Peanut shell as new biosorbent of phenolic compounds from olive mill wastewaters

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Keywords: Adsorption, Biosorbent, Olive mill wastes, Peanut shell, Phenolics
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Olive-mill wastewater (OMW) is a characteristic by-product of olive-oil production and a major environmental problem in the Mediterranean area because of its high and toxic organic load and its low pH. Phenolic compounds are the major contributors to the toxicity of olive mill wastewater. However, these phenolic compounds possess strong antioxidant properties that can turn olive oil residues into an inexpensive source of natural antioxidants (Ena *et al*, 2012).

Generally, many studies on the recovery of polyphenols from OMW have been conducted on small scale and several techniques are used individually or in combination (membrane separation, extraction, adsorption, and chromatographic procedures). Among them, adsorption is generally considered to be the best effective and low cost method. So far, few studies have been carried out using sorbent materials for the removal of polyphenolic compounds contained in OMW. The most popular and widely used adsorbent material for treatment of OMW is activated carbon. However, the relatively high initial cost and the need for a costly regeneration system make the above sorbent 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). Many natural materials have been used as biosorbents for phenol removal, like rice husk, tamarind nutshell, jute stick, avocado kernels, tobacco residues, cereal by-product, pistachio-nut shell ash, coconut shell, and wheat husk. As far as OMW phenols are concerned, Stasinakis *et al* (2008) investigated phenols removal efficiency from OMW by several types of treated olive pomace (dried olive pomace, dried and solvent extracted olive pomace and dried, solvent extracted and incompletely combusted olive pomace). Singh *et al* (2008) investigated the adsorption of both phenol and 2,4-dichlorophenol through the acid treatment of coconut shells, whereas Achak *et al* (2009) used banana peel as a low-cost biosorbent for removing phenolic compounds from OMW yielding an efficiency of 88%. However, in general, little work has been done on the adsorption of phenolic compounds from OMW using novel low cost biosorbents.

Commodity crops, such as peanuts, generate considerable quantities of shells each year, which have little or no value. Peanut shells are low in density and high in volume and are used in animal feed or burned for energy. There have been several reports that peanut shells can be converted into activated carbon and used to absorb various metal ions and organic compounds using sulfuric acid as the activant. The purpose of this work is to investigate the efficiency of peanut shells as biosorbent for removal of phenolic compounds from OMW.

Peanut shells used in this study were collected from a local market in Thessaloniki. The shells were dried at 110 ^{o}C for 1 h, grinded, sieved to obtain particle sizes below 125 μm, and stored in glass containers. The morphological characteristics of peanut shells were observed by scanning electron microscopy (SEM) (Figure 1).

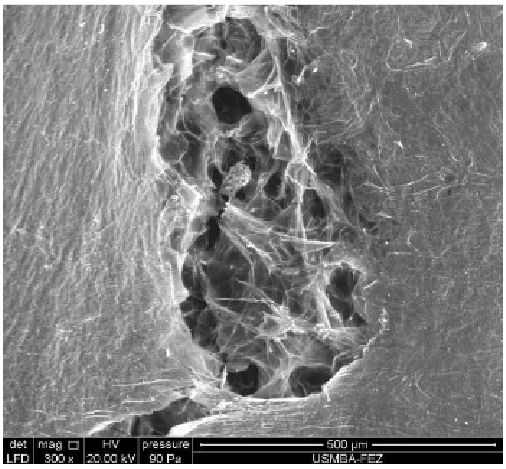

Fig. 1. SEM image of peanut shells.

Initially, the equilibrium time was investigated and afterwards, the effects of sorbent mass concentration (1–3 g/100 mL), solution's pH (2–12), and initial sorbate concentration (50–500 mg/L) on total phenols uptake were studied in batch experiments.

Desorption studies were also used to further aid in elucidating the mechanism of adsorption. If the adsorbed compound on the solid surface can be desorbed by water, the attachment is by weak bonds. If alkaline water (pH 12) is needed, then the adsorption is by ion exchange, whereas if organic acids, like acetic acid, are the most efficient for desorption, then the adsorption is held by the adsorbent through chemisorptions. In addition, the experimental equilibrium data were analyzed using linearized forms of Langmuir and Freundlich isotherms. Using the equilibrium coefficients obtained at different temperatures, various thermodynamic parameters have been calculated. Finally, chemical and thermal regeneration experiments were also performed to investigate whether treated biosorbents could be reused after regeneration.

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