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Ion exchange system for the final purification of olive mill wastewater: Performance of model vs. real effluent treatment

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ABSTRACT

Olive mill wastewater (OMW) is a highly pollutant effluent which can be pretreated through an advanced oxidation process. OMW after this secondary treatment (OMW-2ST) presented high sodium and chloride concentrations, responsible for its high conductivity. In this context, two ion exchange (IE) resins were examined (Dowex Marathon C and Amberlite IRA-67) for final OMW-2ST purification. As this effluent is extremely seasonal and deteriorates within few days, the main parameters affecting IE process were previously optimized with lab-made model OMW-2ST. Then the optimum operating conditions were tested with real OMW-2ST. Evolution of conductivity was evaluated as a function of recirculation time to study the effect of resins disposition and resins dosages and compared with both OMW-2ST. Equilibrium was reached in 10 and 20 min for model and real OMW-2ST, respectively. Furthermore, continuous mode experiments were carried out in to investigate the evolution of conductivity as a function of operating time. Breakthrough time was lower for real versus model OMW-2ST (120 vs. 147.5 min). Minimum 10 g L^{-1} resin dosage ensured 74% and 78% removal efficiencies, thus fulfilling irrigation water legal requirements and rending the production system cost-effective and environmentally respectful. Finally, model OMW-2ST is confirmed as good simulating media to reproduce IE processes.

1. Introduction

Olive oil mill wastewater (OMW) generated by the olive oil production process is the main effluent of this industry, which derives from olives washing wastewater (OWW) and olive vegetation wastewater (OVW). The quantity and compositional characteristics of this effluent depend on several factors such as the variety of the olives, the meteorological conditions and the system of extraction used (Benitez et al., 1997; Raggi et al., 2000). In this work, the problem related to the reclamation of OMW from the two-phase-based system effluent (OMW-2) was investigated.

Regarding the physicochemical properties, what most characterizes this effluent is an acid pH value, black colour, very high chemical oxygen demand (COD) and high concentration of recalcitrant organic matter, such as phenolic compounds and tannins (Rozzi et al., 1998). On the other hand, inorganic compounds such as chloride, sulphate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are usually present in OMW-2 (Garrido Hoyos et al., 2002). The low pH of this wastewater, as well as the presence of phytotoxic and antimicrobial compounds and toxic fatty acids, make it difficult to directly reuse this wastewater. Therefore, the treatment of OMW-2 is a very crucial need for environmental protection and has been studied by several methods highlighting natural evaporation and thermal concentration (Paraskeva and Diamadopoulos, 2006; Annesini and Gironi, 1991), treatments with lime and

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clay (Aktas et al., 2001; Al-Malah et al., 2000), biological treatments (Ammary, 2005; Garrido Hoyos et al., 2002; Taccari and Ciani, 2011) composting (Cegarra et al., 1996; Papadimitriou et al., 1997; Bouranis et al., 1995) and physicochemical procedures such as coagulation–flocculation (Sarika et al., 2005; Martínez Nieto et al., 2011a; Stoller, 2009) and electrocoagulation (Inan et al., 2004; Tezcan Ün et al., 2008).

In our previous research works, OMW-2 was treated at a pilot scale by an advanced chemical oxidation process based on Fenton's reagent followed by a flocculation step and filtration in series through three different kinds of filtrating materials (Martínez Nieto et al., 2010, 2011b). OMW after this secondary treatment (OMW-2ST) presented a large reduction of phenolic compounds, COD and suspended solids. Nevertheless, the effluent stream exhibited high concentrations of dissolved monovalent and divalent ions, which cannot be removed by conventional physicochemical treatments.

Among physicochemical methods for water purification such as chemical reactions, electro-flotation, reverse osmosis and adsorption, ion exchange (IE) technology is very attractive because of the relative simplicity of application and due to the low cost and the effectiveness to remove ions from wastewaters, particularly from diluted solutions (Pintar et al., 2001; Valverde et al., 2006). The use of IE technique depends on several factors such as contact time, operating temperature, pH, flow rate, initial pollutant concentration and resin characteristics (Caetano et al., 2009).

IE resins have also found an increasing application in the drinking water treatment sector over the last few decades, especially when there is a high concentration of natural organic matter (NOM) in contaminated water since high percentages on the removal efficiency of NOM by IE process are found (Eilers, 2008).

In this sense, selective resins can reduce the residual concentration of sodium, total iron chloride and phenols below the maximum standard limits established by the Drinking Water Directive. Council Directive 98/83/EC set the maximum concentration in drinking water at 200 $\mu g\,L^{-1}$ for iron, 200 $mg\,L^{-1}$ for sodium and 250 $mg\,L^{-1}$ for chloride (European Commission, 1998). Phenols concentration is not established by the last European legislation. However, there is a previous directive in which maximum phenols level is set at 5 $\mu g\,L^{-1}$ (European Commission, 1980).

In this research study, IE is presented as an efficient alternative for the purification of OMW-2ST, where iron, sodium, chloride and phenols are the major pollutants. With the goal of achieving the parametric requirements for reusing the final treated effluent in the process or at least for discharge in public waterways, a bench scale study was undertaken to evaluate the performance of a combination of two IE columns working in serial connection. With this regard, the performance of two IE resins, that is, Dowex Marathon C, a strong-acid cation exchange resin, and Amberlite IRA-67, a weak-base anion exchange resin, was examined. Moreover, as one of the main issues of this kind of wastewater stream is that it is extremely seasonal (olive oil campaign lasts 90 days/year) and deteriorates very quickly (within a few days) model OMW-2ST was prepared in the lab. The main parameters affecting the proposed IE process were formerly optimized with the lab-made model OMW-2ST stream, and subsequently the optimum operating conditions were tested and contrasted with real OMW-2ST. Evolution of conductivity and pollutants concentrations were followed as a function of recirculation time (in recirculation mode) and operating time (in continuous mode) and compared with both OMW-2ST, and the efficacy of the model OMW-2ST as simulating media of real OMW-2 prepared was also corroborated.

Table 1 – Physicochemical characteristics of OMW-2ST.

Factor	Value
pH	7.78–8.17
Conductivity ($mS\,cm^{-1}$)	3.15–3.55
COD ($mg\,L^{-1}$)	120.5–226.6
Total phenolic compounds ($mg\,L^{-1}$)	0.39–0.98
[Cl^-] ($mg\,L^{-1}$)	875.83–1045.03
[Na^+] ($mg\,L^{-1}$)	534.01–728.71
Total [Fe] ($mg\,L^{-1}$)	0.04–0.4

2. Experimental

2.1. Model water solutions

Model water simulating pretreated OMW-2ST was prepared in the laboratory by dissolving reagent-grade sodium chloride, iron (III) chloride 30% (w/w) aqueous solution and phenol (all of them provided by Panreac) in double distilled water. These water solutions were prepared prior to the start of the experiments, stored at 4 °C and brought to room temperature before being used.

The physicochemical composition of the OMW-2ST effluent is reported in Table 1 (Ochando-Pulido et al., 2012a,b; Víctor-Ortega et al., 2014a). The desired concentrations for chloride and sodium were fixed at the highest values registered on average at the outlet of the OMW-2 secondary treatment: approximately 1050 $mg\,L^{-1}$ and 750 $mg\,L^{-1}$, respectively, whereas about 1 $mg\,L^{-1}$ and 0.4 $mg\,L^{-1}$ for phenol and total iron concentrations.

2.2. Real OMW samples

Wastewater samples were collected from different olive oil mills in the South of Spain, operating with the two-phase centrifugation system (OMW-2).

OMW-2 samples were conducted to the aforementioned secondary treatment thoroughly described in former works by the Authors (Martínez Nieto et al., 2011a,b; Hodaifa et al., 2013a,b), before being subjected to the final IE purification process. Chemical oxygen demand (COD), total phenolic compounds (TPh), sodium, chloride, total iron, electroconductivity (EC) and pH were measured in the outlet stream samples of the secondary treatment as well as of the IE system, respectively.

2.3. Ion exchange process

Strong-acid cation exchange Dowex Marathon C resin and weak-base anion exchange Amberlite IRA-67 resin, both provided by Sigma Aldrich, were used in this study. Their properties and specifications are reported Table 2.

Both resins present similar total exchange capacities. Dowex Marathon C presents styrene-DVB matrix whereas Amberlite IRA-67 matrix is based on a tertiary amine (see Table 2). On the other hand, it is worthy to point out that strong-acid cationic resin presents effective pH throughout the whole pH range (i.e. 0–14). However, effective pH range for the weak-base anionic resin is 0–7.

The bench-scale IE equipment, used in this research study, consisted on two IE columns operating in serial connection