Processing of Cereals and Derived-By-Products

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Cereals have been one of the major food resources for human diets and animal feed for thousands of years, and a large quantity of by-products is generated throughout the entire processing food chain, from farm to fork. These by-products mostly consist of the germ and outer layers (bran) derived from dry and wet milling of the grains, of the brewers' spent grain generated in the brewing industry, or comprise other types obtained from the breadmaking and starch production industries. Cereal processing by-products are an excellent low-cost source of various compounds such as dietary fibres, proteins, carbohydrates and sugars, minerals and antioxidants (such as polyphenols and vitamins), among others. Often, they are downgraded and end up as waste or, in the best case, are used as animal feed or fertilizers. With the increase in world population coupled with the growing awareness about environmental sustainability and healthy life-styles and well-being, the interest of the industry and the global market to provide novel, sustainable and innovative solutions for the management of cereal-based by-products is also growing rapidly.

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1. Introduction

A society without hunger but with quality and safe food for all is one of the largest challenges for humanity. It has been calculated that 1.3 billion tons of food loss and waste are generated every year from all stages of the food manufacturing process, chiefly food production and consumption [1]. The latter corresponds to approximately one-third of the food produced in the world for human consumption that is lost or becomes waste every year [2]. Paradoxically, an impressive one-third of the world's soil has been lost in the last 40 years, 2.3 billion square kilometres of land area are being degraded and almost 5 million of people died from hunger just in 2020 [2].

These losses result from the whole food (and feed) value chain, i.e., from the harvest step, passing through the postharvest processing, industrial processing and commercialization, to the final consumption by the consumers (transportation, storage, home processing and waste). Food losses also include food processing by-products, which remain as side streams during the production of target products among all sectors of food production. Of course, the negative impact of these losses is even greater if the required inputs such as land, energy and water resources are taken into consideration. This scenario has raised a global interest and the Zero Hunger and the Responsible Consumption and Production of food plans have been included in the seventeen Global Sustainability Goals of the United Nations (UN), which represent an Agenda for global action up to 2030 and defines the sustainable development at the economic, social and environmental dimensions [3]. The "Farm to Fork Strategy—for a fair, healthy and environmentally-friendly food system" [4] is also a good example of the European Union (EU) set of strategies and actions on the scope of "The European Green Deal" towards the EU's economy sustainable [5]. These policies are in line with the strategies and commitments of the Food and Agriculture Organization (FAO) of the United Nations towards a sustainable future.

Over decades, the EU has developed and put into force some world's highest environmental standards, dating back from 2008 when the EU waste management law established a legal framework to treat wastes [6]. The directive 2008/98/EC [7] is of major importance since it gave priority to the reduction of the waste at the source, followed by reuse, recycling, and recovery, i.e., the 3 R's policy following the hierarchy: Reduce, Reuse and Recycle. The 3 R's policy is often replaced by the 5 R's concept, i.e., Reduce, Reuse, Recycle, Rethink and Renew. In that respect, the utilization of by-products from Agro-food manufacturing industry affects industrial branches with underestimated capacity and growing amounts of by-products, against the trends of sustainability principles [8].

The term "cereals" refers to members of the Gramineae family and determines nine species: wheat (Triticum spp.), rye (Secale spp.), barley (Hordeum spp.), oat (Avena spp.), rice (Oryza spp.), millet (Pennisetum spp.), corn (Zea spp.), sorghum (Sorghum spp.), and triticale (x Triticosecale Wittmack)—which is a hybrid of wheat and rye. Furthermore, pseudocereals are non-grasses with similar end-uses to cereals (or true grasses); these flours have gained high popularity among scientists, technicians, and consumers, and encompass the well-known buckwheat (Fagopyrum esculentum), amaranth (Amaranthus spp.), quinoa (Chenopodium spp.), and others such as chia (Salvia spp.), cañihua and pit seed goosefoot (Chenopodium spp.), breadnut (Brosimum alicastrum), celosia (Celosia spp.) and wattle seeds (Acacia spp.).

2. Processing of Cereals and the Derived By-Products

A detailed description of cereal processing and the resulting by-products can be obtained in some complementary literature [9][10][11]. In the present section, a brief description of the various alternatives for cereal processing will be presented and will include the most recent advances in the field.

Cereal by-products continue to represent an unexploited source of many compounds or fractions with high nutritional value and could serve as novel material not only for food and feed production but also for other non-food products. Besides the food industry, bioethanol industry represents an important alternative for the use of cereal by-products.

The milling industry is the major supplier of cereal by-products. The steps performed before milling result in a by-product called "grain screenings" mainly containing all the cereal seeds that do not fulfil grading specification. Besides the refined cereal flours, cereal bran and germ are separately obtained during milling, with the latter used subsequently for the production of cereal germ oil. Cereal bran is considered the main by-product from cereal milling. It contains the coat seed and aleurone layer from the milling of the cereal grains after sieving out the endosperm. Milling of cereals comprises steps such as cleaning and grading before breaking down the grains and sifting to obtain different fractions based on size-exclusion separation in sieves. Depending on the mill used, the cereal grains are broken into smaller pieces by grinding, cutting or crushing to any desired size specification, depending on the final use. Accordingly, different by-products are produced during cereal processing. According to Ma et al. [12], and as expected, flours with smaller particle size had higher amounts of damaged starch but also lower levels of sulfhydryl content of gluten protein leading to alteration of the quality characteristics of the flours. Depending on the desired traits of the final product (i.e., refined flour, starch and gluten), appropriate milling processes and equipment may be applied, e.g., jet milling combined with successive grindings in cascade and air classification are employed to isolate starch from flours resulting in a final product containing <2% (dry basis, d.b.) of residual protein and very low amounts of lipids and pentosans [13].

Besides the refined wheat flours, nowadays the market requests the production of other types of flours such as wholemeal or enriched/biofortified flours with plant-based products. For whole wheat flour production, the wheat kernels are ground without separating the endosperm from germ and bran. Even though the consumers' awareness and acceptance for the consumption of whole grain products is increasing, the industry still needs to focus on the optimization of such products due to the high number of whole grain-avoiders on the cause of poor organoleptic characteristics [14]. Different techniques such as physical, chemical and enzymatic have been applied to this purpose. Besides the increasing of the nutritional value of the final products, these methods aim at reducing negative effects as well as at improving food texture and sensory attributes. Wheat protein that represents a by-product from the industrial production of starch, finds an end-use in the bakery industry to enrich flours for bread and pasta.

Bran from rice, obtained after polishing brown rice, contains grain parts such as pericarp, aleurone and embryo. It is considered as having prebiotic potential because of the beneficial compounds presented therein, such as dietary fibres, essential fatty acids, polyphenols and antioxidants. Bran from rice must be stabilized before use to avoid lipid oxidation and deterioration of its quality and organoleptic characteristics. Recently it has been used in (micro/nano) encapsulate matrices for probiotics showing high encapsulation efficiency and enhanced protection to simulated gastrointestinal tract and storage conditions [15][16]. In addition, it was successfully added in yoghurts in order to increase its antioxidant activity, causing a decrease in syneresis and viscosity values [17]. Further treatment of rice bran can result in the extraction of valuable bioactive compounds such as phenolic compounds. Enzymatic treatments can be alternatively used to minimize the negative effects of traditional extraction methods (chemical degradation or disruption of plant cell wall matrices by acid or base hydrolyses) on the extractability and antioxidant activity of the phenolics. Kim and Lim [18] observed that commercially available carbohydrate enzymes increased the efficiency of phenolic acid extraction from rice bran suggesting the use of this enzymatic treatment to improve the antioxidant activity of the rice bran. In addition to the cereal bran, their oils and cakes are also considered cereal by-products. In the case of rice bran oil, the main components are unsaturated fatty acids (mainly oleic and linoleic acids), and phytochemicals such as phytosterols, vitamin E and γ-oryzanol, which have significant antioxidant activity and important role in the inhibition of some chronic diseases [18]. In terms of the nutritional value of cereal lipids, the importance is well recognized of the relative high content of polyunsaturated fatty acids (PUFA) with different chain lengths, present in free form (free fatty acids) and the acylated forms of triacylglycerols (TAG), diacylglycerols (DAG) and, in relative minor amounts, the monoacylglycerols (MAG). As DAG and MAG, the presence of polyunsaturated sterol esters (SE), as well as sterols and stanols, reveals the high nutritional value of cereals [19][20][21][22][23][24][25][26]. The extraction methods employed affect the quality of the resulting oil. Compared to the conventional methods, the environment-friendly supercritical carbon dioxide extraction (SC-CO_2) results in better quality bran oils with better physicochemical and antioxidant properties [27]. Rice bran oil can be used to enrich diets since it provides immune enhancement along with other bioactive properties [28]. From the industrial production of starch, rice protein is derived that is not considered for food purposes but only for animal feed [29].

Maize is processed by using two different milling techniques (dry and wet milling), depending on the desired product, giving rise to the production of maize bran/fibre. The dry milling method is employed to obtain the maize endosperm fraction to be used as meals, flours, or grits, resulting also in the production of maize bran fraction (from maize pericarp), while the maize germ remains with the latter, representing a by-product that can be used for the oil production. Besides bran, the cake from maize is considered a residual cereal by-product, obtained from the extraction of oil during the process of de-oiling maize germ. Aqueous extract of maize cake, rich in dietary fibres, that remains after obtaining maize oil, has been utilized for the fortification of cakes with edible fibres to produce health-promoting food products [30]. On the other hand, during wet milling of maize, the grain is first steeped in water and sulphur dioxide to soften the kernels and facilitate the separation of the desired products: starch and germ (for oil extraction). Wet milling of maize results in by-products such as maize fibre from the pericarp and maize protein, while various solids are obtained during steeping. The milling industry is facing with increasing amounts of maize bran obtained by the dry milling process of maize because of the growing demand of maize flour for the bakery industry. This by-product represents a potential source of polymers (typically composed by 50% heteroxylans and 20% cellulose) with high added value for the food industry. In addition, it contains ca. 4% phenolic acids, mainly ferulic and diferulic acids [31]. Further extraction of heteroxylans from maize bran results in water-soluble maize bran gum, another by-product for the use in the food industry [32]. In addition to numerous technological applications in the food, nutraceutical and pharmaceutical industries, maize bran gum can be used as a carrier of bioactive compounds in the intestine. It has the ability to form hydrogels that have the potential for transferring thermosensitive bioactive compounds in the food industry [33]. Besides the milling industry, maize is used as the largest source for bioethanol production and other renewable biofuels such as biodiesel and biogas. One of the significant by-products is the fraction of dried distiller's grain with solubles (DDGS). They are used as a raw material for the extraction of arabinoxylans (AXs) [34]. Theoretically, maize bran and fibres consist of the pericarp coating but in the case of maize fibres for starch production, maize pericarp is usually mixed with cell wall materials from the maize endosperm, whereas, during ethanol production, maize bran is mixed with soluble fractions from distiller's grains [35].

Milling and malt-based alcoholic beverage (mainly brewer's grains) by-products are the main residual products from the barley processing industry. Only hull-less barley varieties are used for food purposes, whereas hulled barley is preferred for malting. Fine flour and course meal are obtained as milling by-products of pearled barley [35][36] whereas the spent grains are the main by-product from brewing. The spent grains have been used as a substrate for immobilization of different enzymes such as trypsin, lipases and laccases [37][38].

Bran from rye and triticale is considered as a by-product obtained after milling. Oat bran is also produced during milling to obtain flours for human consumption. It contains mainly hulls and residues from other processes performed also on the oats such as dehulling, rolling and flaking [36]. In general, endosperm moieties are found in cereal bran of these grains depending on the efficiency of the milling process.

In general, bran is used for the biofortification of refined wheat flour used for breadmaking and other bakery goods. Bread biofortification with bran or whole meal of maize, rice, oat, rye, barley and wheat results in technological changes such as the decrease in loaf bread volume, while the content of water, mineral content, fibres, phytates and antioxidant activity are increased and, in addition, the quality of volatile compounds is also affected [39][40][41][42]. The presence of bran in bakery is linked with increased water absorption and low loaf volume due to the weakening of the dough structure from the disruption of the gluten network. Bran processing is likely to be a route to optimize its incorporation in health-promoting foods with biological activity and/or technological functionalities. For instance, it was reported the enhancement of bread quality by lowering the whole wheat flour particle size [43]. As an alternative to the conventional milling processes referred earlier, recent processes such as microfluidization and micron technology are used to reduce the particle size. The microfluidization process is used to reduce the size of the bran particles to submicron scales and reorganize the fibre composition, as well as to open their dense microstructure, increasing health-beneficial properties such as hydration properties and bio-accessibility of bound phytochemicals, resulting in increased antioxidant activities [44][45]. Ortiz de Erive et al. [46] have successfully produced high-fibre bread with similar loaf volume to the control bread by replacing 20% of the wheat flour with microfluidized corn bran. Similar to the microfluidization process, micron technology is used to reduce the particle size of biomaterials and, consequently, to increase the level of released bioactive compounds. As a matter of fact, micron technology improves the functional properties and bio-accessibility of dietary fibres and other bioactive compounds [47]. In addition to the bakery, wheat bran can be used to yield functional nanomaterials from the derived polysaccharide arabinoxylan (AX). The chemically modified AX can be used as a functional nanomaterial for gene delivery [48] or to produce physically immobilized xylanases [38].

3. Conclution

Besides the environmental and economic aspects, discarded cereal- and pseudocereal-based by-products represent an important loss of valuable biomass and nutrients, including many biochemical compounds such as edible fibres, hemicelluloses, β-glucans, resistant starch, arabinoxylans, mono-, di-, oligo- and polysaccharides and other carbohydrates, proteins, bioactive peptides, amino acids and enzymes, lipids (mono- and polyunsaturated fatty acids in free forms, acylglycerols and sterol esters, stanols, glycolipids and phospholipids), polyphenols (phenolic acids, gallotannins, procyanidins, etc.) and other bioactive phytochemicals, vitamins, minerals and other micronutrients, nucleic acids, etc. Cereal-based by-products can be converted as well into biopolymers and bioplastics, biofertilizers and biofuels (bioethanol, biodiesel, bio-butanol and biogas). Their application in fermentative processes can lead to the production of single cell proteins and oils, enzymes and bioactive microbial metabolites.

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