## Low cost biosorbents of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies

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Olive mill wastewater (OMW) is the main liquid effluent of the olive oil production process. OMW is a major environmental problem, because of its high and toxic organic load. Many studies on the recovery of polyphenols from OMW are conducted on small scale and several techniques are used individually or in combination. These techniques largely comprise membrane separation, extraction, adsorption, and chromatographic procedures.

Among them, physical adsorption method is generally considered to be the best effective, low cost, and most frequently used method for the removal of phenolic compounds. Most conventional adsorption plants use activated carbon. Both chemical and thermal regeneration of carbon are expensive, impractical on a large scale, produce additional effluent, and result substantial loss of adsorbent. Thus, many researchers have focused their efforts on optimizing adsorption by development of novel low-cost adsorbents with high adsorptive capacity. The abundance and availability of natural materials, biosorbents, and waste materials from agriculture make them good sources of raw material for activated carbon. Application of waste materials is gradually becoming of great concern, because these wastes are unused resources and can cause serious disposal problems.

In this work two food wastes - pomegranate peel and orange juice by-product – were used as biosorbents for removal of phenolic compounds from OMW. Orange juice by-product is abundant, cheap, and readily available. It is largely composed of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments, and other low molecular weight compounds. As far as the pomegranate peels are concerned, pomegranate has been well documented for its potential health benefits. Since the juice yield of pomegranates is less half of the fruit weight, very large amounts of by-product wastes, such as peels, are formed every year. Orange juice by-product was washed with distilled water, boiled, dried in an oven, and milled, and the powder was passed through standard ASTM sieves. Pomegranate peels were dried in an oven, milled, and used for ultrasound-assisted extraction of phenolic compounds. After extraction, the solid residue of the filtration was dried and passed through sieves.

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transport process. Adsorption kinetics has been proposed to elucidate the adsorption mechanism. In this work, in order to investigate the mechanism of phenolic compounds adsorption on the two investigated biosorbents and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction, the capability of pseudo-first-order and pseudosecond-order kinetic models was examined (Goud et al., 2005). Since neither the pseudo-first-order and pseudo-second-order kinetic model can identify the diffusion mechanism, the interparticle diffusion model was also used to analyze and elucidate the diffusion mechanism (Banat et al., 2004). Different parameters, such as sorbent mass concentration, temperature, solution's pH, initial sorbate concentration, and sorbent particle size (classes passed through standard ASTM sieves) were analyzed for their effects on kinetic models constants.

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 (Achak et al., 2009). 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 such as  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  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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