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Comparison between different ion exchange resins combinations for final treatment of olive mill effluent

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ABSTRACT

Industrial wastewater is subjected to strict environmental legislation, thus making its adequate management a key issue. In this research work, the final purification of two-phase olive mill wastewater (OMW-2) was investigated through four ion exchange resins (a weak-acid cation exchange resin, a strong-acid cation exchange resin, a weak-base anion exchange resin and a strong-base anion exchange resin). Central composite design was used for the optimization of the IE processes. Results revealed that the only final treated OMW-2ST effluent fulfilling the legislated requirements for drinking water was the one from the combination of the strong-acid cation exchange resin and the weak-base anion exchange resin. The proposed IE process yielded up to 88% removal of these pollutants when the initial pH, operating temperature and flow rate were set to 5.1, 26.8 °C and 12.1 $L\,h^{-1}$, respectively. Under these conditions, the achieved concentrations for all contaminants in the final stream were maintained below the maximum established limits. Finally, high treated effluent volume recovery (28 L) could be achieved in continuous mode under the optimal operating conditions found, complying with standards for reuse in the production process.

1. Introduction

Nowadays, water resources are becoming insufficient in order to satisfy the increasing demand of water worldwide. Water scarcity specially concerns agricultural irrigation, which represents the largest demand of fresh water worldwide, that is, more than 70% of the total water consumption [1]. However, the possibility of using regenerated wastewater for irrigation purposes would solve this problem and bring very positive environmental and economic impacts.

In this regard, olive oil industry, which is currently one of the main agro-industrial activities in the Mediterranean Basin countries, generates one of the most highly polluted agro-industrial effluents known nowadays: olive mill wastewater (OMW). This effluent is mainly characterized by high organic carbon content, particularly phenols and polyphenols, which are highly polluting. OMW disposal into the environment causes severe deteriorations such as coloring of natural waters, serious threat to the aquatic life, pollution in surface and ground waters, alterations in soil quality, phytotoxicity and odour nuisance [2,3].

An average-sized modern olive oil factory currently generates 10–15 m^3 of OMW daily. Only in Spain, the main olive oil producer worldwide, this raises a total volume of more than 9 million m^3 of OMW per year, which represents a huge amount of this highly contaminant effluents. Furthermore, olive oil production is steadily growing worldwide and it is now an emergent agro-food industry in China and several other countries such as the USA, Australia and the Middle East. Hence, the treatment of OMW is becoming a task of global concern.

Chemical remediation strategies are thereafter required for the depuration of this wastewater [4–7]. In former works, a treatment process based on Fenton's reaction was optimized with the aim of removing the organic and phenolic pollutants of OMW-2. The treatment process comprises natural precipitation to remove coarse particles followed by Fenton-like advanced oxidation, flocculation–sedimentation and filtration through olive stones in series (secondary treatment, ST) [5,8,9]. However, high levels of monovalent ions, mainly sodium and chloride, as well as iron, are found in OMW-2ST, derived from the dosage of the catalyst and neutralizing agents during the secondary treatment [9,10]. In addition, a significant phenols amount above maximum legislated standard level (0.005 $mg\,L^{-1}$) [11] was present in this secondary-treated OMW-2ST effluent and iron concentration exceeded the maximum

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levels allowed by the European legislation for drinking water (0.2 mg L^{-1}) [12].

On the other hand, the measured electroconductivity (EC) values in the effluent at the outlet of the secondary treatment are well above the range 2–3 mS cm^{-1}, thus presenting hazardous salinity levels according to the standards established by the Food and Agricultural Association (FAO) with the goal of reusing the regenerated water for irrigation purposes [13].

Therefore, a tertiary treatment is necessary for final purification of OMW-2ST. With this regard, membrane technology has been employed in the last decades for final treatment of this effluent [14–17]. However, membrane fouling plays an important role in the industrial scale-up of this broad applied technology and, this drawback is especially relevant in the case of wastewater purification processes [15,18,19].

On the other side, novel IE resins developed over the past few decades have promoted this technology as a suitable separation and purification process for wastewater treatment [20–22]. In this sense, IE is considered a green and simple technology, capable of achieving high removal efficiencies and selectivity [20,21]. There are various studies focused on the use of IE resins for the elimination of sodium and chloride ions in aqueous media [23–25]. Also, several research works have been described in the literature for the removal of iron and phenolic species by means of IE technology [26–33].

In this research study, the final purification of OMW-2ST is addressed through different combinations of four IE resins: a weak-acid cation exchange resin, a strong-acid cation exchange resin, a weak-base anion exchange resin and a strong-base anion exchange resin. The main objective was the optimization of the final purification of OMW-2 by means of the different IE systems comprising two of these resins in serial connection (one cationic and one anionic).

Firstly, recirculation mode experiments were carried out to examine the impacts of the main operating parameters on the IE process performance – operating temperature, initial pH and flow rate – as well as the interactions among them. For this purpose, the IE processes base on the different IE resins were modelled by means of central composite design (CCD).

Subsequently, continuous experiments were performed under the optimum operating conditions found for each pair of resins in order to find the best IE resins combination for its application in the purification of OMW-2ST at industrial scale. Finally, water quality standards for reusing the purified olive mill effluent in the olive oil production process and thus reducing the environmental impact were checked.

2. Experimental section

2.1. Materials

In the present work, samples of OMW were taken from olive oil mills located in the South of Spain, which operate with the modern two-phase olive oil extraction procedure. Firstly, these samples were conducted to the secondary treatment thoroughly described in previous works by the Authors [9,10,15]. The effluent after the secondary treatment, hereafter referred as OMW-2ST, was the feed stream 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, following standard methods [34]. The physicochemical composition of the OMW-2ST samples is reported in Table 1.

Table 1
Physico-chemical characterization of OMW-2ST.

Factor	Value
pH	6.82 ± 0.55
Conductivity, mS cm^{-1}	4.35 ± 0.30
COD, mg L^{-1}	162.0 ± 1.2
Total phenolic compounds, mg L^{-1}	0.012 ± 0.001
[Cl^-], mg L^{-1}	1250 ± 3
[Na^+], mg L^{-1}	870 ± 5
[Total iron], mg L^{-1}	0.9 ± 0.1

Weak-acid and strong-acid cationic resins as well as weak-base and strong-base anionic resins Amberlite IRA-67 resins (Dowex MAC 3, Dowex Marathon C, Amberlite IRA-67 and Amberlyst A26, respectively) all of them provided by Sigma Aldrich, were used in this work in order to cover all kinds of IE resins. Dowex MAC 3 was conditioned in sulfuric acid while Dowex Marathon C was conditioned in hydrochloric acid solution. Then, both resins were washed with water before being used in the IE experiments. On the other hand, Amberlite IRA-67 and Amberlyst A26 resins were treated with sodium hydroxide solution and then were washed with water following the advice of the resin manufacturer. Typical physical and chemical characteristics of the used resins are described in Table 2.

2.2. Ion exchange equipment

Fig. 1 shows the flow diagram of the IE process. A bench-scale IE equipment was used to evaluate the performance of the combination of two IE columns operating in serial connection for the purification of OMW-2ST. The IE columns employed in this study were made of an acrylic tube with dimensions 540 mm height × 46 mm internal diameter. The columns are provided with a mobile upper retaining grid, which could be fixed in the column to adjust it as a fixed bed or a semi-fluidized bed. The IE device (MionTec) was equipped with a peristaltic pump (Ecoline VC-380) and a temperature-controlled thermostatic bath (Precisterm JP Selecta).

2.3. Recirculation IE experiments

The IE removal efficiencies of sodium, chloride, iron and phenolic compounds from OMW-2ST were addressed by performing IE experiments in recirculation mode. The flask containing the 2 L feed solution was magnetically stirred continuously during the whole course of the experiments. The contact time was varied from 0 to 60 min. The initial pH, operating temperature and flow rate ranges studied are reported in Table 3. Each experiment was carried out twice to check the reproducibility of the results.

The percent of removal efficiency of the contaminant species was defined as follows:

$$\%\ \text{Removal efficiency} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final species' concentration (mg L^{-1}), respectively.

2.4. Experimental design and optimization of IE operating parameters

In this work, the impacts of the main operating variables on the IE removal of chloride, sodium, phenols and iron ions in OMW-2ST was examined by means of experimental design for all the possible IE resins combinations. The proposed IE processes was modelled by means of CCD.

The application of experimental design techniques in IE process development can result in improved product yields, reduced process variability, closer confirmation of the output response to the nominal and target requirements and reduced development time