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Chapter

Brazilian Caatinga: Phenolic Contents, Industrial and Therapeutic Applications

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Abstract

Phenolic compounds, mainly represented by flavonoids, tannins and coumarins, bioactive molecules with various applications, have antioxidant, photoprotective, antimicrobial, anti-inflammatory and even antitumor properties. The main mechanism of action of phenolic compounds is due to the transfer of electrons to free radicals, which leads to the interruption of oxidative reactions. The flora of the Brazilian caatinga is full of species with high concentrations of these compounds, which are possibilities for researching new pharmaceutical products and functional foods, and may even generate technological and economic impact, contributing directly or indirectly to the development of communities that are inserted in this context. This is extremely important, considering the large amount of ecotoxic residues resulting from the industrial chain, where it is necessary to use methods to reduce this impact on the environment, such as adsorption, oxidation, biotransformation, liquid-liquid partition and hybrid techniques. This shows the need to reuse this waste and even improve production processes in order to make the most of the content of these compounds with varied applications that sometimes end up being underused. This chapter brings some of the main species involved in this context, their contributions to health and possible applications at a technological, industrial and even sustainable level.

Keywords: Phenolic compounds, Folk Medicine, Ethnopharmacology, Industrial, Therapeutic

1. Introduction

Brazil is often mentioned as a country with great diversity, which takes into account its historical miscegenation considering the participation of native peoples, colonizers and immigrants from the most varied countries [1], relating this also with its biodiversity contained in its ecosystems that are divided into six biomes: Amazon,

Atlantic Forest, Caatinga, Cerrado, Pantanal and Pampa [2]. This characteristic contributes to the modification of the human relationship with the environment, as well as in the extraction of its resources and its applications, contributing to the development, but having an impact on the preservation of the typical species of each of these environments. A problem that has attracted the attention of researchers, since natural alternatives can, on the one hand, minimize environmental damage, such as, for example, the use of natural pigments instead of synthetics or the reprocessing of waste from the production chain [3], however on the other hand, the extraction of these resources in an indiscriminate way can lead to important environmental imbalances, in addition to threatening species with extinction [4].

The use of plants, whether for technological, medicinal, food, commercial or even religious purposes, is directly interconnected with the knowledge shared through generations within the cultural apparatus of the people who cultivate or live in their surroundings, knowledge that can be registered and monitored through ethnobotanical, ethnogeographic and ethnopharmacological studies, mainly [5, 6]. Since their properties are related to the content of secondary metabolites carried by these plant species, chemical components that are synthesized by plants to defend itself against pathogens and predators or to favor germination, thus associated with the production and maintenance strategy of the species and that are called secondary because they are not associated with the growth, development and structure of species. Among these metabolites are the essential oils, alkaloids, quinones, saponins and phenolic compounds, which include tannins, flavonoids and coumarins [7, 8].

Phenolic compounds, which are substances that have an aromatic ring with one or more hydroxy substituents [9], in the plants that synthesize them, act as allelopathic, preventing other species from interfering with their growth and development, fighting pests, including microorganisms and parasites, promote coloring and characteristic odors, protect against ultraviolet radiation [10] and are potent antioxidants, a function that is one of the most explored when using these compounds for medicinal purposes [11], and is also the largest source of antioxidants in human food, present in leaves, fruits and teas. The application of these resources, however, can be optimized, in order to promote their use also at a technological level, considering their versatility [12]. The present study intends to address these applications, highlighting these compounds as a source of innovations and sustainable development.

2. Caatinga: initial considerations, geographic and cultural aspects

The biome Caatinga extends in the northeast of Brazil, covering the states of Ceará, Rio Grande do Norte, with greater distribution in the states of Paraíba and Pernambuco, in addition to the southeast of Piauí, west of Alagoas and Sergipe, north and center of Bahia and part of Minas Gerais, as illustrated in **Figure 1** [13]. Its name comes from the Tupi Guarani language that means “White Forest”, due to the dry seasons, where only the trunks and shrubs, without leaves, remain in the environment. It is the only biome found exclusively in Brazil, one of the least studied and, consequently, one of the least protected, where only 2% of the region is inside of a protected area. For this reason, the Caatinga continues to be one target of deterioration and changes in its territory, caused by the non-responsible use of its natural resources [14].

The caatinga weather has extreme characteristics, with high solar radiation and low cloudiness, presenting the lowest average annual humidity, low evapotranspiration and

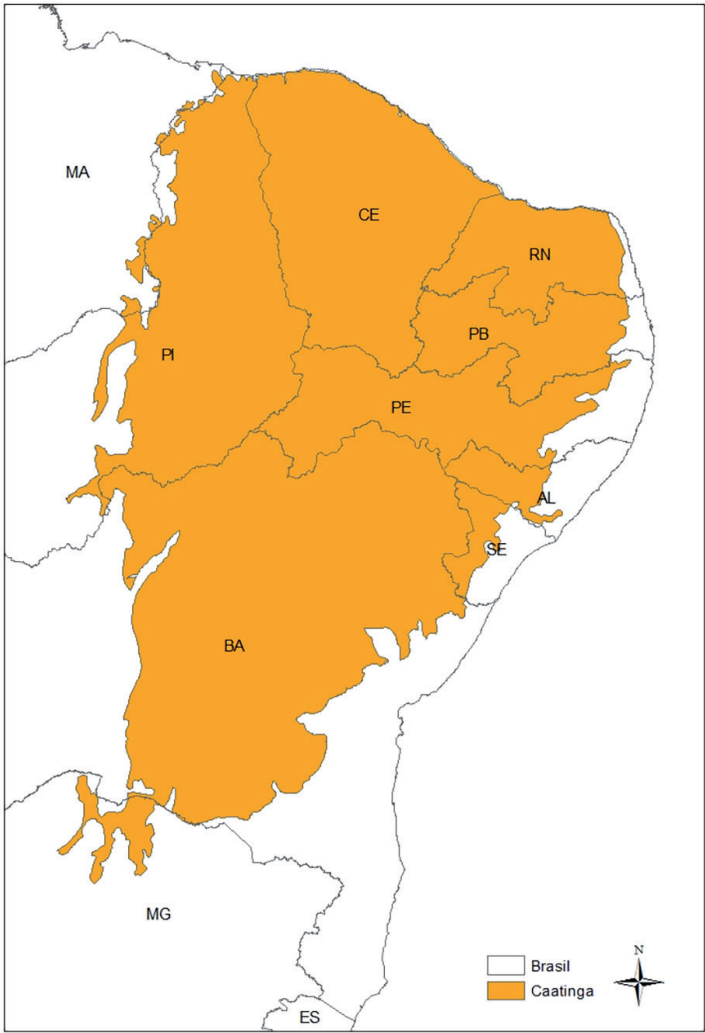


Figure 1.
Geographical location of the caatinga biome. Map available in the National Forest Information System of the Brazilian Forest Service.

irregular and sparse occurrence of rain through the year [15]. And despite being highly threatened, the caatinga is seen as a poor area, a common view about arid and semi-arid areas around the world. However, the caatinga exhibits a vast biodiversity, adapted to the difficult climatic conditions and is also associated with the source of natural resources, such as wood and medicinal plants. Some of these characteristics can be seen in **Figure 2**, which shows an area of the caatinga in the state of Pernambuco [16]. In the northeastern semiarid, the application of these resources is quite popular, considering the socioeconomic component, since there is a large concentration of families dependent on subsistence agriculture and cattle raising that frequently applies these species as low cost medicinal and food alternatives [17].

The environment adversities, however, end up bringing a high concentration of secondary metabolites in the plant species of the caatinga, including the phenolic compounds, since these compounds respond to the stress caused by the environment, in order to promote survival [18], which can make these resources have different applicability and have a excellent application, as medicinal purpose, in the treatment of effluents, such as natural pigments, in leather tanning for cultural or commercial purposes, in the production of wines, in the optimization of functional foods, among other applications. It is necessary to bring attention, in this case, to the conscious use



Figure 2.
Vegetation in the Brazilian caatinga, in the state of Pernambuco.

of these resources aiming to reduce the impact on the environment, with less degradation and predatory extraction, but under the guidance of using natural resources without bringing ecological imbalances that encompass both flora and fauna [19].

Ethnobiology and ethnoecology have already shown that the knowledge of local communities on use, management, including ethnic, biological and cultural implications, is extremely important for the issue of conservation of natural resources [20]. Ethnobotanical surveys have been carried out in recent decades in areas of the caatinga in order to register their species, their importance related to botany, preservation and also the development of new medicines. So, studies with this purpose can be useful, by increasing the focus on these environments. Since ethnopharmacological studies have revealed that many people who live within the context of the caatinga use their species as the first source of healing, using these alternatives for the treatment of various illnesses, such as coughs and colds, wound healing, with antimicrobial, antiparasitic and pesticide purposes, and even chronic diseases such as hypertension and diabetes. With majoritarian use of the species bark, considering that it is the part that is available throughout the year, even in the dry periods, followed by the leaves and seeds and fruits. The most cited species in these studies are mentioned in Section 4 [21].

3. Phenolic compounds in caatinga plant species: methods for obtaining, characterizing and purifying

Phenolic compounds are a group of substances easily found in nature, present in several plant species [22]. In this group are flavonoids, tannins, coumarins and other phenolic acids that are essential for the development of plants, acting mainly in the protection of stress caused by the environment, such as insects, infections, UV radiation, among others [23]. They are metabolites with increasing pharmacological interest, among the activities attributed to them are anti-inflammatory, antioxidant and antibacterial [24]. The chemical structure of these chemical species has similarities as well as specificities.

Flavonoids, tricyclic compounds with an arrangement of 15 atoms, have activities both in the species where they occur and in a medicinal way, regarding protection

against various pathogens, including fungi and bacteria, in addition to viruses and insects; photoprotection and antioxidant action, mainly, also acting as anti-inflammatories, through enzymatic modulation. Tannins are characterized by their astringency, which guarantees, in the species in which they are observed, defense against predators, beside antioxidant and antimicrobial activity, in addition of the ability to combine itself with macromolecules such as proteins to form insoluble complexes [25]. Their structures can be viewed in **Figure 3**.

Coumarins also have antioxidant effects and in plants they act as enzyme inhibitors, in the control of plant growth, in respiration, photosynthesis and in defense against infections and their biological applications are associated with their ability to make non-covalent interactions with protein structures, having a broad spectrum of biological activities, including the synthesis of a potent anticoagulant, warfarin. This is the most popular application of coumarins in medical sciences, which have served as a basis for new research that pursues the development of new synthetic alternatives with better response and fewer side effects, such as risks of bleeding when using these drugs [26].

The extraction is one of the first stages of studies with medicinal plants, being extremely important in the results obtained, as it interferes in the qualitative and quantitative tests of the metabolites, playing a fundamental role in the result of the processing of pharmaceutical and food products. This stage can suffer interference from several factors such as temperature, extraction time, solvent and part of the plant used, besides seasonal effects, considering that environmental aspects can bring modifications in the final chemistry composition of the species [27]. Before that, it is necessary to proceed the identification of the species to be studied by confirming botanical parameters, including macro and microscopic tests, considering the possibility of mistakes, due to morphological and even synonymic similarities of the popular names of these species [27]. From then on, a phytochemical study begins, which must go through extraction processes that can be identified in **Figure 4**.

In order to promote a higher yield of these resources extracted from plants, to guarantee their use at the technological level, whether for medicinal, food or in the production chain, in general, studies appear with the objective of optimizing, mainly, methods of extraction, addressing issues such as solvent, temperature, pH, quantity of material, standardization of new techniques and procedures or updating of protocols already in use [28]. The extraction time is one of the parameters that is often optimized, considering that the longer the extraction time, higher the difficulty

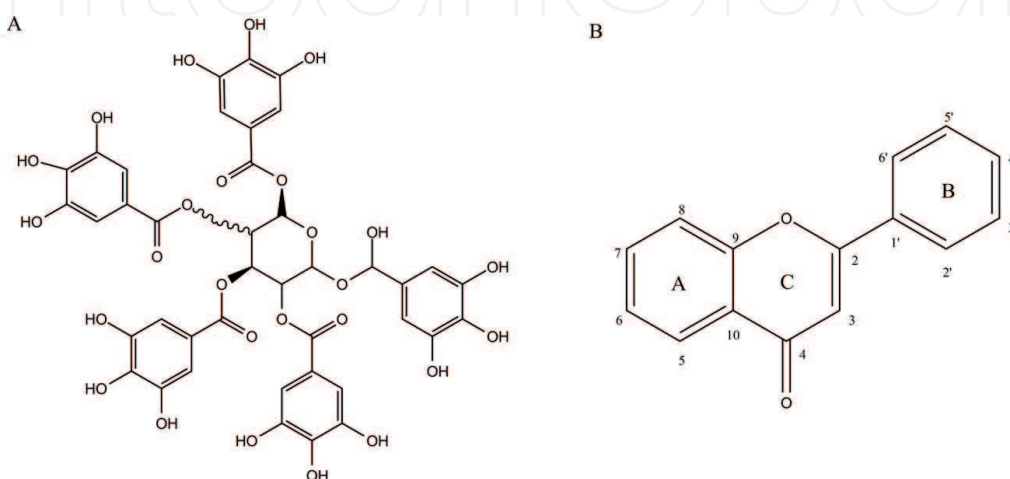


Figure 3.
Structural representation of tannins (A) and flavonoids (B).

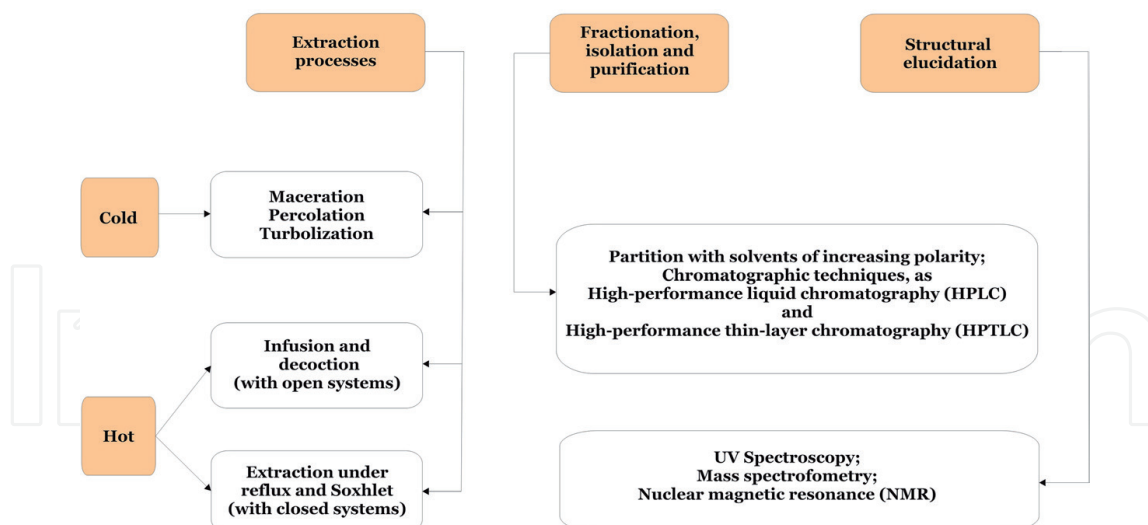


Figure 4.
Classical methods in the stages of studies with medicinal plants.

to apply the method on a large scale, beside the potential material loss due to degradation, since these compounds, being antioxidants, also end up undergoing degradation by the action of light [29].

To assist in the quantification of phenolic compounds, it is possible to use simple spectrophotometer techniques, favoring efficiency of the process and also reducing costs at this stage, maintaining the quality of the analysis. For the research of flavonoids, the standard for performing the calibration curve is rutin. For tannins, tannic acid can be used as a standard and the coumarins, can be analyzed through the Borntrager reaction with a calibration curve using 1,2-benzopyrone as a standard [30].

4. Medicinal and nutritional applications of phenolic compounds and related plant species

From the development of public policies that include natural products and medicinal plants in Brazil, these alternatives have become even more viable in primary health care. This has been observed since the year 2006, when the National Program of Medicinal Plants and Herbal Medicines was created, which provides an identification of the population with the treatments they use, considering that this knowledge comes, in most cases, from the community itself [31]. Several of the species that are used in traditional medicine in Brazil have a high concentration of phenolic compounds in their composition, with the associated mechanisms of action relating precisely to these chemical components and several of the species associated with these strategies are highlighted in ethnopharmacological studies [5].

Coumarins are also phenolic compounds and stand out for having a widely used representative, due to their anticoagulant potential, warfarin, an oral anticoagulant traditionally used in thrombophilic disorders which has its chemical representation indicated in **Figure 5**, where it is possible to identify the various phenolic groups present in its structure. In the caatinga biome, among the main representative species rich in coumarins, is the amburana (*Amburana cearensis*). This potential can serve as a basis, including for the study of synthetic alternatives, for the identification of optimized pharmaceutical products [26].

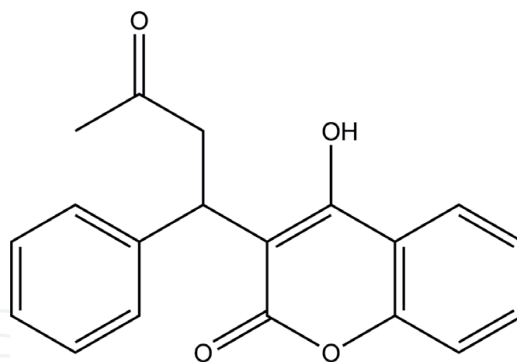


Figure 5.
Structural representation of a phenolic compound widely used in medicine as an anticoagulant (coumarin).
Warfarin.

Some of the main species of the caatinga with a high content of phenolic compounds are shown in **Table 1**, some of them can also be seen in **Figure 6** with their respective representations in studies that use High-performance thin-layer chromatography (HPTLC) as part of the research. These cited species are frequently referenced in ethnopharmacological studies, especially those with a focus on medicinal activity, whether by antimicrobial, antioxidant, anti-inflammatory action, among others [17, 32].

In Nutrition, some medicinal plants can also be considered functional foods, and the beneficial effects occur, since the compounds can act simultaneously on different cellular targets. Among the bioactive compounds already identified are soluble and insoluble fibers, antioxidants (such as polyphenols, carotenoids, tocopherols, phytosterols, isoflavones, organosulfur compounds), plant steroids and phytoestrogens [41]. However, the prescription of medicinal plants must be performed with caution considering the possibility of side effects and interactions with drugs and nutrients, which can generate organic imbalances [42]. Among phytochemicals, there is a growing interest in the discovery and identification of phenolic compounds that occur naturally in plant species, with the aim of finding new and promising sources of antioxidants for human health [43]. In food, they are responsible for color, astringency, aroma and oxidative stability [44].

The main food sources of phenolic compounds are citrus fruits, such as lemon, orange and tangerine, in addition to other fruits such as cherry, grape, plum, pear, apple and papaya, being found in greater concentration in the pulp and in the fruit juice, in addition to green pepper, broccoli, red cabbage, onions, garlic and tomatoes, which are also excellent sources of these compounds [45]. In addition, we can emphasize some plants that belong to the caatinga biome that have a great antioxidant potential and also potential for nutritional use, such as *Moringa oleifera*, characterized as nutritious and with a wide variety of uses, almost all parts of it can be used, its leaves being a food source to combat malnutrition [46], in addition to containing considerable amounts of proteins and several micronutrients, among them vitamin A, vitamin C, potassium, iron and calcium. They are also a good source of phytonutrients, such as carotenoids, and tocopherols [47].

These plants are also classified as unconventional food plants (UFP), because although they are edible, they are commonly underutilized, neglected and even considered weeds. Although not widespread, UFPs are alternatives for food and income improvement for family farmers, and can also be grown in urban backyards, adding food value to meals and even giving an exotic touch to some dishes. They are characterized by rusticity, weather resistance, longevity and great adaptability to different climates and regions. They are, in general, less demanding in fertility and irrigation,

Scientific name	Popular name	Use/composition/mechanisms
<i>Amburana cearensis</i>	Amburana	Its composition comprises mainly flavonoids and coumarins. Making it have an excellent anti-inflammatory action, being also mentioned as having a possible bronchodilator action, not yet fully elucidated [17, 32, 33].
<i>Anacardium occidentale</i>	Cashew tree	It also has, as well as the species mentioned above, antimicrobial action, in wound healing and as an anti-inflammatory, mainly due to the presence of tannins and flavonoids. In addition, it also stands out for its efficiency as an antioxidant, which leads people to use the tea made from cashew barks also to prevent diseases [17, 32].
<i>Anadenanthera colubrina</i>	Angico	It stands out for its high tannin content, with efficient application against infections in general, especially those affecting the skin [17, 32].
<i>Mimosa tenuiflora</i>	Jurema preta	One of the most popular species, according to ethnopharmacological studies applied in the caatinga. It has a very high concentration of tannins, being useful as an antimicrobial, anti-inflammatory and wound healing [17, 32].
<i>Momordica charantia</i>	São Caetano melon	Its fruits, leaves and roots are used for the treatment of diabetes, colic and as a healing agent [34] also presents a gastroprotective effect, due to the presence of bioactive compounds [35]. It is characterized as a plant rich in nutrients and considered quite versatile. Its fruits contain a high number of vitamins, including those of the B complex and minerals [36].
<i>Schinus terebinthifolius</i> Raddi	Aroeira vermelha	Excellent alternative as anti-inflammatory, wound healing, antimicrobial and antioxidant. The main mechanisms of action are related to the capacity of scavenging free radicals (antioxidant activity), interference in microbial cell walls, making these species act as an antifungal, antibacterial and also antiparasitic, some flavonoids can interfere in the performance of proteins and enzymes by hydrophobic interactions, promoting modulations that leads to anti-inflammatory effect, mostly because of the great content of tannins and flavonoids, which also participate in wound healing process, promoting a cover that offers defense against contaminations helping in the hemostasis phase. At the same time, cell signaling can occur, influencing the inflammatory phase by interference in the work of macrophages, responsible for combating possible contaminants [37, 38].
<i>Selaginella convoluta</i> (Arn.) Spring	Jericho	Antimicrobial, antioxidant and anti-inflammatory effects, with similar mechanisms. In addition to being associated with use as an antidepressant and antinociceptive, mechanisms of which have not yet been fully elucidated, but which may also be related to interactions with protein sites and enzymes [39, 40].

Table 1.
Caatinga plants with high concentration of phenolic compounds/medicinal use.

easy in maintenance and can be planted using seeds or seedlings. With extremely diversified possibilities of flavors and very interesting nutritional characteristics, the UFPs contribute to the improvement of the local diet in the communities involved, and are also a true cultural rescue [48].

From that definition, these plants are also distinguished for being considered for localized, regional and/or seasonal consumption, with limited distribution and with no established production chain [48]. In addition, if carried out in a sustainable manner, it can be considered a form of land use with low impact on agriculture, associated with environmental conservation. Thus, the dissemination of studies carried out to the communities can help in a better direction of the use of these resources, where through them it can contribute to an improvement of health, as well as provide strategies to fight hunger in these localities, using these species in favor of the individuals who live in their surroundings [49].

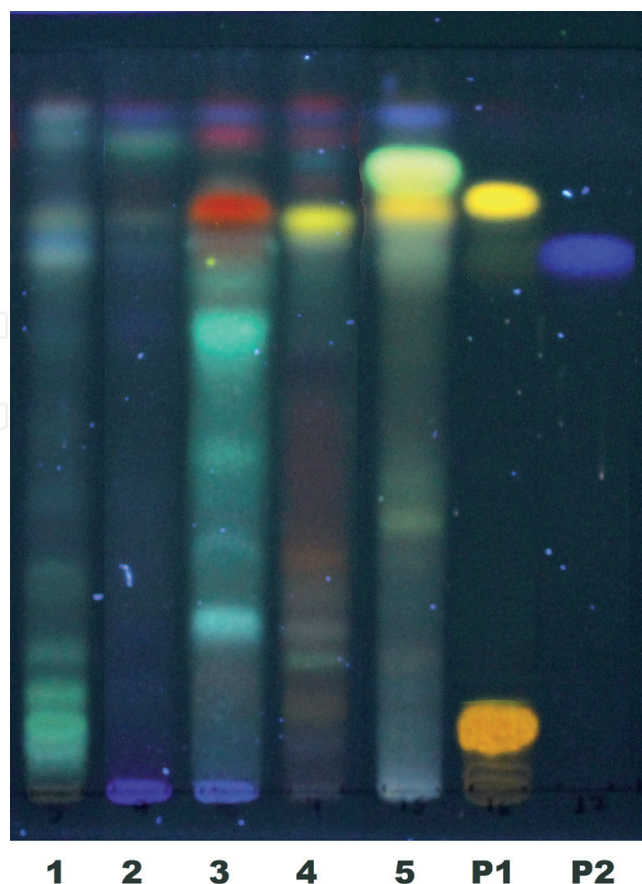


Figure 6.
 High performance thin-layer chromatography (HPTLC) of the crude extract of Caatinga plants. 1 – *Mimosa tenuiflora* (*Jurema preta*); 2 – *Anacardium occidentale* (*caju roxo*); 3 – *Myracrodruon. Urundeuva* (*aroeira do sertão*); 4 – *Anadenanthera colubrina* (*Angico*); 5 – *Amburana cearensis* (*amburana*); P1 – Rutine + quercetin; P2 – Gallic acid.

5. Phenolic compounds with technological application and economic potential

Among the main technological applications for phenolic compounds, as mentioned, its use as a medicinal alternative stands out, where these and other metabolites, medicinal plants and herbal medicines can assist in self-care, making individuals as protagonists of their own care, and also, in reducing health costs. In the Brazilian health system, this alternatives are applied inside the so-called integrative and complementary practices, where they are present, ensured by the legislation, including the official pharmacopeia of the country, in which is possible to consult the monographs with techniques of extraction and basic information about some of the plants used popularly, always remembering that in order to be considered within these official means, these plants, as well as herbal medicines need to undergo studies that prove their efficacy and toxicity patterns, in order to guarantee safety in its use [50–52].

Within the context of medicines, phytotherapeutic drugs of wide use are also highlighted, which are rich in phenolic compounds, such as flavonoids, present in *Ginkgo biloba* L, where they contribute with antioxidant action; Passion fruit (*Passiflora spp*), from which drugs that act as anxiolytics are extracted, where in this case, the flavonoids act mainly as markers for indication of quality in the extraction, a function that is facilitated due to its fundamental structure, which usually has 15 atoms of carbon

arranged in rings, forming a tricyclic compound. The tannic compounds are also noteworthy. Some of them present in the species *Hamamelis virginiana* L. that favor its hemostatic activity, since one of the main characteristics of tannins, in addition to promoting the antioxidant effect, is also able to bind to molecules and macromolecules, such as proteins, for example, being able to contribute to the stabilization in the treatment of injuries, of the most diverse types [27].

In addition, from the perspective of nutrition, there is a growing concern with the food supply capacity at global scale, as well as a high consumption of processed foods and fast food is identified, considering the fast pace of life that people in general maintain. Because of this, the incorporation of these biological assets, such as phenolic compounds and the integration of plant species that are, underutilized or neglected in food, can be an alternative to compose food products that promote health, at the same time that they become productive pathways for families and their financial support, from the moment that a resignification of these alternatives is promoted [53].

This positive health effect resulting from phenolic compounds application of nutrition, is what justifies the action of wines as potent antioxidants, since it is estimated that in its composition it contains more than 200 polyphenols, among flavonoids, tannins and anthocyanins, mainly. And although the grape is not a typical species of the caatinga, there is an increase in investments in the northeast region of Brazil, in which the caatinga is also part, in the so-called São Francisco valley. And this profile generates interaction with the environment, its modification and helps in economic and human development [54].

Another application of caatinga species, such as Babaçu (*Orbignya phalerata* (Mart.)), for example, can also contribute to the production of biodiesel, being, therefore, an alternative to consider in the formulation of sustainable energy sources, in addition to having the possibility of using all parts of the species in this process, which also impacts sustainability demands, considering that all portions can be processed for application in the production of inputs and products, such as brushes and carpets, in food, from the preparation of vegetable oils, chocolates, foods and cakes [55].

The action of flavonoids as photoprotectors has also leveraged research for their cosmetic application. Considering that caatinga species are rich in these metabolites, they can be sources of pharmaceutical inputs or the purification and isolation of these compounds can serve as a basis for synthesizing new molecules that promote the potentiation of the photoprotective effect. Such activity is mainly due to its chemical structure with double conjugated bonds, which directly interferes with the absorption process in the region of ultraviolet A (UVA) and ultraviolet B (UVB) [56].

6. Reprocessing waste containing phenolic compounds in its composition as a sustainability initiative

The current scenario involves all the problems in which globalization and development is involved in the so-called fourth industrial revolution, where, in addition to the competitiveness of the market, there is an urgent need for sustainable proposals and measures within development systems, in order to provide growth with significantly less impact on the environment. From the 1990s, this paradigm shift is observed when we see that development needs sustainable attitudes, where the concept of Triple Bottom Line (TBL) begins to be considered, which understands

the viability of companies' businesses according to the dynamics between economic, social and environmental aspects [57].

Based on this, the reprocessing of residues, mainly those resulting from agribusiness, which is one of the economic sections that most impact the environment, can be an alternative to maximize the efficiency of the production process, meeting the needs related to sustainability. It is clear, from studies published in recent years, that the use of these materials resulting from this reprocessing has high versatility, being able to meet, for example, demands of the food chain [58], and civil construction [59].

As an example of reprocessing, we can mention the contribution of one of the most endemic species of the caatinga, the cashew tree (*Anacardium occidentale* L.), which has several applications: medicinal, food and industrial in general. From this production process, the cashew nut is obtained, its fruit, which contributes economically both to the local product and to exports; as well as cashew nut shell liquid (CNSL), which is seen as a by-product and is still little used in Brazil, while in other countries, some of those who acquire this liquid from Brazil and with the appropriate technology employed, perform its reprocessing as becoming a product of high added value, used as resins and polymers, in addition to additives, surfactants, drugs, pesticides, among others, configuring itself as an alternative with high potential for profitability and which continues to be underutilized [60].

However, phenolic compounds need to be quantified so that they can be used with these purposes safely, considering that these compounds can also, if accumulated, generate complications for the environment, being necessary to maintain safe concentrations when developing new alternatives that contain them. Where it is observed that there is a need to reduce the concentration of phenolic compounds in wastewater in an increasing way, requiring increasingly efficient technologies in this process. In Italy, a law aims to guarantee the quality of fresh, coastal, brackish and marine waters from polluting waste discharge locations, stipulates that waste water must contain a limit value of total phenols before disposal 0.05 mg/L and that, if the disposal is done in freshwater, these waters, after disposal, must contain up to 0.01 mg/L of total phenols, being considered safe for the environment, not putting in risk the health and quality of marine organisms. The reuse of waste can be a tool to reduce the accumulation of these compounds in nature [57].

In Brazil, this concentration varies according to the destination that the wastewater will have and this is divided into four classes. Class 1: the water must be free of phenolic compounds, intended for domestic use without having undergone previous treatment; Class 2: water used for domestic use, irrigation and recreation, which has undergone previous treatment, can contain 0.001 mg/L; Class 3: it can also contain a concentration of 0.001 mg/L, where this water is destined for domestic use or for disposal in places where there is a need for environmental preservation, fauna and flora; Class 4: the concentration can reach 1 mg/L, for which this water can be used for purposes that demand less quality standards such as some domestic uses, industrial use, irrigation, among others. When it is necessary to treat these effluents with high concentrations of phenolic compounds, various techniques can be used. Some of them are described below [57].

Adsorption Methods are the most traditional for the treatment of wastewater with organic contaminants. For phenolic compounds, the continuous flow fixed bed technique is widely used, which generally consists of a cylinder containing an adsorbent inside, with activated carbon (most common compound), with inlet and outlet, through which it is fed by residual water. Factors that interfere with a good efficiency of the technique are the concentration of contaminants in the wastewater and the feed

flow rate. For phenolic compounds, a good efficiency is when the concentration of these compounds is small in the wastewater in addition to a low flow rate [58]. The advantage of considerably reducing the concentration of phenolic compounds in wastewater, allowing for their safe disposal, concomitantly generates. As a disadvantage, the formation of solid waste formed by activated carbon with adsorbed phenolic components, considering that their improper disposal will also cause environmental damage [59].

Another traditional method is the Advanced Oxidation Processes (OAP's) also known as Fenton reaction. The reaction consists in the formation of hydroxyl radicals (HO^\bullet) and Fe^{+3} as a product of the interaction between Fe^{+2} and hydrogen peroxide (H_2O_2). Hydroxyl radicals will react with organic compounds, such as phenols, giving rise to organic radicals that interact with oxygen in the environment, causing a series of degradation of these compounds, generating mainly carbon dioxide and water as products. With the advancement of technologies, the association with other techniques shows that there is a decrease in the reaction time, as this reaction occurs slowly, in addition to a significant increase in the formation of hydroxyl radicals, consequently increasing the degradation of organic compounds [60].

And then came the Eletro-Fenton and Foto-fenton techniques. Electro-fenton consists in the use of electrodes composed of transition metals such as manganese oxide (MnO_x) and nickel oxide (NiO_x) that act as catalysts, increasing efficiency and decreasing the reaction time, accelerating the process [61]. In the case of Foto-Fenton, its principle is the use of ultraviolet radiation not as a catalyst, but as a photolytic agent. In the Fenton reaction, the Fe^{+2} ion with hydrogen peroxide, forming Fe^{+3} . Ultraviolet radiation works by recovering the Fe^{+2} ions by reducing, by photolysis, the nox number

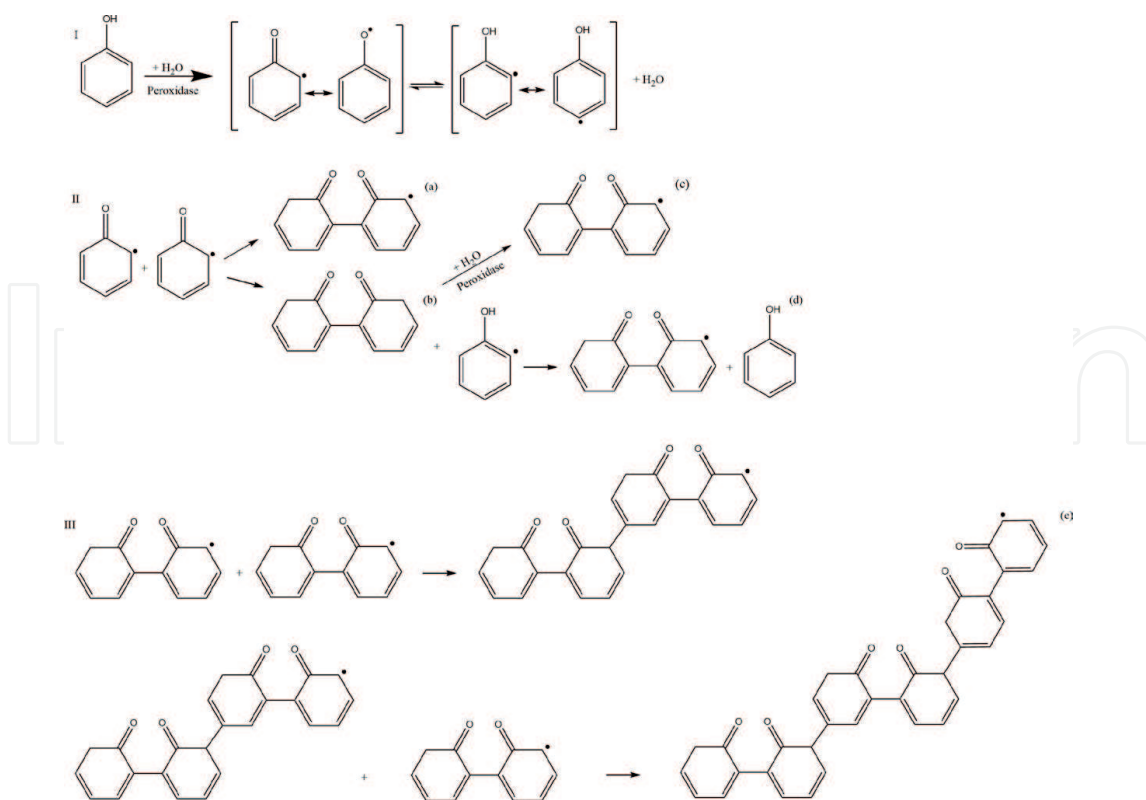


Figure 7.

Polymerization scheme of phenolic compounds by peroxidases, with the following sequence: I. phenol oxidation step with formation of phenoxyl radical and water as product; II. Radical dimerization step; III. Polymerization itself; (a) dimer radical; (b) non-radical dimer; (c) radical dimer formation via the peroxidase pathway; (d) radical dimer formation by reaction with phenoxyl radical; (e) insoluble polymer.

of Fe^{+3} , which makes the system always have the Fe^{+3} ion as the producing agent of hydroxyl radicals in a continuous process. The advantage of this method is that both the ultraviolet radiation used can be either by lamps or by sunlight, which reduces costs [62].

Some microorganisms, such as Gammaproteobacteria, Actinobacteria, Betaproteobacteria and Alphaproteobacteria, can absorb certain types of phenolic compounds and use them as substrates for vital biochemical reactions. From this, the use of biomass from aerobic microorganisms immobilized on solid supports, usually membranes, through which they are subjected to direct contact with wastewater under aerobic conditions, a process called biofiltration, may be interesting alternatives [63].

The use of enzymes can also be a good alternative in the biopurification process of wastewater containing phenolic compounds, especially peroxidases, which are oxidoreductive enzymes capable of oxidizing aromatic compounds and, furthermore, when oxidation occurs in phenolic compounds in the presence of hydrogen peroxide, polymerization of these compounds occurs, forming insoluble precipitates that are easily removed by physical processes of solid-liquid separation (**Figure 7**). The peroxidases can be used pure obtained by commercialization or contained in crude extracts of plants such as horseradish, soybean, turnip, garlic, sweet potato, radish and sorghum for which it is a cheaper alternative and as functional as using purified enzymes [64].

Liquid-liquid partition is a well-known and used way of extracting and purifying substances. It consists of a mix of two immiscible liquids in which one of the liquids has the solute that migrates to the other liquid phase by affinity according to its polarity. Usually, an aqueous phase and an organic phase are used that vary in more or less polar, so it is chosen according to the solute in question. The most commonly used traditional organic solvents are ethanol, methanol, acetone, ethyl acetate and hexane. Taking the characteristics of this technique into consideration, it was seen that it could be used for the removal of phenolic compounds from wastewater, where the choice of solvent occurs according to the physicochemical properties of the phenolic compounds [65].

However, these solvents have several disadvantages, as they are as toxic as the residues themselves, are flammable, generate atmospheric gases, and are non-biodegradable. With this in mind, the technique was linked to biopurification, replacing traditional solvents with solvents considered “clean” or “green”. Called neoteric solvents, their use minimizes environmental impacts, reuse of the solvent itself, reducing process costs, in addition to increasing the efficiency of removal of residual compounds. Neoteric solvents encompass ionic liquids, eutectic solvents, biologically-based solvents and supercritical fluids [65].

Methods that combine more than one technique for the bio-depuration process, called hybrid technologies, can be a very promising alternative. Cavitation is a phenomenon in which tiny bubbles form within a system from the very intense agitation of molecules in a liquid by ultrasound. Cavitational reactors cause this agitation to generate a high energy content in the system. This technology by itself is not so interesting for the treatment of wastewater on an industrial scale, since it demands high costs and causes operational problems when referring to the dissipation of the generated energy. However, when combined with known bio-depuration methods and used as oxidative or catalytic (enzymatic) methods, it can be viable on a large scale. Basically, cavitation reactors will add energy to the medium, facilitating the formation of reactions [66].

Cavitation associated with hydrogen peroxide causes the formation of hydroxyl radicals without the need for the presence of Fe^{+2} in the system, but in well-controlled conditions of pH and temperature, as disorders in this regard can cause the radicals to interact with the hydrogen peroxide itself forming water. Some disadvantages of

the photo-fenton technique, such as inhibition of the reach of ultraviolet radiation by interaction with non-interesting contaminants on the surface of the waste water, as well as limitations on mass transfer, can be reduced or eliminated when associated with cavitation, in addition to an increase in the production of free radicals, a technique called oxidative Sonophotocavitation [66].

The association of cavitation with Electro-Fenton, in addition to helping in the formation of free radicals, the movement of molecules helps the solution to remain mixed and acts to clean the electrodes, removing crusts formed in the process that hinder the exchange of energy between the electrodes and the solution. In combination with oxidative enzymes (peroxidases), cavitation helps to eliminate some disadvantages of the process, such as increasing the useful life and decreasing the inactivation of these enzymes, in addition to being able to act synergistically in the production of radicals, increasing the polymerization of phenolic compounds [66].

7. Future perspective, industrial, therapeutics and sustainability applications

It becomes important to envision the perspective of promoting the integration of academic studies and the industry for the joint development of strategies using the species mentioned, in order to bring together objectives and set concrete goals for possible application, thus contributing to the increasing number of alternatives such as these arrive at the final development, with economic gain, valorization of the local component, academic contribution and for the general community, culminating in added value in conjunction with sustainable development strategies. Which is a necessity imposed by our current reality [67].

For example, the products that have the grape, as its raw material, in addition to wines, are items of high added value, highlighting the participation of grape juice, these products can provide good responses at the commercial and economic level [60]. However, the large scale of production ends up generating waste, which can also be reprocessed for other applications, becoming sustainable alternatives for local development, including the generation of food alternatives, such as the production of flour, also rich in phenolic compounds, with good sensory acceptability and large-scale applicability [68, 69].

Within this context, a major transformation occurred in the so-called São Francisco Valley, in northeastern Brazil and also inserted within the extension where the caatinga grows. From irrigation strategies, this region became one of the main producers of grapes and wines in the country, also participating in exportation in this area, promoting the addition of economic value to that region, generating employment and development. This demonstrates that with the correct investment, the region in which the caatinga is located can, with its own means, grow and develop, also in a sustainable way, since production can reuse all waste associated with the production chain [54].

And this theme can be highlighted considering the following situations: 1. The caatinga region can use these resources sustainably in order to guarantee the livelihood of the families that are inserted in this context. 2. The presence of finished products on the pharmaceutical market, either as medicines or as functional foods, makes it clear that these species can be applied for these purposes, adding value. 3. There is a need to expand studies that promote the visibility of this region in general, as there are still unexplored potentials [69, 70].

8. Conclusion

Phenolic compounds are present in several of the endemic species of this biome, characteristically Brazilian, the Caatinga. The underutilization of these species impacts on a loss of applicability and potential profitability, which can, if applied, leverage the production processes in this location that comprises the Northeast region of Brazil, favoring sustainable development with added value not only to elaborated products, but to the very identity of the communities that depend on the processing of these alternatives. The applications can be diverse, either for use in food, as functional foods, or in traditional medicine, where it adds value even to the cultural factor related to families that pass this knowledge on plants to the generations away. They also participate in industrial and civil construction activities, among other areas. This appreciation also ends up increasing the identity of these communities and their peoples who contribute directly or indirectly to raising the use of plant species, making them feel represented. Therefore, initially, the greatest value to add with the best use of these alternatives is social improvement.

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