



# Dephenolization, dearomatization and detoxification of olive mill wastewater with sonication combined with additives and radical scavengers



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## ABSTRACT

In this study, the effects of some additives [manganese (III) oxide ( $\text{Mn}_3\text{O}_4$ ),  $\text{Cu}^{+2}$ ,  $\text{Fe}^0$  and potassium iodate ( $\text{KIO}_3$ )] and some radical scavengers [sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), perfluorohexane ( $\text{C}_6\text{F}_{14}$ ) and *t*-butyl alcohol ( $\text{C}_4\text{H}_{10}\text{O}$ )] on the sonication of olive mill effluent wastewater (OMW) were investigated since the wastewaters of this industry are removed with low efficiencies. The maximum total phenol and total aromatic amines (TAAs) removal efficiencies were 88% and 79%, respectively, at 60 °C with only 150 min sonication. The maximum phenol removal was found as 98% with 19  $\text{mg L}^{-1}$  perfluorohexane and 5  $\text{mg L}^{-1}$   $\text{Fe}^0$  while the maximum TAAs removal was 99% with 16  $\text{mg L}^{-1}$   $\text{KIO}_3$ . Catechol, tyrosol, quercetin, caffeic acid, 4-methyl catechol, 2-phenylphenol (2-PHE) and 3-phenyl phenol (3-PHE) were detected as phenol intermediates while trimethylaniline, aniline, *o*-toluidine, *o*-anisidine, dimethylaniline, ethylbenzene and duren were identified as TAAs in the OMW. The maximum acute toxicity removals were 96% and 99% in *Vibrio fischeri* and *Daphnia magna*, respectively. Total phenol, TAAs and the toxicity in an OMW were removed efficiently and cost-effectively through sonication.

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## 1. Introduction

Agro-industrial wastewaters such as olive-oil mill effluent wastewaters (OMW) are amongst the most polluting industrial effluents and increasing concern has been expressed about their treatment and safe disposal, since they cause considerable environmental problems (coloring of receiving waters, a serious threat to aquatic life, pollution of surface and ground waters, alterations in soil quality, phytotoxicity and odor nuisance) particularly in the Mediterranean Sea region due to its high organic chemical oxygen demand (COD), polyphenol, aromatic amines concentration, and organic content [1–3].

The organic content of the OMW mainly consists of phenols, polyphenols, polyalcohols, sugars, tannins, pectins and lipids at concentrations as high as 150  $\text{g COD}_{\text{dis}} \text{L}^{-1}$ . The COD is also high, ranging from 45 to 130  $\text{g L}^{-1}$  in the OMW [4–6]. The concentration of phenolic acids in the OMW may vary from as low as 0.05–0.2  $\text{g L}^{-1}$  to as high as 10  $\text{g L}^{-1}$  depending on the type and origin of the effluent [7]. The CNMR spectra of the OMW showed that aliphatic carbon substituted by oxygen and nitrogen and including the methoxyl groups of aromatic ethers (50 and 110 ppm), double bonded or aromatic carbon (110 and 160 ppm) and carboxylic

carbon in ester or amide (160–200 ppm). The resonances observed between 40 and 105 ppm were generated by carbons bound directly to an oxygen heteroatom asin alcohols and carbohydrates or nitrogen as in amines, amino acids and amides (C–N, N–H) [8]. The aromatic region (110–160 ppm) can be divided into three parts, one between 110 and 130 ppm for unsubstituted aromatic carbons, another between 130 and 145 ppm for C-substituted aromatic carbons and the last between 145 and 160 ppm for N substituted aromatic organics [9,10].

Significant numbers of studies were focused on the efficient treatment of the OMW including various chemical, physical, physicochemical and biological treatments or combinations of them [2–7]. Over the past few years, various advanced oxidative processes, and many hybrid technologies, were used to completely or partially degrade the COD and the polyphenols [11]. Usually, the OMW is inappropriate for direct biological treatment and the alternative treatment technologies mentioned above did not give sufficient removals for pollution parameters (COD, phenol and polyphenols). Even though, all of these methods are practicable and effective, they cannot be used ubiquitously with high efficiency and may generate hazardous by-products [11].

Recently, significant interest has been shown in the application of ultrasound for the degradation of the OMW [12,13]. Sonochemical reactions are induced by directing high frequency waves by producing cavitation bubbles which creates extreme temperature,

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ending with pyrolytic fragmentation reactions [12,13]. Ultrasonic action produces radicals such as hydrogen, hydroxyl, hydroperoxyl radicals ( $H\cdot$ ,  $OH\cdot$ ,  $OOH\cdot$ ). The compression cycles generated by the ultrasound waves lead to the cavitation process responsible for chemical reactions: ultrasonic waves can induce the chemical process inside of the cavitation bubble [14,15]. Solute molecules that cannot diffuse to the cavitation bubbles are attacked by  $OH\cdot$  formed from the dissociation of water [11].

The researches performed for the sono-destruction of the OMW are limited to a few studies and lower removals were obtained for the pollutants: phenolic compounds like *p*-coumaric acid and *p*-hydroxybenzaldehyde in the OMW were sono-deconstructed at 150 W sonication power at 19 kHz throughout 240 min sonication. 45% and 47% sonochemical removals were observed for these polyphenols while the total phenol removal was 49% [4,5,15]. Vassilakis et al. [16] found seven phenolic compounds namely hydroxytyrosol, tyrosol, homovanillyl alcohol, protocatechuic acid, caffeic acid, 4-hydroxybenzoic acid, vanillic acid and 3,4-dihydroxyphenylglycol in the OMW with sonication at 21 kHz after 150 min sonication with  $COD_{dis}$  and total phenol removals of around 56% and 60%, respectively. Adrian et al. [17] found 56% and 58%  $COD_{dis}$  and phenol removals in a OMW with  $H_2O_2$ /sonication process while benzoic acid, cinnamic acid and resorcinol were detected as phenol derivatives. 14% phenol removal was achieved in a study performed by Atanassova et al. [12] at 150 W power at 80 kHz frequency after 240 min sonication while the phenol removal decreased to 6.03% with 10% NaCl. In the study undertaken by Entezari and Pétrier [18] 53% phenol removal was observed at 23 kHz frequency after 220 min sonication. The studies investigating the aromatic amines and color removals in OMW with sonication exhibited low aromatic amines (41%) and color removals (44%) [3,4]. Kallel et al. [5] exhibited low aromatic amines removals (45%, 58%) with 190 min sonication at a frequency of 56 kHz at a power of 340 W. Electrocoagulation which is one of the advanced treatment methods removed only 65% of polyphenols present in the OMW [19]. The operational costs are high in the decolorization and dephenolization of OMW using electrocoagulation processes [4–6,20].

As mentioned above the sonication studies on the treatment of OMW did not include the sonication mechanisms of the polyphenol and aromatic amines. In recent studies the contributions of the radical scavengers and of the additives on the removal of the polyphenol and aromatic structures in the OMW were not investigated. The novelty of this work is to detect the main sonication mechanisms for the polyphenol and aromatic amines at increasing sonication times (60, 120 and 150 min) and sonication temperatures (25, 30 and 60 °C). The destruction metabolites of polyphenols and aromatic amines in the OMW were identified. The effects of some radical scavengers ( $Na_2CO_3$ , perfluorohexane and *t*-butyl alcohol) and some additives ( $Mn_3O_4$ ,  $Cu^{+2}$ ,  $Fe^0$  and  $KIO_3$ ) on the removals of phenol and aromatic amines in the OMW were investigated in a sonicator with a power of 640 W and a frequency of 35 kHz. The techno-economical feasibility of sonication was correlated with other treatment systems. Furthermore, the toxicity of the OMW to *Daphnia magna* (water flea) and to *Vibrio fischeri* (bacteria) was investigated.

## 2. Results and discussion

### 2.1. Role of sonication intensity and power density on the removals of total phenol and TAAs removals in OMW

The maximum total phenol (88%) (Fig. 1a) and TAAs (79%) (Fig. 1b) removals were obtained at a sonication frequency of 35 kHz, at a sonication power of 640 W, at a sonication intensity

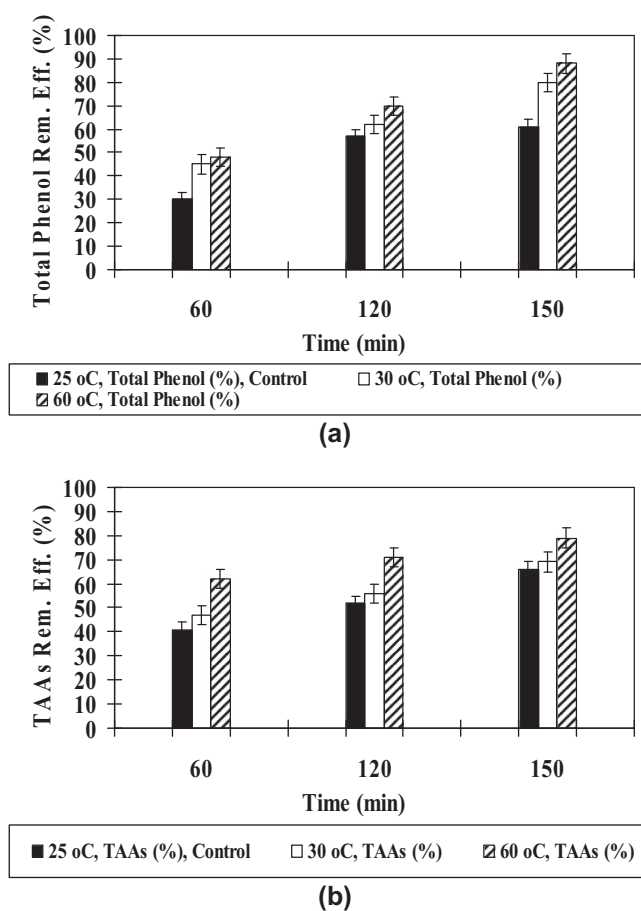


Fig. 1. Effect of increasing sonication time and temperature on the (a) total phenol and (b) TAAs removal efficiencies in OMW at an initial total phenol concentration = 2990 mg L<sup>-1</sup>, at an initial TAAs concentration = 1990 mg L<sup>-1</sup>, at sonication power = 640 W, sonication frequency = 35 kHz and at pH = 5.4 (n = 3, mean values with SD).

of 51.4 W cm<sup>-2</sup>, and at a specific energy of 11.5 kWh kg<sup>-1</sup> COD<sub>dis</sub><sup>-1</sup> at 60 °C after 150 min sonication time (Table 1) without some additives and radical scavengers.

### 2.2. Effect of increasing sonication time and temperature on the total phenol removal efficiencies in OMW

30%, 57% and 61% total phenol removal efficiencies were measured at an influent total phenol concentration of 2990 mg L<sup>-1</sup> after 60, 120 and 150 min sonication times, respectively, at pH = 5.4 and at 25 °C (Fig. 1a). It was found that the total phenol removal efficiencies in the OMW increased from 30% up to 57% as the sonication time was increased from 60 to 120 min at 25 °C. The maximum total phenol removal efficiency was 61% after 150 min sonication time at pH = 5.4 and at 25 °C. The total phenol removals increased by 15%, 5% and 19% after 60, 120 and 150 min, respectively, at pH = 5.4 and at 30 °C, compared to the control at 25 °C (Fig. 1a). 48%, 70% and 88% total phenol removals were found after 60, 120 and 150 min, respectively, at pH = 5.4 and at 60 °C (Fig. 1a). The maximum total phenol removal was 88% after 150 min at pH = 5.4 and at 60 °C. The Kruskal–Wallis test statistics showed that the effects of increasing sonication time (from 60 up to 120 and 150 min) and temperature (from 25 to 30 and 60 °C) on the phenol removals are not differed and these differences are not significant (Mann–Whitney *U*-test statistic = 2.98, *p* < 0.10) after 60 and 120 min at all increasing temperatures. Although the

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