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Utilizing solar energy for the purification of olive mill wastewater using a pilot-scale photocatalytic reactor after coagulation-flocculation

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ABSTRACT

This study investigated the application of a solar-driven advanced oxidation process (solar Fenton) combined with previous coagulation/flocculation, for the treatment of olive mill wastewater (OMW) at a pilot scale. Pre-treatment by coagulation/flocculation using $FeSO_4 \cdot 7H_2O$ (6.67 $g\,L^{-1}$) as the coagulant, and an anionic polyelectrolyte (FLOCAN 23, 0.287 $g\,L^{-1}$) as the flocculant, was performed to remove the solid content of the OMW. The solar Fenton experiments were carried out in a compound parabolic collector pilot plant, in the presence of varying doses of H_2O_2 and Fe^{2+}. The optimization of the oxidation process, using reagents at low concentrations ($[Fe^{2+}] = 0.08\,g\,L^{-1}$; $[H_2O_2] = 1\,g\,L^{-1}$), led to a high COD removal (87%), while the polyphenolic fraction, which is responsible for the biorecalcitrant and/or toxic properties of OMW, was eliminated. A kinetic study using a modified pseudo first-order kinetic model was performed in order to determine the reaction rate constants. This work evidences also the potential use of the solar Fenton process at the inherent pH of the OMW, yielding only a slightly lower COD removal (81%) compared to that obtained under acidic conditions. Moreover, the results demonstrated the capacity of the applied advanced process to reduce the initial OMW toxicity against the examined plant species (*Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*), and the water flea *Daphnia magna*. The OMW treated samples displayed a varying toxicity profile for each type of organism and plant examined in this study, a fact that can potentially be attributed to the varying oxidation products formed during the process applied. Finally, the overall cost of solar Fenton oxidation for the treatment of 50 m^3 of OMW per day was estimated to be 2.11 € m^{-3}.

1. Introduction

Olive oil production is one of the most important agricultural activities in the Mediterranean basin. According to Avraamides and Fatta (2008), there are approximately 750 million productive olive trees (*Olea europea* L.) worldwide, with the countries of the Mediterranean basin concentrating 97% of the world olive oil production. Although olive oil is a product of exceptional nutritional value, its production is associated

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with several adverse effects on the environment, mainly due to the formation of high amount of OMW (Badawy et al., 2009).

The physicochemical characteristics of OMW are rather variable, depending mainly on the cultivation soil, climatic conditions, olive variety, use of pesticides and fertilizers, degree of fruit ripening, harvesting time, and extraction process (Niaounakis and Halvadakis, 2006; Kallel et al., 2009). Nevertheless, OMW is characterized by high organic load (typically 130–150 g L^{-1} COD; 10–30 g L^{-1} DOC; 0.5–25 g L^{-1} phenolic compounds), high inorganic concentration, and acidic pH (Gernjak et al., 2004). According to the literature, the organic matter of OMW consists of a great variety of pollutants, including polysaccharides, sugars, phenolic compounds, tannins, polyalcohols, proteins, organic acids and lipids (El Hadrami et al., 2004; Canizares et al., 2007).

In Cyprus, olive oil production is one of the most traditional industries. According to data obtained from governmental sources, approximately 35 olive mills are registered in Cyprus, producing approximately 7500 tonnes oil per year. Water use in oil production is about four times the amount of oil produced, suggesting that Cyprus produces more than 25,000 tonnes per year of OMW (Anastasiou et al., 2011). In Cyprus, the most common practice for the management of OMW includes the use of evaporation ponds and the subsequent discharge of solids in landfills and/or on soil. While evaporation ponds offer a good way of reducing the liquid portion of the wastewater, they do not contribute in the reduction of its toxicity, while they simultaneously impart an odor problem to the areas where such waste is stored. Furthermore, evaporation results in the loss of large quantities of water, which is an important and limited resource in Cyprus. At the moment there is no European legislation regulating OMW disposal, and standards are left to be set by individual countries.

The problems associated with the OMW are mainly related to its toxic character due to the presence of phenolic compounds, which cannot be degraded by biological treatment (Martins and Quinta-Ferreira, 2011). The improper disposal of OMW into the environment, or to urban wastewater treatment plants, is prohibitive due to its potential threat to surface and groundwater, or due to its toxicity to microorganisms used in treatment plants. Despite being recognized as a hazardous residue, land disposal of OMW remains the most diffused approach along the Mediterranean basin (Justino et al., 2009). Phytotoxic effects on soil properties have been reported to occur when this waste is used directly as an organic fertilizer (Paredes et al., 2001). In addition, the acidic pH and the polyphenols' complexing abilities increase the solubility of heavy metals in the environment (Gernjak et al., 2004).

Through the years, researchers have tested a variety of technologies for OMW treatment. It is evident from the literature, that a single process cannot offer an efficient and viable solution to the problem. Conventional biological processes (aerobic or anaerobic) have shown moderate efficiencies in terms of OMW mineralization (Paraskeva and Diamadopoulos, 2006; Ouzounidou et al., 2010). Aerobic treatment of OMW by three microorganisms, namely *Geotrichum* sp., *Aspergillus* sp. and *Candida tropicalis*, led to an average reduction in terms of COD and total phenolic compounds of 52.5–62.8% and 44.3–51.7%, respectively (Fadil et al., 2003). Anaerobic processes have resulted in 60–70% of COD removal, while total phenolic compounds have been removed by 50–80% (Marques et al., 2001; El Hajjouji et al., 2008; Martinez-Garcia et al., 2009).

In addition to biological processes, various physicochemical processes such as coagulation/flocculation and membrane filtration and separation processes have also been employed for the OMW treatment. The use of direct flocculation with polyelectrolytes for the treatment of OMW showed that two polyelectrolytes, one anionic and one cationic, failed to yield separation, whereas a minimum dose of 2.3–3 g L^{-1} was required. Nearly complete reduction of solids was observed in subsequent analysis, while COD and BOD reduction was up to 55 and 23%, respectively (Sarika et al., 2005). The pre-treatment of OMW by means of coagulation/flocculation combining various inorganic materials and organic poly-electrolytes was investigated by Ginos et al. (2006). Combining lime or ferrous sulphate with cationic poly-electrolytes led to significant solids removal, while COD and total phenolic compounds (TP) removal varied between 10-40% and 30–80%, respectively. The reduction of OMW organic content was also attempted through the use of combined methodologies (i.e. physicochemical and biological). According to Dhaouadi and Marrot (2008), the integration of biological treatment with membrane filtration for the OMW treatment led to moderate COD abatement, depending on the dilution factor and the oxygen transfer to the mixed liquor contained in the membrane bioreactor (MBR).

Within this context, the application of advanced remediation strategies is required either to fulfill legislative requirements for direct disposal into landfills or, when economically wiser, to reduce toxicity and improve biodegradability to allow a posterior inexpensive bioprocess (Hodaifa et al., 2013). Advanced oxidation processes (AOPs) are known for their capability to mineralize a wide range of organic compounds. These processes are based on the *in situ* generation of very reactive and oxidizing free radicals, principally the hydroxyl radicals (HO•). The versatility of the AOPs is enhanced by the fact that there are many ways of producing HO•. During the last several years, AOPs have been extensively studied for the OMW treatment through ozonation (Beltran-Heredia et al., 2001; Canizares et al., 2007), photo-Fenton (Gernjak et al., 2004; Rizzo et al., 2008; Nieto et al., 2011; Hodaifa et al., 2013), TiO_2 photocatalysis (Gernjak et al., 2004; Badawy et al., 2009), electrochemical oxidation (Giannis et al., 2007; Chatzisymeon et al., 2009a; Belaid et al., 2013) and wet air oxidation (Chatzisymeon et al., 2009b). Mantzavinos and Kalogerakis (2005) presented a comprehensive review on the OMW treatment by the application of various AOPs. A process of particular interest is photo-Fenton, as it can be powered by sunlight with wavelengths of $\lambda < 580$ nm, thus lowering the process operational costs (Michael et al., 2012). From the engineering point of view, simplicity in both equipment and operation has postulated photo-Fenton system as one of the most economic alternatives for treating those effluents. In the literature, sufficient information can be found with regard to the OMW treatment using the Fenton reagent. Nevertheless, all the works so far have been carried out in laboratory-scale reactors. To the best of authors' knowledge, only two studies are available on the solar Fenton process application at a pilot scale (Gernjak et al.,