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Chapter

Purple Corn Cob: Rich Source of Anthocyanins with Potential Application in the Food Industry

Andreea Stănilă, Teodora Daria Pop and Zorița Maria Diaconeasa

Abstract

As every year, the entire food chain generates huge amounts of food loss and waste, and there is a great interest in solving the inefficient waste management by implementing the sustainability concept for achieving “waste-to-wealth” goal. This refers to recovering renewable bioactive compounds from food wastes in order to use them as low-cost source of value-added ingredients for different industries. In this way, this work focuses its attention on purple corn cob, a by-product that was not very used in food industry. Purple corn has gained attention due to its capability of coloring food and beverages and the evidence of the antioxidant, anti-inflammatory, and cardiovascular health benefits. As the production is growing year by year, the amounts of waste produced is rising. As a result, purple corn cob caught our attention, reason why in this study we concentrate to summarize and emphasize the compounds that give the color of this waste, anthocyanins.

Keywords: anthocyanins, bioactive compounds, food waste, purple corn cob, food industry

1. Introduction

To date, adding coloring to food and drink color is as significant as it has always been, especially in a society where the quantity of processed food has increased rapidly over the previous half-century. Being the first attribute that potential buyers are aware of, color plays a vital role in motivating the customer to purchase the product [1]. Over the last few years, the food industry’s interest in natural colorants replacing synthetic ones has increased, mainly due to safety issues [2]. Among natural alternatives for synthetic dyes, anthocyanins represent an important class of compounds that provide red to a blue color to food by incorporating into aqueous systems. Also, in the European Union and Japan, anthocyanins are recognized as food colorants with the code E-163 [3].

Purple corn (*Zea mays* L.) represents a rich source of anthocyanins, originated in South America, mainly Peru, and cultivated also in Ecuador, Bolivia, and Argentina. Generally, it is used for the preparation of traditional drinks and desserts, generating important quantities of residues, and its disposal involves major economic expenses [4, 5]. Besides this, generated wastes can cause major environmental problems due

to their high organic charge. However, over the last decades, using these residues has been encouraged as they are good sources of potentially useful bioactive chemicals, and valorizing them might be a viable technique for mitigating their environmental implications and thereby improving the food industry's sustainability [5].

As a major route for their valorization, the recovery of bioactive molecules from food by-products has gained popularity. In this framework, the present review aims to highlight purple corn's capability to be an available source of bioactive compounds with several potential applications, focusing our work on its food industry utilization.

2. Purple corn cob is a rich source of bioactive compounds

The current state of knowledge shows us that purple corn cob represents a rich source of phenolic compounds, especially phenolic acids, flavonoids, and anthocyanins [6, 7].

Purple corn gained attention mainly because of its rich content in anthocyanins, but comparing the seeds (0.5–6.8 mg/g fresh weight) with the cob, the reported values regarding anthocyanins content were higher for the latest (0.8–71.5 mg/g fresh weight) [4].

Based on the previous statement, our focus is on a purple corn cob, as the anthocyanins content makes them potential contributors as natural colorants, varying from blue to red tonalities. Despite their great coloring capacity, these compounds have been increasingly used in the food industry due to their ability to confer bioactive properties to the products [8]. Along with a great coloring capacity, anthocyanins act as antioxidants and antibacterial compounds and help prevent cardiovascular diseases, cancer, diabetes, and have neuroprotective effects [9–13].

Regarding the anthocyanins content, some researchers characterized the purple corn cob. Among them, Díaz-García et al., obtained higher values than other studies, 41.32 ± 0.95 mg C3GE/g DW, compared with 9.30–15.16 mg C3GE/g DW, both using pH differential measurement [4, 14]. Using the same method, Lao and Giusti [15] obtained for the purple corn cob values ranging from 3.1 to 100.3 mg C3G/g. By using a conventional spectrophotometric method, Pascual-Teresa et al. obtained 34 g per 100 g powder, expressed in cyanidin-3-monoglucoside [16]. Another study showed that the anthocyanin content of purple corn cob was calculated to be 92.3 ± 2.1 mg/100 g, expressed in cyanidin-3-glucoside [17]. A much higher value of anthocyanins was presented in another study, where the authors obtained 1219.4 mg/100 g [18]. The comparison between the anthocyanin contents in purple corn cob is difficult as there are several factors to consider, including the harvesting region, methods used by researchers, storage time, and genetic differences [19].

The profile of anthocyanins present in purple corn cob has been characterized by Fernandez-Aulis et al., by identifying the structures using HPLC method, are fragments corresponding to cyanidin, pelargonidin, and peonidin, and they are: cyanidin-3-glucoside, cyanidin-3-(6''-malonyl) glucoside, pelargonidin-3-glucoside, peonidin-3-glucoside, pelargonidin-3-(6''-malonyl) glucoside, and peonidin-3-(6''-malonyl) glucoside, which was in accordance with the previous reports. Among these, the main anthocyanin was cyanidin-3-(6''-malonyl) glucoside obtained in case of enzymatic assisted extraction [20]. Moreover, cyanidin-3-(6''-ethylmalonyl) glucoside, pelargonidin-3-(6''-ethylmalonyl) glucoside, and peonidin-3-(6''-ethylmalonyl) glucoside are three more compounds identified by Pascual-Teresa et al. besides those mentioned above [16].

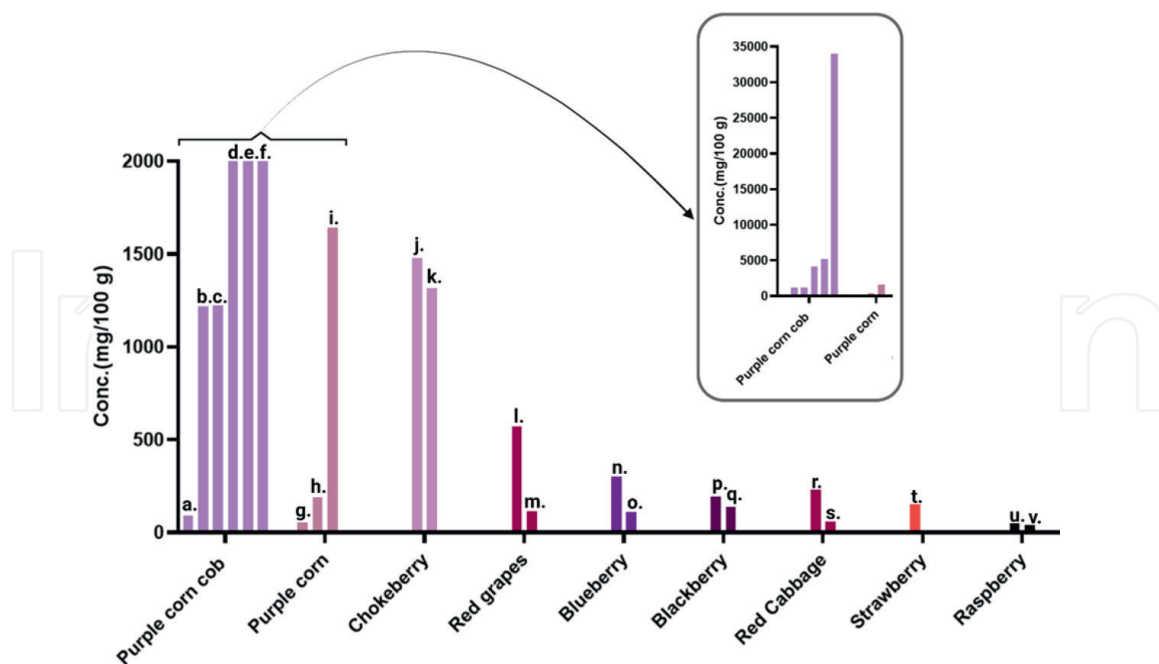


Figure 1. Comparison between rich in anthocyanin sources and purple corn cob based on the concentration (mg/100 g), reported by different authors a—[17], b—[18], c—[14], d—[4], e—[15], f—[16], g—[17], h—[7], i—[21], j—[22], k—[23], l—[24], m—[25], n—[26], o—[27], p—[28], q—[29], r—[30], s—[31], t—[32], u—[33], v—[34].

The reported results suggest that purple corn cob can be considered a promising source of anthocyanins, and this statement can be strengthened by comparing values with other dietary sources, remarked for their rich content in anthocyanins. As shown in **Figure 1**, purple corn cob is a valuable waste that can be successfully used as a rich source of anthocyanins, and by this, an important number of applications can be taken into consideration.

Throughout the years, purple corn gained attention due to its recognized antioxidant property, becoming consumed as food, but also incorporated in new products, fact highlighted too by international data bases, as in 2009, Peru exported total value of US\$9,782,564, while in 2013, the export reached the approximate value of US\$17,981,398 [19, 35]. In 2015, AgriFutures Australia reported a total of 7000 tones as being traded globally each year, with the majority producer, Peru, and for 348 tones, China [36]. National Institute of Statistics and Information Science analyzed the purple corn production index from 1990 to 2018, highlighting the fact that the data reached an all-time high in April 2018 [37]. As the production is rising and the consumption per capita has increased from 6.8 to 12.3 kg per year [19], the amount of generated waste is also recording higher values, the cob representing 15% of the purple corn ear [38]. Also, taking into consideration its richness in bioactive compounds and its growing range of applications, purple corn cob is becoming a topic of interest for future studies.

3. Anthocyanin recovered from by-products

3.1 Extraction methods

As anthocyanins are found as secondary plant metabolites in the case of purple corn cob, it is important to take into consideration their extraction and isolation from

the tissue with adequate method, as their main issue is their high susceptibility to degradation, when isolated. Among the factors that affect anthocyanins' stability, the most referred are pH, when it has values above 7, explaining the requirement of acidified environment for most of the extraction protocols and temperature. The last one impacts the levels of anthocyanin extracted, a higher temperature being likely to induce degradation and impact in this way the extraction factor [39]. An ideal extraction procedure for food-grade anthocyanins would maximize pigment output while reducing degradation and changing the natural state of the target compounds [40]. When choosing the extraction method, it is important to take into consideration the application, as for food industry the solvents play a decisive role. In most of the times, anthocyanins' extraction is conducted by grinding, drying or lyophilizing the matrices, or soaking fresh materials into solvents such as water, ethanol, methanol, acetone, or others. As mentioned, the solvents are frequently acidified to make the extraction process easier and to keep the pigments stable during the process. Other possible influences on anthocyanin extraction that should be considered beside pH and temperature are time, solid:liquid ratio, assistance with microwave, ultrasound, and sonication [3]. In the case of purple corn cob, different optimized extraction techniques have been developed, both conventional and new methods (**Table 1**), taking into consideration the time, temperature, and solid: liquid ratio. In this way, Yang and Zhai [17] macerated the matrices and used methanol as solvent, the same one used by Li et al. in their study [41]. Another solvent used by Nisi et al. is acetone, but due to safety concerns, these two, methanol and acetone, are not desirable if the extract is used in food applications. The same author tested also the efficacy of water and ethanol solvent, by comparing with acetone, and the results were similar [42]. Also, Lao and Giusti optimized an extraction protocol using a combination of water and ethanol (EtOH), which is food-friendly. Besides analyzing the best extraction ratio, they focused also on its acidity in order to increase extraction efficiency [3]. Yang et al.'s work focused on choosing the optimum conditions for the extraction of anthocyanins from purple corn cob taking into account the main factors related to the process, including solvent, acid, solvent concentration, and acid concentration, using a mixture of solvent and water. The maximum yield for purple corn cob extraction was obtained with 80% methanol and 1% citric acid, and using ethanol, the best conditions were obtained with 80% solvent and 0.5% citric acid [43]. Based on safety concerns related to certain organic solvents, Rajha et al. managed to study the efficiency in terms of anthocyanins' extraction using β -cyclodextrin-water as solvent, β -cyclodextrin being generally recognized as safe (GRAS) solvent. They suggested a low-cost extraction protocol for the valorization of purple corn cobs, obtaining the best extraction rate using 39.8 mg/mL β -cyclodextrin at 68.8°C for 60.4 min [44].

Recently, there is a focus on reducing or eliminating the use of toxic solvents by taking advantage of the potential that emerging extraction strategies have, which are capable of reducing the processing time, maintaining also the bioactivity of the compounds [48]. Piyapanrungrueang et al. realized a comparison study between the conventional extraction methods and the emerging ones, having a purple corn cob hybrid as matrices. They characterized and optimized methods for conventional, ultrasound-assisted extraction, microwave-assisted one, and for ohmic heating. By taking into consideration the amount of anthocyanin extracted, energy efficiency, and color value, the best method for extracting anthocyanin from purple corn cob is the microwave-assisted one [45]. There are also other authors that optimized emerging methods for extracting anthocyanins as presented in **Table 1**. When choosing the extracting protocol, the future applications should be taken into consideration, as

Method	Solvent	Acidity	Time	Temp (°C)	Solid:liquid ratio	Anthocyanin content mg/100 g (DW)	Ref.
Conventional extraction methods	Methanol (MeOH)	0%	24h	4°C	1:4	92.3 ± 2.1	[17]
	MeOH	1% HCl	12h/extraction (3 times)	4°C	1:10	0.49–4.6%	[41]
	Acetone 70%	0.01% HCl	12 h	RT	1:50 w/v	931 ± 44	[42]
	EtOH 50%	0.01% HCl 6M	Overnight	RT	1:50 w/v	854 ± 24	[42]
	Water	0.01% HCl	90 min	RT	1:20	1004.22 ± 10.3	[18]
					1:50	754.15 ± 4.5	
					1:100	735.58 ± 11.35	
	Water	0.01% HCl	Not mentioned	RT	—	610	[3]
	EtOH	0.01% HCl	Not mentioned	RT	—	340	
	20% EtOH	0.01% HCl	Not mentioned	RT	—	1060	
	50% EtOH	0.01% HCl	Not mentioned	RT	—	1430	
	80% EtOH	0.01% HCl	Not mentioned	RT	—	1190	
	80% EtOH	0.5% C ₆ H ₈ O ₇	24 h	4°C	1:50	485	[43]
	90% EtOH	0.5% C ₆ H ₈ O ₇	24h	4°C	1:50	262	
	80% MeOH	1% C ₆ H ₈ O ₇	24h	4°C	1:50	590	
	80% EtOH	0.5 % CH ₃ COOH	24h	4°C	1:50	423	
	80% MeOH	0.5% CH ₃ COOH	24h	4°C	1:50	504	
	β-cyclodextrin (25 mg/mL)	0%	29.9 min	52.5°C	Not mentioned	1439	[44]
	β-cyclodextrin (25 mg/mL)	0%	105 min	79.9°C	Not mentioned	1557	
	β-cyclodextrin (39.8 mg/mL)	0%	149.6 min	36.2°C	Not mentioned	1404	
β-cyclodextrin (39.8 mg/mL)	0%	60.4 min	68.8°C	Not mentioned	2608		
β-cyclodextrin (49.8 mg/mL)	0%	105 min	52.5°C	Not mentioned	2497 mg/100g		
Water	0%	5 min	70°C	1:20	366.1 ± 4.7	[45]	

Method	Solvent	Acidity	Time	Temp (°C)	Solid:liquid ratio	Anthocyanin content mg/100 g (DW)	Ref.
Emerging extraction methods	Ultrasound-assisted extraction						
	50% EtOH	0%	30 min	65°C	1:20	240 mg/100 g	[46]
	Water	0%	5 min	80°C	1:20	382.7 ± 9.1	[45]
	80% EtOH	1% lactic acid	20 min	25°C	1:10	2431	[20]
	Microwave-assisted extraction						
	95% EtOH	1.5 M HCl	19 min	RT	1:20	185.1	[47]
	90% EtOH	1% lactic acid	1 min	25°C	1:10	1977	[20]
	Water	0%	2 min	83–91°C	1:20	397.1 ± 11.6	[45]
	Ohmic heating extraction						
	Water	0%	3.5 min	80°C (220V)	1:20	328.0 ± 4.5	[45]

Table 1.
Optimized extraction techniques: conventional and new methods.

there are plenty possibilities for anthocyanin from purple corn cob. Related to this, the next chapter focuses its attention on studies that emphasize purple corn cob's applications in different industries.

3.2 Recent studies and future perspective

In terms of using the cobs in order to minimize the waste production, Nisi et al. proposed a quick and cheap extraction method to obtain anthocyanin with the aim of using them as dye for different natural fibers. Moreover, they managed to recover and use all the material to produce nutraceuticals and pigmented litter for pets [42]. In this framework of the biorefinery approach in valorizing purple corn cob, authors proposed a natural dye for fabrics, showing also ultraviolet protection of the dyed clothes. They present the final product as having good durability, acceptable stability, excellent aesthetic appearance and also sustainable, since are dyed with natural pigments. Also, they demonstrated that the extract possesses good anti-inflammatory properties, highlighting the possibility of incorporating in food products to take advantage of its full potential related to health benefits. The purple lignocellulosic solid residue is considered feasible for animal bedding, which can be compostable, nulling in this way the waste produced [42].

Within the same frame, Gullón et al. characterized purple corn cob's potential in order to comprehend whether it can be used as multifunctional ingredient for food and pharmaceutical industries and what properties does it possess [5]. After the extraction conditions of bioactive compounds from purple corn cob were successfully performed, oligosaccharides and phenolic compounds, including flavonoids and anthocyanins were characterized. The bioactive compounds showed complex structures as the extract was stable at high temperatures when subjected to thermogravimetric analysis. Overall, their research concluded that purple corn cob represents a sustainable source of bioactive compounds with economical value, therefore improving the food industry's competitiveness [5].

Regarding its culinary applications, purple corn cob is used as a base ingredient in the process of obtaining traditional drink *chicha morada* and dessert named *mazamorra morada*. For both of them, the whole corn including the corn cob is boiled in order to extract the color. To obtain the drink, some fruits, spices, and sugar are mixed together. Besides these, the dessert requires a binder followed by cooking. Regarding the heat treatments that can affect the product nutritional quality, some studies concluded that thermal processing such as boiling, roasting, or frying is associated with a decrease in bioactive compounds, as they are not stable in such conditions [19].

Also related to food industry, a recent study developed and optimized a low-calorie tea formulation containing purple corn cob, stevia as sweetener, cinnamon, and clove as flavoring and quince as a pH regulator that improves the color. The product exhibits enhanced antioxidant capacity, which, in future studies, will be evaluated on human volunteers in order to offer information on the true impact of the new antioxidant product [4]. In a similar area of products, Wattanathorn et al. [49] obtained a functional drink containing the extract of purple corn cob and pandan leaves, being the first study that showed that a polyphenol-rich supplement can improve cognitive function in a menopausal animal model. The functional drink has a cognitive boosting effect that is comparable to donepezil, a common medicine used to treat memory problems today. In this way, the product based on purple corn cob extract and pandan leaves can be used as a viable supplement to lower the risk of memory deterioration in menopausal women, which is simple to achieve, based on its advantages and low raw material prices. Clinical trial research and subchronic toxicity, one the other hand, are necessary [49].

As presented, purple corn cob is a valuable source of bioactive compounds, with different possible applications, but related to food industry, several studies need to be made in order to benefits from its full potential.

4. Conclusions

As one of the humanity's greatest difficulties is to live in a society without hunger but with high quality and safe food, it can be assumed that global food loss and waste must be dramatically decreased, because the inefficient waste management causes environmental damages. In this framework, circular bioeconomy represents a great potential approach for reducing these insufficiencies by implementing the term "waste-to-wealth," which refers to the converting of renewable biological supplies with high-end commerce, into valuable resources for a longer period of time, with no waste generation. In this context, agri-food by-products and wastes are of great interest as they are rich in bioactive compounds, which gives them multiple applications.

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Conflict of interest

The authors declare no conflict of interest.

Acronyms and abbreviations


C3GE cyanidin-3-glucoside
DW dry weight
RT room temperature

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