

Adsorption - desorption of phenolic compounds from olive mill wastewater using a novel low cost biosorbent

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Olive mill wastewater (OMW) is a 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). OMW is the main liquid effluent of the olive oil production process and its disposal in nearby aquatic receivers is one of the biggest problems of the olive oil production, as it causes high phytotoxicity with strong negative effect on the environment such as the alteration of the soil quality and the threat of plant growth. The main reason of these effects is 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 concerns further utilization of OMW by recovering useful byproducts such as phenolic compounds, achieved using several techniques individually or in combination. Among them, physical adsorption is considered as the best effective, low cost and most used method for the OMW polyphenols removal. Physical adsorption relies on the interaction between the solid surface and the adsorbed molecules, which has a physical nature. The adsorbent materials which have already been used for OMW treatment are bentonite, zeolite, and soil (Santi *et al.*, 2007). Activated carbon is the most popular and widely used adsorbent material for OMW treatment. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent (Achak *et al.*, 2009).

Thus, researchers have focused on optimizing the adsorption process by development of novel, low-cost adsorbents with high adsorptive capacity, originating from food industry byproducts. These adsorbent materials are called “biosorbents” and some of these are pomegranate, banana and orange 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 a fruit cultivated from ancient times. Pomegranates are rich in aril (seeds), the percentage of which ranges from 50 to 70% of total fruit (Mohagheghi *et al.*, 2011) and contain the highest concentration of total polyphenols in comparison with other fruits. Due to the large annual production of pomegranate seeds as a by-product of the juice industries, the seeds could have more beneficial applications than being used as animal feed or in cosmetology. In this study, pomegranate seeds were used as biosorbent for removal of polyphenols from OMW.

OMW was collected from a three-phase mill in Lesbos island and filtered. 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. Batch experiments took place in order to study the effects of equilibrium time, sorbent mass concentration, temperature, solution's pH, initial sorbate phenolic concentration, and sorbent particle size on total phenols uptake (Fig. 1) and to determine the optimum adsorption conditions. The experimental data were fitted in different adsorption isotherms (Langmuir, Freundlich, and Temkin isotherms) to find out the most suitable models describing the experimental findings. In order to investigate the mechanism of the process and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction, the capability of pseudo-first-order, pseudo-second-order, and interparticle diffusion model was examined. The investigated process parameters were analyzed for their effects on kinetic models' constants.

Pomegranate seeds were also chemically (99% methanol and 4N sodium hydroxide) (Fig. 2) and thermally (at 100, 150, 200, and 250 °C) (Fig. 3) activated, in order to investigate the adsorbent activation effect on total phenols uptake.

Finally, desorption studies in hydrochloric acid were also conducted using all three materials (not activated, thermally activated, and chemically activated) investigating the equilibrium time, the solution's pH and the solid to liquid ratio, in order to determine the optimum desorption conditions.

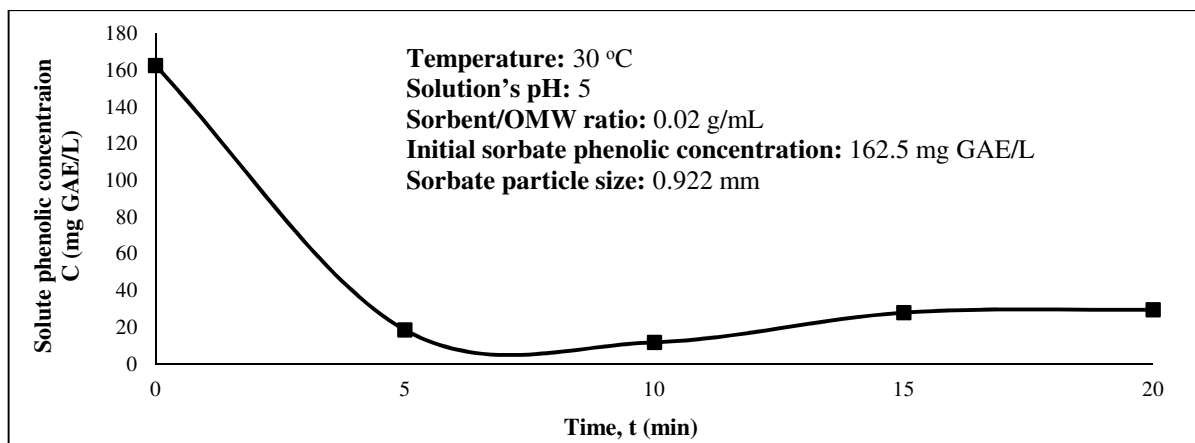


Fig. 1. Sorption of phenolic compounds on pomegranate seeds at specific process conditions.

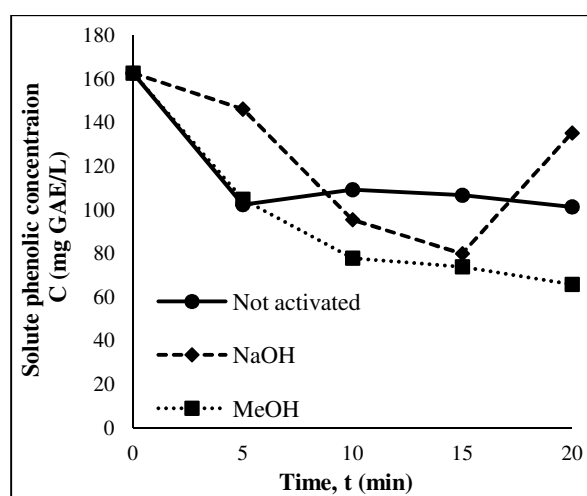


Fig. 2. Effect of chemical activation of pomegranate seeds on solute phenolic concentration.

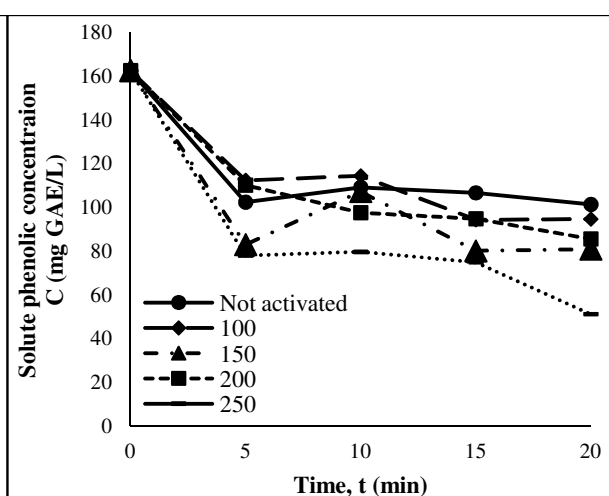


Fig. 3. Effect of thermal activation of pomegranate seeds on solute phenolic concentration.

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