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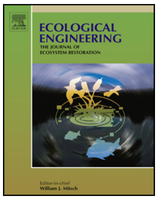

Impacts of integrated strong-acid cation exchange and weak-base anion exchange process for successful removal of saline toxicity from model olive mill wastewater

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ABSTRACT

In the present work, the performance of a fixed-bed ion exchange (IE) process comprising novel strong-acid cation exchange and weak-base anion exchange resins was examined for the removal of the ionic species, that is, sodium and chloride ions, responsible for the high salinity of olive mill wastewater from an olive mill working with the two-phase decanting technology exiting a primary–secondary treatment (OMW-2ST). Sodium IE efficiency was found to increase with an increment in the pH value up 5, whereas the optimum pH for chloride IE was equal to 1. Equilibrium behaviour of both species was accurately predicted by Langmuir isotherm, showing sodium uptake is 53.9% higher than for chloride. Sodium and chloride removal efficiencies decreased (from 97.0 to 74.0% and from 95.0 to 77.0%, respectively) when their initial concentration increased from 250 to 1000 mg L^{-1}. Finally, the integrated IE system in continuous mode ensured 80–90% average removal efficiencies for both ionic species and conductivity. IE efficiency loss below 5% after several regeneration cycles is a technical-economical key fact. The final treated effluent complied with the standards established by the Food and Agricultural Association (FAO) with the goal of reusing the regenerated water for irrigation purposes.

1. Introduction

Olive oil industry, which is widely known to be currently one of the main agro-industrial activities of the Mediterranean Basin countries, by-produces mainly two wastewater streams: the first one comes from the washing of the fruit, and is therefore called olives washing wastewater (OWW), and the second one is generated in the extraction of the olive oil, thus referred to as olive oil washing wastewater, OOW, a mixture of the olive-fruit humidity along with process-added water. These effluents are commonly known as olive mill wastewater (OMW).

In traditional olive oil mills working with the ancient batch press method, increasingly less used, between 0.4 and 0.6 m^3 of OMW were generated per ton of processed olives, while currently an average-sized modern olive oil factory leads to a sensibly higher amount of OMW: up to 10–15 m^3 of OOW daily, in sum to 1 m^3 d^{-1} of OWW (Table 1). Taking the case of 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 pollutant effluents. What is more, olive oil production is steadily growing worldwide and it is now an emergent agro-food industry in China and many other countries such as the USA, Australia and the Middle Earth. Hence, the treatment of the olive mill effluents is becoming a task of global concern.

In the two-phase olive oil extraction system, water injection is only practiced in the final vertical centrifugation step, and thus the volume of liquid effluent by-produced (OMW-2) is reduced by one third on average if compared to the amount required for the three-phase system (OMW-3) (Table 1). The two-phase system appears to be more ecological, and for this reason this system has been strongly promoted in Spain. Nevertheless, the three-phase technology is still surviving in other countries where the scarcity of financial support has not permitted the technological switch yet.

Purification of the effluents from both decanting processes is specifically addressed to be a hard task given their highly variable physico-chemical composition, which also depends on edapho-climatic and cultivation parameters, the type, quality and maturity of the olives (Niaounakis and Halvadakis, 2006; Paraskeva and Diamadopoulos, 2006; Hodaifa et al., 2008). OMW-2 and OMW-3 are among the heaviest polluted agro-industrial effluents, typically characterized by strong odor nuisance, acid pH, intensive violet-dark color and high saline toxicity, reflected by significant electroconductivity (EC) values (Table 2). In these effluents, major organic pollutants concentration is found, among which we should

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Table 1
Flow rates of the different effluents of continuous extraction processes (Mendoza et al., 1996).

Effluent flow rate, L kg^{-1}	3-phase extraction	2-phase extraction
Washing of olives (OWW)	0.06	0.05
Horizontal centrifuge	0.90	0
Vertical centrifuge	0.20	0.15
Cleaning	0.05	0.05
Total	1.21	0.25

highlight phenolic compounds, organic acids, tannins and organo-halogenated contaminants, mostly phytotoxic and recalcitrant to biological degradation. The presence of these substances would be hardly reflected by measurements of the biological oxygen demand (BOD_5), therefore the chemical oxygen demand (COD) seems to be more appropriate as a key parameter together with the total phenolic compounds (TPh) concentration (Table 2).

Uncontrolled disposal of these effluents causes serious environmental impacts, such as soil contamination, underground leakage and water body pollution (Hodaifa et al., 2008; Mendoza et al., 1996; Rozzi et al., 1988). However, at the moment there is no specific European legislation concerning the regulation of olive mill discharges, and standard procedures are delegated to individual countries. In spite of this fact, Directive 2000/60/CE highlights the necessity of conferring maximum protection to water and introducing the idea of the use of regenerated wastewater, thus encouraging the establishment of a legal framework capable of achieving this goal. Direct disposal of these effluents to surface waters or municipal sewage systems is thereof forbidden, and OMW cannot either be disposed directly for irrigation purposes as a general rule, though controlled partial discharge on suitable terrains is still allowed in some EU countries like Italy (Niaounakis and Halvadakis, 2006; Paraskeva and Diamadopoulos, 2006).

Until now, different treatments for the management and reclamation of OMW have been proposed (Niaounakis and Halvadakis, 2006). Biological treatment of OMW is a hard task and right now not applied on a large scale due to the resistance of OMW to biological degradation (Garrido Hoyos et al., 2002; Marques, 2001; Fountoulakis et al., 2002; Ammary, 2005; Taccari and Ciani, 2011). Other treatment processes have been developed in time, such as lagooning or natural evaporation and thermal concentration (Paraskeva, 2006; Annesini and Gironi, 1991 Annesini and Gironi, 1991), treatments with lime and clay (Aktas et al., 2001; Al-Malah et al., 2000), composting (Cegarra et al., 1996; Papadimitriou et al., 1997; Bouranis et al., 1995), physico-chemical procedures as coagulation–flocculation (Sarika et al., 2005; Martínez Nieto et al., 2011a; Stoller, 2009) and electrocoagulation (Inan et al., 2004; Tezcan Ün et al., 2006), advanced oxidation processes including ozonation (De Heredia and Garcia, 2005), Fenton's reagent (Martínez Nieto et al., 2011b; Hodaifa et al., 2013) and photocatalysis (Stoller and Bravi, 2010) and also electrochemical (Papastefanakis et al., 2010; Tezcan Ün et al., 2008 Cañizares et al., 2006) and hybrid processes (Grafias et al., 2010; Lafi et al., 2009; Khoufi et al., 2006; Rizzo et al., 2008).

Table 3
Water quality according to Food and Agriculture Organization (FAO).

EC, mS cm^{-1}	Water quality	Hazardous due to salinity
0–1	Excellent–good	Low–medium
1–3	Good–poor	High
>3	Poor–non-acceptable	Very high

Small size and geographical dispersion of traditional olive oil mills has made the management of OMW rather cost-ineffective. Nevertheless, these typical small olive oil mills are recently tending to group into bigger cooperatives. This fact can be an advantage for suitable treatment processes of these highly polluted effluents.

Within this framework, olive mill wastewater from an olive mill working with the two-phase decanting technology (OMW-2) was conducted to a primary–secondary treatment in previous work carried out in our research group by Martínez-Nieto et al., comprising Fenton's advanced oxidation, flocculation and filtration through cost-free olive stones in series (Martínez Nieto et al., 2011a,b, 2010). This depuration sequence succeeded to solve the problem related to the presence of phenolic compounds and achieved very high reduction of the organic pollutants load (COD), suspended solids and total phenolic compounds, also exploiting a by-product residue of the proper olive oil production process, olive stones.

However, conventional and advanced physicochemical treatments are not able to abate the high salinity exhibited by OMW-2, principally in form of dissolved monovalent species such as sodium and chloride ions, which after the proposed treatment is increased owed to the addition of the catalyst ($FeCl_3$) and neutralizing agent (NaOH) (Martínez Nieto et al., 2011b; Hodaifa et al., 2013). EC values in the primary–secondary-treated OMW-2 (OMW-2ST) are well above the range 2–3 mS cm^{-1}, thus presenting hazardous salinity levels according to the standard limits established by the Food and Agricultural Association (FAO) with the goal of reusing the regenerated water for irrigation purposes (Table 3).

In this regard, the use of ion exchange (IE) technology can be a potential solution for the reclamation of these highly contaminated OMW-2 effluents. IE exhibits a series of characteristics which make it more attractive than classic separation processes, that is, simplicity, effectiveness, selectivity, recovery and relatively low cost (Inoue, 2003; Savari et al., 2008). Moreover, resins beds are modular and have a small footprint, they can be tailored to remove monovalent and divalent ionic species apart from organic pollutants, they can also be successfully regenerated by using common acids and bases, and regeneration cycles can be minimized. What is more, IE processes can also be a suitable alternative to membrane technology for the final purification of OMW-2 (Ochando-Pulido et al., 2012a,b,b), given that IE processes do not require high pressure pumps, variable speed drives and attendant control systems (Bassandeh et al., 2013), thus implying lower capital and operating costs.

In the present research work, the performance of a fixed-bed IE process comprising novel strong-acid cation exchange and weak-base anion exchange resins was fully examined for the removal of the ionic species responsible for the high salinity of OMW-2ST.

Table 2
Characteristics of effluents of batch or continuous olive oil extraction processes.

Process	ID	COD, g O_2 L^{-1}	BOD_5, g O_2 L^{-1}	TSS, g L^{-1}	TPh, g L^{-1}	pH	EC, S cm^{-1}
Olives cleaning	OWW	0.8–2.2	0.3–1.5	8–18	0–0.1	5.5–6.6	2.5–3.0
Batch press	OMW-P	130–130	90–100	10–12	1.0–2.4	4.5–5.0	2.0–5.0
Three phase	OMW-3	30–220	5–45	5–35	0.3–7.5	3.5–5.5	2.0–7.9
Two phase	OMW-2	4–18	0.8–6.0	2–7	0.1–1.0	3.5–6.0	1.5–2.5

TSS: total suspended solids.