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Functionality, stability and technological challenges of natural polyphenols in food matrices

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ABSTRACT

Objective: To examine the presence, stability, and functionality of natural polyphenols in commercial food matrices. The effects of industrial processing and the emerging technological benefits for their protection were also considered.

Design/Methodology/Approach: A review of natural polyphenols in fruits, vegetables, cereals, and beverages (alcoholic and non-alcoholic) was conducted. The oxidation mechanisms present in food matrices and the stability of the molecules during processing were described. Emerging technologies, such as encapsulation, for preserving the antioxidant functionality of natural polyphenols were analyzed.

Results: Natural polyphenols are present in a variety of foods; their composition is linked to the type of food, the plant tissue, and the growing and post-harvest handling conditions. Fruits are notable for their phenolic acids, anthocyanins, and flavonoids. Vegetables are predominantly composed of hydroxycinnamic acids and flavonoids, cereals contain lignans and resorcinols, and beverages contain flavonols, catechins, and resveratrol. Food processing reduces the bioavailability and functionality of polyphenols through oxidation, heat, pH, and exposure to oxygen. Techniques combined with heat treatments, such as microwaves, ultrasound, and bioprocesses, particularly encapsulation, help preserve natural polyphenols and improve their stability and solubility.

Limitations/Implications of the study: The loss of natural polyphenols during industrial processing reduces their antioxidant activity. Emerging technological alternatives applicable to the production of functional foods are needed.

Findings/Conclusions: Natural polyphenols are molecules with varied bioactivity in different food matrices. Their stability depends on the food and the processing applied. Emerging technologies exist to preserve food functionality, including encapsulation, an effective strategy.

Keywords: Natural polyphenols, functional stability, Food processing, encapsulation.

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INTRODUCTION

Natural polyphenols (NPs) are a group of molecules produced by plants; they are secondary metabolites formed in response to internal or external stressors (such as UV radiation, insects, fungi, and animals). Chemical processes produce synthetic polyphenols; they exhibit high stability and efficacy but can cause toxicity (Delgado-Arenas, 2019), which is why NPs are preferred for consumption. Currently, more than 8,000 NPs are registered, in which an aromatic group forms the basis of their structure and is linked to one or more hydroxyl groups (Di Lorenzo *et al.*, 2021; Rana *et al.*, 2022). Polyphenols can be grouped into flavonoids (anthocyanins, flavonols, flavones, isoflavones, flavanones, and stirbenes) and non-flavonoids, which include phenolic acids, tannins, stirbenes, and lignans, among others. Previously, polyphenols were categorized as antinutritional components, without an essential function in human nutrition; however, various studies have recognized that polyphenols are molecules with antioxidant, anti-inflammatory, anti-allergic, and anti-hyperglycemic functions, as well as a direct connection with favorable responses in metabolic pathways and the gut microbiota (Ramaiah *et al.*, 2024). The antioxidant functionality of polyphenols has been demonstrated in several studies where they can eliminate reactive oxygen species (ROS) and chelate transition metals (Zhong *et al.*, 2020); they have been considered as potentially useful in the control of degenerative diseases, specifically due to their ability to inhibit cyclooxygenase and lipoxygenase, enzymes responsible for the inflammatory process, and acetylcholinesterase, associated with the development of Alzheimer's or Parkinson's diseases (Nwidu *et al.*, 2019).

Antioxidant capacity is a functionality that can be measured in *in vitro* and *in vivo* assays. In particular, food matrices are evaluated using *in vitro* assays; these quickly measure bioactive compounds, and results are known within product batches. The most commonly used assays are those that employ a free radical to neutralize electron and hydrogen transfer mechanisms or the chelation of transition metals, such as the DPPH method (using the 2,2-diphenyl-1-picrylhydrazyl radical), the ABTS method (using the 2,2'-azino-bis-(3-ethylthiazolinebenzenesulfonic acid-6) radical), the FRAP assay (using ferric reduction), and the ORAC assay (measuring oxygen radical absorption capacity), among others (Munteanu & Apetrei, 2021; Lang *et al.*, 2024). Natural particles have been a focus of interest for the functional food industry. However, the presence of natural particles in food does not guarantee that functionality will remain intact throughout the agricultural chain, post-harvest, and processing. It has been observed that factors such as growing conditions, post-harvest practices, and the presence of Oxygen levels, hours of sunlight, chemical composition, and heat treatments can cause the degradation, oxidation, or imbalance of NPs in the food matrix (Tian *et al.*, 2025), directly affecting their stability and functionality. Therefore, it is necessary to study how NPs behave in food matrices to ensure their preservation and leverage their functionality in food processing. This review analyzes the presence and characteristics of NPs in various food matrices, the oxidation mechanisms that can affect their stability and functionality, and the limitations encountered during processing. The second section addresses emerging technologies proposed as alternatives to improve and/or preserve bioactivity in processed foods. Overall, the aim is to understand the current challenges and opportunities for maintaining NP functionality in the food industry.

Natural polyphenols in foods

The concentration and composition of polyphenols in plant-based foods vary according to genetic, environmental, and physiological factors specific to each crop. Maturity level, climatic conditions, and post-harvest handling influence polyphenol biosynthesis. The type of plant tissue, such as peel, leaves, pulp, and seed, varies in the content and structural diversity of polyphenols (Aneklaphakij *et al.*, 2021). Several studies have reported that plants of the same species exhibit significant variation in phenolic content due to overexposure to solar radiation or to nutrient availability, which affects enzymatic activity in the phenylpropanoid pathways (Aneklaphakij *et al.*, 2021; Rienth *et al.*, 2021). Therefore, it can be explained that polyphenols are distributed in complex ways across different food matrices, from fruits and vegetables to cereals and alcoholic and non-alcoholic beverages, which constitutes a line of work to understand their behavior during food processing.

Fruits are recognized sources of NPs, with berries, citrus fruits, drupes, pomes, and tropical fruits containing the highest levels. Berries are reported to contain 30 to 2000 mg/100g of total polyphenols (TPs), exhibiting a broad polyphenol profile characteristic of each species, notably anthocyanins, ellagitannins, and proanthocyanidins (Arena *et al.*, 2023). The polyphenols in citrus fruits are primarily flavone glycosides, followed by polymethoxylated flavones, anthocyanins, and traces of hydroxycinnamic acids. The NPs found in bottled orange juice are hesperidin, narirutin, and didymin (65, 13, and 15 mg/250 mL of TPs, respectively) (Sanches *et al.*, 2022). Pome fruits (pear, apple, and quince) and drupes (cherry, peach, plum, and nectarine) primarily contain a mixture of TPs compounds, including chlorogenic acids, anthocyanins, flavonols, catechins, and proanthocyanidins. Specifically, hydroxycinnamic acid and anthocyanins predominate in drupes, while neochlorogenic acid is the most prevalent in other pomos (Lujan *et al.*, 2023). The variation in TPs content among tropical fruits is significant, ranging from 15 to 143 mg/100 g. Guava contains the highest amount (126 mg/100 g), followed by kiwifruit (116 mg/100 g), mango (104 mg/100 g), and pomegranate juice (44 mg/100 ml) (Domínguez-Rodríguez *et al.*, 2021).

Hydroxycinnamic acids predominate in leafy vegetables; lettuce contains 5-caffeoylquinic acid and quercetin glycosides; spinach is high in flavonols derived mainly from quercetagetin. Swiss chard contains up to 1320 mg/100 g, including vitexin 2”-O-xyloside and kaempferol 3-Ogentiobioside. Onions have a higher quercetin content (3.2, 12, and 17 mg/100g in white, yellow, and red onions, respectively). Root vegetables, specifically the cell wall of carrots, contain 5-caffeoylquinic acid, coumaroylquinic acids, and esterified feruloyl acids; black carrots contain anthocyanins (xylosylglucosylgalactoside). Celery contains up to 14 mg/100g of TPs, notably furanocoumarins (8-methoxypsoralen and isopimpinelin), while Swiss chard has 410 mg/g of TPs. Colored potatoes contain twice as many NPs as white potatoes; the main polyphenol is chlorogenic acid (14). mg/100 g) (Kuppusamy *et al.*, 2020; Yuan *et al.*, 2020).

The NPs in the pericarps of cereals such as barley, buckwheat, maize, oats, rice, rye, sorghum, and wheat mainly contain phenolic acids (free or bound: 4-hydroxybenzoic acid and ferulic acid), flavonoids, and resorcinols. Barley flour has been quantified at up to 73 mg/100 g of PCs (Deng *et al.*, 2021), while buckwheat reports 37 and 8 mg/100 g of PCs for whole and refined flours, respectively. Maize kernels have a PC content of 179 mg/100 g, notably containing ferulic acid, synaptic acid, p-coumaric acid, 2-hydroxybenzoic acid, caffeic acid, and syringic acid. Specifically, red, blue, purple, and orange corn varieties are predominantly composed of anthocyanins, while whole grain flours have been identified as containing lignans such as syringaresinol, oxomatairesinol, and hydroxymatairesinol (Suriano *et al.*, 2021). Oats, consumed as rolled oats, whole grain oats, and whole grain oat flour, have a protein content of 26, 39, and 82 mg/100 g, respectively. The polyphenol mixture includes phenolic acids (ferulic acid, vanillic acid, 4-hydroxybenzoic acid, caffeic acid, and vanillin), avenanthramides (N-caffeoyl-5-hydroxyanthranilic acid, N-feruloyl-5-hydroxyanthranilic acid, and N-p-coumaroyl-5-hydroxyanthranilic acid), and lignans (hydroxymatairesinol, lariiresinol, matairesinol, pinoresinol, and syringaresinol) (Raguindin *et al.*, 2021). Rice grain contains ferulic acid (23 mg/100 g of refined flour and 91 mg/100 g of whole grain flour), followed by p-coumaric acid and resorcinols (5-heneicosylresorcinol, 5-heptadecylresorcinol, and 5-nonadecylresorcinol). Colored varieties such as black rice contain anthocyanins (cyanidin 3-glucoside) (Ramos *et al.*, 2023). Sorghum contains up to 413 mg/100g of protein, mainly proanthocyanidins, phenolic acids, and lignans (Kumari *et al.*, 2021). Wheat contains protein in the endosperm and bran, with concentrations 15 times higher in the endosperm. Protein contains phenolic acids (ferulic acid, p-coumaric acid, synaptic acid, caffeic acid, vanillic acid), alkylresorcinols (5-heneicosenylresorcinol and 5-heneicosylresorcinol), lignans, anthocyanins, and flavones (Tian *et al.*, 2021).

Beers and wines are rich in TPs (quantified by the Folin method). Beer contains xanthohumol, isoxanthohumol, 6-prenylnaringenin, ferulic acid, gallic acid, vanillic acid, p-coumaric acid, and synaptic acid, with TPs concentrations of 52, 42, and 28 mg/100 mL for ale, dark beer, and light beer, respectively. The concentration and type of polyphenols depend on the ingredients, processing, aging, and storage (Cortese *et al.*, 2020; Šibalić *et al.*, 2021). Grape polyphenols are highest in the seed (60%) and skin (30%), followed by the pulp and stem (<10%). During winemaking, NPs are obtained through vinification; the quantity and type of NPs depend on the grape species, the process, time and type of aging; including phenolic acids, styrbenes, flavonols, dihydroflavonols, anthocyanins (malvidin 3-O-glucoside, malvidin 3-O-(6-acetyl-glucoside)), catechins and proanthocyanidins, in TPs concentrations of 216, 32 mg/100 ml in red wine and white wine, respectively. Wine resveratrol has high biological activity; it occurs as aglycones (trans- and cis-resveratrol), glycosides (trans- and cis-piceid), and dimers (viniferin and pallidol) (Dos Santos *et al.*, 2022; Pereira-Coelho *et al.*, 2023).

Coffee and tea are the non-alcoholic beverages with the highest TPs content. Green coffee beans contain approximately 45 chlorogenic acids. When making the beverage, roasted beans are used, and this process influences the variability of TPs composition, as do bean maturity, storage, and brewing methods. The main components are phenolic acids, including 5-caffeoylquinic, ferulic, p-coumaric, 4-hydroxybenzoic, and vanillic acids. The only lignan identified was secoisolariciresinol, with TPs concentrations of 87-212 mg/mL (Mehari *et al.*, 2021; Alnsour *et al.*, 2022). Brewed tea contains up to 40% TPs; its content varies depending on the serving size. Green tea contains 7 catechins ((+)-gallocatechin, (+)-gallocatechin 3-O-gallate, (−)-epicalocatechin, (−)-epicalocatechin 3-O-gallate, (−)-epicatechin and (−)-epicatechin 3-O-gallate), phenolic acids, flavonoids and proanthocyanidins (65.7, 12.5, 5.3 and 5.5 mg/100 mL, respectively) (Abdullah & Mazlan, 2020), and for black tea a fermentation must be carried out in which thearubigins and theaflavins are formed by the oxidation of polyphenols. Cocoa beans store up to 2% w/w of protein in the cotyledon. When the beans are fermented, and cocoa powder is obtained, the protein composition is 5624 mg/100 g, consisting mainly of flavonols (catechins and proanthocyanidins). During chocolate processing, epicatechins and phenolic acids are formed, while clovamide and deoxyclovamide predominate in cocoa liquor (see Figure 1).

Effects of industrial processing on food matrices

The food industry uses technology to process food to provide microbiologically safe edible products, improve the digestibility of some nutrients, and develop the organoleptic characteristics of smell and texture. Processing induces structural changes within the food matrix and affects the polyphenols present naturally or added to prevent oxidation in easily degraded foods (Cao *et al.*, 2021). Food processing can include thermal and mechanical treatments, refrigeration, drying, and fermentation (Conte *et al.*, 2023), which cause significant changes in structure and composition, with effects that may be desirable or undesirable (Arfaoui, 2021). In particular, exposure to pro-oxidant metals and/or oxygen-rich atmospheres, heat, and pH changes promotes oxidation reactions that lead to the loss of molecules and their functionality (Cao *et al.*, 2021). Food quality is also affected by oxidation, compromising the functionality of native proteins, lipids, carbohydrates, and polyphenols. Oxidation influences the bioavailability, functionality, and stability of bioactive components during processing and storage (Conte *et al.*, 2023; Dini & Grumetto, 2022).

Protein oxidation is another cause of food spoilage, resulting in the loss of thousands of pesos' worth of products that are not consumed as intended. Amino acid side chains

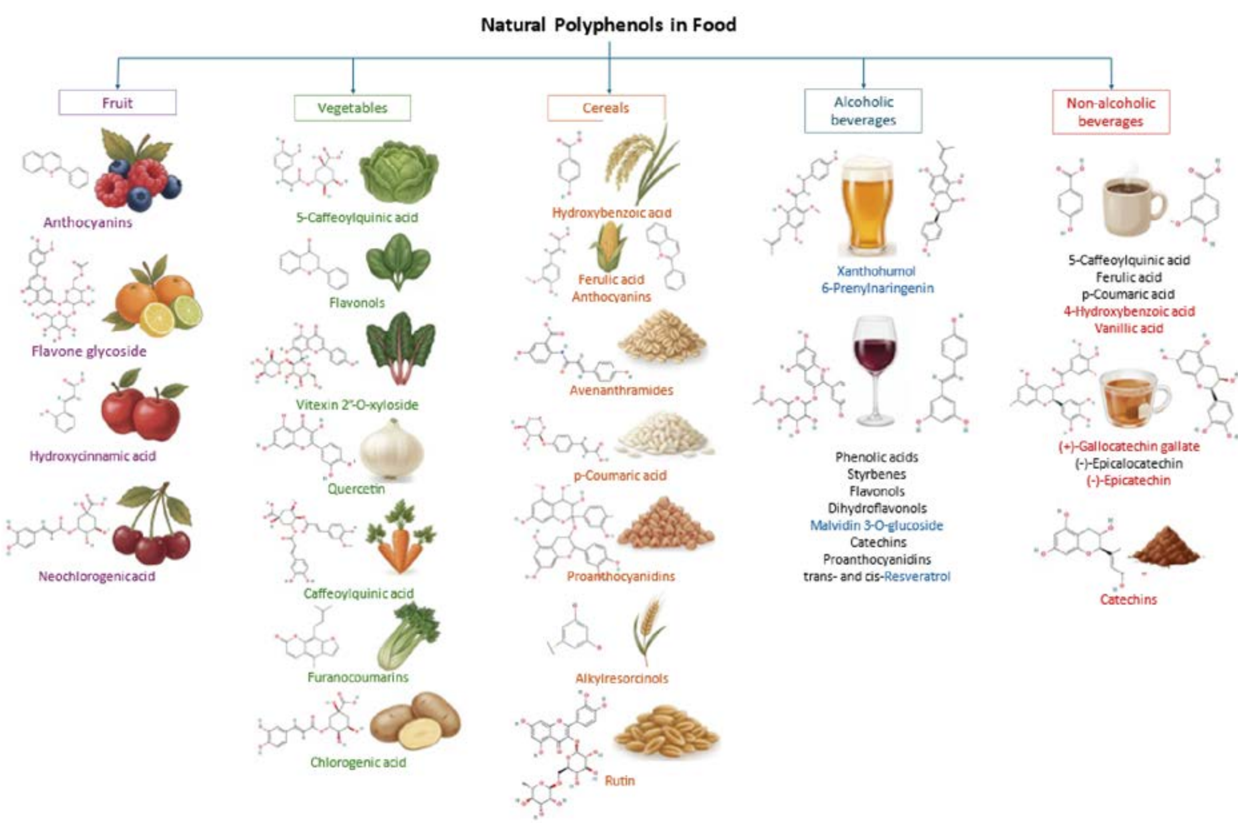

Figure 1. Chemical structure and food source of natural polyphenols.

can undergo oxidation reactions, altering protein function and compromising food quality. Protein oxidation is primarily a consequence of the presence of free radicals, heat treatments that modify protein structure, and myoglobin or metal catalysts (Davies, 2016). Protein oxidation promotes the generation of hydroxyperoxides, carbonyls, and sulfoxides, and the solubilization of proteins through the breaking of peptide bonds. Carbonylation of protein groups is similar to lipid oxidation. In the first stage, a hydrogen atom is removed from the protein structure by a reactive oxygen species, generating a protein free radical (P•) in the presence of molecular oxygen. The P• transforms into a peroxyl radical, which can react with another protein and trigger oxidative reactions. In the second stage, an alkoxyl radical is formed (Domínguez *et al.*, 2021). In meat products, the protein carbonylation process results in loss of juiciness and tenderness, color changes, decreased protein digestibility, and impaired functionality.

Lipid oxidation occurs in three stages: the first is initiation, in which a hydrogen atom is removed from an unsaturated fatty acid (RH) by a reactive species, generating an alkyl radical (R•). Endogenous enzymes, metalloproteins, light, and high temperatures are recognized as catalysts for this first stage, generating radicals such as the hydroxyl radical, the superoxide anion, singlet oxygen, the lipid radical, or the peroxyl-lipid radical. In the second stage, atmospheric oxygen reacts with the alkyl radical, forming a peroxyl radical. This promotes the removal of another hydrogen atom from a neighboring fatty acid, continually forming alkyl radicals. In this phase, it is common for products to develop a rancid odor, resulting from lipid peroxidation and the formation of aldehydes, ketones, and malondialdehyde (Hennebelle *et al.*, 2024). In the third stage, termination and direct interaction between two radicals result in dimers, trimers, or fatty acid polymers. Especially in food matrices of animal origin, polyoxygenated cholesterol derivatives are produced, which are potentially toxic (Wu *et al.*, 2024).

In the case of fried foods with high fat and carbohydrate content, deterioration occurs due to the generation of lipid-free radicals, resulting from thermal oxidation or auto-oxidation (Zeb, 2019). Protein-rich foods subjected to heat treatments above 250 °C and in the presence of free radicals form heterocyclic amines (Fernández *et al.*, 2012). The presence of these compounds has been linked to chronic degenerative diseases caused by the consumption of processed and ultra-processed foods. Processed food matrices are susceptible to oxidation but can self-regulate when they contain native antioxidants, such as vitamins, carotenoids, and polyphenols, which can neutralize reactive oxygen species and reduce deterioration. This self-regulation depends on the stability and concentration of the antioxidants. However, when intrinsic antioxidant capacity is lost, the addition of antioxidant-rich extracts, such as polyphenols, provides stability to the processes. The changes that polyphenols undergo during processing are, in many cases, desirable, even if they involve some loss, due to the desired sensory quality of the final product. In the case of grape fermentation, aged wines degrade anthocyanins, thereby achieving sensory stability. In barley malting, a pretreatment for beer production, up to 60% of flavonoids are lost; however, polyphenol derivatives are generated that give each type of beer its characteristic profile. The decaffeination process eliminates 9% of chlorogenic acid, and roasting the grain reduces polyphenols by 67% to 90%.

Packaged tea contains fewer polyphenols than tea consumed directly due to pasteurization. In the case of grains, most of the NPs on the outside of the seeds are lost during the mechanical refining process; however, some NPs can be retained in whole-grain flours. Tortillas made with corn in Latin American countries use nixtamalization (an alkaline-thermal process), in which the presence of Ca^{2+} and the temperature reduce the total polyphenol content by 78-90%. Pearling oats reduces avenanthramides by 58-83%. Flaked sorghum loses up to 90% of its proanthocyanidin polymers. Products made with whole-wheat flour retain 80% of their total polyphenol content, while those made with refined flour have a low NPs content. Baked potatoes contain 80% less 5-caffeoylquinic acid, microwaved potatoes retain 55% of the same polyphenol, and fried potatoes do not contain 5-caffeoylquinic acid. (Dao & Friedman, 1992; Peaterson *et al.*, 2001; Rothwell *et al.*, 2013).

Emerging technologies for polyphenol protection

Foods selected to preserve polyphenol functionality employ technologies that reduce polyphenol loss, such as vacuum thermal processing, microwaves, and ultrasound. Alternatives to thermal treatment also exist, such as high-pressure, freeze-drying, and bioprocesses, which reduce polyphenol loss and improve bioaccessibility (Conte *et al.*, 2023). Encapsulation is a preferred bioprocess due to its high specificity and ease of implementation. Polyphenol encapsulation can involve the use of proteins, lipids, polysaccharides, or mixtures thereof as carriers. This preserves the antioxidant activity of the polyphenol because the carriers prevent it from interacting with oxygen and water. The advantages of polyphenol encapsulation, beyond stabilizing them, include preventing the development of unwanted odors or flavors, improving aqueous solubility, controlling release, and increasing bioavailability. Encapsulation techniques depend on the desired physical state, core compound, required particle size, and sensitivity to high temperatures. Notable techniques include freeze-drying, fluidized bed coating, spray drying, cocrystallization, extrusion, spray cooling, coacervation, emulsification, nanoencapsulation, and molecular inclusion.

Freeze-drying and spray-drying are commonly used techniques for removing water from food matrices with encapsulation effects; they require expensive equipment with limited operating capacity (Ramírez *et al.*, 2015). Fluidized bed coating is a technique that involves coating particles suspended in air; it uses various coating materials, such as starch derivatives, gums, proteins, and cellulose in solution, among others (Lipin & Lipin, 2022). Co-crystallization modifies the crystalline structure of sucrose to an irregular structure with pores into which molecules of interest can be incorporated (Pawar *et al.*, 2021). Extrusion is a technique that forces a polymer solution, along with the molecules to be encapsulated, through a small orifice into a gelling solution. This technique uses sodium alginate as the polymer, and chlorine solution is commonly used as the gelling agent. The disadvantage of this encapsulation method is the loss of encapsulated molecules, and its industrial application is very expensive (Nurhudan *et al.*, 2021). Spray cooling is similar to spray drying, except that a cooling chamber is used instead of a drying chamber; the coating materials employed are lipid-based, such as waxes, fats, fatty alcohols, and polyethylene glycols. Coacervation uses the principle of phase separation of a hydrocolloid from a solution, followed by the deposition of the coacervate phase formed around the molecule of interest suspended in a medium; this technique is mainly used with high-value-added compounds due to their high cost (Sing & Perry, 2020). Emulsification involves dispersing one liquid in another as small droplets; it requires a stabilizing emulsifier, and drying is used to obtain encapsulated powders.

Nanoencapsulation is a constantly evolving technique that generates particles ranging from 1 to 1000 nm. It includes nanospheres and nanocapsules. Nanospheres are matrices in which the molecule of interest is adsorbed to the surface. At the same time, nanocapsules contain the molecule of interest within a cavity with an internal liquid core surrounded by a polymer network. This results in greater bioavailability, solubility, and controlled release (Naskar *et al.*, 2022). Molecular inclusion is a supramolecular technology that confines molecules of interest, called guests, within a polymer matrix. Interactions between the interior and exterior can be controlled because the guest fits within a circularly surrounding molecule through specific hydrophobic and/or hydrophilic interactions. The main encapsulating polymer used for molecular inclusion is cyclodextrin (Arce-Vazquez *et al.*, 2016). This technique offers significant advantages, including achieving desirable biocompatibility, high targeting and safety, a unique molecular structure, and easy functionalization. Inclusion complexes overcome the limitations of nanoparticle encapsulation.

CONCLUSION

This review confirms that natural polyphenols are an abundant group of molecules with antioxidant properties and are of interest to human health. However, their stability depends on agronomic factors and the mechanical conditions during processing. Polyphenol groups in food are closely associated with factors of genetic variability, environmental stress, and physiological maturity. Historically considered antinutritional, NPs are now recognized for their antioxidant, anti-inflammatory, and regulatory functions in metabolic processes, which are associated with consumer health. Therefore, NPs can be used in the development of functional foods; however, their sensitivity to oxidation, heat, pH, and light limits their direct application.

Furthermore, it is emphasized that food matrices possess self-regulatory mechanisms that balance oxidation via compounds such as carotenoids, vitamins, and natural polyphenols. This capacity can be affected when processing conditions favor oxidative reactions, leading to degradation or reduced functionality. The loss of NPs during processes such as cooking, roasting, nixtamalization, or refining can be excessive. Still, it is sometimes desirable due to its contribution to improving sensory characteristics. NPs preservation can be achieved through emerging technologies, such as minimal-intensity processes, bioprocesses, and, especially, encapsulation strategies. These represent alternatives for improving the stability and bioavailability of NPs. The appropriate integration of these technologies can foster the development of processed foods with effective functionality for the contemporary food industry.

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