

# Batch and continuous adsorption of phenolic compounds from olive mill wastewater using a novel low cost biosorbent

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Olive mill wastewater (OMW) is the main liquid effluent of the olive oil production process. OMW is an aqueous, dark, foul smelling turbid liquid with high organic content (57.2-62.1%) and acidic character (pH 2.2-5.9) (Dermeche *et al*, 2013). The disposal of OMW in nearby aquatic receivers is one of the biggest problems of the olive oil production process, as it causes high phytotoxicity with strong negative impact on soil quality and plant growth, due to its high concentration of phenolic compounds (up to 80 g/L), low pH, and toxic fatty acids. This problem has been extensively investigated during the last years without finding a solution, which is technically feasible, economically viable, and socially acceptable.

The present trend is towards further utilization of OMW by recovering useful byproducts such as polyphenols, using several techniques conducted on small scale, individually or in combination. Among them, physical adsorption, in which the interaction between the solid surface and the adsorbed molecules has a physical nature, is generally considered to be the best effective, low cost, and most frequently used method for the removal of phenolic compounds. Many adsorbent materials have been used for OMW treatment, such as soil, bentonite, zeolite (Santi *et al*, 2007) and activated carbon (Bertin *et al*, 2004). Although activated carbon is the most popular and widely used adsorbent material for OMW treatment, the relatively high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent (Achak *et al*, 2009).

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. Such adsorbent materials are orange peels, banana peels, pomegranate peels, olive pomace, and wheat bran (Namasivayam *et al*, 1996; Stasinakis *et al*, 2008; Achak *et al*, 2009; Ali *et al*, 2013; Achak *et al*, 2014).

Pomegranate (*Punica granatum* L.) is one of the oldest known edible fruit that contains the highest concentration of total polyphenols in comparison with other fruits studied. Pomegranates are rich in aril, the percentage of which ranges from 50 to 70% of total fruit and comprises of 78% juice and 22% seeds (Mohagheghi *et al*, 2011). According to Eikani *et al* (2012), pomegranate seeds show average contents of about 37–143 g/kg of fruit. Due to the large annual production of pomegranate seeds as a by-product of the juice and concentrate industries, the seeds could have more beneficial applications in industries instead of being used as animal feed or in commercial cosmetic products. In this work, pomegranate seeds were used as biosorbent for removal of phenolic compounds from OMW.

Pomegranate seeds 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. Initially, batch experiments took place, in order to determine the optimum adsorption conditions, investigating the equilibrium time and afterwards the effects of sorbent mass concentration, temperature, solution's pH, initial sorbate phenolic concentration, and sorbent particle size on total phenols uptake (Fig. 1). Different adsorption isotherms (Langmuir and Freundlich isotherms) were used to find out most suitable models describing the experimental findings. In order to investigate the mechanism of phenolic compounds adsorption on the investigated biosorbent and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction, the capability of pseudo-first-order and pseudo-second-order kinetic models was examined. 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. The examined process parameters 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

For continuous adsorption experiments, a column was packed with a known mass of pomegranate seeds using different sorbent's particle sizes. Diluted OMW with different total phenols concentrations was delivered up flow to the column using a peristaltic pump at various flow rates. To obtain breakthrough curves, samples were periodically collected from the top of the column and analyzed for residual concentration of total phenols. The effects of the process variables on adsorption yield were studied. Finally, pomegranate seeds were thermally (at 100, 150, 200, and

250°C) and chemically (99% methanol and 4N sodium hydroxide) activated, in order to investigate the adsorbent activation effect on total phenols uptake.

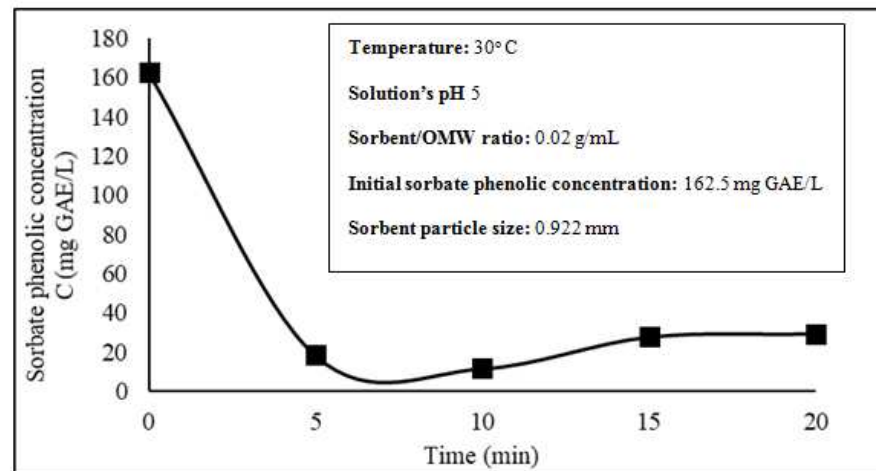


Figure 1. Sorption of phenolic concentration on pomegranate seeds at specific process conditions.

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