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Transformation of Eggshells, Spent Coffee Grounds, and Brown Onion Skins into Value-Added Products

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Abstract

Unlike other wastes from the agri-food industry (straw, corn, cob, stalks, seeds, husks) widely used in biorefineries as feedstock for the production of high-value products (chemicals, biofuels and bioenergy), eggshells, spent coffee grounds, and brown onion skins have not yet found a suitable place in sustainable production, but are mainly landfilled burdening the environment. This paper aims to point out the great potential of eggshells, spent coffee grounds, and brown onion skins as secondary raw materials in sustainable development, with minimal production of waste streams.

Keywords: *eggshells, spent coffee grounds, brown onion skins, value-added products, "zero-waste" model*

1. Introduction

Sustainable production from its conceptual introduction by Agenda 21 [1] to the present time represents an industrial development that meets the needs of current generations without compromising the ability of future generations to meet their needs [2]. It should be noted that this definition does not include only activities related to the environmental protection, but also a whole range of activities related to the protection of natural, cultural and social values that are closely connected to material goods. Therefore, sustainable development includes a series of technical, technological, economic and social changes carried out by the needs of present and future generations. One of the pillars of sustainable development is the circular economy model, which aims to ensure sustainable development at every stage of product creation, processing and transformation by creating a "closed-loop" economy [3]. The new value is created through a "closed loop", approaching a model that avoids the creation of waste, i.e., the "zero waste" model. One of the five major challenges of sustainable waste management in the agri-food industry using the "zero-waste" model [4] is the development of innovative waste utilization techniques for the production of chemicals, fine chemicals, bioactive compounds, enzymes, and functional materials (Fig. 1.). These products have at least twice the added value of the products derived from currently prevailing outdated waste management strategies, which are not consistent with sustainable development. Outdated waste management strategies result in low value-added products such as animal feed, treated waste from the processes of composting, anaerobic digestion, and incineration, which can also have a negative impact on the environment and ultimately and most undesirably result in landfilling [5].

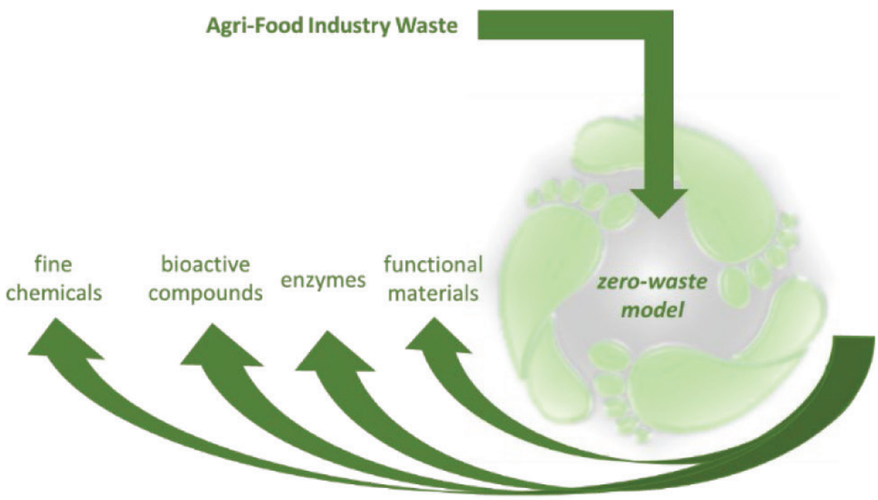

Fig. 1. Schematic presentation of possible products within "closed loop" economy from agri-food industry waste

Since food industry produces large amounts of waste, which mostly present an environmental problem, there is a need for its characterization and valorization in order to develop a model of its cost-effective recovery. Waste from the agri-food industry has the potential for the production of very valuable semi-finished products and products intended for further use in the food, pharmaceutical and biotechnology industries, and the concept of valorization is being intensively introduced into the management of agricultural and food waste [6].

Among the numerous wastes generated in the agri-food industry, eggshells, spent coffee grounds and brown onion skins are particularly "suitable" candidates (raw materials) for the preparation of enzymes (lysozyme), fine chemicals and/or functional materials as carriers for the immobilization of enzymes. The latter is supported by the available information on their structure, chemical composition and current knowledge on their potential use. The usage of innovative transformation techniques of this waste could result in protein-based carriers (eggshell membrane) and cellulose and/or hemicellulose based carriers (spent coffee grounds and brown onion skins). This has also been proved by research within the framework of a project funded by the Croatian Science Foundation "Immobilization of Lipases on Functionalised Carriers Produced from Selected Agro-Food Industrial Waste – ImoLipWaste" conducted by a research group at the Faculty of Food Technology of Osijek.

2. Are the eggshells a waste?

The eggshells are waste from the agri-food, pharmaceutical and biotechnology industries, family farms and crafts, but also restaurants and households, whose total annual production can be estimated based on data on the total mass of hen eggs produced, and the fact that the eggshell accounts for between 10–11% of the total egg mass [7]. According to the Food and Agriculture Organization (FAO), a total of 78949,623 t of chicken eggs was produced in the world in 2018, of which 7,770,000 t in the European Union, including the United Kingdom, and 47,150 t in the Republic of Croatia [8]. Consequently, it can be estimated that in 2018 the world generated at least 7,894,962 t of eggshell as waste, of which 777,000 t in the European Union and 4,715 t in the Republic of Croatia. It is crucial to emphasize that about 15 to 20% of the total eggs produced are further used in chicken hatcheries, and after hatchery remained eggshells becomes a waste.

The research by [9,10,11] indicates the potential of the eggshells as a carrier for enzyme immobilization. In addition, the eggshell is a very "cheap" source of natural calcium in the form of calcium carbonate, from which inorganic and organic calcium salts can be produced by relatively simple processes. Organic and inorganic calcium salts are used in the food, pharmaceutical and chemical industries (additives, food supplements), as well as for the production of calcium-based fertilizers for agricultural purposes [7]. Among the numerous methods for obtaining calcium salts from eggshells, the best known are those based on dissolving calcium carbonate from calcified matrix in dilute solutions of acids such as hydrochloric, acetic and o-phosphoric acid. In addition to calcium salts, eggshell membranes are also formed as a by-product during dissolution with acids (Fig. 2.). In addition to being an inexpensive source of collagen and hyaluronic acid for the pharmaceutical and cosmetic industries [7], eggshell membranes also have great potential to be used as a carrier for enzyme immobilization [12]. This is supported by numerous studies focused on the development of biosensors based on the enzyme immobilization on eggshells membranes as solid support [13]. When the production of calcium salts by eggshell treatment with dilute acids is compared to the the eggshell membranes production for biosensor development, it can be observed that ground eggshells are used for the production of salts, and intact eggshells or eggshell halves for biosensor related eggshells membranes production. Moreover, in biosensor development, partial decalcification of the eggshells by

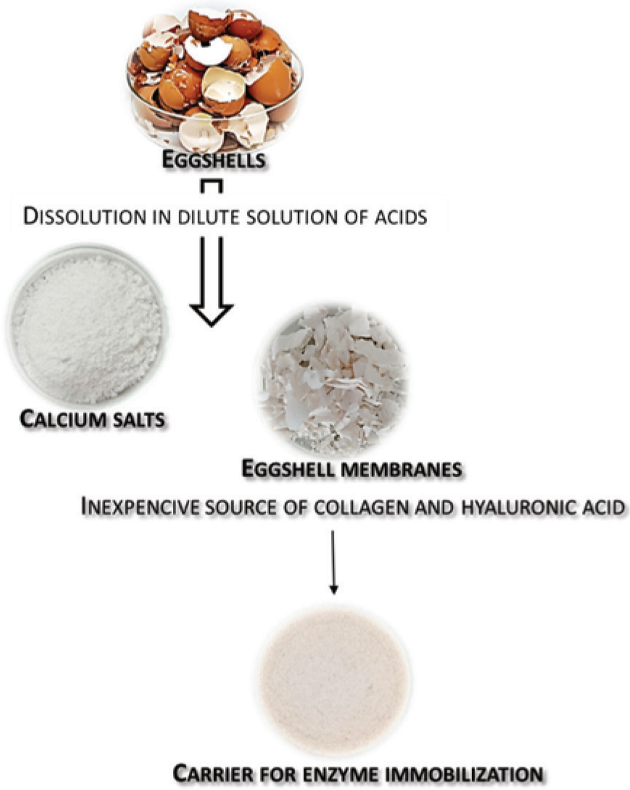

Fig. 2. Possible "zero-waste" model of eggshell waste transformation

acids is performed in order to facilitate the separation of large pieces of the eggshell membranes from the remaining eggshells. Accordingly, it seems quite likely that these two types of production processes could be combined for simultaneous production of calcium salts and larger pieces of eggshell membranes, using halves and/or larger pieces of eggshells instead ground ones. This would greatly facilitate the process of eggshell membrane separation and handling. Furthermore, produced eggshell membranes could be uniformly milled to particle size necessary for enzyme immobilization.

The exploitation of eggshells for the production of value-added products has great potential, related to its rich composition of various high-value compounds, Eggshells have already found its application in the production of feed for livestock and pets, organic fertilizers and soil improvers, compost and biogas, as well as, raw materials for cosmetic industry, active implantable medical products, in vitro diagnostic medical devices, veterinary medical products and for the pharmaceutical industry. By use of innovative transformation techniques and advanced technical and technological solutions, it is possible to prevent the occurrence of risks for humans and animals and to use eggshells for the production of products for human consumption.

3. Hidden treasure behind a cup of coffee

Coffee, a beverage made from roasted and ground coffee beans, is one of the three most popular beverages besides tea and water. Coffee is a tree-like plant shrub from the *Rubiaceae* family, and originates from the Ethiopian province of Kafa. The average annual coffee production in the world exceeds 10 million tons, leaving behind about 6 million tons of spent coffee grounds after the production and consumption of about 2.3 trillion cups of coffee [8]. The aforementioned seems to be quite a good reason for the serious exploration of the possibility of using spent coffee grounds for the production of value-added products and/or secondary raw materials, rather than its landfilling. Namely, spent coffee grounds possess a significant nutritional value, as well as, large proportion of various valuable biocomponents, which can be further used in pharmaceutical, biochemical/chemical, food industry and civil engineering. According to the literature [14] spent coffee grounds contains about 60% of water-insoluble lignocellulosic material or about 50% of insoluble fibers in dry matter with domination of cellulose and hemicellulose, about 13.6-17.5% proteins, 10-15% lipids, 4% of total polyphenols and 2.5% of condensed tannins in dry matter. Since spent coffee ground components differ in polarity, they can be isolated by the use of standard

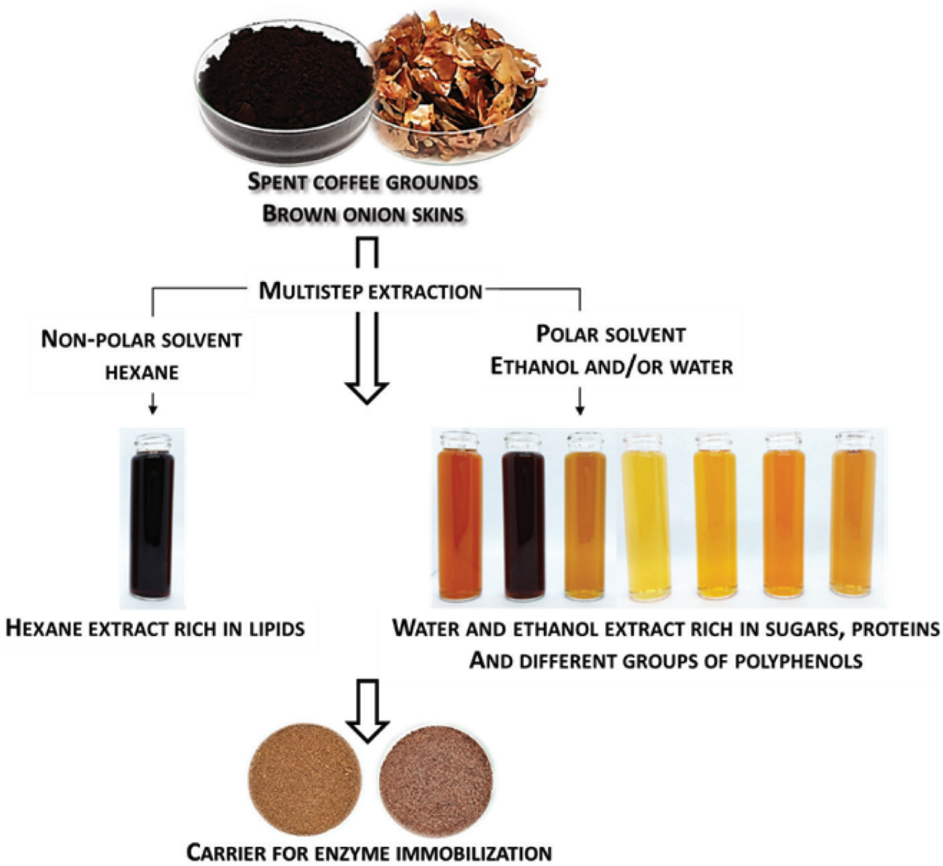

Fig. 3. Possible "zero-waste" model of spent coffee grounds and brown onion skins transformation

extraction methods with different solvents ranging from non-polar to polar, as well as by innovative extraction techniques (Fig. 3.) including supercritical CO_2 extraction and subcritical ethanol and water extraction [15].

4. All sides of the brown onion skins

For the most of the world's population, onion (Allium cepa L.) is a daily part of the diet and one of the oldest cultivated plants in the world. According to FAO 104 million tons of onions were produced worldwide in 2020, with 16,350 tons in Croatia [8]. With the increased need for processed onions, the production of waste biomass from onions also increases. About 37% of the total mass of fresh onions is classified as waste during processing. Depending on the type of onion processing, two types of waste are distinguished. Waste biomass of onions after calibration and packaging is the outer shell of the so-called onion skin, while waste biomass of onions lagging behind industrial onion production includes onion skins, two outer fleshy layers, roots, upper and lower bulbs, and waste includes small, deformed, diseased or damaged bulbs [16]. This type of onion waste is a major problem for the industry because it cannot be used as animal feed due to its characteristic strong and sharp smell, and it cannot be used as an organic fertilizer due to the development of phytopathogens such as *Sclerotium cepivorum*. The use of onion waste as a potential source of functional ingredients is one of the ways to valorize it (Fig. 3.), especially with food industry modern trends connected to the growing need for the production of functional foods. Nevertheless, the chemical composition of onion waste can vary significantly and therefore it is necessary to determine the content of target compounds separately. However, onion waste is generally identified as a source of flavor compounds, fibers, non-structural carbohydrates and polyphenols, which opens opportunities for its further use as a source of functional food ingredients to improve antioxidant and prebiotic quality of new products [17,18].

5. ImoLipWaste Project

Waste from the agri-food industry, which is widely available, could be used for the production of "cheap" enzyme immobilization carriers, subsequently leading to the reduction in waste disposal costs, due to the usage of produced waste for carrier production and selling, instead of cost-effective waste disposal. In the long run, such an approach could make an additional profit, instead of the costs in the industry, especially if bioactive components present in the extracts would be further used as additional products. Such an approach has been used within the ImoLipWaste project research where appropriate techniques for the transformation of eggshell, spent coffee ground and brown onion skin wastes into functional materials based on protein fibers (Fig. 2.) and/or lignocellulosic material (Fig. 3.) for enzyme immobilization was used, and obtained by-product extracts for further use/production was evaluated. Based on the project preliminary research, it seems that economy-based production of "cheap" carriers for enzyme immobilization from eggshells, spent coffee grounds and brown onion skins, is inevitably connected to the production of bioactive components present in the extracts during carrier preparation, where achieving of the greatest profit using "zero-waste" model approach can be obtained. Among the variety of bioactive compounds present in the aforementioned waste, the most prominent was found lysozyme (eggshells), caffeine (spent coffee grounds) and quercetin (brown onion skins).

The material remaining after the extraction of bioactive compounds from eggshells, spent coffee grounds and brown onion skins, presents the carriers for lipase immobilization, which can be used in food, biochemical, chemical and/or pharmaceutical industry. The usage of the immobilized lipases reduces production and operational costs due to the fact that immobilized lipases can be re-used in the production process. Moreover, such an approach enables sustainable industrial production and creates added value for waste/by-products of the agri-food industry, which is the basis of circular management. Furthermore, immobilized lipases open the possibility for developing new production technologies, such as the transition from batch to continuous processes. The introduction of continuous processes instead of batch processes reduces the size of the reactor and therefore the investment costs, facilitates process control in the event of minor deviations in product quality.

6. Conclusions

It is to be expected that in the next few decades new and/or improved existing technologies will follow the trend of sustainable production, enabling the better utilization of agri-food waste for everything for which fossil reserves are still used today. Besides its potential use in the energy production (bioenergy/biofuels), agri-food industry waste clearly represents the material for the production of multiplicity of various high-value added biomaterials where approach to the "zero-waste" model can be achieved. However, such an approach clearly requires the use of innovative techniques.

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