The importance of the cashew nut (*Anacardium occidentale* L.) coat: a review

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ABSTRACT

The cashew (Anacadium occidentale L.) is a major source of income for farmers in the Northeast of Brazil. The cashew nut is composed of three parts: shell, nut, and brown film- known as coat. The coat represents 1% to 3% of the nut total weight and is a rich source of polymeric hydrolysable tannins, as polyphenols. The lipid fractions are particularly comprised by fatty acids, oleic (C18: 1) and linoleic (C18: 2). This study reviewed the cashew nut coat, in light of the scientific advances achieved in recente years. The aspects examined were: separation process between the coat and the cashew nut, coat chemical composition considering nutrients and other bioactive compounds of primary and secondary metabolism, biological and microbiological activities and technological applications.

Keywords: *Cashew nut coat, phenolic compounds, Anacardium occidentale L.*

INTRODUCTION:

The cashew tree (*Anacardium occidentale*) is a Brazilian plant widely available in the coastal region, extending from the Amazon to the Northeast. It is distributed in many tropical regions of the world, among which are: Mozambique, Tanzania, Kenya, Guinea Bissau, Indonesia, Thailand, Vietnam [1, 2], and India [3]. The cashew nut trade began in the early 1920s. India was a pioneer in processing and trading these nuts in industrial scale, and it remains the top cashew nut producer in the world, followed by Vietnam and Brazil [4].

In Brazil, the cashew nut agribusiness is concentrated in the Northeast region. Together, the states of Ceará, Piauí, and Rio Grande do Norte are responsible for 95% of the total production. The sale of cashew nut contributes significantly to the local economy, creating more than 300,000 jobs in the Northeast [5]. According to IBGE (the Brazilian Institute of Geography and Statistics), Brazil has close to 775,000 hectares dedicated to cashew groves, area that practically remains unchanged over the past 10 years. The total cashew nut production ranges around 276,000 tons per year [6].

The cashew tree has been considered a great source of phytotherapics for centuries. Its application in popular medicine is described in the literature. Common uses include: analgesic [7], diuretic [8], antiseptic for oral hygiene [9], asthenia treatment, respiratory problems, genital infections, and skin diseases [10].

Literature reports evidences of its successful uses as a hyperglycemic [11], an antimicrobial [12, 13], antioxidant [14, 15], anti-inflammatory [16, 17], anti-ulcerogenic [18], and antiophidic [19].

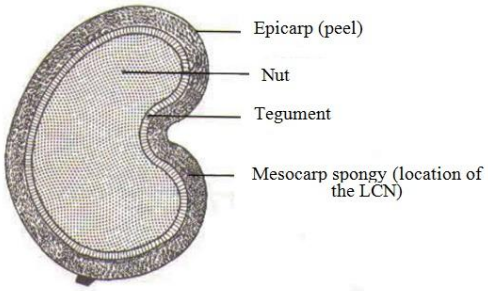
To make the observations, chemical constituents were isolated and identified from many parts of cashew tree. From the chemical study of the leaf, it is highlighted the occurrence of flavonoids such as: agathisflavone, apigenin, kanferol, myricetin, quercetin, quercetin-3-O-glicopiranosil, quercetin-3-O-ramnopiranosil, robustflavone, and amentoflavone [20]. The Ethyl gallate was isolated from the flowers [21]. Its bole shell shows the gallic acid as a major component. The steroids were obtained as tannins hydrolysis product: myo-inositol, cholesterol, campesterol, stigmasterol, and sitosterol [22]. The *occidentosídeo(-)-salipurposídeo* were isolated from the nut shells [23, 24], naringenin, naringenin-7-O-(6"-O-p-coumaroyl)- β-Dglycosylates [25], naringenin-5β-glycosylates[23]. Various phenolic sources were selected for the coat study, in which (+)-catechin and (-)-epicatechins were isolated [21]. In addition, pharmacological activities were tested in one of the bioactive compound classes and those that attracted more interest were phenolic lipids, mainly for its antioxidant properties [26, 27].

Although there are many studies on the cashew tree, a detailed research on the coat is scarce. The subject has received more attention only in recent years, for its functional potential [4]. However, there is little information on the chemical structure and the physicochemical and functional properties of the cashew nut coat. Therefore, in this review, four themes will be addressed: (i) cashew nuts processing and waste generation (coat) (ii) chemical and metabolic composition, (iii) biological activities, and, (iv) possible industrial applications.

• THE CASHEW NUT

The cashew nut consists of three parts: shell, coat and nut. The weight of a nut may vary from 2g to 30g, and the average weight is around 7.0g. The Figure 1 shows a cross section of cashew nuts.

Figure 1. Cross section of a cashew nut



Source: [4].

The shell, which is 65% to 70% of the nut's weight, consists of an epicarp coriaceous, crossed by a spongy mesocarp, whose alveoli are filled with a caustic and flammable liquid, the CNSL (Cashew Nutshell liquid) [28]. The film, or coat, represents around 3% of the nut's weight, it is rich in tannins [29], and the nut, the edible part, formed by two ivory cotyledons, represent approximately 28% to 30% of its weight. In the industrial process, the average yield is only 21% [30]. The CNSL consists of a dark brown liquid, viscous, acre and caustic, rich in phenolic compounds (anacardium acid, cardol, cardonol, and 2-metilcardol) [31, 32].

The cashew nut coat is a thin protective layer of the nut (Figure 1). It was initially utilized to maintain the operation of boilers, on CNSL extraction and in cattle feed [33]. These remain the most used applications to date. Numerous authors have observed the coat's phenolic activity, opening doors for many studies related to tannins applicability. Varnishes manufacture, elaborated from resins obtained from tannin extracts of the coat, are cited as one of its industrial applications [34]. The cashew nut coat represents an environmental problem for the producing regions because due to the high production of nuts and, consequently, coat, the manufacturing plants have no use for this residue, except for utilizing it to power boilers [35].

• CASHEW NUT PROCESSING

The cashew nut processing aims to obtain the whole nut, fully dehulled, white-ivory, spotless, and good sized [36]. The cashew industrialization (peduncle and nut) can be divided, at least, in two types of processing: the nut processing industry and the peduncle manufacturing industry. The first aims to obtain cashew nuts (CN), with cashew nutshell liquid (CNSL), nut shell, film (rich in tannin), and cashew nut oil as its main by-products. The peduncle manufacturing industry, in turn, has segments in beverages, sweets, condiments, flours, and feeds industries, among others.

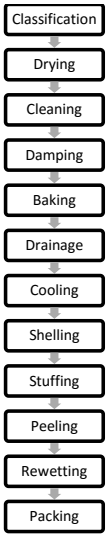
The cashew nut processing is performed, predominantly, by mechanized and semi-mechanized systems in large factories. This process may also take place in establishments classified as micro or small homemade production, cooperatives, and producer associations (with capacity of process up to one ton/day). The average yield of these processes is approximately 23%, i.e., 4.35 kg of raw nuts are necessary to produce one kilogram of nut [28].

The handmade process of nut processing is still widely adopted in small farms in the Northeast of Brazil, especially in the states of Piauí and Bahia. Other countries (Africa, India, Sri Lanka, and Vietnam) also utilize this process due to the availability of low cost labor and for its higher yield of the whole nuts, around 85% to 95% [37]. This process has many drawbacks, linked mainly to poor hygiene conditions of the settings [38].

The Brazilian industry of cashew nut processing utilizes both mechanized and semi-mechanized segment. The mechanized segment consists of 12 processing plants with the capacity of processing about 90% of the Brazilian production [39], and the semi-mechanized segment consists of over one hundred mini factories, with capacity of processing 20,000 tons per year (Paiva, S. N. et al., 2006). The mechanized industrial processing of cashew nuts is represented according to the Flowchart 1.

• NUT AND COAT SEPARATION PROCESSES FROM CASHEW NUT

Flowchart 1: Cashew processing phases in mechanized system



The processing starts with the nuts' arrival in the industry. First, they are weighed and taken to sunlight exposure aiming to reduce moisture (from 7% to 10%) to avoid deterioration problems and, thus, leading to the maturation of the nut by the action of infrared and ultraviolet rays [40]. The nuts remain drying for a period that can reach up to seven days, and a classification by size is, then, performed, following a previous cleaning using vibrating screens or perforated plates [41].

The nuts, after being dried, cleaned, and sorted, may be stored in sacks, stacked on pallets arranged on a waterproof floor [42, 43]. Then, they are cleaned and stored in bins, which are immersed in water for a period ranging from 140 to 330 min [44]. Nut roasting is usually carried out in an autoclave at 110°C/10 min, or in a household pan [45].

The CNSL, first noble product of the processing, is extracted during roasting process. The dehulling or shelling may be performed by centrifugation ("Stutervant" process) or cutting ("Oltremare" process) [29].

After shelling, drying aims to reduce nut moisture from 2.5% to 4.0%, wherefore the coat, firmly adhered, becomes brittle and can easily be removed. Drying is performed by greenhouse (between 60°C to 80°C) for 6 to 8 hours. In many cases, the nut is submitted to a wetting process by saturated steam (between 1 or 2 minutes), which facilitates the coat separation from the nut [46].

The nut tends to decrease in size and the coat becomes brittle with dehydration, weakly adhering to the nut. Then, the shelling is carried out taking advantage of this physical change. The coat removal is done by injecting compressed air to break or release the coat, or by a shelling cylinder with brushes, or using an electric rotary cylinder [46, 47].

The shelling with rotary cylinder, activated by an electric motor at low speed, consists of submitting the nuts to friction on a perforated screen, promoting the partial release of the coat. In a shelling cylinder with brushes, the nuts are placed on a wood table or galvanized sheet provided with metal screen, where they are submitted to friction through the bristle brushes to obtain the nuts partially without coat. In any of these operations one may obtain nuts up to 70% without coat. The remaining shell is submitted to a manual scraping process with shelling knives [43].

• COAT CHEMICAL COMPOSITION

Thousands of chemical constituents may be present in plant tissues, although, largely, in low concentrations. Even under these conditions, several of these constituents are responsible for features such as color, flavor and taste, besides nutritional and nutraceuticals effects [48-50].

Among the chemical constituents identified in the cashew nut coat, one can highlight the following classes: terpenes, flavonoids, terpenoids, catechins, epicatechins, tannins, and sterols. Phenolic compounds are considered as the primary responsible for pharmacological activity [51-59].

Studies performed [60] to determine the cashew nut coat (CNC) mineral composition, show that it contains more protein, fiber, calcium, magnesium, phosphorus than corn, but with less energy if compared to values reported for that grain (Table 1).

Table 1: Chemical and mineral composition of the cashew nut coat

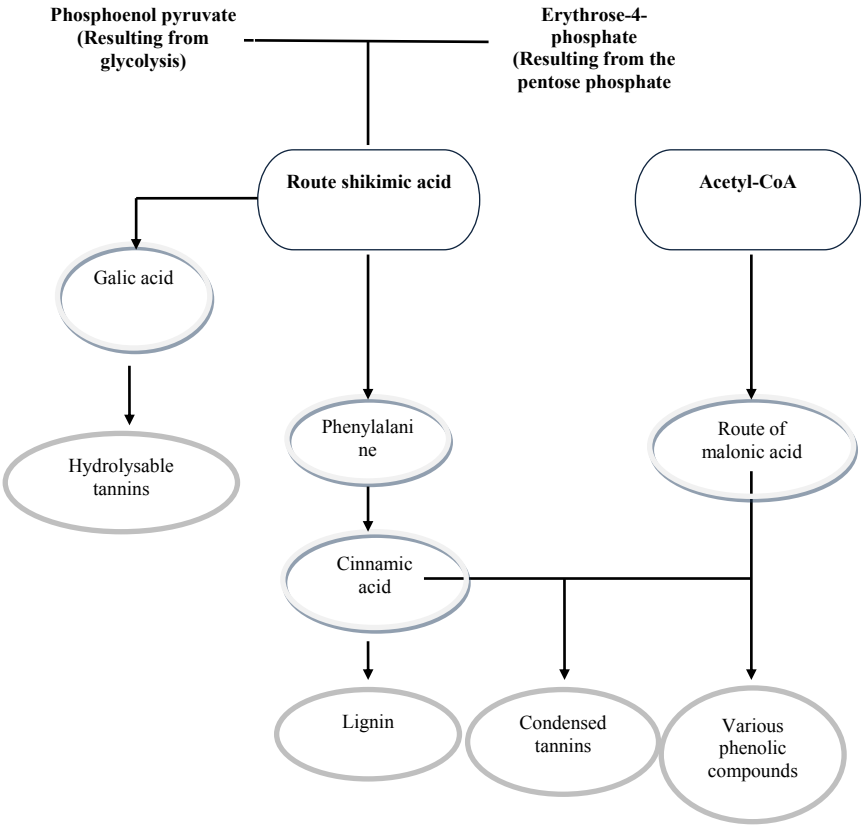
ANALYSIS	NTC (g/Kg)	Corn (g/Kg)
Dry matter (DM)	905	890
Crude protein	190	88
Crude fiber	103	22
Ether extract	20,1	38
Ash	20,2	13
Calcium	5,6	0,2
Phosphorus	1,9	2,8
Magnesium	5,8	1,2
Tannins	1,8	--
Metabolizable energy	7,12	14,02

Source: [59].

• METABOLISM, PRIMARY AND SECONDARY METABOLITES

Plants primary biosynthetic process is the photosynthesis, which uses solar energy for organic compounds production, grouped according to common features of primary and secondary metabolites. The primary metabolites, essential for organism survival are: sugars, amino acids, fatty acids, nucleotides, and polymers. Some of these metabolites are used as precursors in the synthesis of other compounds, in enzymatically catalyzed reactions, such as shikimic acid (precursor of several aromatic compounds), acetate (a precursor of fatty acids, polyphenols, isoprene, prostaglandins, among others), and aliphatic amino acids (alkaloids biosynthesis), summarized in flowchart 2 [61].

Flowchart 2: Some primary metabolites routes



Source: Adpt [62].

- PRIMARY METABOLITES DERIVED OF FATTY ACID PRESENTED IN COAT (CNC)

The fatty acid is an essential primary metabolite for plants and animals. It is derived from a biosynthetic route of acylpolimalonato (AcetylCoA), creating long carbon chains. Its dehydrogenation and/or oxidation may give rise to heterocyclic, triglyceride, and lipid compounds [63].

The cashew nut coat has a high amount of ether extract (Table 1), characteristic that arises one's interest in understanding its lipid composition [64]. The main fatty acids found in the coat are shown in Table 2.

The coat's lipid composition values vary based on different factors such as sample preparation, sample homogenization with solvents, phase separation, and solvents removal. Sample preparation depends on its nature, harvest local, extraction forms, storage period, and temperature [65]. During the lipidic extraction, some conditions are

considered, such as operational costs, implementation speed, ease execution, to include the care to prevent lipid and hydrolysis oxidation and degradation during analysis and storage stages [66].

Table 2 analysis allows the comparison of two extractive methods performed by [67] and [68], with extraction solvents (chloroform/ methanol/ water) and (ethyl acetate/ hexane), respectively.

Table 2: Fatty acid composition CNC

FATTY ACIDS	[67](%)	[68] (g/kg)
Lauric acid (C12: 0)	0,2	-
Myristic acid (C14: 0)	0,3	-
Physeteric acid (C14: 1)	0,4	-
Palmitic acid (C16: 0)	16,4	-
Palmitoleic acid (C16: 1)	1,1	-
Hexadecodienóico acid (C16: 2)	1,4	-
Stearic acid (C18: 0)	6,4	40,9± 6,3
Oleic acid (C18: 1)	35,3	214±33,2
Linoleic acid (C18: 2)	30,4	68,6± 10
Linolenic acid (C18: 3)	5,8	-
Gadoleic acid (C20: 1)	1,6	-
Fatty acids	0,8	-

(-) not analised.

One of the advantages of the method used by [67] is the formation of a biphasic system from solvents proportions added during the extraction process, based on the liquid-liquid balance theory of three components (chloroform/ methanol/ water). The methodology used by [64] was performed following the method used by [69], which analyzes stearic, oleic, and linoleic acids, for being of great importance in the extract and oil characterizations. Unlike the previous method [67], the authors sought solvents like ethyl acetate and hexane, to replace the chloroform. The analysis based on gas chromatography was coupled to mass spectrum which allowed the quantification of the fatty acids present in the coat.

The stearic acid content (4.1g/100g) in the coat was higher than those found in peanut (1.30g/100g), hazelnut (0.94g/100g), coconut (1.10g/100g), nut (0.55g/100g), pistachio (0.98g/100g), and walnut (1.37g/100g)[70]. The oleic acid content (21.40g/100g) showed a higher concentration than the nut (0.98g/100g), coconut (2.10g/100g), Brazil nut (18.5g/100g), and walnut (11.4g/100g), while the linoleic acid content of the coat (6.9g/100g) was greater than the one present in coconut (0.68g/100g) and macadamia (1.74g/100g) [71-73]. The linoleic acid is a phospholipid component, responsible for cytoplasmic membrane structure and function [74]. According to that study, a diet rich in polyunsaturated fatty acids has anti-spreader effects of diseases, such as: diabete type 2, hyperlipidemic, cardiovascular disease, inflammatory rise, cancer, and osteoporosis.

• SECONDARY METABOLITES PRESENTED IN THE COAT (CNC) OF *ANACARDIUM OCCIDENTALE* L.

Secondary metabolites are responsible for maintaining the plant, i.e., the interaction with the native environment. Generally, they have a complex structure, low molecular weight, and remarkable biological activity, protecting the plant against pathogens and microbial attacks, and herbivorous actions. It is produced by plants in various stress situations including nutrient deficiency, salinization, water scarcity, and high exposure to UV radiation, leading to the production of more polar compounds [63, 75, 76]. Secondary metabolites are divided into three classes: phenolic compounds (phenols, phenolic acids, coumarins, flavonoids, tannins, and lignins); terpenes (carotenes, steroids, polysoprenos, saponins, and triterpenes), and alkaloids (nitrogenous compounds) [76, 77].

Phytochemical research is one of the most widely used methods for the isolation and purification of secondary metabolites, aiming at identifying the chemical constituents of a given plant specie or evaluating its presence [78].

Whenever there is no chemical study available on species of interest, the preliminar phytochemical analysis may indicate the relevant groups of secondary metabolites therein. The extracts prepared from plants are submitted to tests which allows the characterization of the main groups containing the organic substances of interest [63].

Researchers [79] and [80] identified in cashew nuts classes of secondary metabolites as alkaloids, polyphenols, and saponins. Among the classes of secondary metabolites, the more prevalent in the coat are: tannins, phenolics, and flavonoids (catechin, epicatechin, and epigallocatechin). Studies with coat (CNC) pointed that phenolic constituents highlight the hydrolysed tannins with polymeric proto anthocyanidins. Table 3 presents a phytochemical analysis of the cashew nut coat extracted by solventes of different polarities [68].

Table 3: Coat (CNC) chemical profile of *Anacardium occidentale* L. using different solvents.

PHYTOCHEMICAL	**Solvent**		
	Ethanol	Ethyl acetate	Acetone
Alkaloids	✖	✖	✖
Carbohydrates	✖	✓	✓
Steroids	✖	✖	✖
Phenolic	✓	✓	✓
Flavonoids	✖	✖	✓
Glycosides	✖	✖	✖
Volatile oils	✓	✓	✓
Triterpenoids	✓	✖	✓
Xantoproteins	✖	✓	✓

(✖) Not detected (✓) Present

Source: [79].

Natural compounds have a different solubility behavior depending on the chemical nature of different functional groups present and may vary from simple to highly polymerized substances. In addition, there is also the possibility of interaction between the various compound classes, such as carbohydrates and proteins. These interactions may form insoluble complexes, thus, compromising the reliability of the obtained data. The development of a single extraction procedure, capable of recovering all compounds present in the sample, is improbable, since a small fraction of these compounds are soluble in the solvent utilized [81-83]. The use of diferent solvents explains the differences in results shown in Table 3. The CNC ethanolic extracts resulted in the presence of various phytochemical compounds such as triterpenoid, phenolic, and volatile oils. The extract with ethyl acetate showed a different combination of phytochemicals- phenols, volatile oils, xantho proteins, and carbohydrates. However, the extract containing acetone was effective in dissolving triterpenoids, phenolics, volatile oils, flavonoids, xantho proteins, and carbohydrates [79].

• PHENOLIC COMPOUNDS

The outer layers of plant materials such as shells and coat have a high content of phenolic compounds. They act in the defense against pathogens, parasites and predators' attacks, besides contributing to the formation of a variety of colors found in plants [83].

Studies have shown that the content assessment of phenolic compounds present in the CNC depends on the extraction method and type. In ethanol extracts [4] obtained directly from the coat, the concentration of total phenols is approximately 185.44mg/ Gallic Acid Equivalent (GAE). But [27] used ethanol to prepare the extract, under stirring, at 37°C, for a period of 3hrs and, when analyzing the amount of phenolic compounds, they observed that the coat presented a higher total phenolic content (243mg/GAE) than the ethanolic extract at room temperature (Table 4).

Studies performed with CNC degreasing ethanolic extracts, carried out by [84] showed a different behavior with temperature variation, indicating that elevating temperatures resulted in an increase of the phenol content. They obtained 790.9 mg/EAG as a maximum point (130°C), whereas in low temperature (70°C) there was a decrease in the phenolic compound content (701.2mg/ GAE). The explanation for this variation is a consequence of the conjugates phenolic compounds released during the thermic treatment and the production of Maillard Reaction Products (MRP) [85-87].

Another related study, [88], analyzed the content yields of soluble and conjugated phenolic compounds in ethanolic extracts of raw coat, when submitted to high and low temperatures. The highest yields of phenolic extracts were 44.2 ± 1.4g/100g of degreased flour, and its total phenolic content was 347.99 ± 6.88g/g of degreased flour, in which the CNC was submitted to 130°C for 33 min (Table 4).

These results are similar to the study performed by [89] and [90] in hazelnut coat and its derivatives, where roasting (175°C/5 min) increased by 40% the total peanut coat phenolic compounds in comparison to the raw coat. The authors concluded that the thermic treatment increased the phenolic compound concentrations in the coat, and its results were consistent with similar studies performed using hazelnuts and peanuts [90, 91].

Table 4: Content of CNC total phenolic compounds submitted to diferente methods

Extract	Submitted treatment	Total phenolic compounds (TPC)	Reference
Ethanol	Shaker 37°C/3hrs	243 mg /g GAE	[27]
Ethanol	Ambient temperature	185,44±12,04 mg /g GAE	[4]
Ethanol (80%)	Degreased (hexane)	656,2±23,0 mg /g GAE	[84]
Ethanol (80%)	Degreased (hexane) 70ºC/ 6hrs	701, 2 ± 21,1 mg /g GAE	[84]
Ethanol (80%)	Degreased (hexane) 130°C/33min	790,9±15,4 mg /g GAE	[84]
Ethanol (80%)	Degreased (hexane)	269,05±9,77 mg $GAE/g_{degreased\ sample}$	[88]
Ethanol (80%)	Degreased (hexane) 70ºC/ 6hrs	308,50,9±6,88 mg $GAE/g_{degreased\ sample}$	[88]
Ethanol (80%)	Degreased (hexane) 130°C/33min	347,51±9,35 mg $GAE/g_{degreased\ sample}$	[88]

Phenolic compounds are the most important products of a plant secondary metabolism, acting on the growth, reproduction and natural development of plants and vegetables. Most of them come from phenylalanine amino acids and, in some plants, from tyrosine. Although animal tissues do not synthesize phenolic compounds, the presence of this type of structure may be attributed to plants ingestion [92, 93]. The three largest groups of phenolic compounds

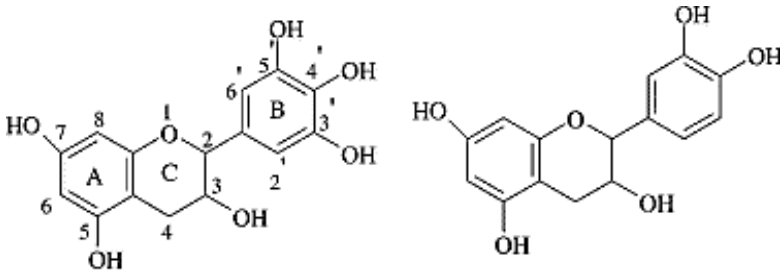
found in animal diet are flavonoids, phenolic acids, and polyphenols (tannins). Phenolic acids comprise benzoic acid and its derivatives (hydroxybenzoic, gallic, and ellagic, among others), cinnamic acid and its derivatives (coumaric, caffeic, ferulic, and chlorogenic, among others). The tannins are polimers with a high molecular weight, divided into two classes: hydrolysable tannins- comprising gallic acid polymers or ellagic (found in fruits and nuts), and the condensed tannins, catechin, or epicatechin polymers [61].

Several phenolic compounds have been found in CNC, such as tannins, flavonoids, catechins and epicatechins, and, in smaller proportions, phenolic acids (syringic, gallic, and coumaric). Studies performed [84] highlight that the values of these acids in extreme conditions can reach 0.974 ± 0.030; 5.705 ± 0.001; and 0.693 ± 0.043mg/g MS degreased (Table 4). These acids are also present in other nuts for instance cashew nuts, hazelnuts, and pine coat [89, 94, 95].

• TANNINS

The tannins of cashew nut coat have been studied over the years as a hydrolysable tannins source. The tannin quantitative estimation in the CNC shows that from 82.5% of total polyphenols, 80% are tannins, while the remainder are phenolic constituents [34, 96]. Further studies elucidated and identified the tannins present in the coats (Figures 3 and 4), indicating the presence of procyanidin as its main constituent [34].

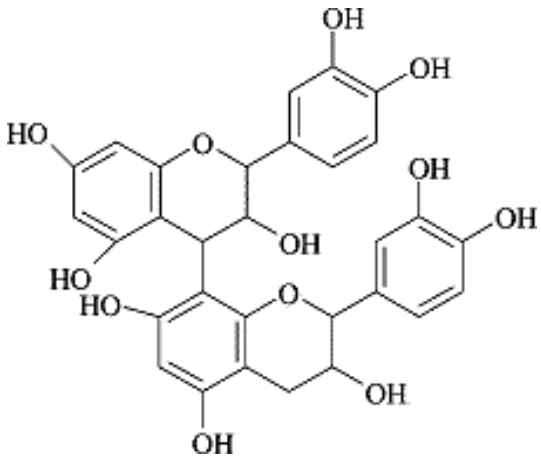
Figure 3: Tannins structure of cashew nut coat (a) delphinidin and (b) cyanidin



(a) (b)

Source:[34].

Figure 4: Existing catechin in the cashew nut coat.



Source:[34].

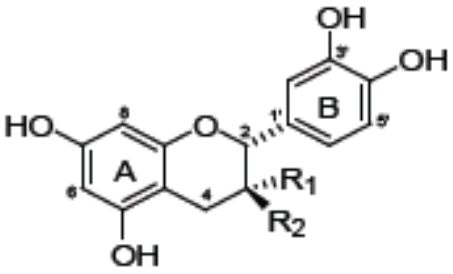
• CATECHINS

Catechins belong to the flavonoid group of flavanols class. They present a phenyl benzopyran basic skeleton without the carbonyl at carbon 4 and without unsaturation in linking carbons 2 and 3 (Figure 5) [63, 97]. Catechins have beneficial effects on human health, (+) – catechin and (-) - epicatechin have recently received much attention being considered as protective agents against cardiovascular disease and cancer [86, 98, 99].

Researchers [84, 88] observed that the catechin, epicatechin, and epigallocatechin content found in the degreased samples of cashew nut coat were 47.28mg/g; 28.29mg/g; and 2.0mg/g, respectively.

While evaluating the cashew nut coat extract, one can observe that the HPLC/MS spectrum of the phenolic extract reveals two prominent peaks with maximum absorption at 278nm, highlighting the presence of phenolic compounds such as the catechins[68]. Autors reported the presence of catechins and epicatechins in the coat, through analysis of RMN spectrum of samples isolated from fractioning by column chromatography in silica gel and in ethyl acetate phase (Figure 5)[4].

Figure 5: Structures of (+) - catechin and (-) - epicatechin isolated in CNC



7: R_1=H; R_2=OH
8: R_1=OH; R_2=H

Source: [4].

• OTHER CLASSES OF SECONDARY METABOLITES

The exposure of the human body to free radicals from various sources, leads to the development of defense mechanisms (endogenous defenses) to eliminate these free radicals [100, 101]. These endogenous defenses may be enzymatic or non-enzymatic. The enzymatic antioxidant defenses are in large number and are located throughout the body, both intracellular and extracellular. Among others, the superoxide dismutase, catalase, glutathione peroxidase, and glutathione reductase are examples of these defenses. Non-enzymatic antioxidant defenses highlight compounds such as glutathione, γ-tocopherol (vitamin E), ascorbic acid (vitamin C), lipoic acid, and carotenoids [101, 102].

Bioactive compounds in cashew nut coats were analysed and it was observed the presence of these compounds in greater quantities than those found in the cashew nut (Table 6) [68]. The presence of high amounts of carotenoids (β-carotene, lutein, and α-zeaxanthin) in the coat is of great importance for the development of cashew nuts during germination. The coat protects it from insects, microbial infection, and sunlight through the enclosure containing the cashew nutshell liquid (CNSL)[64]. After breaking the shell, the antioxidant protection function contained in the coat is

activated [103]. According to [104], carotenoids play an important role in cancer prevention and atherosclerosis.

Table 6: Carotenoids, tocopherols and thiamine in the cashew nuts coat

Bioactive compounds	Concentration (mg/KgDM)
β-carotene	218 ± 11,8
Lutein	525 ± 45,2
α- zeaxanthin	7,0 ± 2,2
α-tocopherol	10,1 ± 0,7
γ-tocopherol	10,6 ± 0,6
Thiamine	3,0 ± 0,5

1 Values are means ± standard deviation of 10 separate determinations (n = 10).

Source: [64]

The levels of α- and γ-tocopherols in cashew nut coat are 10.1 and 10.6mg/kg of MS, respectively (Table 6). Tocopherols are reported to constitute an essential part of biological membranes, showing a protective role against lipid peroxidation of membrane, lipoproteins, and fats [105]. Thiamine was also found in CNC (3.0mg/kg of MS).

The coat has a high amount of functional compounds, but its composition may not be described in its entirety because natural constituents are yet to be studied. Moreover, a great number of identified compounds, already isolated and with determined chemical structure, have no specific biological activity, either in terms of their functions, or potential uses, especially therapeutic.

• ANTIOXIDANT ACTIVITY

Research involving antioxidant compounds from natural sources, as plant extracts and its components, have been extensively developed for utilization in foods, in industrial applications, and in animal organisms. This includes diferent parts, such as seeds (soybeans, peanuts, cotton, mustard, canola, rice, and sesame), fruits (grapes, citrus fruits and peppers), leaves (green tea, rosemary, thyme, and oregano), and others (onion seedlings, sweet potato, and oats) [106-108].

The search for natural antioxidants has been intensified since the 1980s, in an attempt to replace total or partially synthetic antioxidants. Deleterious effects are attributed to the animal organism when used in high doses [109]. The possible adverse health risks that the irregular and/or indiscriminate use of synthetic antioxidants may present to humans contribute to the high rejection of this additive type. Emphasis has been placed on the identification and purification of new natural compounds with antioxidant activity, which can act alone or synergistically with other additives to prevent oxidative deterioration of foods and restrict the utilization of synthetic antioxidants [89].

Natural antioxidants attract particular interest, especially the ones present in popular foods. Diseases as cancer, atherosclerosis, arthritis, diabetes, and heart-related problems, along with processes responsible for the body's aging may be related to the presence of ROS (reactive oxygen species) in the body [110, 111]. Studies indicate that certain bioactive compounds present naturally in foods may inhibit these processes, due to natural antioxidant qualities [112].

In vitro techniques allow a quick selection of substances and/or potentially interesting mixtures. The principles which guide these methods include the capture of the peroxyl radical (ORAC, TRAP), metal reduction power (FRAP, CUPRAC), capture of the hydroxyl radical (deoxyribose method), capture of organic radicals (ABTS, DPPH), quantification of products formed during lipid peroxidation

(TBARS, LDL oxidation, and co-oxidation of β- carotene), RANCIMAT, standard automated method to determine the oxidative stability of oils, fats and lipid food [113-117].

Numerous studies and different methodologies were applied to the cashew nut coat to measure its antioxidant activity, such as DPPH (2.2-diphenyl-1- picryl-hydrazyl), co-oxidation of β-carotene/linoleic acid, ABTS (2.2'-bis-azino 3-ethylbenzthiazoline-6-sulfonic), ORAC (kidnapping of peroxyl radical), capture of hydrogen peroxide (H2O2), kidnapping of hydroxyl-deoxirribose radical, inhibition of LDL oxidation (inhibition of the lipid peroxidation), FRAP (antioxidant parameter of the reduced ferric ion), and the RANCIMAT [117-122].

The analysis of the cashew nut coat antioxidant activity was performed using different methods. With the ABTS method, the antioxidant activity was measured by the samples discoloration with ABTS + radical concentration in relation to the coat extract and a synthetic antioxidant, BHA (butylated hydroxyanisole), comparing them. Its potential was also measured using the following methods: Kidnapping of hydrogen peroxide (H_2O_2), kidnapping of hydroxyl-deoxirribose radical, LDL, and FRAP (Table 7)[27].

The results are expressed in EC50 (mg.mL-1), which correspond to the amount of extract required to reduce the DPPH radical in 50%. Thus, the smaller the EC50, the better is the extract antioxidant capacity is. From the data obtained in different tests, it became evident that the CNC effectiveness order is: ABTS> superoxide> deoxyribose> LDL> FRAP (Table 7). Based on the results, one can say that the coat extract is a more potent antioxidant than the ferric reducer.

Table 7: CNC antioxidant activity

Antioxidant activity method	**EC_{50} (µg/mL)**
ABTS	1,30±0,02
FRAP	6000±0,24
LDL	24,66±0,32
Abduction of hydrogen peroxide (H_2O_2)	10,69±1,13
Abduction of hydroxyl-radical deoxyribose	17,70±0,05

Source: [27]

Other authors [123] investigated the nut coat ethanolic extract potential to kidnap the DPPH radical. The results obtained, expressed by antioxidant activity, were analyzed at concentrations ranging from 25 to 250 µg/mL, in which the coat had inhibition variations from 12% to 40%.

The phenolic compounds present in vegetables show a high antioxidant activity [124, 125]. Literature [88] evaluated the coat phenolic extract antioxidant activity through diverse methodologies, varying the drying temperature (Table 8). These studies show that the extracts studied had a high antioxidant potential, which was compared with a BHA synthetic antioxidant.

Table 8: Evaluating the temperature variation of cashew nut coat antioxidant potential using different methodologies

Methods	Processing conditions			Control
	$T_{ambiance}$	T 70°C/6hrs	T 130°C/33min	BHA[(1)]/Catechin[(2)]
Lipid-oxidation TBARS (eq.MDA-malondialdehyde / kg extract)	2,75±0,34	2,34±0,31	2,75±0,18	2,12±0,15[(1)]
Co-oxidation β-carotene / Linoleic acid (coef. Ativi. Antiox. / G extract)	370	365	345	-
Peroxidation of LDL oxidation - inibition (%)	46,05±0,24	41,51±0,72	43,66±2,13	40,00±1,52 [(2)]
Induction of DNA H_2O_2 (%)	87	91	84	-
Rancimat (inflection Factor)	2,83±0,05	1,57±0,02	1,48±0,01	2,48±0,13[(1)]

Values expressed as mean ± standard deviation (n = 3); (-) Not reviewed.

Although the coat has a high percentage of catechins in its composition as seen on Table 8 [64, 88, 96, 126], other antioxidant compounds, i.e. the tocopherol, the thiamine, and/or phenolics, may influence the quantification of the catechin, thus justifying the variations in its analysis.

The oxidation rate of lipids, proteins, and DNA by the superoxide radical is relatively low. However, its importance as an oxidative process is connected to its capacity to generate other reactive oxygen species, as hydroxyl radical (•OH), which has high reactivity.

• BIOLOGICAL ACTIVITIES

The use of plants as medicinal agents in the treatment of many diseases has been investigated since the most ancient civilizations. Many researches have been developed based on the uses of vegetables used in folk medicine, leading to new drugs. Nowadays, there is an increased global interest and demand for herbal medicines due to their extensive biological activities, while presenting less toxicity than the synthetic drugs, and lower production costs. Current estimates indicate that around 80% of people from developing countries still rely on traditional drugs obtained from many plant species [127-130].

After two centuries of studies, the natural products chemistry continues to be a challenge and an important research field for diverse science areas (chemical, biological, medical, agronomic, botanical, and pharmacological). The motivation behind this demand resides in the high pharmacological potential observed in natural products, that can be optimized by detection, isolation, and purification processes, especially with advances in spectral techniques [infrared (IR), mass spectrometry (MS), and nuclear magnetic resonance (NMR)] to the structural elucidation of new compounds and complexes [131].

Many parts of the cashew tree (Anacardium occidentale L.) have been studied for their biological potential. In folk medicine, the cashew tree has been used for diverse purposes. The juice of its pseudo fruit is utilized as antipyretic and antacid, it is also used in the treatment of premature aging and in skin remineralization processes [132, 133]. The tree's root and bole have been utilized as anti-inflammatory agents and in diarrhea treatment [134]. The cashew tree leaf is widely used for diarrhea and cramps treatment. In Nigeria, cashew the tree leaf extract has been used to reduce blood pressure and blood sugar [133]. Some Surinam tribes utilize cashew seed oil as a vermicide for butterfly larvae. In Brazil, the bole shell tea is used as an astringent to stop the bleeding after teeth extraction [134]. The cashew juice and bole shell tea are common remedies for diarrhea used by local residents throughout the Amazon.

A wine made from the pseudo fruit is utilized in dysentery treatment in other Amazon areas [12, 135-137].

Hence, the therapeutic potential of the *Anacardium occidentale* L. becomes evident due to its large usage in biological activities. It has a low cost and is widely available, thus, attracting the interest of scientists aimed at taking advantage of its popular features.

Literature shows that, used in pharmacological activities, cashew tree is an anti-inflammatory plant [16, 133, 134, 138, 139], antidiabetic [140-142], inhibitor of the acetylcholinesterase enzyme [142], used in the treatment of acute gastritis and stomach ulcers [135]. Isolated, substances of the fruit are proven to inhibit tyrosinase [143]. Nonetheless, it is utilized as an antiseptic for skin diseases and vaginal astringent treatment [144-149].

All the plant parts show antimicrobial activities both to gram negative and positive bacteria, as well as a potent anti-inflammatory action when compared to acetylsalicylic acid [150]. Other plant therapeutic actions include inhibiting the formation of dental bacterial plaque, besides being utilized against *Leishmania* (*Viannia*) brasiliensis [12, 137, 151, 152]. Both the bole shells and leaves have a large quantity of polyphenols, especially tannins, which are primarily responsible for the pharmacological properties [146, 153, 154].

Anacardic acids- phytochemical components of cashew nut extract- present in all parts (shell, coat, and nut), have been used to reduce cellular aging effect and helps to inhibit and kill some cancer cells [155, 156]. Besides the anacardic acids, these tests included the cardol, hydroxybenzoic acid, salicylic acid, and kaempferol tannins.

• ANTIMICROBIAL ACTIVITY

The indiscriminate use of antimicrobials, commonly marketed and utilized in infectious disease treatments, and the microorganism mutation observed in recent years, led to the increase of microbial resistance to multiple drugs [157, 158]. Secondary metabolites and complex structure compounds, such as alkaloids, terpenoids, and phenolics, as well as their derivatives, have been under investigation to confirm their medicinal and healing properties.

Studies show that different parts of *Anacardium occidentale* L. may present activities against some bacteria and fungi. The activity of the *Anacardium occidentale* L. was observed *in vitro* [159]. The shell extract on Streptococcus species, presented activities for the *S. mitis*, *S. mutans,* and *S. sanguis*, present in the gingival supra bacterial biofilm. The extract may be used therapeutically in the odontology as an antibacterial agent. The antifungal potential of the cashew shell extracts against *C. tropicalis* and *C. stellatoidea* was observed [160].

The antibacterial activity of the cashew nut extract using 10 bacterial lineages was evaluated [161]. The researchers observed that 4 bacteria (*Proteus mirabilis, Shigella sonnei, Staphylococcus aureus, and Staphylococcus spp. Coagulase*) were sensitive to the extract, and the others (*Escherichia coli, Enterobacter aerogenes, Streptococcus pyogenes, Klebsiella pneumoniae, Providencia spp., and Pseudomonas aeruginosa*) were resistant to cashew nut extract.

Studies performed with hydroalcoholic extract coming from the cashew tree (*Anacardium occidentale Linn.)* produced significant antimicrobial activity *in vitro* on the *Staphylococcus aureus* lineages from hospital human rise resistant and sensitive to methicillin, becoming an effective therapeutic alternative for infections caused by *Staphylococcus aureus*. This low cost alternative is easily accessible to the population, as it's use is already widespread in folk medicine [162]. The extract of cashew tree leaves observed showed activity against *Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus cereus, Salmonella enterica serovar typhimurium,* and *Klebsiella pneumoniae*, demonstrating the high efficiency of the plant[163].

Polyphenols isolated from the nut, like the anacardio acid and the cardonol, showed high antimicrobial inhibition in fungi and bacteria (*C. albicans, C. Utilis, S. aureus, and S. mutans*) [164, 165]. Phenolic acids such as caffeic, ferulic and ρ-coumaric acid have been reported as antifungal [166,

167]. Studies [168] evaluated coat extracts (acetone and ethanol) and verified that the coat offers antimicrobial activity against some bacteria considered pathogenic to humans, being two gram-positive bacteria (*Micrococcus luteus and Staphylococcus aureus*) and four gram-negative bacteria (*Salmonella typhi, Klebsiella pneumoniae, Escherichia coli, and Pseudomonas aeruginosa*). Table 9 shows the results comparing the coat extract with the commercial antibiotic.

Table 9: Comparison of the inhibition zones by coat extracts in comparison to a commercially traded antibiotic

Microorganism	Extract (6mg/100µL)			Amicacina
	Aquoso	Acetona	Etanólico	(30 mcg / mL)
Escherichia coli	13	21	34	27
Klebsiella pneumoniae	-	24	18	29
Micrococcus luteus	14	24	28	24
Pseudomonas aeruginosa	-	19	31	29
Salmonella typhi	-	22	27	24
Staphylococcus aureus	11	21	27	34

(-) Not analised

Source: [168].

The results of Table 9 show that the three extracts (water, acetone, and ethanol) of *Anacardium occidentale* exhibited, effectively, antimicrobial activity against six bacterial strains with zones of inhibition that ranged from 12.0 to 34.0mm. The extracts showed a wide activity spectrum compared with a pattern antibiotic, Amikacin (30 mcg/mL) and the coat ethanolic extract obtained a higher potential in comparison with other extracts and with the Amikacin.

• CHEMICAL APPLICATIONS

The cashew nut coat has diverse constituents with applications covering the food industry, medicinal, petrochemical, cosmetics, and other areas of the chemical industry.

In the coat chemical composition it has a significant amount of fatty acids (stearic, oleic, and linoleic acid), which are responsible for many applications. Plant extracts, which have stearic acid in their compositions are commonly used in processes that are intended to form a stable and resistant base, like the cosmetics segment, the production of vegetable creams and chewing gums, and the textile industry [169-171].

Vegetable oils rich in oleic acid were studied for the possible inhibition and/or reduction of mammary tumors and on the cervix, these were induced in rats and showed significant and promising results for future work [172-187].

There are many applications for phenolic compounds. Besides phenol and other common metabolic compounds, many derivatives with diverse applications, are available, among them are: coadjuvant function at inflammatory processes treatments [188]; preservative in foods; hypoglycemic activity; and inhibitory effect on enzymatic activity and on platelet aggregation [188], blockage in the formation of cells responsible for diseases such as cancer, atherosclerosis, arthritis, diabetes, cardiovascular diseases, and processes responsible for the body aging; and antioxidants, among others [110, 189-195]. The antioxidant activity is usually attributed to soluble phenolic compounds of small chains. Researchs suggests that polyphenols with high molecular weight, such as prothocyanidins and hydrolysable tannins, are 15 to 30 times more effective than simple phenols [195].

Studies involving catechins have demonstrated its high antioxidant potential [196-202] besides the antimicrobial

inhibition [203-207], antimutagenic [208, 209], melanoma and metastasis inhibition [210-213], in the treatment of diseases like hepatitis [214], HIV [215-217], hypertension [218], and obesity [219, 220], respiratory tract [221]. Due to their antioxidant potential mentioned, the catechins have extended applications in both human health as in food applications and industry to the stability of oils and fats, acting against thermal and oxidative stress [222-227].

Besides the biological applications in antioxidant and antimicrobial activities, cashew nut coat extracts, rich in tannins, were studied [34], in phenol-formaldehyde resin formulations for the varnishes preparation. The resins were uniform, with smooth coverage without pores or any other defects, thus, providing a good quality varnish (enamels with good brightness, flexibility, scratch, and corrosion resistance).

• FINAL CONSIDERATIONS

This review reported the potential applications of the cashew nut coat. Despite being a waste of the cashew nut processing, due to its diverse chemical constituents it presents potential benefits to human health and other relevant economical possibilities. This chemical potential has been reported repeatedly in the literature when addressing the use of important fatty acids, phenolic, tannins, catechins, and bioactive compounds (β-carotene, lutein, α- zeaxanthin, α-tocopherol, γ-tocopherol, and thiamine). Its compounds are responsible for antioxidant, antimicrobial and biological activities, already proven in the literature. Thus, the cashew nut coat has diverse perspective for application in many areas of industry as pharmaceuticals, cosmetics, petroleum or food.

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