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Final purification of synthetic olive oil mill wastewater treated by chemical oxidation using ion exchange: Study of operating parameters

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ABSTRACT

In this research work, ion exchange (IE) is presented as a suitable option for purification of olive oil mill wastewater (OMW) previously treated by means of a secondary treatment (OMWST). This pretreatment consisted in Fenton-like oxidation process, followed by coagulation–flocculation and filtration through olive stones. The parametric requirements for drinking water production or at least for public waterways discharge were achieved using a combination of two IE columns working in series at bench scale. The IE resins used in this study were Dowex Marathon C and Amberlite IRA-67. The effect of contact time, operating temperature and flow rate on simultaneous removal of sodium, total iron, chloride and phenols (the major pollutant species in OMWST) were investigated. Removal percentages of sodium, chloride and total iron increased with incrementing the contact time. Equilibrium was obtained in about 30 min for all ions and ion concentrations values determined were lower than the maximum levels for drinking water standards. On the other hand, adsorption efficiencies of sodium, total iron and chloride ions were found to be not considerably affected by the operating temperature. The highest phenols removal percentage (around 100%) was obtained in the first minutes for 298 K and 10 L/h.

1. Introduction

Olive oil mill wastewater (OMW) generated by the olive oil production process is the main effluent of this industry. OMW derives from olives washing wastewater (OWW) and olive vegetation wastewater (OVW). Around 1.8 10^6 t of olive oil are produced annually worldwide and the Mediterranean countries are the major producers. For this reason, OMW represents a serious environmental problem in the Mediterranean basin and concretely in the southern European countries [1]. The amount of this effluent and its physicochemical properties are influenced by several factors such as the variety of the olives, the meteorological conditions and the extraction process [2].

In the two-phase-based system the volume of OVW yielded (OVW-2) is reduced by one third as water injection is used only in the final vertical centrifugation step. Most of the organic matter stays in the solid waste ("alpeorujo"). This waste contains more humidity than its equivalent from the three-phase system (60% in two-phase systems vs. 45% in three-phase ones, OVW-3) and therefore OVW-2 presents lower pollutants load [3]. In this work, the problem related to the reclamation of OVW-2 effluent was investigated.

In particular, what most characterizes this effluent is an acid pH value, black color, very high chemical oxygen demand (COD) and high concentration of recalcitrant organic matter, such as phenolic compounds and tannins [4]. This is one of the highest organic loads of known concentrated effluents, which is 100–150 times higher than that of domestic wastewater. On the other hand, inorganic compounds such as chloride, sulfate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are usually present in OMW [5].

The low pH of this wastewater, as well as the presence of phytotoxic and antimicrobial compounds and toxic fatty acids, makes it difficult to directly reuse this wastewater. Accordingly, the treatment of OMW is a very crucial need for environmental protection and has been studied by several methods such as composting, evaporation ponds, thermal, physicochemical and biological treatments, land spreading and membranes filtration [6–16].

In previous research works, OMW from two-phase continuous centrifugation process 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 [17,18].This depuration sequence

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achieved a large reduction of phenolic compounds, COD and suspended solids. Nevertheless, after this treatment OMW presented a significant concentration of dissolved monovalent and divalent ions, which cannot be removed by conventional physicochemical treatments.

The IE process comprises the interchange of ions between a solution and an insoluble solid, i.e., polymeric or mineral ion exchangers such as IE resins (functionalized porous or gel polymer), natural or synthetic zeolites, montmorillonite, clay, etc. In a wastewater treatment system undesirable ions in water supply are replaced with innocuous ions. Water decontamination consists of removal of ionic pollutants such as phosphate, chloride, nitrate, ammonia, which appear in various types of agricultural, domestic and industrial wastewaters, or heavy metals discharged in effluent from electroplating plants, metal finishing operations, as well as a number of mining and electronics industries [19]. Physicochemical methods of water purification such as chemical reactions, electro-flotation, reverse osmosis and adsorption may be under given conditions more effective than IE technology. However, the latter process is considered very attractive because of the relative simplicity of application and in many cases it has been proven to be an economic and effective technique to remove ions from wastewaters, particularly from diluted solutions [20,21]. The use of IE technique depends on various factors such as temperature, pH, flow rate, contact time, initial pollutant concentration and adsorbent characteristics [22].

There are many studies on the adsorption of metal ions on IE resins, which have been reported in literature. Several studies of selective removal of heavy metal ions by IE which include removal of Pb(II), Hg(II), Cd(II), Ni(II), V(IV,V), Cr(III,VI), Cu(II) and Zn(II) from water and industrial wastewaters have been carried out in the last years [23–26]. Otherwise, there are many reports on the use of IE in hydrometallurgical applications for the recovery or purification of metal solutions or for effluent treatment, including the primary recovery of gold, uranium and rhenium, and the purification of cobalt electrolyte to ensure high-purity metal [27].

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 the contaminated water, since high percentages on the removal efficiency of NOM by IE process are found [28]. Phenolic compounds can also be successfully removed from wastewaters by IE technology [29–32]. In case of phenols, Caetano et al. [22] evaluated a strong anion exchange resin (Dowex XZ), a weak anion exchange (AuRIX 100) and non-functionalized resin (Macronet MN200) to remove phenol from aqueous solution.

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 [33]. Phenol concentration is not established by any directive, but it is important to avoid it as much as possible as it is phytotoxic and recalcitrant to biological degradation.

To the best of our knowledge, there are no previous studies in literature reported on the use of IE technology for drinking water production from OMW. In this research study, IE is presented as an efficient alternative for purification of OMW previously treated by means of the secondary treatment above described (OMWST), where iron, sodium, chloride and phenols are the major pollutants.

With the idea of achieving the parametric requirements for drinking water production or at least public waterways discharge, and close the loop or zero-discharge in olive-oil extraction plant, a bench scale study was undertaken to evaluate the performance of a combination of two IE columns working in serial connection for the purification of OMWST. The aim of this work consists in investigating simultaneous removal of sodium, total iron, chloride and phenol species from synthetic water simulating OMWST using Dowex Marathon C and Amberlite IRA-67 resins. With this purpose, study the influence of several factors such as contact time, operating temperature and flow rate was carried out in a semi-batch IE system.

Table 1
Physicochemical analysis of OMW determined after secondary treatment (OMWST) [17,34].

Physicochemical properties	Parametric value
pH	7.78 – 8.17
Conductivity, mS/cm	3.15 – 3.55
COD, mg/L	121 – 227
Total phenols, mg/L	0.39 – 0.98
[Fe] Total, mg/L	0.04 – 0.4
$[Cl^-]$, mg/L	876 – 1045
$[Na^+]$, mg/L	534 – 729

2. Materials and methods

2.1. Model water solutions

All experiments were carried out using model water simulating pretreated OMWST prepared 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. Model 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 OMWST effluent is reported in Table 1 [17,34]. The desired concentrations for chloride and sodium were fixed at the highest values registered on average at the outlet of the OMW secondary treatment: approximately 1045 mg/L and 730 mg/L, respectively, whereas about 1 mg/L and 0.4 mg/L for phenol and total iron.

2.2. Ion Exchange system

Strong-acid cation exchange Dowex Marathon C and weak-base anion exchange Amberlite IRA-67 resins, both provided by Sigma–Aldrich, were used in this study. Their properties and specifications as reported by the suppliers are shown in Table 2. Dowex Marathon C is generally used for softening and demineralization applications. Otherwise, Amberlite IRA-67 is widely used for industrial water treatment systems as well as pharmaceutical, chemical and food processing industries.

A bench-scale IE equipment was used to evaluate the performance of a combination of two IE columns operating in serial connection for the purification of OMWST. IE columns employed in this study were made of an acrylic tube of 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

Table 2
Properties of Dowex Marathon C and Amberlite IRA-67 IE resins.

Properties	Dowex Marathon C	Amberlite IRA-67
Type	Strong-acid cation	Weak-base anion
Matrix	Styrene-DVB, gel	Tertiary amine
Ionic form as shipped	H^+	OH^-
Particle size	0.55–0.65 nm	0.5–0.75 mm
Effective pH range	0–14	0–7
Total exchange capacity	1.80 eq/L	1.60 eq/L
Shipping weight	800 g/L	700 g/L