Review

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Cocoa waste valorization: a review and sustainability analysis of green technologies

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Abstract: Cocoa residues – notably cocoa pod husks and cocoa bean shells – can be valorized for biocompound recovery, bioenergy production, and waste reduction. This review analyzed 1115 publications related to this field to identify key research trends. Interest is increasing in compounds such as theobromine, bioactive substances, adsorption processes, and byproducts like biogas. Terms including 'biomass', 'biogas', 'theobromine', 'cocoa pod husk', and 'cocoa shell' emerged as central themes, along with extraction methods and sustainability. The environmental impact of three extraction methods – ultrasound (US), supercritical water extraction (SWE), and natural deep eutectic solvents (NADES) – was assessed using the Path2Green sustainability metric. Their respective scores were −0.386 for US, −0.05 for SWE, and 0.341 for NADES. The results highlight cocoa waste valorization as a growing field, driven by sustainability and circular economy goals. © 2025 The Author(s). *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

Key words: cocoa pod husk; cocoa bean shell; ultrasound; supercritical water extraction; natural deep eutectic solvents

Introduction

Theobroma cacao is an important crop and a source of economic development in several countries. Global production in 2023–2024 reached approximately 4.5×10^9 kg, with exports from October to December 2023 totaling 2.36×10^9 kg.[1] An estimated 5 to 6 million smallholder farmers account for over 90% of global cocoa production.[2] Following the World Cocoa Conference in April 2024,[3] concern for improving farmers' livelihoods contributed to a significant price increase – from \$2.284 per kg in July to \$2.584 in December 2024.[4,5]

Chocolate is the primary confectionery product derived from cocoa. It includes various forms such as tablets, candies, bites, truffles, cocoa powder, cocoa liquor, and paste. Cocoa semifinished products are also used widely in the

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manufacture of cookies, ice cream, breakfast cereals, desserts, gums, baked goods, and other processed foods.[6,7]

Cocoa pod husk (CPH), cocoa bean shell (CBS), and cocoa mucilage (CM) are the main wastes from the cocoa industry.[8] Only 20% to 30% of the cocoa pod is grain; 60% to 70% is CPH, and 100–150 L of CM is produced when 1 ton of cocoa grain is soaked.[7] Given their volume and relevance, the proper utilization of these residues is essential for achieving zero-waste production within the framework of the circular economy and sustainable development goals.

Cocoa waste contains a wide range of bioactive compounds, including tannins, pectin, proteins, lipids,[8,9] methylxanthines (theobromine, caffeine),[10] polyphenols (catechin, epicatechin), anthocyanins, flavonoids (quercetin), and organic acids. It also provides minerals, dietary fiber, and starch, and can be converted into various energy sources – such as biogas, biodiesel, bioethanol, and biohydrogen – as well as biodegradable materials, including polyhydroxyalkanoates (PHA), polylactic acid (PLA),[11] pectins, xylose, cellulose, and lignin (Fig. 1).[7–9,12–14]

Conventional extraction processes consume chemical solvents like methanol and ethanol, which contaminate water, air, and the ground; they also need more energy and extraction time. Emerging technologies, such as ultrasound (US), microwave (MW), pulsed electric fields (PEF), super/subcritical fluid extraction (SFE), and natural deep eutectic solvents (NADES), among others, possess various advantages such as selectivity and more efficient biocompound recovery, and they have a lower environmental impact; they use less energy, produce less waste, and need less time for the extraction process.

This review presents, for the first time, a bibliometric analysis of research on cocoa waste valorization, focusing on the main compounds extracted and trends in related publications. It includes an analysis of these compounds and a review of the green extraction techniques employed in the field. Finally, it offers a sustainability assessment comparing the environmental performance of three green extraction methods – supercritical water extraction (SWE), US, and NADES – to evaluate their environmental friendliness.

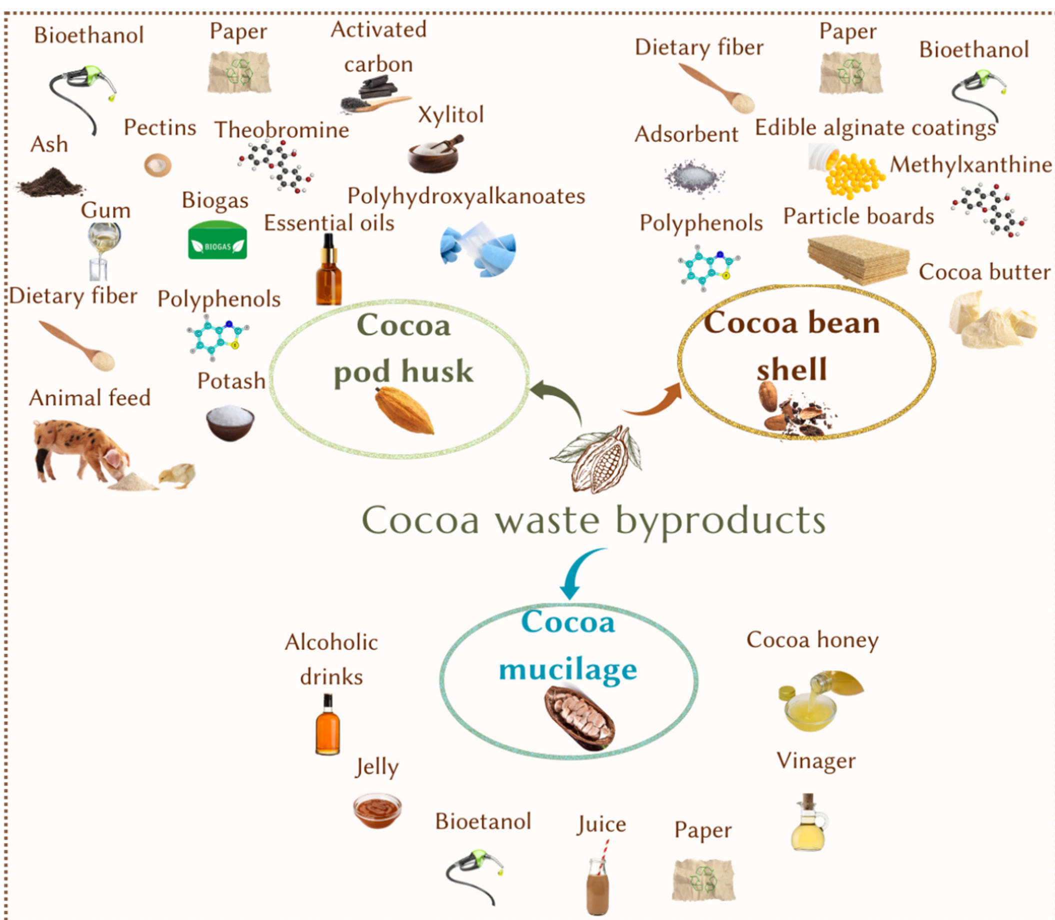

Figure 1. Cocoa waste byproducts.

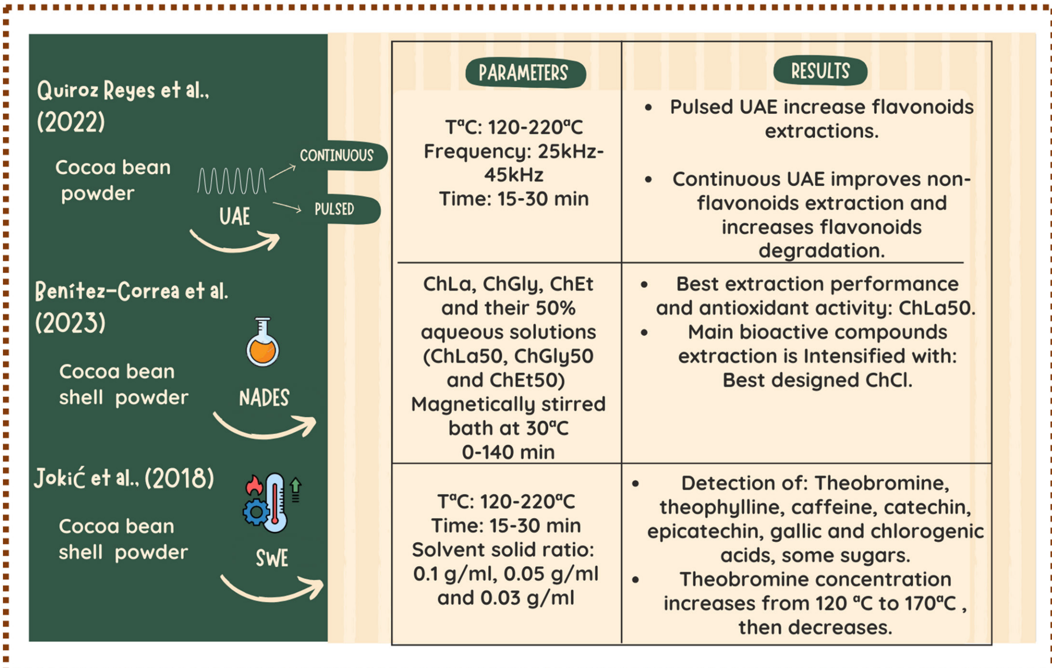

Figure 2. Comparison of methodologies in selected articles for sustainability analysis.

Methodology

The analysis was based on the Scopus database, with the search conducted in August 2024 and covering publications up to 2023. The keywords used were *quercetin* OR *theobromine* OR *methylxanthines* OR *waste* OR *valorization* OR *biomass* AND *Theobroma* OR *cacao*. The search criteria focused on key components extracted from cocoa waste and their valorization. A total of 1115 documents were retrieved and analyzed using VOSviewer and Bibliometrix. The VOSviewer was used to generate keyword distribution maps, grouping author keywords into clusters for analysis. Bibliometrix identified leading authors and produced a thematic map based on the most frequent keywords, applying the InfoMap clustering algorithm with a 250-word limit and a minimum cluster frequency of 5. The bibliometric analysis highlights the main research areas, most cited documents, leading authors and affiliations, and key trends in the field.

For the environmental analysis, three extraction techniques – US, SWE, and NADES – were selected for their versatility, performance, and comparability. The environmental scores of these methods were assessed using a Path2Green metric proposed in the literature.[15] This was based on 12 principles of green extraction. These principles evaluate various stages of the process, including pre-extraction and postextraction procedures. Each principle was also assessed individually, applying weighted scores: economic aspects (weight = 1), societal aspects (weight = 2), and environmental aspects (weight = 3). Three representative studies were compared: Article 1 – ultrasound extraction using an organic solvent (0.8% 2 mol/L HCl in water–methanol, 50:50 v/v)[16]; Article 2 – conventional extraction using a eutectic solvent (choline chloride:lactic acid, 1:2, with 50% water w/w)[17]; and Article 3 – SWE (Fig. 2).[18]

Results

Overview and trends in cocoa waste research

The analysis highlights publication trends between 2013 and 2023, during which 709 documents were identified, accounting for 63.59% of the total records in the Scopus database as of 2023. Over the past decade, academic interest in cocoa-derived compounds – such as quercetin, theobromine, and methylxanthines – as well as in themes including 'waste', 'biomass', and 'valorization', has grown considerably. The number of publications increased from 44 in 2013 to 96 in 2023. A marked rise occurred in 2018, with 67 publications, after which the upward trend continued (Fig. 3). The primary research areas include agricultural and biological sciences (25.5%), environmental science (11.8%), and biochemistry, genetics, and molecular biology (11.3%).

A co-occurrence analysis of author keywords identified 95 terms, which were grouped into color-coded clusters (Fig. 4a). Several keywords span multiple topics, linking different

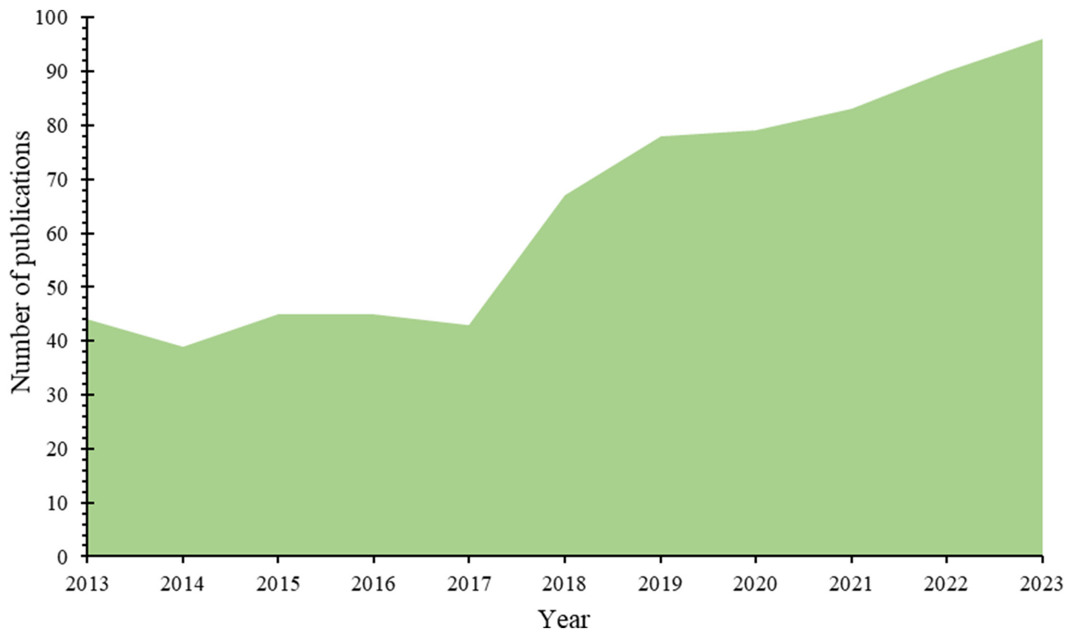

Figure 3. Evolution of cocoa-related research between 2013 and 2023.

clusters. The thickness of the connecting lines reflects the strength of association between terms.[19] Similarly, the temporal evolution of publications up to 2023 is shown in Fig. 4b, also color-coded by cluster. Biocompounds of interest that can be obtained from *T. cacao* – including polyphenols (flavanols, catechin, epicatechin), methylxanthines (theobromine, caffeine), flavonoids, procyanidins, and theophylline – appear in the yellow, purple, brown, and sky-blue clusters. The terms 'biomass' and 'bioenergy' form a red cluster linking cocoa and waste-related research. Byproducts such as 'biochar', 'biogas', 'bioethanol', and 'activated carbon' are also present, along with application terms like 'adsorption' and 'biosorption'. The nine clusters and their components are summarized in Table 1.

The conceptual structure of the database was analyzed using a thematic map generated with Bibliometrix, based on the most frequently used author keywords (Fig. 5). This map identifies niche, basic, motor, and emerging or declining themes, according to their degree of development (density) and relevance (centrality) within the research field. Keywords such as 'biomass', 'biogas', and 'agroindustrial waste' are classified as well-developed, highly relevant motor themes. 'Pyrolysis', 'cocoa pod husks', and 'agricultural waste' also appear as motor themes, though less developed and central than the former group. 'Adsorption', 'cocoa shell', and 'kinetics' are identified as less prominent motor themes, suggesting emerging areas with potential for further research.

Basic themes that are highly relevant but not yet well developed include 'theobromine', 'cocoa', and 'caffeine', which appear within the same cluster. Less relevant and less developed topics include '*Theobroma cacao*', 'agroforestry', and 'climate change'. In contrast, 'cocoa pod husk', 'pectin', and 'response surface methodology' show limited current relevance but have strong potential for future research. Other keywords found among the basic themes – such as 'biochar', 'cocoa shells', and 'soil' – also exhibit modest relevance but remain promising areas for further investigation. The term 'agricultural waste', identified as a motor theme, highlights a core focus of this article, as does the byproduct 'biogas'. 'Theobromine', although placed among the basic themes, is also closely related to the article's central topic. 'Cocoa shell' and 'cocoa pod husks' appear in both basic and motor themes, emphasizing their importance and potential for development in this research context.

Review of cacao waste and compounds of interest

Cocoa pod husk

Cocoa pod husk constitutes 70% of the total *T. cacao* fruit.[7] It contains acidic phenolics such as ferulic acid, which exhibit antioxidant, antibiotic, and antifungal activity, as well as cardiovascular and neuroprotective effects. Ferulic acid also has potential antidiabetic properties, primarily by regulating blood glucose and lowering blood sugar levels.[20] The antibacterial effects of cocoa pod husk have been demonstrated against *Porphyromonas gingivalis* and

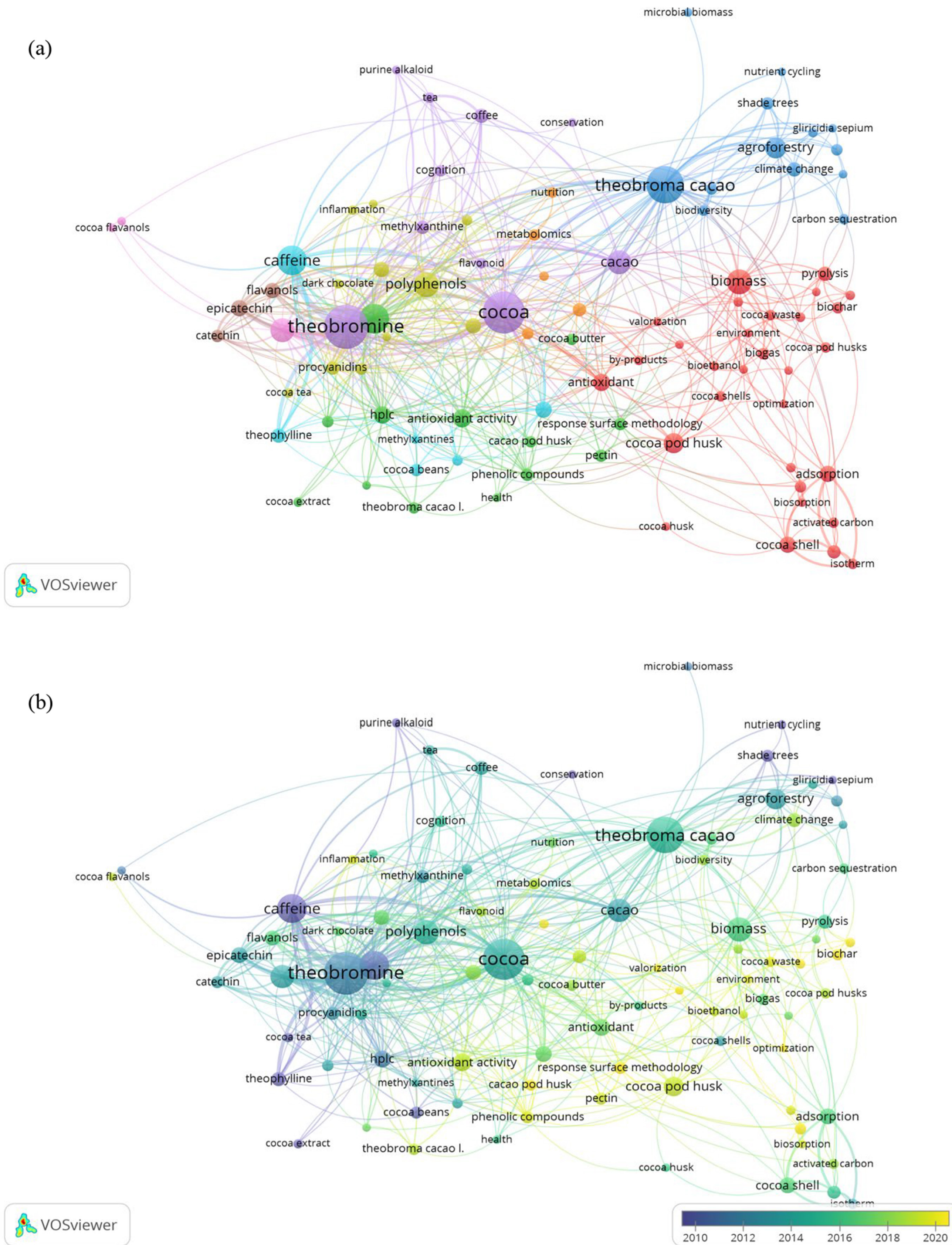

Figure 4. (a) Clustering of the most frequent authors' keywords. (b) Clustering of terms over time.

Table 1. Clusters based on the analysis of author key words.

Cluster	Number of items	Keywords on VOSviewer network
1	30	Activated carbon, adsorption, agricultural waste, agro-industrial waste, antioxidant, bio-oil, biochar, bioenergy, bioethanol, biogas, biomass, biosorption, by-products, cocoa husk, cocoa pod husk, cocoa shell, cocoa shells, cocoa waste, environment, heavy metals, isotherm, kinetics, lignocellulosic biomass, optimization, pre-treatment pyrolysis, soil, valorization, waste
2	13	Alkaloids, antioxidant activity, cacao pod husk, chocolate, cocoa butter, cocoa extract, health, HPLC, pectin, phenolic compounds, phenols, response surface methodology, *Theobroma cacao* L.
3	13	Agroforestry, biodiversity, carbon sequestration, carbon stocks, climate change, Ghana, *Gliricidia sepium*, microbial biomass, nutrient cycling, shade trees, sustainability, *Theobroma cacao*, *Theobroma grandiflorum*
4	11	Antioxidants, catechins, cocoa powder, cocoa tea, dark chocolate, flavonoids, inflammation, oxidative stress, polyphenol, polyphenols, procyanidins
5	10	Cacao, cocoa, coffee, cognition, conservation, flavonoid, methylxanthine, pure alkaloid, tea, theobromine
6	6	Caffeine, cocoa beans, fermentation, methylxanthines, *Theobroma cacao* L., theophylline
7	5	Bioactive compounds, cocoa bean shell, extraction, metabolomics, nutrition
8	3	Catechin, epicatechin, flavanols
9	3	Cocoa flavanols, metabolism, methylxanthines

Streptococcus mutans, pathogens involved in periodontal disease and dental caries.[21]

The quercetin content,[22] reported 3.58 mg of quercetin in CPH. In contrast, another study measured 84.36 ± 2.31 mg quercetin per ml using ethanol extract and 88.46 ± 3.12 mg quercetin per ml with aqueous extract from cocoa waste.[23] However, the authors did not specify the source of the waste – whether cocoa pod husk, cocoa bean shell, or a mixture thereof – nor the proportions used; they only indicated that the waste originated from espresso cocoa production.

Dietary fiber from CPH is a widely used byproduct in agroindustry, incorporated into products such as pork sausages, bread, and muffins.[24–26] The addition of CPH powder improved bread volume and texture hardness.[25] In pork sausages, it enhanced flavor acceptability by improving emulsion stability and apparent viscosity.[24] In chocolate muffins, CPH fiber replaced oil effectively, resulting in higher moisture content, a more tender texture, and reduced hardening during storage.[26]

Pectin with antibacterial activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Escherichia coli*, *Salmonella typhi*, and *Shigella* spp. has been extracted from CPH,[27] and also serves as an effective agent for probiotic encapsulation.[28] Pectins derived from CPH are used in edible films, as gum replacers, and as structural materials for microparticle-based drug delivery systems.[14] Xylitol, another byproduct of CPH, is used widely in the food and pharmaceutical industries.[29,30] A gel recovered from cocoa pod extracts has also been shown *in vivo* to improve skin moisture and reduce wrinkles. Activated carbon from CPH is effective in removing methylene blue,[31] and cocoa pod ash filtrate is used in the production of African black soap and conditioning cleansing creams.[32]

Cocoa bean shell

Cocoa bean shell, another byproduct of the cocoa industry, constitutes approximately 20% of the cocoa bean and 2.1% to 2.3% of the cocoa pod. It has various applications, including use as a pigment, in paper production, and in the preparation of tea, as well as for fiber-, methylxanthine-, and polyphenol-rich extracts. The latter exhibit antiglucosyltransferase activity, inhibiting dental caries.[33] The main polyphenols are catechin and epicatechin (3.5 mg g^{-1}), along with methylxanthines such as theobromine (9.89 mg g^{-1}) and caffeine.[14] Cocoa bean shell also contains flavonols such as quercetin and has been used as an adsorbent for heavy metals in water treatment, as well as in the production of biofuels, biochar, and animal feed.[13] It has further potential in industrial applications, including antimicrobial textiles, bandages, and food packaging, through its use in the synthesis of silver nanoparticles, which show antimicrobial activity against *E. coli*, *Listeria monocytogenes*, *S. aureus*, *Salmonella enteritidis*, *Cronobacter sakazakii*, and *Klebsiella pneumoniae*.[34] Cocoa bean shell nanofibrils have been incorporated into edible alginate coatings for fruit packaging, reducing respiration rate and delaying postharvest deterioration of Andean blueberries.[35]

Regarding quercetin content, researchers analyzed CBS and its cell wall material (CWM) from two cacao varieties –

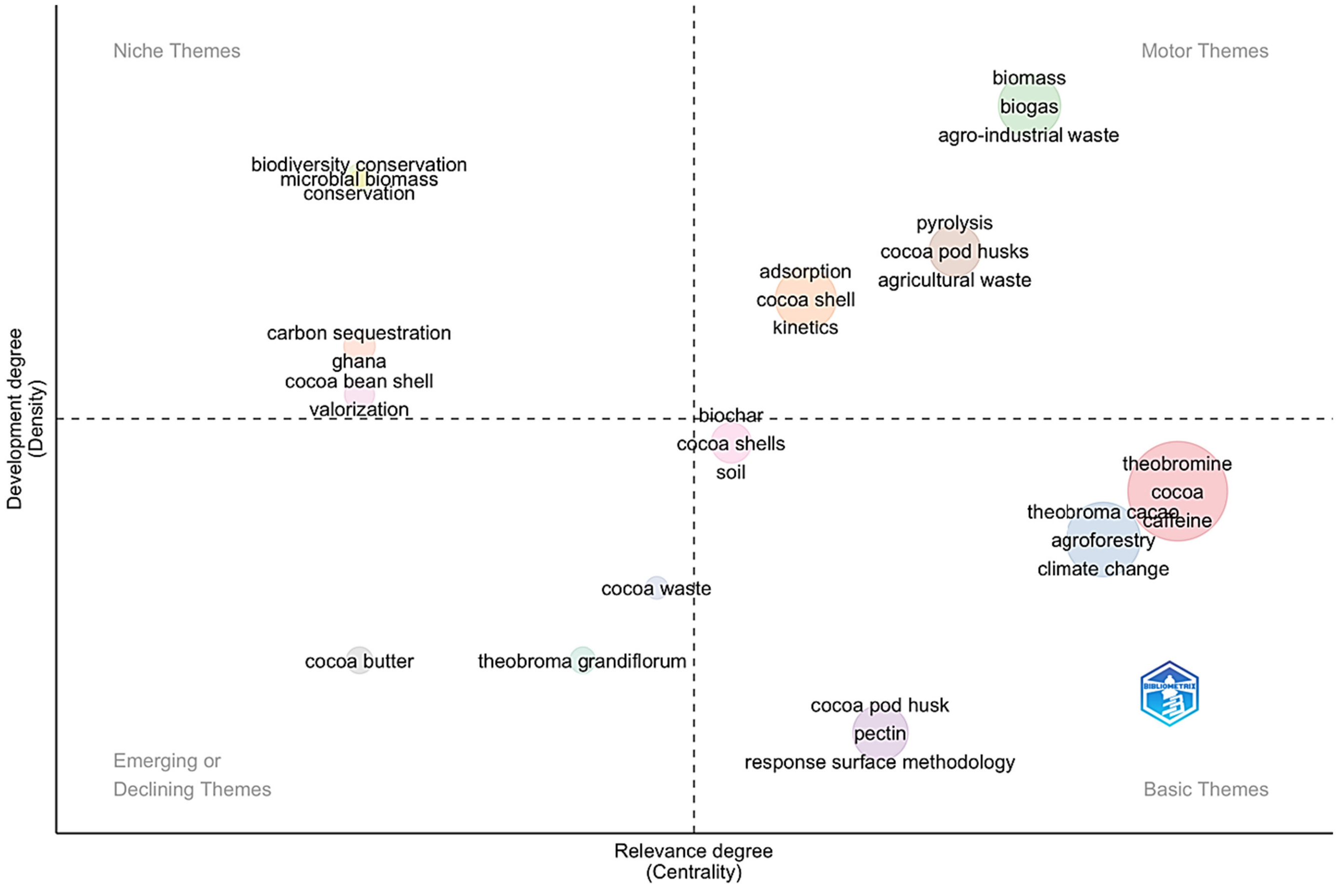

Figure 5. Density visualization map of conceptual structure.

Nacional/Arriba (NAC) and CCN51 – across fermentation, drying, and roasting stages.[36] The quercetin levels in CBS and in CWM CBS were as follows. For fermented CCN51, the levels were 2.1 ± 0.1 ng kg^{-1} in CBS and 4.6 ± 0.5 ng kg^{-1} in CWM. For dried CCN51, they were 3.1 ± 0.3 ng kg^{-1} in CBS and 6.0 ± 1.1 ng kg^{-1} in CWM. For roasted CCN51, the values were 0.4 ± 0.04 ng kg^{-1} in CBS and 0.5 ± 0.003 ng kg^{-1} in CWM. In roasted NAC, quercetin was 0.8 ± 0.1 ng·kg^{-1} in CBS and was not detected in CWM.

Results from two Venezuelan cocoa varieties showed that quercetin extraction from CBS was 5.64 mg kg^{-1} for Ocumare_2C and 61.5 mg kg^{-1} for Ocumare_1C. Their contribution to the total phenolic content was 3.8%, whereas quercetin alone represented less than 0.5%.[37] Regarding cocoa beans, the sum of individual anthocyanins and flavanols has been reported to vary with processing conditions.[38] In that study, these compounds decreased as roasting air temperature increased from 110 °C to 150 °C, except for catechin and quercetin. The authors noted that increasing air relative humidity to 5.0% significantly reduced losses of epicatechin, procyanidin B2, procyanidin C1, and anthocyanins. At higher temperatures and humidity, catechin and quercetin aglycone levels increased, and quercetin glycosides decreased.

Cocoa mucilage

Cocoa mucilage, constituting up to 9.9% of the cocoa bean, is also a valuable byproduct.[13] It can be processed into juice or cacao honey and fermented to produce alcoholic beverages, vinegar, citric acid, and jelly.[39] High-grade pectin extracted from cocoa pulp juice is comparable to that from common fruit sources such as apples, lemons, and pawpaw. Cocoa mucilage also contains fermentable sugars (9% to 13%), minerals (Ca, K, Mg, Na, P), and organic acids including citric, malic, acetic, oxalic, lactic, and fumaric acids, as well as protein, fiber, fat, sugars, polyphenols, and vitamin C.[40,41]

Table 2 presents the chemical composition of cocoa waste. However, these values vary in the literature due to factors such as variety, origin, and extraction technique. Carbohydrate content in CPH has been reported to range from 74.7% to 78.9%, with protein content ranging from 6.3% to 7.2%, and fat content ranging from 0.2% to 0.7%.[13] These values differ

Table 2. Chemical composition of cocoa pod husk (CPH), cocoa bean shell (CBS), and cocoa mucilage (CM).

	CPH (%)	CBS (%)	CM (%)	References
CHO	29.04–32.3	17.8–23.2	10.7–68.35	[14]
Protein	4.21–10.74	15.9	0.4–5.5	
Fat	1.5–2.24	8.49	1.91–3.54	
Lignin	14.6–23.38	42.28–45.61	ND	
Cellulose	24–35	15.1	ND	
Hemicellulose	8.7–11	ND	ND	
Tannins	5.2	3.3–4.5	ND	
Pectin	6.1–9.2	ND	0.57–1.5	
Theobromine	0.3	1.3	ND	[8]
Catechin	0.00289	0.00265	ND	[56]
Epicatechin	0.0067	0.02164	ND	
Caffeine	0.00052	0.00496	ND	

Abbreviation: ND, not determined.

from those in Table 2. Similarly, CBS has been reported to contain 58.6% carbohydrates, 6.2% proteins, and 1.8% fats.[42] Likewise, CM has been reported to contain 4.10 ± 0.5% carbohydrates, 0.53 ± 0.06% protein, and 1.00 ± 0% fat.[43]

Esters, alcohols, aldehydes, furans, pyrazines, terpenes, hydrocarbons, and ketones have been identified in both CPH and CBS.[44] Biofuels such as bioethanol can also be obtained from CPH, CBS, and CM, and biogas can be obtained from CPH. Biodegradable materials for packaging, such as polyhydroxyalkanoates, can also be derived from cocoa waste.[9] Figure 1 illustrates cocoa waste and byproducts.

Greener extraction

Among the 'green' techniques used to recover biocompounds from cocoa waste are microwave-assisted extraction (MAE), SFE, US, PEF, enzymatic extraction (EE), SWE, ultrasonic–microwave-assisted extraction (UMSE),[12] deep eutectic solvents (DES), and pressurized liquid extraction (PLE).[45] These methods are considered 'green' because they typically require less solvent, time, and energy, resulting in lower environmental impact than conventional extraction methods. They generate less pollution in air, water, and soil, and consume fewer resources. They also often yield higher extraction efficiency and, in some cases, improved product quality.[46,47]

Microwave-assisted extraction

The extraction mechanism in MAE involves intense heating generated by the combined effects of ionic conduction and dipole rotation induced by nonionizing radiation.[12] For pectin extraction from CPH, MAE yields products with higher molecular weight, lower degree of esterification, and elevated galactose content.[48–50] Microwave-assisted extraction has also been employed to extract polyphenols and polysaccharides from CBS for pectin-based film production, with the phenolic compounds showing high antioxidant activity.[51] Anthocyanins have been extracted from cocoa peel using MAE under optimal conditions – 60 mesh particle size, 0.0625 w/v sample-to-solvent ratio, 10 min extraction time, and 450 W microwave power, yielding 1.434 mM.[52] Phytosterols (β-sitosterol) were extracted under optimal conditions of 70 °C, 500 W, and 10 min, achieving a maximum yield of 3 546.1 mg 100 g^{-1}, which was 13% higher than that obtained by conventional maceration.[53] Catechin has also been extracted from cocoa husk using MAE, with results indicating that longer extraction times improve yield.[54]

Ultrasound

Acoustic cavitation occurs when sound waves (20 kHz to 10 MHz) propagate through a liquid medium, generating alternating compression and expansion cycles that form microbubbles. These bubbles eventually implode, enhancing mass transfer and mixing, and thereby facilitating the diffusion of target molecules from the matrix to the bulk solvent.[55] Ultrasound is a selective technique that enables the extraction of purer products by increasing pectin solubility and improving extraction yields.[12]

This nondestructive method offers several advantages, including enhanced efficiency, shorter processing times, improved product quality, and extended shelf life.[56] Ultrasound-assisted extraction (UAE) has achieved the recovery of high yields of bioactive compounds from CBS, and its combination with MAE at 90 °C yielded the highest levels of antiradical activity and bioactive compounds, such as melanoidins, polyphenols, and proanthocyanidins.[57] Similarly, the extraction of phenolic compounds and flavonoid compounds from CBS powder, along with associated antioxidant properties, has been optimized using US.[58] Ultrasound has also been applied to optimize phenolic extraction and enrich bioactive compound content in CBS.[59,60]

Another study applied US extraction to CPH and CBS, optimizing conditions to maximize extraction of phenolic compounds, and optimizing Trolox equivalent antioxidant capacity (TEAC), ferric reducing antioxidant power (FRAP), and oxygen radical absorbance capacity (ORAC).[61] Under optimal conditions, UAE also yielded the highest anhydrouronic acid content and the maximum degree of esterification from the three main cocoa wastes: CPH, CBS, and CM.[62]

Ultrasonic-microwave simultaneous extraction

Ultrasonic-microwave simultaneous extraction is a quick, effective, and economical technique that combines ultrasonic and microwave technologies to maximize their individual effects. In pectin extraction, UMSE also removes impurities, increases yield, and modifies the degree of esterification.[12] The molecular weight of pectin extracted from fig skin using ultrasonic-microwave technology was significantly higher than that of jackfruit pectin.[48] This method combines the high-energy effects of microwave heating and ultrasonic cavitation to enhance extraction efficiency.[63] Flavonoids extracted from *Dioscorea involucrata* leaves using UMSE exhibited superior antioxidant capacity to conventional extraction methods.[64]

A synergistic effect between US and MAE has been reported in the extraction of compounds from CBS, such as melanoidins, polyphenols, and proanthocyanidins.[57] Ricinine extraction from castor cake, a residue of castor oil production, was optimized using UMSE, achieving maximum yield in less time.[65] Similarly, enzymatic pretreatment combined with UMSE maximized the extraction of essential oils and flavonoids (epicatechin, rutin, isoquercitrin, myricetin, and quercetin) from *Baeckea frutescens*.[66]

Pulsed electric field

The electroporation phenomena produced during PEF extraction enables recovery of biocompounds from raw material; by applying electric pulses, cell membranes are disrupted, releasing intracellular content. This innovative technique has recently expanded to applications such as pretreatments, biocompound extraction, microbial inactivation, microalgae biorefinery, liquid food pasteurization,[46] drying, peeling, freezing, and food preparation,[67] among others.[68] A PEF was applied to a CBS–choline chloride–lactic acid (ChLa) suspension, improving metabolite extraction and the bioactivity of the CBS extract. However, the authors do not recommend this process due to negligible effects of the treatment caused by the sample's low electrical conductivity. On the other hand, PEF increased polyphenol extraction yield from CBS as a pretreatment under optimal conditions (1.74 kV/cm for 118.54 min, with 39.15% ethanol), resulting in higher recovery of polyphenols and methylxanthines than with conventional extraction.[69]

Supercritical fluid extraction

In a supercritical state, a fluid exhibits mixed liquid and gas properties at temperatures and pressures above its critical point; such a fluid is called a supercritical fluid (SCF). Supercritical fluids have high solute diffusivity and low viscosity, enabling excellent mass transfer. Supercritical fluid extraction involves bringing the SCF into contact with the raw material's solute in an extraction chamber, allowing solvent-solute equilibration to maximize compound extraction from solid to liquid phase, followed by target compound separation through solvent depressurization.[47] Common solvents include water, liquid CO_2, ethane, propane, ethanol, and butane.[70] Dimethyl ether, a more recent solvent derived from biomaterials, is also used for extracting oils from plant seeds.

Scientists extracted higher yields of fat (94.73%) and caffeine (90%) from cocoa shell powder using supercritical CO_2.[71] However, theobromine could not be extracted under optimal conditions (6000 psi, 313 K, 90 min) due to its low solubility. Supercritical CO_2 extraction with ethanol as a co-solvent increased phenolic compounds and antioxidant activity in cocoa husk.[72] Another study optimized extraction time, temperature, pressure, ethanol concentration, and particle size to extract polyphenols from the same source using the same method.[73] Combined PLE and SFE yielded the highest antioxidant activity and phenolic content from cocoa bean hulls in less time than conventional Soxhlet extraction.[74] Fats and methylxanthines (theobromine and caffeine) were extracted efficiently from CBS with supercritical CO_2; however, theobromine remained in the waste.[71]

Subcritical water extraction

Characterized by high yields, low cost, and safety, this technique reduces energy use and produces higher quality extracts in less time. Water is applied at temperatures above its boiling point under high pressure to maintain its liquid

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state.[75] As temperature increases, water polarity decreases significantly, resembling methanol or ethanol. Liquid water maintained below the critical point at temperatures above boiling is termed 'subcritical water'.[76]

Properties such as solubility, mass transfer and extraction capacity change in water with varying temperature and pressure,[77] and this forms the basis of subcritical water extraction. Subcritical water extraction of CPH yielded higher phenol content (10.9%), required one-third of the time, and produced pectin with higher molecular weight (750 kDa) than obtained in conventional extraction.[78] Similarly, total phenolic content (catechin, epicatechin, gallic, and chlorogenic acids) from cocoa shells varied significantly with temperature in subcritical water extraction, ranging from 27.26 mg GAE g^{-1} (120 °C, 75 min, 20 mL g^{-1}) to 130.33 mg GAE g^{-1} (220 °C, 75 min, 20 mL g^{-1}). However, at higher temperatures, 5-HMF was also recovered, prompting recommendations to optimize the extraction process.[18]

Enzymatic extraction

Enzyme catalysts enable the natural extraction, modification, or formation of complexes.[79] This method accesses chemicals typically unavailable via conventional solvent extraction by releasing compounds bound to inner surfaces.[80] Its specificity allows targeted compound extraction under mild aqueous conditions.[81]

By hydrolyzing cellulose or hemicellulose, enzymes break down cell walls, releasing pectins. The most commonly used enzymes for this extraction are cellulase, protopectinase, hemicellulase, and xylanase. This approach yields higher-quality, more homogeneous, and purified pectin with improved gel-forming properties.[12] It is also used to extract carotenoids, essential oils, chlorophyll, and phenolic compounds.[82]

Enzymatic extraction of pectin from CPH slightly outperformed acid hydrolysis and sonication-assisted methods, while also reducing environmental impact due to lower acid use. Enzymatic extraction produced higher pectin content (up to 10.20 g per 100 g) with galacturonic acid at 52.06 g per 100 g pectin than traditional methods.[83] An optimized enzyme combination was studied to enhance sugar release from CPH for poultry feed, resulting in a 42% to 53% increase in sugar release and a 7% to 14% reduction in crude fiber, thereby improving digestibility.[84]

Deep eutectic solvents

Organic carbonates, DES, water (normal, subcritical, and supercritical), biosolvents, and supercritical CO_2 are considered 'green solvents'.[85] Deep eutectic solvents are inexpensive, biodegradable solvents composed of at least two compounds. When mixed in appropriate molar ratios, their melting points are significantly lower than those of the individual components, producing a eutectic mixture.[86] Solvent pairs containing hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) form this eutectic phase. Examples of HBDs include urea and acetamide, while choline chloride (ChCl) and tetrabutylammonium chloride serve as HBAs in DES.[85] Choline chloride, a quaternary ammonium salt, is the most common DES component.[86] Caffeine and theobromine from CPH were extracted using DES, with ultrasound-probe assisted extraction (UPAE; 3 min, constant duty cycle, 200 W) yielding higher extraction efficiency than heat stirring-assisted extraction (HSE; 1 h, 30 min).[87]

Natural DES can recover polar and nonpolar compounds, which improves the extraction performance.[88–90] They offer superior extraction efficiency and solubilizing capacity compared with conventional solvents,[91,92] improving the solubility of phytochemicals in aqueous solutions.[88] Natural DES are formed by hydrogen bonding between organic acids, amino acids, sugars, sugar alcohols, and polyalcohols.[85] Key properties include low volatility, tunable viscosity, water solubility, high thermal stability, and strong solubilizing power.[93] Additional advantages include nonflammability, acceptable pharmaceutical toxicity, and ease of preparation,[94,95] making NADES attractive for the valorization of industrial waste.[96]

Several studies have reported significant effects on extraction efficiency based on the choice of HBD in NADES,[97] underscoring the importance of selecting appropriate components for specific bioactive targets. Polyphenols from cocoa byproducts have been extracted using NADES for the fortification of chocolate milk, with sensory evaluation confirming safety, acceptability, and no requirement for solvent removal.[98] This eliminates the need for purification steps, presenting a clear advantage. Pulsed electric field combined with NADES was the most effective method for extracting bioactive compounds from CBS, outperforming ultrasound-assisted NADES extraction and conventional methods.[68] Chlorogenic acid extraction from cocoa and coffee waste was also 84 times higher using NADES than with water.[99]

Pressurized liquid extraction

This combination of techniques can be distinguished by operating parameters (subcritical or supercritical) and the type of solvent used,[100] both of which influence the range of natural compounds extracted. The method permits the use of solvents with different polarities, thereby broadening the spectrum of biocompounds recovered.[101–105] In the

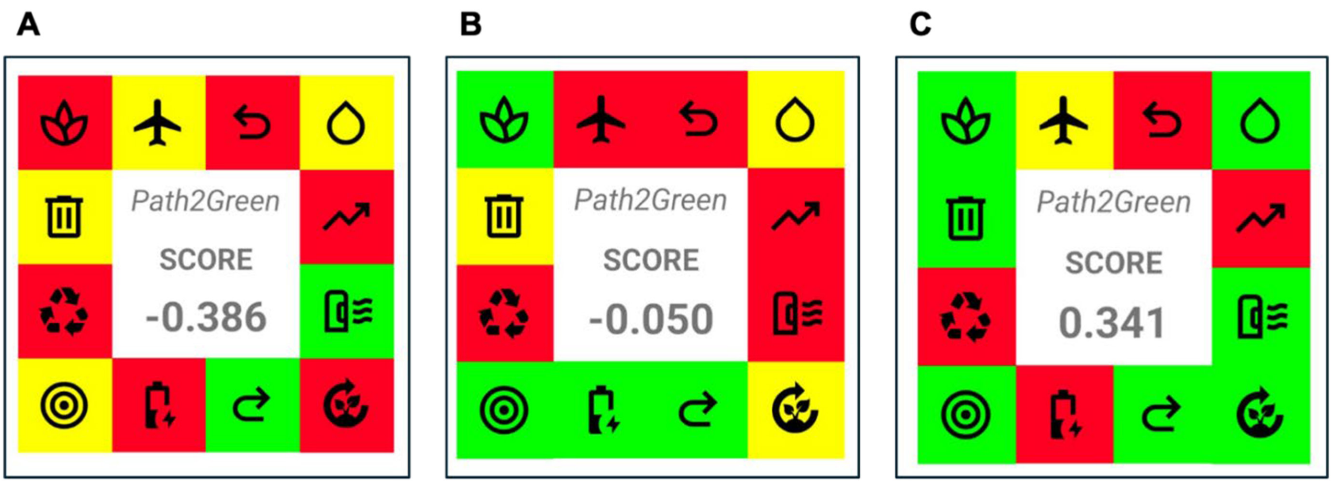

Figure 6. Pictogram depicting the final score of Path2Green metric. (a) Article 1: Ultrasound assisted extraction (UAE) using an organic solvent;[16] (b) Article 2: Conventional extraction using a eutectic solvent,[17] and (c) Article 3: Subcritical water extraction (SWE).[18]

subcritical state, PLE utilizes heated, pressurized solvents at temperatures above their atmospheric boiling points.[55] Under these conditions, solvent viscosity and surface tension decrease, enhancing penetration into the matrix and weakening solute–matrix interactions. Changes in distribution coefficients further improve the solubilization of target molecules in the solvent.[106–108]

Depending on the solvent used, PLE is referred to by different names:

- Solvent-based PLE, also known as accelerated solvent extraction (ASE), pressurized hot-solvent extraction (PHSE), or pressurized fluid extraction (PFE).
- Water-based PLE also termed subcritical water extraction, pressurized hot water extraction (PHWE), pressurized low-polarity water extraction (PLPW), or superheated water extraction (SHWE).
- Phytonic process, a patented method based on HCF-134a (1,1,1,2-tetrafluoroethane), which operates at lower temperatures and pressures.[109]

In one study,[110] solvent-based PLE using absolute ethanol was applied. Theobromine and caffeine yields from CBS increased with temperature, accompanied by reduced extraction time and enhanced antioxidant activity. However, flavanol content decreased at 90 °C due to thermal degradation; similar declines were observed for catechin, epicatechin, procyanidin B2, and alkaloids.

Sustainable analysis for the extraction process

Modern extraction methods can cause significant environmental impacts if not carefully managed.[111,112] Consequently, there is growing demand for extraction processes that are both efficient and sustainable. Achieving these objectives in a single process is challenging, as multiple steps require separate evaluation. Recently, the Path2Green metric was developed to assess extraction sustainability[113]; based on 12 green extraction principles, it enables a comprehensive analysis to be conducted by evaluating each principle individually.

The Path2Green metric includes criteria for both pre-extraction and postextraction procedures. Accordingly, three methods for extracting bioactive compounds from cocoa samples were selected and compared for sustainability using the Path2Green mobile app (suggested methods: via WhatsApp or USB connection - https://pubs.rsc.org/en/content/articlelanding/2024/gc/d4gc02512a) and considering its 12 principles: 1: Biomass; 2: Transport; 3: Pretreatment; 4: Solvents; 5: Scaling; 6: Purification; 7: Yield; 8: Post-Treatment; 9: Energy; 10: Application; 11: Repurposing; and 12: Waste Management. Each principle is scored from −1 to 1, with scores closer to 1 indicating better adherence to green principles. The resulting pictogram (Fig. 6) shows the final score and overall extraction performance.

The first selected method (Article 1) employs UAE with an acidified solvent mixture (0.8% hydrochloric acid (2 mol L^{-1}) in water–methanol 50:50 v/v) to recover phenolics, flavonoids, flavan-3-ols, nonflavonoids, and proanthocyanidins from cocoa beans.[16] Two UAE modes were used: pulsed UAE (PUAE) and continuous UAE (CUAE), with temperatures from 120 °C to 220 °C and frequencies ranging from 25 to 45 kHz. The second method (Article 2) is a conventional extraction using three eutectic solvents – choline–lactic acid (ChLa), choline–glycerol (ChGly), and choline–ethanol

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Table 3. 'Twelve principles' scores for each evaluated method using the Path2Green metric.

Path2Green metric principles	Ultrasound assisted extraction using organic solvents	Conventional extraction using a eutectic solvent	Subcritical water extraction	Principle weighting
1. Biomass: Select biomass that is naturally sourced or requires minimal resource usage for production	−0.75	1	1	6
2. Transport: Preserving biomass integrity while minimizing transport's environmental impact	1	−0.5	1	5
3. Pretreatment: Optimization for pretreatment avoidance and cost-effective techniques	−0.7	−0.2	−0.2	2.5
4. Solvents: Minimize solvent usage, prioritizing those of biological origin, biodegradable and nontoxic	0	0	1	6
5. Scaling: Ensure reproducibility and a continuous extraction flow	−1	−1	−1	5
6. Purification: Final application dictates the extent of purification	0.5	−0.5	1	2.5
7. Yield: Maximize the utilization and valorization of the biomass	−0.5	0	1	4
8. Post-treatment: Functionalization of natural products postextraction to maximize their benefits	0.50	0.50	0.5	2.5
9. Energy: Prioritize using clean energy sources and high-efficiency extraction techniques	−0.5	0.50	−0.5	4
10. Application: Ensure safety for applications in several domains	0	0.66	1	4.5
11. Repurposing: Trace strategies to perform closed-loop extraction systems, preferably using nonvirgin materials	−1	−1	−1	6
12. Waste management: Refine waste reduction and ensure effective waste management	0	0	1	6

(ChEt) – and their 50% aqueous solutions (ChLa50, ChGly50, ChEt50). Extraction was performed in a magnetically stirred bath at 30 °C for 0 to 140 minutes to identify the optimal solvent combination (choline chloride:lactic acid 1:2 with 50% water w/w) for polyphenols from CBS.[17] The third method (Article 3) uses subcritical water extraction (SWE) with 85% water and 15% ethanol (m/m) to extract valuable compounds from CBS (Fig. 2).[18] Concentrations of 0.1, 0.05, and 0.03 g mL^{-1} were tested over 15 to 30 min at temperatures from 120 °C to 220 °C.

The extraction techniques obtained Path2Green scores of −0.386, −0.05, and 0.341, respectively. Figure 6 presents the final score pictograms, and Table 3 summarizes the 12 green chemistry principle scores evaluated for each method.

The extraction process using subcritical water (Article 3) scored highest, making it the most sustainable method analyzed. It achieved the highest ratings in principles 4, 6, 7, 10, and 12, unlike the other methods. For principle 4 (Solvents: minimize solvent use, prioritizing biologically derived, biodegradable, and nontoxic solvents), Article 3 employed 85% water and 15% ethanol (m/m). Both solvents are recommended under the CHEM21 guidelines.[114] The ethanol amount used was confirmed to be nontoxic. In contrast, Article 1 was penalized under this principle for using an acidified water–methanol (50:50 w/w) solution (0.8% HCl 2 mol L^{-1}), considered problematic by CHEM21 due to methanol's environmental and health risks. Article 2 also incurred a penalty because its eutectic solvent (choline chloride:lactic acid 1:2 with 50% water w/w), despite yielding the highest extraction efficiency, contains lactic acid, which CHEM21 classifies as problematic for aquatic toxicity.[114] Although lactic acid is naturally derived and biodegradable, its poor separation efficiency increases energy consumption in purification. This finding underscores the need for thorough evaluation of alternative solvents, which may still pose environmental risks and require careful assessment before application.

Using an environmentally friendly solvent in subcritical water extraction contributed to Article 3's highest scores for principles 6 (Purification: final application determines purification extent) and 10 (Application: ensure safety across uses). Subcritical water extraction yields a ready-to-use, nontoxic extract that requires no further purification. This extract is suitable for cosmetics, pharmaceuticals, skincare, cleaning, and hygiene, where the presence of ethanol poses no issue. In contrast, other methods require post-treatment to remove toxic solvents, which reduces overall sustainability. Toxic, nonvolatile solvents are especially difficult to eliminate due to low volatility. Ready-to-use methods employing nontoxic eutectic formulations should therefore be prioritized.[115]

Article 3 achieved the highest scores for principles 7 (Yield: maximize biomass valorization) and 12 (Waste management: minimize waste and ensure effective handling) due to its exhaustive extraction approach. After subcritical water extraction, the solid residue was washed with water to recover remaining soluble compounds, maximizing cocoa shell biomass use. High-pressure extraction also provided higher yields than conventional methods.

Differences among the articles were also noted in relation to the raw materials used, particularly under principles 1 (Biomass: Select biomass of natural origin or that requires minimal resource input for production) and 2 (Transportation: Preserve biomass integrity while minimizing the environmental impact of transport). Under principle 1, Article 1 was penalized for using cocoa from a polyculture agroindustrial system, whereas the other articles utilized cocoa shells, which are classified as industrial waste and thus enhance process sustainability.[116] Under principle 2, only Article 2 was penalized, as it sourced raw materials from another country, thereby increasing the carbon footprint and associated environmental impact.

The Path2Green metric also highlights the environmental, economic, and social challenges associated with the methods studied. Articles 1 and 3 were penalized under principles 3, 5, 8, 9, and 11, while Article 2 was penalized under all except principle 9. Under principle 3 (Pretreatment: Optimize to avoid pretreatment and use economical techniques), all articles included pretreatment steps necessary to enhance extraction selectivity. Article 1 employed chemical pretreatment, involving peeling, grinding, and degreasing cocoa beans with hexane at a 1:6 ratio. In contrast, Articles 2 and 3 used physical pretreatment through grinding. Physical methods are generally preferred for biomass preparation due to their simplicity, cost-effectiveness, and minimal use of reagents, energy, and time.[15]

Chemical pre-treatments, nonetheless, often raise environmental concerns due to the use of chemicals that generate hazardous waste and release pollutants, justifying the greater penalty (−0.7) imposed on Article 1. This consideration also relates to principle 8 (Post-treatment: Functionalization of natural products post-extraction to maximize their benefits), as all extraction processes require post-treatment steps to enhance the quality, bioavailability, or stability of the extracts.

Regarding principle 5 (Scaling: ensuring reproducibility and a continuous extraction flow), all processes were performed using batch systems, which are more challenging to scale, leading to lower scores. For principle 9 (Energy: prioritize the use of clean energy sources and high-efficiency extraction techniques), the articles utilizing modern extraction methods, such UAE and SWE, were penalized due to the high energy demand of these techniques. This explains why Article 2 received a higher score in this category. Finally, in principle 11 (Repurposing: Outlining strategies to carry out closed-loop extraction systems, preferably using non-virgin materials), all articles received low scores, as none presented a recycling strategy. This challenge is not exclusively related to the methods presented, as even the waste generation inherent to the extraction process becomes inevitable.

Comparing different extraction methods using Path2Green metric highlights the complexity of achieving sustainable extraction processes for cocoa samples. The subcritical water extraction method stood out as the most sustainable, mainly due to the choice of more environmentally friendly solvents and the reduction in post-treatment steps. Thus, careful selection of solvents and maximum biomass recovery are relevant to accomplishing sustainability. Nevertheless, the analysis reveals that each method has challenges, such as using eutectic solvents, which is proposed as a green alternative. However, it was penalized due to presence of problematic compounds, which reinforces the need for thorough analysis before their application.

The application of the 12 principles of the Path2Green metric also showed that the sustainability of an extraction process depends not only on the solvents used but also on factors such as the origin of the biomass, energy efficiency, and the pretreatment and post-treatment steps. Penalizing modern extraction techniques that require high energy, such as UAE and SWE, is still a challenge. The results of this analysis thus highlight the superiority of the subcritical water extraction method and point to critical areas where removal methods can be improved to achieve a balance between environmental, economic, and social impacts. A better approach to waste treatment is needed in the publications analyzed.

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This review also noted the lack of studies correlating natural eutectic solvents and other green extraction techniques with the sustainable extraction of cocoa bio-compounds and encouraged further research in this area.

This study paves the way for future investigations into the extraction of compounds from cocoa waste and, in particular, the development of sustainable solvents and the optimization of scalable removal processes. Developing these technologies could contribute significantly to advancing greener and more sustainable extraction processes and removal practices in the cocoa industry.

Discussion and conclusion

Analysis has revealed that trends in cocoa waste research is primarily associated with fields such as agricultural and biological sciences, environmental science, biochemistry, genetics, and molecular biology. In contrast, agricultural waste represents a broader and more established area, identified in the analysis as a 'motor theme' due to its high relevance and direct connection to the present study. Similarly, terms such as 'biogas', 'theobromine', 'cocoa pod husk', and 'cocoa shell' appeared among both motor and basic themes, underscoring their significance to this line of research.

Greener extraction techniques can demonstrate enhanced performance when combined. For example, integration of supercritical CO_2 and pressurized liquid extraction yielded higher total phenolic content (from 35 to 51 mg GAE g^{-1}) and antioxidant activity (from 115 to 177 μg mL^{-1}, EC_{50} values) compared with individual methods.[74] Similarly, pectin was extracted from CPH using subcritical water extraction and supercritical CO_2.[78] Subcritical water extraction alone achieved higher yields (10.9%) in less time (30 min) than conventional citric acid extraction (7.4% to 8.3% in 95 min), with increased selectivity (galacturonic acid and degree of methyl esterification) and purity. When subcritical water extraction was combined with supercritical CO_2 extraction of polyphenols, no significant differences in yield or pectin quality were observed, supporting the feasibility of their integration in a biorefinery approach.[55] Combining SFE and PLE improved antioxidant activity and phenolic content from cocoa bean hulls.[74] More efficient extraction of theobromine and caffeine from cocoa bean shells was also achieved by combining ES with MAE, compared with DES alone.[117] These findings highlight the strong potential for integrating green extraction techniques in the recovery of bioactive compounds from cocoa waste.

A variety of biocompounds can be recovered from cocoa waste, including polyphenols, methylxanthines, organic acids, pectins, and dietary fiber, with applications in the food industry, cosmetics, human health, and bioremediation. Isoquercetin has been extracted from cocoa shell at a yield of 1.01 ± 0.09 mg·g^{-1}, and from CPH using three treatments: CPHF1 (untreated, immediately frozen), CPHF2 (10 min in boiling water), and CPHF3 (3 h at room temperature followed by 10 min of boiling). The corresponding isoquercetin contents were 0.20 ± 0.08, 0.09 ± 0.09, and 0.09 ± 0.07 mg·g^{-1}, respectively, indicating that the absence of heat treatment yields higher isoquercetin levels in CPH.[118] Isoquercetin is more water-soluble than quercetin due to its additional glucose moiety, enhancing its bioavailability. This makes isoquercetin a promising yet underexplored biocompound for recovery from cocoa waste.

Another relevant point is that concentrations of compounds obtained from cocoa waste vary, depending on the extraction technique, variety, and origin.[119] Likewise, types and levels of phenolic compounds in cocoa beans depend on cocoa type and are significantly affected by roasting conditions; high temperatures notably have been found to alter flavan-3-ol concentrations.[38] This behavior could also apply to cocoa bean shells and cocoa pod husks in future research.

Regarding sustainable analysis, the environmental score obtained using the Path2Green metric for the extraction techniques that were studied prompts further reflection on green extraction technologies. This metric, with its specific characteristics and parameters, facilitates objective and consistent evaluation of extraction efficiency and resource intensity. Although detailed information on extracted products and efficiencies may vary across studies, Path2Green allows valid comparison within the defined context and aligns with other methods used in the literature to evaluate resource intensity in extraction processes, such as Agree and Egroscale. These metrics do not replace full environmental analyses required for international certification but provide insight into the environmental performance of extraction techniques. The significant challenge of achieving higher extraction yields that are both efficient and rapid, while producing fewer pollutants, requires further research to identify optimal techniques or combinations. Such efforts should aim to minimize environmental impact through comprehensive analysis.

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Conflict of interest

The authors declare no conflict of interest.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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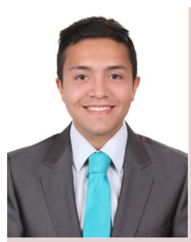

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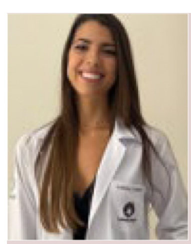

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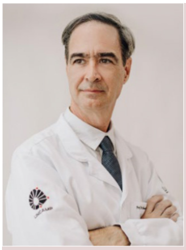

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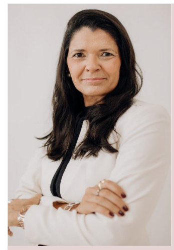

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