

# Adsorption of phenolic compounds from olive mill wastewaters on spent coffee grounds: Isotherms, kinetics, pure phenols adsorption

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Olive oil is considered to be one of the most widely consumed oils worldwide, with economic importance for many countries, especially Mediterranean basin countries such as Greece. During olive-oil production, significant amounts of degradation-resistant organic matter and phenolic components with antimicrobial and phytotoxic properties are generated, rendering it a severe environmental threat.

Commonly, since there is an absence of an explicit regulation regarding olive mill waste discharge, the management of this liquid waste known as “Olive Mill Wastewater” or OMW consists of its disposal onto the soil or discharge in nearby aquatic receivers (Paraskeva and Diamadopoulos, 2006). Aiming to minimize environmental pollution, the research community has focused its efforts on the development of novel techniques regarding OMW depollution. Among them, adsorption is considered to be the most effective and low-cost method for the recovery of valuable compounds from OMW (Elgarahy *et al* 2019; Rahmanian *et al* 2014; Singh *et al* 2008). However, the prohibitive cost of commonly used adsorbents, as well as the need for their regeneration led researchers to the investigation and development of novel, inexpensive biosorbents originating from food industry wastes (Ververi and Goula, 2019).

The aim of the present study is the recovery of bioactive components from OMW using coffee industry by-products. Spent coffee grounds (SCG) are the primary solid by-product generated during brewing of coffee powder (Zuorro and Lavecchia, 2012). SCG is an inexpensive solid waste, which is abundant after coffee beverage production. According to Murthy and Naidu (2012) and Mata *et al* (2018), 1 ton of green coffee beans can generate up to 650 kg of SCG, while for the preparation of 1 kg of coffee beverage around 2 kg of wet SCG are produced.

Primarily, OMW was collected from a three-phase mill in Lesvos island and filtered. SCG were dried at 45 °C for 24 h to reach a moisture content of about 3% w/w and were used for the extraction of phenolic compounds. After extraction, solid residue of the filtration was dried. Batch adsorption experiments took place in order to study equilibrium time and the effects of initial sorbate phenolic concentration, sorbent mass concentration, temperature and solution's pH on total phenols uptake with a view to determine the optimum adsorption conditions. The maximum adsorption yield observed was 45.44% after 20 min, at 30 °C and pH of 8.0, with initial phenolic concentration of 162.5 mg/L and sorbent ratio of 0.02 g/mL. This value can be considered relatively low, however, in comparison with other methods that have been studied for OMW depollution, it can be characterized as satisfactory, especially due to the fact that SCG used were not thermally or chemically treated.

In order to investigate the mechanism of OMW adsorption, batch adsorption experiments of aqueous solutions of the main phenolic compounds of OMW were also conducted, both individually for each compound and as a mixture at concentrations at which they are found in OMW, thus simulating the phenolic content of this by-product.

The sorption of phenolics was also investigated as a function of concentration at 30°C in the range of 50–500 mg/L using 1 g of adsorbent, 50 mL of adsorbate solution, 20 min shaking time at a shaking speed of 300 rpm, and a pH of 8. Equilibrium relationships between sorbent and sorbate were described by sorption isotherms, the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. The experimental data were fitted to Langmuir, Freundlich, and Temkin isotherms.

In order to investigate the mechanism of phenolics adsorption on the proposed 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 model to describe the adsorption data was examined. The effects of the investigated process parameters on kinetic models' constants were also analyzed. Findings of the present study seem promising for future applications of SCG as biosorbent for the adsorption of bioactive and value-added compounds from food industry by-products.

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