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Pilot scale hybrid process for olive mill wastewater treatment and reuse

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ABSTRACT

A novel process has been developed at pilot scale for the treatment of olive mill wastewater (OMW), which combines electro-Fenton, anaerobic digestion and ultrafiltration. Application of electro-Fenton procedure in semi-continuous mode permitted high removal efficiencies of chemical oxygen demand (COD) (50%) and monophenolic compounds (95%). This pre-treatment was found to enhance the anaerobic activity of an up-flow anaerobic filter (300 l) significantly. In the bioreactor, COD removal efficiency of 75% was reached at a hydraulic retention time of 4.5 d and an organic loading rate of 10 g COD l^{-1} d^{-1}. The use of ultrafiltration technology as a post-treatment completely detoxified the anaerobic effluent and removed its high molecular mass polyphenols. An economic calculation of this treatment process revealed that a surplus of energy of 73.5 kWh could be recovered after the treatment of 1 m^3.

1. Introduction

Olive oil production is a highly important activity for the economies of the Mediterranean countries, constituting one of the major agro-industrial activities for countries as diverse as Italy, Spain, Greece, Turkey and Tunisia. The production process releases a notoriously polluting wastewater usually named olive mill wastewater (OMW). OMW is becoming a serious environmental problem, due to its high organic chemical oxygen demand (COD) concentration, phytotoxic properties and because of its resistance to biodegradation due to its high polyphenol [1,2] and organic content [3].

Due to the current lack of appropriate alternative technologies to treat OMW, much of the OMW in the Mediterranean area is discharged directly into rivers and the sea. At best it is stored in evaporation ponds, where anaerobic conditions are quickly established leading to malodours, breading of insects and risks of surface and groundwater contamination [4]. Also, reuse of the OMW by distribution in agricultural soils as an organic fertilizer was studied [5]. Unfortunately, the addition of such quantity of OMW causes significant shifts in the structure and the function of the microbial community, which in turn may influence the viability of the soil for agriculture. The effects of OMW on the biological and physico-chemical characteristics of the soil are well documented [6,7].

OMW treatment usually comprises a physico-chemical method aiming at the removal of organic matter from the liquid phase. This is generally done by means of chemical coagulation–flocculation [8] and membrane separation [9]. However, these processes suffer from serious drawbacks such as high cost, low efficiency and sludge disposal problems. Therefore, research efforts have been directed towards the development of efficient treatment technologies including various advanced oxidation technologies and biological processes.

Anaerobic digestion is usually the basic biological process for OMW treatment since it has many advantages compared to aerobic treatment. Yet, anaerobic digestion cannot deal with the high organic load of OMW that needs to be diluted several times prior to treatment, thus introducing serious cost and environmental implications. In addition to this, the presence of some classes of inhibitory and/or toxic compounds such as polyphenols and lipids makes OMW inappropriate for direct biological treatment [10].

Advanced oxidation processes (AOPs) such as Fenton's reagent, ozone, UV, UV/H_2O_2, UV/Fenton, and ultrasound, based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been used with an increasing interest due to their high oxidant power. These hydroxyl radicals have a strong oxidation potential that can achieve two alternative goals: the

Abbreviations: AF, anaerobic filter; BI, bioluminescence inhibition; BOD_5, biological oxygen demand; COD, chemical oxygen demand; GI, germination index; HMM, high molecular mass; HRT, hydraulic retention time; LMM, low molecular mass; OMW, olive mill wastewaters; TMP, transmembrane pressure; TSS, total suspended solids; VFA, volatile fatty acids.

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Table 1
Characteristics of settled raw OMW, EF-treated OMW after sedimentation (EF-Sed), anaerobic effluent (AEff), permeate from membrane having cut-off 25 kDa (P) and Tunisian discharge limits (TDL)

Parameters	OMW	EF-Sed	AEff	P	TDL
pH	5.20	6.50	8.17	8.30	6.5–8.5
Coloration	72 ± 5	25 ± 2	20.5 ± 3	5.3 ± 1.5	–
COD ($g\,l^{-1}$)	95 ± 5	45 ± 2	11 ± 1	5.3 ± 1	0.09
BOD_5 ($g\,l^{-1}$)	19 ± 2	22 ± 1	3.8 ± 0.4	1.8 ± 0.2	0.03
TSS ($g\,l^{-1}$)	15 ± 4	2.5 ± 0.7	1.5 ± 0.5	0	0.03
Lipids ($g\,l^{-1}$)	9.8 ± 1.2	0.7 ± 02	Not detected	Not detected	–
Polyphenols ($g\,l^{-1}$)	11.5 ± 1.6	2.5 ± 0.8	1.2 ± 0.4	0.5 ± 0.2	–
Monomers ($mg\,l^{-1}$)	2740 ± 50	876 ± 27	496 ± 12	159 ± 7	0.002

reduction of the COD content of wastewater up to the desired maximum allowable concentration value through the mineralization of recalcitrant pollutants and the enhancement of the biodegradability of treated effluents with the aim of making their subsequent biological treatment possible [11]. Recently, a new advanced oxidation process induced by electrochemistry was proposed as an alternative process. Electro-Fenton (EF) approach consisted of either adding ferrous iron or reducing ferric iron electrochemically with simultaneous production of hydrogen peroxide upon the reduction of oxygen on several electrodes [12].

This study reports on the development of a novel three-step method for the treatment of OMW at pilot scale. The first step of this method consisted of a semi-continuous electro-Fenton treatment to achieve oxidation of the toxic and recalcitrant organic compounds such as polyphenols. The second step consisted of an anaerobic biological treatment of the pre-treated wastewater using an anaerobic filter (AF) of 300 l capacity, for bulk COD removal and the biodegradation of phenols and most of the organic acids. The third step consisted of an ultrafiltration as a post-treatment for complete detoxification and color removal allowing water recovery and reuse for agricultural purposes. Microbial toxicity and phytotoxicity reduction capacity of each step of the pilot plant treatment were also investigated.

2. Materials and methods

2.1. Wastewater

Fresh OMW was obtained from a discontinuous olive oil processing plant located in Sfax (southern Tunisia). Table 1 shows the typical characteristic parameters of OMW from the region. This OMW is characterized by substantial organic matter content and high TSS content, resulting in an average total COD concentration of 95 $g\,l^{-1}$ and a TSS concentration of 15 $g\,l^{-1}$. Very high content of toxic compounds was reflected by the low value of BOD_5 in comparison with the COD value. The low biodegradability of this effluent was due to the presence of toxic polyphenolic compounds (11.5 $g\,l^{-1}$) and also the acid pH (5.2) (Table 1).

2.2. Description of the whole process

The complete pilot plant used in this study is shown in Fig. 1. Raw OMW was pre-stored in a 300 l static separator (D1) in order to remove suspended solids. Suitable H_2O_2 and H_2SO_4 (adjustment of pH) quantities were added in the first tank (T1). From this tank, OMW effluent was fed into the EF-reactor at a 9 $l\,h^{-1}$ rate of alimentation using a pump (P1). After 4 h of residence time, the EF-treated

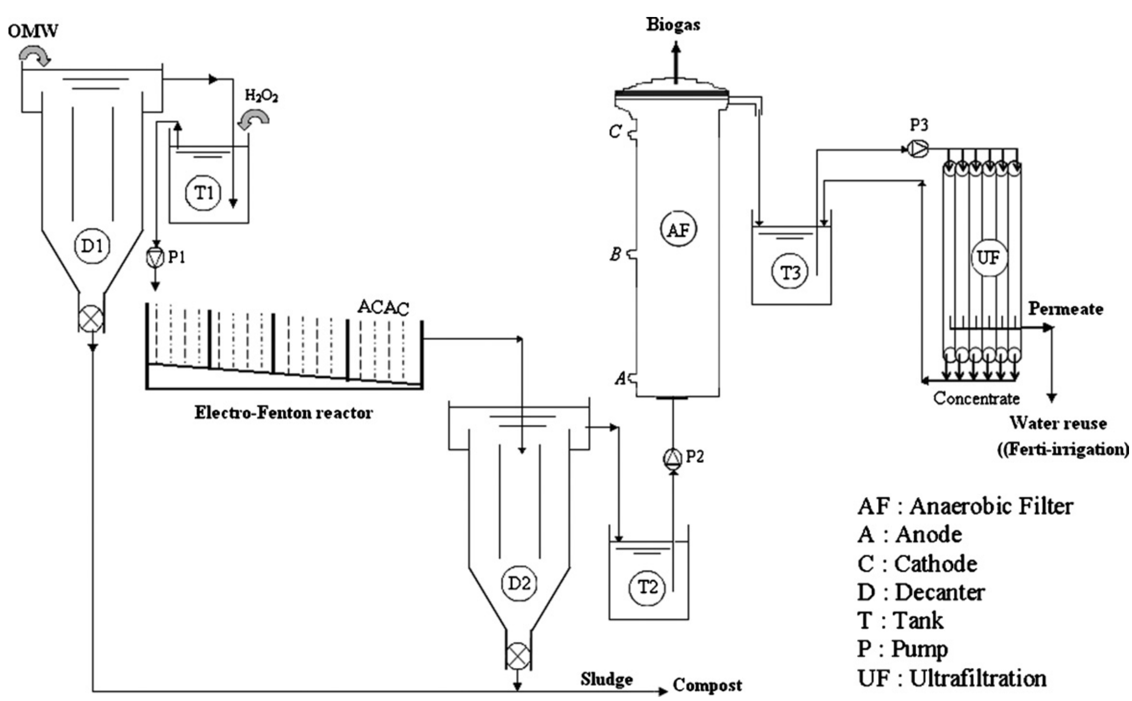

Fig. 1. Schematic flow diagram of pilot plant for OMW treatment.