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Dry fractionation of olive pomace as a sustainable process to produce fillers for biocomposites

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ABSTRACT

Olive pomace (OP) is the agro-industrial residue of olive oil extraction composed of residual pulp and stone. This work aims at exploring the possibility of using dry fractionation (combination of grinding and sorting processes) to produce pulp-rich and stone-rich fractions with the highest purity and yield. The physical-chemical characteristics (composition, thermal stability, color, surface free energy) of the obtained powders were discussed in relation to the applied processes. It was shown that dry fractionation could be successfully used to convert OP into valuable fractions using processes avoiding the consumption of water and the generation of effluents or co-products. Results revealed that the separation of the pulp from the stone using friction solicitations in a ball mill operating in mild conditions (2 min at a frequency of 15 Hz) was as efficient as wet fractionation in terms of powder characteristics, achieving a total yield of 99.4% against only 82.1% in the case of wet fractionation and without using water while a water:biomass ratio of 5:1 was required for wet fractionation. Produced powders exhibited contrasted biochemical composition (either rich in lignin or cellulose) and surface free energy, and were thermally stable up to at least 210 °C. It was concluded that they could be interestingly used as raw resources for the production of fillers that will be further incorporated in polymer matrices to produce a range of biocomposites.

1. Introduction

In recent years, an increasing public concern has been noticed over the harmful effects of fossil-based plastic materials on the environment. The development of alternative materials that are both biodegradable and produced from natural resources is thus gaining considerable attention owing to environmental, economical, societal and technical advantages as compared to conventional synthetic polymers. Lignocellulosic fillers based biocomposites constitute a promising answer since they allow to joint current requirements regarding the need to reduce our dependence to fossil resources, environmental pollution, while offering a way of sustainable eco-conversion of lignocellulosic solid wastes and by-products. A large range of lignocellulosic residues obtained from agro-food industries have already been explored and effectively used as fillers in biocomposites due to their interesting properties, biodegradability, high availability and low price [1]. Among this available lignocellulosic biomass, one valuable lignocellulosic biomass is olive pomace [2,3]. Recently, some studies highlighted the potential of olive pomace (OP) as reinforcing agents in polymer matrix [4,5].

Over 95% of the world's olive trees (*Oleaeuropeae*) are found in the Mediterranean basin, due to environmental factors that make the soil and the climate ideal for their cultivation, flowering and production of their fruit. Among the emerging producing countries, Algeria is considered as a new extra-virgin olive oil exporter. *Chemlal* is the most common olive cultivar grown in this country, with 40% of the orchards. Recently, this variety has become associated with high olive oil production, due to its large distribution and its high olive oil yield, *i.e.* 18 L/100 kg of olives [6]. One hectare of olive tree originates on average about 2500 kg of olives. Generally, 100 kg of olives produce 20 L of oil, 35 kg of olive pomace and 100 L of wastewater [7]. So, about 875 kg of OP are generated by hectare. It is estimated that the production of OP reaches 2,881,500 tons/year worldwide [8]. OP is not easily degradable under natural conditions and its disposal causes serious environmental problems, particularly in the Mediterranean countries, where abundant quantities are produced during a short period of the year. It is responsible of inhibition of microorganisms' activities, reduction in the seed germination, and alteration of soil porosity and humus concentration. Thus, in order to reduce its harmful environmental impact, several works have been recently dedicated to its valorization in various fields, such as animal feed, composting, energy and biofuels, cosmetics, food industry, and pharmaceutical areas. Only few studies are describing the use of olive pomace

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(quasi exclusively olive stone) as raw materials for the production of reinforcing fillers [3,4,5]. The intrinsic characteristics of fillers obtained from agro-residues, including their composition and surface properties, are considered as key criteria for their use in composite materials and should be thus well controlled [9]. Furthermore, many studies demonstrated that the development of biocomposites at industrial scale requires a better control of the filler/matrix interface, which can be tricky in the case of fillers derived from heterogenous and complex agro-residues.

The olive fruit can be structurally separated into three compartments, *i.e.* (1) the skin, called epicarp, which contains chlorophylls, carotenoids and anthocyanins that account for the color, (2) the pulp or flesh, called mesocarp, which is the reserve supply of all the constituents (oil, ashes, proteins, cellulose and lignin), and (3) the stone, called woody endocarp, which contains the seed and is mainly composed of crude cellulose [10]. OP is a mixture of residual skin, pulp and fragments of the crushed stone. The distribution of the various constituents and the physical-chemical characteristics of the OP are complex and fluctuate according to the fruit variety, cultivation practices, geographical origin, stage of maturity, storage time and process of oil extraction [7]. The structural heterogeneity and complexity of OP constitute one of the obstacles to subsequent eco-conversion especially in biocomposites application. Existing pre-treatments used to separate the pulp from the olive stone are based on chemical multistep processes consuming large amounts of water and chemicals and generating effluents that have to be treated. They include cleaning and washing with hot water [2,3,11,12,13], with hot water and solvent (acetone-hexane) to remove the pulp [14], or hot treatment by solvent (acetone and/or hexane) followed by separation with ventilation of the stone from the pulp [4,5].To raise this bottleneck and allow a better exploitation of OP, it would be more relevant to apply a non-polluting fractionation process in order to produce contrasted powders whose properties will be adapted to composite applications.

In this context, dry fractionation appears as a promising alternative for the production of pulp-rich and stone-rich fractions without any consumption of water nor chemicals and therefore generate very few wastes [15,16]. Dry fractionation processes combining grinding and sorting technologies (air classification, electrostatic separation or sieving) have attracted a great deal of attention due to their use in various fields including electronic waste valorization, food industry, pharmaceuticals, ceramics and materials science [17,18]. Dry fractionation has been widely applied to several lignocellulosic biomasses with promising results, namely wheat straw [15,19], rice straw [17], bagasse [16] and rapeseed press cake [20]. To our knowledge, these processes have never been applied to the treatment of OP.

In this context, the present study aimed at exploring the use of dry fractionation to produce pulp-rich and stone-rich fractions with the highest purity and yield from crude OP, that could be further used as raw resources for the production of fillers for biocomposites. Different milling modes (compression, shearing and impact, friction) were considered and combined by selecting appropriate equipment (knife milling, impact milling, ball milling). The ground powders were then separated in interesting fractions by sorting steps (sieving or electrostatic fractionation). Some intrinsic properties (color, biochemical composition, surface free energy and thermal stability) of the resulting fractions were characterized and discussed in relation to the applied dry fractionation route. These properties were characterized in such a way (i) to assess the efficiency of the sorting route and (ii) to estimate the potentiality of using obtained fractions as raw resources for the production of fillers, with a focus of the estimated affinity with polymer matrices. A wet separation process was tested for comparison. Finally, in view to draw an optimized biorefinery scheme for the conversion of OP, different added-value routes of valorization were proposed for each resulting powders, besides to their potential application as fillers in biocomposites.

2. Materials and methods

2.1. Materials

Olive pomace was obtained from the oil extraction of the *Chemlal* variety using a traditional press system. It was kindly supplied by local olive producers in the region of Azazga (Tizi-Ouzou) in north-central Algeria, in February 2016. This residue was composed of partially crushed stones, pulp and skin. Olive pomace was dried in ambient air for three days and then, stored at 4 °C and shielded from the light until its use. Only one batch of olive pomace was considered in the present study.

Sulfuric acid, arabinose, xylose and glucose (SIGMA-ALDRICH), formamide, diiodomethane (Acros Organics, Geel, Belgium), ethylene glycol (Aldrich chemical Co. Inc., Milwaukee, USA) and glycerol (Merck, Darmstadt, Germany) were used for characterization of olive pomace fractions.

2.2. Fractionation of olive pomace

Fractionation of crude olive pomace was carried out to produce pulp-rich and stone-rich fractions following different routes (Fig. 1). All the obtained fractions came from the same initial olive pomace batch.

2.2.1. Wet fractionation

200 g of crude OP were mixed with 1 L of distilled water and left during 24 h at room temperature. Then, this suspension was placed under agitation at 400 rpm and 30 °C for 24 h. The mixture was first sieved through a 1 mm sieve in order to separate the humid stone-rich fraction from the humid pulp-rich fraction. The residual liquid fraction was centrifuged at 10,000 rpm during10 min in order to separate the pulp-rich fraction from the liquid effluent. The two obtained fractions were dried in an oven at 50 °C during 24 h and were designated as wS (stone-rich fraction) and wP (pulp-rich fraction) (Fig. 1).

2.2.2. Dry fractionation

The crude OP was first ground using a knife milling (SM 300, Retch, Germany) with a grid size of 4 mm, and then passed through a second grinding with a grid size of 2 mm to obtain the fraction F0. Then, two types of sorting were tested in order to separate the pulp from the stone, *i.e.* sorting according to the particle size by sieving (route A1), sorting according to the particle surface charge by electrostatic separation (route A2). Given the crumbly character of the pulp tissue that can be easily mechanically detached from the stone, another sorting route has been investigated, *i.e.* friction (route B) using mild conditions of ball milling without preliminary grinding of crude OP (Fig. 1).

2.2.2.1. Sorting by sieving (route A1). 200 g of F0 sample were passed into a ROTEX mechanical sieve through a 0.8 mm mesh for 10 min. Two fractions were obtained. The first one contained the particles with a diameter greater than or equal to 0.8 mm and corresponded to the stone-rich fraction (dS1) while the fraction constituted of particles with a size smaller than 0.8 mm represented the pulp-rich fraction (dP1).

2.2.2.2. Electrostatic sorting (route A2). 200 g of F0 were further ground using impact milling (Hosokawa-alpine, type UPZ, Augsburg, Germany) with a grid size of 0.3 mm. Resulting fine particles displayed a median diameter, measured by laser granulometry (d_{50}), of about 100 μm. A pilot-scale TFS (TEP System, Tribo Flow Separations, Lexington, USA) was used for the electrostatic fractionation (EsF), using fine particles as starting material. This technology is based on the separation of particles according to their surface properties (chemical composition and charges), in which lignocellulosic particles are trained in a charging