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Utilization and Valorization Of Citrus Fruit By-Products: A Review

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Abstract: Citrus fruits are among the most cultivated fruits around the globe. The production increased due to the rising demands as humans becoming more aware of the health concerns and the nutrients confined in these citrus fruits. Vitamin generated by the juice from citrus-processing industries accounts for almost 50% from the initial fruits mass and the remaining considered underutilized. Hence, these citrus wastes undergo extraction processes to obtain the valuable chemicals compounds in the citrus wastes such as pectin, flavonoids, essential oils and phenols as raw materials and source of energy. The article aims to present the high-value compound in the citrus wastes and their extraction methods for obtaining the value-added products as well as their corresponding applications.

Keywords: Citrus Wastes, Valorization, Extraction Methods, Pectin, Essential Oils

1. Introduction

Citrus sinensis, commercially known as the orange tree is one of the most vital fruit crops in the world. It is grown in more than 100 countries globally, predominantly in tropical and subtropical areas where favourable soil and climate changes affects citrus cultivation. These citrus fruits are marketed mainly as fresh fruits and as processed juice [1]. The genus of *Citrus* fruits includes *C. sinensis* (sweet orange), *C. reticulata* (tangerine), *C. limon* and *C. aurantifolia* (lemon and lime) and *C. paradisi* (grapefruit) as the major worldwide basis. While sour orange (*C. quarantium*), citron (*C. medica*) and shaddock (*C. grandis*) comprised the bulk of minor *Citrus* species. In addition, Citrus fruits can be fragmented into two sections; the flesh and peel as shown in Fig 1. Flavedo and albedo confined in the peel. Most of us will see the flavedo, the outermost layer of these fruits upon arriving at the market. The flavedo or also known as exocarp, confines the cellulosic materials for the most part and also bears the oil glands and pigments. Albedo is the inner part of the citrus fruit, located next to the flavedo, rich in pectin and usually this part is removed before eating. The endocarp is divided into several sections namely segments. Juice vesicles (or juice sac) are the pulps, filling these segments [2].

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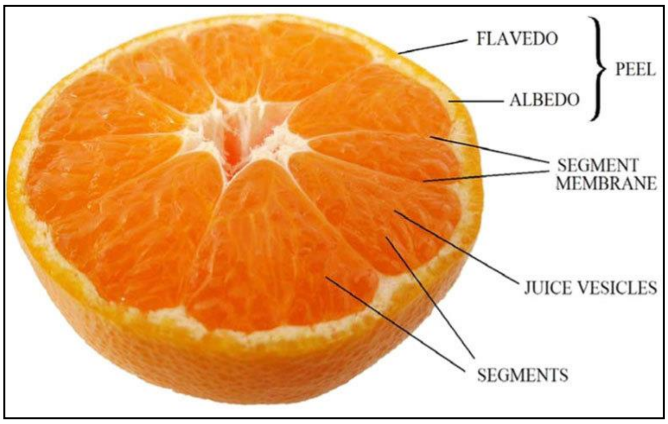

Figure 1: Segments of the Citrus fruit [3]

An enormous amount of by-products and residues by the peels are produced during the processing of the citrus fruits. They are discarded or dumped as they do not add values to the products. On another viewpoint, these materials are not part of the food chain making them considered wastes. During juice extraction processing, citrus wastes include more than half of the whole fruits and mainly consists of peels and pressed pulps residual generated by the juicing manufacturing industry, discarded fruits for commercial reasons (such as damaged fruits, different sizes, expired etc.) and fruit discarded that limit the production due to regulations [1].

Over times, these waste products led to significant disposal issues since there were no satisfactory disposal means other than dumping on land alongside the production site. Part of large tracts of land presents an arising risk to local water courses due to the putrefying wastes and in some cases leads to uncontrolled methane production. If it is not managed properly, the major environmental problems associated with citrus peels is its highly fermentable carbohydrate content that escalates its degradation [2].

1.1 Citrus wastes disposal management systems

Three types of wastes commonly generated during the processing of citrus fruits which are solid (such as peels, seeds, rags and sludge), liquid (consists of cannery effluents, overflow of can-cooler, fruit-washing, peeling and sectioning waste waters) and distilled effluents which include the citrus molasses, citric acid and pectin's effluents and peel oil plants. Traditionally and most common citrus wastes management methods are composting, anaerobic digestion, thermolysis, incineration and gasification. Moreover, various methods are used for disposing the citrus waste for instance, the effluents are either released directly into lakes, dumped in the pond, discharged into groves or wells or city sewage system management [6]. Direct disposal of wastes from citrus fruits without proper processing eventually bring about environmental problems. Thus, it is requisite and our responsibility to treat these citrus wastes systematically at the early stage in food industries and other correlate areas.

2. Valorization of citrus by-products

The phrase waste valorization refers to activities of any industrial processing aimed at reusing, recycling or composting from wastes, residues, useful products or sources of energy [4]. It generally takes form in one of the following activities; (i) residue or by-products processing into raw materials, (ii) exploitation of discarded finished or semifinished products as raw materials or sources of energy,

(iii) waste materials' utilization during stages in the manufacturing process and lastly (iv) incorporation of residues materials to finished products. According to environmental regulation, wastes types used in valorization are typically considered non-hazardous and differs from household wastes. This is because, waste valorization involves a large magnitude of production-related wastes and by-products' processing and is much more homogeneous [4][5].

Chemical composition confined in the solid citrus wastes including soluble sugars (6-8%), primarily fructose, glucose and sucrose. Structural polysaccharides (1.5-3%) like cellulose, hemicellulose and pectin. Besides that, lignin-like compounds for examples flavonoids and essential oils (83-97%) particularly D-limonene could also be found in these solid residues [7][8]. Several factors such as growing conditions, variety and climatic changes influenced the relative composition of citrus waste [8]. The sustainable potential of citrus wastes utilization is to be used as biofuel by converting them into bioethanol, as a source of renewable energy. A source of renewable energy and value-added derived products depends on the chemical composition for biorefinery processes [7]. These by-product valorizations offer several benefits which are environmental protection, economic gains and consumers' lives improvements, thanks to the use of natural products. Extraction of citrus essential oils can be used in various foods, as a food flavouring ingredient. In pharmaceuticals due to its antibacterial and anti-inflammatory effects. As well as daily-used products such as soaps, perfumes and cosmetics [8].

3. Utilization of citrus wastes into environmentally sustainable products

3.1 Direct use of citrus wastes

Citrus by-products are directly utilized as feedstuff. Introducing citrus wastes for ruminant nutrient is possible due to the availability of soluble fibers and ruminant's ability to ferment a large amount of fibers [9]. One of the applications of citrus wastes is it use as an organic fertilizer in agriculture industry. Aside from citrus fruits, there are also several agro-wastes being studied and used including banana peels, watermelon, pineapple and papaya. In 2015, Lim et al conducted a research and studied the production of citrus fertilizers using the fermentation method. The effectiveness of the citrus-based fertilizers was determined by applying them on mustard plants. However, results show that the citrus has low pH, illustrated high acidity that needs to be redeveloped for better characteristics [10].

Orange peels conversion into fertilizers by composting are successfully achieved by adjusting the pH value, C/N ratio and moisture content to 6.3, 24:1 and 60% moisture content respectively. The modified substrate was piled under shelter and entirely composted within 30 days, with regular turning and watering and thermophilic phase between 65-70 days [11]. In another study proven that Citric peel powder has high Nitrogen content (9.1 mg/g) combined with the alkaline peel powder with high Phosphorous content (4.2 mg/g) and Potassium (2.1 mg/g). Acidic peel (citric powder) helps minimise the soil salinity while alkaline peel powder is used to reduce the presence of acidity content in the soil [12].

Besides, citrus peel could also act as a cost-effective and efficient biosorbents to remove dye, metals and organic pollutants from an industrial water stream. The predominant type of polysaccharides in the citrus wastes cell walls is pectin which accounts 40% of the dry matter. Pectin substance are commonly known to strongly bind metal cations in aqueous solution due to the carboxyl functions of galacturonic acid [13].

3.2 Extraction of high-value chemical compound

3.2.1 Pectin

Pectin is a polysaccharides polymer compound present at higher plants, widely distributed in the cell walls of the roots, stems, leaves and oranges. It is the main component for dietary fibers with excellent gelling and emulsion stabilities. Presently, pectin is widely used in the food industry, pharmaceutical and chemical industries and other specific applications. As citrus peels confine high levels of pectin, it can be reused and recycle as raw materials for pectin extraction. Pectin substances are commonly used in the commercial and home production of jams, jellies, confectionary products and baking fillings due to its gelling ability [11]. It is also being processed as a thickeners and stabilizers in milk products, as chocolate milk and as cosmetics emulsifiers, cold creams and soap [2][15]. Pectin is also suggested as a drug carrier injected intramuscularly because pectin delayed the drug absorption enabling more prolonged effect such as in insulin-pectin and pectin-penicillin preparations. Pectin is industrially extracted in a chemical way with incorporation of strong acids such as hydrochloric, nitric, oxalic and sulfuric acids but they are environmentally hazardous [11][18]. Therefore, 'green labeled' pectin could be produced by an alternative of enzyme usage such as pectinolytic, cellulolytic and hemicellulolytic [2]. Pectin extraction from citrus peels can be optimized with regards to the concentration of enzyme, water: peel ratio, temperature and treatment duration. Increased of pectin liberation achieved at 37°C (compared to 25℃) for 24 h. Water: peel ratio less than 12:1, could reduce the pectin released period [11].

In additions, pectin and its derivatives also appear to have inherent therapeutics properties specifically in malfunction and digestive tract cases. It is prepared and employed as a supportive measure for infant diarrhea and other alimentary tract disorders cases [14]. One of the hot topics currently is in food packaging to develop innovative active packaging, based on natural antioxidant and antimicrobial agents where citrus wastes are incorporated. Sustainable, biodegradable PLA-based active packaging is developed by incorporating the natural antioxidants from agri-food wastes. The antioxidants from orange peels wastes are extracted through hydro-alcoholic extraction then spray-dried with pectin or cyclodextrins as carrier materials [15].

3.2.2 Citrus Essential Oils (CEOs)

Citrus essential oils are a mixture of complex hydrocarbon and oxygenated derivatives consisting of functional groups such as aldehydes, alcohols, ketones and other molecules including esters and organic acids. These essential oils contained in oil glands or sacs located in flavedo [2][6][11]. Factors such as variety, seasons, geographic locations and ripening stages influenced the variety of CEOs composition in the citrus fruits. There are around 20-60 compounds exists per CEO. D-limonene is the prime component with concentrations varies between 32% and 98% depends on the citrus genus a hydrocarbon classified as cyclic terpene [2][6]. Citrus wastes as a source of D-limonene as shown in Fig. 2, also used for building chemical structure such as biosolvent as an alternative of halocarbon solvent. Fragrance compound can also be produced from D-limonene [9].

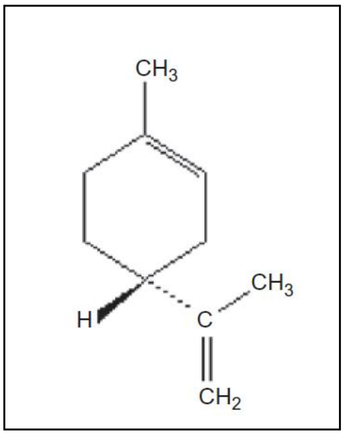

Figure 2: Illustration of D-limonene chemical structure [11]

Extraction of essential oil from the citrus peels is viable since this by-product has high added value. Techniques for EOs extraction such as supercritical fluid extraction, ultrasound, subcritical water extraction, the process of control drop pressure and microwave steam distillation (MSD) are more compatible compared to steam distillation (SD) and hydrodistillation as there two methods prolonged extraction time and thus chemical modification and loss occur [2]. The applications of CEOs spread from cosmetics, packaging, pharmaceuticals and formulation of food [11][16]. MSD technique accelerated the extraction process without changing the composition of volatile oil. MSD effectiveness over SD is contributed by the cell structure pronounced alteration, specifically compartment of cell wall by microwaves [6]. In this modern era, consumer's growing health concerns make them turn their views from commercial antimicrobial into natural microbials to manage food contamination and deterioration. Essential oils possess these properties against a broad spectrum of pathogens. Extraction of CEOs from citrus wastes also benefits as an antifungal agent. The employment of citrus essential oils helps to minimize the fungal growth and contamination while extending the shelf-life of food products. Essential oil of *C. Limon* was used to controls pathogens of fungal plants that attacking the grapevines [16].

4. Conclusion

Citrus fruits are included among the most widely cultivated and commercially beneficial in tropical and subtropical areas. It confined valuable juice vitamins and important dietary in our life. The huge amounts of citrus wastes are actively processed in order for high-value compounds such as flavonoids, phenolic, d-limonene, pectin and cellulose in the citrus wastes for greener products development. The potential extraction methods for these chemical compounds including microwave extraction, ultrasonic and supercritical fluid extraction are also important as an alternative of traditional techniques. Thus, these products can be actively used in pharmaceuticals, food industries, packaging and food formulations industries.

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