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Biological treatment performance of hypersaline wastewaters with high phenols concentration from table olive packaging industry using sequencing batch reactors

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ABSTRACT

Biological treatment of hypersaline wastewaters such as fermentation brine from table olive processing (FTOP), was carried out using four sequential biological reactors (SBRs). These wastewaters were characterized by conductivities higher than 90 mS cm^{-1} together with COD and total phenols concentration values of more than 15 g L^{-1} and 1000 mg L^{-1}, respectively. In order to increase the organic removal efficiency and to reduce the hydraulic retention time (HRT), extra nutrients were added and pre-treatment by adsorption was performed. Results showed that the COD/N/P relationship, in the FTOP, of 250/5/1 was appropriate for the biological process reaching COD removal efficiencies of around 80%. The FTOP adsorption pre-treatment with powder activated carbon for the reduction of phenols concentration to 400 mg L^{-1} led to a HRT reduction from 40 to 15 days, maintaining the COD and total phenols removal percentages around 78% and 97%, respectively. On the other hand, γ-*Proteobacteria* was the main bacterial class, representing around 74% of the microbial community in the reactors.

Introduction

Industrial activity related to olive processing is concentrated on Mediterranean countries such as Spain, Italy, Greek, Tunisia and Morocco [1]. The average world production of table olives, between 2010 and 2015, was 2,531,600 ton [2].

Table olive processing (TOP) is performed in three steps: (1) debittering; olives are submerged in a NaOH solution (1–2% w/v) during 8–12 h, and the natural olive bitterness is removed, because oleuropein is hydrolyzed. (2) Rinsing; to eliminate the alkali excess. (3) Fermentation; olives are submerged in brine (4–8% w/v) of NaCl for several months. During this time lactic fermentation is performed and the organoleptic properties of olives are improved [3]. Throughout the TOP, large quantities of wastewater (about 3.9–7.5 m^3 per ton of green olives) are produced [1]. Usually, these effluents are stored in evaporation ponds (risk of surface and groundwater contamination, bad odors . . .) or even discharged into the sea or rivers. Strict environmental regulations have led to the research on the appropriate treatment of this industrial wastewater.

Wastewater generated in the fermentation brine of table olive processing (FTOP) only represents 20% of the total volume within the global industry. Nevertheless, these effluents contribute to 85% of the global wastewater pollution [1,4]. Therefore, if FTOPs are treated separately, the overall management of wastewater will be improved.

The FTOP is an acidic effluent (pH around 4) with a very high conductivity (between 70–90 mS cm^{-1}) and high organic matter concentration (between 7 and 20 g L^{-1} in terms of chemical oxygen demand), which includes phenolic compounds in concentrations between 700 and 1500 mg L^{-1}. These variations are mainly due to the olive characteristics (variety, maturation degree . . .) and to the olive processing [5].

Unlike the biological treatment of olive oil mill wastewaters, which have been studied in many investigations [6,7], there are only a few authors dealing with the FTOP effluents. Some authors have reported results on the treatment of the global wastewater

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[8], the alkaline wastewaters [9,10] and the washing water [11]. However, there is a lack of results regarding FTOP biological treatment. There has also been very few works focusing on the removal of the chemical oxygen demand (COD) and phenolic compounds from other saline wastewaters. Moreover, the studies that have been carried out used simulated wastewater [12,13]. It is known that the biological treatment of hypersaline wastewater involves great difficulties [14–16], since high salt concentrations can produce plasmolysis and loss of cells activity. In the same way, hydrophobicity and settlement properties of the activated sludge will decrease. In addition, phenolic compounds can inhibit the biomass because of their bactericidal effect [17,18]. Thus, the reduction of phenol concentration before the biological treatment could enhance the process performance. For it, adsorption can be tested, since other authors reported successful results of this technique for phenols removal and other organic compounds like dyes from other wastewaters [19–25].

The aim of this work is to perform a direct biological treatment of FTOP wastewater in order to reduce the COD and phenol compounds. The previous biomass acclimation was already reported [26]. In that work COD removal efficiencies were around 88% and phenols were almost completely removed. However, to achieve these results a high hydraulic retention time (HRT = 40 days) was required. In the present work, two strategies were carried out to reduce the HRT to get an economically viable full-scale treatment: extra nutrients were added to the FTOP (nitrogen and phosphorous) and the concentration of COD and phenols in the FTOP were reduced by a previous adsorption with powder activated carbon (PAC).

Materials and methods

Wastewater

Fermentation brine was provided by a table olive packaging industry located in Comunidad Valenciana (Spain). Experiments were carried out with four fermentation brine samples, named from FTOP-1 to FTOP-4. The FTOPs were previously filtered in a 60 μm sieve in order to reduce the suspended solids concentration. Additionally, some FTOPs were treated with PAC and these samples were named FTOP-$_{PAC}$. Before their use, all wastewater samples were stored at 4 °C. Table 1 shows the main characteristics of the different samples of FTOP and FTOP-$_{PAC}$ wastewaters used in the experiments. The parameters were measured in triplicate and the average value has been presented. Filtration was necessary for PAC removal after the adsorption process, which eliminated suspended solids as shown in the table.

It can be observed that the FTOPs are acidic effluents. The pH in these five samples was 4.2 ± 0.4. FTOP-1, FTOP-2 and FTOP-2$_{PAC}$ had very similar conductivities, around 94 mS cm^{-1}, meanwhile this parameter decreased in FTOP-3$_{PAC}$ and FTOP-4$_{PAC}$ to 79 mS cm^{-1} (lower concentration of NaCl into the brine preparation). FTOP-2$_{PAC}$ was treated with the PAC to obtain a total phenols concentration of 400 mg L^{-1}. Similarly, FTOP-3$_{PAC}$ and FTOP-4$_{PAC}$ were treated with PAC to reduce the total phenols concentration to 200 mg L^{-1}. The adsorption process also reduced the COD considerably. Thus, COD values of 6710 and 5465 mg L^{-1} were reached. On the other hand, only FTOP-2 required additional nutrients to achieve the relationship COD/N/P of 250/5/1. The mass of urea and KH_2PO_4 required to meet the stoichiometric ratio of 250/5/1 and 10% in excess of this values was calculated.

The HPLC analysis of the FTOPs showed that the main phenolic compounds in all of the samples were hydroxytyrosol and tyrosol. These results agree with those reported by other authors [27,28]. Hydroxytyrosol concentration is explained by the acid and enzymatic hydrolysis of oleuropein. Tyrosol may be produced from the hydrolysis of ligstroside. The presence of other phenolic compounds such as caffeic, gallic, *p*-hydroxyphenylacetic, vanillic . . . , depend on the cultivar and olive maturation stage [29].

Analysis

The FTOP samples were characterized by the following analysis: pH, conductivity, soluble COD (filtered to 0.45 μm), total phenols (T.Ph), phenolic profile (analysis of simple phenolic compounds with HPLC), chloride (Cl^-), total nitrogen (N_T), total phosphorus (P_T), turbidity, suspended solids (SS) and volatile suspended solids (VSS).

The parameters measured in the effluents from the SBRs were: pH, conductivity, soluble COD (filtered to 0.45 μm), turbidity, T.Ph and phenolic profile. In the SBRs mixed liquor suspended solids (MLSS) and volatile suspended solids (MLVSS) were measured and the ratio MLVSS/MLSS was calculated.

The percentages of COD and T.Ph removed during the biologic treatment were calculated from experimental measurements and according to the following equations:

$$\text{COD removal}\,(\%) = \frac{\text{COD}_0 - \text{COD}_{\text{effluent}}}{\text{COD}_0} \times 100 \quad (1)$$

$$\text{T.Ph removal}\,(\%) = \frac{\text{T.Ph}_0 - \text{T.Ph}_{\text{effluent}}}{\text{T.Ph}_0} \times 100 \quad (2)$$

where COD_0 and $T.Ph_0$ were the concentration values (mg L^{-1}) for these parameters in FTOP and $COD_{effluent}$ and $T.Ph_{effluent}$ were the concentration (mg L^{-1}) for these parameters in the effluent.

Also, food-to-microorganism ratio (*F*/*M*) was calculated as an operating parameter of the SBRs (Eq. (1)) [30]:

$$F/M = \frac{\text{COD}_0 \times Q}{V_R \times \text{MLVSS}} \quad (3)$$

where Q is the daily wastewater volume fed to SBR (L day^{-1}), V_R was the volume reaction (L) and MLVSS was the mixed liquor volatile suspended solids (mg L^{-1}).

The pH and conductivity measurements were carried out with pH-Meter GLP 21+ and EC-Meter GLP 31+ (Crison), respectively.

Table 1
FTOPs characteristics.

Characteristics	FTOP-1	FTOP-2	FTOP-2$_{PAC}$	FTOP-3$_{PAC}$	FTOP-4$_{PAC}$
pH	4.0 ± 0.1	3.7 ± 0.1	3.7 ± 0.1	4.4 ± 0.2	4.5 ± 0.2
Cond. (mS cm^{-1})	94.2 ± 0.2	94.1 ± 0.1	94.1 ± 0.3	78.8 ± 0.3	79.0 ± 0.1
COD (g L^{-1})	17.70 ± 0.12	21.50 ± 0.08	16.72 ± 0.06	6.71 ± 0.02	5.47 ± 0.03
N_T (mg L^{-1})	365 ± 3	352 ± 2	320 ± 8	205 ± 12	247 ± 7
P_T (mg L^{-1})	75 ± 1	76 ± 2	65 ± 2	35 ± 5	23 ± 2
Cl^- (g L^{-1})	50.01 ± 0.25	44.93 ± 0.32	44.93 ± 0.12	38.48 ± 0.09	40.17 ± 0.11
T.Ph (mg TY L^{-1})	1109 ± 23	1550 ± 34	400 ± 12	200 ± 13	200 ± 4
SS (mg L^{-1})	936 ± 15	1237 ± 43	408 ± 21	250 ± 9	407 ± 11
VSS (mg L^{-1})	466 ± 8	511 ± 22	182 ± 12	117 ± 11	203 ± 9