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COCOA BEAN SHELL – A PROMISING BY-PRODUCT RICH IN BIOACTIVE COMPOUNDS

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review

Summary

Nowadays, when we are increasingly becoming a generation of large quantities of waste materials from various industries, there is an emerged need for certain solutions to suppress waste or make it more economical in some other way. Some by-products from the different food industries are rich in various bioactive compounds which could be utilized in other production processes. Finding the purpose and use of these compounds could be valuable for future generations. One of those by-products is cocoa bean shell (CBS), by-product in the processing of cocoa and its products, that has already proven to contain large amount of different bioactive compounds like theobromine, caffeine, specific phenolic compounds as well as dietary fibres and other valuable compounds which will be reviewed in this paper. CBS could be used in the production of functional products or even in food industry, cosmetic or pharmaceutics due to its high nutritional value what also makes it an economically acceptable raw material.

Keywords: by-product, cocoa bean shell, bioactive compounds, utilization

Introduction

During the production of different products in the food industry, large quantities of waste are also produced (Nguyen, 2014) that pollute the environment and cause major economic problems around the world. Consequently, people begin to think and explore in the direction of utilization and application of by-products from the food industry (Manzano et al., 2017; Okiyama et al., 2017; Pavlović et al., 2019; Viganó et al., 2015).
The fact of growing world population and disappearing raw materials, with a real threat of reduced food sources, does not surprise that the awareness is raising about the needs of storage and re-usage of materials that once were just a waste (Panak Balentić, 2018). Different types of waste are thrown away near the factories polluting the soil, nearby lakes and rivers, creating the major ecological problem while actually, those waste has the potential to be reused (Hamzat and Adeola, 2011).

By-products of the cocoa industry

Cocoa beans, as fermented and dried seeds of the *Theobroma cacao* plant are used as a main ingredient in the production of chocolate and its products. In Ghana, this raw material is called "golden pod" and has a "premium status" on the market because the cultivation of this plant is a tradition of private farms across the country, with the unique culture in the production of high quality dried cocoa beans. The main process in the cocoa industry includes a wide range of intermediate products that include cocoa liquor, cocoa butter, cocoa cake and raw cocoa powder. Cocoa pulp juice is a by-product used in the production of industrial alcohol and alcoholic beverages while the pod husks and shells are used as animal feed or fertilizer. After harvest, crucial chocolate precursors are formed in the fermentation process due to diverse biochemical transformation inside the cocoa beans. The fermentation step depends mostly on type of the seed, climate, season, diseases, turning, quantity of beans and pre-conditioning of the pulp (Afoakwa et al., 2013). It is known how during the process of fermentation significant amounts of certain phenolic compounds migrate from cocoa bean to the shell making this by-product rich in these compounds. So enriched cocoa bean shell (CBS) could be a potential source of bioactive compounds in different industries like food, cosmetic or pharmaceutics (Hernández-Hernández et al., 2018). Research on waste disposal in the way of finding new solutions for the use of different by-products would certainly reduce waste accumulation in a world that has become serious ecological and economical problem today.
CBS is a part of cocoa bean, which is separated from the cotyledon together with the nib before or after roasting (Arlorio et al., 2005). Since CBS is a waste in cocoa processing with certain bioactive compounds (Awarikabey et al., 2014), it is necessary

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to further explore and find suitable applications for its usage.

Bioactive compounds of CBS

While cocoa bean is only about 33% of the cocoa plant, 67% is considered as waste (Campos-Vega et al., 2018). It is already known how cocoa is included in the promotion of health due to the valuable bioactive compounds (Scapagnini et al., 2014) that can be extracted or even eliminated by various extraction methods. In this way, its further use in the food industry is enabled, leading again to the creation of new technologies (Awarikabey et al., 2014). Besides bioactive compounds (1.4%), CBS contains proteins (18.2%), carbohydrates (68.9%), fats (2.4%) and some minerals (9.1%) (Jurić and Nutrizio, 2014). CBS has been used also as fertilizer and as feed in animal nutrition (Afoakwa et al., 2013).

Methylxantines

From valuable bioactive compounds, CBS primarily contains methylxanthines theobromine and caffeine while theophylline concentrations are negligible (Okiyama et al., 2017; Pavlović et al., 2019). All three methylxanthines have similar psychoactive effects but different effects on the human organism (Okiyama et al., 2017). In cocoa fruit, theobromine is synthesized both in pericarp and in cotyledons of cocoa seeds. It accumulates firstly in young leaves, and during the ripening phase, its concentration decrease in the pericarp while in the cotyledons its concentration increases probably due to its migration from the pericarp. Theobromine is synthesized from AMP (Adenosine MonoPhosphate) and metabolised by demethylation via xanthine as well as in the seed and leaves of the cocoa plant. The rippening phase, growing as well as soil composition and climatic conditions significantly affect the methylxanthine content in cocoa plant (Smit, 2011). In the fermentation stage, the proportion of theobromine in the bean is decreased by cca 25% due to the migration of the methylxanthines from the beans to the CBS (Okiyama et al., 2017; Smit, 2011; Timbie et al., 1978). Theobromine, as naturally present in the plant, serves as its defense mechanism (Hartati, 2010). In addition to being toxic in larger quantities, some authors pointed how theobromine possess many pharmacological properties such as anticancer, diuretic and stimulative. The use of CBS in animal nutrition was found questionable primarily because of larger theobromine amounts which can have adverse effects such as damage to the reproductive and developmental system of animals (Adamafio, 2013). The higher quantities of caffeine limit the use of CBS in animal feed depending on the species and year of the animal (Hamzat and Adeola, 2011). The European Union restricted the theobromine quantity in feed to 300 mg/kg what means 13.7% w/w of CBS (Oduro-Mensah et al., 2018). Conclusions lead to the development of some of its removal methods so that such by-products can get even wider, better purpose and usage. Some methods of detheobromination are hot water extraction, alkaline treatment as well as treatment by microorganisms (Adamafio, 2013).

Phenolic compounds

Phenolic compounds are secondary metabolites found in pigment cells of cotyledons which perform different functions in the plant (Hernández – Hernández et al., 2017). Polyphenols are involved in plants growth and reproduction as well as in its protection from various pests. The polyphenol profile of every plant differs within the variety of each species (Bravo, 2009). Strong antioxidant activity of certain phenolic compounds reduces oxidative stress (Santos et al., 2017) and improves cardiovascular function (Aprotosoaie et al., 2016). Certain phenolic compounds migrate from cocoa beans into CBS during various stages in the production process such as fermentation, roasting and alkalization, thus reducing the polyphenol content in cocoa beans and increasing their content in CBS. That makes this by-product rich in these compounds. Strong antioxidant activity of CBS could also be associated with procyanidines (Ismail and Lye Yee, 2006; Okiyama et al., 2017). The most common phenolic compounds in cocoa are epicatechin (even about 35% of total phenolic content), catechin and procyanidine. Other cocoa bean polyphenols are galocatechin, epigallocatehin, epicatechin-3-*O*-gallate, quercetin, quercetin 3-glucoside, quercetin-3-arabinoside, clovamide and deoxycyclovamide (Hernández-Hernández et al., 2017). During the fermentation process, which may last from 5 to 10 days, the combination of endogenous and microbial enzymatic activities, with a temperature increase of about 50 °C, and diffusion of the metabolites inside and outside the cotyledon, results in polymerization of polyphenols as well as their ability to react with other compounds and thus the creation of certain complexes. For this reason, fermentation is a very important and most responsible step in reducing the content of flavan-3-ols in cocoa beans, specifically (-) – epicatechin. The amount of reduced polyphenols definitely depends on the degree of fermentation. The process of drying, after fermentation step, due to the decrease in water content also contributes to the reduction of polyphenols in the beans, depending mostly on climatic conditions (Di Mattia et al., 2017). Hernández – Hernández et al. (2017) mentions different authors who refer to positive properties of phenolic compounds like antitumour, anti-inflammatory, antineurodegenerative, antibacterial and anticancer properties.

Other compounds of CBS

Dietary fibres

When consumed, dietary fibres are already known to be beneficial for the human health as well as for body function. CBS contains about 60% dietary fibres according to dry weight. 80% of those total fibres are insoluble dietary fibres while 17% are soluble ones and are mainly pectic substances (11.78% of the total dietary fibres). Their amount mostly depends on external factors such as climate and soil quality. High day and night temperatures, with a sufficient moisture, help to accumulate these compounds in CBS. Low amount of water soluble pectins in CBS was reported in non-fertile and non-volcanic soils. Also, the difference in the content of the water soluble pectins and the polyphenol content has been reported previously to be in relation to the heterogeneity of the seed coming from neighbor plantations, making the cocoa origin as a significant quality parameter (Bruna et al., 2009).
CBS were also characterized to have the high pectin ability in gel formation and is widely used in the production of jams, jellies, frozen foods and foods with reduced caloric value (Arlorio et al., 2001). The proportion of fibre in CBS depends on whether they are roasted or not. It is also concluded that in roasted seeds and shells, formation of Maillard compounds increases the fibre content (Redgwell et al., 2003). A positive constituent is that CBS contains fibres, but some monogastrics are unable to digest them, and because of that, some ways of improving their digestibility have been demonstrated by fermentation with *Plerotus* spp., while theobromine degradation was achieved by fermentation with *Aspergillus niger*. Certainly, prior using those methods, it is necessary to conduct an analysis on mycotoxicity (Bentil, 2012).

Lipid profile

Fatty acids are involved in transport and storage of energy in the body as they are essential compounds of all membranes and are also gene regulators (Rustan and Devon, 2005). Essential fatty acids are those that are needed for the biological functioning of the body and which the body cannot synthesize itself. Human body needs two such essential fatty acids: linoleic (C18: 2n-6) and α-linolenic (C18: 3n-3) acid (Glick and Fischer, 2013).
In addition to interesting bioactive profile, the CBS has also an interesting fatty acid composition, similar to that of cocoa butter. The main fatty acids of CBS are palmitic and oleic, while linoleic acid is even twice as much in CBS than in cocoa butter (Okiyama et al., 2017; El-Saied et al., 1981). Following the comparison of the chemical composition of CBS fat and cocoa butter fat, it can be noticed the similarity and higher nutritional value of CBS fat (El-Saied et al., 1981). Also, it was found how during the fermentation process some microorganisms affect the changes in lipid profile because the content of saturated fatty acids decreases in CBS extracts while the content of some unsaturated fatty acids (oleic, linoleic and gamma-linolenic fatty acids) which are important for our health, increases (Lessa et al., 2018).

Vitamin D

The CBS from fresh unfermented cocoa beans dried in the sun, may contain small amounts of vitamin D while the fermented ones can contain a much larger amounts. This is probably due to a specific precursor that is converted to vitamin D during exposure to sunlight. Knapp and Coward (1935) decided to make an experiment and determine how the fermentation step, as well as type of drying, affect the vitamin D content in the CBS. The fermented beans are usually put on tables and dried by turning in the sun during 6 days at least. Some beans can be also artificially dried. Yeasts, that contain ergosterol, develop during the fermentation process of the cocoa beans, and during the drying process in the tropical sun, ergosterol is converted into vitamin D. It was also noticed how this was only the case when CBS had been exposed to sunlight. During the process of artificially drying, vitamin D was absent in the CBS (Knapp and Coward, 1935). By adding a CBS into animal food, it is proven the increase of vitamin D content also in animal milk and butter (Knapp and Churchman, 1937).

Biogenic amines

Potentially toxic compounds such as biogenic amines like tyramine and the non-nutritive compounds such as phytic acid and trypsin inhibitors, do not reduce the possibility of further usage of CBS as a source of pectin. The pectin gel obtained from the CBS can be purified with ethanol and 2-propanol. Some studies pointed how biogenic amines can cause heart palpitations, hyper and hypotension, dizziness, headache and facial redness. The amount of these compounds in CBS is relatively small and has no toxic effect (Arlorio et al., 2001).

HMF

In the food industry, because of different operation conditions and due to the chemical composition of raw materials, the synthesis of hydroxymethylfurfural (HMF), also 5-(hydroxymethyl)furfural, is a common occurrence in food. The reasons are mainly accumulation of simple sugars as well as some polysaccharides, proteins and amino acids, low pH and high temperatures (Kowalski et al., 2013). Jokić et al. (2018) investigated bioactive compounds in CBS extracts obtained after subcritical water extraction (SWE) and demonstrated how at higher temperatures HMF was detected in extracts. This is one of the reasons why it is always important to optimize the extraction procedure to obtained desired compounds in the final extract.

Thermal treatment such as roasting (especially foods rich in carbohydrates) also greatly contributes to the formation of HMF. Also, many polysaccharides are susceptible to hydrolysis in the acidic medium and can be transformed into simple sugars, which are starting material for the formation of HMF. HMF is a heterocyclic aldehyde with six carbon atoms, aldehyde and alcohol functional group. The basic substrates of HMF formation are monosaccharides fructose and glucose, and disaccharide sucrose which is easily transformed to both of them. Fructose dehydration is more effective and faster than glucose dehydration and occurs in three stages. The last step of dehydration forms the final structure of HMF. Due to possible adverse effects of HMF on human health, it is necessary to take into account the reduction of this compound in food by alteration in its possible production (Kowalski et al., 2013).

Some potential usage of CBS

CBS as a by-product in the cocoa industry has been still discarded regardless of its high nutritional value. Apart from being a source of fibre, it is a potential source of antioxidants, due to its high phenolic content (explained in text above), which makes it a good source as a raw material for further use. This high content of dietary fibre makes it interesting as an ingredient in food preparation (Martín-Cabrejas et al., 1994; Martínez et al., 2012; Okiyama et al., 2017). Relatively high values of dietary fibres together with phenolic compounds imply that this by-product is interesting to the food industry, in the manufacture of confectionery products, bakery or in the preparation of low calorie dietetic and fibre-rich products (Nsor-Atindana et al., 2012). The another innovative approach would be adding isolated polyphenolic compounds and water-soluble pectins from CBS further in chocolate, making it richer in antioxidant composition (Bruna et al., 2009).

Some studies have proven that the phenolic compounds of CBS that are added to some types of meat can reduce lipid oxidation with their antioxidant properties. Therefore, they can be recommended for oils that are intended for frying as a replacement for synthetic antioxidants (Okiyama et al., 2017). This can improve their quality and their stability without affecting the color of the oil. When added to oils, the formation of free fatty acids and peroxide levels is slowed down while antioxidant activity increased (Manzano et al., 2017).

Looking the situation today, when economic gains and profits are most important to the producers, the usage of antibiotics is increasing in livestock treatment and have preventive maintenance on their health. Resistance to pathogenic bacteria is becoming more frequent, and excessive use of antibiotics leads to their residues in the environment, which becomes serious environmental problem. Evidence is also made by various confirmatory studies where traces of antibiotics are found in some local and waste waters. It is the reason because some authors mention the use of by-products of tropical plants such as CBS as possible substitutions for antibiotics in animal feed due to substantial antimicrobial potential, improving the health of domestic animals on farms. Bioactive compounds of those by-products can influence pathogenic bacteria, avoiding the damage of the cell itself. Some bioactive compounds may act synergistic and increase antimicrobial activity against pathogenic bacteria. Certainly, these assumptions and research require extra caution because some bioactive compounds may be toxic (Guil-Guerrero et al., 2016).

As an adsorbent, CBS is mostly effective in removing heavy metals such as lead, chrome, cadmium, etc. There is also an increase in pH value and release of calcium, magnesium, potassium and sodium from the CBS as well (Meunier et al., 2003). Among all other natural materials, CBS with its low porosity is widely used in metal decontamination of soil (Meunier et al., 2004). The CBS based activated carbons show the potential for usage as an adsorbent in various water or wastewater treatments, as some studies confirm (Ahmad et al., 2012). It is also recommended usage of CBS in the biofiltration of wastewaters in the food production as well as biogas production. Some studies mention also the usage of phenolic extracts in prevention of dental cavities (Okiyama et al., 2017). Other authors concluded that CBS is a promising precursor for activated carbon for usage in adsorption of whey proteins (Pereira et al., 2014).

The CBS can be chemically modified based on diazonium chemistry. Because of the fast, simple preparation and the wide range of reactive functional groups of aryl diazonium salts, they are ideal for modifying surface properties of various materials and so as the CBS. These compounds grafted on the CBS surface changing its properties and making it a suitable adsorbent to remove pollutants such as heavy metals, gases or industrial dyes (Fioresi et al., 2017).
The CBS can be used as a fertilizer because it forms a humus substrate, but does not decompose easily, which can lead to its accumulation during the season (Nair, 2010).
The possibility of water bounding and polysaccharide composition makes the CBS suitable as a raw material for preparing fibre-based formulations. The various composition of CBS can be changed by various extraction methods and techniques, given the extracts interesting not only because of its aroma but also for its protein and saccharide content (Dongowski et al., 1991). An example is the addition of this compound (soluble cocoa dietary fibre) into the muffins as a substitute for fat, thus altering the dough properties. Except pleasant colors, it increases the density of dough, making its texture softer and smoother and reducing its later hardening. Disadvantages were difficulty to chewing and swallowing, stickiness and bitter taste (Okiyama et al., 2017).
Important facts are also expensive sources of protein concentrates that make the basis of animal feed. CBS is recommended for the ruminant diet but with the addition of certain compounds to improve the taste or dilute the toxic effects of CBS substances that could affect the used diet (Aregheore, 2002). In addition to being used as fuel for boilers, livestock feed and preparation of fertilizers, this by-product could be used as a food, cosmetic or pharmaceutical additive or food supplement with high nutritional value and due to that become an economically acceptable raw material (Okiyama et al., 2017).

Conclusion

The CBS, which is a food industry by-products produced in large quantities in the world, contains valuable bioactive compounds. Given its nutritional value, this by-product could become a raw material in newer productions, thereby reducing the amount of waste in the world. As a rich source of some bioactive compounds including theobromine, caffeine, flavonoids and dietary fibres which can be isolated by different extraction techniques, CBS can also be used in preparation of large spectrum of functional products.

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Conflicts of Interest

The authors declare no conflict of interest.

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