Novel Low-Cost Biosorbents of Phenolic Compounds from Olive Mill Wastewaters †

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Abstract: Olive oil is one of the most widely used oils in the world with economic importance for many countries. Olive oil extraction generates large amounts of solid (cake) and liquid waste (olive mill wastewater, OMW), which pose a chronic environmental problem due to their disposal on the landfill and water recipients. Thus, the research community is in search of techniques, individually or in combination, in order to detoxify waste. The common treatment methods belong to a one-dimensional waste treatment approach, which is depollution. A practical way to overcome the financial obstacle of depollution is to develop treatment schemes that combine depollution with recovery of valuable ingredients, such as phenolics. The toxicity of this waste is mainly due to the high concentration of phenolic compounds, which, however, have strong antioxidant activity, turning OMW into an economical raw material for the recovery of bioactive compounds. Adsorption is generally considered to be the most effective and low-cost method for the removal of phenolics. So far, few studies have been carried out using sorbents for the removal of phenolics from OMW. However, the relatively high initial cost and the need for a costly regeneration system render common sorbents less economically viable. Thus, many researchers have focused their efforts on optimizing adsorption process by development of novel, low-cost adsorbents with high adsorptive capacity, originating from food industry byproducts (biosorbents). The objective of this work is to provide a comprehensive summary of the biosorbents used for OMW management.

Keywords: olive mill wastewater; food wastes; adsorption; phenolic compounds; biosorbents; polyphenols recovery

1. Introduction

Olive oil is one of the most widely used oils in the world with economic importance for many countries. This agro-industrial activity generates large amounts of wastes such as solid (cake) and liquid (olive mill wastewater, OMW), which pose a severe environmental pollution.

There are two ways of olive oil extraction: traditional pressing and centrifugation systems, which are used over the last decades. As for centrifugation systems, there are two different types—the two-phase and three-phase systems. At present, more and more modern olive mills use the continuous three-phase extraction process system, which generates two streams of waste: a solid waste (~30% of raw material weight) called “orujo” or “olive cake,” and a liquid waste (50% of raw material weight) called “olive mill wastewater” (OMW) [1].
2. OMW Composition

In Mediterranean countries, more than 2.4 million tons of olives are produced every year, which correspond to 95% of total world production. Due to the fact that 90% of this amount is destined for olive oil production, the proper treatment of OMW is crucial [2]. As a waste, OMW consists of a dark liquid, with an intense odor, high turbidity, high organic content, and relatively low pH (Figure 1).

OMW is considered to be a great environmental hazard when not properly treated, as it contains high concentrations of organic compounds such as organic acids, lipids, alcohols, and polyphenols (Table 1).

According to literature, more than 30 phenolic compounds have been detected in OMW, the total concentration of which ranges from 0.5 to 24.0 g/L, depending on the processing system used for olive oil extraction [3]. Research on the phenolic profile of OMW shows that flavonoids represent 45–65% of the total phenolic content, while flavanols and proanthocyanidins consist of the main flavonoid subgroups [4]. In addition, hydroxytyrosol appears to be the most dominant phenolic compound in OMW, representing approximately 55–70% of total phenolic content [5].

3. OMW Treatment

There are several ways for OMW management (depollution), which can be divided into three categories: physical and physicochemical processes (thermal methods, flocculation, adsorption), biological processes (aerobic and anaerobic), and a combination of both. All aforementioned methods present the same financial obstacle, as the size of most olive mills is relatively small. Waste management schemes that combine depollution with the extraction of valuable compounds is a possible way of overcoming this financial burden. Consequently, the profit from the extraction of these compounds could compensate for the cost of waste treatment. In order to fractionate valuable compounds derived from OMW, processing methods have been employed in recent approaches. Phenolic compounds, dietary fibers, and squalene are considered to be the most popular constituents isolated from OMW.
4. Adsorption

The recovery of OMW polyphenols has been mainly studied on small scale and many methods have been used, either individually or in combination (membrane separation, extraction, adsorption, and chromatographic procedures). Out of all these methods, physical adsorption is thought to be the most economical and effective. The efficiency of the adsorption and desorption methods influence significantly the ability of such waste treatment applications to create profit margins. To date, only a few studies have been conducted on the recovery of OMW phenolic compounds using a variety of sorbent materials (Figure 2).

Figure 2. Adsorption capacities of various adsorbents for phenolic compounds [12].

5. Biosorbents

Although some of the sorbents mentioned above achieve sufficient adsorption capacities, the high initial and regeneration costs render these materials less economically viable options. Therefore, numerous studies have been focused on the optimization of adsorption methods utilizing innovative, low-cost, and highly efficient adsorbents generated from food industry wastes (biosorbents) (Table 2). Although most of these sorbents (biosorbents) constitute food industry by-products or agricultural wastes, they offer many advantages. The most important are their low cost, their availability, and the fact that they can be easily regenerated.

Table 2. Bioabsorbent materials for the selective adsorption of waste compounds.

| Biosorbent                        | Waste                                         | Reference |
|----------------------------------|-----------------------------------------------|-----------|
| Azolla                           | Polyphenols from olive mill wastewater        | [13]      |
| Banana peel                      | Phenolic compounds from olive mill wastewaters| [14]      |
| Nutshells                        | Phenolic compounds from aqueous solutions     | [15]      |
| Oil palm kernel shell            | Organic and inorganic pollutants in palm oil mill effluent (POME) | [16] |
| Olive pomace                     | Total phenols from olive mill wastewater      | [17]      |
| Olive stone and pulp             | Total phenols from olive mill wastewater      | [6]       |
| Pomegranate peel and orange juice by-product | Phenolic compounds from olive mill wastewaters | [18] |
| Pomegranate seeds                | Phenolic compounds from olive mill wastewaters| [19]      |
| Wheat bran                       | Phenolic compounds from olive mill wastewaters| [20]      |
| Wheat husk                       | Phenols from aqueous solution                 | [21]      |

Such adsorbent materials are banana peels, olive pomace, wheat bran, etc. Stasinakis et al. [17] investigated total phenol removal efficiency from OMW by several types of treated olive pomace...
(dried olive pomace, dried and solvent extracted olive pomace, and incompletely combusted olive pomace). Goud et al. [15] investigated the adsorption of phenols through the treatment of nutshells, whereas Achak et al. [14] used banana peel as a low-cost solution biosorbent for removing phenolic compounds from OMW yielding an 88% removal. The efficiency of pomegranate peels and orange juice by-product in removing the total OMW phenolics was investigated by Ververi and Goula [18], reporting a 93.1 and 89.5% removal, respectively. However, in general, little work has been done on the adsorption of phenolic compounds from OMW using novel low-cost biosorbents.

7. Conclusions

Olive oil extraction generates a variety of by-products. Most of these wastes are valorized as animal feed or discharged in the environment, posing a severe threat for the environment. The potential use of these by-products for the recovery of bioactive and health-promoting ingredients, such as polyphenols, is remarkable. On the other hand, food production also generates high amounts of by-products, which can be utilized for the adsorption of bioactive compounds from OMW. In this way, two by-products of the food industry can be utilized with the ultimate purpose of incorporating the extracted bioactive compounds as functional ingredients in novel food products. However, further studies are needed in order to fully evaluate the potential of these by-products for the extraction of phenolic compounds and investigate the optimum conditions of these procedures.

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