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Review

Citrus processing wastes: Environmental impacts, recent advances, and future perspectives in total valorization

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ABSTRACT

The recent advances and future perspectives in the complete valorization of citrus processing waste (CPW), a by-product of citrus processing industries, are presented in this review paper. First, the importance of valorization of CPW to develop a bio-economy and to reduce its negative environmental impacts is assessed. A brief survey of applications of native/modified CPW for nanoparticle, bio-sorbent, and biofertilizer production is presented. As the core part of the valorization scheme and regarding the environmental aspects, the perspectives for the application of CPW are via green extraction techniques, e.g., microwave- and ultrasound-assisted extractions, and biochemical processes. Furthermore, green extraction and biochemical techniques result in processes' intensification toward integrated biorefinery models. The superiority of green extraction techniques over traditional techniques, challenges for implementation, and the valuable extracts obtained by these methods as well as a summary of their analytical techniques are discussed. The challenges of bioconversion of CPW to biofuels and fermentative products and strategies to overcome them are later presented. Finally, a literature review on using the concept of green chemistry for the integrated biorefinery of CPW and its engineering challenges is presented and a biorefinery scheme is proposed accordingly.

1. Introduction

According to the Food and Agriculture Organization (FAO), a total of 636,544,883 and 1,106,133,866 tons of fruits and vegetables, respectively, was produced in 2012 (FAOSTAT-FAO statistical database, 2015). Citrus fruits are the most consumed fruits in the world, because of their nutritional values and health benefits, as a result of having appreciable amounts of secondary metabolites (Lv et al., 2015). Brazil, China, India, Mexico, Spain, and the USA produce over two-thirds of the world's citrus fruits (Paggiola et al., 2016). The genus *Citrus* includes several important fruits, with dominantly sweet orange, mandarin, grapefruit, lime, and lemon (Mamma and Christakopoulos, 2014; Zheng et al., 2016). Over 61% of the world's citrus fruit production is the share of sweet orange. Sweet orange (or *Citrus sinensis*) varieties can be classified into three groups: common oranges (also called white or blonde oranges), navel oranges, and pigmented oranges or blood oranges (Stinco et al., 2016). While the first group is mainly intended for use in juice production industries, the pulpy texture of the second group and the reddish coloration of the third group make them favorable for fresh consumption.

The citrus processing industries are usually involved in four main steps. After being harvested, citrus fruits are transported to production plants. Afterwards, the fruits are graded in a preliminary step, and after removal of debris, they are stored to be ready for water-washing cleaning, in the second step. At the third step, the fruits' juice is extracted via pressing and centrifugation; the juice is then heated to activate pectic enzymes, and transferred to syrup tanks for concentration and adding citric acid, enzymes, and vitamin C, to obtain the best quality. Finally, the juice is filled into packages, boiled to sterilize, and the packs are labeled (see Fig. 1) (Ngoc and Schnitzer, 2009; Taghizadeh-Alisaraei et al., 2017).

Approximately one-third of citrus fruits is utilized for processing, which produces *ca.* 50–60% organic waste. CPW has a low pH level (3–4) and is characterized by having high organic matter (95% of total solids) and high water content (around 80–90%). Table 1 summarizes the proximate composition of major citrus fruits' byproducts produced in citrus processing industries. This composition includes some fats, free sugars (e.g., glucose, fructose, and sucrose), organic acids, carbohydrate polymers (cellulose, hemicellulose, and pectin), enzymes (pectinesterase, phosphatase, and peroxidase), flavonoids, essential oils (mainly limonene), and pigments (Boukroufa et al., 2015). The organic acids in orange processing waste, i.e., citric, malic, malonic, and oxalic acids,

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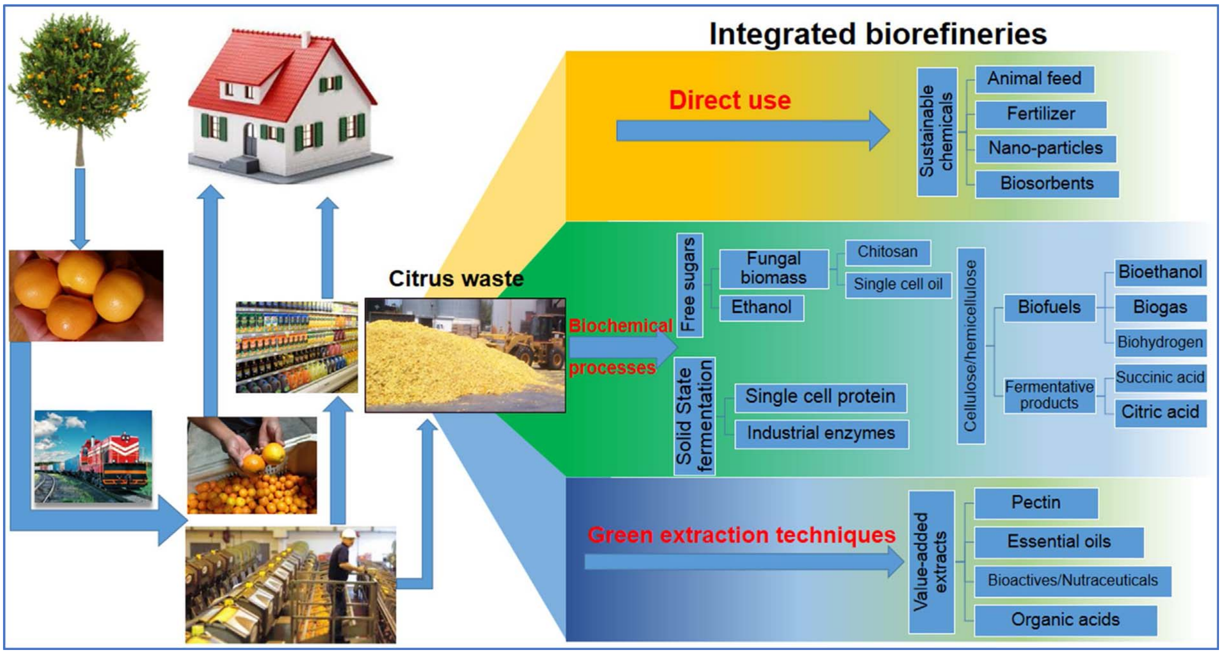

Fig. 1. View of citrus fruit supply chain and the waste valorization.

Table 1
Proximate composition of some major citrus fruits' by-products (% of dry basis).

Waste	Ash	Sugar	Fat	Protein	Flavonoid	Pectin	Lignin	Cellulose	Hemicellulose	Refs.
Lemon peels	2.52	6.52	1.51	7.00	12.54	13.00	7.56	23.06	8.09	Marín et al. (2007)
Sweet orange peels	2.56	9.57	4.00	9.06	4.50	23.02	7.52	37.08	11.04	Marín et al. (2007)
Citrus waste[a]	3.73	22.9[b]	3.78[c]	6.07	–	25.00	2.19	22.00	11.09	Pourbafrani et al. (2010)
Citrus waste[a]	4.75	33.09[b]	–	–	–	15.30[d]	1.95	8.82	7.96[e]	Satari et al. (2017)
Kinnow mandarin	3.23	31.58	–	5.78	–	22.6	0.56	10.10	4.28	Oberoi et al. (2011)

[a] Mixture of orange and grapefruit peels, seeds, and leaf residues after juice extraction.
[b] Sum of glucose, sucrose, and fructose.
[c] Limonene.
[d] Galacturonan.
[e] Sum of arabinan, xylan, galactan, and mannan.

together compose approximately 1% of dry weight (Angel Siles Lopez et al., 2010). In citruses, citric acid is the dominant organic acid and generally lemon juice has the highest acidity with over 48 g/L citric acid (Karadeniz, 2004). The taste of juice is primarily affected by the sugars and organic acids, while volatile organic compounds are associated with its aroma. Noteworthy, when CPW is obtained from a juice production factory, it also contains citrus seeds, which are characterized by having high oil content, with dominantly C_{16} and C_{18} fatty acids profile (Anwar et al., 2008). Regarding negative impacts of production of such a huge amount of CPW to the environment and also the contribution of the CPW-derived products to the bioeconomy, the valorization of CPW to food, feed, and fuels is a necessity.

The aim of valorization of CPW in the present study is via three main platforms (Fig. 1): direct use of native/modified CPW, biochemical processes, and green extraction techniques. The paper primarily summarized the direct utilization of CPW for producing nanoporous materials, biosorbent for heavy metals (unmodified or chemically modified), and biofertilizer. The recent advances in the literature on the using green extraction techniques, i.e., microwave- and ultrasound-assisted extraction, and biochemical processes for biofuels and fermentative products production were presented and critically analyzed. Challenges of implementation of the green chemistry for CPW valorization and in integrated biorefinery platforms were discussed. The solutions for some of the problems and questions to be answered in the future for fully utilization of this waste were finally discussed.

2. The importance of CPW valorization: environmental and economic aspects

The valorization of CPW has a great potential for transition toward a bioeconomy. Besides, the negative impacts of citrus processing industries to the environment make the valorization schemes more important. The importance is to mitigate the negative environmental effects via introducing green valorization schemes that lead to an integrated biorefinery platform.

2.1. Emergence of bioeconomy and the share of CPW

The global population is exponentially expanding and consequently the demands for human food and feeds are advancing. Industrialized nations are heavily dependent on crude oil and natural gas for their energy, chemicals, and materials demands. Nonetheless, the political instability of some Middle East oil suppliers and also the recent fluctuations of oil price make this dependency more challenging (Reboredo et al., 2016). Besides, the petroleum supplies are limited resources and there have been always environmental concerns regarding their use. Therefore, the ability to meet market demands yet minimize environmental collapse has been of great importance for the future of the mankind's life on earth. In this regard, different countries have passed legislation to move towards bio-based economy for the future (Inghels et al., 2016). The emerging "bioeconomy" is "a new concept coined by