propriedades do composto principal, como cor, volume, densidade aparente, reatividade, durabilidade, sensibilidade à pressão e ao calor e fotossensibilidade (ARPAGAUS *et al*., 2018; ASSADPOUR; JAFARI, 2017).

Além disso, a microencapsulação por atomização vem sendo mais largamente empregada pela indústria alimentícia pelo baixo custo em comparação com os demais processos como liofilização que chegam a ser 30 a 50 vezes mais caras (PUDZIUVELYTE *et al*., 2019). Esta técnica visa prolongar a vida útil do produto, protegendo os componentes ativos contra a degradação durante o armazenamento e/ou processamento e mantendo a funcionalidade, além de mascarar *flavours*, odores ou sabores indesejados (JAFARI *et al*., 2017). A atomização de compostos ativos aumenta a biodisponibilidade destes e melhora a solubilidade de compostos pouco solúveis (PUDZIUVELYTE *et al*., 2019).

2.7.2. Liofilização

A liofilização é uma técnica baseada na remoção da água por sublimação que é utilizada para se obter vários produtos industriais. O desempenho do processo é fortemente dependente da escolha adequada das condições operacionais e, portanto, há necessidade de uma extensiva análise de seus efeitos no tempo de processamento e na qualidade do produto obtido. Essa tecnologia foi desenvolvida para superar as perdas de compostos responsáveis pelos aromas nos alimentos, os quais são muito suscetíveis às

modalidades de processamento que empregam temperaturas elevadas, como a secagem convencional (SALAZAR; ALVAREZ; ORREGO, 2017).

A técnica da liofilização mantém a alta qualidade dos alimentos e bioprodutos, incluindo a aparência, nutrientes, sabor e alta capacidade de reidratação. O processo consiste principalmente em congelamento e desidratação sob pressão reduzida. Um processo de liofilização bem-sucedido resulta em matrizes altamente porosas e desidratadas com alta capacidade de reidratação, que é uma propriedade importante da liofilização (HARNKARNSUJARIT *et al.*, 2016). Apesar destas vantagens, as amostras liofilizadas exibem uma alta higroscopicidade, e, podem ser adversamente afetadas pela umidade durante o armazenamento. Sob a influência de umidade e oxigênio, componentes sensíveis ao oxigênio podem rapidamente se decompor. A liofilização aumenta a porosidade, e consequentemente, a área do produto que está exposta à atividade de radicais livres (MATERSKA, 2014).

Alimentos liofilizados são produtos com alto valor agregado por reter grande parte de seus nutrientes originais, uma vez que se empregam baixas temperaturas em seu processamento. Entretanto, seu custo é expressivamente maior quando comparado aos produtos secos por outras técnicas, necessitando-se, assim, de pesquisas que minimizem os custos operacionais.

2.7.3. Estudos sobre microencapsulação de extratos de vegetais e subprodutos

A atomização e a liofilização são amplamente utilizadas para a microencapsulação de extratos de resíduos e outros compostos bioativos de fontes naturais, por exemplo, a casca de uva (*Vitis labrusca* var. Bordo) (KUCK; NORENA, 2016), o extrato de erva-mate (*Ilex paraguariensis*) (NUNES *et al*., 2015) e o resíduo de acerola (REZENDE *et al*., 2018).

Diversos estudos utilizando microencapsulação por atomização de extratos de compostos bioativos foram publicados, como exemplos, microencapsulação de extrato de polifenóis de semente de uva (YADAV *et al*., 2020); de compostos fenólicos de cranberry (ZHANG *et al*., 2020); de compostos bioativos de cagaita (*Eugenia dysenterica*) (DAZA *et al*., 2016); de antocianinas de *chokeberry* (PIECZYKOLAN; KUREK, 2019); de compostos bioativos de bagaço de amora (SANTOS *et al*., 2019), e de polifenóis de chicória vermelha e couve roxa (ZANONI *et al*., 2020). Entretanto Sharayei, Azarpazhooh e Ramaswamy (2020) utilizaram a microencapsulação por

liofilização em extratos de compostos fenólicos da casca de romã e obtiveram bons resultados. Também encontram-se na literatura estudos que utilizam as duas técnicas de microencapsulação (atomização e liofilização) de extratos de compostos bioativos com diferentes agentes encapsulantes. Ramírez, Giraldo e Orrego (2015) avaliaram a estabilidade de polifenóis de frutos encapsulados por atomização e liofilização, utilizando maltodextrina e goma arábica, como agentes encapsulantes. Rezende et al. (2018) estudaram a microencapsulação por atomização e por liofilização de compostos bioativos da polpa e do resíduo da acerola utilizando goma arábica e maltodextrina como agentes encapsulantes, enquanto que Agudelo et al. (2017) analisaram o efeito da preservação da retenção de antioxidantes em diferentes pós de toranja obtidos por liofilização e por atomização.

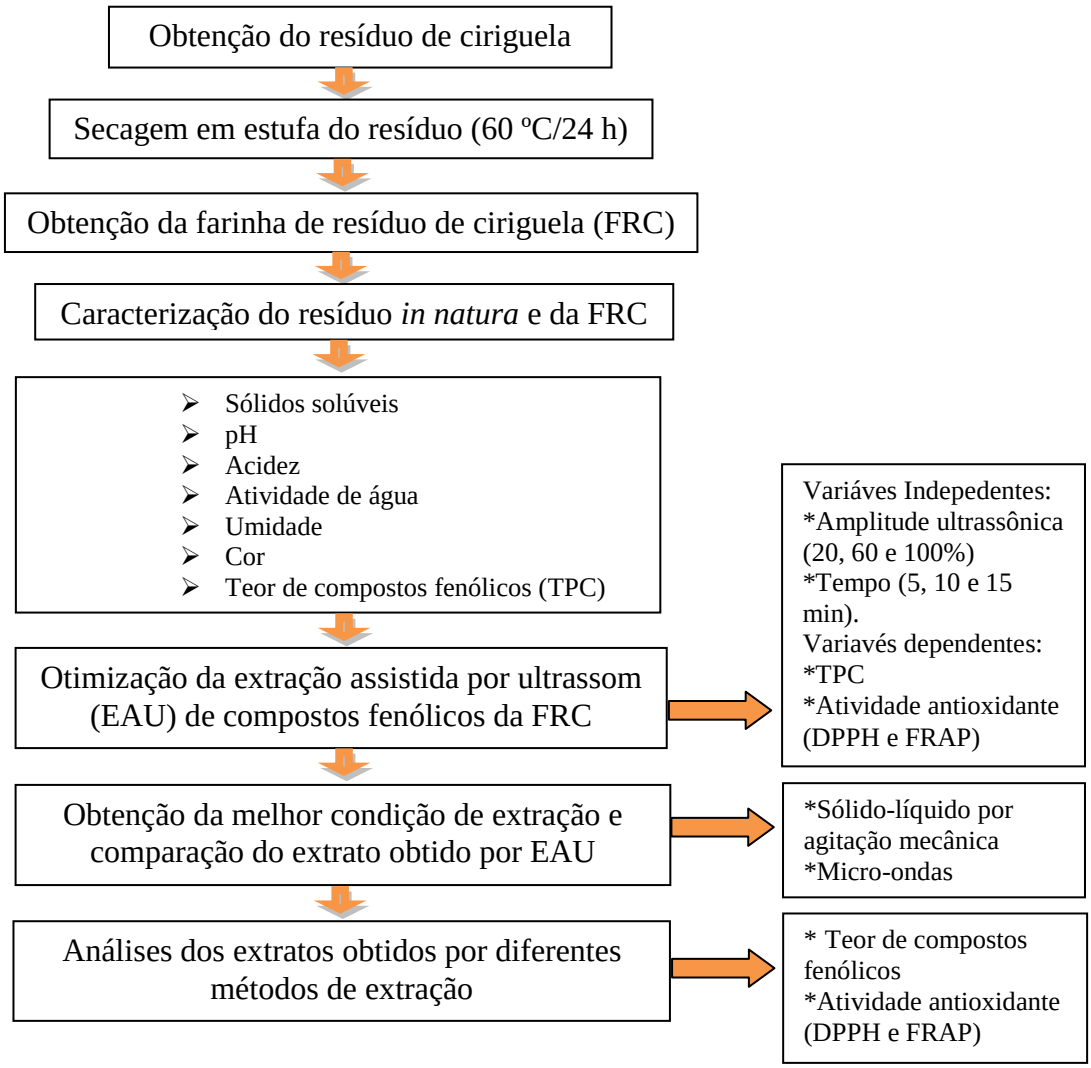
Com base nos diversos estudos de extração e microencapsulação de compostos fenólicos de vegetais e seus subprodutos, citados anteriormente, uma alternativa para o aproveitamento tecnológico do resíduo da ciriguela é a sua utilização na produção de extratos microencapsulados, de modo a obter um extrato rico em compostos bioativos que possua elevado teor de compostos fenólicos. É importante otimizar o processo de extração e microencapsulção de extrato da farinha de resíduo de ciriguela visando obter um extrato com maior concentração de compostos fenólicos e consequentemente, maior atividade antioxidante. Esses aspectos, juntamente com o crescente interesse global em tecnologias de extração emergentes, que visam à minimização dos impactos ambientais, justificam a utilização deste subproduto gerado nas indústrias de processamento de frutas.

3. MATERIAL E MÉTODOS

3.1 Desenho experimental e local de execução da pesquisa

O desenho experimental desta pesquisa foi dividido basicamente em 3 fases: a primeira etapa (Figura 5) compreendeu a obtenção do resíduo de ciriguela e processamento da farinha de resíduo de ciriguela (FRC), até a caracterização e obtenção dos extratos de compostos fenólicos obtidos por diferentes métodos de extração. Esta etapa da pesquisa foi realizada no Laboratório de Processamento de Alimentos, e no Laboratório de Análises Físico-químicas, ambos locados no Departamento de Ciências do Consumo (DCC) da Universidade Federal Rural de Pernambuco (UFRPE).

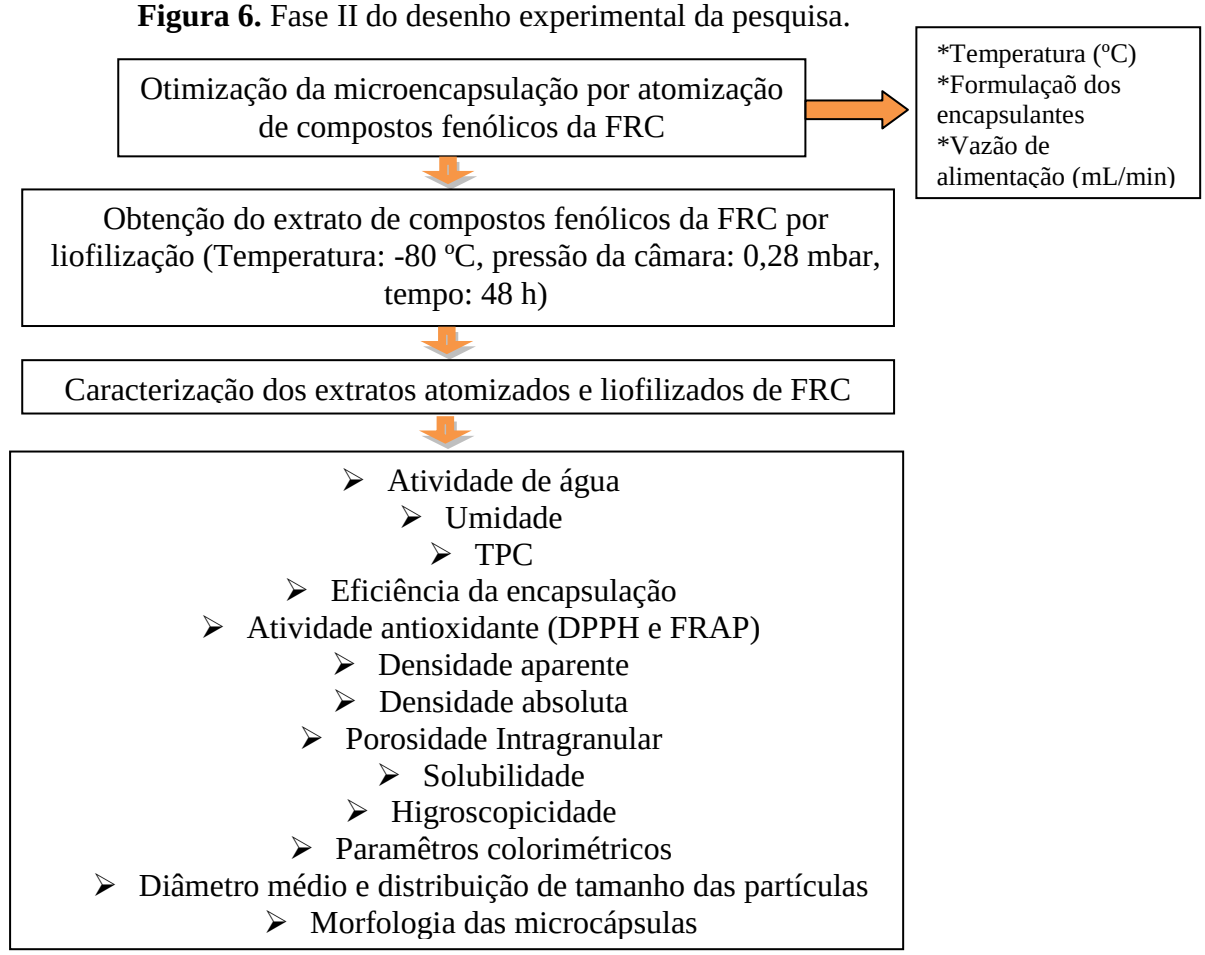
Figura 5. Fase I do desenho experimental da pesquisa.



A segunda fase experimental (Figura 6) consistiu da realização do planejamento experimental da microencapsulação por atomização do extrato de

compostos fenólicos de FRC, realizado no Laboratório de Processamento de Alimentos da UFRPE. E também foi realizada a comparação entre o extrato atomizado otimizado e o extrato liofilizado. A produção do extrato liofilizado foi realizada no Centro de Apoio ao Pesquisador (CENAPESQ) da UFRPE. Além da caracterização física, físico-química e tecnológica, determinação de compostos fenólicos e da atividade antioxidante dos extratos em pós, realizada no Laboratório de Análises Físico-químicas do DCC da UFRPE.

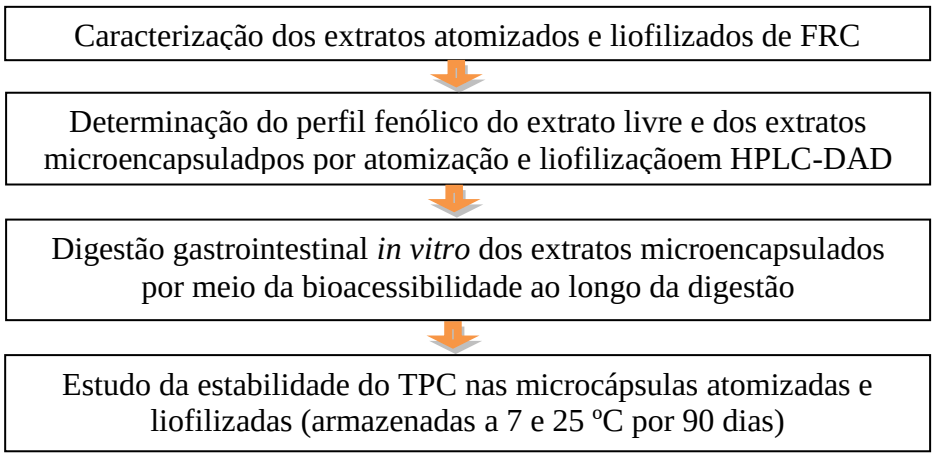
Figura 6. Fase II do desenho experimental da pesquisa.



A terceira fase (Figura 7) foi basicamente a caracterização dos extratos atomizado e liofilizado (perfil fenólico por HPLC, digestão gastrointestinal *in vitro* e estudo da estabilidade). O perfil fenólico por HPLC foi realizado no Laboratório de Cromatografia Líquida, do Departamento de Tecnologia em Alimentos, do Instituto Federal do Sertão Pernambucano (IFSertãoPE), Campus Petrolina. A digestão gastrointestinal *in vitro* foi realizada no Laboratório de Microbiologia de Alimentos, do Centro de Educação e Saúde (CES), da Universidade Federal de Campina Grande

(UFCG). E o estudo da estabilidade foi realizado no Laboratório de Análises Físico-químicas do DCC da UFRPE.

Figura 7. Fase III do desenho experimental da pesquisa.



3.2. Obtenção do resíduo

Os resíduos da polpa de ciriguela (cascas e caroços) foram fornecidos por uma indústria de polpas de frutas congeladas, localizada em João Pessoa/PB. Os frutos foram cultivados na Paraíba (07º 09' S 36º 49' W), a extração da polpa foi realizada pela indústria de polpas. Foram disponibilizados 50 kg de subprodutos (cascas e caroços) de ciriguela, que foram transportados em caixas térmicas mantendo a temperatura (7 ± 2 ºC) até o laboratório de Processamento de Alimentos do DCC da UFRPE. Após a separação manual dos caroços das cascas, rendeu aproximadamente 11 kg de cascas de ciriguela.

3.3. Obtenção da farinha de resíduo de ciriguela (FRC)

As cascas da ciriguela foram separadas dos caroços manualmente e submetidas à secagem a 60 °C por 24 h (CALDAS et al., 2018), em estufa com circulação de ar (Marconi®, modelo MA035), até atingir umidade igual ou inferior a 10%, em seguida trituradas em moinho multi uso TE 631/2 (Tecnal) e peneirada #40 (425 µm). Foram produzidos aproximadamente 3,5 kg de FRC, que foi armazenada em sacos de polietileno de baixa densidade, envolvidos com papel laminado a -22 ºC.

3.4. Análises físicas e físico-químicas do resíduo *in natura* de ciriguela e da FRC

A determinação de sólidos solúveis foi realizada com refratômetro digital de marca Reichert® (r2 i300 - USA), e os resultados foram expressos em °Brix; o pH foi analisado por meio de medidas diretas utilizando pHmetro com eletrodo de vidro (AAKER®); a atividade de água (a_w) foi determinada com o auxílio de um analisador de atividade de água (DECAGON®, AQUA LAB - 4TE) a 25°C; a umidade foi determinada em balança de infravermelho (MARTE® – IDSO – Piracicaba/SP) a 105 ºC, com resultados expressos em (%), enquanto a acidez titulável foi realizada por método titulométrico, com resultados expressos em g de ácido cítrico/100 g de FRC (AOAC, 2019).

A cor foi avaliada em colorímetro (Minolta® CR 400, Konica Minolta, Sensing Inc), utilizando-se os padrões de cor do sistema CIELab – "Comission Internationale de L'Eclairage": *L** (luminosidade) variando do branco (L=100) ao preto (L=0), *a** que caracteriza a coloração na região do vermelho (+a*) ao verde (-a*), e *b** que indica a coloração no intervalo do amarelo (+b*) ao azul (-b*) (YILDIZ; RABABAH; FENG, 2016). O colorímetro foi previamente calibrado com um padrão branco antes de cada análise, usando como fonte de luz uma lâmpada de xenônio, iluminante C (Y=92.78; x=0.3139; y=0.3200), ângulo de observação de 10º e área de medição de 8 mm de diâmetro (YILDIZ; RABABAH; FENG, 2016).

3.5. Análise de compostos fenólicos da FRC

Para quantificação de compostos bioativos da FRC foi realizada a extração convencional, utilizando maceração da FRC e solventes em almofariz. 10 g de FRC foram adicionadas a 40 mL de etanol-água a 80% (solvente selecionado em testes pré-liminares), seguido de agitação constante por 20 min em agitador magnético (Fisatom 752A - São Paulo/Brasil) com auxilio de barra magnética, centrifugação (2500 rpm equivalente a 1500 *g*/10 min) e filtração. O extrato obtido foi armazenado em vidros âmbar sob congelamento na temperatura de -22 ºC.

Os compostos fenólicos totais foram determinados por método espectrofotométrico pela absorbância a 725 nm, utilizando reagente de Folin Ciocaulteu (Sigma Aldrich®, St. Louis, MO, USA), segundo metodologia descrita por Wettasinghe e Shahidi (1999). Resumidamente, em um tubo de ensaio foram adicionados 0,5 mL do extrato de cada amostra, 8,0 mL de água destilada e 0,5 mL do reagente Folin-

Ciocaulteu. Após 3 min, 1,0 mL de solução de carbonato de sódio foi adicionado e deixado reagir por 60 min no escuro. O teor de compostos fenólicos totais foi determinado por interpolação da absorbância das amostras contra uma curva padrão preparada a partir das soluções aquosas de ácido gálico (0,1-1 mg/mL) e os resultados foram expressos em mg de equivalente de ácido gálico (EAG)/g de FRC.

3.6. Obtenção dos extratos de FRC

Inicialmente foi realizado o planejamento experimental da extração por ultrassom dos compostos fenólicos da FRC, e em seguida o extrato otimizado foi comparado aos extratos obtidos pela extração por método convencional (sólido-líquido por agitação mecânica) e pela extração assistida por micro-ondas.

3.6.1. Extração assistida por ultrassom (EAU)

Para obtenção do extrato de compostos fenólicos por EAU, a FRC juntamente com o solvente (etanol a 80%, acidificado com 0,1% de HCl) foram submetidos a sonda ultrassônica (modelo QR1000, Ultronique, Ecosonics, São Paulo/Brasil) com potência máxima de 1000 Watts (W) e frequência ultrassônica de 20 kHz. O extrato obtido foi filtrado e armazenado em recipiente âmbar a -20 ºC.

Para a EAU da FRC utilizou-se o planejamento experimental Box-Behnken (Tabela 1) com 8 pontos fatoriais (níveis ± 1) e 5 pontos centrais (nível 0), totalizando 13 ensaios. Conforme o estudo de Sharayei *et al*. (2019), as variáveis independentes foram: amplitude ultrassônica (20, 60 e 100%) e tempo de exposição ao ultrassom (5, 10 e 15 min), e as variáveis dependentes foram: teor de compostos fenólicos, atividade antioxidante por DPPH e FRAP.

Os dados obtidos no planejamento experimental foram ajustados à Equação 1 (AZARPAZHOOH; RAMASWAMY, 2012):

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{i<j} \sum \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \epsilon \quad \text{(Eq. 1)}$$

onde: Y representa a resposta prevista, β_0 o coeficiente de regressão constante, βi, βjj e βij os coeficientes lineares, quadráticos e de interação, respectivamente, Xi e Xj as variáveis independentes e ε o ruído ou erro.

A qualidade dos modelos polinomiais ajustados foi expressa pelo coeficiente de regressão (R^2), R^2 ajustado, precisão adequada (AP) e coeficiente de variação (CV).

Tabela 1. Planejamento experimental codificado e decodificado da extração por ultrassom da farinha de resíduo de ciriguela (FRC).

Ensaio	Amplitude ultrassônica (%)	Tempo de exposição ao ultrassom (min)
01	0 (60)	0 (10)
02	0 (60)	+1 (15)
03	0 (60)	0 (10)
04	-1 (20)	+1 (15)
05	-1 (20)	0 (10)
06	+1 **(**100)	0 (10)
07	-1(20)	-1 (5)
08	+1(100)	-1 (5)
09	0 (60)	0 (10)
10	0 (60)	-1 (5)
11	0 (60)	0 (10)
12	+1 **(**100)	+1 (15)
13	0 (60)	0 (10)

3.6.2. Extração por método convencional (sólido-líquido por agitação mecânica)

A extração dos compostos fenólicos por método convencional foi realizada utilizando maceração da FRC e solventes em almofariz. Para tanto, 10 g de FRC foram adicionados a 40 mL de etanol-água a 80% acidificado com 0,1% de HCl, seguido de agitação constante por 60 min em agitador magnético, com auxílio de barra magnética, centrifugação (2500 rpm equivalente a 1500 x *g*/10 min) e filtração (condições definidas em testes preliminares). O extrato obtido foi armazenado em vidros âmbar sob congelamento na temperatura de -22 ºC.

3.6.3. Extração assistida por micro-ondas (EAM)

Para obtenção do extrato de compostos fenólicos por micro-ondas, a FRC juntamente com o solvente (etanol a 80%, acidificado com 0,1% de HCl) foram colocados no equipamento de micro-ondas CEM Discover (modelo Discover System

908005) utilizando potência de 800W, temperatura de 120 ºC e tempo de extração de 15 min (condições definidas em testes preliminares). Após a exposição às ondas eletromagnéticas o sobrenadante obtido foi filtrado e armazenado em recipiente âmbar a -22 ºC.

3.7. Análises dos extratos obtidos por diferentes métodos de extração

3.7.1. Teor de compostos fenólicos (TPC)

O teor de compostos fenólicos foi realizado conforme citado anteriormente no item 3.5.

3.7.2. Capacidade de Sequestrar o Radical DPPH$^{\bullet}$ (EC 50%)

Foi realizado segundo método descrito por Brand-Williams et al. (1995) modificado por Sanchez-Moreno et al. (1998). O extrato foi diluído em três diferentes concentrações de fenólicos totais (2, 3 e 9 µg/mL) e adicionado à solução de DPPH$^{\bullet}$ (1,1-difenil-2-picrilhidrazil) em metanol (0,1M). A absorbância a 517 nm foi monitorada em espectrofotômetro (Shimadzu UV-1650PC, São Paulo/Brasil) até a reação atingir o platô.

A atividade de eliminação de radicais foi calculada conforme Ramadan et al. (2003), como porcentagem da descoloração do DPPH$^{\bullet}$ usando a Eq. (2):

$$DPPH^{\bullet}\ \% = [(ADPPH - AS)/ADPPH] \times 100 \qquad \text{(Eq. 2)}$$

onde AS é a absorbância da solução quando a amostra é adicionada em um nível particular e ADPPH é a absorbância da solução de DPPH$^{\bullet}$.

A concentração da amostra que fornece metade do máximo (50%) da atividade de eliminação de radicais (EC_{50}) é uma medida da eficácia de uma substância na inibição de uma função biológica ou bioquímica específica. Ela foi calculada por interpolação do gráfico da porcentagem de atividade de eliminação de radicais em relação à concentração da amostra.

Os resultados foram expressos em EC_{50} (concentração de extrato em µg/mL capaz de reagir com 50% do radical presente na solução de DPPH$^{\bullet}$).

3.7.3. Poder de redução do ferro – FRAP

O ensaio do poder antioxidante redutor férrico (FRAP- Ferric Reducing Antioxidant Power) foi conduzido de acordo com a metodologia relatada por Thaipong et al. (2006). A absorbância utilizada foi 593 nm, utilizando um espectrofotômetro (Shimadzu UV-1650PC, São Paulo - Brasil). A atividade antioxidante por FRAP foi expressa em µmol de equivalente ferroso por g de extrato (µmol $Fe^{2+/}$g).

3.8. Microencapsulação do extrato de compostos fenólicos da FRC

O método de extração que produziu o extrato com maior concentração de compostos fenólicos foi escolhido para dar continuidade à pesquisa. As condições ótimas de extração foram de acordo com os dados obtidos do planejamento experimental. Ao extrato rotaevaporado por 15 min a 40 ºC e em seguida diluído em água destilada (para facilitar a passagem pelo bico atomizador) e foram adicionado(s) o(s) agente(s) encapsulante(s) (goma arábica e maltodextrina), de acordo com a quantidade de sólidos totais para cada ensaio do planejamento.

3.8.1. Microencapsulação por atomização

A encapsulação foi realizada em atomizador modelo MSD 1.0 (LABMAQ do Brasil LTDA). Os agentes carreadores utilizados foram: maltodextrina 10DE (Ingredion – São Paulo/Brasil) e goma arábica (Dinânica – São Paulo/Brasil), por apresentarem baixo custo e/ou alta eficiência no encapsulamento de compostos bioativos.

O extrato de FRC juntamente com a formulação de agente encapsulante foram homogenizados por 5 min em homogenizador Turratec (Tecnal/TE-102 – Piracicaba, São Paulo/Brasil) utilizando velocidade de 14.000 rpm. Na microencapsulação por atomização a concentração de sólidos totais da solução final foi fixada em 30% (27% de material de parede e 3% do material de recheio/extrato), enquanto a vazão de alimentação da mistura foi fixada em 0,60 L/h, utilizando bico injetor de 1,2 mm de diâmetro, fluxo de ar de 30 m^3/h e pressão do ar de 0,6 bar.

Foi realizado um planejamento experimental 2^3 composto por 8 pontos fatoriais (níveis ± 1) e 3 pontos centrais (nível 0), totalizando 11 ensaios (Tabela 2). As variáveis independentes foram: temperatura (T), formulação do encapsulante (F) e vazão de alimentação (V, mL/min). Os dados obtidos foram ajustados à Equação 3:

$$Y = \beta_0 + \beta_1 T + \beta_2 F + \beta_3 V + \beta_4 TF + \beta_5 TV + \beta_6 FV$$

(Eq. 3)

onde Y é a resposta, β_0 é o coeficiente de regressão constante, β_1, β_2 e β_3 são os coeficientes lineares, T, F e V são as variáveis independentes e β_4, β_5, β_6 são os coeficientes de efeito de interação.

As variáveis de resposta (dependentes) foram: umidade, atividade de água, teor de compostos fenólicos, eficiência de encapsulamento, cor e atividade antioxidante por DPPH e FRAP.

Tabela 2. Planejamento experimental codificado e descodificado da microencapsulação por atomização do extrato de compostos fenólicos da FRC.

Ensaio	Temperatura (°C)	Formulação do encapsulante	Vazão de alimentação (mL/min)
01	-1 (130)	-1 (0% M / 100% GA)	-1 (0,40)
02	+1(170)	-1 (0% M / 100% GA)	-1 (0,40)
03	-1 (130)	+1 (100% M / 0% GA)	-1 (0,40)
04	+1 (170)	+1 (100% M / 0% GA)	-1 (0,40)
05	-1 (130)	-1 (0% M / 100% GA)	+1 (0,80)
06	+1 (170)	-1 (0% M / 100% GA)	+1 (0,80)
07	-1 (130)	+1 (100% M / 0% GA)	+1 (0,80)
08	+1 (170)	+1 (100% M / 0% GA)	+1 (0,80)
09	0 (150)	0 (50% M / 50% GA)	0 (0,60)
10	0 (150)	0 (50% M / 50% GA)	0 (0,60)
11	0 (150)	0 (50% M / 50% GA)	0 (0,60)

M=maltodextrina e GA=goma arábica.

3.8.2. Microencapsulação por liofilização

A liofilização foi utilizada como controle/padrão no processo de microencapsulação, realizada em liofilizador (Christ Alpha 1-4 LD Plus) disponível no CENAPESQ (Centro de Apoio à Pesquisa da UFRPE). Na microencapsulação por liofilização foi utilizada temperatura de liofilização (-80 ºC), vácuo da câmara (0,28

mbar), tempo de 48 h, e agente carreador (utilizando as condições otimizadas na secagem por atomização).

3.9. Análises dos extratos microencapsulados por atomização e liofilização

3.9.1. Umidade, atividade de água, cor e teor de compostos fenólicos

Conforme citado anteriormente para caracterização da FRC no item 3.3.

3.9.2. Atividade antioxidante por DPPH e FRAP

Conforme citado anteriormente para análise dos extratos de FRC no item 3.6.

3.9.3. Eficiência da encapsulação (EE)

Para determinação do teor total de fenólicos do microencapsulado (TTF), 100 mg do microencapsulado foram dispersos em 1 mL da solução etanol:ácido acético:água destilada (50:8:42 v/v). A mistura foi agitada em vortex por 1 min, e filtrada em microfiltro (Syringe Filters K18-230) com poros de diâmetro de 0,22 µm (SAÉNZ, et al., 2009). O teor de fenólicos foi determinado por método espectrofotômetro, com espectro de absorção registrado no comprimento de onda de 725 nm, utilizando o reagente de Folin-Ciocalteu (Merk – Darmstadt/Alemanha) e curva padrão de ácido gálico (WETTASINGHE; SHAHIDI, 1999). Os resultados foram expressos em µg de equivalente de ácido gálico por mg microcápsulas (pó) (µg EAG/mg^{-1}).

O teor de fenólicos totais na superfície da microcápsula (TFS) foi determinado segundo procedimento descrito por Saénz et al. (2009). 100 mg do microencapsulado foram dispersos em 1 mL de etanol:metanol (1:1 v/v), levemente agitados por 5 min e filtrados em microfiltro (Syringe Filters K18-230) de 0,22 µm. O teor de fenólicos foi determinado utilizando o reagente de Folin-Ciocalteu (Merk) e curva padrão de ácido gálico (WETTASINGHE; SHAHIDI, 1999).

A eficiência do encapsulamento (EE) foi calculada considerando a Equação 4 proposta por MAHDAVI et al. (2016).

$$EE\ (\%) = \frac{TTF - TFS}{TTF} \times 100 \qquad \text{(Eq. 4)}$$

onde: EE=Eficiência da encapsulação; TTF= Teor de Fenólicos totais das microcápsulas e TFS= Teor de fenólicos totais da superfície das microcápsulas.

3.10. Caracterização física dos extratos de compostos fenólicos microencapsulados por atomização e liofilização

O extrato otimizado microencapsulado por atomização e o extrato liofilizado foram escolhidos para dar continuidade à pesquisa, e consequentemente foram caracterizados quanto as variáveis físicas descritas abaixo.

3.10.1. Densidade aparente

A densidade aparente foi determinada de acordo com procedimento descrito por Barbosa-Canovas e Juliano (2005) e Caparino et al. (2012), com algumas modificações. Foram transferidas 2 g de amostra para uma proveta graduada de 10 mL, onde o pó foi compactado batendo a proveta 50 vezes sobre a bancada.

A densidade foi calculada de acordo com a Equação (5) e o resultado expresso em g/mL:

$$\rho_{ap} = m/v \qquad \text{(Eq. 5)}$$

onde: m é a massa da amostra (g); V é o volume total que o pó ocupou na proveta (mL).

3.10.2. Densidade absoluta

Determinada por meio de metodologia proposta por Caparino et al. (2012), a 25 ºC em um picnômetro com termômetro.

3.10.3. Porosidade intragranular (ε)

Calculada de acordo com Caparino et al. (2012), utilizando a Equação (6):

$$\varepsilon = 1-\rho_{ap}/\rho_{abs} \qquad \text{(Eq. 6)}$$

onde: ρ_{ap} é a densidade aparente (g/mL) e ρ_{abs} é a densidade absoluta (g/mL) da amostra.

3.10.4. Solubilidade

Determinada de acordo com a metodologia descrita por Cano-Chauca et al. (2005). 1 g da amostra foi diluído em 100 mL de água destilada, agitado em agitador magnético (Fisatom, modelo 752) por 5 minutos, formando uma solução aquosa, que

em seguida foi centrifugada a 3000 rpm (equivalente a 1800x*g*) por 5 minutos em centrífuga (Cientec, modelo CT-6000R). Uma alíquota de 25 mL do sobrenadante foi colocada em placa de Petri, esterilizada e previamente pesada e levada para estufa com circulação e renovação de ar (Marconi, modelo MA-035) a 105 ºC por 5 h. Ao término do processo a placa foi pesada em balança analítica e a solubilidade obtida através da diferença de peso.

3.10.5. Higroscopicidade

Determinada de acordo com a metodologia proposta por Cai e Corke (2000), modificada. Cápsulas com 1 g de extrato microencapsulado foram colocadas em um recipiente hermético contendo uma solução saturada de NaCl (umidade relativa de 75,29%) a 25 ºC e, após uma semana foram pesadas. A higroscopicidade foi expressa em g de umidade adsorvida por 100 g de massa seca da amostra (g/100g).

3.10.6. Diâmetro médio e distribuição de tamanho das partículas

Determinada em aparelho com difração a laser (Microtrac, modelo S3500), disponível no Laboratório Multiusuário de Nanotecnologia do CETENE (Centro de Tecnologias Estratégicas do Nordeste – CETENE), acoplado a um aparelho de ultrassom comum de bancada para aumentar a dispersibilidade da amostra. O líquido sedimentador utilizado foi isopropanol, visto que as partículas não são solúveis neste composto. Uma pequena quantidade de amostra foi dispersa em isopropanol e submetida a leituras de distribuição do tamanho de partículas. O diâmetro médio foi determinado com base no diâmetro médio de uma esfera do mesmo volume (diâmetro de Broucker, D[4,3]), geralmente utilizado para caracterizar partículas de pó.

3.10.7. Morfologia das partículas

Foi realizado por meio da microscopia eletrônica de varredura (MEV), modelo (Vega 3, Tescan, Brno, Czech Republic) disponível no Centro de Apoio à Pesquisa (CENAPESQ) da Universidade Federal Rural de Pernambuco. As amostras foram fixadas em porta-espécimens metálicos (*stubs*) com uma fita adesiva de dupla face condutora convencional, em seguida metalizadas com ouro em um metalizador (Leica, modelo EM SCD500), a uma taxa de recobrimento de 15 nm de espessura, por 80 segundos e corrente de 40 mA e, observadas em um microscópio eletrônico de

varredura (FEI, modelo Quanta 200 FEG), operando com 20 kV. A aquisição das imagens foi realizada pelo software, XT microscope.

3.11. Parâmetros colorimétricos

3.11.1. Cromaticidade

A cromaticidade (C) é a relação entre os valores de a* e b*, onde se obtém a cor real do objeto analisado. Foi calculada conforme a equação:

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

(Eq. 7)

onde: C: cromaticidade; a*: intensidade da cor vermelha a verde do extrato microencapsulado; b*: intensidade da cor amarela a azul do extrato microencapsulado.

3.11.2. Ângulo de tonalidade (Hue-angle)

É o ângulo formado entre a* e b*, indicando a saturação da cor do produto. Para cálculo do ângulo de tonalidade foi utilizada a equação:

$$H^{o} = \tan^{-1} b^{*}/a^{*}$$

(Eq. 8)

onde: H^{o}: ângulo de tonalidade; a*: intensidade da cor vermelha a verde do extrato microencapsulado; b*: intensidades da cor amarela a azul do extrato microencapsulado.

3.11.3. Diferença de cor

A variação na diferença de cor (ΔE*) em pós microencapsulados obtidos por atomização e liofilização foi calculado pela Equação (9) (CAI & CORKE, 2000), com base na análise de cor do extrato livre antes do encapsulamento e do extrato microencapsulado reconstituído (1g de extrato/10 mL de água).

$$\Delta E^{*} = (L^{*} - L_{0})^{2} + (a^{*} - a_{0}^{*})^{2} + (b^{*} - b_{0}^{*})^{2})^{0,5}$$

(Eq. 9)

Onde: ΔE*: é a diferença total de cor; L_0* e L*: são as luminosidades das amostras do extrato livre e do extrato microencapsulado reconstituído, respectivamente; a_0* e a*: são as intensidades da cor vermelha a verde das amostras do extrato livre e do extrato microencapsulado reconstituído, respectivamente; b_0* e b*: são as intensidades da cor

amarela a azul das amostras do extrato livre e do extrato microencapsulado reconstituído, respectivamente.

3.12. Perfil fenólico em HPLC-DAD

Amostras (1 g) de pós microencapsulados de extrato de FRC foram adicionadas a 10 mL de metanol/6 mol L^{-1} HCl. As amostras foram submetidas à extração por ultrassom a 40 kHz por 30 min a 25 °C (UNIQUE, modelo USC-1800, Brasil). Em seguida, o extrato foi centrifugado a 3000×*g* por 20 min (centrífuga SL-701; Solab, São Paulo, Brasil), e o sobrenadante (extrato fenólico) foi coletado. Uma alíquota de 1 mL do extrato foi filtrada em filtro seringa membrana (Zhejiang Alwsci Technologies-China) de 0,45 µm (PTFE) e utilizada para identificação e quantificação de compostos fenólicos por HPLC.

Os compostos fenólicos individuais foram determinados seguindo a metodologia validada por Padilha et al. (2017), com adaptações de Dutra et al. (2018) em gradiente e tempo de execução para quantificação de estilbenos, flavonóis e flavanonas, utilizando um cromatógrafo líquido Agilent 1260 Infinity LC System (Agilent Technologies, Santa Clara – EUA) acoplado a um detector de arranjo de diodos (DAD) (modelo G1315D). A separação cromatográfica dos compostos fenólicos foi realizada em uma coluna Zorbax Eclipse Plus RP-C18 (100 × 4,6 mm, 3,5 µm) e na pré-coluna Zorbax C18 (12,6 × 4,6 mm, 5 µm). A coleta e análise dos dados foram realizadas no software OpenLAB CDS ChemStation Edition (Agilent Technologies, Santa Clara – EUA). A temperatura utilizada foi de 35 °C e o volume de injeção foi de 20 µL da amostra, previamente diluída na fase A, e filtrada através de membrana de 0,45 µm (Millex Millipore, Barueri, SP, Brasil). O fluxo de solvente foi de 0,8 mL min^{-1}. O gradiente utilizado na separação foi de 0-5 min: 5% B; 5–14 min: 23% B; 14–30 min: 50% B; 30–33 min: 80% B onde o solvente A era uma solução de ácido fosfórico (0,52 M - pH = 2,0) e o solvente B era metanol acidificado com 0,5% H_3PO_4. A detecção dos compostos foi feita em 220, 280, 320, 360 e 520 nm, e a identificação e quantificação por comparação com padrões externos. Os resultados foram expressos em µg/g DW.

3.13. Digestão gastrointestinal *in vitro*

O procedimento de digestão gastrointestinal foi realizado imitando as condições

gastrointestinais fisiológicas, avaliadas em três fases sequenciais (oral, estômago e intestino delgado incluindo diálise), conforme Rodrigues-Roque et al. (2013) e Dutra et al. (2017). As alíquotas do extrato de compostos fenólicos microencapsulado reconstituído (50 mL) foram misturadas com 5 mL de solução salivar (2,38 g de Na_2HPO_4, 0,19 g de KH_2PO_4, 8 g de NaCl e 200 mL de amilase) em frascos âmbar. A mistura foi homogeneizada durante 10 minutos num banho de água a 37 ± 2 °C a 95 g. Depois, as amostras foram acidificadas até pH 2,0 com 1 mL de uma preparação de pepsina porcina (13 mg de pepsina em 5 mL de HCl a 0,1 M) para dar um volume final de 5 mL e posteriormente incubadas a 37 °C em agitação a 95 x *g* durante 1 h, para simular a digestão gástrica. No final da digestão pós-gástrica, a mistura foi imediatamente arrefecida num banho de gelo e uma alíquota de 1 mL foi removida e armazenada a -18 ºC. O restante da amostra foi submetido à digestão intestinal. Os segmentos de membrana de diálise foram cortados a 30 cm de comprimento e preenchidos com 25 mL de água/$NaHCO_3$ (0,5 M). A quantidade necessária de $NaHCO_3$ (0,5 M) para titular a digestão gástrica a pH 7,5 foi a contida na membrana de diálise. Cada 20 mL de digestão gástrica foi colocada num tubo de polietileno, e uma membrana de diálise foi completamente imersa até atingir um pH de 5,0. Depois, foram adicionados a cada tubo 5 mL de pancreatina (0,12 g) e sais biliares (40 mg de glicodesoxicolato em 1 mL de solução salina), taurodesoxicolato (25 mg em 1 mL de solução salina), taurocolato (40 mg em 1 mL de solução salina). As amostras foram incubadas sob agitação (95 rpm) a 37 °C durante 2 h para completar a fase intestinal. Por último, a membrana de diálise foi retirada e enxaguada com água destilada. Os compostos fenólicos disponíveis para absorção estavam dentro da membrana de diálise (fração bioacessível). Em seguida a fração bioacessível foi analisada em HPLC, conforme Caldas et al. (2018), para determinação do perfil de compostos fenólicos presentes após a digestão gastrointestinal simulada.

3.14. Estudo da estabilidade

As microcápsulas atomizadas e liofilizadas do extrato de compostos fenólicos da FRC foram armazenadas conforme Nunes et al. (2015) com modificações a diferentes temperaturas (7 e 25 ± 1 ºC). As amostras foram colocadas em embalagens plásticas

flexíveis laminadas (Zip lock) e armazenadas no escuro por 90 dias. Foi avaliado o TPC (conforme item 3.5) a cada 15 dias.

3.15. Análise estatística

Os dados experimentais foram analisados e apresentados como valores médios e desvios-padrão de dados obtidos em triplicata. A análise de variância (ANOVA), o teste de falta de ajuste (teste F), a determinação dos coeficientes de regressão, a otimização dos processos foram executados utilizando a Metodologia de Superfície de Resposta (RSM) e o teste de diferenças de médias (Teste Tukey) foram realizados com o auxílio do software Statistica versão 12.0 (StatSoft Inc., Tulsa, EUA) ao nível de 5% de significância. A correlação de Person's foi realizada utilizando o R Studio Build 461 (RStudio Inc., Boston, EUA).

REFERÊNCIAS

ABREU, D. J. M.; CARVALHO, E. E. N.; VILAS BOAS, E. V. B.; ASQUIERI, E. R.; DAMIANI, C. Ultrasound-assisted extraction of red mombin seed oil (*Spondias purpurea* L.): phenolic profile, fatty acid profile and chemical characterization of the cake, residue from the oil extraction. **Grasas Aceites**, v. 73(1), e451, 2022.

ADETUNJI, L. R.; ADEKUNLE, A.; ORSAT, V.; RAGHAVAN, V. Advances in the pectin production process using novel extraction techniques: A review. **Food Hydrocolloids**, v. 62, p. 239–250, 2017.

AHMAD, N.; ZUO, Y.; LU, X.; ANWAR, F.; HAMEED, S. Characterization of free and conjugated phenolic compounds in fruits of selected wild plants. **Food Chemistry**, v. 90, p. 80-89, 2016.

AIRES, A.; CARVALHO, R.; SAAVEDRA, M. J. Reuse potential of vegetable wastes (broccoli, green bean and tomato) for the recovery of antioxidant phenolic acids and flavonoids. **International Journal of Food Science and Technology**, v. 52, p. 98–107, 2017.

AGUDELO, C.; BARROS, L.; SANTOS-BUELGA, C.; MARTÍNEZ-NAVARRETE, N.; FERREIRA, I. C. F. R. Phytochemical content and antioxidant activity of grapefruit (*Star Ruby*): A comparison between fresh freeze-dried fruits and different powder formulations. **LWT - Food Science and Technology**, v. 80, p. 106-112, 2017.

AGUIAR, J.; ESTEVINHO, B. N.; SANTOS, L. Microencapsulation of natural antioxidants for food application - the specific case of coffee antioxidants - a review. **Trends in Food Science and Technology**, v. 58, p. 21–39, 2016.

ALBARICI, T. R.; FREITAS, D. M.; PESSOA, J. D. C. Atividade antioxidante pelo método ORAC (Capacidade de Absorção de Radicais de Oxigênio). In T. R. ALBARICI; D. M. FREITAS (Eds.). **Protocolos de análises para polpa de açaí: um guia prático de consulta** (pp. 33–38). São Carlos: Livros Científicos (ALICE) – Embrapa Instrumentação Agropecuária, 2009.

ALBAYRAK, S.; ATASAGUN, B.; AKSOY, A. Comparison of phenolic components and biological activities of two *Centaurea* sp. obtained by three extraction techniques. **Asian Pacific Journal of Tropical Medicine**, v. 10, n. 6, p. 599-606, 2017.

ALBUQUERQUE, J. G.; DUARTE, A. M.; CONCEIÇÃO, M. L. AQUINO, J. S. Integral utilization of seriguela fruit (*Spondias purpurea* L.) in the production of cookies. **Revista Brasileira de Fruticultura**, v. 38, n. 3, 2016.

ALBUQUERQUE, M. A. C.; LEVIT, R.; BERES, C.; BEDANI, R.; LEBLANC, A. M.; SAAD, S. M. I.; LEBLANC, J. G. Tropical fruit by-products water extracts as sources of soluble fibres and phenolic compounds with potential antioxidant, anti-inflammatory, and functional properties. **Journal of Functional Foods**, v. 52, p. 724– 733, 2019.

AL-DHABI, N. A.; PONMURUGAN, K.; JEGANATHAN, P. M. Development and validation of ultrasound-assisted solid-liquid extraction of phenolic compounds from waste spent coffee grounds. **Ultrasonics Sonochemistry**, v. 34, p. 206–21, 2017.

ALI, K.; MALTESE, F.; CHOI, Y. H.; VERPOORTE, R. Metabolic constituents of grapevine and grape-derived products. **Phytochemistry Reviews**, v. 9, n. 3, p. 357-378, 2010.

ALLEY, M. C.; SCUDIERE, D. A.; MONKS, A.; HURSEY, M. L.; CZERWINSKI, M. J.; FINE, D. L.; ABBOTT, B. J.; MAYO, J. G.; SHOEMAKER, R. H.; BOYD, M. R. Feasibility of drug screening with panels of human tumor cell lines using a microculture tetrazolium assay. **Cancer Research**, v. 48, p. 589-601, 1988.

ANUÁRIO BRASILEIRO DE FRUTICULTURA, 2017. Cleonice de Carvalho et al.– Santa Cruz do Sul: Editora Gazeta Santa Cruz, 2017.

AOAC - Official Methods of Analysis of the Association of Official Analytical Chemists: Official Methods of Analysis of AOAC International. 21st Edition, AOAC, Washington DC, 2019.

ARES, A. M.; BERNAL, J.; NOZAL, M. J.; TURNER, C.; PLAZA, M. Fast determination of intact glucosinolates in broccoli leaf by pressurized liquid extraction and ultra high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry. **Food Research International**, v. 76, p. 498–505, 2015.

ARPAGAUS, C.; COLLENBERG, A.; RÜTTI, D.; ASSADPOUR, E.; JAFARI, S. M. Nano spray drying for encapsulation of pharmaceuticals. **International Journal of Pharmaceutics,** v. 546, n.1–2, p.194–214, 2018.

ASHOKKUMAR, M. Applications of ultrasound in food and bioprocessing. **Ultrasonics Sonochemistry**, v. 25, p. 17–23, 2015.

ASSADPOUR, E.; JAFARI, S. M. Spray drying of folic acid within nano-emulsions: optimization by Taguchi approach. **Drying Technology**, v. 35, n. 9, p.1152–60, 2017.

ASSADPOUR, E.; JAFARI, S. M.; FARIDI ESFANJANI, A. Protection of phenolic compounds within nanocarriers. **CAB Reviews**, v. 12, n.57, p. 1–8, 2017.

ASPÉ, E.; FERNÁNDEZ, K. The effect of different extraction techniques on extraction yield, total phenolic, and anti-radical capacity of extracts from *Pinus radiata* Bark. **Industrial Crops and Products**, v. 34, p. 838–844, 2011.

AUGUSTO, P. E. D.; CRISTIANINI, M.; IBARZ, A. Effect of temperature on dynamic and steadystate shear rheological properties of siriguela *(Spondias purpurea* L.) pulp. **Journal of Food Engineering**, v.108, p. 283 – 289, 2012.

AZARPAZHOOH, E.; RAMASWAMY, H. S. Modeling and optimization of microwave osmotic dehydration of applecylinders under continuous-flowspraymodeprocessing conditions. **Food and Bioprocess Technology**, v. 5, n.5, p.1486–1501, 2012.

BAKIĆ, M. T.; PEDISIĆ, S.; ZORIĆ, Z.; DRAGOVIĆ-UZELAC, V.; GRASSINO, A. N. Effect of microwave-assisted extraction on polyphenols recovery from Tomato peel waste. **Acta Chimica Slovenica**, v. 66, p. 367–377, 2019.

BANERJEE, J.; SINGH, R.; VIJAYARAGHAVAN, R.; MACFARLANE, D.; PATTI, A. F.; ARORA, A. Bioactives from fruit processing wastes: Green approaches to valuable chemicals. **Food Chemistry**, v. 225, p. 10–22, 2017.

BARBA, F. J.; ZHU, Z.; KOUBAA, M.; SANT'ANA, A. S.; ORLIEN, V. Green alternative methods for the extraction of antioxidant bioactive compounds from winery wastes and by-products: A review. **Trends in Food Science and Technology**, v. 49, p. 96–109, 2016.

BARBA, A. A.; CALABRETTI, A.; D'AMORE, M.; PICCINELLI, A.L.; RASTRELLI, L. Phenolic constituents levels in cv. Agria potato under microwave processing. **LWT - Food Science and Technology,** v. 41, p. 1919–1926, 2008.

BARBOSA-CÁNOVAS, G.V.; JULIANO, P. Physical and chemical properties of food powders. In: ONWULATA, C. **Encapsulated and powdered foods.** Boca Raton: Taylor & Francis, p.39-71, 2005.

BARROS, R. G. C.; ANDRADE, J. K. S.; DENADAI, M.; NUNES, M. L.; NARAIN, N. Evaluation of bioactive compounds potential and antioxidant activity in some Brazilian exotic fruit residues. **Food Research International**, v. 102, p. 84–92, 2017.

BATAGLION, G. A.; SILVA, F. M. A.; EBERLIN, M. N.; KOOLEN, H. H. F. Determination of the phenolic composition from Brazilian tropical fruits by UHPLC–MS/MS. **Food Chemistry**, v. 180, p. 280-287, 2015.

BENJAMIN, S. R.; OLIVEIRA NETO, J. R.; MACEDO, I. Y. L.; BARA, M. T. F., CUNHA, L. C.; CARVALHO, L. A. F.; GIL, E. S. Electroanalysis for quality control of acerola (*Malpighia emarginata*) fruits and their commercial products. **Food Analytical Methods**, v. 8, p. 86–92, 2015.

BEN-OTHMAN, S.; JÕUDU, I.; BHAT, R. Bioactives from agri-food wastes: present insights and future challenges. **Molecules**, v. 25, p. 510-544, 2020.

BHAT, R. Sustainability Challenges in agro-food sector; Wiley Blackwell Publishers: West Sussex, UK, 2017; p. 720.

BICAS, J. L.; MOLINA, G.; DIONISIO, A. P.; BARROS, F. F. C.; WAGNER, R.; MAROSTICA JR.; M. R., PASTORE, G. M. Volatile constituents of exotic fruits from Brazil. **Food Research International**, v. 44, p. 1843–1855, 2011.

BLASI, F.; URBANI, E.; SIMONETTI, M. S.; CHIESI, C.; COSSIGNANI, L. Seasonal variations in antioxidant compounds of Olea europaea leaves collected from different Italian cultivars. **Journal of Applied Botany and Food Quality**, v. 89, p. 202–207, 2016.

BRAND-WILIAMS, W.; CUVELIER, M.E.; BERSET, C. Use of a free radical method to evaluate antioxidant activity. **Food Science and Technology,** v. 28, p.25-30. 1995.

BUNIOWSKA, M.; CARBONELL-CAPELLA, J. M.; FRIGOLA, A.; ESTEVE, M. J. Bioaccessibility of bioactive compounds after non-thermal processing of an exotic fruit juice blend sweetened with Stevia rebaudiana. **Food Chemistry**, v. 221, p. 1834–1842, 2017.

CAI, Y. Z.; CORKE, H. Production and properties of spray dried *Amaranthus* betacyanin pigments. **Journal of Food Science**, v.65, p.1248-1252, 2000.

CAI, Z.; QU, Z.; LAN, Y.; ZHAO, S.; MA, X.; WAN, Q.; LI, P. Conventional, ultrasoundassisted, and accelerated-solvent extractions of anthocyanins from purple sweet potatoes. **Food Chemistry**, v. 197, p. 266–272, 2016.

CALDAS, T. W.; MAZZA, K. E. L.; TELES, A. S. C.; MATTOS, G. N; BRÍGIDA, A. I. S.; CONTE-JUNIOR, C. A.; BORGUINI, R. G.; GODOY, R. L. O.; CABRAL, L. M. C.; TONON, R. V. Phenolic compounds recovery from grape skin using conventional and nonconventional extraction methods. **Industrial Crops & Products**, v.111, p. 86–91, 2018.

ÇAM, M.; IÇYER, N. C.; ERDOGAN, F. Pomegranate peel phenolics: Microencapsulation, storage stability and potential ingredient for functional food development. **LWT – Food Science and Technology**, v. 55, n.1, p. 117–123, 2014.

CANO-CHAUCA, M.; RAMOS, A. M.; STRINGHETA, P. C. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. **Innovative Food Science e Emerging Technologies**, v.6, p.420-428, 2005.

CAO, L.; SI, J. Y.; LIU, Y.; SUN, H.; JIN, W.; LI, Z.; ZHAO, X.; PAN, R. L. Essential oil composition, antimicrobial and antioxidant properties of *Mosla chinensis Maxim*. **Food Chemistry**, v. 115, n.3, p. 801-805, 2009.

CAPARINO, O. A.; TANG, J.; NINDO, C. L.; SABLANI, S. S.; POWERS, J. R. FELLMAN, J. K. Effect of drying methods on the physical properties and microstructures of mango (*Philippine* 'Carabao' var.) power. **Journal of Food Engineering**, v.111, p.135-148, 2012.

CAPPATO, L. P.; FERREIRA, M. V. S.; MORAES, J.; PIRES, R. P. S.; ROCHA, R. S.; SILVA, R.; NETO, R. P. C.; TAVARES, M. I. B.; FREITAS, M. Q.; RODRIGUES, F. N.; CALADO, V. M. A.; RAICES, R. S. L.; SILVA, M. C.; CRUZ, A. G. Whey acerola-flavoured drink submitted Ohmic Heating: Bioactive compounds, antioxidant capacity, thermal behavior, water mobility, fatty acid profile and volatile compounds**. Food Chemistry,** v. 263, p. 81-88, 2018.

CARVALHO, A. V., DA SILVEIRA, T. F. F., DE MATTIETTO, R. A., DO OLIVEIRA, M. S., DE, P., & GODOY, H. T. Chemical composition and antioxidant

capacity of açaí (*Euterpe oleracea*) genotypes and commercial pulps. **Journal of the Science of Food and Agriculture**, v. 97, p. 1467–1474, 2017.

CARVALHO, I. T.; ESTEVINHO, B. N.; SANTOS, L. Application of microencapsulated essential oils in cosmetic and personal healthcare products – a review. **International Journal of Cosmetic Industry**, v. 38, n. 2, p. 109–119, 2016.

CASSOL, L.; RODRIGUES, E.; NOREÑA, C. P. Z. Extracting phenolic compounds from *Hibiscus sabdariffa* L. calyx using microwave assisted extraction. **Industrial Crops & Products,** v. 133, p. 168–177, 2019.

CASTANEDA-VALBUENA, D.; AYORA-TALAVERA, T.; LUJÁN-HIDALGO, C.; ÁLVAREZ-GUTIÉRREZ, P.; MARTÍNEZ-GALERO, N.; MEZA-GORDILLO, R. Ultrasound extraction conditions effect on antioxidant capacity of mango by-product extracts. **Food and Bioproducts Processing**, v. 127, p. 212-224, 2021.

CELLI, G. B.; GHANEM, A.; BROOKS, M. S. Bioactive encapsulated powders for functional foods — a review of methods and current limitations. **Food and Bioprocess Technology**, v. 8, n. 9, p. 1825-1837, 2015.

CHAN, C. H.; YEOH, H. K.; YUSOFF, R.; NGOH, G. C. A first-principles model for plant cell rupture in microwave-assisted extraction of bioactive compounds. **Journal of. Food Engineering**, v. 188, p. 98–107, 2016.

CHEEKE, J. D. N. Fundamentals and applications of ultrasonic waves. 2nd edition. Boca Raton:CRC Press, 2012. 504p.

CHEMAT, F.; ROMBAUT, N.; SICAIRE, A. G.; MEULLEMIESTRE, A.; FABIANO-TIXIER, A. S.; ABERT-VIAN, M. Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review. **Ultrasonics Sonochemistry**, v. 34, p. 540–560, 2017a.

CHEMAT, F., ROMBAUT, N., MEULLEMIESTRE, A., TURK, M., PERINO, S., FABIANOTIXIER, A. S.; ABERT-VIAN, M. Review of green food processing techniques. Preservation, transformation, and extraction. **Innovative Food Science and Emerging Technologies**, v. 41, p. 357–377, 2017b.

CHEMAT, F.; ZILL-E-HUMA; KHAN, M. K. Applications of ultrasound in food technology: Processing, preservation and extraction. **Ultrasonics Sonochemistry**, v. 18, n. 4, p. 813–835, 2011.

CHEN, G.; CHEN, S.; ZHAO, Y.; LUO, C.; LIB, J.; GAO, Y. Total phenolic contents of 33 fruits and their antioxidant capacities before and after in vitro digestion. **Industrial Crops and Products**, v. 57, p. 150-157, 2014.

CHENG, X.; ZHANG, M.; XU, B.; ADHIKARI, B.; SUN, J. The principles of ultrasound and its application in freezing related processes of food materials: A review. **Ultrasonics Sonochemistry**, v. 27, p. 576–585, 2015.

CHEN, J.; , THILAKARATHNA, W. P. D. W.; ASTATKIE, T.; RUPASINGHE, H. P. V. Optimization of catechin and proanthocyanidin recovery from grape seeds using microwave-assisted extraction. **Biomolecules**, v. 10, p. 243-257, 2020.

CHIRINOS, R.; ROGEZ, H.; CAMPOS, D.; PEDRESCHI, R.; LARONDELLE, Y. Optimization of extraction conditions of antioxidant phenolic compounds from mashua (*Tropaeolum tuberosum* Ruíz & Pavón) tubers. **Separation and Purification Technology,** v. 55, p. 217–225, 2007.

CORRADO, S.; CALDEIRA, C.; ERIKSSON, M.; HANSSEN, O. J.; HAUSER, H. E.; VAN HOLSTEIJN, F.; LIU, G.; ÖSTERGREN, K.; PARRY, A.; SECONDI, L.; STENMARCK, A.; SALA, S.. Food waste accounting methodologies: Challenges, opportunities, and further advancements. **Global Food Security**, v. 20, p. 93-100, 2019.

COSTA, R. G.; ANDREOLA, K.; MATTIETTO, R. A.; FARIA, L. J. G.; TARANTO, O. P. Effect of operating conditions on the yield and quality of açaí (*Euterpe oleracea* Mart.) powder produced in spouted bed. **LWT - Food Science and Techonology**, v. 64, p. 1196-1203, 2015.

COVA, C. M.; BOFFA, L.; PISTOCCHI, M.; GIORGINI, S.; LUQUE, R.; CRAVOTTO, G. Technology and process design for phenols recovery from industrial Chicory (*Chicorium intybus*) leftovers. **Molecules** v. 24, n. 15, p. 2681-2694, 2019.

CVJETKO BUBALO, M.; CURKO, N.; TOMASEVIC, M.; GANIC, K. K.; REDOVNIKOVIC, I. R. Green extraction of grape skin phenolics by using deep eutectic solvents. **Food Chemistry**, v. 200, p. 159–166, 2016.

DADAN, M.; RYBAK, K.; WIKTOR, A.; NOWACKA, M.; ZUBERNIK, J.; WITROWA-RAJCHERT, D. Selected chemical composition changes in microwave-convective dried parsley leaves affected by ultrasound and steaming pre-treatments – An optimization approach. **Food Chemistry,** v. 239, p. 242-251, 2018.

DAI, J.; MUMPER, R. J. Plant Phenolics: Extraction, analysis and their antioxidant and anticancer properties. **Molecules**, v.15, n.10. p. 7313-7352, 2010.

DAVIDOV-PARDO, G.; McCLEMENTS, A. J. Nutraceutical delivery systems: Resveratrol encapsulation in grape seed oil nanoemulsions formed by spontaneous emulsification. **Food Chemistry**, v.167, p. 205-212, 2015.

DAZA, L. D.; FUJITA, A.; FÁVARO-TRINDADE, C. S.; RODRIGUES-RACT, J. N.; GRANATO, D.; GENOVESE, M. I. Effect of spray drying conditions on the physical properties of Cagaita (*Eugenia dysenterica* DC.) fruit extracts. **Food and Bioproducts Processing**, v. 97, p. 20–29, 2016.

DELVA, L.; GOODRICH-SCHNEIDER, R. Antioxidant activity and antimicrobial properties of phenolic extracts from acerola (*Malpighia emarginata* DC) fruit. **International Journal of Food Science and Technology**, v. 48, p.1048–1056, 2013.

DI BATTISTA, C. A.; CONSTENLA, D.; RAMÍREZ RIGO, M. V.; PIÑA, J. Process analysis and global optimization for the microencapsulation of phytosterols by spray drying. **Powder Technology**, v. 321, p. 55–65, 2017.

DROSOU, C.; KYRIAKOPOULOU, K.; BIMPILAS, A.; TSIMOGIANNIS, D.; KROKIDA, M. A comparative study on different extraction techniques to recover red grape pomace polyphenols from vinification byproducts. **Industrial Crops & Products**, v.75, p.141–149, 2015.

DUTRA, R. L. T.; DANTAS, A. M.; MARQUES, D. A.; BATISTA, J. D. F.; MEIRELES, B. R. L. A.; CORDEIRO, A. M. T. M.; MAGNANI, M.; BORGES, G. S. C. Bioaccessibility and antioxidant activity of phenolic compounds in frozen pulps of Brazilian exotic fruits exposed to simulated gastrointestinal conditions. **Food Research International**, v. 100, p. 650–657, 2017.

DUTRA, M. C. P.; RODRIGUES, L. L.; OLIVEIRA, D.; PEREIRA, G. E.; LIMA, M. S. Integrated analyses of phenolic compounds and minerals of Brazilian organic and conventional grape juices and wines: Validation of a method for determination of Cu, Fe and Mn. **Food Chesmitry**, v. 269, p. 157-165, 2018.

ENGELS, C.; GRATER, D.; ESQUIVEL, P.; JIMÉNEZ, V. M.; GANZLE, M. G.; SCHIEBER, A. Characterization of phenolic compounds in jocote (*Spondias purpurea L*) peels by ultra high-performance liquid chromatography/electrospray ionization mass spectrometry. **Food Research International,** v.46, p. 557-562, 2012.

ENSMINGER, D.; BOND, L. J. Ultrasonics: fundamentals, technologies, and applications. 3nd. ed. Boca Raton, FL: CRC Press, 2011. 723p.

EROGLU, E.; TONTUL, I.; TOPUZ, A. Optimization of aqueous extraction and spray drying conditions for efficient processing of hibiscus blended rosehip tea powder. **Journal of Food Processing and Preservation**, v. 42, p. 1–9, 2018.

ESPADA-BELLIDO, E.; FERREIRO-GONZALEZ, M.; CARRERA, C.; PALMA, M.; BARROSO, C. G.; BARBERO, G. F. Optimization of the ultrasound-assisted extraction of anthocyanins and total phenolic compounds in mulberry (*Morus nigra*) pulp. **Food Chemistry**, v. 219, p. 23–32, 2017.

ESTEVEZ, M.; GUELL, C.; LAMO-CASTELLVI, S. D.; FERRANDO, M. Encapsulation of grape seed phenolic-rich extract within W/O/ W emulsions stabilized with complexed biopolymers: evaluation of their stability and release. **Food Chemistry**, v. 272, p. 478–487, 2019.

EZHILARASI, P. N.; INDRANI, D.; JENA, B. C.; ANANDHARAMAKRISHNAN, C. Freeze drying technique for microencapsulation of *Garcinia* fruit extract and its effect on bread quality. **Journal of Food Engineering**, v. 117, p. 513–520, 2013.

FAO (Food and Agriculture Organisation of the United Nations). FAOSTAT domains, crops: In: FOOD and Agriculture Organization, 2018. Disponivel em: http://www.fao.org/faostat/en/#data/QC. Acesso em 03 set 2022).

FARRAG, A.; MOHAMMED EL-MESSERY, T.; MOHAMED EL-SAID, M.; SOLIMAN, T. N.; MOHAMED FAKHR EL-DIN, H. Microencapsulation of grape phenolic compounds using whey proteins as a carrier vehicle. **Journal of Biological Scienses**, v. 18, n. 7, p. 373–380, 2018.

FARIDI ESFANJANI, A.; ASSADPOUR, E.; JAFARI, S. M. Improving the bioavailability of phenolic compounds by loading them within lipid-based nanocarriers. **Trends Food Science and Technology**, v. 76, p. 56–66, 2018.

FANG, Z.; BHANDARI, B. Encapsulation of polyphenols - a review. **Trends in Food Science & Technology**, v.20, p.510-523, 2010.

FERNANDES, R. V. D. B.; BORGES, S. V.; BOTREL, D. A. Gum Arabic/starch/maltodextrin/ inulin as wall materials on the microencapsulation of rosemary essential oil. **Carbohydrate Polymers**, v. 101, p. 524–532, 2014.

FERRARI, C. C.; RIBEIRO, C. P.; AGUIRRE, J. M. Spray drying of blackberry pulp using maltodextrin as carrier agent. **Brazilian Journal of Food Technology**, v.15, p.157-165, 2012.

FIDELIS, J. C. F.; MONTEIRO, A. R. G.; SCAPIM, M. R. S.; MONTEIRO, C. C. F.; MORAIS, D. R.; CLAUS, T.; VISENTAINER, J. V.; YAMASHITA, F. Development of an active biodegradable film containing tocopherol and avocado peel extract. **Italian Journal of Food Science**, v. 27, p. 468–475, 2015.

FRONTUTO, D.; CARULLO, D.; HARRISON, S. M.; BRUNTON, N. P.; FERRARI, G.; LYNG, J. G.; PATARO, G. Optimization of pulsed electric fields-assisted extraction of polyphenols from potato peels using response surface methodology. **Food and Bioprocess Technology**, v. 12, p. 1708–1720, 2019.

FURTADO, G.; SILVA, F.; PORTO, F. S.; SANTOS, A. G. Secagem de polpa de ciriguela pelo método de camada de espuma. **Revista Brasileira de Produtos Agroindustriais**, v. 12, p. 9–14, 2010.

GARCIA-CASTELLO, E. M.; RODRIGUEZ-LOPEZ, A. D.; MAYOR, L.; BALLESTEROS, R.; CONIDI, C.; CASSANO, A. Optimization of conventional and ultrasound assisted extraction of flavonoids from grapefruit (*Citrus paradisi* L.) solid wastes. **LWT - Food Science and Technology**, v. 64, n.2, p. 1114-1122, 2015.

GARCIA-MENDOZA, M. DEL P.; ESPINOSA-PARDO, F. A.; BASEGGIO, A. M.; BARBERO, G. F.; MARÓSTICA JUNIOR, M. R.; ROSTAGNO, M. A.; MARTÍNEZ, J. Extraction of phenolic compounds and anthocyanins from juçara (*Euterpe edulis Mart*.) residues using pressurized liquids and supercritical fluids. **The Journal of Supercritical Fluids**, v. 119, p. 9– 16, 2017.

GHARSALLAOUI, A.; ROUDAUT, G.; CHAMBIN, O.; VOILLEY, A.; SAUREL, R. Applications of spray drying in microencapsulation of food ingredients: An overview. **Food Research International**, v.40, p.1107-1121, 2007.

GOGOI, P.; CHUTIA, P.; SINGH, P.; MAHANTA, C. L. Effect of optimized ultrasound-assisted aqueous and ethanolic extraction of *Pleurotus citrinopileatus* mushroom on total phenol, flavonoids and antioxidant properties**. Journal of Food Process Engineering**, v. 42, n. 6, p. 1-12, 2019.

GOOT, A. J.; PELGROM, P. J. M.; BERGHOUT, J. A. M.; GEERTS, M. E. J.; JANKOWIAK, L.; HARDT, N. A.; BOOM, R. M. Concepts for further sustainable production nof foods. **Journal of Food Engineering**, v. 168, p.42–51, 2016.

GROSS, J. Carotenoids. In: GROSS, J. Pigments in fruits. London: Academic Press, 1987. p. 87-186, 303 p.

GUANDALINI, B. B. V.; RODRIGUES, N. P.; MARCZAK, L. D. F. Sequential extraction of phenolics and pectin from mango peel assisted by ultrasound. **Food Research International**, v. 119, p. 455–461, 2019.

GULLÓN, B.; LÚ-CHAU, T. A.; MOREIRA, M. T.; LEMA, J. M. Rutin: A review on extraction, identification and purification methods, biological activities and approaches to enhance its bioavailability. **Trends in Food Science and Technology**, v. 67, p. 220–235, 2017.

HABIBI, F.; RAMEZANIAN, A. Vacuum infiltration of putrescine enhances bioactive compounds and maintains quality of blood orange during cold storage. **Food Chemistry,** v. 227, p. 1–8, 2017.

HARNKARNSUJARIT, N.; KAWAI, K.; WATANABE, M.; SUZUKI, T. Effects of freezing on microstructure and rehydration properties of freeze-dried soybean curd. **Journal of Food Engineering**, v. 184, p. 10-20, 2016.

HEERES, H.L. Regulatory Requirements for valorisation of food-chain co-products in the European Union. In Handbook of waste management and co-product recovery in food processing; Waldron, K.W., Ed.; CRC Press: Boca Raton, FL, USA, 2009.

HOHNOVÁ, B., ŠALPLACHTA, J.; KARÁSEK, P. Pressurized hot water extraction followed by high-performance liquid chromatography for determination of polyphenols in *Sambucus nigra* L. branches in dependence on vegetative period of the plant. **Journal of Food and Nutrition Research**, v. 56, n. 3, p. 299–303, 2017.

HOU, K.; BAO, M.; WANG, L.; ZHANG, H.; YANG, L.; ZHAO, H.; WANG, Z. Aqueous enzymatic pretreatment ionic liquidelithium salt based microwaveeassisted extraction of essential oil and procyanidins from pinecones of *Pinus koraiensis.* **Journal of Cleaner Production**, v. 236, 117581, 2019.

HUANG, H. W.; HSU, C. P.; YANG, B. B.; WANG, C. Y. Advances in the extraction of natural ingredients by high pressure extraction technology. **Trends in Food Science & Technology**, v. 33, n. 1, p. 54–62, 2013.

HUI, Y. H. **Handbook of fruit and vegetable flavors**. Wiley, p. 1095, 2010.

INFANTE J.; ROSALEN, P. L.; LAZARINI, J. G.; FRANCHIN, M.; ALENCAR, S. M. Antioxidant and anti-inflammatory activities of unexplored Brazilian native fruits. **PLoS ONE**, v. 11, n. 4, e0152974, 2016.

JAFARI, S. M.; GHALENOEI, M. G.; DEHNAD, D. Influence of spray drying on water solubility index, apparent density, and anthocyanin content of pomegranate juice powder. **Powder Technology**, v. 311, p. 59–65, 2017.

JEDDOU, K. B.; BOUAZIZA, F.; ZOUARI-ELLOUZIA, S.; CHAARIA, F.; ELLOUZ-CHAABOUNIA, S.; ELLOUZGHORBELA, R.; NOURI-ELLOUZC, O. Improvement of texture and sensory properties of cakes by addition of potato peel powder with high level of dietary fiber and protein. **Food Chemistry**, v. 217, p. 668–677, 2017.

JESUS, M. S.; GENISHEVA, Z.; ROMANÍ, A.; PEREIRA, R. N.; TEIXEIRA, J. A.; DOMINGUES, L. Bioactive compounds recovery optimization from vine pruning residues using conventional heating and microwave-assisted extraction methods. **Industrial Crops & Products**, v. 132, p. 99-110, 2019.

KADERIDES, K.; PAPAOIKONOMOU, L.; SERAFIM, M.; GOULA, A. M. Microwave-assisted extraction of phenolics from pomegranate peels: Optimization, kinetics, and comparison with ultrasounds extraction. **Chemical Engineering & Processing: Process Intensification**, v. 137, p. 1–11, 2019.

KANG, J.; LIU, L.; LIU, M.; WU, X.; LI, J. Antibacterial activity of gallic acid against Shigella flexneri and its effect on biofilm formation by repressing mdoH gene expression. **Food Control,** v. 94, p. 147–154, 2018.

KASAPIDOU, E.; SOSSIDOU, E.; MITLIANGA, P. Fruit and vegetable co-products as functional feed ingredients in farm animal nutrition for improved product quality. **Agriculture**, v. 5, n. 4, p. 1020-1034, 2015.

KATOUZIAN, I.; JAFARI, S. M. Nano-encapsulation as a promising approach for targeted delivery and controlled release of vitamins. **Trends Food Science Technology**, v. 53, p. 34–48, 2016.

KRINGEL, D. H.; DIAS, A. R. G.; ZAVAREZE, E. R.; GANDRA, E. A. Fruit wastes as promising sources of starch: Extraction, properties, and applications. **Starch – Stärke**, v.72, 1900200, 2020.

KRISHNAN, R. Y.; RAJAN, K. S. Microwave assisted extraction of flavonoids from Terminalia bellerica: Study of kinetics and thermodynamics. **Separation and Purification Technology**, v. 157, p. 169–178, 2016.

KUCK, L. S.; NORENA, C. P. Z. Microencapsulation of grape (*Vitis labrusca* var. Bordo) skin phenolic extract using gum arabic, polydextrose, and partially hydrolyzed guar gum as encapsulating agents. **Food Chemistry**, v. 194, p. 569–576, 2016.

LABUSCHAGNE, P. Impact of wall material physicochemical characteristics on the stability of encapsulated phytochemicals: a review. **Food Research International**, v. 107, p. 227–247, 2018.

LAURENTIIS, V.; CORRADO, S.; SALA, S. Quantifying household waste of fresh fruit and vegetables in the EU. **Waste Management**, v. 77, p. 238-251, 2018.

LAVELLI, V.; HARSHA, P. S. C. S.; LAUREATI, M.; PAGLIARINI, E. Degradation kinetics of encapsulated grape skin phenolics and micronized grape skins in various water activity environments and criteria to develop wide-ranging and tailor-made food applications. **Innovative Food Science and Emerging Technologies**, v. 39, p. 156 – 164, 2017.

LEE, H. S.; LEE, H. J.; YU, H. J.; JU, W.; KIM, Y.; KIM, C. T.; KIM, C. J.; CHO, Y. J.; KIM, N.; SUH, H. J. A comparison between high hydrostatic pressure extraction and heat extraction of ginsenosides from ginseng (*Panax ginseng CA* Meyer). **Journal of the Science of Food and Agriculture**, v. 91, n. 8, p. 1466–1473, 2011.

LEE, Y.; CHANG, Y.H. Microencapsulation of a maca leaf polyphenol extract in mixture of maltodextrin and neutral polysaccharides extracted from maca roots. **International Journal of Biological Macromolecules**, v. 150, p. 546–558, 2020.

LESJAK, M.; BEARA, I.; SIMIN, N.; PINTAC, D.; MAJKIC, T.; BEKVALAC, K.; ORCIC, D.; MIMICA-DUKIC, N. Antioxidant and anti-inflammatory activities of querce tin and its derivatives. **Journal of Functional Foods**, v. 40, p. 68–75, 2018.

LIU, C.; XUE, H.; SHEN, L.; LIU, C.; ZHENG, X.; SHI, J.; XUE, S. Improvement of anthocyanins rate of blueberry powder under variable power of microwave extraction. **Separation and Purification Technology**, v. 226, p. 286–298, 2019.

LOMBARDI, G.; COSSIGNANI, L.; GIUA, L.; SIMONETTI, M. S.; MAURIZI, A.; BURINI, G.; COLI, R.; BLASI, F. Phenol composition and antioxidant capacity of red wines produced in Central Italy changes after one-year storage. **Journal of Applied Botany and Food Quality**, v. 90, p. 197–204, 2017.

LUCAS-GONZÁLEZ, R.; VIUDA-MARTOS, M.; PÉREZ ÁLVAREZ, J. A.; JUANA FERNÁNDEZ-LÓPEZ, J. Changes in bioaccessibility, polyphenol profile and antioxidant potential of flours obtained from persimmon fruit (*Diospyros kaki*) co-products during in vitro gastrointestinal digestion. **Food Chemistry**, v. 256, p. 252–258, 2018.

LUTHRIA, D. L. Influence of experimental conditions on the extraction of phenolic compounds from parsley (*Petroselinum crispum*) flakes using a pressurized liquid extractor. **Food Chemistry**, v. 107, n. 2, p. 745–752, 2008.

MAHDAVI, S.A.; JAFARI, S.M.A; ASSADPOOR, E.; DEHNADA, D. Microencapsulation optimization of natural anthocyanins with maltodextrin, gum Arabic and gelatin. **International Journal of Biological Macromolecules**, v.85, p.379–385, 2016.

MALDONADO-ASTUDILLO, Y. I.; ALIA-TEJACAL, I.; NÚNEZ-COLÍN, C. A.; JIMÉNEZ-HERNÁNDEZ, J.; PELAYO-ZALDÍVAR C.; LÓPEZ-MARTÍNEZ, V.; ANDRADE-RODRÍGUEZ, M.; BAUTISTA-BANOS, S.; VALLE-GUADARRAMA, S. Postharvest physiology and technology of *Spondias purpurea* L. and *S. mombin* L. **Scientia Horticulturae,** v. 174, p. 193–206, 2014.

MANE, S.; BREMNER, D. H.; TZIBOULA-CLARKE, A.; LEMOS, M. A. Effect of ultrasound on the extraction of total anthocyanins from Purple Majesty potato. **Ultrasonics Sonochemistry**, v. 27, p. 509–514, 2015.

MANGANG, K. C. S.; CHAKRABORTY, S.; DEKA, S. C. Optimized microwave-assisted extraction of bioflavonoids from *Albizia myriophylla* bark using response surface methodology. **Journal of Food Science Technology**, v. 57, p. 2107-2117, 2020.

MANTHEY, J. A.; GUTHRIE, N.; GROHMANN, K. Biological properties of citrus flavonoids pertaining to cancer and inflammation. **Current Medicinal Chemistry,** v. 8, p. 135–153, 2001.

MARIĆ, M.; GRASSINO, A. N.; ZHU, Z.; BARBA, F. J.; BRNČIĆ, M.; RIMAC BRNČIĆ, S. An overview of the traditional and innovative approaches for pectin extraction from plant food wastes and by-products: Ultrasound-, microwaves-, and enzyme-assisted extraction. **Trends in Food Science & Technology**, v. 76, p. 28–37, 2018.

MARINELLI, V.; SPINELLI, S.; ANGIOLILLO, L.; DEL NOBILE, M. A.; CONTE, A. Emerging techniques applied to by-products for food fortification. **Journal of Food Science Technology**, v. 57, n. 3, p. 905–914, 2020.

MATERSKA, MAŁGORZATA. Bioactive phenolics of fresh and freeze-dried sweet and semi-spicy pepper fruits (*Capsicum annuum* L.*).* **Journal of Functional Foods**, v.7, p. 269-277, 2014.

McGUIRE, R. G. Reporting of objective color measurements. **HortScience**, v.27, p. 1254-1555, 1992.

MENA-GARCÍA, A.; RODRÍGUEZ-SÁNCHEZ, S.; RUIZ-MATUTE, A. I.; SANZ, M. L. Exploitation of artichoke byproducts to obtain bioactive extracts enriched in inositols and caffeoylquinic acids by microwave assisted extraction. **Journal of Chromatography A**, v. 1613, p. 460703, 2020.

MERCALI. G. D.; JAESCHKE, D. P.; TESSARO, I. C.; MARCZAK, L. D. F. Degradation kinetics of anthocyanins in acerola pulp: Comparison between ohmic and conventional heat treatment. **Food Chemistry**, v. 136, p. 853–857, 2013.

MICHALSKA, A.; WOJDYŁO, A.; HONKE, J.; CISKA, E.; ANDLAUER, W. Drying-induced physico-chemical changes in cranberry products. **Food Chemistry**, v. 240, p. 448–455, 2018.

MILANI, G.; CURCI, F.; CAVALLUZZI, M. M.; CRUPI, P.; PISANO, I.; LENTINI, G.; CLODOVEO, M. L.; FRANCHINI, C.; CORBO, F. Optimization of microwave-

assisted extraction of antioxidants from bamboo shoots of phyllostachys pubescens. **Molecules,** v. 25, p. 215-225, 2020.

MINATEL, I. O.; BORGES, C. V.; FERREIRA, M. I.; GOMEZ, H. A. G.; CHEN, C.-Y. O.; LIMA, G. P. P. Phenolic compounds: Functional properties, impact of processing and bioavailability. **Phenolic Compondus - Biological Activity**, v. 8, p. 1–24, 2017.

MOREIRA, S. A.; ALEXANDRE, E. M. C.; PINTADO, M.; SARAIVA, J. A. Effect of emergent non-thermal extraction technologies on bioactive individual compounds profile from different plant materials. **Food Research International**, v. 115, p. 177–190, 2019.

MORENO, T., DE PAZ, E., NAVARRO, I., RODRÍGUEZ-ROJO, S., MATÍAS, A., DUARTE, C., SANZ-BUENHOMBRE, M., COCERO, M. J. Spray Drying Formulation of polyphenols-rich grape marc extract: Evaluation of operating conditions and different natural carriers. **Food and Bioprocess Technology**, v. 9, n. 12, p. 2046–2058, 2016.

MOSELE, J. I.; MACIÀ, A.; ROMERO, M.; MOTILVA, M.; RUBIÓ, L. Application of in vitro gastrointestinal digestion and colonic fermentation models to pomegranate products (juice, pulp and peel extract) to study the stability and catabolism of phenolic compounds. **Journal of Functional Foods**, v. 14, p. 529–540, 2015.

MOSER, P.; TELIS, V. R. N.; ANDRADE NEVES, N.; GARCÍA-ROMERO, E.; GOMEZ-ALONSO, S.; HERMOSÍN-GUTIERREZ, I. Storage stability of phenolic compounds in powdered BRS Violeta grape juice microencapsulated with protein and maltodextrin blends. **Food Chemistry**, v. 214, p. 308–318, 2017.

MOSMAN, T. Rapid colorimetric assay for cellular growth and survival: application to proliferation and cytotoxicity assays. **Journal of Immunological Methods**. 65: 55-63. 1983.

MUSIELAK, G.; MIERZWA, D.; KROEHNKE, J. Food drying enhancement by ultrasound – A review. **Trends in Food Science and Technology**, v. 56, p. 126–141, 2016.

NAWI, N. M.; MUHAMAD, I. I.; MARSIN, A. M. The physicochemical properties of microwave-assisted encapsulated anthocyanins from *Ipomoea batatas* as affected by different wall materials. **Food Science Nutrition**, v. 3, p. 91–99, 2015.

NAYAK, B.; DAHMOUNE, F.; MOUSSI, K.; REMINI, H.; DAIRI, S.; AOUN, O.; KHODIR, M. Comparison of microwave, ultrasound and accelerated-assisted solvent extraction for recovery of polyphenols from *Citrus sinensis* peels. **Food Chemistry**, v. 187, p. 507–516, 2015.

NIPORNRAM, S.; TOCHAMPA, W.; RATTANATRAIWONG, P.; SINGANUSONG, R. Optimization of low power ultrasound-assisted extraction of phenolic compounds from mandarin (*Citrus reticulata Blanco* cv. Sainampueng) peel. **Food Chemistry**, v. 241, p. 338–345, 2018.

NOREEN, H.; SEMMAR, N.; FARMAN, M.; JAMES McCULLAGH, J. S. O. Measurement of total phenolic content and antioxidant activity of aerial parts of medicinal plant *Coronopus didymus*. **Asian Pacific Journal of Tropical Medicine**, v. 10, n. 8, p. 792-801, 2017.

NUNES, G. L.; BOAVENTURA, B. C. B.; PINTO; S. S.; VERRUCK, S.; MURAKAMI, F. S.; PRUDÊNCIO, E. S.; AMBONI, R. D. M. C. Microencapsulation of freeze concentrated *Ilex paraguariensis* extract by spray drying. **Journal of Food Engineering**, v.151, p. 60–68, 2015.

OMENA, C. M. B.; VALENTIM, I. B.; GUEDES, G. S.; RABELO, L. A.; MANO, C. M.; BECHARA, E. J. H.; SAWAYA, A. C. H. F.; TREVISAN, M. T. S.; COSTA, J. G.; FERREIRA, R. C. S.; SANT'ANA, A. E. G.; GOULART, M. O. F.; Antioxidant, anti-acetylcholinesterase and cytotoxic activities of ethanol extracts of peel, pulp and seeds of exotic Brazilian fruits Antioxidant, anti-acetylcholinesterase and cytotoxic activities in fruits. **Food Research International**; v.49, p. 334–344, 2012.

OROIAN; M.; DRANCA, F.; URSACHI, F. Comparative evaluation of maceration, microwave and ultrasonicassisted extraction of phenolic compounds from própolis. **Journal of Food Science Technology**, v. 57, n. 1; p. 70–78, 2020.

OZDAL, T.; SELA, D. A.; XIAO, J.; BOYACIOGLU, D.; CHEN, F.; CAPANOGLU, E. The reciprocal interactions between polyphenols and gut microbiota and effects on bioaccessibility. **Nutrients**, v. 8, n. 2, p. 78, 2016.

PADILHA, C. V. S.; MISKINIS, G. A.; SOUZA, M. E. A. O.; PEREIRA, G. E.; OLIVEIRA, D.; BORDIGNON-LUIZ, M. T.; LIMA, M. S. Rapid determination of flavonoids and phenolic acids in grape juices and wines by RP-HPLC/DAD: Method validation and characterization of commercial products of the new Brazilian varieties of grape. **Food Chesmistry**, v. 228, p. 106-115, 2017.

PAL, C. B. T.; JADEJA, G. C. Microwave-assisted extraction for recovery of polyphenolic antioxidants from ripe mango (*Mangifera indica* L.) peel using lactic acid/sodium acetate deep eutectic mixtures. **Food Science and Technology International**, v. 26, n. 1, p. 78–92, 2019.

PASHAZADEH, B.; ELHAMIRAD, A. H.; HAJNAJARI, H.; SHARAYEI, P.; ARMIN, M. Optimization of the pulsed electric field -assisted extraction of functional compounds from cinnamon. **Biocatalysis and Agricultural Biotechnology**, v. 23, 2020.

PAZ, M.; GÚLLON, P.; BARROSO, M. F.; CARVALHO, A. P.; DOMINGUES, V. F.; GOMES, A. M.; BECKER, H.; LONGHINOTTI, E.; DELERUE-MATOS, C. Brazilian fruit pulps as functional foods and additives: Evaluation of bioactive compounds. **Food Chemistry**, v. 172, p. 462–468, 2015.

PELLEGRINI, M.; LUCAS-GONZALEZ, R.; FERNÁNDEZ-LÓPEZ, J.; RICCI, A.; PÉREZ-ÁLVAREZ, J. A.; LO STERZO, C.; VIUDA-MARTOS, M. Bioaccessibility of

polyphenolic compounds of six quinoa seeds during in vitro gastrointestinal digestion. **Journal of Functional Foods**, v. 38, p. 77–88, 2017.

PHISUT, N. Spray drying technique of fruit juice powder: some factors influencing the properties of product. **International Food Research Journal**, v.19, p.1297-1306, 2012.

PIECZYKOLAN, E.; KUREK, M. A. Use of guar gum, gum arabic, pectin, beta-glucan and inulin for microencapsulation of anthocyanins from chokeberry. **International Journal of Biological Macromolecules**, v. 129, p. 665–671, 2019.

PINTAĆ, D.; MAJKIĆ, T.; TOROVIĆ, L.; ORCIĆ, D.; BEARA, I.; SIMIN, N.; MIMICAE-DUKIĆ, N.; LESJAK, M. Solvent selection for efficient extraction of bioactive compounds from grape Pomace. **Industrial Crops and Products**, v, 111, p. 379-390, 2018.

POLLINI, L.; COSSIGNANI, L.; JUAN, C.; MAÑES, J. Extraction of phenolic compounds from fresh apple pomace by different non-conventional techniques. **Molecules,** v. 26, 4272, 2021. https://doi.org/10.3390/molecules26144272

PÓŁTORAK, A.; WYRWISZ, J.; MOCZKOWSKA, M.; MARCINKOWSKA-LESIAK, M.; STELMASIAK, A.; RAFALSKA, U.; WIERZBICKA, A.; SUN, D. W. Microwave vs. convection heating of bovine gluteus medius muscle: impact on selected physical properties of final product and cooking yield. **International Journal of Food Science and Technology**, v. 50, n. 4, p. 958–965, 2015.

PUDZIUVELYTE, L.; MARKSA, M.; JAKSTAS, V.; IVANAUSKAS, L.; KOPUSTINSKIENE, D. M.; BERNATONIENE, J. Microencapsulation of *Elsholtzia ciliata* Herb ethanolic extract by spray-drying: impact of resistant-maltodextrin complemented with sodium caseinate, skim milk, and beta-cyclodextrin on the quality of spray-dried powders. **Molecules**, v. 24, n. 8, p. 1461, 2019.

PU, Y. Y.; SUN, D. W. Prediction of moisture content uniformity of microwave-vacuum dried mangoes as affected by different shapes using NIR hyperspectral imaging. **Innovative Food Science and Emerging Technologies**, v. 34, p. 348–356, 2016.

PU, Y. Y.; SUN, D. W. Combined hot-air and microwave-vacuum drying for improving drying uniformity of mango slices based on hy- perspectral imaging visualization of moisture content distribution. **Biosystems Engineering**, v. 156, p. 108–119, 2017.

PUTNIK, P.; LORENZO, J. M.; BARBA, F. J.; ROOHINEJAD, S.; JAMBRAK, A. R.; GRANATO, D.; MONTESAN, D.; BURSAĆ KOVAČEVIĆ, D. Novel food processing and extraction technologies of high-added value compounds from plant materials. **Foods**, v. 7, p. 106–122, 2018.

QUIROZ, J. Q.; TORRES, A. C.; RAMIREZ, L. M.; GARCIA, M. S.; GOMEZ, G. C.; CAMARGO, J. R. Optimization of the microwave-assisted extraction process of bioactive compounds from annatto seeds (*Bixa orellana* L.). **Antioxidants**, v. 8, p. 37, 2019.

RAFIEE, Z.; BARZEGAR, M.; ALI, M.; MAHERANI, B. Nanoliposomal carriers for improvement the bioavailability of high – Valued phenolic compounds of pistachio green hull extract. **Food Chemistry**, v. 220, p. 115–122, 2017.

RAHMAN, M. M.; RAHAMAN, M. S.; ISLAM, M. R.; RAHMAN, F.; MITHI, F. M.; ALQAHTANI, T.; ALMIKHLA, M. A.; ALGHAMDI, S. Q.; ALRUWAILI, A. S.; HOSSAIN, M. S.; et al. Role of phenolic compounds in human disease: Current knowledge and future prospects. **Molecules**, v. 27, p. 233, 2022.

RAMADAN, M. F., KROH, L. W., & MORSEL, J. T. Radical scavenging activity of black cumin (*Nigella sativa* L.), coriander (*Coriandrum sativum* L.), and Niger (*Guizotia abyssinica* Cass.) crude seed oils and oil fractions. **Journal of Agricultural and Food Chemistry**, v. 51(24), p. 6961–6969, 2003.

RAMÍREZ, M. J.; GIRALDO, G. I.; ORREGO, C. E. Modeling and stability of polyphenol in spray-dried and freeze-dried fruit encapsulates. **Powder Technology**, v. 277, p. 89–96, 2015.

REIN, M. J.; RENOUF, M.; CRUZ-HERNANDEZ, C.; ACTIS-GORETTA, L.; THAKKAR, S. K.; PINTO, M.D. S. Bioavailability of bioactive food compounds: A challenging journey to bioefficacy. **Nutraceuticals Themed Section**, v. 75, n. 3, p. 588–601, 2013.

RÉ, M. I. Microencapsulation by spray drying. **Drying Technology**, v. 16, n. 6, p. 1195-1236, 1998.

RENARD, C. M. G. C. Extraction of bioactives from fruit and vegetables: State of the art and perspectives. **LWT - Food Science and Technology**, v. 93, p. 390–395, 2018.

RE, R; PELLEGRINI, N.; PROTEGGENTE, A.; PANNALA, A.; YANG, M.; RICE-EVANS, C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. **Free Radical Biology and Medicine**, v.26, n.9/10, p.1231–1237, 1999.

REZENDE, Y. R. R. S.; NOGUEIRA, J. P.; NARAIN, N. Comparison and optimization of conventional and ultrasound assisted extraction for bioactive compounds and antioxidant activity from agro-industrial acerola (*Malpighia emarginata DC*) residue. **LWT - Food Science and Technology**, v. 85, p. 158-169, 2017.

REZENDE, Y. R. R. S.; NOGUEIRA, J. P.; NARAIN, N. Microencapsulation of extracts of bioactive compounds obtained from acerola (*Malpighia emarginata* DC) pulp and residue by spray and freeze drying: Chemical, morphological and chemometric characterization. **Food Chemistry,** v.254, p. 281-291, 2018.

RIBEIRO, A. M.; ESTEVINHO, B. N.; ROCHA, F. Microencapsulation of polyphenols - The specific case of the microencapsulation of *Sambucus nigra* L. extracts - A review. **Trends in Food Science & Technology**, v. 105, p. 454-467, 2020.

ROCCHETTI, G.; BLASI, F.; MONTESANO, D.; GHISONI, S.; MARCOTULLIO, M. C.; SABATINI, S.; COSSIGNANI, L.;LUCINI, L. Impact of conventional/non-

conventional extraction methods on the untargeted phenolic profile of *Moringa oleifera* leaves. **Food Research International**, v. 115, p. 319–327, 2019.

RODRIGUES-AMAYA, B. B. **A guide to carotenoid analysis in foods**. ILST Press. p. 64, 1999.

RODRIGUES, F. A. R.; BOMFIM, I. S.; CAVALCANTI, B. C.; PESSOA, C.; GONCALVES, R. S. B.; WARDELL, J. L.; WARDELL, S.M.S.V.; SOUZA, M. V. Mefloquine–oxazolidine derivatives: a new class of anticancer agents. **Chemical biology & drug design**, v. 83, p. 126-131, 2014.

RODRÍGUEZ-ROQUE, M. J.; ROJAS-GRAÜ, M. A.; ELEZ-MARTÍNEZ, P.; MARTÍN-BELLOSO, O. Changes in vitamin C, phenolic, and carotenoid profiles throughout in vitro gastrointestinal digestion of a blended fruit juice. **Journal of Agricultural and Food Chemistry,** v. 61, p. 1859–1867, 2013.

ROMBAUT, N.; TIXIER, A.-S.; BILY, A.; CHEMAT, F. Green extraction processes of natural products as tools for biorefinery. **Biofuels, Bioproducts and Biorefining**, v. 8, n. 4, p. 530–544, 2014.

ROMERO-DIEZ, R.; MATOS, M.; RODRIGUES, L.; BRONZE, M. R.; RODRIGUEZ-ROJO, S.; COCERO, M. J.; MATIAS, A. A. Microwave and ultrasound pre-treatments to enhance anthocyanins extraction from different wine lees. **Food Chemistry**, v. 272, p. 258–266, 2019.

ROUTRAY, W.; ORSAT, V. Microwave-assisted extraction of flavonoids: A review. **Food Bioprocess Technology**. v.5, n.2, p.409–424, 2012.

ROSELLÓ-SOTO, E.; BARBA, F. J.; PARNIAKOV, O.; GALANAKIS, C. M.; LEBOVKA, N.; GRIMI, N.; VOROBIEV, E.. High voltage electrical discharges, pulsed electric field, and ultrasound assisted extraction of protein and phenolic compounds from Olive Kernel. **Food Bioprocess Technology,** v. 8, p. 885–894, 2015.

ROY, S.; LINGAMPETA, P. Solid wastes of fruits peels as source of low cost broad spectrum natural antimicrobial compounds furanone, furfural and benezenetriol. **International Journal of Research in Engineering and Technology**, v. 3, n. 7, p. 273-277, 2014.

SADEGHI, A.; HAKIMZADEH, V.; KARIMIFAR, B. Microwave assisted extraction of bioactive compounds from food: A review. **International Journal of Food Science and Nutrition Engineering**, v. 7, n. 1, p. 19–27, 2017.

SAÉNZ, C.; TAPIA, S.; CHÁVEZ, J.; ROBERT, P. Microencapsulation by spray drying of bioactive compounds from cactus pear (*Opuntia ficus-indica*). **Food Chemistry,** v.11, p.616–622, 2009.

SALAZAR, N. A.; ALVAREZ, C.; ORREGO, C. E. Optimization of freezing parameters for freeze-drying mango (*Mangifera indica* L.) slices. **Drying Technology**, v.36, n.2, p.192-204, 2017.

SALEEM, M.; SAEED, M. T. Potential application of waste fruit peels (orange, yellow lemon and banana) as wide range natural antimicrobial agente. **Journal of King Saud University – Science**, v. 32, p. 805–810, 2020.

SALIM, N. S. M.; SINGH, A.; RAGHAVAN, V. Potential utilization of fruit and vegetable wastes for food through drying or extraction techniques. **Novel Techniques in Nutrition and Food Science**, v. 1, n. 2, p. 15-27, 2017.

SAMOTICHA, J.; WOJDYŁO, A.; GOLIS, T. Phenolic composition, physicochemical properties and antioxidant activity of interspecific hybrids of grapes growing in Poland. **Food Chemistry,** v. 215, p.263-273, 2017.

SÁNCHEZ-MORENO, C.; LARRAURI, J. A.; SAURA-CALIXTO, F. A procedure to measure the antiradical efficiency of polyphenols. **Journal of the Science of Food and Agriculture**, v.76, n.2, p.270-276, 1998.

SANTANA NETO, D. C.; FERREIRA, V. C. S.; ARAÚJO, I. B. S.; MEIRELES, B. R. L. A.; CORDEIRO, A. M. T. M.; SILVA, F. A. P. Solid–liquid extraction of bioactive compounds from *Spondias mombin* L. by-products: optimization and identifcation of phenolic profle. **Brazilian Journal of Chemical Engineering**,v. 39, p. 511–525, 2022.

SANTHALAKSHMY, S.; BOSCO, S. J. D.; FRANCIS, S.; SABEENA, M. Effect of inlet temperature on physicochemical properties of spray-dried jamun fruit juice powder. **Powder Technology**, v.274, p.37-43, 2015.

SANTOS, S. S.; RODRIGUES, L. M.; COSTA, S. C.; MADRONA, G. S. Antioxidant compounds from blackberry (*Rubus fruticosus*) pomace: Microencapsulation by spray-dryer and pH stability evaluation. **Food Packaging and Shelf Life**, v. 20, p. 100177, 2019.

SARABANDI, K.; SADEGHI MAHOONAK, A.; HAMISHEKAR, H.; GHORBANI, M.; JAFARI, S. M. Microencapsulation of casein hydrolysates: physicochemical, antioxidant and microstructure properties. **Journal Food Engineering**, v. 237, p. 86–95, 2018.

SCHIASSI, M. C. E. V.; SOUZA, V. R.; LAGO, A. M. T.; CAMPOS, L. G.; QUEIROZ, F. Fruits from the Brazilian Cerrado region: Physico-chemical characterization, bioactive compounds, antioxidant activities, and sensory evaluation. **Food Chemistry,** v. 245, p. 305–311, 2018.

SEPÚLVEDA, L.; ROMANÍ, A, AGUILAR, C. N.; TEIXEIRA, J. Valorization of pineapple waste for the extraction of bioactive compounds and glycosides using autohydrolysis. **Innovative Food Science & Emerging Technologies**, v. 47, p. 38–45, 2018.

SETTE, P.; FERNANDEZ, A.; SORIA, J.; RODRIGUEZ, R.; SALVATORI, D.; MAZZA, G. Integral valorization of fruit waste from wine and cider industries. **Journal of Cleaner Production**, v. 242, p. 118486, 2020.

SHAMAEI, S.; SADEGH, S.; AGHBASHLO, M.; TSOTSAS, E.; KHARAGHANI, A. Microencapsulation of walnut oil by spray drying: Effects of wall material and drying conditions on physicochemical properties of microcapsules. **Innovative Food Science & Emerging Technologies**, v.39, p. 101-112, 2017.

SHARAYEI, P.; AZARPAZHOOH, E.; RAMASWAMY, H. S. Effect of microencapsulation on antioxidant and antifungal properties of aqueous extract of pomegranate peel. **Journal Food Science Technology**, v. 57, n. 2, p.723–733, 2020.

SHARAYEI, P.; AZARPAZHOOH, E.; ZOMORODI, S.; RAMASWAMYC, H. S. Ultrasound assisted extraction of bioactive compounds from pomegranate (*Punica granatum* L.) peel. **LWT - Food Science and Technology**, v. 101, p. 342–350, 2019.

SHAVANDI, A.; BEKHIT, A. E. A.; SAEEDI, P.; IZADIFAR, Z.; KHADEMHOSSEINI, A. Polyphenol uses in biomaterials engineering. **Biomaterials,** v. 167, p. 91-106, 2018.

SHISHIR, M. R. I.; CHEN, W. Trends of spray drying: A critical review on drying of fruit and vegetable juices. **Trends in Food Science & Technology**, v.65, p. 49-67, 2017.

SILVA, R. V.; COSTA, S. C. C.; BRANCO, C. R. C.; BRANCO, A. In vitro photoprotective activity of the *Spondias purpurea* L. peel crude extract and its incorporation in a pharmaceutical formulation. **Industrial Crops and Products**, v. 83, p. 509-514, 2016.

SUN, Y.; XUE, H. K.; LIU, C. H.; LIU, C.; SU, X. L.; ZHENG, X. Z. Comparison of microwave assisted extraction with hot reflux extraction in acquirement and degradation of anthocyanin from powdered blueberry. **International Journal of Agricultural and Biological Engineering**, v. 9, n. 6, p. 186–199, 2016.

TABELA BRASILEIRA DE COMPOSIÇÃO DE ALIMENTOS - TACO / NEPA – UNICAMP.- 4. ed. rev. e ampl. Campinas: NEPA UNICAMP, 2011.

TAN, S.P.; KHA, T.C.; PARKS, S.; STATHOPOULOS, C.; ROACH, P.D. Optimising the encapsulation of an aqueous bitter melon extract by spray-drying. **Foods**, v. 4, p. 400–419, 2015.

TAO, Y.; ZHANG, Z.; SUN, D. W. Kinetic modeling of ultrasoundassisted extraction of phenolic compounds from grape marc: influence of acoustic energy density and temperature. **Ultrasonics Sonochemistry**, v. 21, n. 4, p. 1461–1469, 2014.

THAIPONG, K.; BOONPRAKOB, U.; CROSBY, K.; CISNEROS-ZEVALLOS, L.; BYRNE, D. H. Comparison of ABTS, DPPH, FRAP, and ORAC assays for estimating antioxidant activity from guava fruit extracts. **Journal of Food Composition and Analysis**, v. 19, n. 6-7, p. 669-675, 2006.

TODISCO, K. M.; CASTRO-ALVES, C. C. C.; GARRUTI, D. S.; COSTA, J. M. C.; CLEMENTE, E. The use of headspace solid-phase microextraction (HS-SPME) to

Assess the quality and stability of fruit products: An example using red Mombin pulp (*Spondias purpurea* L.). **Molecules,** v. 19, p. 16851-16860, 2014.

TOLEDO-MERMA, P. R.; CORNEJO-FIGUERO, M. H.; CRISOSTO-FUSTER, A. D. R.; STRIEDER, M. M.; CHAÑI-PAUCAR, L. O.; NÁTHIA-NEVES, G.; RODRÍGUEZ-PAPUICO, H.; ROSTAGNO, M. A.; MEIRELES, M. A. A.; ALCÁZAR-ALAY, S. C. Phenolic compounds recovery from pomegranate (*Punica granatum* L.) by-products of pressurized liquid extraction. **Foods**, v. 11(8), 1070, 2022.

TOMAS, M.; TOYDEMIR, G.; BOYACIOGLU, D.; HALL, R.; BEEKWILDER, J. C. E. The effects of juice processing on black mulberry antioxidants. **Food Chemistry**, v. 186, p. 277–284, 2015.

TONON, R. V.; FREITAS, S. S.; HUBINGER, M. D.; Spray drying of açai (*Euterpe oleraceae* Mart.) juice: effect of inlet air temperature and type of carrier agent. **Journal of Food Processing and Preservation**. v. 35, p. 691–700, 2011.

TRUJILLO-MAYOL, I.; CÉSPEDES-ACUÑA, C.; SILVA, F. L.; ALARCÓN-ENOS, J. Improvement of the polyphenol extraction from avocado peel by assisted ultrasound and microwaves. **Journal of Food Process Engineering**, v. 42, n. 6, p. 1-11, 2019.

TSANG, Y. F.; KUMAR, V.; SAMADAR, P.; YANG, Y.; LEE, J.; OK, Y. S.; SONG, H.; KIM, K. H.; KWON, E. E.; JEON, Y. J. Production of bioplastic through food waste valorization. **Environment International**, v. 127, p. 625-644, 2019.

TSAO, R. Chemistry and biochemistry of dietary polyphenols. **Nutrients,** v. 2, n. 12, p. 1231–1246, 2010.

VAN HERPEN, E.; VAN DER LANS, I. A.; HOLTHUYSEN, N.; NIJENHUIS-DE VRIES, M.; QUESTED, T. E. Comparing wasted apples and oranges: An assessment of methods to measure household food waste. **Waste Management**, v. 88, p. 71-84, 2019.

VERRUCK, S.; PRUDENCIO, E. S. Ultrassom na indústria de alimentos: aplicações no processamento e conservação . Ponta Grossa (PR): Atena Editora, 2018.

VIAPIANA, A., WESOLOWSKI, M. The phenolic contents and antioxidant activities of infusions of *Sambucus nigra* L. **Plant Foods for Human Nutrition**, v. 72, n. 1, p.82–87, 2017.

VINATORU, M.; MASON, T. J.; CALINESCU, I. Ultrasonically assisted extraction (UAE) and microwave assisted extraction (MAE) of functional compounds from plant materials. **Trends in Analytical Chemistry**, v. 97 (Suppl. C), p. 159–178, 2017.

WALDRON, K. Handbook of waste management and co-product recovery in food processing; Woodhead Publishing: Cambridge, UK, 2009.

WANG, J. Optimization of ultrasound-assisted extraction of phenolic compound from wheat bran. **Food Chemistry**, v. 106, p. 804–810, 2008.

WEN, L.; ZHANG, Z.; RAI, D.; SUN, D. W.; TIWARI, B. K. Ultrasound-assisted extraction (UAE) of bioactive compounds from coffee silverskin: Impact on phenolic content, antioxidant activity, and morphological characteristics. **Journal of Food Process Engineering**, v. 42, n. 6, p. 1-11, 2019.

WETTASINGHE, M.; SHAHIDI, F. Evening primrose meal: a source of natural antioxidants and scavenger of hydrogen peroxide and oxygen-derived free radicals. **Journal of Agricultural and Food Chemistry**, v.47, p.1801-1812, 1999.

YADAV, K.; BAJAJ, R. K.; MANDAL, S.; MANN, B. Encapsulation of grape seed extract phenolics using whey protein concentrate, maltodextrin and gum arabica blends. **Journal of Food Science Technology**, v. 57, n. 2, p. 426-434, 2020.

YILDIZ, G.; RABABAH, T.; FENG, H. (2016). Ultrasound-assisted cutting of Cheddar, Mozzarella and Swiss Cheeses – Effects on quality attributes during storage. Innovative **Food Science and Emerging Technologies**, v. 37, p. 1–9, 2016.

ZANONI, F.; PRIMITERRA, M.; ANGELI, N.; ZOCCATELLI, G. Microencapsulation by spray-drying of polyphenols extracted from red chicory and red cabbage: Effects on stability and color properties. **Food Chemistry**, v. 307, 125535, 2020.

ZHANG, J.; ZHANG, C.; CHEN, X.; QUEK, S. Y. Effect of spray drying on phenolic compounds of cranberry juice and their stability during storage. **Journal of Food Engineering**, v. 269, 109744, 2020.

ZHAO, Y.; WANG, P.; ZHENG, W.; YU, G.; LI, Z.; SHE, Y.; LEE, M. Three-stage microwave extraction of cumin (*Cuminum cyminum* L.) Seed essential oil with natural deep eutectic solventes. **Industrial Crops & Products**, v. 140, n. 111660, 2019.

ZEKOVIĆ, Z.; PINTAĆ, D.; MAJKIĆ, T.; VIDOVIĆ, S.; MIMICA-DUKIĆ, N.; TESLIĆ, N.; VERSARI, A.; PAVLIĆ, B. Utilization of sage by-products as raw material for antioxidants recovery - Ultrasound versus microwave-assisted extraction. **Industrial Crops and Products**, v. 99, p. 49–59, 2017.

ZULKIFLI, S. A.; GANI, S. S. A.; ZAIDAN, U. H.; HALMI, M. I. E. Optimization of total phenolic and flavonoid contents of defatted pitaya (*Hylocereus polyrhizus*) seed extract and its antioxidant properties. **Molecules**, v. 25, p. 787, 2020.

4. RESULTADOS

A apresentação dos resultados dos experimentos foi realizada em forma de artigos, de acordo com as normas estabelecidas pelo Programa de Pós-Graduação em Ciência e Tecnologia dos Alimentos (Norma Complementar nº 56/2014).

ARTIGO I (Anexo 1). Ultrasound-assisted extraction of bioactive compounds from ciriguela (*Spondias purpurea* L.) peel: Optimization and comparison with conventional extraction and microwave (Publicado em 2021 no Arabian Journal of Chemistry (1878-5352): Fator de Impacto JCR 2022 (6.212); CiteScore (9.8); Disponível em: https://doi.org/10.1016/j.arabjc.2021.103260).

ARTIGO II. Microencapsulation by spray-drying and freeze-drying of phenolics obtained from ciriguela peel: Chemical, morphological and chemometric characterization of microcapsules.

ARTIGO III. Effect of coating material on microencapsulation by spray-drying and freeze-drying of phenolic compounds extracted from ciriguela peel residue.

ARTIGO I. Ultrasound-assisted extraction of bioactive compounds from ciriguela (*Spondias purpurea* L.) peel: Optimization and comparison with conventional extraction and microwave

Marcony Edson da S. Júnior[a], Maria Vitória R. L. Araújo[b], Anderson Andrade de Santana[b], Flávio Luiz H. da Silva[a], Maria Inês S. Maciel[a*]

[a]Food Science and Technology Graduate Program, Technology Center, Federal University of Paraíba, João Pessoa, Brazil.

[b]Laboratory of Physical-Chemical Analysis of Food, Department of Consumer Sciences, Federal Rural University of Pernambuco, Recife, Brazil.

*Corresponding author (Maria Inês S. Maciel).

E-mail address: m.inesdcd@gmail.com

Fone: + 55 81 33206536 / Fax: +55 81 33206540

ABSTRACT

The ciriguela (*Spondias purpurea* L.) residue resulting from its pulp and juice processing stands out due to the high content of bioactive compounds. This study aimed to optimize the ultrasound-assisted extraction (UAE) process of phenolic compounds from ciriguela peel. The response surface method was used to investigate the effects of process-independent variables (ultrasonic amplitude, UA): 20%, 60% and 100%, and ultrasonic exposure time (T): 5, 10 and 15 min on the dependent variables (content of total phenolic compounds (TPC), DPPH - 1,1-diphenyl-2-picrylhydrazyl free radical scavenging (IC_{50}) and ferric reducing-antioxidant power (FRAP) of ciriguela peel extract. The UA and time influenced TPC, IC_{50} and antioxidant activity by FRAP. However, the antioxidant activity of DPPH had no significant influence on the variables used. Ideal conditions were set at UA = 100% (200 W) and T = 15 min. The extract of phenolic compounds from the ciriguela peel obtained by optimized ultrasound was compared with other extraction techniques (conventional and microwave-assisted). UAE showed better results concerning the extraction yield of phenolic compounds and high antioxidant activity (35.15 mg GAE/g, IC 50 = 0.19 mg/mL), compared to conventional extraction (30.10 mg GA/g and IC 50 = 1.68 mg/mL) and microwave-assisted (23.31 mg GA/g and IC 50 = 4.29 mg/mL). These results demonstrate the efficacy and better usefulness of the ciriguela residue in obtaining the extracts of bioactive compounds using the ultrasound-assisted extraction technique.

Keywords: Phenolic compounds; Antioxidants; Extraction; Ultrasound; Microwave.

1. Introduction

Brazil is a country with favorable geographical and climatic characteristics for fruit production. In the semiarid region, the Caatinga biome has an immense biodiversity of fruits, particularly those of the genus *Spondias*, mainly ciriguela (*Spondias purpurea* L.), which originated in Mexico and Central America. This fruit is rich in secondary metabolites, particularly phenolic compounds and is of biological interest (Maldonado-Astudillo et al., 2014).

In recent decades, there has been an increase in the international consumption of tropical fruits. Considering this increase, the processing of fruits into products such as juices and beverages showed high growth, mainly due to the possibility of producing new sources of functional and healthy ingredients (Jeddou et al., 2017). However, this high growth in the pulp and fruit juice industries has generated a large volume of waste,

which can be exploited for the production of highly valued substances (Ben-Othman et al., 2020; Saleem and Saeed, 2020). Fruit residues are rich in bioactive compounds. However, these substances degrade easily during food extraction, processing and storage (Renard, 2018).

The extraction of the compounds of interest present in fruit residues can generate products with high added value (Kringel et al., 2020). This extraction can be carried out by conventional methods, using maceration and/or agitation with solvents and by Soxhlet extraction, which is based on the capture of the compounds of interest from a solute or matrix, with or without heat. However, it requires long times to reach the maximum concentration of the compounds of interest and a high solvent demand and thermal degradation due to the long processing time (Caldas et al., 2018). Considering these disadvantages, more sustainable methods are sought, in which solvent consumption and the extraction time are minimized and the extraction yield is increased (Pintać et al., 2018).

The recent interest in operating an environmentally sustainable way as well as safety and economic aspects led to the best choice of applying new “green” extraction techniques (Noroozi et al., 2021). The innovative or nonconventional technologies that have been used include the application of pulsed electric fields, ultrasound-assisted extraction (UAE), microwave-assisted extraction, high pressure and solvent acceleration (Putnik et al., 2018). UAE stands out and uses mechanical waves that present frequencies between 20 and 100 kHz (Dadan et al., 2018). UAE has several advantages: shorter processing time, better penetration, low solvent consumption, higher yield, good reproducibility, improves the extraction rate and quality of the extract, allows the possibility of using more economical and safer alternative solvents for the environment and health (Chemat et al., 2017b; Marić et al., 2018). The UAE process allows complete extraction of target compounds in short time mainly via production of hydrodynamic cavitation phenomenon. Different stages of hydrodynamic cavitation phenomenon were: nuclei formation, expansion phase, maximum radius, collapse phase, explosion and release of energy (Noroozi et al., 2021).

The main contribution of this manuscript was the consideration of the possibility of the valorization of ciriguela peel generated during ciriguela processing or beverage production. The growing global interest in emerging extraction technologies, which aim to minimize environmental impacts, justifies the use of ciriguela residue as a source of antioxidants, which have a high content of phenolic compounds. Since the use of RSM

has not been reported yet for modeling the UAE of phenolic compounds from ciriguela peel, the aim of this study was to evaluate and optimize the extraction process of phenolic compounds from using UAE from ciriguela peel, maximizing the yield of phenolic compounds and antioxidant activity of ciriguela peel extracts, in addition to comparing conventional and microwave-assisted extraction processes.

2. Materials and methods

2.1. Materials

Ciriguela residues (*Spondias purpurea* L.) were supplied, as a byproduct, by the fruit pulp industry, located in João Pessoa, Paraíba, Brazil (07º 09' S 36º 49' W).

2.2. Chemicals

Ethanol (Vetec, Rio de Janeiro, Brazil) and distilled water were used for extraction. Folin-Ciocalteu phenol reagent, gallic acid ($C_7H_6O_5$), 2,4,6-tripyridyl-s-triazine (TPTZ) and 2,2-diphenyl-1-picrylhydrazyl radical ($DPPH^{\bullet}$) were obtained from Sigma Aldrich (St. Louis, MO, USA).

2.3. Obtaining the ciriguela residue flour (FRC)

The ciriguela peels were separated from the seeds manually and subjected to drying at 60 °C for 24 h (Caldas et al., 2018) in an oven with circulation and air renewal (Marconi; model MA035) until the moisture reached at or below 10%. Next, they were crushed in a 631/2 multiuse mill (Tecnal) and sieved using a sieve mesh #40 (425 μm). The FRC was packed in 140-micron low-density polyethylene bags, wrapped with laminated paper and frozen at -18°C for further analysis.

2.4. Extraction processes of phenolic compounds

2.4.1 Preliminary analysis

In order to optimize the extraction conditions, initially preliminary extractions were carried out using UAE. The extractions were performed at specified conditions, ultrasound power (120 W) and extraction time (10 min). To evaluate the extracts by ultrasound, water (100%) and ethanol (20%, 50% and 80%) were used as solvents, acidified with 0.1% HCl. Ethanol is in compliance with good manufacturing practice

and it is considered as a GRAS (generally-recognized-as-safe) solvent (Santos et al., 2010).The parameters used were: 10 g of FRC mixed with 40 mL of the solvent, was placed in a 100-mL beaker and submitted to an ultrasonic probe (Ultronique, Ecosonics) that has an ultrasonic frequency of 20 kHz. The extract was filtered using Whatman Nº 2 filter paper. The extracts were stored in amber bottle which were kept in a freezer (-20ºC) until analysis.

2.4.2 Ultrasound-assisted extraction (UAE)

Ultrasound experiments were carried out using 10 g of FRC placed in an extraction unit with 40mL of solvent (selected in the pre-tests). The sample container was covered with aluminum-foil paper to prevent oxidative change from light. In the UAE procedure, the sonicator (QR1000 Ultronique, Ecosonics - Brazil) used in this study has a constant frequency of 20 kHz, that has a maximum power of 1000 Watts (W) and a horn microtip with diameter of 25.4 mm. UAE process variables including ultrasonic intensity and time were investigated as outlined in Table 3. However, the temperature was controlled using a water bath around the extraction flask. The obtained extracts were filtered and kept in the dark at -20 ºC for further analysis.

The UAE optimization of FRC phenolic compounds was developed using Statistica 7.0 software (StatSoft, Tulsa, USA). The central experimental design, comprised 8 factorial points (levels ± 1) and 5 central points (level 0). The independent variables were ultrasonic amplitude (UA) (20, 60 and 100%) and time (t) of exposure to ultrasound (5, 10 and 15 min), and the dependent variables (response) were the total phenolic compounds (TPC), ferric reducing-antioxidant power (FRAP) and 1,1-diphenyl-2-picryl hydrazyl (DPPH) free radical scavenging activity expressed as the IC_{50}.

Five replicates of the central point of the experimental design were used to estimate the value of the pure error and sum of squares. Because the various responses were the result of the interactions of the independent variables, the data for all the responses were adjusted to the second-order polynomial regression equation, Eq. (1).

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \epsilon \quad (1)$$

158 Where Y represents the predicted response, β_0 is the constant regression coefficient, βi,
159 βjj and βij are the linear, square and interaction coefficients, respectively, Xi and Xj are
160 the independent variables, and ε is noise or error (Azarpazhooh and Ramaswamy,
161 2012). The quality of the adjusted polynomial models was expressed by the regression
162 coefficient (R^2), adequate precision (AP) and variation coefficient (CV).
163 The experimental data were adjusted to the proposed model, and analysis of
164 variance (ANOVA), the lack of fit test (F test), determination of the regression
165 coefficients and obtaining the response surfaces were performed using Statistica 7.0
166 software (StatSoft, Tulsa, USA) at the 5% significance level.
167
168 *2.4.3. Microwave-assisted extraction (MAE)*
169 For microwave extraction, 0.33 g of FRC was mixed with 20 mL of ethanol-
170 water (80%), and then the mixture was subjected to a CEM Discover microwave
171 (Discover System model 908005) using a power of 800 W, a temperature of 120ºC and
172 an extraction time of 15 min (Best result of preliminary analysis). After exposure to
173 electromagnetic waves, the supernatant obtained was filtered and stored in an amber
174 container at -20ºC until further analysis.

175 *2.4.4. Conventional extraction by maceration (MCE)*
176 Three replicates (10.0 g) of FRC were extracted in 40 mL of 80% ethanol-water
177 (v/v), by using a dynamic maceration, brought to room temperature (25ºC) and kept
178 under stirring for 1 h. After extraction, suspended solids were removed by filtration
179 through qualitative filter paper and the extracts obtained were stored at -20°C until
180 further analysis.
181
182 *2.5. Physico-chemical analysis of FRC*
183 *2.5.1. Soluble solids and Titratable acidity*
184 The according to the methodology described by A.O.A.C. (2006). Soluble solids
185 was expressed as °Brix and acidity were expressed as g of citric acid/100 g of FRC.
186 *2.5.2. pH*
187 The pH was measured directly measurements using a pH meter with a glass
188 electrode (AAKER).
189 *2.5.3. Moisture*

The moisture content was determined using an infrared moisture balance (MARTE-IDSO, São Paulo, Brazil) and heating at 105°C for 30 minutes. The results are expressed as (%) (A.O.A.C., 2006).

2.5.4. Water activity

Water activity was measured using a water activity analyzer (DECAGON, AQUA LAB - 4TE) at 25 °C.

2.5.5. Color

The color was evaluated in a colorimeter (Minolta CR 400; Konica Minolta, Sensing Inc.), using the color standards of the CIELab ("Commission Internationale de L'Eclairage"). The instrumental color was determined on the surface of the ciriguela residue flour. The colorimeter was previously calibrated with a white standard before each analysis using a xenon lamp, illuminant C (Y = 92.78; x = 0.3139; y = 0.3200), an observation angle of 10° and a measuring area of 8 mm in diameter.

2.6. Analysis of bioactive compounds and antioxidant activity

2.6.1. Total phenolic compounds (TPCs)

The TPC content was determined spectrophotometrically, where the absorbance was quantified at 725 nm using Folin–Ciocalteu reagent and ethanol as the solvent, according to the methodology described by Wettasinghe and Shahidi (1999). Briefly, the reaction was conducted in test tubes. An amount of 0.5 mL of each sample was incubated with 8.0 mL of distilled water and 0.5 mL of Folin-Ciocalteau reagent. After 3 min 1.0 mL of sodium carbonate solution was added and left to react for 60 min in the dark. The TPCs was calculated using a standard curve prepared from the aqueous solutions of gallic acid (0.1-1 mg/mL) and results were expressed in mg of gallic acid equivalent (GAE)/g of FRC.

2.6.2. Antioxidant activity by DPPH

The determination of the free-radical scavenging capacity was evaluated with the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) as described by Brand-Williams et al. (1995) and modified by Sanchez-Moreno et al. (1998). The extract was diluted at three different concentrations of total phenolics. Briefly, 0.1 mL of appropriately diluted FRC extracts samples was added to 3.9 mL of DPPH (0.03 mg/ml) in methanol. The decrease in absorbance at 517 nm was monitored until the reaction

reached a plateau (30 min) of reaction, using a spectrophotometer (Shimadzu UV-1650 PC). The results were expressed as the IC_{50} (concentration of the extract in μg/mL that can react with 50% of the radicals present in the DPPH solution).

2.6.3. Ferric reducing antioxidant power (FRAP)

The FRAP test was performed according to the methodology reported by por Thaipong et al. (2006). The absorbance was measured at 593 nm, using a spectrophotometer (Jenway 6705 UV/Vis). FRAP reagent was freshly prepared by mixing a 10 mM 2,4,6-tris (1-pyridyl)-5-triazine (TPTZ) solution in 40 mM HCl with a 20 mM, $FeCl_3$ solution and 0.3 M acetate buffer (pH 3.6) in a proportion 1:1:10 (v/v/v). A calibration curve was prepared with aqueous solution of $FeSO_4$ (2.5, 5.0, 7.5 and 10 mg/L). In test tube 90 μL of the filtered and duly diluted extract with 270 μL of distilled water and 2.7 mL of FRAP reagent. Then, the reaction mixture was incubated at 37 °C for 30 min. Antioxidant activity by FRAP were expressed as μmol of ferrous equivalent per g of extract (μmol Fe^{2+}/g).

2.7. Statistical analysis

All the experiments were performed in triplicate, and the results were expressed as the mean values ± standard deviation. Statistical analysis of the model was performed using Statistica 7.0 software.

3. Results and discussion

3.1. Physico-chemical properties

The data on the soluble solid content, pH, titratable acidity, moisture and colorimetric parameters of the FRC are presented in Table 1.

The FRC presented 4.63 °Brix of soluble solids (Table 1), indicating the presence of water-soluble compounds and substances, such as sugars, acids, vitamin C and some pectins (Maldonado-Astudillo et al., 2014). The pH (3.79) characterized FRC as an acid product. The FRC acidity obtained as 1.57 g/100 g of citric acid (Table 1) was similar to that reported in the study by Neris et al. (2017), which characterized ciriguela peel and obtained 1.66 g/100 g of citric acid. The water activity found in the FRC (0.178) was considered a low value (the value varies from 0 to 1). The presence of moisture in plant matter indicates the possibility of microbial growth during storage (Shardul et al., 2013), and FRC showed low moisture (5.83%). The colorimetric

parameters (L a* b*) remained on the positive side, indicating a shade of red to yellow, and the value of L was 61.86, indicating that the FRC has clear luminosity.

Table 1

Physico-chemical characterization of FRC.

Parameters	Mean values ± SD
Soluble solids (ºBrix)	4.66 ± 0.15
pH	3.79 ± 0.15
Acidity (g/100g citric acid)	1.57 ± 0.06
Aw	0.178 ± 0.04
Moisture (%)	5.83 ± 0.01
L*	61.86 ± 1.05
a*	16.26 ± 0.34
b*	31.52 ± 0.17

Means ± standard deviation (n = 3).

3.2. Preliminary experiments – solvent selection

Selection of the best solvent for extraction by UAE was based on the values of phenolic compounds of the extracts. Table 2 shows the data on phenolic compounds from the extracts obtained using water and ethanol (20, 50 and 80%) as solvent.

Table 2

Extraction of phenolic compounds from FRC using different solvents.

Solvents	TPC (mg GAE/g of FRC)
Water	23.04^{c} ± 1.50
Etanol 20%	43.70^{b} ± 0.37
Etanol 50%	45.93^{b} ± 2.29
Etanol 80%	56.38^{a} ± 0.98

Means ± standard deviation (n = 3).

Means in each column followed by different superscript letters were significantly different (p> 0.05), by Tukey's test.

Ethanol has been found to possess the highest affinity for phenolics and hence it is the first choice for the extraction of phenolic compounds from fruit and vegetable waste (Ramić et al., 2015). Table 2 shows that the extract obtained with 80% ethanol

had a higher content of phenolic compounds. This was expected because the solubility of polyphenols increases with increasing concentrations of ethanol (He et al., 2016). Noroozi et al. (2021) studying continuous ultrasound-assisted extraction of *Cucurbita pepo* seeds, revealed that with increasing ethanol concentration, the phenolic compounds recovery increased and reached a maximum value at the ethanol concentration of around 80%, and then slightly decreased. This is because the polarity of the solvent decreases, and the similarity in the solvent to the polyphenols polarity increases, causing an increase in the solubility of polyphenols. Increase in ethanol concentration increases the yield of phenolic compound until a maximum ethanol concentration and then it has negative effect on the yield. The ethanol concentration near 100% i.e. highly pure ethanol solvent causes dehydration of the tissue of plant along with denaturation of the protein leading to decreased yield at such high concentration (Kumar et al., 2021). Caldas et al. (2018) observed that the highest phenolic content was found for medium values of ethanol concentration (60%), within the studied range (8-92%), which may be related to the different polarities of phenolics present in grape skin. Savic and Savic Gajic (2020) analyzed the extraction of polyphenols from wheatgrass (*Triticum aestivum* L.) obtained maximum yield of phenolic compounds using 56% ethanol concentration.

3.3 Experimental design of FRC by UAE

The contents of the experimental variables used in this study and the results obtained for the quality parameters of the experimental design are shown in Table 3. TPC ranged from 14.56 to 35.15 mg GAE/g of FRC, antioxidant activity by IC_{50} from 0.19 to 3.51 mg/mL and antioxidant activity by FRAP from 7.624,40 to 17.373,73 µmol Fe^{2+}/g.

ANOVA for the quadratic model of the response surface is shown in Table 4. Not significant variables were omitted, and the other coefficients were used in the final predictive equations. The data showed a good fit with Eq. (1), which was statistically acceptable at $p < 0.05$.

The adequacy of the model was also evaluated by the residuals, which represent the difference between the observed and predicted values of the response (Maran et al., 2017). The residuals are thought of as the elements of variation unexplained by the regression model (Savic Gajic et al., 2019). The obtained residuals are plotted against the expected values in the normal probability plot (Figure 1 a, b and c). The obtained

plots of the model after excluding nonstatistically significant terms indicate that the residuals are normally distributed. The slight deviation of points from the straight line in the reduced model indicates a better prediction of the regression model.

Table 3

Face-centered composite design 3^2 of UAE using two variables and the resulting quality response parameters of the FRC extract.

Exp. n0	UA (%)	Time (min)	TPC (mg GAE/g of FRC)	IC 50 (mg/mL)	FRAP (µmol Fe^{2+}/g)
1	60 (0)	10 (0)	29.40±0.68	1.46±0.13	15.403,95±23.82
2	60 (0)	15 (+1)	30.01±0.98	1.03±0.08	15.653,02±63.52
3	60 (0)	10 (0)	28.96±0.30	1.40±0.14	14.290,19±45.91
4	20 (-1)	15 (+1)	22.53±0.18	2.17±0.23	11.456,33±67.92
5	20 (-1)	10 (0)	20.42±0.48	2.52±0.09	10.857,03±30.40
6	100(+1)	10 (0)	28.03±0.25	2.64±0.04	14.657,94±85.25
7	20 (-1)	5 (-1)	14.56±0.54	3.51±0.04	7.624,40±38.18
8	100 (+1)	5 (-1)	21,70±0,10	2.99±0.06	12.148,17±90.78
9	60 (0)	10 (0)	29.73±0.20	1.96±0.07	15.749,00±57.54
10	60 (0)	5 (-1)	25.06±0.60	2.97±0.07	9.573,12±34.99
11	60 (0)	10 (0)	29.05±0.30	1.95±0.16	16.462,94±74.69
12	100 (+1)	15 (+1)	35.15±0.43	0.19±0.02	17.373,73±29.19
13	60 (0)	10 (0)	29.43±1.22	1.48±0.17	15.770,72±97.94

UA: Ultrasound Amplitude.
TPC: Total Phenolic Compound.
FRAP: Ferric Reducing Antioxidant Power.
DPPH: scavenging activity of DPPH.
IC50: The concentration of extract required to scavenge 50% of 2, 2-diphenyl-1-picryl-hydrazyl free radical.
*Analytical results are the means ± SD (n = 3).

Table 4

ANOVA for the response surface quadratic model.

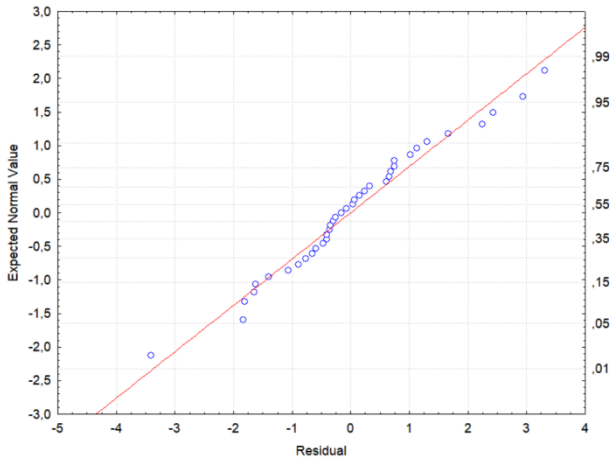
Source	Df	TPC (mg GAE/g of FRC)	IC 50 (mg/mL de fenol)	FRAP (µmol Fe^{2+}/g)
Regression	4	984.98*	24.61*	2929070.19*
Residual	34	73.12	5.87	229854.43
Lack of fit	4	63.21*	4.55*	157999.76*
Pure Error	30	9.90ns	1.31ns	71854.67ns
Cor Total	38	1058.10	30.48	3158924.62
R-Squared		0.93	0.81	0.93

ns: Not significant ($p > 0,05$).

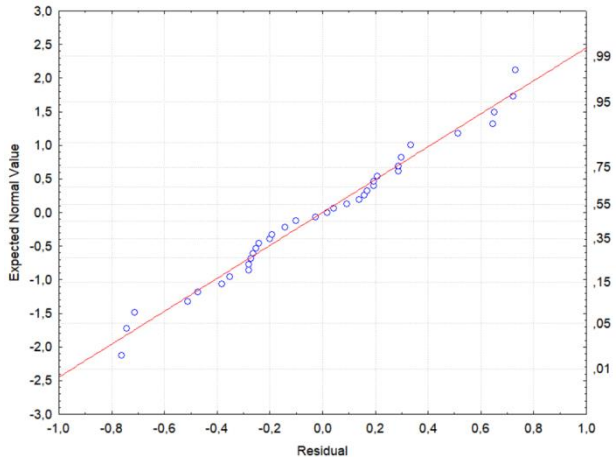
*Significant at ($p < 0,05$).

Fig. 1 Normal probability plot of studentized residuals for the reduced polynomial model: (a) TPC; (b) IC50; (c) antioxidant activity by FRAP.

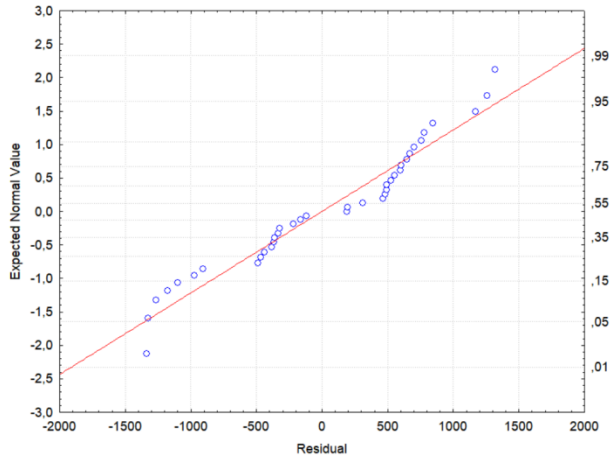
(a)



(b)



(c)



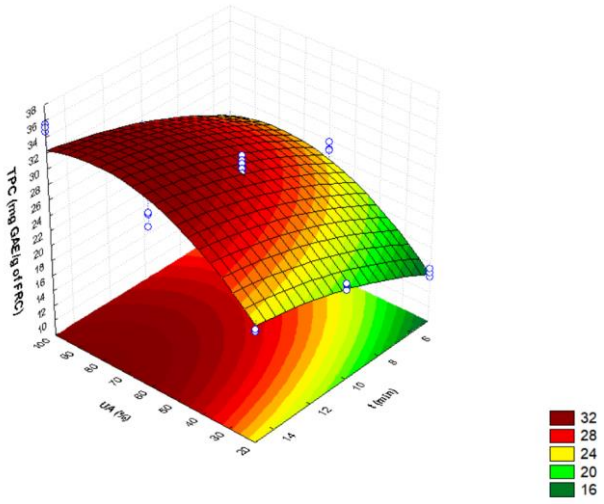
3.3. Effect of process variables on TPC

341 The TPC of the FRC extracts and ANOVA of the results obtained are presented
342 in Tables 3 and 4, respectively. Data analysis showed that the TPC was significantly
343 affected by UA and t ($p < 0.05$). Additionally, it was possible to determine the
344 significant regression coefficients for the TPC, as shown in Eq. (2).

345 $$TPC = 25.26 + 4.56X_1 + 4.39X_2 + 2.29X_1^2 + 0.63X_2^2 \quad (2)$$

346 The variables that significantly influenced the model for TPC were as follows:
347 UA (X_1 and X_1^2) and t ($X_2^{2)}$, as shown in Table 4. The lack of fit was significant for the
348 TPC model, however, when the pure error value is low, that is, the reproducibility is
349 very good, resulting in a false result of lack of fit, since the Fcalculated value is high
350 due to the denominator being very low. Therefore, it does not explain the lack of fit.
351 The model has statistical and predictive significance, and there is no lack of fit. To
352 visualize the influence of variables on the TPC, the response surface graph (Fig. 2) was
353 constructed.

354 **Fig. 2** Effect of the interaction of process variables on the extraction of TPC from FRC.



355

356 As observed in tests 4, 2 and 12 (Table 3), the TPC increased slowly with the
357 increase in UA and reached a peak at 100% UA, both obtained using 15 min of
358 extraction time and resulting in 22.53, 30.01 and 35.15 mg GAE/g of FRC, respectively.
359 Significant increases in TPC were observed as the UA range was increased during the
360 extraction of phenolic compounds from the pomegranate peel (Sharayei et al., 2019).
361 Opposite results have been obtained in some studies in which UA was not a significant
362 factor in the extraction of phenolic compounds (Espada-Bellido et al., 2017; Saifullah et
363 al., 2020).

364 The increase in UA causes an additional effect of cavitation and temperature
365 increase, causing the explosion of bubbles, resulting in material swelling, solvent

uptake, and pore enlargement in the materials (Bimark et al., 2019; Gam et al., 2020; Gogoi et al., 2018). Cavitation effect works by imploding cavitation bubbles and thermal effect works by swelling and loosening the cell structure, which increase solute solubility and diffusivity (Poodi et al., 2018). The increase of ultrasonic power accelerates the destruction of cell walls, thereby promoting the extraction of the TPC into the extraction solvent (Gam et al., 2020). In addition, the penetration of the solvent into the solid matrix is improved, facilitating the mass transfer rate of phenolic compounds from the food matrix to the solvent (Gogoi et al., 2018).

The extraction time showed a positive linear effect on the extraction of phenolic compounds from FRC and led to a gradual increase in the TPC. Similar results were obtained in the study of extraction of antioxidants from plum seeds (Savic and Savic Gajic, 2021). The contact time allows for a higher mass transfer rate, resulting in better extraction efficiency. The operating time is very important during extraction because it helps to reduce electricity consumption as the operating time decreases (Chakraborty et al., 2020). The same effect was obtained in other studies (Fernandes et al., 2020; Saifullah et al., 2020).

As the extraction time increased, a higher TPC was obtained, according to tests 7 (14.56 mg GAE/g of FRC), 5 (20.42 mg GAE/g of FRC) and 4 (22.53 mg GAE/g of FRC), using 20% of ultrasonic amplitude and extraction time of 5, 10 and 15 minutes, respectively (Table 3). Gogoi et al. (2018) observed that the increase in extraction time from 8.00 to 14.00 min increased the yield of phenolic compounds, which subsequently decreased with a further increase in treatment time. Opposite results were obtained in some studies in which time was not a significant factor in the ultrasound-assisted extraction of phenolic compounds (Jovanovic et al., 2017; Li et al., 2016).

3.4. Effect of process variables on the antioxidant activity by DPPH (IC_{50})

IC_{50} represents the concentration of the extract necessary to inhibit 50% of DPPH free radicals. The following equation describes the IC_{50} predicted by the model (Eq. 3) according to the coded and significant variables ($p \leq 0.05$).

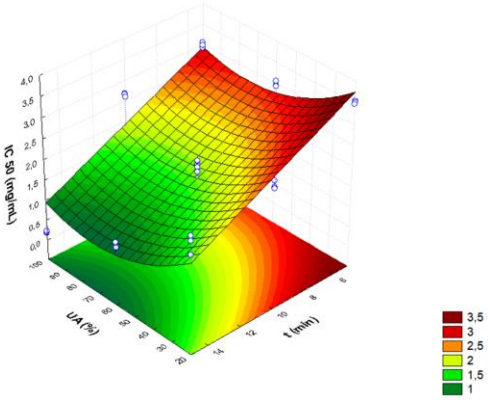
$$IC_{50} = 2.14 - 0.39X_1 - 1.01X_2 - 0.29X_1^2 \quad (3)$$

The variables that significantly influenced the model for IC_{50} were UA (X_1 *and* X_1^2), and t (X_2). The not significant value of the lack of fit showed that the model was considered predictive for IC50 (R^2=0.81) (Table 4). The not statistically significant

terms could be excluded from the second order polynomial equation in order to improve the prediction ability of the proposed model. The regression coefficients indicate that the linear effects and quadratic effect UA have a negative impact on the response.

UA caused a negative signal effect in IC_{50}, and the increase in IC_{50} was related to the increase in UA (Fig. 3). Similar results were obtained by Sharayei et al. (2019), in which the IC_{50} increase was observed when a UA up to 60% was used; additionally, when the UA was further increased, the IC_{50} decreased. Li et al. (2016) reported significant increases in the antioxidant activity (DPPH) as the ultrasound time was increased. In a study of the extraction of phenolic compounds from pomegranate peel, an increase in UA up to 60% was observed to increase the antioxidant activity (Sharayei et al., 2019).

Fig. 3 Effect of the process variables on the IC_{50} of extracts of FRC phenolic compounds.



3.5. Effect of the process variables on the antioxidant activity by FRAP

Through factorial experimental design, it was possible to determine the significant regression coefficients for antioxidant activity by FRAP, as shown in Eq. (4).

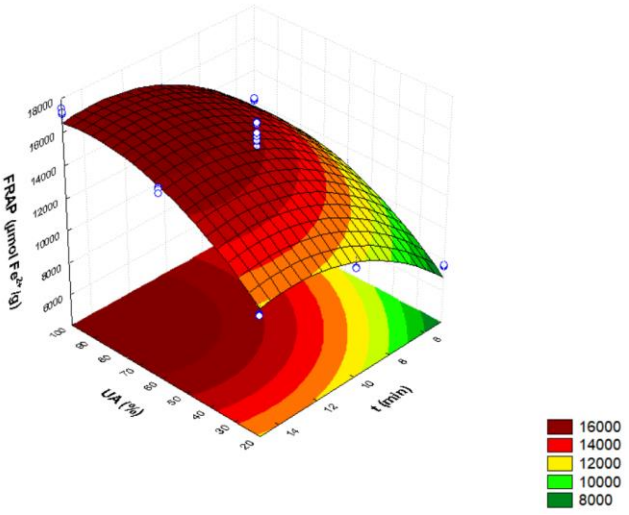
$$FRAP = 12883.45 + 2357.01X_1 + 2484.01X_2 + 820.78X_1^2 + 926.32X_2^2 \quad (4)$$

However, only the linear terms UA (X_1 and X_1^2) and t (X_2 and X_2^2) ($p \leq 0.05$) showed positive signal effects in the extraction. The not significant value of the lack of fit showed that the model was considered predictive for antioxidant activity by FRAP (R^2=0.93) (Table 4). The lack of fit was significant for antioxidant activity by FRAP model, however, when the pure error value is low, that is, the reproducibility is very good, resulting in a false result of lack of fit, since the Fcalculated value is high due to

the denominator being very low. Therefore, it does not explain the lack of fit. The model has statistical and predictive significance, and there is no lack of fit.

The increase in UA likely promoted more efficient extraction of phenolic compounds, resulting in the increased antioxidant activity by FRAP (Fig 4). This effect may be due to the cavitation process and vibration mechanics produced by the pressure of ultrasonic radiation, which can accelerate the penetration of solvents and improve the extraction efficiency and antioxidant activity of the obtained extracts (Wang et al., 2016).

Fig. 4 Effect of the influence of process variables on the antioxidant activity by FRAP using FRC extracts.



Tests 7, 10 and 8, all using an extraction time of 5 min, showed significant increases in the antioxidant activity by FRAP as the UA was increased (7.624,40 (20% UA), 9.573,12 (60% UA) and 12.148,17 µmol Fe^{2+}/g (100% UA), respectively (Table 3). The same trend was obtained by several authors using UAE (Chen et al., 2018; Li et al., 2016; Sharayei et al., 2019). UAE contribute to more efficient extraction of the compounds, improving the cavitation phenomena, mechanical agitation, and process efficiency and facilitating the transport of bioactive compounds, in addition to contributing to the reduction of extraction time (Chakraborty et al., 2020).

Higher FRAP values were obtained when longer extraction times were used (Fig. 4). Li et al. (2016) also reported significant increases in antioxidant activity by FRAP as the ultrasound time was increased.

3.6. Comparison of different extraction methods in the recovery of phenolic compounds from FRC

The optimization of the extraction of FRC phenolic compounds resulted in a higher content of phenolic compounds and high antioxidant activity using the following optimal extraction conditions—UA (100%) and t (15 min). Comparing the total phenolic compounds obtained by different methods, it could be noted that the ultrasound-assisted extraction was significantly more efficient (Table 5).

Table 5

Extraction of phenolic compounds from FRC using different extraction methods.

Methods of extraction	TPC (mg GAE/g of FRC)	IC 50 (mg/mL)	FRAP (µmol Fe^{2+}/g)
Ultrasound	$35.15^{a} \pm 0.43$	$0.19^{a} \pm 0.02$	$17.373,73^{a} \pm 29.19$
Microwave	$23.31^{c} \pm 0.17$	$4.29^{c} \pm 0.03$	$15.784,15^{a} \pm 80.16$
Conventional	$30.10^{b} \pm 0.07$	$1.68^{b} \pm 0.11$	$16.040,50^{a} \pm 25.13$

*Means ± standard deviation (n = 3).

Means in each column followed by different superscript letters were significantly different (p> 0.05), by Tukey's test.

The extract obtained in the UAE showed greater phenolic recovery, indicating that the application of ultrasonic waves is a promising alternative, aiming to increase the extraction yield of phenolic compounds (Table 5). This can be seen in other studies (Caldas et al., 2018; Fernandes et al., 2020; Martínez-Ramos et al., 2020; Rezende et al. 2017) who investigated the recovery of phenolic compounds from grape residue, jabuticaba peel, mango peel and acerola residue, respectively, using different extraction methods. Compared to the UAE with maceration and soxhlet extraction, the UAE gives higher yields of desired compounds for shorter extraction times and at lower temperatures (Savic Gajic et al., 2019). The higher extraction efficiency using the UAE was due to the effect of cavitation (Vinatoru et al. 2017), facilitating the penetration of the solvent through the healthy cells is better, which reflects the increase in the mass transfer (Savic and Savic Gajic, 2020).

The higher rate extraction for UAE is attributed to the cavitation process, which causes the rupture of cellular structures and greater penetration of the solvent into the internal structure of the particles, increasing the intraparticle diffusivity (Chemat et al.,

2017). During sonication, ultrasonic waves create shock waves within the cell wall and liquid jets are formed as a result of cavitation of the liquid media due to compression and rarefaction cycle of ultrasonic waves (Gogoi et al., 2019). Cavitation is a process that results in swelling of the material, increased temperature, solvent absorption, softening of plant surfaces and enlarged pores in materials, factors that are favorable to mass transport (Chakraborty et al., 2020; Gam et al. 2020).

The conventional techniques require the use of organic solvent for the extraction of bioactive compounds from plant material. In addition to evaporation and recycling of the solvent after using these techniques. These facts cause the increase of solvent consumption, energy consumption and generation of hazardous solvent residues after its evaporation from the sample (Savic Gajic et al., 2021). Meregalli et al. (2020) compared conventional extraction and UAE in the extraction of bioactive compounds obtained from red araçá and observed an increase of 23.45% in the levels of phenolic compounds and a 25.00% reduction in the time of extraction using UAE compared with conventional extraction by maceration. Additionally, ultrasonic extraction produced a higher yield of propolis phenolic compounds than extraction by maceration and microwave (Oroian et al., 2020). Bimakr et al. (2017) investigated the effects of ultrasound-assisted extraction on the extractive value (EV) of bioactive phenolics from Malva sylvestris leaves and its comparison with agitated bed extraction (ABE) technique. In comparasion the free radical scavenging activity (FRSA) and TPC analyses results revealed that UAE afforded extracts with relatively higher FRSA and TPC values compared with ABE in much shorter time (48.77 min). Opposite results were obtained in some studies evaluated the impact of different extraction methods of phenolic compounds (Da Rocha and Noreña, 2020; Rocchetti et al., 2019).

4. Conclusions

Ciriguela peel (*Spondias purpurea* L.) is considered a sustainable source of natural antioxidants and phenolic compounds. The optimum condition of the UAE of phenolic compounds from the FRC extract was obtained using an ultrasonic amplitude (UA) of 100% and a time (t) of 15 min. The extraction process affected the content of bioactive compounds and antioxidant activity. In this work, the impacts of different extraction technologies (including conventional and nonconventional) that is, mechanical agitation, ultrasound and microwave—were evaluated in terms of

recovering phenolic compounds from ciriguela peel. Additionally, UAE was more efficient in recovering the compounds of interest.

References

AOAC - Association of Official Analytical Chemists. Official Methods of Analysis of Association of Official Analytical Chemists International, 18th ed. Gaithersburg: AOAC International, 2006.

Azarpazhooh, E., Ramaswamy, H. S., 2012. Modeling and optimization of microwave osmotic dehydration of applecylinders under continuous-flowspraymodeprocessing conditions. Food Bioproc. Tech. *5*(5), 1486–1501.

Ben-Othman, S., Jõudu, I., Bhat, R., 2020. Bioactives from Agri-Food Wastes: Present Insights and Future Challenges. Molecules. 25, 510-544. https://doi:10.3390/molecules25030510.

Bimakr, M., Ganjloo, A., Noroozi, A., 2019. Effect of acoustic cavitation phenomenon on bioactive compounds release from Eryngium caucasicum leaves. J. Food Meas. Charact. 13, 1839–1851. https://doi.org/10.1007/s11694-019-00103-w

Bimakr, M., Ganjloo, A., Zarringhalami, S., Ansarian, E., 2017. Ultrasound-assisted extraction of bioactive compounds from Malva sylvestris leaves and its comparison with agitated bed extraction technique. Food Sci Biotechnol (2017) 26(6), 1481–1490. https://doi.org/10.1007/s10068-017-0229-5

Brand-Wiliams, W., Cuvelier, M.E., Berset, C., 1995. Use of a free radical method to evaluate antioxidant activity. Food Sci. Technol. 28, 25-30. https://doi.org/10.1016/S0023-6438(95)80008-5.

Caldas, T. W., Mazza, K. E. L., Teles, A. S. C., Mattos, G. N., Brígida, A. I. S., Conte-Junior, C. A., Borguini, R. G., Godoy, R. L. O., Cabral, L. M. C., Tonon, R. V., 2018. Phenolic compounds recovery from grape skin using conventional and nonconventional extraction methods. Ind. Crops Prod. 111, 86–91. http://dx.doi.org/10.1016/j.indcrop.2017.10.012.

Chakraborty, S., Uppaluri, R., Das, C., 2020. Optimization of ultrasound-assisted extraction (UAE) process for the recovery of bioactive compounds from bitter gourd using response surface methodology (RSM). Food Bioprod. Process. 120, 114–122. https://doi.org/10.1016/j.fbp.2020.01.003.

Chemat, F., Rombaut, N., Sicaire, A. G., Meullemiestre, A., Fabiano-Tixier, A. S., Abert-Vian, M., 2017. Ultrasound assisted extraction of food and natural products.

554 Mechanisms, techniques, combinations, protocols and applications. A review. Ultrason.
555 Sonochem. 34, 540–560. https://doi.org/10.1016/j.ultsonch.2016.06.035.
556
557 Chen, S., Zeng, Z., Hu, N., Bai, B., Wang, H., Suo, Y., 2018. Simultaneous
558 optimization of the ultrasound-assisted extraction for phenolic compounds content and
559 antioxidant activity of Lycium ruthenicum Murr. fruit using response surface
560 methodology. Food Chem. 242, 1–8. http://dx.doi.org/10.1016/j.foodchem.2017.08.105.
561
562 Dadan, M., Rybak, K., Wiktor, A., Nowacka, M., Zubernik, J., Witrowa-Rajchert, D.,
563 2018. Selected chemical composition changes in microwave-convective dried parsley
564 leaves affected by ultrasound and steaming pre-treatments – An optimization approach.
565 Food Chem. 239, 242-251. https://doi.org/10.1016/j.foodchem.2017.06.061.
566
567 Da Rocha, C. B., Noreña, C. P. Z., 2020. Microwave-Assisted Extraction and
568 Ultrasound-Assisted Extraction of Bioactive Compounds from Grape Pomace. Int. J.
569 Food Eng. 16, 20190191. https://doi.org/10.1515/ijfe-2019-0191.
570
571 Espada-Bellido, E., Ferreiro-González, M., Carrera, C., Palma, M., Barroso, C. G.,
572 Barbero, G. F., 2017. Optimization of the ultrasound-assisted extraction of anthocyanins
573 and total phenolic compounds in mulberry (*Morus nigra*) pulp. Food Chem. 219, 23–32.
574 https://10.1016/j.foodchem.2016.09.122.
575
576 Fernandes, F. A. N., Fonteles, T. V., Rodrigues, S., Brito, E. S., Tiwari, B. K., 2020.
577 Ultrasound-assisted extraction of anthocyanins and phenolics from jabuticaba
578 (Myrciaria cauliflora) peel: kinetics and mathematical modeling. J. Food Sci. Technol.
579 57, 2321–2328. https://doi.org/10.1007/s13197-020-04270-3.
580
581 Gam, D. H., Yi Kim, S., Woo Kim, J., 2020. Optimization of Ultrasound-Assisted
582 Extraction Condition for Phenolic Compounds, Antioxidant Activity, and
583 Epigallocatechin Gallate in Lipid-Extracted Microalgae. Molecules. 25, 454.
584 https://10.3390/molecules25030454
585
586 Gogoi, P., Chutia, P., Singh, P., Mahanta, C. L., 2019. Effect of optimized ultrasound-
587 assisted aqueous and ethanolic extraction of Pleurotus citrinopileatus mushroom on total
588 phenol, flavonoids and antioxidant properties**.** J. Food Process Eng. 42(6), 1-12.
589 https://doi.org/10.1111/jfpe.13172.
590
591 He, B., Zhang, L. L., Yue, X. Y., Liang, J., Jiang, J., Gao, X. L., Yue, P. X., 2016.
592 Optimization of ultrasound-assisted extraction of phenolic compounds and anthocyanins
593 from blueberry (*Vaccinium ashei*) wine pomace. Food Chem. 204, 70–76.
594
595 Jeddou, K. B., Bouaziza, F., Zouari-Ellouzia, S., Chaaria, F., Ellouz-Chaabounia, S.,
596 Ellouzghorbela, R., Nouri-Ellouzc, O., 2017. Improvement of texture and sensory
597 properties of cakes by addition of potato peel powder with high level of dietary fiber

598 and protein. Food Chem. 217, 668–677.
599 https://doi.org/10.1016/j.foodchem.2016.08.081.
600
601 Jovanovic, A. A., Dordevic, V. B., Zdunic, G. M., Pljevljakusic, D. S., Savikin, K. P.,
602 Godevac, D. M., Bugarski, B. M., 2017. Optimization of the extraction process of
603 polyphenols from Thymus serpyllum L. herb using maceration, heat- and ultrasound-
604 assisted techniques. Sep. Purif. Technol. 179, 369–380.
605 https://doi.org/10.1016/j.seppur.2017.01.055.
606
607 Kringel, D. H., Dias, A. R. G., Zavareze, E. R., Gandra, E. A., 2020. Fruit Wastes as
608 Promising Sources of Starch: Extraction, Properties, and Applications. Stärke. 72,
609 19000200. https://doi.org/10.1002/star.201900200.
610
611 Kumar, K., Srivastav, S., Singh, Sharanagat, V. S., 2021. Ultrasound assisted extraction
612 (UAE) of bioactive compounds from fruit and vegetable processing by-products: A
613 review. Ultrasonics – Sonochemistry. 70, 105325.
614 https://doi.org/10.1016/j.ultsonch.2020.105325
615
616 Li, H. Z., Zhang, Z. J., Xue, J., Cui, L. X., Hou, T. Y., Li, X.-J., Chen, T., 2016.
617 Optimization of ultrasound-assisted extraction of phenolic compounds, antioxidants and
618 rosmarinic acid from perilla leaves using response surface methodology. Food Sci.
619 Technol. 36, 686–693. http://dx.doi.org/10.1590/1678-457x.13516.
620
621 Maldonado-Astudillo, Y. I., Alia-Tejacal, I., Núnez-Colín, C. A., Jiménez-Hernández,
622 J., Pelayo-Zaldívar, C., López-Martínez, V., Andrade-Rodríguez, M., Bautista-Banos,
623 S., Valle-Guadarrama, S., 2014. Postharvest physiology and technology of Spondias
624 purpurea L. and S. mombin L. Sci. Hortic. 174, 193–206.
625 https://doi.org/10.1016/j.scienta.2014.05.016.
626
627 Maran, J.P.; Manikandan, S.; Nivetha, C.V.; Dinesh, R., 2017. Ultrasound assisted
628 extraction of bioactive compounds from Nephelium lappaceum L. fruit peel using
629 central composite face centered response surface design. Arab. J. Chem. 10, 1145–1157.
630
631 Marić, M., Grassino, A. N., Zhu, Z., Barba, F. J., Brnčić, M., Rimac Brnčić, S., 2018.
632 An overview of the traditional and innovative approaches for pectin extraction from
633 plant food wastes and by-products: Ultrasound-, microwaves-, and enzyme-assisted
634 extraction. Trends Food Sci. Technol. 76, 28–37.
635 https://doi.org/10.1016/j.tifs.2018.03.022.
636
637 Martínez-Ramos, T., Benedito-Fort, J., Watson, N. J., Ruiz-López, I. I., Che-Galicia,
638 G., Corona-Jiménez, E., 2020. Effect of solvent composition and its interaction with
639 ultrasonic energy on the ultrasound-assisted extraction of phenolic compounds from
640 Mango peels (Mangifera indica L.). Food Bioprod. Process. 122, 41-54.
641 https://doi.org/10.1016/j.fbp.2020.03.011.

Meregalli, M. M., Puton, B. M. A., Camera, F. D., Amaral, A. U., Zeni, J., Cansian, R. L., Mignoni, M. L., Backes, G. T., 2020. Conventional and ultrasound-assisted methods for extraction of bioactive compounds from red araçá peel (*Psidium cattleianum* Sabine). Arab. J. Chem. 13, 5800-5809. https://doi.org/10.1016/j.arabjc.2020.04.017.

Neris, T. S., Loss, R. A., Guedes, S. F., 2017. Caracterização físico-química da seriguela (*Spondias purpurea* L.) coletadas no município de Barra do Bugres/MT em diferentes estágios de maturação. Nat. Resour. 7(1), 9-18. https://doi.org/10.6008/SPC2237-9290.2017.001.0002.

Noroozi, F., Bimakr, M., Ganjloo, A., Aminzare, M., 2021. A short time bioactive compounds extraction from *Cucurbita pepo* seed using continuous ultrasound-assisted extraction. J. Food Meas. Charact. 15, 2135–2145. https://doi.org/10.1007/s11694-021-00810-3

Oroian, M., Dranca, F., Ursachi, F., 2020. Comparative evaluation of maceration, microwave and ultrasonicassisted extraction of phenolic compounds from própolis. J. Food Sci. Technol. 57, 70–78. https://doi.org/10.1007/s13197-019-04031-x.

Pintać, D., Majkić, T., Torović, L., Orcić, D., Beara, I., Simin, N., Mimicae-Dukić, N., Lesjak, M., 2018. Solvent selection for efficient extraction of bioactive compounds from grape Pomace. Ind.Crops Prod. 111, 379-390. https://doi.org/10.1016/j.indcrop.2017.10.038.

Poodi, Y., Bimakr, M., Ganjloo, A., Zarringhalami, S., 2018. Intensification of bioactive compounds extraction from Feijoa (*Feijoa sellowiana* Berg.) leaves using ultrasonic waves. Food Bioprod. Process. 108, 37-50. https://doi.org/10.1016/j.fbp.2017.12.004

Putnik, P., Lorenzo, J. M., Barba, F. J., Roohinejad, S., Jambrak, A. R., Granato, D., Montesan, D., Bursać Kovačević, D., 2018. Novel food processing and extraction technologies of high-added value compounds from plant materials. Foods. 7, 106–122. https://doi10.3390/foods7070106.

Renard, C. M. G. C., 2018. Extraction of bioactives from fruit and vegetables: State of the art and perspectives. LWT-Food Sci. Technol. 93, 390–395. https://doi.org/10.1016/j.lwt.2018.03.063.

Rezende, Y. R. R. S., Nogueira, J. P., Narain, N., 2017. Comparison and optimization of conventional and ultrasound assisted extraction for bioactive compounds and antioxidant activity from agro-industrial acerola (*Malpighia emarginata DC*) residue. LWT - Food Sci. Technol. 85, 158-169. http://dx.doi.org/10.1016/j.lwt.2017.07.020.

686 Rocchetti, G., Blasi, F., Montesano, D., Ghisoni, S., Marcotullio, M. C., Sabatini, S.,
687 Cossignani, L., Lucini, L., 2019. Impact of conventional/non-conventional extraction
688 methods on the untargeted phenolic profile of *Moringa oleifera* leaves. Food Res. Int.
689 115, 319–327. https://doi.org/10.1016/j.foodres.2018.11.046.
690
691 Saifullah, Md., McCullum, R., McCluskey, A., Vuong, Q., 2020. Comparison of
692 conventional extraction technique with ultrasound assisted extraction on recovery of
693 phenolic compounds from lemon scented tea tree (Leptospermum petersonii) leaves.
694 Heliyon. e03666. https://doi.org/10.1016/j.heliyon.2020.e03666.
695
696 Saleem, M., Saeed, M. T., 2020. Potential application of waste fruit peels (orange,
697 yellow lemon and banana) as wide range natural antimicrobial agente. J. King Saud
698 Univ. Sci. 32, 805–810. https://doi.org/10.1016/j.jksus.2019.02.013 101.
699
700 Sánchez-Moreno, C., Larrauri, J. A., Saura-Calixto, F., 1998. A procedure to measure
701 the antiradical efficiency of polyphenols. J. Sci. Food Agric. 76(2), 270-276.
702 https://doi.org/10.1002/(SICI)1097-0010(199802)76:2<270::AID-JSFA945>3.0.CO;2-
703 9.
704
705 Santos, D., Veggi, P.C., Meireles, M.A., 2010. Extraction of antioxidant compounds
706 from Jabuticaba (*Myrciaria cauliflora*) skins: yield, composition and economical
707 evaluation. J. Food Eng. 101, 23–31.
708
709 Savic, I. M., Savic Gajic, I. M., 2020. Optimization of ultrasound-assisted extraction of
710 polyphenols
711 from wheatgrass (*Triticum aestivum* L.). J Food Sci Technol. 57(8), 2809–2818.

712 Savic Gajic, I. M., Savic, I. M., Gajic, D. G., Dosic, A. 2021. Ultrasound-assisted
713 extraction of carotenoids from Orange peel using olive oil and its encapsulation in ca-
714 alginate beads. Biomolecules. 11, 225. https://doi.org/10.3390/biom11020225

715 Savic, I. M., Savic Gajic, I. M., 2021. Optimization study on extraction of antioxidants
716 from plum seeds (*Prunus domestica* L.). Optimization and Engineering. 22, 141–158.
717 https://doi.org/10.1007/s11081-020-09565-0

718 Savic Gajic, I., Savic, I., Boskov, I., Žeraji´C, S., Markovic, I., Gajic, D. 2019.
719 Optimization of ultrasound-assisted extraction of phenolic compounds from black locust
720 (*Robiniae Pseudoacaciae*) flowers and comparison with conventional methods.
721 Antioxidants. 8, 248.

722 Sharayei, P., Azarpazhooh, E., Zomorodi, S., Ramaswamyc, H. S., 2019. Ultrasound
723 assisted extraction of bioactive compounds from pomegranate (*Punica granatum* L.)
724 peel. LWT - Food Sci. Technol. 101, 342–350.
725 https://doi.org/10.1016/j.lwt.2018.11.031.

Shardul, K., Swati, J., Prajakta, K., Prafullachandra, T., Santos, H, P., Arun, R., 2013. Proximate analysis of peel and seed of *Annona Squamosa* (Custard Apple) fruit. Res. J. Chem. Sci. 3(2), 92-94.

Thaipong, K., Boonprakob, U., Crosby, K., Cisneros-Zevallos, L., Byrne, D. H., 2006. Comparison of ABTS, DPPH, FRAP, and ORAC assays for estimating antioxidant activity from guava fruit extracts. J. Food Compost. Anal. 19(6-7), 669-675. https://doi.org/10.1016/j.jfca.2006.01.003.

Vinatoru, M., Mason, T. J., Calinescu, I., 2017. Ultrasonically assisted extraction (UAE) and microwave assisted extraction (MAE) of functional compounds from plant materials. Trends Anal Chem. 97, 159–178.

Wang, W., Jung, J., Tomasino, E., Zhao, Y., 2016. Optimization of solvent and ultrasound-assisted extraction for different anthocyanin rich fruit and their effects on anthocyanin compositions. LWT – Food Sci. Technol. 72, 229–238. https://doi.org/10.1016/j.lwt.2016.04.041.

Wettasinghe, M., Shahidi, F., 1999. Evening primrose meal: a source of natural antioxidants and scavenger of hydrogen peroxide and oxygen-derived free radicals. J. Agric. Food Chem. 47, 1801-1812. https://doi.org/10.1021/jf9810416.

ARTIGO II. Microencapsulation by spray-drying and freeze-drying of phenolics obtained from ciriguela peel: Chemical, morphological and chemometric characterization of microcapsules

Abstract

Microcapsules of ciriguela peel extracts obtained by ultrasound-assisted extraction were prepared by spray drying, whose results were compared with those of freeze-drying as a control. The effects of spray-drying air temperature, feed flow rate and ratio of encapsulating agents (maltodextrin and arabic gum) were studied. Encapsulation efficiency, moisture content, total phenolic compounds (TPC), water activity, hygroscopicity, solubility, colorimetric parameters, phenolic profile by HPLC/DAD, simulated gastrointestinal digestion and morphology of spray-dried and freeze-dried microcapsules were evaluated, as well as their stability of TPC during 90 days storage at 7 and 25 °C. Spray-dried extracts showed values of moisture content, water activity, hygroscopicity and solubility within the expected ranges for powder products, and the use of arabic gum as an encapsulating agent ensured the highest encapsulation efficiency and TPC content. Spray-dried extract showed higher encapsulation efficiency (98.83%) and TPC (476.82 mg GAE g^{-1}) than freeze-dried extract. The most abundant compounds in the liquid extract of ciriguela peel flour were rutin (342.59 ± 45.08 μg g^{-1}), epicatechin gallate (228.63 ± 12.78 μg g^{-1}), chlorogenic acid (228.31 ± 5.67 μg g^{-1}) and quercetin (181.02 ± 6.28 μg g^{-1}). Rutin and myricetin were the major flavonoids in the atomized extract, while quercetin and kaempferol were in the freeze-dried one. The simulated gastrointestinal digestion test of microencapsulated extracts revealed the highest TPC contents after the gastric phase and the lowest one after the intestinal one. Rutin was the most abundant compound after the digestion of both spray-dried (68.74 μg g^{-1}) and freeze-dried (93.98 μg g^{-1}) extracts. Scanning electronic microscopy examination of the atomized extract showed the presence of spherical microcapsules with smooth surface, while those of the lyophilized extract had extensive wrinkles and more rough surface. Atomized microcapsules had higher phenolic compounds contents after 90 days of storage at 7 °C compared to those stored at 25 °C, while the lyophilized ones showed no significant difference between the two storage temperatures. The ciriguela agro-industrial residue can be considered an interesting alternative source of phenolic compounds that could be used, in the form of bioactive compounds-rich powders, as an ingredient in pharmaceutical, cosmetic and food industries.

Keywords: antioxidant activity; phenolic compounds; powder extract; encapsulating agents.

1. Introduction

In Brazil, it stands out the consumption of ciriguela (*Spondias purpurea* L.), a species belonging to the genus *Spondias*, which comprises more than 600 species concentrated mainly in the tropical regions of Africa, Asia and Central America (AUGUSTO et al., 2012; BARROS et al., 2017). From a phytochemical point of view, ciriguela is rich in secondary metabolites, mainly phenolic compounds (MALDONADO-ASTUDILLO et al., 2014), the main of which are gallic acid, kaempferol, quercetin and isorhamnetin (DUTRA et al., 2017; MACEDO et al., 2019). Thanks to their important antioxidant effects, phenolic compounds are beneficial to human health; they can in fact act as potential agents to prevent and treat diseases related to the oxidative stress and even to control cancer (INSANG et al., 2022), in addition to having proven antibiotic, antiallergic, anti-inflammatory and photochemical protection effects (AGUDELO et al., 2017). In addition, they can be used as substitutes for synthetic antioxidants as well as to produce functional foods, drugs and cosmetics (SHAVANDI et al., 2018; RENARD, 2018).

The main by-products of fruit processing are peels and seeds, whose extracts contain a considerable amount of valuable substances with potential application in food, cosmetic and pharmaceutical industries (SZABO et al., 2018; BEN-OTHMAN; JÕUDU; BHAT, 2020). Compared to other extraction methods, ultrasound assisted extraction stands out, because it is a simple, green and low cost process that uses acoustic energy to improve the release and diffusion of target compounds from various matrices, makes less use of solvents and requires lower temperatures and shorter extraction time (REZENDE; NOGUEIRA; NARAIN; 2017; CALDAS et al., 2018; GUANDALINI et al., 2019). There are numerous limitations in the application of these extracts due to the instability of bioactive compounds under conditions of high temperature and presence of oxygen, light and enzymes, as well as pH variations (RIBEIRO; ESTEVINHO; ROCHA, 2019). These bottlenecks can be overcome by microencapsulation techniques, which are capable of increasing the stability of these compounds by protecting them from environmental adverse effects thanks to the incorporation of a protective matrix (LEE; CHANG, 2020; AGUILERA-CHÁVEZ et al., 2022).

Among them, spray-drying, or atomization, is the most popular microencapsulation method (PUDZIUVELYTE et al., 2019; ZHANG et al., 2020). This

technique, which consists of transforming a fluid suspension into dry particles, is widely used to encapsulate heat-sensitive food ingredients, such as bioactive compounds, using an encapsulating agent that acts as a coating material (ZANONI et al., 2020; INSANG et al., 2022; AGUILERA-CHÁVEZ et al., 2022). Commonly used encapsulating agents are biopolymers such as maltodextrin with different dextrose equivalents and arabic gum. Variations in the quantity and type of coating agent result in different encapsulation efficiencies and in powders with different physical properties and (SHISHIR & CHEN, 2017).

The need for environmental protection, which has boosted the search for a better use of raw materials and waste, and the growing global interest in emerging extraction technologies justify the use of ciriguela waste to produce phenolic compounds-rich microencapsulated extracts. Given the above, the main objective of the present work was to study the influence of temperature, feed flow rate and ratio of encapsulating agents (maltodextrin and gum arabic) on the microencapsulation by spray-drying of ciriguela waste extracts prepared by ultrasound-assisted extraction. It was also compared the TPC stability of the spray-dried extract with that of a control powder prepared by freeze-drying over 90-day storage at different temperatures (7 and 25 °C), for its possible use as a functional ingredient in food, cosmetic and pharmaceutical applications.

2. Materials and Methods

Materials

Ciriguela fruits were produced in the state of Paraíba (07° 09' S 36º 49' W). Ciriguela pulp by-products (peel and seed) were provided, after pulp extraction, by a frozen fruit pulp factory located in João Pessoa, PB, Brazil. After manual separation, 50 kg of ciriguela by-products yielded approximately 11 kg of ciriguela peel.

Chemicals

All chemicals used in this study were obtained from Sigma-Aldrich (St. Louis, MI, USA) or Merck (Darmstadt, Germany).

Preparation of ciriguela peel flour (CPF)

Ciriguela peel was subjected to drying at 60 °C for 24 h (CALDAS et al., 2018)

in an oven with air circulation and renewal (Model MA035/5, Marconi, Piracicaba, SP, Brazil) until reaching moisture below 10%. Then they were ground in a multipurpose mill (model TE 631/2, Tecnal, Piracicaba, SP, Brazil) and sieved through a 40-mesh (425 μm) screen. The resulting ciriguela peel flour (CPF) was stored in low-density 140-μm thick polyethylene bags, wrapped with laminated paper, and frozen to -20 °C for later analyses.

Physicochemical and chemical characterization of ciriguela residue in natura and ciriguela peel flour

Soluble solids were determined with a digital refractometer (model r^2i300, Reichert, Depew, NY, USA) and expressed in °Brix. The pH was analyzed using a pH-meter (HANNA, model HI 2210). The water activity (a_w) was determined with a water activity meter (Decagon 4TE, Aqualab, Pullman, WA, USA) at 25°C. The moisture content was determined on an infrared balance (model ID50, Marte Científica, São Paulo, SP, Brazil) at 105 ºC, and the results were expressed in %. Titrable acidity was determined titrimetrically, and the results were expressed in g of citric acid/100g CPF (AOAC, 2016).

Determination of total phenolic compounds in *in natura* ciriguela residue and ciriguela peel flour

Ten g of CPF and 10 g ciriguela residue were separately extracted in 40 mL of solvent [80 % (v/v) ethanol-water acidified with 0.1 % (v/v) hydrochloric acid] by using a dynamic maceration, brought to room temperature (25ºC) and kept under stirring for 1 h. After extraction, suspended solids were removed by filtration through qualitative filter paper and the extracts obtained were stored at -22°C until further analysis.

The content of total phenolic compounds (TPC) in both *in natura* ciriguela residue and CPF was determined on a spectrophotometer (model UV-1650PC, Shimadzu, São Paulo/Brazil) at 725 nm using Folin-Ciocalteu reagent, according to the methodology described by Wettasinghe & Shahidi (1999). Briefly, 0.5 mL of each sample were incubated in a test tube with 8.0 mL of distilled water and 0.5 mL of Folin-Ciocalteu reagent. After 3 min of reaction, 1.0 mL of sodium carbonate solution was added, and the mixture was left to react for 60 min in the dark. The TPC content was calculated using a standard curve prepared from aqueous gallic acid solutions (0.1-1.0

mg/mL^{-1}), and the results were expressed in mg of gallic acid equivalents (GAE) g^{-1} of CRF.

Ultrasound-assisted extraction

Ten g of CRF with 40 mL of solvent [80 % (v/v) ethanol-water acidified with 0.1 % (v/v) hydrochloric acid] were placed in a 100-mL beaker and subjected to the action of a ultrasonic probe (model QR1000 Eco-sonic, Ultronique, Sao Paulo, SP, Brazil), using 1000 W power, 20 kHz frequency and 15 min exposure time (Silva Júnior et al., 2021). The extracts obtained were filtered and kept in the absence of light at -20 °C for later analyses.

Microencapsulation of ciringuela peel flour extracts

Spray-drying

Microencapsulation by atomization was performed in a spray-dryer (model MSD 1.0, Labmaq do Brasil, Ribeirão Preto, SP, Brazil). The carrier agents used were maltodextrin 10DE (Ingedion, Mogi-Guaçu, SP, Brazil) and gum arabic (Dinâmica Química Contemporânea, Indaiatuba, SP, Brazil). Extracts together with the encapsulating agent formulation were homogenized in Turrax (model TE-102, Tecnal – Piracicaba, São Paulo/Brazil) using a speed of 14.000 rpm for 5 minutes. The content of total solids in the suspension (wall material plus extract) was fixed at 30%, and atomization was performed using 1.2 mm diameter injector nozzle, 30 m^3 h^{-1} air flow rate and 0.6 bar air pressure.

Runs were carried out according to a 2^3-full experimental design composed of 8 factorial points (levels ± 1) and 3 central points (level 0), totaling 11 runs (Table 1).

Temperature (*T*), ratio of encapsulating agents (*F*) and feed flow rate (*V*) were the independent variables, while moisture content, water activity, hygroscopicity, solubility, TPC content, encapsulation efficiency and chromatic parameters were the response variables. The data obtained were adjusted to Equation 1:

$$Y = \beta_0 + \beta_1 T + \beta_2 F + \beta_3 V + \beta_4 TF + \beta_5 TV + \beta_6 FV + \beta_7 TFV \quad (1)$$

where Y is the response, β_0 is the constant regression coefficient, β_1, β_2 and β_3 are the linear coefficients, T, F and V are the independent variables, and β_4, β_5, β_6 and β_7 are the coefficients of the interaction effects TF, TV, FV and TFV, respectively.

Table 1. Matrix of the experimental design used for microencapsulation by spray-drying of ciriguela residue flour extract, with indication of the coded and real levels of the independent variables. M = maltodextrin; GA = gum arabic.

Run	Temperature (°C)	Ratio of encapsulating agents (%)	Feed flow rate (mL min^{-1})
1	-1 (130)	-1 (0% M / 100% GA)	-1 (0.40)
2	+1(170)	-1 (0% M / 100% GA)	-1 (0.40)
3	-1 (130)	+1 (100% M / 0% GA)	-1 (0.40)
4	+1 (170)	+1 (100% M / 0% GA)	-1 (0.40)
5	-1 (130)	-1 (0% M / 100% GA)	+1 (0.80)
6	+1 (170)	-1 (0% M / 100% GA)	+1 (0.80)
7	-1 (130)	+1 (100% M / 0% GA)	+1 (0.80)
8	+1 (170)	+1 (100% M / 0% GA)	+1 (0.80)
9	0 (150)	0 (50% M / 50% GA)	0 (0.60)
10	0 (150)	0 (50% M / 50% GA)	0 (0.60)
11	0 (150)	0 (50% M / 50% GA)	0 (0.60)

Freeze-drying

Microencapsulation by freeze-drying, used as a control, was performed for 48 h in a lyophilizer (model Alpha 1-4 LD Plus, Martin Christ, Osterode am Harz, Germany) at -80 °C and 0.28 mbar chamber pressure, using the optimum encapsulating agents formulation established for microencapsulation by spray-drying.

Analysis of extracts microencapsulated by spray-drying and freeze-drying

Moisture content, water activity and total phenolic compounds content

These characteristics of the microencapsulated extracts were determined by the same methodologies used for *in natura* ciriguela residue and CPF.

Hygroscopicity

The hygroscopicity of microencapsulated extracts was determined according to the methodology described by Cai and Corke (2000) with some modifications. Briefly, one g samples of each microencapsulated extract were placed at 25 °C in an airtight container containing a saturated NaCl solution (75.29% relative humidity) and weighed after one week. Hygroscopicity was expressed in g of moisture absorbed per 100 g of sample dry mass (g/100g).

Solubility

The solubility in water of microencapsulated extracts was determined according to the methodology reported by Cano-Chauca et al. (2005). To this purpose, 1.0 g samples of each powder were suspended in 100 mL of distilled water, stirred for 5 min in a magnetic stirrer (model 752, Fisatom, São Paulo, SP, Brazil) and centrifuged at 3000 rpm (1800 × *g*) for 5 min in a centrifuge (model CT-6000R, Cientec, Belo Horizonte, MG, Brazil). A 25-mL supernatant aliquot was placed in a pre-weighed sterilized Petri dish and kept at 105 ºC for 5 h in oven. The plate was then weighed on an analytical balance, and the solubility determined by weight difference.

Chromatic parameters

The chromatic parameters of microencapsulated extracts were evaluated with a colorimeter (model CR 400, Konica Minolta, Sensing Inc., Osaka, Japan), using the color standards of the Commission Internationale de L'Eclairage (CIELab) system, namely, luminosity (L^*) ranging from white (100) to black (0), intensity of the green ($-a^*$) to red ($+a^*$) component of light, and intensity of the blue ($-b^*$) to yellow ($+b^*$) component.

The variation in color (ΔE^*) compared to the *in natura* extract was calculated by Equation (2) (CAI & CORKE, 2000):

$$\Delta E^* = \sqrt{(L^* - L_0)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2} \quad (2)$$

where L_0^* and L^*: are the luminosities of the samples of the free extract and the reconstituted microencapsulated extract, respectively; a_0^* and a^*: are the red to green color intensities of the free extract and reconstituted microencapsulated extract samples, respectively; b_0^* and b^*: are the intensities of the yellow to blue color of the samples of the free extract and the reconstituted microencapsulated extract, respectively.

Encapsulation efficiency

The phenolics contents in microencapsules (TMPC) and on microcapsules surface (SMPC) were determined spectrophotometrically at 725 nm according to Saénz et al. (2009), after reaction with the Folin-Ciocalteu reagent and using a gallic acid standard curve (WETTASINGHE & SHAHIDI, 1999). The results were expressed in mg of gallic acid equivalents per g of microcapsules (mg GAE/g^{-1}).

The microencapsulation efficiency (*ME*) was calculated by Equation (3) according to Mahdavi et al. (2016):

$$ME\ (\%) = \frac{\mathrm{TMPC} - \mathrm{SMPC}}{\mathrm{TMPC}} \times 100 \qquad (3)$$

Apparent density

The apparent density of microcapsules (ρ_{ap}) was determined according to the procedure described by Barbosa-Canovas and Juliano (2005) and Caparino et al. (2012), with some modifications. Two g of sample were transferred to a 10-mL graduated test tube, where the powder was compacted by beating it 50 times on the bench. ρ_{ap}, expressed in g/mL, was calculated according to Equation (4):

$$\rho_{ap} = m/V \qquad (4)$$

where m is the sample mass (g) and V the total volume occupied by the powder in the tube (mL).

Absolute density

The absolute density (ρ_{abs}) was determined at 25 °C by means of a pycnometer provided with thermometer according to the methodology proposed by Caparino et al. (2012) and expressed in g mL^{-1}.

Intragranular porosity

The intragranular porosity (ε) was calculated according to Caparino et al. (2012) using Equation (5):

$$\varepsilon = 1 - \frac{\rho_{ap}}{\rho_{abs}} \quad (5)$$

DPPH· scavenging capacity

The 1,1-diphenyl-2-picrylhydrazyl radical (DPPH·) scavenging capacity of microcapsules was assessed according to the method described by Brand-Williams et al. (1995) and modified by Sanchez-Moreno et al. (1998). The extract was diluted up to three different TPC concentrations by its addition to a 0.1 M DPPH· solution in methanol. The absorbance at 517 nm was monitored with a spectrophotometer (model UV-1650PC, Shimadzu, São Paulo, SP, Brazil) until the reaction reached a plateau. The results were expressed according to Ramadan et al. (2003). The inhibition percentage (IC_{50}), i.e., the sample concentration needed to inhibit the DPPH• radical formation by 50%, was obtained according to Equation (6):

$$\text{DPPH\%} = \frac{A_{DPPH} - A_S}{A_{DPPH}} \times 100 \quad (6)$$

where A_S is the absorbance of the sample suspension and A_{DPPH} is the absorbance of the DPPH solution.

The sample concentration providing IC_{50} was calculated by interpolation from the graph of radical-scavenging activity percentage against sample concentration.

Ferric reducing antioxidant power

The ferric reducing antioxidant power (FRAP) of microcapsules was determined by monitoring the absorbance at 593 nm (Thaipong et al., 2006), and the results were expressed as µmol of ferrous equivalent per g of powder (µmol Fe^{2+} g^{-1}).

Profile of phenolic compounds by HPLC-DAD

One g samples of microencapsulated extracts were added to 10 mL of 6.0 M HCl in methanol and submitted for 30 min to extraction under ultrasonication at 25 °C and 40 kHz (model USC-1800, Unique, Indaiatuba, SP, Brazil). The extract was then centrifuged at 3000 × *g* for 20 min (model SL-701, Solab, Piracicaba, SP, Brazil). A 1.0-mL aliquot of the supernatant was filtered through a politetrafluoroetilene syringe filter with 0.45-µm pore diameter and used to identify and quantify the phenolic compounds by High Performance Liquid Chromatography (HPLC).

The methodology validated by Padilha et al. (2017), with adaptations by Dutra et

al. (2018) on gradient and runtime, was used to quantify individual phenolic compounds using an Agilent 1260 Infinity LC System (Agilent Technologies, Santa Clara, CA, USA) coupled to a diode arrangement detector (DAD) (model G1315D). Separation of phenolic compounds was performed in a Zorbax Eclipse Plus RP-C18 column (100 × 4.6 mm, 3.5 μm) and a Zorbax C18 precolumn (12.6 × 4.6 mm, 5 μm). Data collection and analyses were carried out using the software OpenLAB CDS ChemStation Edition (Agilent Technologies). After dilution in solvent A (0.1 M phosphoric acid solution, pH 2.0), samples were filtered through a membrane with 0.45-μm pore diameter (Millex Millipore, Barueri, SP, Brazil) and injected (20 μL). The oven temperature was 35 °C, the eluent a mixture of solvents A and B (metanol acidified with 0.5% phosphoric acid), and the eluent flow rate 0.8 mL min^{-1}. The gradient used in the separation was 0–5 min: 5% B, 5–14 min: 23% B, 14–30 min: 50% B, 30–33 min: 80% B. Detection of compounds was done at 220, 280, 320, 360 and 520 nm, and the identification and quantification by comparison with external standards. The results were expressed in μg g^{-1} dry weight.

Simulated gastrointestinal digestion

The gastrointestinal digestion simulation was performed, according to Rodrigues-Roque et al. (2013) and Dutra et al. (2017), mimicking the physiological gastrointestinal conditions, i.e., considering two sequential phases in stomach (gastric) and small intestine including dialysis (intestinal). Microencapsulated extract aliquots (50 mL) were mixed with 5 mL of simulated salivary solution (2.38 g Na_2HPO_4, 0.19 g KH_2PO_4, 8 g NaCl, and 200 U/L of α-amylase) in amber vials. After homogenization of the mixture for 10 min in a water bath at 37 ± 1 °C and 95 × *g*, the samples were acidified to pH 2.0 with 1.0 mL of a porcine pepsin solution (13 mg pepsin in 5 mL of 0.1 M HCl) and later incubated at 37 °C under agitation at 95 × *g* for 1 h to simulate gastric digestion. The mixture was then immediately cooled in an ice bath, and a 1.0-mL aliquot was stored at -18 °C, while the rest of the sample was submitted to intestinal digestion. Thirty cm long dialysis membrane segments were filled with 25 mL of a 0.5 M $NaHCO_3$ solution, which was used to titrate the gastric digestate at pH 7.5. Each 20-mL sample of gastric digestate was placed in a polyethylene tube, and a dialysis membrane was completely immersed until pH 5.0 was reached. Then, 5.0 mL of pancreatine (0.12 g) and bile salts solution (40 mg glycodeoxycholate, 25 mg taurodeoxycholate, 40 mg taurocholate in 1.0 mL of saline) were added to each tube.

The samples were incubated under agitation of 95 rpm at 37 °C for 2 h to complete the intestinal phase. Finally, the dialysis membrane was removed and rinsed with distilled water. The bioaccessible fraction of phenolic compounds transferred within the dialysis membrane was then analyzed by HPLC to determine the profile of residual phenolic compound after simulated gastrointestinal digestion.

Average diameter and particle size distribution

The average diameter and particle size distribution were determined on a laser diffraction analyzer (model S3500, Microtrac, Largo, FL, USA) coupled to a common bench ultrasound device to increase sample dispersibility. A small amount of sample was dispersed in isopropyl alcohol as a carrying fluid and subjected to particle size distribution readings. The average diameter was determined based on the average diameter of a sphere of the same volume (Brouckere diameter, D[4.3]), which is generally used to characterize powder particles.

Particle morphology

The morphology of microparticles was examined with a scanning electron microscope (SEM) (model Vega 3, Tescan, Brno, Czech Republic). The samples were fixed in metallic specimen holders (stubs) with a conventional electrically conductive double-sided adhesive tape, metallized with gold in a metallizer (model EM SCD500, Leica, Wetzlar, Germany) at a coating rate of 15 nm thickness for 80 seconds and a current of 40 mA, and examined with the above SEM operating at 10 kV. Image acquisition was performed using the XT microscope software.

Storage stability of microcapsules

Microcapsules were stored according to Nunes et al. (2015) with some modifications. The samples (1.0 g) were placed in flexible laminated packages (Zip lock), kept at two different temperatures (7 and 25 ± 1 ºC) and stored for 90 days. The TPC content was determined at 0, 15, 30, 45, 60, 75 and 90 days.

Statistical analysis

Experimental data were analyzed and presented as means plus standard deviations of triplicate measurements. Analysis of variance (ANOVA), *F*-test for lack of fit, determination of regression coefficients and generation of response surfaces were

done with the aid of Statistic 7.0 software (Statsoft, Tulsa, OK, USA) at 5% error probability.

3. Results and Discussion

Characterization of the in natura *ciriguela residue and ciriguela peel flour*

Table 2 lists the results of the physicochemical characterization of *in natura* ciriguela residue and ciriguela peel flour (CPF).

The waste drying process resulted in a total solids content in CPF within the range found by other authors for flours of different fruit residues (ALBUQUERQUE et al., 2016; REIS et al., 2017). The pH values of both *in natura* ciriguela residue and CPF are in the range of acid foods, which suggests inhibition of the growth of most pathogenic and deteriorating microorganisms. This value is in agreement with that reported by Albuquerque et al. (2016) (3.17) for ciriguela whole flour. The water activity (a_w) of CPF (0.178 ± 0.004) was much lower than that of *in natura* residue, which indicates that it can be considered microbiologically safe (LEONG et al., 2011).

Table 2. Physicochemical characterization of the *in natura* ciriguela residue and the ciriguela peel flour (CPF).

Parameter	*In natura* residue	CPF
Soluble solids (ºBrix)	0.90 ± 0.01	4.63 ± 0.15
pH	3.86 ± 0.02	3.79 ± 0.15
Water activity (a_w)	0.983 ± 0.001	0.178 ± 0.004
Titratable acidity (g/100g citric acid)	0.51 ± 0.04	0.93 ± 0.01
Moisture content (%)	69.57 ± 2.26	5.83 ± 0.15
Total phenolic compounds (mg GAE.g^{-1})	11.60 ± 0.20	25.97 ± 0.42

*Values are means ± standard deviation (n = 3). Different letters in the same column indicate significant differences among powders ($p < 0.05$). GAE = gallic acid equivalents.

Experimental design of ciriguela peel extract microencapsulation

Table 3 shows the results of the quality parameters (water activity, moisture content, hygroscopicity and solubility) of the CPFs prepared by spray-drying according to the experimental design shown in Table 1.

Table 3. Analyses of ciriguela peel flours prepared by spray-drying according to the experimental design shown in Table 1.

Run	Water activity (a_w)	Moisture content (%)	Hygroscopicity (g/100g)	Solubility (%)	*ME* (%)	TPC (mg GAE g^{-1} powder)
1	$0.207^{bcd} \pm 0.004$	$4.85^{abc} \pm 0.17$	$13.99^{b} \pm 0.28$	$86.43^{b} \pm 0.91$	$99.14^{ab} \pm 0.07$	$385.91^{c} \pm 1.13$
2	$0.183^{e} \pm 0.003$	$5.03^{ab} \pm 0.04$	$12.16^{de} \pm 0.22$	$87.84^{ab} \pm 1.76$	$99.84^{a} \pm 0.02$	$370.95^{d} \pm 1.42$
3	$0.225^{ab} \pm 0.001$	$4.23^{cde} \pm 0.10$	$11.20^{e} \pm 0.10$	$88.93^{ab} \pm 0.21$	$93.47^{f} \pm 0.44$	$190.45^{j} \pm 0.56$
4	$0.200^{cde} \pm 0.009$	$3.16^{f} \pm 0.13$	$11.73^{de} \pm 0.08$	$92.20^{a} \pm 0.46$	$76.83^{g} \pm 0.76$	$218.48^{h} \pm 1.99$
5	$0.188^{de} \pm 0.007$	$5.58^{a} \pm 0.21$	$15.24^{a} \pm 0.13$	$89.79^{ab} \pm 2.00$	$98.40^{bc} \pm 0.09$	$454.66^{a} \pm 2.60$
6	$0.235^{a} \pm 0.002$	$4.53^{bcd} \pm 0.22$	$14.92^{ab} \pm 0.24$	$88.77^{ab} \pm 2.22$	$98.35^{bc} \pm 0.09$	$432.69^{b} \pm 1.42$
7	$0.155^{f} \pm 0.002$	$3.65^{ef} \pm 0.29$	$14.15^{ab} \pm 0.39$	$89.39^{ab} \pm 2.14$	$95.53^{e} \pm 0.22$	$219.24^{h} \pm 1.42$
8	$0.225^{ab} \pm 0.001$	$4.07^{de} \pm 0.26$	$12.30^{de} \pm 0.88$	$88.47^{ab} \pm 0.99$	$98.23^{c} \pm 0.12$	$201.82^{i} \pm 0.56$
9	$0.218^{abc} \pm 0.016$	$4.19^{cde} \pm 0.26$	$12.57^{d} \pm 0.13$	$88.02^{ab} \pm 0.23$	$97.13^{d} \pm 0.04$	$279.66^{g} \pm 0.98$
10	$0.210^{bc} \pm 0.008$	$4.46^{bcd} \pm 0.37$	$13.80^{bc} \pm 0.52$	$89.49^{ab} \pm 2.00$	$95.54^{e} \pm 0.06$	$290.27^{f} \pm 1.42$
11	$0.204^{bcde} \pm 0.010$	$4.61^{bcd} \pm 0.45$	$12.65^{cd} \pm 0.65$	$89.19^{ab} \pm 1.93$	$97.68^{cd} \pm 0.02$	$296.89^{e} \pm 2.15$

*Values are means ± standard deviation (n = 3). Different letters in the same column indicate significant differences among powders ($p < 0.05$). *ME* = microencapsulation efficiency; TPC = total phenolic compounds content; GAE = gallic acid equivalents.

The results of analysis of variance (ANOVA) applied to linear models (Equation 1) of each response variable, omitting the non-significant terms, are gathered in Table 4.

Table 4. Results of the analysis of variance (ANOVA) applied to linear models of response variables.

Source	Water activity	Moisture content (%)	Hygroscopicity (g/100g)	Solubility (%)	*ME* (%)	TPC (mg GAE/g of powder)
Regression	0.014702^{*}	12.57281^{*}	49.46205^{*}	57.8693	1219.093	263356.6
Residual	0.002213	1.89926	7.46184	56.9365	30.531	4027.7
Lack of fit	0.000651^{*}	0.17479^{ns}	0.90142^{ns}	1.1931^{ns}	21.391^{*}	3261.4^{*}
Pure Error	0.001562^{ns}	1.72447^{ns}	6.56042^{ns}	56.8998^{ns}	9.140^{ns}	506.3^{ns}
Total	0.016915	14.47207	56.92389	114.8058	1249.624	267384.3
R-Squared	0.87	0.87	0.87	0.50	0.97	0.98

ns: Not significant ($p > 0.05$). *Significant at ($p < 0.05$); Df = degrees of freedom; *ME* = microencapsulation efficiency; TPC = total phenolic compounds contents; GAE = gallic acid equivalents.

As is known, a_w, moisture content and hygroscopicity are important characteristics for the stability and storage of any powder, while solubility is associated with its eventual reconstitution. All a_w values of spray-drying microencapsulated extracts (0.155-0.235) (Table 3) were lower than the threshold limit (0.3) below which powders can be considered stable (DAMODARAN; PARKIN, 2017) and resistant to

the attack of both spoilage microorganisms and enzymes responsible for lipid oxidation (JANISZEWSKA-TURAK et al., 2017). a_w values close to those obtained in this study were reported for different bioactive compounds-rich microencapsulated extracts (ARCHAINA et al., 2017; KUCK; NOREÑA, 2016; NGUYEM et al., 2021; REZENDE et al., 2018; ZHANG et al., 2020).

This response was significantly influenced by inlet air temperature (*T*), interaction between temperature and feed flow rate (*TV*) and interaction between the ratio of encapsulating agents and feed flow rate (*FV*), according to Equation (7):

$$a_w = 0.205 + 0.008T + 0.020TV - 0.009FV \quad (7)$$

The higher the temperature, the lower the a_w value of powder extracts, which indicates its positive effect on this response similar to that observed by Tulek et al. (2020) for atomized lemongrass extract. The higher temperature, the lower the aw value of the powdered extracts, which indicates their positive effect on this response, similar to that observed by Tulek et al. (2020) for atomized extract of lemongrass. When using a high feed flow rate of (0.80 mL min-1) and combined with 100% gum arabic as an encapsulating agent, the extracts showed lower $a_{W,}$ probably due not only to the influence of the *T*x*V* and *F*x*V* binary ($p < 0.05$) (*Figures 1S and 2S of the Supplementary Material*), but also the ability of gum arabic to incorporate water molecules thanks to the presence of proteins and hydrophilic groups in its composition (ZHANG et al., 2020). Similarly, Bednarska & Janiszewska-Trak (2020) and Janiszewska-Tuk et al. (2017) observed that the greater the addition of gum arabic, the lower the aw values of chokeberry and carrot powder juices, respectively.

Moisture contents in the 1–6% range are sought by industry to ensure stability of powder products during storage (DAMODARAN; PARKIN, 2017). All moisture contents obtained in this study, varying from 3.16 to 5.58% (Table 3), fell within this range and were close to those reported in several studies for different atomized fruit extracts or by-products, such as cagaita (*Eugenia dysentrica* DC) (DAZA et al., 2016), grape (*Vitis labrusca var*. Bordo) skin (KUCK; NOREÑA, 2016) and grape pomace (TSALI; GOULA, 2018), acerola residue (REZENDE et al., 2018), pineapple peel (LOURENÇO et al., 2020), maca leaf (LEE; CHANG, 2020), cranberry juice (ZHANG et al., 2020), cocoa pod husk (NGUYEN; TRA; LE, 2021), and mulberry (*Morus alba* L.) leaf (INSANG et al., 2022).

Moisture content was significantly influenced by the linear effects of *T* and *F* as well as the ternary interaction between *T*, *F* and *V* ($p < 0.05$) (Tables 3 and 4), according to Equation (8):

$$\text{Moisture content} = 4.39 - 0.18T - 0.61F + 0.33TFV \quad (8)$$

ANOVA showed a coefficient of determination (R^2) of 0.87 (Table 4), indicating that fitting of experimental data to this model was more than satisfactory. In particular, the decrease in microcapsule moisture content resulting from an increase in air inlet temperature (*Figures 3S and 4S of the Supplementary Material*). The temperature had a negative effect on the moisture of the powders, higher inlet air temperature (170 °C) produced extracts in powders with lower moisture contents, probably due to different drying rates between the droplets of the feed solution and the air of drying due to their different physical properties (LOURENÇO et al., 2020). The same negative effect of air temperature on moisture content has been reported for different phenolic compounds-rich atomized extracts (DAZA et al., 2016; LOURENÇO et al., 2020; SHAMAEI et al., 2017; TSALI & GOULA, 2018). According to Kaderides et al. (2015), the higher the temperature difference between drying air and particles, the higher the heat transfer rate to the particles, thus causing a driving force for moisture removal. The powders produced with gum arabic as an encapsulating agent exhibited the highest moisture contents and (*Figure 3S of the Supplementary Material*), confirming the trend observed by Pudziulyte et al. (2019) for *Elsholtzia ciliata* essential oil microcapsules. According to Tran and Nguyen (2018), gum arabic has higher capacity of absorbing water from surrounding environments than maltodextrin.

The hygroscopicity of powders, varying from 11.20 to 15.24 g of water absorbed/100 g of sample (Table 3), was low, which promises to facilitate their conservation and preserve their color and content of bioactive compounds. This response variable was significantly influenced by *T*, *F*, *V* and ternary *T*x*F*x*V* interaction ($p < 0.05$) (Tables 3 and 4), according to Equation (9):

$$\text{Hygroscopicity} = 13.15 - 0.43T - 0.86F + 0.94V - 0.48TFV \quad (9)$$

Hygroscopicity values close to those of this study were reported for different spray-dried extracts (ARCHAINA et al., 2017; DAZA et al., 2016; KUCK; NOREÑA,

2016; REZENDE et al., 2018). More hygroscopic powders were produced when higher feed rates were used. This response was influenced mainly and positively by *V* and negatively by *F* (*Figure 5S of the Supplementary Material*). Similar results were obtained by Bednarska & Janiszewska-Trak (2020) for chokeberry juice powder.

Water solubility of atomized extracts, ranging from 86.43 to 92.20% (Table 3), fell within the solubility range reported for other atomized fruit extracts or by-products (ARCHAINA et al., 2017; LOURENÇO et al., 2020; PUDZIUVELYTE et al., 2019; REZENDE et al., 2018). It was significantly influenced by *F* and by the *F*x*V* and *T*x*V* binary interactions ($p < 0.05$), according to Equation (10):

$$\text{Solubility} = 88.96 + 0.77F - 0.82TV - 0.94FV \quad (10)$$

This model, however, was not predictive due to a too low R^2 value (0.5) (Table 4), so the effect of each variable on powders solubility were illustrated in the form of Pareto Graph (*Figure 7S of the Supplementary Material*). The maltodextrin/gum arabic ratio in the coating agents formulation had a positive effect on water solubility, in that, powders produced with maltodextrin were more soluble, although the solubility of all them was high (Figure 8S of the Supplementary Material). The high solubility of powders produced in this work can be related to the high solubility of the selected encapsulating agents (LABUSCHAGNE, 2018) as well as the product granulometry, in that, the lower the particles size, the greater the surface area available for hydration (KUCK; NORENA, 2016). As shown in Figure 9S (Supplementary Material), the most soluble microencapsulated extracts were those produced using the lowest feed flow rate and maltodextrin as a wall material.

The microencapsulation efficiency (*ME*) of atomized extracts ranged from 76.83 to 99.84% (Table 3), indicating that the selected formulation of encapsulating agents was very efficient in protecting phenolic compounds. This response was significantly influenced by all independent variables and their combinations ($p < 0.05$) according to Equation (11):

$$ME = 95.46 - 1.66T - 3.95F + 2.65V - 1.82TF + 2.32TV + 3.21FV + 2.51TFV \quad (11)$$

The model had statistical and predictive significance with R^2 of 0.97. When the value of pure error is low as in this case, i.e., the reproducibility is very good, the lack

of fit, even though significant (Table 4), is a false result due to the fact that the *F*-calculated value is high because of the very low denominator value. This model was validated through ANOVA before building the response surface charts illustrated in Figure 1.

The atomized extracts produced with gum arabic showed the highest *ME* values, in agreement with the results obtained by Pudziulyte et al. (2019) for microcapsules of *E. ciliata* essential oil. It has been reported that *ME* of microencapsulated extracts would be related to the combination of encapsulating agents used, which would be responsible for different filmogenic properties, keeping the active principle protected (KUCK; NORENÃ, 2016).

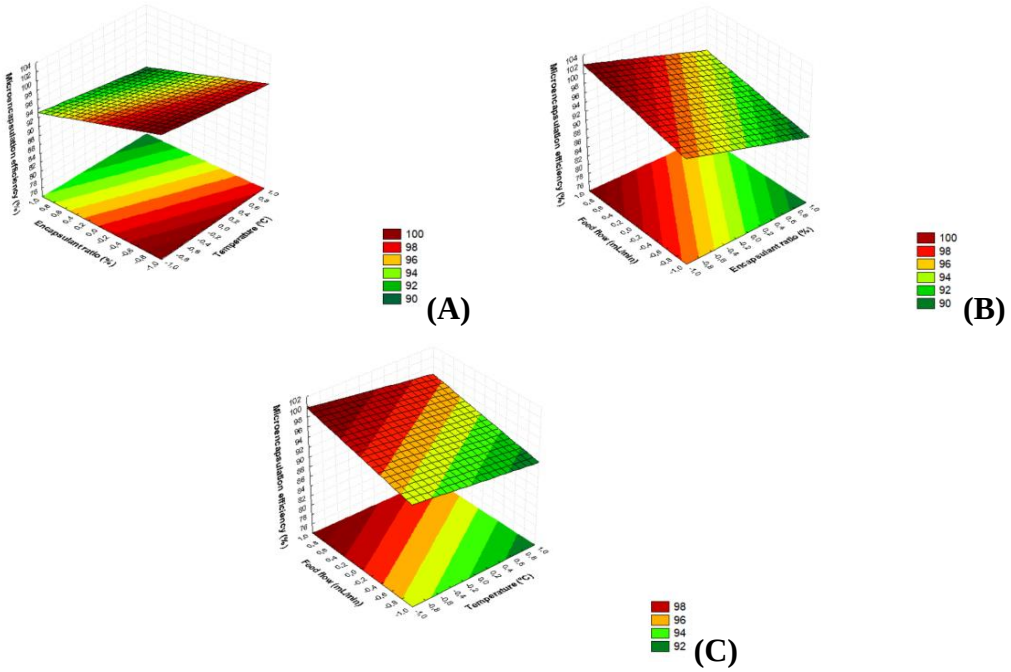


Figure 1. Response surfaces of the efficiency of ciriguela residue extracts encapsulated by spray-drying as a function of (a) temperature and ratio of encapsulating agents; (b) feed flow rate and ratio of encapsulating agents; and (c) feed flow rate and temperature.

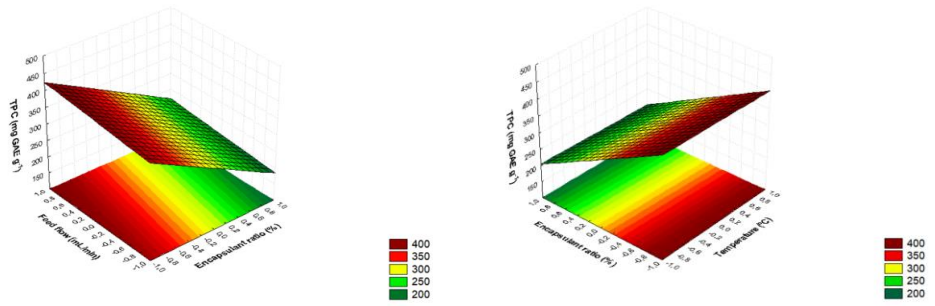
The TPC content of atomized extracts, which ranged from 190.45 to 454.66 mg GAE g^{-1} (Table 3), was significantly influenced by *F*, *V*, *TF*, *TV*, and *FV* (Table 4) according to Equation (12):

$$\text{TPC content} = 303.72 - 101.77F + 17.82V + 5.94TxF - 6.55TxV - 14.79FxV \quad (12)$$

The high R^2 value (0.98) compensates for the significant lack of fit for same reasons as for *ME* (Table 4), indicating that the model has statistical and predictive

significance. The influence of independent variables on this response is illustrated by the response surfaces in Figure 2.

Since the ratio of coating agents in the encapsulating formulation was the variable that most influenced this response, followed by the *FV* interaction, the highest TPC contents were obtained using gum arabic (Figures 2A and B). Similar result was reported for spray-drying of grape (*V. labrusca* var. Bordo) skin extract (KUCK; NOREÑA, 2016). This special gum arabic capacity of encapsulating TPC has been related to its structure, being a highly branched sugar heteropolymer with small protein content, which allows to protect these compounds mainly during the critical early phase (KUCK; NOREÑA, 2016; REZENDE et al., 2018). As a result, all the runs performed using the mixture of encapsulating agents (9, 10 and 11) also led to TPC contents higher than those obtained only with maltodextrin, similarly to what was observed by Rezende et al. (2018) for atomized acerola residue extract.



(A) **(B)**

Figure 2. Response surfaces of the total phenolic compounds (TPC) content of ciriguela residue extracts encapsulated by spray-drying as a function of (a) ratio of encapsulating agents and feed flow rate and (b) ratio of encapsulating agents and temperature.

Selection of the best conditions for ciriguela residue extract spray-drying and freeze-drying

According ANOVA applied to results from runs performed according to the above experimental design, the optimal conditions for microencapsulation by spray-drying of CPF extracts were a temperature of 150 °C, a feed flow rate of 0.80 L h^{-1} and 100% gum arabic as a coating agent. Microencapsulation by freeze-drying, used as a control, was performed with the same encapsulating agent. Table 5 lists the results of physicochemical parameters and antioxidant activity of ciriguela residue extracts microencapsulated by both drying methods.

ME, TPC content, antioxidant activity by the DPPH method, apparent density and intragranular porosity showed statistically significant differences ($p < 0.05$) between atomized and lyophilized extracts, while antioxidant activity by the FRAP method did not ($p > 0.05$) (Table 5). These results suggest the importance of using different methods for the safe and conclusive determination of antioxidant activity, as each method has its own specificities and acts better in a specific field (REZENDE et al., 2018). Higher values of *ME*, TPC content and antioxidant activity by DPPH were obtained for the spray-dried extract ($p < 0.05$). On the other hand, Ramírez et al. (2015), when studying the stability of freeze-dried and spray-dried fruits, observed greater retention of polyphenols in the former encapsulates.

Table 5. Physicochemical parameters and antioxidant activity of ciriguela residue extracts microencapsulated by spray-drying and freeze-drying.

Parameter	Spray-drying*	Freeze-drying*
TPC content (mg GAE g^{-1})	$486.82^{b} \pm 3.04$	$532.96^{a} \pm 0.58$
Microencapsulation efficiency (%)	$98.83^{a} \pm 0.07$	$88.76^{b} \pm 0.42$
DPPH (%)	$68.21^{a} \pm 0.59$	$48.84^{b} \pm 0.59$
FRAP (µmol Fe^{2+} g^{-1})	$4.826,48^{a} \pm 49.65$	$4.802,01^{a} \pm 23.41$
Moisture content (%)	$4.51^{a} \pm 0.12$	$4.35^{a} \pm 0.20$
Solubility (%)	$89.02^{a} \pm 1.37$	$86.37^{a} \pm 2.36$
Hygroscopicity (g 100g)	$14.83^{a} \pm 0.07$	$14.84^{a} \pm 0.30$
*L**	$89.73^{a} \pm 0.39$	$88.42^{b} \pm 0.38$
*a**	$-0.07^{a} \pm 0.03$	$-0,05^{a} \pm 0.03$
*b**	$13.07^{b} \pm 0.33$	$17,11^{a} \pm 0.36$
ΔE *	$55.04^{a} \pm 2.04$	$53.17^{a} \pm 1.67$
Apparent density (g mL^{-1})	$0.25^{b} \pm 0.01$	$0.31^{a} \pm 0.01$
Absolute density (g mL^{-1})	$1.06^{a} \pm 0.01$	$1.07^{a} \pm 0.01$
Intragranular porosity (%)	$70.44^{a} \pm 0.86$	$64.37^{b} \pm 0.95$

*Values are means ± standard deviation (n = 3). Different letters in the same column indicate significant differences among powders ($p < 0.05$). *ME* = microencapsulation efficiency; TPC = total phenolic compounds content; GAE = gallic acid equivalents; DPPH = antioxidant activity by the DPPH method; FRAP = antioxidant activity by the ferric reducing antioxidant power method; *L** = luminosity; *a** = intensity of green/red component of light; *b** = intensity of yellow/blue component of light; ΔE*= difference in color.

Luminosity (*L**) values were close to 90.00 (Table 5), indicating that atomized and lyophilized extracts had color close to white, similarly to what was observed for atomized cagaita extract (DAZA et al., 2016). According to Comunian et al. (2011), these results are due to the dilution effect of the white encapsulating agents. Although microencapsulation by spray-dring, due to high inlet air temperature, can lead to darkening reactions responsible for color loss (CALISKAN; DIRIM, 2016), the

intensity of green/red component of light (a^*) and difference in color (ΔE^*) showed no significant difference between the two extracts, unlike the intensity of yellow/blue component of light (b^*) ($p < 0.05$). Taking the colorimetric parameters as a whole (L^*, a^*, b^*), it can be concluded that the CPF extract microcapsules can be considered of greenish-yellow color like those obtained from mulberry (*M. alba* L.) leaf (INSANG et al., 2022).

Physical parameters showed no significant differences between atomized and lyophilized extracts ($p > 0.05$), except for apparent density and intragranular porosity that were 24% higher (0.31 ± 0.01 g mL^{-1}) and 8.6% lower ($64.37 \pm 0.95\%$), respectively, for the lyophilized extract (Table 5). It is noteworthy that these characteristics play an important role in controlling the degree of rehydration and reconstitution of powders.

Phenolics profiles in liquid and microencapsulated extracts and during simulated gastrointestinal digestion

The profile of phenolic compounds was investigated by HPLC-DAD in both the liquid extract and the microcapsules prepared by spray-drying and freeze-drying using 100% gum arabic as a coating agent (Table 6). Phenolic acids, flavanols and flavonols were identified as the four major groups, while flavanones, stilbenes and anthocyanins were detected in lower amounts. Although the contents of identified phenolics varied statistically between the two powders ($p < 0.05$), as expected, their qualitative profile (Table 6) was relatively similar to that observed for frozen ciriguela pulp (DUTRA et al., 2017) and ciriguela bark (ENGELS et al., 2012; SILVA et al., 2016). This shows that after microencapsulation of ciriguela residue extract, the microcapsules still had phenolic compounds with biological activities of interest such as antioxidant, antimicrobial and anti-inflammatory attributed to the various phenolic compounds found (DUTRA et al., 2017; KANG et al., 2018).

Table 6. Phenolics profile in liquid (control), spray-dried and freeze-dried ciriguela residue extracts.

Phenolic compound (μg g^{-1})	Retention time (min)	Liquid extract (control)	Spray-dried extract	Freeze-dried extract
Phenolic acids				
trans-Caftaric acid	13.4	$14.09^{a} \pm 0.26$	ND	ND
Chlorogenic acid	14.6	$228.31^{a} \pm 5.67$	$40.09^{b} \pm 1.53$	$17.72^{c} \pm 0.17$
Caffeic acid	17.1	$18.01^{a} \pm 3.03$	ND	ND
p-Coumaric acid	23.3	$15.45^{a} \pm 0.62$	ND	ND
Flavanols				
Procyanidin B1	12.6	$5.96^{b} \pm 0.12$	ND	$16.74^{a} \pm 0.22$
Procyanidin B2	16.9	$15.47^{a} \pm 0.37$	ND	ND
Catechin	14.6	$60.95^{b} \pm 0.93$	$16.59^{c} \pm 0.07$	$93.94^{a} \pm 0.67$
Epicatechin	19.3	$105.71^{a} \pm 2.02$	$22.40^{b} \pm 0.06$	ND
Epigallocatechin gallate	20.2	$28.96^{b} \pm 0.48$	$53.62^{a} \pm 0.99$	ND
Epicatechin gallate	25.3	$228.63^{a} \pm 12.78$	$71.23^{b} \pm 0.41$	$41.85^{c} \pm 1.02$
Procyanidin A2	26.4	$80.40^{a} \pm 4.70$	$83.70^{a} \pm 4.28$	$35.08^{b} \pm 0.55$
Flavonols				
Myricetin	23.9	$65.85^{a} \pm 0.24$	$21.60^{b} \pm 0.52$	$17.15^{b} \pm 0.40$
Rutin	25.3	$342.59^{a} \pm 45.08$	$82.69^{b} \pm 0.70$	$54.66^{c} \pm 0.35$
Quercetin	25.7	$181.02^{a} \pm 6.28$	$11.75^{c} \pm 0.08$	$26.77^{b} \pm 0.90$
Kaempferol	27.0	$5.32^{c} \pm 0.02$	$12.84^{b} \pm 0.26$	$70.46^{a} \pm 1.33$
Isorhamnetin	27.9	ND	$54.78^{a} \pm 0.54$	ND
Flavanones				
Hesperidin	27.1	$92.48^{a} \pm 5.09$	$80.34^{b} \pm 2.07$	ND
Stilbenes				
trans-Resveratrol	29.2	$26.38^{a} \pm 0.86$	ND	ND
Anthocyanins				
Petunidin 3-glucoside	24.7	$7.19^{a} \pm 1.45$	ND	ND

*The results are expressed as mean ± standard deviation (n = 3). Values expressed in μg g^{-1} dry matter. Means followed by the same letters in the same line do not differ by the Tukey's test at 5% error probability. ND – not detected.

Rutin (342.59 ± 45.08 μg g^{-1}), epicatequin gallate (228.63 ± 12.78 μg g^{-1}), chlorogenic acid (228.31 ± 5.67 μg g^{-1}) and quercetin (181.02 ± 6.28 μg g^{-1}) were the most abundant phenolic compounds in the CPF liquid extract. Chlorogenic acid was the only phenolic acid found in spray-dried (40.09 ± 1.53 μg g^{-1}) and freeze-dried (17.72 ± 0.17 μg g^{-1}) extracts. Catechin content was significantly higher ($p < 0.05$) in the lyophilized extract (93.94 ± 0.67 μg g^{-1}) compared to both liquid and atomized extracts (Table 6). Isorhamnetin was present only in the atomized sample, while epicatequin, epigallocatechin gallate and hesperidin were only detected in the free and atomized extracts. Rutin was the major flavonol in both liquid (342.59 ± 45.08 μg g^{-1}) and atomized (82.69 ± 0.70 μg g^{-1}) extracts, while kaempferol was in the lyophilized one (70.46 ± 1.33 μg g^{-1}). Santana Neto et al. (2022) observed similar phenolic acids' profle

to that of this study in extract ciriguela residue, and among the flavonoids identified, rutin had the highest level.

trans-Caftaric acid, caffeic acid, *p*-coumaric acid, *trans*-resveratrol and petunidin 3-glucoside were found only in liquid extract. In this regard, it has been reported that, when fruits are subjected to processing, including maceration, crushing, microencapsulation or freezing, oxidation and/or degradation of antioxidant compounds may occur (BARBOSA et al., 2016; BUNIOWSKA et al., 2017; DUTRA et al., 2017; TOMAS et al., 2015).

The contents of phenolic compounds recovered after each phase (oral, gastric and intestinal) of simulated gastrointestinal digestion of microencapsulated extracts are listed in Table 7. It is noteworthy that the higher this residual content, the greater the resistance of microcapsules to gastric conditions. The highest values were found after the gastric phase ($p < 0.05$), while the minor ones after the latter, i.e., the intestinal one. Similar result was reported for flour from persimmon (*Diospyros kaki*) fruit co-product during in vitro gastrointestinal digestion (GONZÁLEZ et al., 2018).

While in the post-gastric phase most phenolic compounds were identified, in the post-intestinal phase there was a significant reduction in the amount of compounds. This tendency may be related to digestion conditions, mainly due to changes in gastric pH (pH 2.0) and intestine (pH 7.5) (YUCETEPE; ALTIN; OZÇELIK, 2021). The acidic conditions of the gastric phase probably contributed to the release of the compounds.

During gastric digestion, several phenolic acids, flavanols and flavonols were detected, highlighting the significant phenolic content available for absorption. However more research is needed to investigate the dynamics of absorption of phenolic compounds in the stomach. The transition from gastric to intestinal digestion reduced the bioaccessibility of most compounds, but did not increase the bioaccessibility of procyanidin A2 from the atomized extract.

Regarding the microcapsule production method, freeze-drying ensured greater phenolic compound content than spray-drying, except for epigallocatechin gallate and quercetin. Most phenolic compounds were completely degraded after the gastric phase, except for epicatechin gallate and rutin in the freeze-dried extract, while procyanidin A2 was detected only after the intestinal phase in the spray-dried one. Finally, the highest concentrations of epicatechin gallate and rutin ($p < 0.05$) were detected after the gastric phase, similarly to what was observed for persimmon fruit co-product flour (GONZÁLEZ et al., 2018).

Table 7. Phenolic compounds contents (μg g^{-1}, mean values ± standard deviation, n = 3) obtained during simulated gastrointestinal digestion of spray-dried and freeze-dried ciriguela residue extracts.

Compound (μg g^{-1})	Sample	Phase		
		Oral	Gastric	Intestinal
Chlorogenic acid	Spray-dried	ND	36.06^{B} ± 2.39	ND
	Freeze-dried	ND	45.29^{A} ±0.32	ND
Procyanidin B1	Spray-dried	ND	11.80^{B} ± 0.91	ND
	Freeze-dried	ND	14.67^{A} ±0.46	ND
Catechin	Spray-dried	ND	32.99^{B} ± 0.95	ND
	Freeze-dried	ND	35.53^{A} ±0.02	ND
Epicatechin	Spray-dried	ND	11.22^{B} ± 0.22	ND
	Freeze-dried	ND	95.45^{A} ± 0.57	ND
Epigallocatechin gallate	Spray-dried	ND	29.49^{A} ± 0.26	ND
	Freeze-dried	ND	ND	ND
Epicatechin gallate	Spray-dried	33.10^{b} ± 0.57	50.69^{Ba} ± 0.98	ND
	Freeze-dried	ND	59.98^{Aa} ± 8.41	17.10^{Ab} ± 0.27
Procyanidin A2	Spray-dried	ND	ND	37.90 ± 1.66
	Freeze-dried	ND	ND	ND
Rutin	Spray-dried	23.61^{Bb} ± 0.20	68.74^{Ba} ± 1.97	ND
	Freeze-dried	28.74^{Ab} ± 0.64	93.98^{Aa} ± 2.00	21.24^{c} ± 0,16
Quercetin	Spray-dried	ND	66.53^{A} ± 3.17	ND
	Freeze-dried	ND	10.64^{B} ± 0.27	ND

ND: No detection. Different superscript lowercase letters on the same line indicate a statistically significant difference ($p < 0.05$) for the same compound obtained by the same microencapsulation method at different stages of gastrointestinal digestion. Different superscript capital letters in the same column indicate a statistically significant difference ($p < 0.05$) based on t-test, for the same compound at the same stage of gastrointestinal digestion obtained by different microencapsulation methods.

A total of three compounds were detected after the intestinal phase of digestion and six were not detected. This finding is consistent with several studies that found a considerable decrease in phenolic compounds after gastrointestinal digestion (GONZÁLEZ et al., 2018; PEANPARKDEE; BOROMPICHAICHARTKUL; IWAMOTO, 2021; NIGNPENSE et al., 2022). The loss of these compounds may have been caused by conditions in the intestinal environment that were unfavorable to its stability, such as alkaline pH, pancreatin, and bile secretions (PODIO et al., 2019). After the intestinal phase, the presence or absence of phenolic compounds revealed the variable chemical behavior of phenolic compounds. For example, quercetin, which is extracted in relatively large amounts during gastric digestion, is not detected after

intestinal digestion. A similar result was found in the study by Nignpense et al. (2022). This is consistent with evidence that quercetin has low solubility in alkaline media such as water and intestinal juice (GAO et al., 2009).

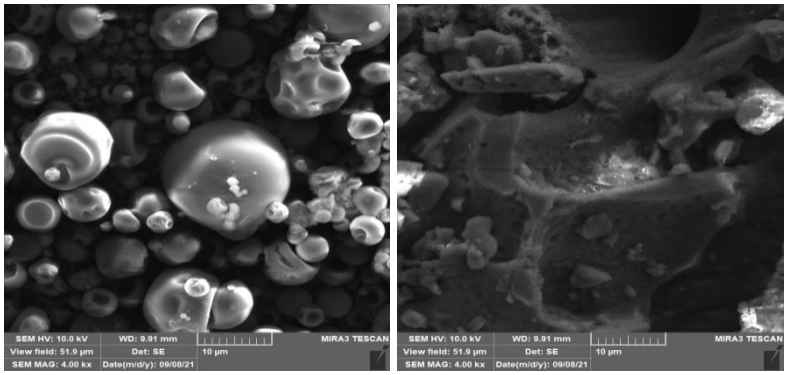
The chemical characteristics of phenolic compounds, such as solubility, hydrophobicity, molecular weight or even isomer configuration, are influencing their stability in the course of digestion (BARBA et al., 2017). The decrease of most phenolic compounds during in vitro digestion, regardless of the FRC extract microencapsulation method, may be related to the release of proteins and fibers by enzymatic degradation. Since both proteins and carbohydrates are able to interact with phenolic compounds and block their detection through spectrophotometric analysis (ALTIN et al., 2019; YUCETEPE; ALTIN; OZÇELIK, 2021). Changes in the simulated digestive environment's pH can convert anthocyanins and transform some phenolics into different structural formulas with various chemical properties (KIM et al., 2020).

Average diameter and particle size distribution

The particle size of powder extracts has been associated with important characteristics such as susceptibility to deterioration, fluidity, appearance and dispersibility (BOTREL et al., 2014). Particle size distribution graphs (Figure 10S of the Supplementary Material) allowed to calculate for atomized and lyophilized microcapsules average diameters (16.75 and 25.19 µm, respectively) within the values reported for spray-drying in general (10-100 µm) (FANG; BHANDARI, 2010) and for other microencapsulated natural products or by-products (FIGUEIREDO et al., 2020; REZENDE et al., 2018; NUNES et al., 2015; PANG et al., 2014). The largest size of freeze-dried particles compared to the spray-dried ones may have been due to the low process temperature as well as the lack of strength to break frozen drops or to change surface during drying (SAIKIA et al., 2015).

Particle morphology

Figure 3 shows the scanning electron micrographs of CPF extracts microencapsulated by spray-drying (a) and freeze-drying (b). Microcapsules prepared by freeze-drying had a more deformed and irregular shape, with extensive wrinkles and more toothed surface than the ones prepared by spray-drying, which had spherical shape, few deformations and a smooth surface, confirming the observations of other authors (NUNES et al., 2015; DAZA et al., 2016; TOLUN; ARTIK; ALTINTAS, 2020).



(a) **(b)**

Figure 3. Scanning electron micrographs of ciriguela peel extract microparticles prepared by (a) spray-drying and (b) freeze-drying.

According to Ballesteros et al. (2017), the quite different conditions of spray-drying and freeze-drying result in different morphology, shape and size of microparticles. Moreover, superficial imperfections, such as wrinkles or cracks, occur when there is slow film formation during droplet microencapsulation (RÉ, 1998). Also the type of encapsulating agent can influence the morphology of microcapsules. In fact, Bernstein & Noreña (2015) obtained similar particles with toothed surface using gum arabic, likely due to sudden moisture loss during microencapsulation (TOLUN; ARTIK; ALTINTAS, 2020). Even the deformations of microcapsules, i.e., irregular spherical shape, shrinks and wrinkles on their surface, may have been due to the use of arabic gum as an encapsulating agent (DAZA et al., 2016).

Storage stability of microcapsules

Microcapsules placed in flexible laminated packages were stored for 90 days at 7 ± 1 ° C, aiming at their use as an additive for low temperature stored products, and 25 ± 1 ° C, representing the room temperature. Figure 4 shows the stability of atomized and lyophilized microcapsules under these conditions in terms of ability to retain their TPC content over time.

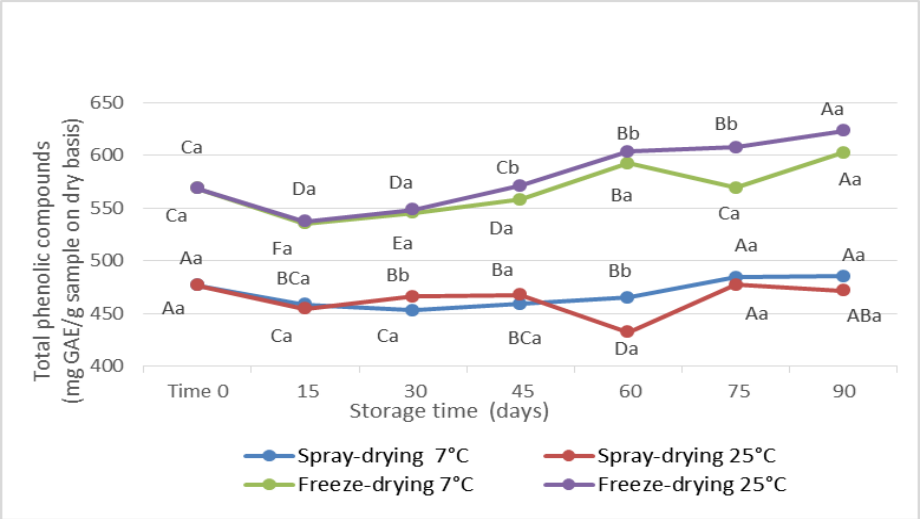


Figure 4. Stability analysis of atomized and lyophilized microcapsules of ciriguela residue extract stored at 7 and 25 °C for 90 days in terms of ability to retain phenolic compounds. Different capital letters indicate statistically significant differences over time for the same powder. Different lowercase letters indicate statistically significant differences between powders obtained by the same encapsulation method, at the same storage time and at different storage temperatures.

The freeze-dried microcapsules of CPF extract did not show any statistically significant difference in their TPC content (602.77-623.41 mg GAE g^{-1}) ($p > 0.05$) after 90 days compared to the beginning (568.86 ± 0.98 mg GAE g^{-1}), regardless of the storage temperature. The spray-dried powder extract started with 476.82 ± 2.04 mg GAE g^{-1}, and at the end of the stability at 7ºC it presented 485.34 ± 1.50 mg GAE g^{-1} and at 25ºC, 471.70 ± 2.47 mg GAE g^{-1}, so there was no significant difference between the start and end time.This small increase in TPC after stability is due to recoveries and formation of polyphenols as a consequence of the hydrolysis of conjugated polyphenols (NUNES et al., 2015; BAKOWSKA-BARCZK; KOLODZIEJCZYK, 2011).

Conclusions

Spray-drying and freeze-drying proved to be suitable processes to prepare ciriguela peel extract microcapsules to be used as a source of phenolic compounds for foods, such as drinks, salty cookies, cookies, bakery products among others, as well as pharmaceuticals and cosmetics. The optimized conditions of microencapsulation by atomization were shown to be a temperature of 150 °C, a feed flow rate of 0.80 L h^{-1} and the use of 100 % gum arabic as an encapsulating agent. Spray-dried extract showed higher TPC (486.82 mg GAE g^{-1}). The fenolic compounds found in greater

concentrations in the liquid extract of ciriguela residue were rutin, epicatechin gallate, chlorogenic acid and quercetin, while rutin and myricetin were the most abundant in the atomized extract, and quercetin and kaempferol in the freeze-dried one. After simulated gastrointestinal digestion of microencapsulated extracts, rutin was the fenolic compound most abundant in microcapsules. Atomized and lyophilized powders, regardless of the temperature (7 or 25 °C), maintained their high content of phenolic compounds almost unvaried for 90 days of storage.

References

AGUILERA-CHÁVEZ, S. L.; GALLARDO-VELÁZQUEZ, T.; MEZA-MÁRQUEZ, O. G.; OSORIO-REVILLA, G. Spray drying and spout-fluid bed drying microencapsulation of mexican plum fruit (*Spondias purpurea* L.) extract and its effect on in vitro gastrointestinal bioaccessibility. **Applied Science**s, v. 12, 2213, 2022.

AGUDELO, C.; BARROS, L.; SANTOS-BUELGA, C.; MARTÍNEZ-NAVARRETE, N.; FERREIRA, I. C. F. R. Phytochemical content and antioxidant activity of grapefruit (*Star Ruby*): A comparison between fresh freeze-dried fruits and different powder formulations. **LWT - Food Science and Technology**, v. 80, p. 106-112, 2017.

ALBUQUERQUE, J. G.; DUARTE, A. M.; CONCEIÇÃO, M. L.; AQUINO, J. S. Integral utilization of seriguela fruit (*spondias purpurea* l.) In the production of cookies. **Revista Brasileira de Fruticultura,** v. 38, n. 3, 2016. http://dx.doi.org/10.1590/0100-29452016229.

ALTIN, G.; AYAR, E. N.; OZCELIK, B. Phenolic-protein interaction: effects on functional properties of phenolics and advantages on delivery of phenolics. **Global Journal of Medical Research: L Nutrition and Food Science**, v. 19, p. 1–11, 2019.

AOAC - Official Method of Analysis: Association of Official Analytical Chemists. 20th Edition, Washington DC, 2016.

ARCHAINA, D.; LEIVA, G.; SALVATORI, D.; SCHEBOR, C. Physical and functional properties of spray-dried powders from blackcurrant juice and extracts obtained from the waste of juice processing. **Food Science and Technology International**, v. 24, n. 1, p. 78–86, 2017.

AUGUSTO, P. E. D.; CRISTIANINI, M.; IBARZ, A. Effect of temperature on dynamic and steadystate shear rheological properties of siriguela *(Spondias purpurea* L.) pulp. **Journal of Food Engineering**, v.108, p. 283 – 289, 2012.

BAKOWSKA-BARCZK, A.M., KOLODZIEJCZYK, P.P. Black currant polyphenols: their storage stability and microencapsulation. **Industrial Crops and Products**, v. 34, p. 3101–3109, 2011.

BALLESTEROS, L. F.; RAMIREZ, M. J.; ORREGO, C. E.; TEIXEIRA, J. A.; MUSSATTO, S. I. Encapsulation of antioxidant phenolic compounds extracted from

spent coffee grounds by freeze-drying and spray-drying using different coating materials. **Food Chemistry**, v.237, p. 623-631, 2017.

BARBA, F. J.; MARIUTTI, L. R. B.; BRAGAGNOLO, N.; MERCADANTE, A. Z.; BARBOSA-CANOVAS, G. V.; ORLIEN, V. Bioaccessibility of bioactive compounds from fruits and vegetables after thermal and nonthermal processing. **Trends in Food Science & Technology**, v. 67, p. 195–206, 2017.

BARBOSA-CÁNOVAS, G.V.; JULIANO, P. Physical and chemical properties of food powders. In: ONWULATA, C. **Encapsulated and powdered foods.** Boca Raton: Taylor & Francis, p.39-71, 2005.

BARBOSA, P. O., PALA, D., SILVA, C. T., SOUZA, M. O., AMARAL, J. F., VIEIRA, R. A. L., ... FREITAS, R. N. (2016). Açai (*Euterpe oleracea* Mart.) pulp dietary intake improves cellular antioxidant enzymes and biomarkers of serum in healthy women. **Nutrition**, v. 32, n. 6, p. 674–680, 2016.

BARROS, R. G. C., ANDRADE, J. K. S., DENADAI, M., NUNES, M. L., NARAIN, N. Evaluation of bioactive compounds potential and antioxidant activity in some Brazilian exotic fruit residues. **Food Research International**, v. 102, p. 84–92, 2017.

BEDNARSKA, M. A.; JANISZEWSKA-TURAK, E. The influence of spray drying parameters and carrier material on the physico-chemical properties and quality of chokeberry juice poder. **Journal of Food Science Technology**, v. 57(2), p. 564–577, 2020.

BEN-OTHMAN, S.; JÕUDU, I.; BHAT, R. Bioactives from Agri-Food Wastes: Present Insights and Future Challenges. **Molecules**, v. 25, p. 510-544, 2020.

BERNSTEIN, A.; NOREÑA, C. P. Z. Encapsulation of red cabbage (*Brassica oleracea* L. var. *capitata* L. f. *rubra*) anthocyanins by spray drying using different encapsulating agents. **Brazilian Archives of Biology and Technology**, v. 58(6), p. 944–952, 2015.

BOTREL, D. A.; BORGES, S. V.; BARROS, R. V. DE; DO CARMO, E. L. Optimization of fish oil spray drying using a protein: inulin system optimization of fish oil spray drying using a protein: inulin system. **Drying Technology**, v. 32(3), p. 279–290, 2014.

BRAND-WILIAMS, W.; CUVELIER, M.E.; BERSET, C. Use of a free radical method to evaluate antioxidant activity. **Food Science and Technology,** v. 28, p.25-30. 1995.

BRAMONT, W. B.; LEAL, I. L.; UMSZA-GUEZ, M. A.; GUEDES, A. S.; ALVES, S. C. O.; REIS, J. H. O.; BARBOSA, J. D. V.; MACHADO, B. A. S. Comparação da Composição Centesimal, Mineral e Fitoquímica de Polpas e Cascas de Dez Diferentes Frutas. **Revista Virtual Quimica.** v.10, n.4, 2018.

BRASIL. ANVISA- Agência Nacional de Vigilância Sanitária. **Resolução RDC nº 272, de 22 de setembro de 2005**. Regulamento Técnico para produtos de vegetais, produtos de frutas e cogumelos comestíveis. Diário Oficial da República Federativa do Brasil, Poder Executivo, Brasília, 23 de setembro de 2005.

BUNIOWSKA, M., CARBONELL-CAPELLA, J. M., FRIGOLA, A., ESTEVE, M. J. Bioaccessibility of bioactive compounds after non-thermal processing of an exotic fruit juice blend sweetened with Stevia rebaudiana. **Food Chemistry**, v. 221, p. 1834–1842, 2017.

CAI, Y. Z.; CORKE, H. Production and properties of spray dried amaranthus betacyanin pigments. **Journal of Food Science**, v.65, p.1248-1252, 2000.

CALDAS, T. W.; MAZZA, K. E. L.; TELES, A. S. C.; MATTOS, G. N; BRÍGIDA, A. I. S.; CONTE-JUNIOR, C. A.; BORGUINI, R. G.; GODOY, R. L. O.; CABRAL, L. M. C.; TONON, R. V. Phenolic compounds recovery from grape skin using conventional and nonconventional extraction methods. **Industrial Crops & Products**, v.111, p. 86–91, 2018.

CALISKAN, G.; DIRIM, S. N. The effect of different drying processes and the amounts of maltodextrin addition on the powder properties of sumac extract powders. **Powder Techonology**, v. 287, p. 308-314, 2016.

CANO-CHAUCA, M.; RAMOS, A. M.; STRINGHETA, P. C. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. **Innovative Food Science e Emerging Technologies**, v.6, p.420-428, 2005.

CAPARINO, O. A.; TANG, J.; NINDO, C. L.; SABLANI, S. S.; POWERS, J. R. FELLMAN, J. K. Effect of drying methods on the physical properties and microstructures of mango (*Philippine* 'Carabao' var.) power. **Journal of Food Engineering**, v.111, p.135-148, 2012.

CARNAVAL, L. S. C. Potencial aplicação do extrato de resíduo de seriguela (*Spondias purpurea L.*) em filmes ativos à base de resíduo de mandioca. **Dissertação (Mestrado)**. Universidade Federal Rural de Pernambuco. Recife, 2019.

COMUNIAN, T.A.; MONTERREY-QUINTERO, E.S.; THOMAZINI, M.; BALIEIRO, J.C.; PICCONE, P.; PITTIA, P.; FAVARO-TRINDADE, C.S. Assessment of production efficiency, physicochemical properties and storage stability of spray-dried chlorophyllide, a natural food colourant, using gum Arabic, maltodextrin and soy protein isolate-based carrier systems. **International Journal of Food Science and Technology**, v. 46 (6), p. 1259–1265, 2011.

DAMODARAN, S., PARKIN, K.L., 2017. Fennema's Food Chemistry. CRC press.

DAZA, L. D.; FUJITA, A.; FÁVARO-TRINDADE, C. S.; RODRIGUES-RACT, J. N.; GRANATO, D.; GENOVESE, M. I. Effect of spray drying conditions on the physical properties of Cagaita (*Eugenia dysenterica* DC.) fruit extracts. **Food and Bioproducts Processing**, v. 97, p. 20–29, 2016.

DUTRA, R. L. T.; DANTAS, A. M.; MARQUES, D. A.; BATISTA, J. D. F.; MEIRELES, B. R. L. A.; CORDEIRO, A. M. T. M.; MAGNANI, M.; BORGES, G. S. C. Bioaccessibility and antioxidant activity of phenolic compounds in frozen pulps of Brazilian exotic fruits exposed to simulated gastrointestinal conditions. **Food Research International**, v. 100, p. 650–657, 2017.

DUTRA, M. C. P.; RODRIGUES, L. L.; OLIVEIRA, D.; PEREIRA, G. E.; LIMA, M. S. Integrated analyses of phenolic compounds and minerals of Brazilian organic and conventional grape juices and wines: Validation of a method for determination of Cu, Fe and Mn. **Food Chesmitry**, v. 269, p. 157-165, 2018.

ENGELS, C.; GRATER, D.; ESQUIVEL, P.; JIMÉNEZ, V. M.; GANZLE, M. G.; SCHIEBER, A. Characterization of phenolic compounds in jocote (*Spondias purpurea L*) peels by ultra high-performance liquid chromatography/electrospray ionization mass spectrometry. **Food Research International,** v.46, p. 557-562, 2012.

FANG, Z.; BHANDARI, B. Encapsulation of polyphenols - a review. **Trends in Food Science & Technology**, v.20, p.510-523, 2010.

FIGUEIREDO, J. A.; TEIXEIRA, M. A.; CAMPELO, P. H.; LAGO, A. M. T.; DE SOUZA, T. P.; YOSHIDA, M. I.; DE OLIVEIRA, C. R.; PEREIRA, A. P. A.; PASTORE, G. M.; SANCHES, E. A.; BOTREL, D. A.; BORGES, S. V. Encapsulation of camu-camu extracts using prebiotic biopolymers: Controlled release of bioactive compounds and effect on their physicochemical and thermal properties. **Food Research International,** v. 137, 109563, 2020.

GAO, Y.; WANG, Y.; MA, Y.; YU, A.; CAI, F.; SHAO, W.; ZHAI, G. Formulation optimization and in situ absorption in rat intestinal tract of quercetin-loaded microemulsion. **Colloids and Surfaces B: Biointerfaces**, v. 71(2), p. 306–314, 2009.

GONZÁLEZ, R. L.; MARTOS, M. V.; ÁLVAREZ, J. A. P.; LÓPEZ, J. F. Changes in bioaccessibility, polyphenol profile and antioxidant potential of flours obtained from persimmon fruit (*Diospyros kaki*) co-products during in vitro gastrointestinal digestion. **Food Chemistry**, v. 256, p. 252–258, 2018.

GUANDALINI, B. B. V.; RODRIGUES, N. P.; MARCZAK, L. D. F. Sequential extraction of phenolics and pectin from mango peel assisted by ultrasound. **Food Research International**, v. 119, p. 455–461, 2019.

INSANG, S.; KIJPATANASILP, I.;, JAFARI, S.; ASSATARAKUL, K. Ultrasound-assisted extraction of functional compound from mulberry (*Morus alba* L.) leaf using response surface methodology and effect of microencapsulation by spray drying on quality of optimized extract. **Ultrasonics Sonochemistry**, v. 82, 105806, 2022.

JANISZEWSKA-TURAK, E., DELLAROSA, N., TYLEWICZ, U., LAGHI, L., ROMANI, S., DALLA ROSA, M., WITROWA-RAJCHERT, D. The influence of carrier material on some physical and structural properties of carrot juice microcapsules. **Food Chemistry**, v. 236, p. 134–141, 2017. https://doi.org/10.1016/j.foodchem.2017.03.134

KADERIDES, K.; GOULA, A. M.; ADAMOPOULOS, K. G. A process for turning pomegranate peels into a valuable food ingredient using ultrasound-assisted extraction and encapsulation. **Innovative Food Science & Emerging Technologies**, v. 31, p. 204–215, 2015.

KANG, J.; LIU, L.; LIU, M.; WU, X.; LI, J. Antibacterial activity of gallic acid against Shigella flexneri and its effect on biofilm formation by repressing mdoH gene expression**. Food Control**, v. 94, p. 147–154, 2018.

KIM, I.; MOON, J. K.; HUR, S. J.; LEE, J. Structural changes in mulberry (*Morus Microphylla*. Buckl) and chokeberry (*Aronia melanocarpa*) anthocyanins during simulated in vitro human digestion. **Food Chemistry**, v. 318, 126449, 2020. https://doi.org/10.1016/j.foodchem.2020.126449.

KRINGEL, D. H.; DIAS, A. R. G.; ZAVAREZE, E. R.; GANDRA, E. A. Fruit Wastes as Promising Sources of Starch: Extraction, Properties, and Applications. **Starch – Stärke**, v.72, 1900200, 2020.

KUCK, L. S.; NORENA, C. P. Z. Microencapsulation of grape (*Vitis labrusca var*. Bordo) skin phenolic extract using gum arabic, polydextrose, and partially hydrolyzed guar gum as encapsulating agents. **Food Chemistry**, v. 194, p. 569–576, 2016.

LABUSCHAGNE, P. Impact of wall material physicochemical characteristics on the stability of encapsulated phytochemicals: a review. **Food Research International**, v. 107, p. 227–247, 2018.

LEE, Y.; CHANG, Y.H. Microencapsulation of a maca leaf polyphenol extract in mixture of maltodextrin and neutral polysaccharides extracted from maca roots. **International Journal of Biological Macromolecules**, v. 150, p. 546–558, 2020.

LEONG, S. L.; PETTERSSON, O. V.; RICE, T.; HOCKING, A. D.; SCHNÜRER, J. The extreme xerophilic mould xeromyces bisporus — growth and competition at various water activities. **International Journal of Food Microbiology**, v.145, p.57–63, 2011.

LOURENÇO, S. C.; MOLDÃO-MARTINS, M.; ALVES, V. D. Microencapsulation of pineapple peel extract by spray drying using maltodextrin, inulin, and arabic gum as wall matrices. **Foods**, v. 9, 718, 2020. doi:10.3390/foods9060718

MACEDO, D.A.; MAFALDO, I.M.; OLIVEIRA, P.M.L.; LIMA, M.S.; MAGNANI, M.; BORGES, G.S.C. Bioaccessibility of phenolic compounds in native and exotic frozen pulps explored in Brazil using a digestion model coupled with a simulated intestinal barrier. **Food Chemistry**, v. 274, p. 202–214, 2019.

MAHDAVI, S. A.; JAFARI, S. M.; ASSADPOOR, E.; DEHNAD, D. Microencapsulation optimization of natural anthocyanins with maltodextrin, gum Arabic and gelatin. **International Journal of Biological Macromolecules**, v. 85, p. 379–385, 2016. https://doi.org/10.1016/j.ijbiomac.2016.01.011

MALDONADO-ASTUDILLO, Y. I.; ALIA-TEJACAL, I.; NÚNEZ-COLÍN, C. A.; JIMÉNEZ-HERNÁNDEZ, J.; PELAYO-ZALDÍVAR C.; LÓPEZ-MARTÍNEZ, V.; ANDRADE-RODRÍGUEZ, M.; BAUTISTA-BANOS, S.; VALLE-GUADARRAMA, S. Postharvest physiology and technology of Spondias purpurea L. and S. mombin L. **Scientia Horticulturae,** v. 174, p. 193–206, 2014.

NIGNPENSE, B. E.; LATIF, S.; FRANCIS, N.; BLANCHARD, C.; SANTHAKUMAR, A. B. The impact of simulated gastrointestinal digestion on the bioaccessibility and antioxidant activity of purple rice phenolic compounds. Food Bioscience, v. 47, 101706, 2022. https://doi.org/10.1016/j.fbio.2022.101706

NGUYEN, V. T.; TRAN, A. X.; LE, V. A. T. Microencapsulation of phenolic-enriched extract from cocoa pod husk (*Theobroma cacao* L.). **Powder Technology**, v. 386, p. 136–143, 2021.

NUNES, G. L.; BOAVENTURA, B. C. B.; PINTO; S. S.; VERRUCK, S.; MURAKAMI, F. S.; PRUDÊNCIO, E. S.; AMBONI, R. D. M. C. Microencapsulation of freeze concentrated Ilex paraguariensis extract by spray drying. **Journal of Food Engineering**, v.151, p. 60–68, 2015.

PADILHA, C. V. S.; MISKINIS, G. A.; SOUZA, M. E. A. O.; PEREIRA, G. E.; OLIVEIRA, D.; BORDIGNON-LUIZ, M. T.; LIMA, M. S. Rapid determination of flavonoids and phenolic acids in grape juices and wines by RP-HPLC/DAD: Method validation and characterization of commercial products of the new Brazilian varieties of grape. **Food Chemistry**, v. 228, p. 106-115, 2017.

PANG, S.F.; YUSOFF, M.M.; GIMBUM, J. Assessment of phenolic compounds stability and retention during spray drying of Orthosiphon stamineus extracts. **Food Hydrocolloids**, v. 37, p. 159–165, 2014.

PEANPARKDEE, M.; BOROMPICHAICHARTKUL, C.; IWAMOTO, S. Bioaccessibility and antioxidant activity of phenolic acids, flavonoids, and anthocyanins of encapsulated Thai rice bran extracts during *in vitro* gastrointestinal digestion. Food Chemistry, v. 361, 130161, 2021. https://doi.org/10.1016/j.foodchem.2021.130161

PODIO, N. S.; BARONI, M. V.; P´EREZ, G. T.; WUNDERLIN, D. A. Assessment of bioactive compounds and their *in vitro* bioaccessibility in whole-wheat flour pasta. **Food Chemistry**, v. 293, p. 408–417, 2019.

PUDZIUVELYTE, L.; MARKSA, M.; JAKSTAS, V.; IVANAUSKAS, L.; KOPUSTINSKIENE, D. M.; BERNATONIENE, J. Microencapsulation of Elsholtzia ciliata Herb Ethanolic Extract by Spray-Drying: Impact of Resistant-Maltodextrin Complemented with Sodium Caseinate, Skim Milk, and Beta-Cyclodextrin on the Quality of Spray-Dried Powders. **Molecules**, v. 24, n. 8, p. 1461, 2019.

RAMADAN, M. F., KROH, L. W., & MORSEL, J. T. Radical scavenging activity of black cumin (*Nigella sativa* L.), coriander (*Coriandrum sativum* L.), and Niger (*Guizotia abyssinica* Cass.) crude seed oils and oil fractions. **Journal of Agricultural and Food Chemistry**, v. 51(24), p. 6961–6969, 2003.

RAMÍREZ, M. J.; GIRALDO, G. I.; ORREGO, C. E. Modeling and stability of polyphenol in spray-dried and freeze-dried fruit encapsulates. **Powder Technology**, v. 277, p. 89–96, 2015.

REIS, D. S.; FIGUEIRO NETO, A.; FERRAZ, A. V.; FREITAS, S. T. Produção e estabilidade de conservação de farinha de acerola desidratada em diferentes

temperaturas. **Brazilian Journal of Food Technology** , Campinas, v. 20, n. e2015083, 2017.

RÉ, M.I. Microencapsulation by spray drying. **Drying Technology: An International Journal**, v. 16:6, p. 1195–1236, 1998.

RENARD, C. M. G. C. Extraction of bioactives from fruit and vegetables: State of the art and perspectives. **LWT - Food Science and Technology**, v. 93, p. 390–395, 2018.

REZENDE, Y. R. R. S.; NOGUEIRA, J. P.; NARAIN, N. Microencapsulation of extracts of bioactive compounds obtained from acerola (*Malpighia emarginata* DC) pulp and residue by spray and freeze drying: Chemical, morphological and chemometric characterization. **Food Chemistry**, v. 254, p. 281-291, 2018.

RIBEIRO, A. M.; ESTEVINHO, B. N.; ROCHA, F. Microencapsulation of polyphenols - The specific case of the microencapsulation of *Sambucus Nigra* L. extracts - A review. **Trends in Food Science & Technology**, *In press*, 2019. https://doi.org/10.1016/j.tifs.2019.03.011

RODRÍGUEZ-ROQUE, M. J.; ROJAS-GRAÜ, M. A.; ELEZ-MARTÍNEZ, P.; MARTÍN-BELLOSO, O. Changes in vitamin C, phenolic, and carotenoid profiles throughout in vitro gastrointestinal digestion of a blended fruit juice. **Journal of Agricultural and Food Chemistry,** v. 61, p. 1859–1867, 2013.

SAÉNZ, C.; TAPIA, S.; CHÁVEZ, J.; ROBERT, P. Microencapsulation by spray drying of bioactive compounds from cactus pear (Opuntia ficus-indica). **Food Chemistry,** v.11, p.616–622, 2009.

SAIKIA, S., MAHNOT, N. K., MAHANTA, C. L. Optimisation of phenolic extraction from *Averrhoa carambola* pomace by response surface methodology and its microencapsulation by spray and freeze drying. **Food Chemistry**, v. 171, p. 144–152, 2015.

SÁNCHEZ-MORENO, C.; LARRAURI, J. A.; SAURA-CALIXTO, F. A procedure to measure the antiradical efficiency of polyphenols. **Journal of the Science of Food and Agriculture**, v.76, n.2, p.270-276, 1998.

SANTANA NETO, D. C.; FERREIRA, V. C. S.; ARAÚJO, I. B. S.; MEIRELES, B. R. L. A.; CORDEIRO, A. M. T. M.; SILVA, F. A. P. Solid–liquid extraction of bioactive compounds from *Spondias mombin* L. by-products: optimization and identifcation of phenolic profle. **Brazilian Journal of Chemical Engineering**, v. 39, p. 511–525, 2022.

SHAMAEI, S.; SEIIEDLOU, S. S.; AGHBASHLO, M.; TSOTSAS, E.; KHARAGHANI, A. Microencapsulation of walnut oil by spray drying: effects of wall material and drying conditions on physicochemical properties of microcapsules. **Innovative Food Science & Emerging Technologies**, v. 39, p. 101-112, 2017.

SHAVANDI, A.; BEKHIT, A. E. A.; SAEEDI, P.; IZADIFAR, Z.; KHADEMHOSSEINI, A. Polyphenol uses in biomaterials engineering. **Biomaterials,** v. 167, p. 91-106, 2018.

SHISHIR, M. R. I.; CHEN, W. Trends of spray drying: A critical review on drying of fruit and vegetable juices. **Trends in Food Science & Technology**, v.65, p. 49-67, 2017. https://doi.org/10.1016/j.tifs.2017.05.006.

SILVA JÚNIOR, M. E.; ARAÚJO, M. V. R. L.; SANTANA, A. A.; SILVA, F. L. H.; MACIEL, M. I. S. Ultrasound-assisted extraction of bioactive compounds from ciriguela (*Spondias purpurea* L.) peel: Optimization and comparison with conventional extraction and microwave. **Arabian Journal of Chemistry**, v. 14, 103260, 2021.

SILVA, R. V.; COSTA, S. C. C.; BRANCO, C. R. C.; BRANCO, A. In vitro photoprotective activity of the *Spondias purpurea* L. peel crude extract and its incorporation in a pharmaceutical formulation. **Industrial Crops and Products**, v. 83, p. 509-514, 2016.

SZABO, K.; CATOI, A. F.; VODNAR, D. C. Bioactive compounds extracted from tomato processing by-products as a source of valuable nutrients. **Plant Foods for Human Nutrition**, v. 73, p. 268–277, 2018.

THAIPONG, K.; BOONPRAKOB, U.; CROSBY, K.; CISNEROS-ZEVALLOS, L.; BYRNE, D. H. Comparison of ABTS, DPPH, FRAP, and ORAC assays for estimating antioxidant activity from guava fruit extracts. **Journal of Food Composition and Analysis**, v. 19, n. 6-7, p. 669-675, 2006.

TRAN, T. T. A.; NGUYEN, H. V. H. Effects of spray-drying temperatures and carriers on physical and antioxidant properties of Lemongrass leaf extract powder. **Beverages**, v. 4, p. 84, 2018.

TOLUN, A.; ARTIK, N.; ALTINTAS, Z. Effect of different microencapsulating materials and relative humidities on storage stability of microencapsulated grape pomace extract. **Food Chemistry**, v. 302, 2020.

TOMAS, M., TOYDEMIR, G., BOYACIOGLU, D., HALL, R., BEEKWILDER, J. C. E. The effects of juice processing on black mulberry antioxidants. **Food Chemistry**, v. 186, p. 277–284, 2015.

TSALI, A.; GOULA, A. M. Valorization of grape pomace: Encapsulation and storage stability of its phenolic extract. **Powder Technology**, v. 340, p. 194-207, 2018.

TÜLEK, Z.; ALAŞALVAR, H.; BAŞYIĞIT, B.; BERKTAS, S.; SALUM, P.; ERBAY, Z.; TELCI, I.; ÇAM, M. Extraction optimization and microencapsulation of phenolic antioxidant compounds from lemon balm (Melissa officinalis L.): Instant soluble tea production. **Journal of Food Processing and Preservation**, v. 45, e14995, 2020. https://doi.org/10.1111/jfpp.14995

WETTASINGHE, M.; SHAHIDI, F. Evening primrose meal: a source of natural antioxidants and scavenger of hydrogen peroxide and oxygen-derived free radicals. **Journal of Agricultural and Food Chemistry**, v.47, p.1801-1812, 1999.

YUCETEPE, A.; ALTIN, G.; OZÇELIK, B. A novel antioxidant source: evaluation of in vitro bioaccessibility, antioxidant activity and polyphenol profile of phenolic extract from black radish peel wastes (*Raphanus sativus* L. var. *niger*) during simulated gastrointestinal digestion. **International Journal of Food Science and Technology**, v. 56, p. 1376–1384, 2021.

ZANONI, F.; PRIMITERRA, M.; ANGELI, N.; ZOCCATELLI, G. Microencapsulation by spray-drying of polyphenols extracted from red chicory and red cabbage: Effects on stability and color properties. **Food Chemistry**, v. 307, 125535, 2020.

ZHANG, J.; ZHANG, C.; CHEN, X.; QUEK, S. Y. Effect of spray drying on phenolic compounds of cranberry juice and their stability during storage. **Journal of Food Engineering**, v. 269, 109744, 2020.

Microencapsulation by spray-drying and freeze-drying of phenolics obtained from ciriguela peel by ultrasound-assisted extraction: Chemical, morphological and chemometric characterization of microcapsules

Supplementary Material

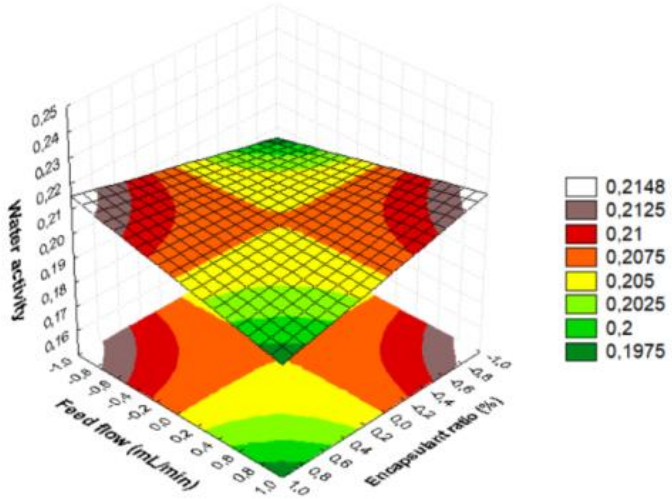


Figure 1S. Response surface of water activity of ciriguela residue extract encapsulated by spray-drying as a function of feed flow rate and ratio of encapsulating agents.

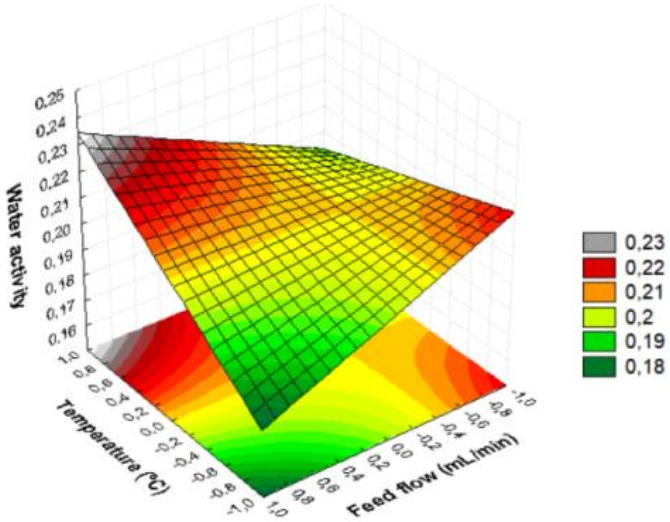


Figure 2S. Response surface of water activity of ciriguela residue extracts encapsulated by spray-drying as a function of temperature and feed flow rate.

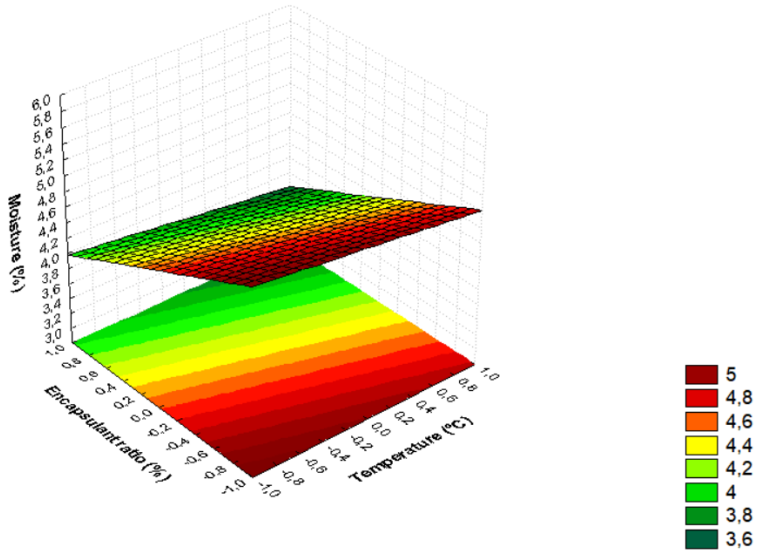


Figure 3S. Response surface of moisture content of ciriguela residue extract encapsulated by spray-drying as a function of temperature and ratio of encapsulating agents.

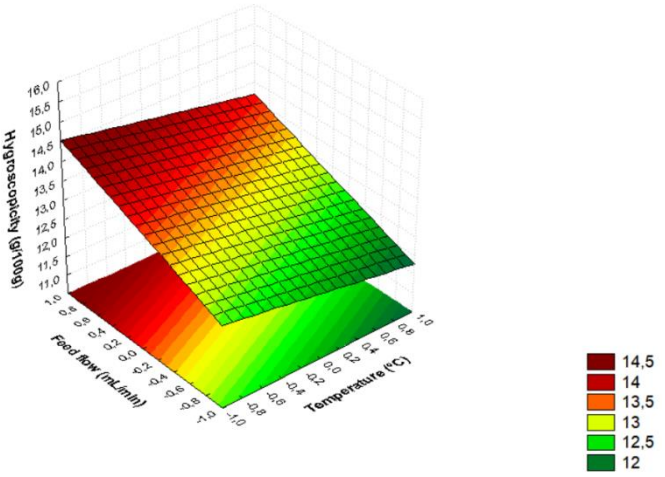


Figure 4S. Response surface of hygroscopicity of ciriguela residue extract encapsulated by spray-drying as a function of feed flow rate and temperature.

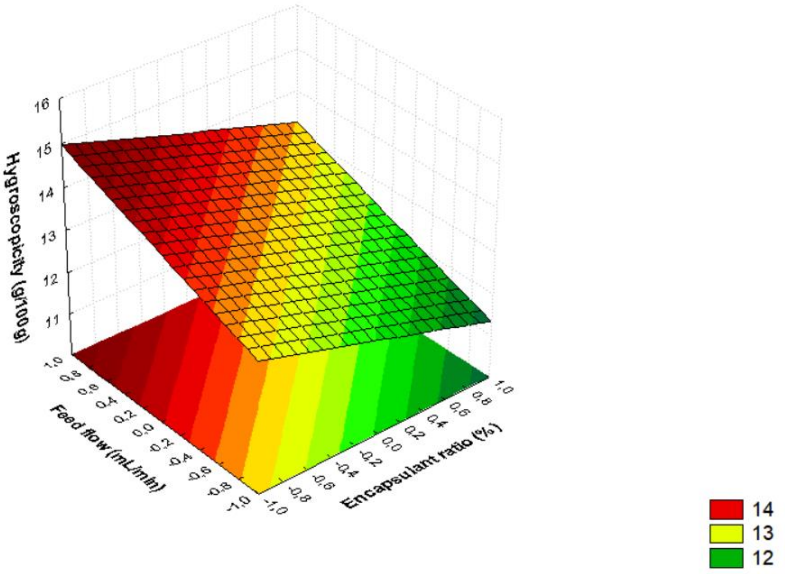


Figure 5S. Response surface of hygroscopicity of ciriguela residue extract encapsulated by spray-drying as a function of feed flow rate and ratio of encapsulating agents.

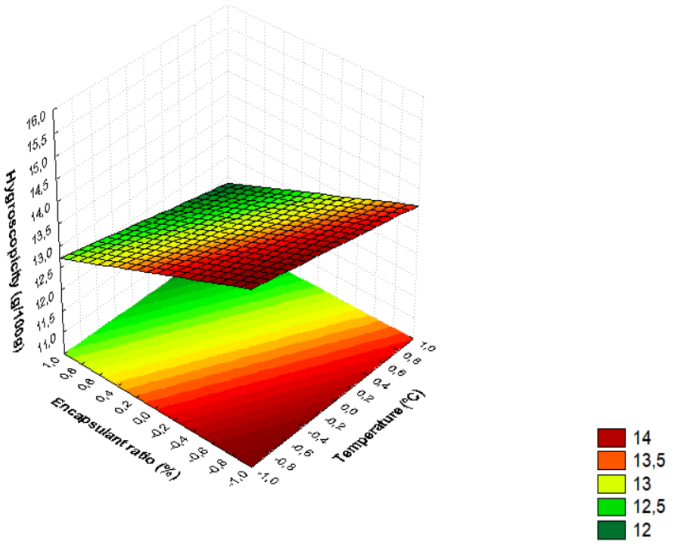


Figure 6S. Response surface of hygroscopicity of ciriguela residue extract encapsulated by spray-drying as a function of temperature and ratio of encapsulating agents.

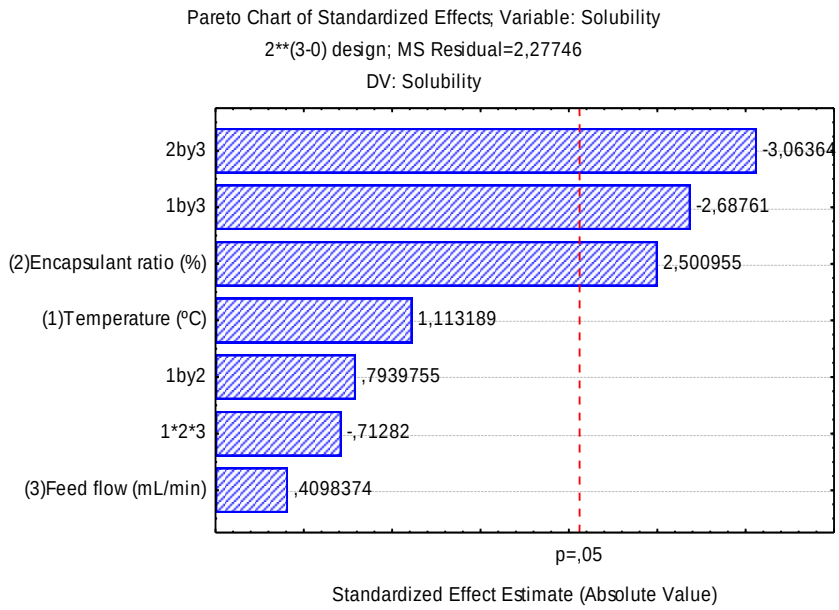


Figure 7S. Pareto Chart of the solubility of ciriguela residue extract encapsulated by spray-drying.

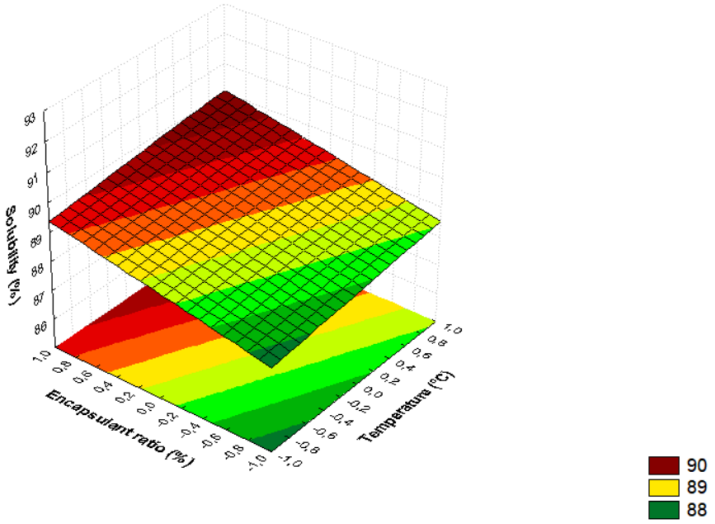


Figure 8S. Response surface of solubility of ciriguela residue extract encapsulated by spray-drying as a function of ratio of encapsulating agents and temperature.

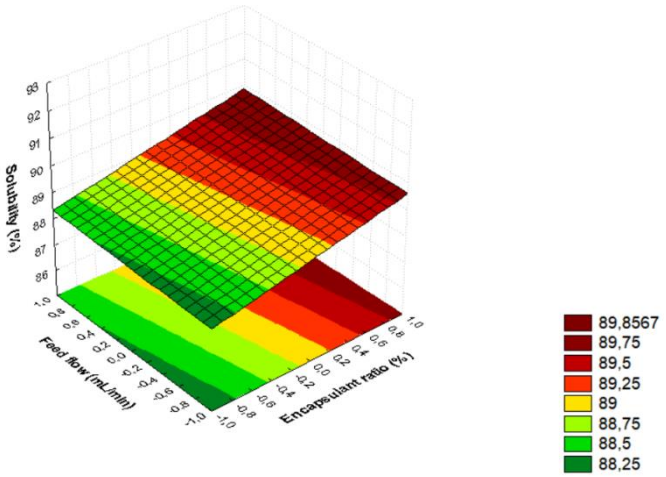
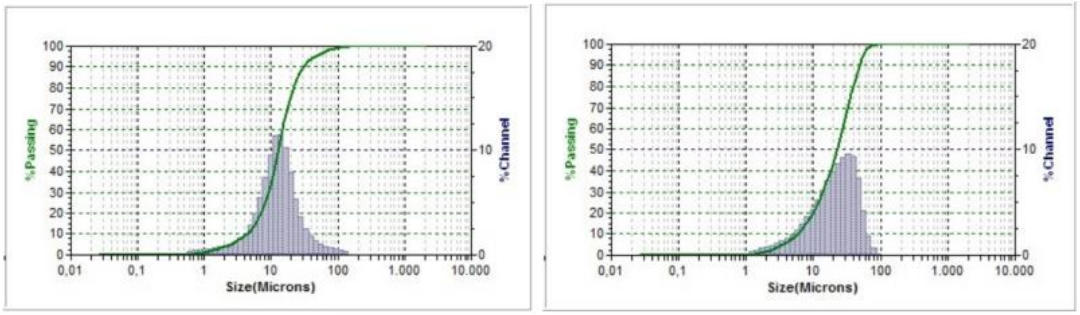


Figure 9S. Response surface of solubility of ciriguela residue extract encapsulated by spray-drying as a function of feed flow rate and ratio of encapsulating agents.



(a) **(b)**

Figure 10S. Particle size distribution of ciriguela residue extracts encapsulated by (a) spray-drying and (b) freeze-drying.

ARTIGO III. Effect of coating material on microencapsulation by spray-drying and freeze-drying of phenolic compounds extracted from ciriguela peel residue

Abstract

Extract of ciriguela residue was microencapsulated by spray-drying and freeze-drying using maltodextrin(M), gum arabic(GA), and mixture (50%M;50%GA) as encapsulating agents. Total phenolic compounds (TPC), antioxidant activity, physicochemical properties, profile of phenolic compounds by HPLC-DAD, and storage stability were evaluated. TPC content of powders ranged 306.93 to 451.25 mg GAE.g^{-1}. Powder spray-dried using GA as encapsulating agent showed higher TPC content and antioxidant activity. Powders freeze-dried had lower moisture content and water activity. Spray-dried microcapsules were of spherical shape, freeze-dried products of irregular structures. Profile of phenolic compounds identified in samples was similar, rutin and quercetin were the major compounds in liquid and freeze-dried extracts, myricetin was predominant in spray-dried ones. Storage stability tests carried out for 45 days at 7 or 25 °C revealed no statistically significant difference in TPC content. Ciriguela agro-industrial residue can be considered a source of TPC and used as ingredient with good antioxidant activity in the food industry.

Keywords: Antioxidant activity; gum arabic; maltodextrin; powdered extract; *Spondias purpurea* L.

INTRODUCTION

Ciriguela (*Spondias purpurea* L.) is a fruit native to the tropical regions of Africa, Asia and Central America (AUGUSTO; CRISTIANINI; IBARZ, 2012; BARROS et al., 2017), the pulp and peel of which are rich in secondary metabolites of biological interest, including in particular phenolic compounds (MALDONADO-ASTUDILLO et al., 2014; SILVA et al., 2016). Phenolics can provide many health-promoting properties such as antioxidant, antimicrobial, anticancer, anti-inflammatory, and antiallergic actions (ASSADPOUR; JAFARI, 2019).

In fruit processing, peel and seeds are the two main by-products, whose extracts contain a considerable amount of bioactive compounds (GOOT et al., 2016). It is

estimated that 40% of the fruit volume is discarded, which generates a large volume of organic waste (DUZZIONI et al., 2013). In the last decades, economic and environmental issues have increased concerns about the large amount of waste generated by the food industry, which could be exploited to produce highly valued ingredients (BEN-OTHMAN; JÕUDU; BHAT, 2020; CALDAS et al., 2018). By-products of the fruit processing industry, such as seeds, kernels, and bagasse, which were earlier considered wastes, possess high potential for use as food supplements (REZENDE; NOGUEIRA; NARAIN, 2018).

In this context, the extraction of bioactive compounds present in the ciriguela residue could increase the commercial value of the raw material and the profitability of fruit processing. Several works have evaluated the recovery of phenolic compounds from fruit skin and seeds by different extraction methods. Ultrasound-assisted extraction is a green, relatively simple, and cheap process that represents a slight modification of the conventional stirring method (CALDAS et al., 2018) and uses acoustic energy and solvents to improve the release and diffusion of target compounds from various matrices (GUANDALINI; RODRIGUES; MARCZAK, 2019; MOREIRA et al., 2019).

Several limitations have been associated with the use of extracts of bioactive compounds in products due to their instability under conditions of high temperature and oxygen during storage as well as the influence of solvent, pH, light, and enzymes (ÇAM; IÇYER; ERDOGAN, 2014; RIBEIRO; ESTEVINHO; ROCHA, 2020). Microencapsulation techniques are alternative processes able to overcome these problems, increasing the stability of these compounds and protecting them from adverse environmental effects by incorporating a protective matrix (LEE; CHANG, 2020). According to a survey made to know the most used encapsulation methods for phytochemicals, spray-drying and freeze-drying appear in about 84% of publications (LABUSCHAGNE, 2018).

However, there is still no work that has described the microencapsulation of the bioactive compounds from ciriguela residue. Thus, this study aimed to encapsulate the extracts of bioactive compounds from agro-industrial peel ciriguela residue by spray-drying and freeze-drying, and to determine the physicochemical characteristics of the resulting powders (moisture content, water activity, solubility, hygroscopicity and color), their antioxidant activity, their stability under typical storage conditions, and the efficiency of phenolic compounds encapsulation.

MATERIALS AND METHODS

Microencapsulating materials, standards and reagents

The ciriguela by-products (peels and seeds) were supplied by a frozen fruit pulp industry, located in João Pessoa, PB, Brazil. The fruits were cultivated in the state of Paraíba (07º 09' S 36º 49' W), and the pulp extraction was carried out by the same factory. 50 kg of ciriguela by-products were made available, which, after manual separation of peels from the seeds, yielded approximately 11 kg of ciriguela peels.

Maltodextrin dextrose equivalent 5 (M 5DE) (MOR-REX® 1905) was purchased from Ingredion (Mogi-Guaçu, SP, Brazil), gum arabic (G9752) and 2,2-diphenyl-1-picrylhydrazyl radical ($DPPH^{\cdot}$) from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA), nitric acid, Folin Ciocalteu reagent, ethanol, phosphoric acid and potassium phosphate monobasic from Merck (Darmstadt, Germany), and methanol from J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water was produced with a purification system (Marte Científica, São Paulo, SP, Brazil). External standards of hesperidin, procyanindin B_1, catechin, procyanidin B_2, trans-caftaric acid, chlorogenic acid, caffeic acid, *p*-Coumaric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA), while epigalocatechin gallate, epicatechin, epicatechin gallate, procyanidin A_2, quercetin 3-glucoside, rutin, myricetin, kaempferol 3-glucoside, and petunidin 3-glucoside from Extrasynthese (Genay, France). *Trans*-resveratrol was obtained from Cayman Chemical Company (Ann Arbor, MI, USA).

Preparation of the ciriguela residue flour

The ciriguela peels were dried at 60 °C for 24 h (CALDAS et al., 2018) in an oven with air circulation (model MA035/5, Marconi, Piracicaba, SP, Brazil) until a moisture content ≤ 10%, then ground in a multipurpose mill (model TE 631/2, Tecnal, Piracicaba, SP, Brazil), and sieved (40 mesh, corresponding to 425 μm). The resulting ciriguela residue flour (CRF) (approximately 3.5 kg) was stored in low-density polyethylene bags, wrapped with laminated paper, and frozen at -18 ºC for further analysis.

Extraction of polyphenols from flour by ultrasound-assisted extraction

To obtain the extract of phenolic compounds by ultrasound-assisted extraction, 10 g of CRF were mixed with 40 mL of 80% etanol – 20% water (v/v) solution acidified

with 0.1% HCl (SILVA JÚNIOR et al., 2021). The mixture was submitted to the action of an ultrasonic probe (Ultronique, Eco-Sonics, São Paulo, SP, Brazil) with a maximum power of 1000 W and 20 kHz ultrasonic frequency for 15 min. The obtained liquid extract was filtered and stored in an amber container at -18 ºC.

Microparticles production and characterization

Microencapsulation by spray-drying

The atomization process was performed in a Mini-Spray dryer MSD 1.0 (Labmaq do Brasil, Ribeirão Preto, SP, Brazil). Three experiments were carried out using M 5DE (treatment 1), gum arabic (treatment 2), or a formulation of 50% M 5DE and 50% gum arabic (treatment 3), as the encapsulating agent. The CRF extracts together with the selected formulation of encapsulating agent and distilled water were homogenized in Turrax (model TE-102, Tecnal) using a speed of 14.000 rpm for 5 minutes and then submitted to spray-drying under the following conditions: 30% total solids concentration in the feeding solution (300 mL), 0.60 L/h feed flow rate, inlet air temperature of 140 ºC, diameter injector nozzle of 1.2 mm, 30 m^3/h flow air pressure and 0.6 bar air pressure.

Microencapsulation by freeze-drying

Microencapsulation was also performed by freeze-drying (model Alpha 1-4 LD Plus, Martin Christ, Osterode am Harz, Germany) at -80 ºC for 48 h using a chamber pressure of 0.28 mbar. Three experiments were carried out using M 5DE (treatment 4), gum arabic (treatment 5), or a formulation of 50% M 5DE and 50% gum arabic (treatment 6) as encapsulating agent.

Determination of bioactive compounds and antioxidant activity

Total phenolics compounds

The total phenolic compounds (TPC) were quantified spectrophotometrically at 725 nm after reaction with the Folin-Ciocaulteu reagent (Sigma Aldrich, St. Louis, MO, USA) in ethanol as a solvent, according to the methodology described by Wettasinghe & Shahidi (1999). Briefly, 0.5 mL of each sample, 8.0 mL of distilled water, and 0.5 mL of the Folin-Ciocalteu reagent were added to a test tube. After 3 min, 1.0 mL of a sodium carbonate solution was added and allowed to react for 60 min in the dark. The content of TPC was determined by interpolating the absorbance of the samples against a

standard curve prepared from aqueous solutions of gallic acid (0.1-1 mg/mL), and the results were expressed in mg of gallic acid equivalent (GAE)/g of microcapsules (powder) (mg GAE/g).

Microencapsulation efficiency

To determine the total phenolic content in microencapsules (TMPC), 100 mg of microencapsules were dispersed in 1.0 mL of a 50:8:42 (v/v/v) ethanol:acetic acid:distilled water solution. The mixture was vortexed for 1 min, filtered through a microfilter with 0.45-µm pore diameter (Syringe Filters K-18) (SAÉNZ et al., 2009), and analyzed after reaction with the Folin-Ciocalteu reagent as described above.

The phenolics content on the microcapsule surface (SMPC) was determined according to the procedure described by Saénz et al. (2009). 100 mg of microcapsules were dispersed in 1.0 mL of 1:1 (v/v) ethanol:methanol solution, gently stirred for 5 min to avoid their rupture, and microfiltered as described above. The phenolics content was assessed in the filtrate using the Folin-Ciocalteu reagent and a gallic acid standard curve (WETTASINGHE & SHAHIDI, 1999).

The microencapsulation efficiency (*ME*) was then calculated by the equation described by Mahdavi et al. (2016):

$$ME\ (\%) = \frac{\mathrm{TMPC} - \mathrm{SMPC}}{\mathrm{TMPC}} \times 100 \quad (1)$$

DPPH· scavenging capacity

The DPPH$^{\bullet}$ scavenging capacity assay was assessed according to the method described by Brand-Williams, Cuvelier, & Berset (1995) and modified by Sanchez-Moreno, Larrauri, & Saura-Calixto (1998). The extract was diluted up to three different concentrations (7.84 - 23.54 µg/mL^{1}) of total phenolics by addition to a 0.1 M solution of 1,1-diphenyl-2-picrylhydrazyl radical (DPPH$^{\bullet}$) in methanol. The absorbance at 517 nm was monitored in a spectrophotometer (model UV-1650PC, Shimadzu, São Paulo, SP, Brazil) until the reaction reached a plateau. The results were expressed according to Ramadan, Kroh, & Morsel (2003). The inhibition percentage (IC_{50}), i.e., the sample concentration needed to inhibit the DPPH$^{\bullet}$ radical formation by 50%, was obtained according to Eq. (2).

$$\mathrm{DPPH\%} = \frac{A_{\mathrm{DPPH}} - A_S}{A_{\mathrm{DPPH}}} \times 100 \quad (2)$$

where A_S is the absorbance of the solution when the sample is added at a particular level and A_{DPPH} is the absorbance of the $DPPH^{\bullet}$ solution.

The sample concentration providing IC_{50} was calculated by interpolation from the graph of radical-scavenging activity percentage against sample concentration.

Ferric reducing antioxidant power

The ferric reducing antioxidant power (FRAP) assay was conducted according to Thaipong et al. (2006) by monitoring the absorbance at 593 nm with the same spectrophotometer, and the results were expressed as μmol of ferrous equivalent per g of extract (μmol Fe^{2+}/g).

Determination of the physicochemical properties of the microencapsulated powders

Water activity and moisture

The water activity (a_w) was determined with a water activity meter (Decagon 4TE, Aqualab, Pullman, WA, USA) at 25°C, while the moisture content on an infrared balance (model ID50, Marte Científica, São Paulo, SP, Brazil) at 105 ºC for 30 min.

Solubility

The solubility of powders in water was determined according to the methodology described by Cano-Chauca, Ramos, & Stringheta (2005) after diluting 1.0 g of sample in 100 mL of distilled water, stirring for 5 min in a magnetic stirrer (model 752, Fisatom, São Paulo, SP, Brazil) and then centrifuging at 3000 rpm (1800 × *g*) for 5 min in a centrifuge (model CT-6000R, Cientec, Belo Horizonte, MG, Brazil). An aliquot of the supernatant (25 mL) was placed in a pre-weighed sterilized Petri dish and kept at 105 ºC for 5 h in the oven with air circulation and renewal described above. At the end of the process, the plate was weighed on an analytical balance, and the solubility obtained by weight difference.

Hygroscopicity

Powders hygroscopicity was determined according to the methodology proposed by Cai & Corke (2000) with some modifications. Plastic capsules with 1.0 g of microencapsulated extract were placed in an airtight container containing a saturated

solution of NaCl (75.29% relative humidity) at 25 °C and weighed after one week. Hygroscopicity was expressed as g of moisture absorbed per 100 g of dry mass of the sample (g/100g).

Colorimetric parameters

The color of powders was evaluated on the surface of the microencapsulated extracts in a colorimeter (model CR 400, Konica Minolta, Sensing Inc., Osaka, Japan), using the color standards of the Commission Internationale de L'Eclairage (CIELab) system, i.e., luminosity (L^*) ranging from white (100) to black (0), intensity of the green ($-a^*$) to red ($+a^*$) component, and intensity of the blue ($-b^*$) to yellow ($+b^*$) component. The colorimeter, previously calibrated with a white standard before each analysis, was operated using as light source a xenon lamp (Illuminant C; Y = 92.78; x = 0.3139; y = 0.3200), observation angle of 10º, and measurement area of 8 mm × 8 mm (YILDIZ; RABABAH; FENG, 2016).

The chroma (C), which is the relationship between the values of a^* and b^*, where the real color of the analyzed object is obtained, was calculated according to the Eq. (3):

$$C = \sqrt{(a^{*2} + b^{*2})} \quad (3)$$

The hue-angle is the angle formed between a^* and b^*, indicating the color saturation of the product. To calculate it, the following Eq. (4) was used:

$$h = \tan^{-1} (b^*/a^*) \quad (4)$$

The variation in color (ΔE^*) in microencapsulated powders obtained by spray-drying and freeze-drying was calculated by Eq. (5) (Cai & Corke, 2000), considering the color parameters of the free extract before encapsulation as a reference:

$$\Delta E^* = \sqrt{(L^* - L_0)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2} \quad (5)$$

where L_0^* and L^*: are the luminosities of the samples of the free extract and the reconstituted microencapsulated extract, respectively; a_0^* and a^*: are the red to green color intensities of the free extract and reconstituted microencapsulated extract samples, respectively; b_0^* and b^*: are the intensities of the yellow to blue color of the samples of the free extract and the reconstituted microencapsulated extract, respectively.

Particle morphology

The morphology of microparticles produced with different encapsulation agents and by different methods was examined with a scanning electron microscope (SEM) (model Vega 3, Tescan, Brno, Czech Republic). The samples were fixed in metallic specimen holders (stubs) with a conventional double-sided adhesive tape, metallized with gold in a metallizer (model DESK V, Denton Vacuum, Moorestown, NJ, USA) at a coating rate of 15 nm thickness, for 80 seconds and a current of 40 mA, and examined with the above SEM operating at 20 kV. Image acquisition was performed using the XT microscope software.

Profile of phenolic compounds by HPLC-DAD

Samples (1.0 g) of microencapsulated powders were added to 10 mL of methanol containing 6.0 M HCl and submitted to extraction under ultrasonication at 40 kHz for 30 min at 25 °C (model USC-1800, Unique, Indaiatuba, SP, Brazil). Afterward, the extract was centrifuged at 3000 × *g* for 20 min (model SL-701, Solab, Piracicaba, SP, Brazil), and the supernatant containing the phenolic compounds was collected. An aliquot of the supernatant (1.0 mL) was filtered through a politetrafluoroetilene syringe filter with 0.45-µm pore diameter and used to identify and quantify the phenolic compounds by High Performance Liquid Chromatography (HPLC).

For this purpose, the methodology validated by Padilha et al. (2017), with adaptations by Dutra et al. (2018) on gradient and runtime, was used to quantify phenolic acids, flavanols, flavonols, flavanones, stilbenes and anthocyanins using the Agilent 1260 Infinity LC System (Agilent Technologies, Santa Clara, CA, USA) coupled to a diode arrangement detector (DAD) (model G1315D). Chromatographic separation of phenolic compounds was performed in a Zorbax Eclipse Plus RP-C18 column (100 × 4.6 mm, 3.5 µm) and the Zorbax C18 precolumn (12.6 × 4.6 mm, 5 µm). Data collection and analyses were carried out using the software OpenLAB CDS ChemStation Edition (Agilent Technologies). Before the injection (20 µL), samples were diluted in solvent A (0.52% phosphoric acid solution, pH 2.0), and filtered through a membrane with 0.45-µm pore diameter (Millex Millipore, Barueri, SP, Brazil). The oven temperature was 35 °C, the eluent a mixture of solvents A and B (metanol acidified with 0.5% phosphoric acid), and the eluent flow rate 0.8 mL/min. The gradient used in the separation was 0–5 min: 5% B, 5–14 min: 23% B, 14–30 min: 50% B, 30–33 min: 80% B. Detection of compounds was done at 220, 280, 320, 360 and 520 nm,

and the identification and quantification by comparison with external standards. The results were expressed in µg/g dry weight. Typical chromatogram of residue extract of ciriguela is available in the Supplementary Material (Fig. S1).

Storage stability tests

The microcapsules produced by spray-dring or freeze-drying were stored according to Nunes et al. (2015) with some modifications. The samples (1.0 g) were placed in flexible laminated packages (Zip lock), kept at two different temperatures (7 ± 1 ºC and 25 ± 1 ºC) and stored for 45 days. The TPC content was determined at 0, 15, 30, and 45 days.

Statistical analysis

Experimental data were analyzed and presented as mean values and standard deviations of triplicate measurements. Results were subjected to analysis of variance (ANOVA), and post hoc comparison of the means was performed by the Tukey's test at $p < 0.05$ using the Statistica (version 12.0, Stat Soft. Inc., Tulsa, OK, USA) software package. Person's correlation was performed using the Build 461 (RStudio Inc., Boston, MA, USA) package.

RESULTS AND DISCUSSION

Bioactive compounds and antioxidant activity

The results of total phenolic compounds (TPC) and the antioxidant activity determined by both DPPH$^{\bullet}$ and FRAP methods of the microencapsulated extracts of ciriguela residue are listed in Table 1.

In general, powders obtained by spray-drying using gum arabic (GA) as the encapsulating agent (treatment 2) showed significantly higher content of TPC and antioxidant activity by DPPH$^{\bullet}$ ($p < 0.05$) than the others, while the one obtained by freeze-drying with 50% maltodextrin 5 Dextrose (M 5DE) and 50% GA (treatment 6) showed the highest antioxidant activity by FRAP.

Table 1. Total phenolic compounds (TPC) and antioxidant activity by both DPPH and FRAP methods of the ciriguela peel extract microencapsulated with maltodextrin 5 Dextrose (M 5DE), gum arabic (GA), and mixture of M 5DE and GA by spray drying and freeze drying.

Treatment	TPC (mg GAE/g dry powder)	DPPH (%)	FRAP (µmol Fe^{2+}/g)
Spray-drying (100% M)	313.93 ± 1.42^{d}	40.67 ± 0.87^{e}	3558.77 ± 71.84^{d}
Spray-drying (100% GA)	451.25 ± 0.98^{a}	63.83 ± 0.78^{a}	4563.62 ± 87.46^{c}
Spray-drying (50% M/50% GA)	407.88 ± 2.92^{b}	58.17 ± 0.88^{b}	4583.72 ± 54.79^{c}
Freeze-drying (100% M)	306.93 ± 3.97^{d}	38.21 ± 0.82^{e}	3238.54 ± 31.35^{e}
Freeze-drying (100% GA)	397.84 ± 3.54^{c}	48.84 ± 0.59^{c}	4832.01 ± 23.41^{b}
Freeze-drying (50% M/50% GA)	398.78 ± 1.99^{c}	43.83 ± 0.48^{d}	6617.20 ± 13.62^{a}

*Results are the means of three determinations (n= 3) ± standard deviations. Different letters in the same column indicate significant differences among microencapsulated extracts ($p < 0.05$).

In particular, the TPC content ranged from 306.93 to 451.25 mg GAE/g dry powder, with the highest value (451.25 mg GAE/g dry powder) being observed for the extract microencapsulated by spray-drying with 100% GA followed by that prepared with 50% M and 50% GA (407.88 ± 2.92 mg GAE/g dry powder), while lower values were detected in those prepared by freeze-drying. To explain this variability, it should be remembered that polyphenol losses can occur during the drying process as the result of several factors: whereas in the spray-drying process, phenolics loss is mainly due to exposure to oxygen and high temperature, in freeze-drying product grinding can lead to degradation of compounds due to the occurrence of oxidation reactions (KUCK; NOREÑA, 2016).

In both drying processes, biopolymers are used as wall materials just to prevent degradation. Although maltodextrin is the biopolymer most commonly used for phenolics encapsulation, some researchers observed an enhancement of encapsulation efficiency when combining it with other biopolymers (RAMÍREZ; GIRALDO; ORREGO, 2015; TOLUN; ARTIK; ALTINTAS, 2016; BUSCH et al., 2017; LEE; CHANG, 2020). Gum arabic, owing to its low viscosity in aqueous solution, its film forming and emulsifying capacities (TSAI; KITAMURA; KOKAWA, 2017), and its peculiar structure, being a highly branched sugar heteropolymer with small protein content (LABUSCHAGNE, 2018), was shown to overcome typical problems related to the use of maltodextrin such as scarce activity on the surface of microcapsules and low emulsifying power (AUGUSTIN; HEMAR, 2009; LABUSCHAGNE, 2018). Taking into account that the lowest TPC contents in microencapsulated ciriguela peel extracts were observed using M regardless of the drying method (313.93 and 306.93 mg GAE/g dry powder for spray-drying (100% M) freeze-drying (100% M), respectively) ($p >$

0.05), gum arabic proved to be a more effective wall material than M to preserve these compounds.

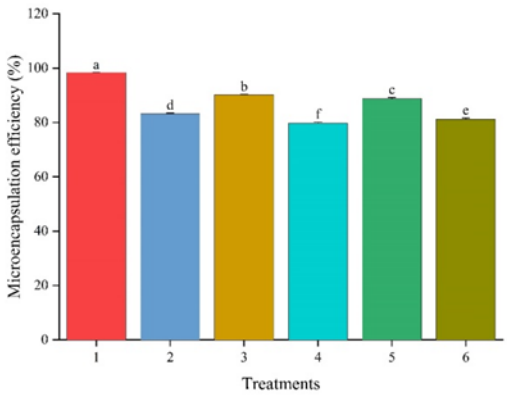
Moreover, the highest TPC content obtained with spray-drying (100% GA) can be justified by the fact that the sample, despite the high temperature used in this process, was exposed to it only for a very short time because microencapsulation occurs instantaneously, thus ensuring the preservation of sensitive compounds (AGUDELO et al., 2017). A similar result was reported by Kuck & Noreña (2016), who investigated the microencapsulation by spray-drying and freeze-drying of phenolic compounds from grape skin (*Vitis labrusca* var. Bordo). TPC contents as high as 785.50-891.00 mg/g dry powder were observed for microencapsulated extracts of maca leaf produced by spray-drying using different formulations of wall materials (LEE; CHANG, 2020), likely due to the high content of these compounds in the raw material.

The antioxidant activity of the microencapsulated powders determined by the DPPH assay, which ranged from 38.21 to 63.83%, followed a trend similar to that of TPC, with the highest value being obtained for the extract spray-dried with 100% GA, followed by that spray-dried with 50% M and 50% GA. Figueiredo et al. (2020), who used a similar method to quantify the antioxidant activity of spray-dried extracts of camu-camu, found the highest antioxidant activity (92.72%) in microparticles produced with maltodextrin as a coating agent, followed by those produced with oligofructose (85.32%) and inulin (82.43%). On the other hand, the antioxidant activity determined by the FRAP assay, which ranged from 3238.54 to 6617.20 μmol Fe^{2+}/g, showed a quite different trend, with the highest values being detected for the extract freeze-dried with 50% M and 50% GA, followed by that freeze-dried with 100% GA. These results confirm the importance of using different tests for the safe and conclusive determination of antioxidant activity, since each method has its own specificities and acts at a particular site of action (REZENDE et al., 2018).

Microencapsulation efficiency (*ME*) of phenolic compounds varied from 79.65 to 98.37% (Fig. 1) and showed statistically significant differences among all treatments. Such high values can be ascribed not only to the selected encapsulating agents (gum arabic and maltodextrin) but also to their high concentration used (30%). Comparable values were reported for microencapsulation by spray-drying of maca leaf polyphenol extract using a mixture of maltodextrin and neutral polysaccharides from roots or arabic gum (79.23-90.61%) (LEE; CHANG, 2020) as well as of jussara (*Euterpe edulis* Martius) fruit extract using inulin (87.66%), arabic gum (87.19%) and maltodextrin

(79.73%) (BERNARDES et al., 2019). On the other hand, the lower values of *ME* of bioactive compounds observed for acerola pulp and residual extracts microencapsulated by spray-drying and freeze-drying (17.25-69.75%) using gum arabic and maltodextrin (REZENDE et al., 2018) were probably due to the low concentration of encapsulating agents used (10%).

Although all treatments allowed to obtain powders with high *ME*, spray-drying using 100% M 5DE stood out showing the highest value (98.37% ± 0.01). Ballesteros et al. (2017) also found the highest *ME* when using 100% maltodextrin as a wall material. This result is of great importance, since it is desirable that most of polyphenols remain trapped within the microcapsules, given that the fraction of those that remain on the surface is more prone to oxidation (ZANONI et al., 2020). On the other hand, freeze-drying led to the lowest *ME* values (79.65 and 81.16% for treatments 4 and 6, respectively) (Figure 1). Such a loss of bioactive compounds during the freeze-drying process could mainly be due to water sublimation, which is able to cause premature release of the encapsulated components and hence their degradation (REZENDE et al., 2018).



*Means followed by different letters in the bars differed significantly by the Tukey's test at 5% probability.

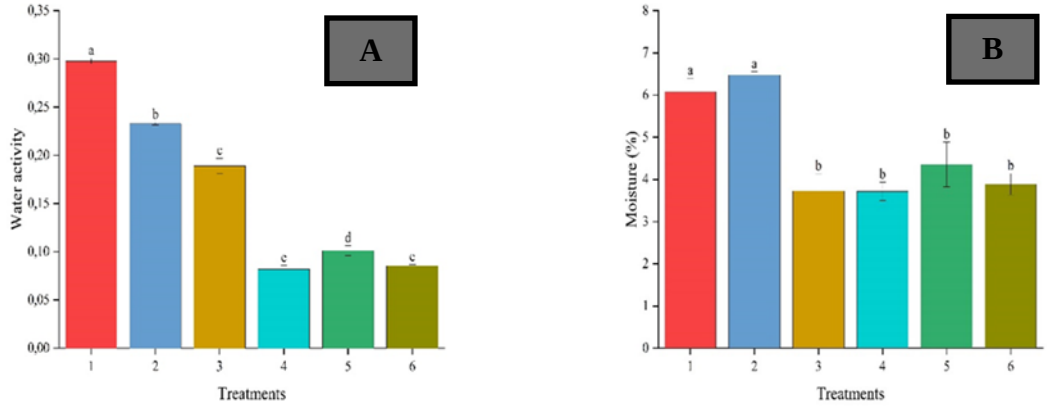
Figure 1. Microencapsulation efficiency of the ciriguela peel extract microencapsulated using different treatments: (1) spray-drying with 100% M 5DE; (2) spray-drying with 100% GA; (3) spray-drying with 50% M 5DE and 50% GA; (4) freeze-drying with 100% M 5DE; (5) freeze-drying with 100% GA; (6) freeze-drying with 50% M 5DE and 50% GA.

3.2. Physical properties of the microencapsulated powders

The water activity (a_w) of microencapsulated powders ranged from 0.081 (treatment 4) to 0.297 (treatment 1), with statistically significant differences among almost all samples ($p < 0.05$) (Fig. 2A). These low values indicate that the prepared

powders are microbiologically stable, being all within the recommended limit to ensure powder stability (< 0.30) (NUNES et al., 2015; ZANONI et al., 2020). Several studies with powdered polyphenol extracts reported a_w values within the range obtained in this study (NUNES et al., 2015; CALISKAN; DIRIM, 2016; KUCK; NOREÑA, 2016; REZENDE et al., 2018; ZANONI et al; 2020). On the other hand, although Daza et al. (2016) detected similar values for cagaita extracts spray-dried using arabic gum, freeze-drying was unsuccessful (0.75). Also, Bernardes et al. (2019) reported a_w values higher than the recommended limit (0.35-0.57) for the extract of phenolic compounds from jussara pulp microencapsulated by spray-drying.

The moisture content varied from 3.72 to 6.47% (Fig. 2B), with significantly higher values ($p < 0.05$) for spray-dried powders prepared by treatments 1 and 2, while the freeze-dried extracts did not show any significant differences among them and treatment 3 ($p > 0.05$) (Fig. 2B). As in this study, Kuck & Noreña (2016) observed significantly lower moisture contents in freeze-dried grape skin extracts than in the spray-dried ones. Similar values were obtained by Rezende et al. (2018) in extracts of bioactive compounds from acerola residue prepared by spray- and freeze-drying. Daza et al. (2016) found moisture contents lower than those of the present study in spray-dried cagaita extracts (2.55 to 5.01%), but higher in freeze-dried one (9.55%). Likewise, Caliskan & Dirim (2016), studying sumac extract powder, found moisture contents between 2.94 and 4.30% in spray-dried samples and between 5.60 and 8.49% in freeze-dried ones.

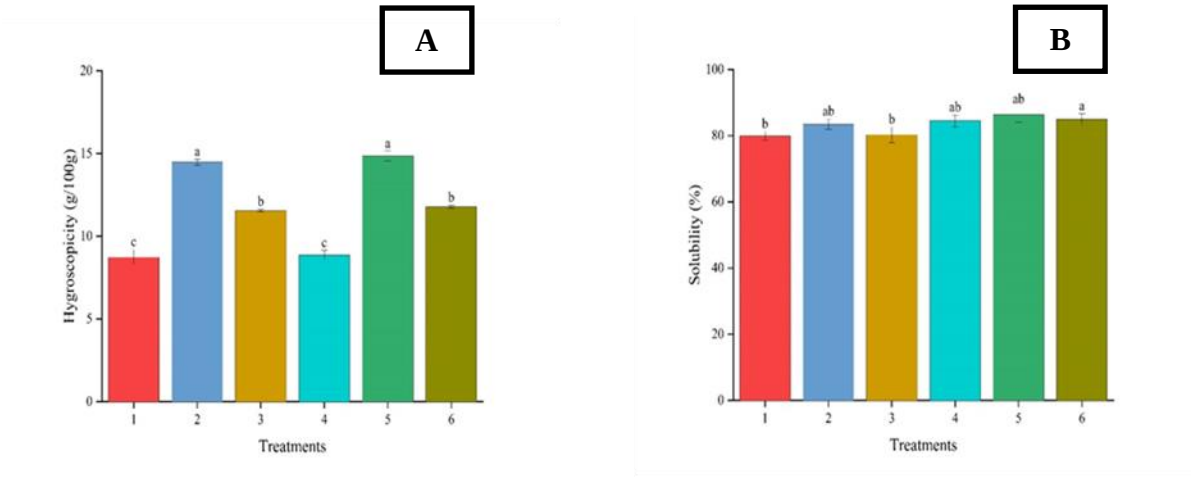


*Means followed by the same letter in the bars do not differ significantly by the Tukey's test at 5% probability.

Figure 2. (A) Water activity; and (B) moisture content of ciriguela peel extract microencapsulated using different treatments: (1) spray-drying, with 100% M 5DE; (2) spray-drying, with 100% GA; (3) spray-drying, with 50% M 5DE and 50% GA; (4) freeze-drying, with 100% M 5DE; (5) freeze-drying, with 100% GA; (6) freeze-drying, with 50% M 5DE and 50% GA.

Hygroscopicity is the ability of a material to absorb moisture from the surrounding environment, and it is an important property to be considered in food processing due to its influence in food stability (DAZA et al., 2016). The hygroscopicity values varied from 8.86 to 14.84 g/100g, with a statistically significant influence of the of encapsulating agent, but not of the microencapsulation method (Fig. 3A). Low hygroscopicity values of powders like these facilitate their conservation as well as the preservation of color and bioactive compounds content. Similar results were reported for spray-dried and freeze-dried extracts of bioactive compounds from acerola residue (REZENDE et al., 2018), spray-dried anthocyanin extract from *Ardisia compressa* K. fruit (ANTONIO-GÓMEZ et al., 2021), and spray-dried cagaita fruit extracts (DAZA et al., 2016).

Water solubility is an important characteristic of powdered products that can affect their properties, especially in relation to dry extract reconstitution or the availability of encapsulated compounds in a food system. Although it depends on various factors, feed composition and particle size are the most impactful (DAZA et al., 2016; REZENDE et al., 2018).



*Means followed by the same letter in the bars do not differ significantly by the Tukey's test at 5% probability.

Figure 3. (A) Hygroscopicity; and (B) solubility of ciriguela peel extract microencapsulated using different treatments: (1) spray-drying, with 100% M 5DE; (2) spray-drying, with 100% GA; (3) spray-drying, with 50% M 5DE and 50% GA; (4) freeze-drying, with 100% M 5DE; (5) freeze-drying, with 100% GA; and (6) freeze-drying, with 50% M 5DE and 50% GA.

Water solubility of all powders produced in this study was high, ranging from 79.93 to 86.37% (Fig. 3B). Even though there was no statistically significant influence of the drying method ($p > 0.05$), the microencapsulated powders obtained by freeze-

drying as a whole exhibited greater solubility than those obtained by spray-drying. Particularly, the solubility of those produced with gum arabic (treatments 2 and 5) showed no significant difference between them, regardless of the method used. The high solubility of all these powders may be related to the high solubility of GA and M, which, when used in combination, proved to ensure proper water solubility and encapsulation efficiency (PAPILLO et al., 2018). Bernardes et al. (2019) reported even higher solubility (> 99.00%) for the extract of phenolic compounds from jussara pulp microencapsulated by spray-drying.

3.3. Colorimetric analysis

Color parameters, namely luminosity (L^*), intensities of the green to red (a^*) and blue to yellow (b^*) components, chroma (C), hue-angle (h) and variation in color (ΔE^*), were used to verify the color difference between initial and final samples (Table 2). The higher L^* values of powders obtained with maltodextrin (92.27 and 92.45 for treatments 1 and 4, respectively) indicate that they were darker than those obtained with gum arabic (89.73 and 88.42 for treatments 2 and 5, respectively), likely due to the formation of differently-colored by-products during the drying process. Kuck & Noreña (2016), analyzing grape skin phenolic extracts microencapsulated with different wall materials, observed that the type of wall material did not influence luminosity of freeze-dried samples, while polydextrose decreased that of samples prepared by spray-drying.

Table 2. Color parameters, namely luminosity (L^*), intensities of the green to red (a^*) and blue to yellow (b^*) components, chroma (C) and hue-angle (h), of ciriguela peel extract microencapsulated with maltodextrin 5 Dextrose (M 5DE), gum arabic (GA) and mixture of 50% M 5DE and 50% GA by spray-drying and freeze-drying.

Treatment	L^*	a^*	b^*	ΔE^*	C	h
1	92.27 ± 0.26^{a}	-1.21 ± 0.05^{a}	11.78 ± 0.34^{e}	53.33 ± 0.83^{a}	11.83 ± 0.34^{d}	84.13 ± 0.06^{e}
2	89.73 ± 0.40^{b}	-0.07 ± 0.03^{d}	13.07 ± 0.33^{d}	55.04 ± 1.66^{a}	13.07 ± 0.33^{d}	89.69 ± 0.14^{a}
3	91.91 ± 0.71^{a}	-0.64 ± 0.04^{c}	12.53 ± 0.95^{de}	52.13 ± 1.09^{a}	12.54 ± 0.95^{d}	87.05 ± 0.34^{c}
4	92.45 ± 0.50^{a}	-0.94 ± 0.04^{b}	15.80 ± 0.18^{c}	51.96 ± 0.47^{a}	15.83 ± 0.18^{c}	86.57 ± 0.17^{c}
5	88.42 ± 0.38^{c}	-0.05 ± 0.04^{d}	17.11 ± 0.37^{b}	53.17 ± 1.36^{a}	17.11 ± 0.37^{b}	89.80 ± 0.13^{a}
6	88.60 ± 0.12^{bc}	-0.55 ± 0.01^{c}	19.63 ± 0.13^{a}	47.85 ± 0.54^{b}	19.63 ± 0.13^{a}	88.39 ± 0.04^{b}

*Results are the means of three determinations (n = 3) ± standard deviations. Different letters in the same column indicate significant differences among extracts ($p < 0.05$). Treatment 1: spray-drying with 100% M 5DE; Treatment 2: spray-drying with 100% GA; Treatment 3: spray-drying with 50% M 5DE and 50% GA; Treatment 4: freeze-drying with 100% M 5DE; Treatment 5: freeze-drying with 100% GA; Treatment 6: freeze-drying with 50% M 5DE and 50% GA.

The results obtained for a^* and b^* (Table 2) show that all intensities were located in the fourth quadrant ($-a^*$, $+b^*$), indicating a tendency to green and yellow components of light. Similar results were reported for spray-dried cagaita fruit extracts

using GA (DAZA et al., 2016). The variation in color (ΔE^*) did not show any significant difference ($p > 0.05$) among most microencapsulated powders (51.96-53.33), except for that produced by freeze-drying with 50% M and 50% GA (treatment 6) that displayed a significantly lower value (47.85 ± 0.54).

C, which indicates the color intensity of foods or products, is directly linked to the concentration of the coloring element (BERNARDES et al., 2019). The higher the value of *C*, the higher the man-perceived saturation of colors. Neutral colors have low saturation, while pure colors have high saturation and, therefore, are brighter in human perception (PATHARE; OPARA; AL-SAID, 2013). There was no statistically significant difference among *C* values of spray-dried samples (treatments 1, 2 and 3), which, taken as a whole, were significantly lower than those of freeze-dried ones (treatments 4, 5, and 6). This means that latter had the desirable feature of higher saturation or color purity. A similar result was obtained by Rezende et al. (2018) for powdered extracts of acerola residue.

The hue-angle is a qualitative attribute of colors traditionally defined as reddish, greenish, etc. The angles 0º (red), 90º (yellow), 180º (green), and 270º (blue) are graphically considered (MCGUIRE, 1992; PATHARE et al., 2013). In the present study, *h* ranged from 84.13 to 89.80 (Table 2); therefore, all spray-dried and freeze-dried samples can be considered to be yellow almost regardless of the type of wall material and drying method. Rezende et al. (2018) reported *h* values between 57.78 and 78.60 for powdered extracts of acerola residue, indicating a tendency to red and yellow hues.

3.4. Correlation analysis

Figure 4 illustrates the results of Pearson's correlation coefficients among the phenolic compounds content, antioxidant activity, and physical properties of microencapsulated ciriguela residue extracts. The correlation analysis revealed that both the DPPH and FRAP scavenging capacities had significant positive correlations with TPC (R = 0.88 and 0.63, respectively, $p < 0.05$), which means that the higher the TPC content of a microencapsulated product, the higher its antioxidant activity. These results are consistent with the positive correlations between antioxidant activity and TPC reported by other researchers for different microencapsulated extracts (AN et al., 2022; DENG et al., 2019; JIANG et al., 2017; REZENDE et al., 2018). Significant positive

correlations were also pointed out between *a** and TPC (R = 0.85, $p < 0.05$), between *h* and *a** (R = 0.97, $p < 0.05$), between *C* and *b** (R =1.00, $p < 0.05$) and, as expected by their strong inter-dependency, between moisture and water activity (R = 0.785, $p < 0.05$).

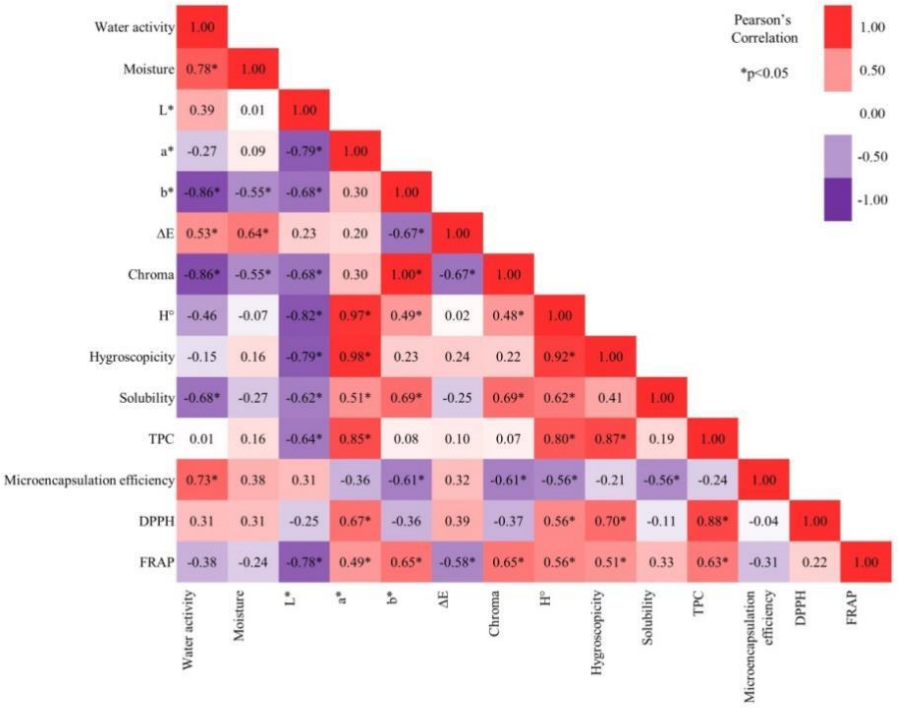


Figure 4. Pearson's correlations among the main characteristics of ciriguela peel extracts microencapsulated using different protocols.

3.5. Particle morphology

Figure 5 shows the scanning electron micrographs of ciriguela peel extracts microencapsulated by both spray-drying (panels A, B, and C) and freeze-drying (panels D, E, and F). Since the two selected coatings, maltodextrin and gum arabic, possess similar morphologies, all the microparticles were irregular and spherical with different sizes. Nonetheless, some differences can be recognized.

The spray-dried microparticles (Fig. 5 A, B, and C) exhibited spherical shape and had different size, few deformations and a smooth surface. These observations are consistent with those reported for a lot of different extracts microencapsulated by this technique (BERNSTEIN; NOREÑA, 2015; DAZA et al., 2016; TOLUN; ARTIK; ALTINTAS, 2020; ZANONI et al., 2020). On the other hand, the microparticles prepared by freeze-drying (Fig. 5 D, E, and F) had a more deformed and irregular shape, with extensive wrinkles and a porous and more serrated surface than those

microencapsulated by spray-drying. A similar morphology was observed by Yadav, Bajaj, Mandal, & Mann (2020) for freeze-dried grape seed extract using blends of whey protein concentrate, maltodextrin and gum arabic as wall materials. These authors suggested that ice supported the frozen structure during freeze-drying, and once ice was removed by sublimation, microcapsules retained the porous structure.

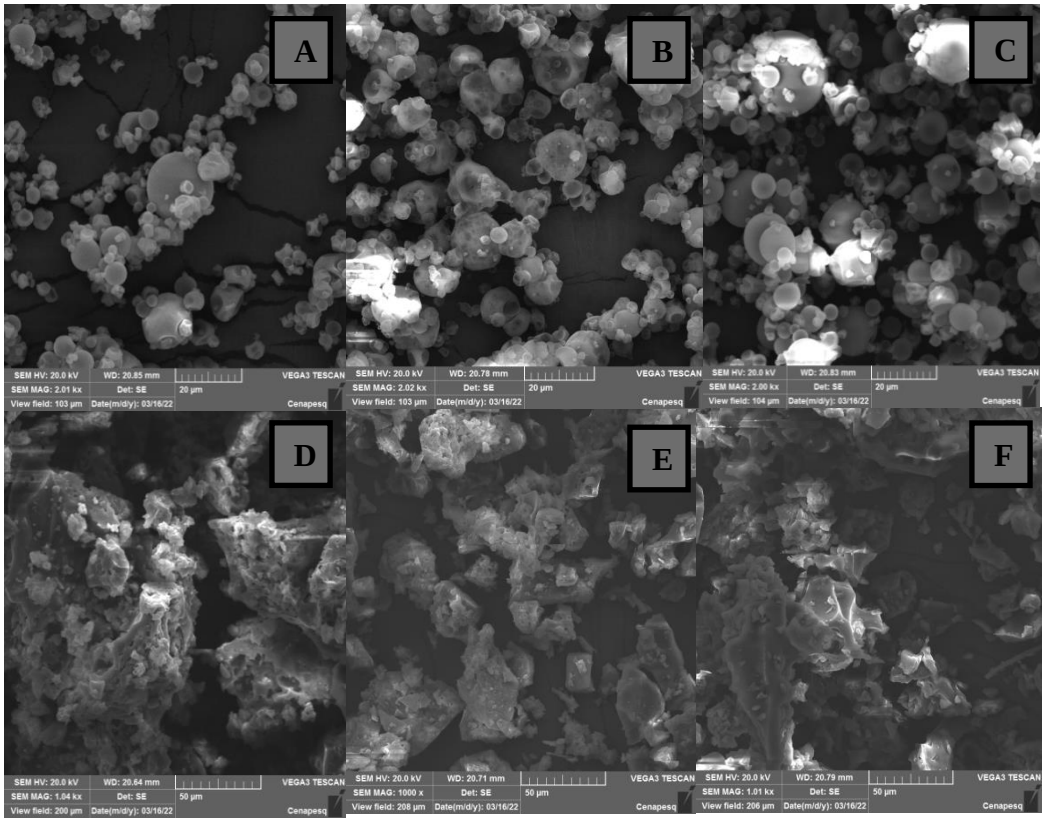


Figura 5. Scanning electron microscopy images of ciriguela peel extract microparticles prepared using different treatments: (A) spray-drying, with 100% M 5DE; (B) spray-drying, with 100% GA; (C) spray-drying, with 50% M 5DE and 50% GA; (D) freeze-drying, with 100% M 5DE; (E) freeze-drying, with 100% GA; (F) freeze-drying, with 50% M 5DE and 50% GA.

Differences in morphology, shape and size of microparticles produced by the freeze-drying and spray-drying processes should be expected due to the quite different drying conditions (BALLESTEROS et al., 2017). The use of gum arabic interfered with the morphology of microcapsules, causing deformations (irregularly spherical shape, shrinkage and dents on the surface) similar to those observed by Daza et al. (2016) and Tolun et al. (2020) using the same encapsulating agent. Such morphological changes are expected to alter the power of encapsulation due to variation in the surface area of the coatings, which can affect the degradation of the encapsulated compounds (BALLESTEROS et al., 2017).

3.6. Phenolics profile by HPLC

An overall comparison of microparticles features revealed that those produced using 50% maltodextrin 5DE and 50% gum arabic by both spray-drying (treatment 3) and freeze-drying (treatment 6) showed the best physicochemical characteristics, good retention of phenolic compounds and high antioxidant activity. Therefore, the phenolics profile by HPLC and stability analysis were performed only on these two powders.

Thirty-one phenolic compounds were investigated in the liquid extract of ciriguela peel by-product as well as in the microcapsules prepared by spray-drying and freeze-drying it (Table 3). Four major groups were identified and quantified by HPLC, namely phenolic acids, flavanols, flavonols and flavanones, plus minor amounts of anthocyanins and stilbenes, whose amounts, however, strongly depended on the sample preparation protocol.

As expected, such profiles are relatively close to those reported for frozen ciriguela pulp (DUTRA et al., 2017) and ciriguela peels (ENGELS et al., 2012; SILVA et al., 2016). Chlorogenic acid was the main phenolic acid found in the liquid extract (228.31 ± 5.67 µg/g of dry matter) and the only one detected in both spray-dried (26.28 ± 0.39 µg/g of dry matter) and freeze-dried (24.10 ± 1.14 µg/g of dry matter) extracts. Whereas epicatechin and epicatechin gallate were the main flavanols detected in the control, epigallocatechin gallate and epicatechin gallate were the most abundant in the spray-dried extract and procyanidin B1, catechin and epigallocatechin gallate in the freeze-dried one (Table 3). Rutin and quercetin were the major flavonols in the liquid and freeze-dried extracts, while myricetin and rutin were predominant in the spray-dried one, followed by kaempferol and quercetin.

As is known, all phenolic compounds are important nutrients and flavor components, whose presence is desirable especially in food products. Microencapsulation by spray drying significantly increased the amounts of the flavanols procyanidin B1 and epigallocatechin gallate and of the flavonols myricetin and kaempferol compared to the liquid extract, but both drying methods significantly reduced those of the flavonols rutin and quercetin ($p < 0.05$). On the other hand, *trans*-resveratrol and petunidin 3-glucoside, belonging to stilbene and anthocyanin classes, respectively, were only found in the liquid extract.

Table 3. Phenolics profiles of the liquid ciriguela peel extract (control) and of microcapsules prepared by spray-drying and freeze-drying it using 50% M 5DE and 50% GA as a wall material.

Phenolic compound (μg/g of dry matter)	Retention time (min)	Liquid extract (control)	Spray-dried microcapsules	Freeze-dried microcapsules
Phenolic acids				
Trans-caftaric acid	13.4	14.09 ± 0.26[a]	ND	ND
Chlorogenic acid	14.6	228.31 ± 5.67[a]	26.28 ± 0.39[b]	24.10 ± 1.14[b]
Caffeic acid	17.1	18.01 ± 3.03[a]	ND	ND
p-Coumaric acid	23.3	15.45 ± 0.62[a]	ND	ND
Flavanols				
Procyanidin B1	12.6	5.96 ± 0.12[c]	12.91 ± 0.12[b]	95.02 ± 0.32[a]
Procyanidin B2	16.9	15.47 ± 0.37[a]	ND	ND
Catechin	14.6	60.95 ± 0.93[b]	11.08 ± 0.06[c]	97.08 ± 2.16[a]
Epicatechin	19.3	105.71 ± 2.02[a]	18.25 ± 2.67[b]	30.06 ± 13.52[b]
Epigallocatechin gallate	20.2	28.96 ± 0.48[b]	70.17 ± 0.26[a]	82.25 ± 13.41[a]
Epicatechin gallate	25.3	228.63 ± 12.78[a]	40.19 ± 0.36[b]	51.64 ± 0.07[b]
Procyanidin A2	26.4	80.40 ± 4.70[a]	36.98 ± 0.17[b]	40.04 ± 1.94[b]
Flavonols				
Myricetin	23.9	65.85 ± 0.24[b]	97.41 ± 1.96[a]	18.53 ± 0.33[c]
Rutin	25.3	342.59 ± 45.08[a]	71.11 ± 1.14[b]	72.92 ± 0.73[b]
Quercetin	25.7	181.02 ± 6.28[a]	56.37 ± 0.67[b]	43.24 ± 0.26[c]
Kaempferol	27.0	5.32 ± 0.02[b]	57.14 ± 7.09[a]	ND
Flavanones				
Hesperidin	27.1	92.48 ± 5.09[a]	74.76 ± 5.10[b]	ND
Stilbenes				
Trans-resveratrol	29.2	26.38 ± 0.86[a]	ND	ND
Anthocyanins				
Petunidin 3-glucoside	24.7	7.19 ± 1.45[a]	ND	ND

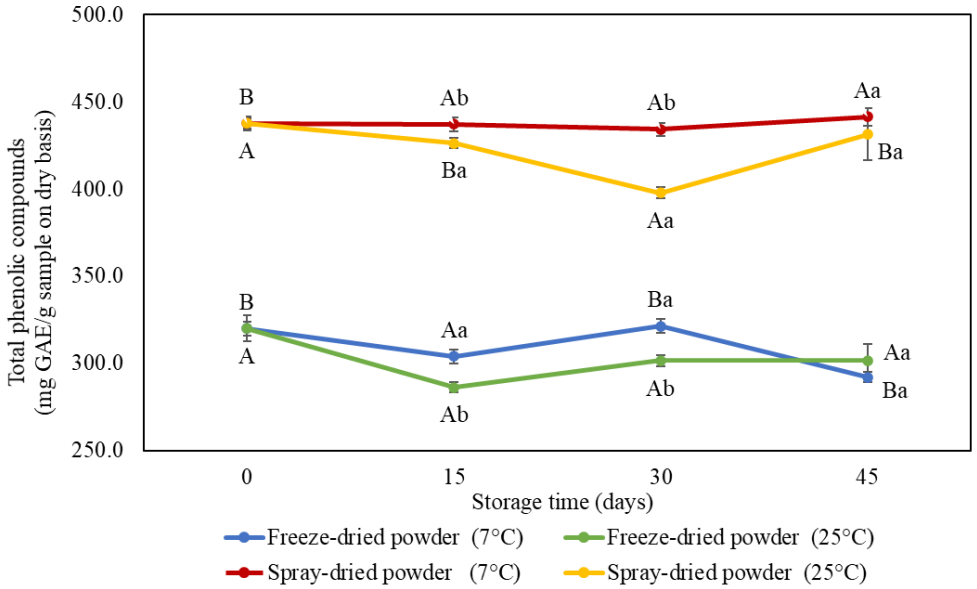
*Results are the means of three determinations (n = 3) ± standard deviation. Different letters in the same column indicate significant differences among samples ($p < 0.05$). ND – not detected.

It has been reported in previous studies that oxidation and/or degradation of antioxidant compounds can occur when fruits are subjected to processing, including maceration, trituration, microencapsulation or freezing (TOMAS et al., 2015; BARBOSA et al., 2016; BUNIOWSKA et al., 2017; DUTRA et al., 2017), which can justify the reductions observed for some less stable phenolic compounds after both spray-drying and freeze-drying.

3.7. Storage stability

One-gram microcapsules prepared by spray-drying and freeze-drying with 50% M and 50% GA were packed in metallized plastic bags, vacuum-sealed, and stored for 45 days at two temperatures, namely 7 ± 1 ºC, aiming to use the powder as an additive

in products stored under refrigeration, and room temperature (25 ± 1 ºC). The 45-days stability profiles of microcapsules produced by spray-drying and freeze-drying are illustrated in Figure 6 in terms of retention of TPC.



*Different capital letters represent statistically significant differences ($p < 0.05$) among different days at the same storage temperature. Different lowercase letters represent statistically significant differences ($p < 0.05$) after the same storage time at different temperatures.

Figure 6. 45-Days storage stability at 7 and 25 ºC of total phenolic compounds entrapped in spray-dried and freeze-dried microcapsules of ciriguela peel extract using 50% maltodextrin 5 DE and 50% gum arabic.

The spray-dried and freeze-dried microcapsules of ciriguela peel extract did not show any statistically significant difference in their TPC contents ($p > 0.05$) after 45 days compared to the beginning (time 0), regardless of the storage temperature. The highest TPC content after 45 days of storage was observed in microcapsules prepared by spray-drying (437.61 and 441.4 mg GAE/g at 7 ºC and 25 °C, respectively). Under refrigeration at 7 °C, the TPC content of spray-dried microcapsules has even increased slightly compared to the initial value, probably due to the formation of polyphenols following the hydrolysis of polyphenol conjugates (BAKOWSKA-BARCZK; KOLODZIEJCZYK, 2011; NUNES et al., 2015).

CONCLUSIONS

In this study, extracts of the phenolic compounds-rich ciriguela agroindustrial residue were dried by spray-drying and freeze-drying using gum arabic and maltodextrin as encapsulating agents. The content of total phenolic compounds (TPC)

showed significant and positive correlations with antioxidant activity determined by both DPPH and FRAP assays. The microencapsulation efficiency was greater than 80% for TPC, and the antioxidant activity was high in all powders. In general, spray- and freeze-dried powders had good physicochemical characteristics, i.e., water activity, moisture, hygroscopicity, solubility, and color parameters. Compared to freeze-drying, the spray-drying treatment led to better morphological characteristics of microcapsules, which showed spherical shape and lower incidence of roughness and fissures. Chlorogenic acid, epicatechin gallate and quercetin were the major phenolic compounds in the liquid extract, while epigallocatechin gallate and myricetin those in the spray-dried extract, and procyanidin B1, catechin and epigallocatechin gallate those in the freeze-dried one. Rutin was one of the most abundant phenolic compounds both in the liquid and in the microencapsulated extracts. The stability of microcapsules rich in phenolic compounds showed no significant difference after 45 days compared to the initial value, regardless of storage temperature and encapsulation method. These characteristics make the microencapsulated powders here developed a promising source of functional ingredientes for nutraceutical foods.

REFERENCES

AGUDELO, C.; BARROS, L.; SANTOS-BUELGA, C.; MARTÍNEZ-NAVARRETE, N.; FERREIRA, I. C. F. R. Phytochemical content and antioxidant activity of grapefruit (*Star Ruby*): A comparison between fresh freeze-dried fruits and different powder formulations. **LWT - Food Science and Technology**, v. 80, p. 106-112, 2017.

AN, N.; SUN, W.; LI, B.; WANG, Y.; SHANG, N.; LV, W.; LI, D.; WANG, L. Effect of different drying techniques on drying kinetics, nutritional components, antioxidant capacity, physical properties and microstructure of edamame. **Food Chemistry,** v. 373, Part B, 2022.

ANTONIO-GÓMEZ, M. V.; SALINAS-MORENO, Y.; HERNÁNDEZ-ROSAS, F.; MARTÍNEZ-BUSTOS, F.; ANDRADE-GONZÁLEZ, I.; HERRERA-CORREDOR, J. A. Optimized Extraction, Microencapsulation, and Stability of Anthocyanins from *Ardisia compressa* K. Fruit. **Polish Journal of Food Nutrition Science**, v. 71(3), p. 299–310, 2021.

ASSADPOUR, E.; JAFARI, S. M. Advances in Spray-Drying Encapsulation of Food Bioactive Ingredients: From Microcapsules to Nanocapsules. **Annual Review of Food Science and Technology**, v. *10*, p. 103-131, 2019.

AUGUSTIN, M. A.; HEMAR, Y. Nano- and micro-structured assemblies for encapsulation of food ingredients. **Chemical Society Reviews**, v. 38(4), p. 902-912, 2009.

AUGUSTO, P. E. D.; CRISTIANINI, M.; IBARZ, A. Effect of temperature on dynamic and steadystate shear rheological properties of siriguela *(Spondias purpurea* L.) pulp. **Journal of Food Engineering**, v. 108, p. 283 – 289, 2012.

BALLESTEROS, L. F.; RAMIREZ, M. J.; ORREGO, C. E.; TEIXEIRA, J. A.; MUSSATTO, S. I. Encapsulation of antioxidant phenolic compounds extracted from spent coffee grounds by freeze-drying and spray-drying using different coating materials. **Food Chemistry**, v. 237, p. 623-631, 2017.

BAKOWSKA-BARCZAK, A. M.; KOLODZIEJCZYK, P. P. Black currant polyphenols: their storage stability and microencapsulation. **Industrial Crops and Products,** v. 34(2), p. 1301–1309, 2011.

BARBOSA, P. O.; PALA, D.; SILVA, C. T.; SOUZA, M. O.; AMARAL, J. F.; VIEIRA, R. A. L.; FOLLY, G. A. F.; VOLP, A. C. P.; FREITAS, R. N. Açai (*Euterpe oleracea* Mart.) pulp dietary intake improves cellular antioxidant enzymes and biomarkers of serum in healthy women. **Nutrition,** v. 32(6), p. 674–680, 2016.

BARROS, R. G. C.; ANDRADE, J. K. S.; DENADAI, M.; NUNES, M. L.; NARAIN, N. Evaluation of bioactive compounds potential and antioxidant activity in some Brazilian exotic fruit residues. **Food Research International**, v. 102, p. 84–92, 2017.

BEN-OTHMAN, S.; JÕUDU, I.; BHAT, R. Bioactives from Agri-Food Wastes: Present Insights and Future Challenges. **Molecules**, v. *25*, p. 510-544, 2020.

BERNARDES, A. L.; MOREIRA, J. A.; TOSTES, M. G. V.; COSTA, N. M. B.; SILVA, P. I.; COSTA, A. G. V. In vitro bioaccessibility of microencapsulated phenolic compounds of jussara (*Euterpe edulis* Martius) fruit and application in gelatine model-system. **LWT - Food Science and Technology**, v. 102, p. 173-180, 2019.

BERNSTEIN, A.; NOREÑA, C. P. Z. Encapsulation of red cabbage (*Brassica oleracea* L. Var. capitata L. f. rubra) anthocyanins by spray drying using different encapsulating agents. **Brazilian Archives of Biology and Technology**, v. 58(6), p. 944 –952, 2015.

BRAND-WILIAMS, W., CUVELIER, M.E., BERSET, C. Use of a free radical method to evaluate antioxidant activity. **Food Science and Technology**, v. 28, p. 25-30, 1995.

BUNIOWSKA, M.; CARBONELL-CAPELLA, J. M.; FRIGOLA, A.; ESTEVE, M. J. Bioaccessibility of bioactive compounds after non-thermal processing of an exotic fruit juice blend sweetened with Stevia rebaudiana. **Food Chemistry,** v. 221, p. 1834–1842, 2017.

BUSCH, V. M.; PEREYRA-GONZALEZ, A.; ŠEGATIN, N.; SANTAGAPITA, P. R.; POKLAR ULRIH, N.; BUERA, M. P. Propolis encapsulation by spray drying: characterization and stability. **LWT - Food Science and Technology**, v. 75, p. 227–35, 2017.

CAI, Y. Z.; CORKE, H. Production and properties of spray dried *Amaranthus* betacyanin pigments. **Journal of Food Science**, v. 65, p. 1248-1252, 2000.

CALDAS, T. W.; MAZZA, K. E. L.; TELES, A. S. C.; MATTOS, G. N.; BRÍGIDA, A. I. S.; CONTE-JUNIOR, C. A.; BORGUINI, R. G.; GODOY, R. L. O.; CABRAL, L. M. C.; TONON, R. V. Phenolic compounds recovery from grape skin using conventional and nonconventional extraction methods. **Industrial Crops & Products**, v. 111, p. 86–91, 2018.

CALISKAN, G.; DIRIM, S. N. The effect of different drying processes and the amounts of maltodextrin addition on the powder properties of sumac extract powders. **Powder Techonology**, v. 287, p. 308-314, 2016.

ÇAM, M.; IÇYER, N. C.; ERDOGAN, F. Pomegranate peel phenolics: Microencapsulation, storage stability and potential ingredient for functional food development. **LWT – Food Science and Technology**, v. 55(1), p. 117–123, 2014.

CANO-CHAUCA, M.; RAMOS, A. M.; STRINGHETA, P. C. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. **Innovative Food Science e Emerging Technologies**, v. 6, p. 420-428, 2005.

DAZA, L. D.; FUJITA, A.; FÁVARO-TRINDADE, C. S.; RODRIGUES-RACT, J. N.; GRANATO, D.; GENOVESE, M. I. Effect of spray drying conditions on the physical properties of cagaita (*Eugenia dysenterica* DC.) fruit extracts. **Food and Bioproducts Processing**, v. 97, p. 20–29, 2016.

DENG, L.-Z.; PAN, Z.; MUJUMDAR, A. S.; ZHAO, J.-H.; ZHENG, Z.-A.; GAO, Z.-J.; XIAO, H.-W. High-humidity hot air impingement blanching (HHAIB) enhances drying quality of apricots by inactivating the enzymes, reducing drying time and altering cellular structure. **Food Control**, v. 96, p. 104–111, 2019.

DUTRA, R. L. T.; DANTAS, A. M.; MARQUES, D. A.; BATISTA, J. D. F.; MEIRELES, B. R. L. A.; CORDEIRO, A. M. T. M.; MAGNANI, M.; BORGES, G. S. C. Bioaccessibility and antioxidant activity of phenolic compounds in frozen pulps of Brazilian exotic fruits exposed to simulated gastrointestinal conditions. **Food Research International**, v. 100, Part 1, p. 650-657, 2017.

DUTRA, M. C. P.; RODRIGUES, L. L.; OLIVEIRA, D.; PEREIRA, G. E.; LIMA, M. S. Integrated analyses of phenolic compounds and minerals of Brazilian organic and conventional grape juices and wines: Validation of a method for determination of Cu, Fe and Mn. **Food Chesmitry**, v. 269, p. 157-165, 2018.

DUZZIONI, A. G.; LENTON, V. M.; SILVA, D. I. S.; BARROZO, M. A. S. Effect of drying kinetics on main bioactive compounds and antioxidant activity of acerola

(*Malpighia emarginata* D.C.) residue. **International Journal of Food Science & Technology**, v. 48(5), p. 1041–1047, 2013.

ENGELS, C.; GRATER, D.; ESQUIVEL, P.; JIMÉNEZ, V. M.; GANZLE, M. G.; SCHIEBER, A. Characterization of phenolic compounds in jocote (*Spondias purpurea L*) peels by ultra high-performance liquid chromatography/electrospray ionization mass spectrometry. **Food Research International**, v. 46, p. 557-562, 2012.

FIGUEIREDO, J. A.; TEIXEIRA, M. A.; CAMPELO, P. H.; LAGO, A. M. T.; DE SOUZA, T. P.; YOSHIDA, M. I.; DE OLIVEIRA, C. R.; PEREIRA, A. P. A.; PASTORE, G. M.; SANCHES, E. A.; BOTREL, D. A.; BORGES, S. V. Encapsulation of camu-camu extracts using prebiotic biopolymers: Controlled release of bioactive compounds and effect on their physicochemical and thermal properties. **Food Research International**, v. 137, 109563, 2020.

GOOT, A. J.; PELGROM, P. J. M.; BERGHOUT, J. A. M.; GEERTS, M. E. J.; JANKOWIAK, L.; HARDT, N. A.; BOOM, R. M. Concepts for further sustainable production nof foods. **Journal of Food Engineering**, v. 168, p. 42–51, 2016.

GUANDALINI, B. B. V.; RODRIGUES, N. P.; MARCZAK, L. D. F. Sequential extraction of phenolics and pectin from mango peel assisted by ultrasound. **Food Research International**, v. 119, p. 455–461, 2019.

JIANG, N.; LIU, C.; LI, D.; ZHANG, Z.; LIU, C.; WANG, D.I.; NIU, L.; ZHANG, M. Evaluation of freeze drying combined with microwave vacuum drying for functional okra snacks: Antioxidant properties, sensory quality, and energy consumption. **LWT-Food Science and Technology**, v. 82, p. 216–226, 2017.

KUCK, L. S.; NOREÑA, C. P. Z. Microencapsulation of grape (*Vitis labrusca* var. Bordo) skin phenolic extract using gum arabic, polydextrose, and partially hydrolyzed guar gum as encapsulating agents. **Food Chemistry**, v. 194, p. 569–576, 2016.

LABUSCHAGNE, P. Impact of wall material physicochemical characteristics on the stability of encapsulated phytochemicals: a review. **Food Research International**, v. 107, p. 227–247, 2018.

LEE, Y.; CHANG, Y.H. Microencapsulation of a maca leaf polyphenol extract in mixture of maltodextrin and neutral polysaccharides extracted from maca roots. **International Journal of Biological Macromolecules**, v. 150, p. 546–558, 2020.

MAHDAVI, S. A.; JAFARI, S. M. A.; ASSADPOOR, E.; DEHNADA, D. Microencapsulation optimization of natural anthocyanins with maltodextrin, gum Arabic and gelatin. **International Journal of Biological Macromolecules**, v. 85, p. 379–385, 2016.

MALDONADO-ASTUDILLO, Y. I.; ALIA-TEJACAL, I.; NÚNEZ-COLÍN, C. A.; JIMÉNEZ-HERNÁNDEZ, J.; PELAYO-ZALDÍVAR C.; LÓPEZ-MARTÍNEZ, V.; ANDRADE-RODRÍGUEZ, M.; BAUTISTA-BANOS, S.; VALLE-GUADARRAMA, S. Postharvest physiology and technology of *Spondias purpurea* L. and *S. mombin* L. **Scientia Horticulturae**, v. 174, p. 193–206, 2014.

McGUIRE, R. G. Reporting of Objective Color Measurements. **HortScience**, v. 27(12), p. 1254-1255, 1992.

MOREIRA, S. A.; ALEXANDRE, E. M. C.; PINTADO, M.; SARAIVA, J. A. Effect of emergent non-thermal extraction technologies on bioactive individual compounds profile from different plant materials. **Food Research International**, v. 115, p. 177–190, 2019.

NUNES, G. L.; BOAVENTURA, B. C. B.; PINTO; S. S.; VERRUCK, S.; MURAKAMI, F. S.; PRUDÊNCIO, E. S.; AMBONI, R. D. M. C. Microencapsulation of freeze concentrated *Ilex paraguariensis* extract by spray drying. **Journal of Food Engineering**, v. 151, p. 60–68, 2015.

PADILHA, C. V. S.; MISKINIS, G. A.; SOUZA, M. E. A. O.; PEREIRA, G. E.; OLIVEIRA, D.; BORDIGNON-LUIZ, M. T.; LIMA, M. S. Rapid determination of

flavonoids and phenolic acids in grape juices and wines by RP-HPLC/DAD: Method validation and characterization of commercial products of the new Brazilian varieties of grape. **Food Chesmistry**, v. 228, p. 106-115, 2017.

PAPILLO, V. A.; LOCATELLI, M.; TRAVAGLIA, F.; BORDIGA, M.; GARINO, C.; ARLORIO, M.; COÏSSON, J. D. Spray-dried polyphenolic extract from Italian black rice (*Oryza sativa* L., var. Artemide) as new ingredient for bakery products. **Food Chesmitry**, v. 269(15), p. 603-609, 2018.

PATHARE, P. B.; OPARA, U. L.; AL-SAID, F. A. Colour measurement and analysis in fresh and processed foods: a review. **Food Bioprocess Technology**, v. 6, p. 36–60, 2013.

RAMADAN, M. F.; KROH, L. W.; MORSEL, J. T. Radical scavenging activity of black cumin (*Nigella sativa* L.), coriander (*Coriandrum sativum* L.), and Niger (*Guizotia abyssinica* Cass.) crude seed oils and oil fractions. **Journal of Agricultural and Food Chemistry**, v. 51(24), p. 6961–6969, 2003.

RAMÍREZ, M. J.; GIRALDO, G. I.; ORREGO, C. E. Modeling and stability of polyphenol in spray-dried and freeze-dried fruit encapsulates. **Powder Technology**, v. 277, p. 89–96, 2015.

REZENDE, Y. R. R. S.; NOGUEIRA, J. P.; NARAIN, N. Microencapsulation of extracts of bioactive compounds obtained from acerola (*Malpighia emarginata* DC) pulp and residue by spray and freeze drying: Chemical, morphological and chemometric characterization. **Food Chemistry**, v. 254, p. 281-291, 2018.

RIBEIRO, A. M.;, ESTEVINHO, B. N.; ROCHA, F. Microencapsulation of polyphenols - The specific case of the microencapsulation of *Sambucus Nigra* L. extracts - A review. **Trends in Food Science & Technology**, v. 105, p. 454-467, 2020.

SAÉNZ, C.; TAPIA, S.; CHÁVEZ, J.; ROBERT, P. Microencapsulation by spray drying of bioactive compounds from cactus pear (*Opuntia ficus-indica*). **Food Chemistry**, v. 11, p. 616–622, 2009.

SÁNCHEZ-MORENO, C.; LARRAURI, J. A.; SAURA-CALIXTO, F. A procedure to measure the antiradical efficiency of polyphenols. **Journal of the Science of Food and Agriculture**, v. 76(2), p. 270-276, 1998.

SILVA, R. V.; COSTA, S. C. C.; BRANCO, C. R. C.; BRANCO, A. In vitro photoprotective activity of the *Spondias purpurea* L. peel crude extract and its incorporation in a pharmaceutical formulation. **Industrial Crops and Products**, v. 83, p. 509-514, 2016.

SILVA JÚNIOR, M. E.; ARAÚJO, M. V. R. L.; SANTANA, A. A.; SILVA, F. L. H.; MACIEL, M. I. S. Ultrasound-assisted extraction of bioactive compounds from ciriguela (*Spondias purpurea* L.) peel: Optimization and comparison with conventional extraction and microwave. **Arabian Journal of Chemistry**, v. 14(8), 103260, 2021.

THAIPONG, K.; BOONPRAKOB, U.; CROSBY, K.; CISNEROS-ZEVALLOS, L.; BYRNE, D. H. Comparison of ABTS, DPPH, FRAP, and ORAC assays for estimating antioxidant activity from guava fruit extracts. **Journal of Food Composition and Analysis**, v. 19(6-7), p. 669-675, 2006.

TOLUN, A.; ALTINTAS, Z.; ARTIK, N. Microencapsulation of grape polyphenols using maltodextrin and gum Arabic as two alternative coating materials: development and characterization. **Journal of Biotechnology**, v. 239, p. 23–33, 2016.

TOLUN, A.; ARTIK, N.; ALTINTAS, Z. Effect of different microencapsulating materials and relative humidities on storage stability of microencapsulated grape pomace extract. **Food Chemistry**, v. 302, 125347, 2020.

TOMAS, M., TOYDEMIR, G., BOYACIOGLU, D., HALL, R., & BEEKWILDER, J. C. E. The effects of juice processing on black mulberry antioxidants. **Food Chemistry**, v. 186, p. 277–284, 2015.

TSAI, F.; KITAMURA, Y.; KOKAWA, M. Effect of gum arabic-modified alginate on physicochemical properties, release kinetics, and storage stability of liquid-core hydrogel beads. **Carbohydrate Polymers**, v. 174(15), p. 1069-1077, 2017.

WETTASINGHE, M.; SHAHIDI, F. Evening primrose meal: a source of natural antioxidants and scavenger of hydrogen peroxide and oxygen-derived free radicals. **Journal of Agricultural and Food Chemistry**, v. 47, p. 1801-1812, 1999.

YADAV, K.; BAJAJ, R. K.; MANDAL, S.; MANN, B. Encapsulation of grape seed extract phenolics using whey protein concentrate, maltodextrin and gum arabica blends. **Journal of Food Science Technology**, v. 57(2), p. 426-434, 2020.

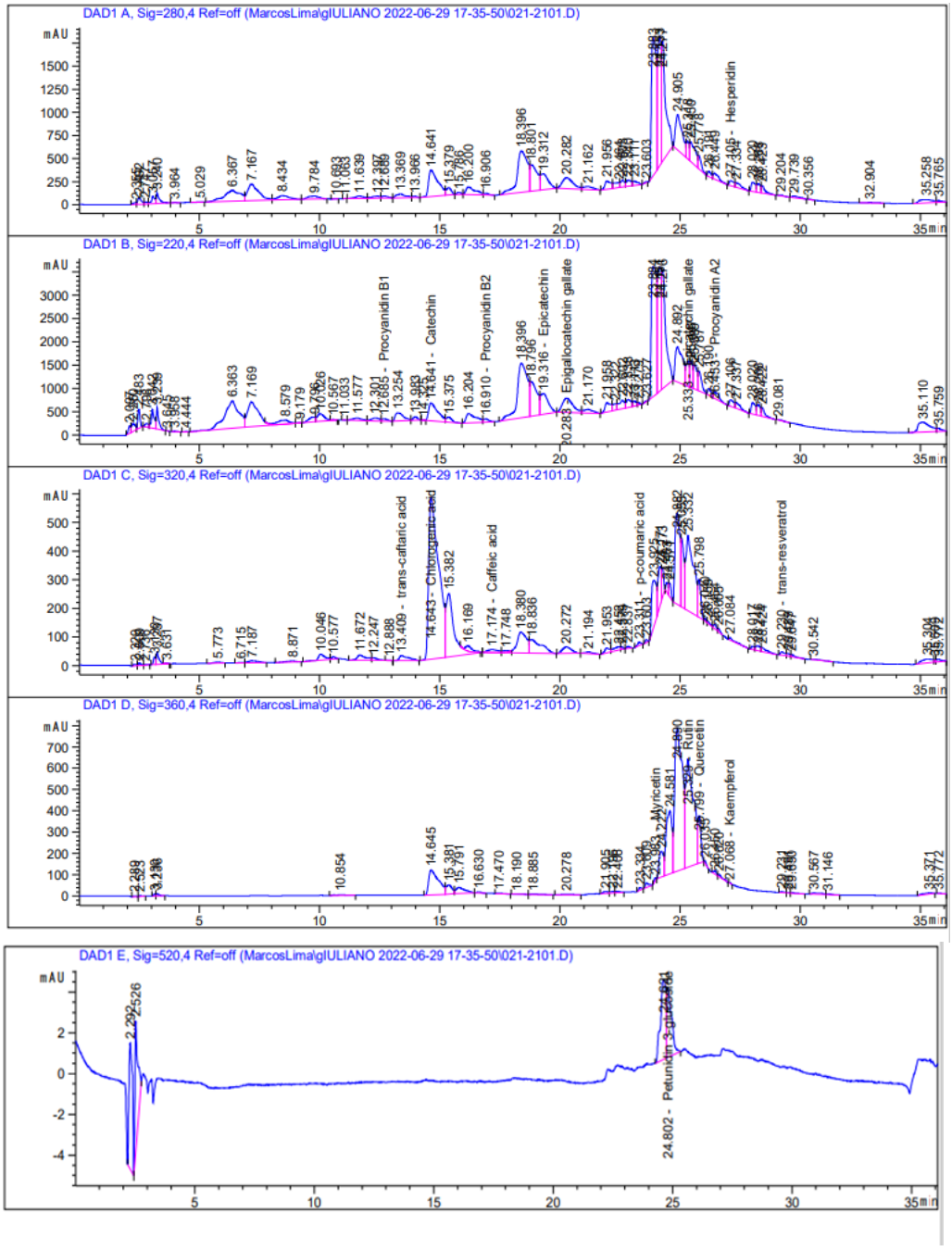
YILDIZ, G.; RABABAH, T.; FENG, H. Ultrasound-assisted cutting of Cheddar, Mozzarella and Swiss Cheeses – Effects on quality attributes during storage. **Innovative Food Science and Emerging Technologies**, v. 37, p. 1–9, 2016.

ZANONI, F.; PRIMITERRA, M.; ANGELI, N.; ZOCCATELLI, G. Microencapsulation by spray-drying of polyphenols extracted from red chicory and red cabbage: Effects on stability and color properties. **Food Chemistry**, v. 307, 125535, 2020.

Effect of coating material on microencapsulation by spray-drying and freeze-drying of phenolic compounds extracted from ciriguela peel residue

Supplementary Material

Fig S1. HPLC-DAD chromatogram of ciriguela residue extract.



5. CONSIDERAÇÕES FINAIS

Diante dos resultados obtidos nos artigos apresentados conclui-se que:

- Casca de Ciriguela (*Spondias purpurea* L.) é considerada uma fonte sustentável de antioxidantes naturais e compostos fenólicos. A condição ótima da extração assistida por ultrassom dos compostos fenólicos do extrato de resíduo da farinha de ciriguela foi obtida utilizando amplitude ultrassônica (UA) de 100% e tempo (t) de 15 min. O processo de extração afetou o teor de compostos bioativos e a atividade antioxidante.
- As condições otimizadas de microencapsulação por atomização do extrato de resíduo de ciriguela foram: temperatura de 150 °C, vazão de alimentação de 0,80 L/h^{-1} e 100 % de goma arábica como agente encapsulante.
- O extrato atomizado apresentou maior TPC (476,82 mg GAE g-1) do que o extrato liofilizado (382,86 mg GAE g-1). Os compostos fenólicos encontrados em maiores concentrações no extrato líquido do resíduo de ciriguela foram rutina, galato de epicatequina, ácido clorogênico e quercetina, enquanto rutina e miricetina foram os mais abundantes no extrato atomizado, e quercetina e kaempferol no liofilizado.
- Após digestão gastrointestinal simulada de extratos microencapsulados, a rutina foi o composto fenólico mais abundante nas microcápsulas.
- Pós atomizados e liofilizados, independente da temperatura (7 ou 25 °C), mantiveram seu alto teor de compostos fenólicos após 90 dias de armazenamento. O conteúdo de compostos fenólicos totais (TPC) apresentou correlações significativas e positivas com a atividade antioxidante determinada pelos ensaios DPPH e FRAP.
- As microcápsulas liofilizadas tinham formato mais deformado e irregular, com rugas extensas e superfície mais dentada do que atomizadas, que tinham formato esférico, poucas deformações e superfície lisa.
- Essas informações tornam os pós microencapsulados aqui desenvolvidos uma fonte promissora de ingredientes funcionais para alimentos nutracêuticos.

ANEXOS

Anexo 1.
Primeira página do Artigo I: Ultrasound-assisted extraction of bioactive compounds from ciriguela (*Spondias purpurea* L.) peel: Optimization and comparison with conventional extraction and microwave

Arabian Journal of Chemistry (2021) **14**, 103260

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Ultrasound-assisted extraction of bioactive compounds from ciriguela (*Spondias purpurea* L.) peel: Optimization and comparison with conventional extraction and microwave

Marcony Edson Silva Júnior [a], **Maria Vitória R.L. Araújo** [b], **Anderson Andrade Santana** [b], **Flávio Luiz H. Silva** [a], **Maria Inês S. Maciel** [a,*]

[a] *Food Science and Technology Graduate Program, Technology Center, Federal University of Paraíba, João Pessoa, Brazil*
[b] *Laboratory of Physical-Chemical Analysis of Food, Department of Consumer Sciences, Federal Rural University of Pernambuco, Recife, Brazil*

Received 25 February 2021; accepted 9 June 2021
Available online 15 June 2021

KEYWORDS

Phenolic compounds;
Antioxidants;
Extraction;
Ultrasound;
Microwave

Abstract The ciriguela (*Spondias purpurea* L.) residue resulting from its pulp and juice processing stands out due to the high content of bioactive compounds. This study aimed to optimize the ultrasound-assisted extraction (UAE) process of phenolic compounds from ciriguela peel. The response surface method was used to investigate the effects of process-independent variables (ultrasonic amplitude, UA): 20%, 60% and 100%, and ultrasonic exposure time (T): 5, 10 and 15 min on the dependent variables (content of total phenolic compounds (TPC), DPPH – 1,1-diphenyl-2-picrylhydrazyl free radical scavenging (IC_{50}) and ferric reducing-antioxidant power (FRAP) of ciriguela peel extract. The UA and time influenced TPC, IC_{50} and antioxidant activity by FRAP. However, the antioxidant activity of DPPH had no significant influence on the variables used. Ideal conditions were set at UA = 100% (200 W) and T = 15 min. The extract of phenolic compounds from the ciriguela peel obtained by optimized ultrasound was compared with other extraction techniques (conventional and microwave-assisted). UAE showed better results concerning the extraction yield of phenolic compounds and high antioxidant activity (35.15 mg GAE/g, IC 50 = 0.19 mg/mL), compared to conventional extraction (30.10 mg GA/g and IC 50 = 1.68 mg/mL) and microwave-assisted (23.31 mg GA/g and IC 50 = 4.29 mg/mL). These results demonstrate

* Corresponding author.
E-mail addresses: marcony172009@hotmail.com (M.E. Silva Júnior), vitoria.lemos.araujo@gmail.com (M.V.R.L. Araújo), andersonandrade1993.s@gmail.com (A.A. Santana), flavioluizh@yahoo.com.br (F.L.H. Silva), m.inesdcd@gmail.com, maria.ismaciel@ufrpe.br (M.I.S. Maciel).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.arabjc.2021.103260