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Ion exchange as an efficient pretreatment system for reduction of membrane fouling in the purification of model OMW

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HIGHLIGHTS

- Removal of sodium, chloride, iron and phenols from synthetic water simulating OMWST
- IE as efficient pretreatment for reduction of fouling on subsequent membrane process
- Sodium, chloride and iron IE was not significantly affected by operating temperature.
- Average efficiencies provided by the proposed IE system in the range 50–80%
- Cation exchange resin followed by anion exchange one yielded the highest efficiency.

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ABSTRACT

Membrane technology is becoming increasingly accepted in the field of wastewater reclamation, but pretreatments are needed to prevent membrane fouling that limits system performance and recovery. In this research work, ion exchange (IE) is presented as an efficient pretreatment for reducing membrane fouling in the purification of olive mill wastewater (OMW). No previous studies are available in scientific literature regarding the treatment of OMW by means of IE technology. OMW was previously conducted to a secondary treatment comprising chemical oxidation with Fenton's reagent, coagulation–flocculation and filtration through olive stones. Chloride, sodium, iron and phenols are the major pollutants in OMW after secondary treatment (OMWST). A bench-scale study was undertaken to evaluate the performance of two IE columns working in serial connection. Simultaneous removal of those pollutants from synthetic water simulating OMWST using Dowex Marathon-C and Amberlite IRA-67 resins was examined by studying the disposition order of both resins in semi-batch system, as well as operating temperature in batch and continuous mode. Results of continuous IE operation verify the patterns observed for the studied species in batch-run experiments. The IE system proposed, with average removal efficiencies (50–80%), will be contributed to reduce concentration polarization and membrane fouling.

1. Introduction

As water becomes scarce and treatment regulations more stringent, purification systems like membranes and ion exchange (IE) processes have drawn more attention because of their attractive separation capabilities. Reverse osmosis (RO) membranes are able to effectively remove most organic and inorganic compounds and microorganisms from raw water and have been applied to drinking water treatment and wastewater reclamation [1,2]. On the other hand, in order to produce water of superior quality like drinking water, the use of IE resins in desalination and wastewater reclamation has become more widespread. IE resins have been developed as a major option for pollutants removal in drinking water treatment [3] and wastewater reclamation over the past few decades [4–8].

Olive mill wastewater (OMW) is a hardly treated by-product generated during olive oil production which constitutes an important environmental problem, since its disposal into watercourses leads to deterioration of natural water bodies, pollution and environmental degradation [9]. This effluent is characterized by an acid pH value, black color, very high and variable chemical oxygen demand (COD) and major concentration of microbial growth inhibiting compounds, such as phenolic compounds and tannins (Table 1). Also inorganic compounds such as chloride, sulfate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are present in OMW [10]. Management of this pollutant effluent is of major importance nowadays, especially in the Mediterranean countries. In this sense, there are some studies concerning OMW treatment by means of membrane filtration processes [11–17]. As water treatment membrane

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Table 1
Characterization of OMW used in the oxidation experiments [23].

Parameters	OMW from Jaén	OMW from Granada
pH	7.24	6.32
Total solids (%, w/w)	0.24	0.83
Total suspended solids (%, w/w)	0.005	0.001
Ash, (%, w/w)	0.08	0.50
Electric conductivity (mS/cm)	2.08	1.17
$[Fe^{3+}]$ (mg/L)	126.4	7.7
Total phenols (mg/L)	44.0	50.6
BOD5 (mg O_2/L)	380.0	1100.0
COD (mg O_2/L)	1672.9	4137.2

systems increase in use throughout the world, pretreatment is needed to prevent fouling on membranes [17–22]. Phenols and some ions, like calcium and iron, are major foulants of membrane systems that cause severe fouling and limit system recovery [18,21].

In our previous studies, an efficient and novel secondary treatment based on an advanced chemical oxidation process which comprises Fenton's reagent was used to break down organic and inorganic compounds of OMW in the laboratory and on a pilot scale [23,24], followed by a flocculation–sedimentation step and filtration-in-series through olive stones as zero-cost filtration medium [25,26]. This depuration sequence succeeded to overcome the problem related to the presence of phenolic compounds and achieved very high reduction of COD and suspended solids concentration. Nevertheless, after this secondary treatment OMW presented a high concentration of dissolved monovalent and divalent ions, which cannot be removed by conventional physicochemical treatments.

IE is a separation process in which harmful or undesirable ions are removed from solution to the resin or other IE material and replaced by others which do not contribute to contamination of the environment, since in most cases the undesirable ion is changed by another one which is neutral within water bodies. The change continues until the ion exchanger achieves ionic equilibrium and then the capacity of the ion exchanger is exhausted and no exchange is possible any longer. After that, the IE column must be removed from service, regenerated and reused after the usage [27]. The method is technologically simple and enables efficient removal of even traces of impurities from solutions. The operational and installation costs of IE processes are sensibly lower compared with other wastewater treatment processes like membrane filtration or granular activated carbon (GAC) filtration process [8]. However, IE resins must be regenerated by chemical reagents when they are exhausted, a factor to be optimized to avoid causing secondary pollution. The uptake of ions by IE resins is rather affected by certain variables such as pH, temperature, flow rate, ionic charge, initial pollutant concentration and contact time.

Many studies on the adsorption of metal ions on IE resins such as Dowex A-1 [28], Duolite GT-73 [29] and NKA-9 [30] have been reported. There are several examples 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 [5,8,31]. Apart from that, 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 [7].

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 [3]. Phenolic compounds can also be successfully removed from wastewaters by IE technology [6,32–34].

Selective resins can reduce the residual concentration of iron, sodium, chloride and phenols, which are the major pollutants in the olive mill wastewater effluent after the secondary treatment (OMWST), to limits which are not harmful for membrane systems performance. On the other hand, IE resins can reduce wastewater salinity which is a main issue causing membrane concentration polarization and fouling problems. In this sense, IE is presented as an efficient pretreatment system for reduction of membrane fouling in the purification of OMW. The aim of this work was to examine the simultaneous removal of iron, sodium, chloride and phenols from synthetic water simulating OMWST using a Dowex Marathon C cation exchange resin and an Amberlite IRA-67 anion exchange resin, in serial connection. The present research work is focused on the disposition of the resins under study and the influence of the operating temperature, with the idea of implementing a combined system based on IE as pretreatment of a subsequent membrane process.

2. Experimental

2.1. OMW treatment

The secondary treatment of OMW consists of various stages: 1) Fenton-like oxidation, 2) flocculation–sedimentation, and 3) olive stones filtration.

2.1.1. Fenton-like oxidation

Olives and olive oil wastewaters were mixed in 1:1 (v/v) proportion in the laboratory to regulate the value of the organic load of OMW entering the depuration system and thus avoid fluctuations in the COD parameter. OMW was then conducted through a secondary advanced oxidation process consisting in chemical oxidation based on Fenton's reagent. OMW was pumped into a stirred reaction tank in which an oxidizing agent (hydrogen peroxide) and a catalyst (ferric chloride) were added as it is shown in Fig. 1. The best catalyst–regarding efficiency and low cost from among tested Mohr salt ($Fe(SO_4)_2(NH_4)_26H_2O$), ferric perchlorate and ferric chloride–and the best catalyst/oxidant concentrations ratio were studied, as well as the optimal operating conditions with regard to pH, stirring velocity and temperature [23,24].

2.1.2. Flocculation–sedimentation

Throughout the Fenton-like oxidation process, OMW pH fell spontaneously to values around 3.0–at which the reaction optimally occurred–owed to the addition of the catalyst. For this reason, a neutralizing agent (sodium hydroxide solution, 5 N) was added in a following stirred tank to the OMW coming out of the Fenton-like oxidation tank, adjusting its pH to neutrality (to pH values between 6.0–9.0, as regulations demand). This way, besides, the iron colloidal particles present in OMW due to the previous addition of the ferric catalyst became precipitated as iron hydroxide. Moreover, to attain rapid separation of the solid–liquid phases, several commercial coagulant–flocculants (QG-2001, QG-2002, DQGALFLOC-130H and Nalco-77171) were tested, leading to the formation of an iron-rich sludge which finally sedimented in a lamelar decanter. The sludge was recirculated to the oxidation tank to reduce the catalyst consumption. The optimum dosage of each flocculant was also studied [35].

2.1.3. Olive stones filtration

In our previous research studies, the profit of olive stones as zero-cost adsorbent medium was investigated in detail [25,26]. Using olive stones directly as adsorbent for metal ions, instead of more expensive materials, such as activated carbon, was stated as an economically and environmentally interesting alternative for this thereby product of the olive oil industry.

Besides, it is well known that the presence of iron is harmful to nanofiltration (NF) and RO membranes, as in its form of insoluble complexes with hydroxyl ions (ferric hydroxide) at neutral and alkaline pH, these large metal hydroxide molecules cannot easily pass through the membrane. As a result, they become deposited on the membrane surface, leading to cake enhanced concentration polarization, pore blockage and