

Treatment of olive mill wastewater by chemical processes: effect of acid cracking pretreatment

B. Hande Gursoy-Haksevenler and Idil Arslan-Alaton

ABSTRACT

The effect of acid cracking (pH 2.0; T 70 °C) and filtration as a pretreatment step on the chemical treatability of olive mill wastewater (chemical oxygen demand (COD) 150,000 mg/L; total organic carbon (TOC) 36,000 mg/L; oil-grease 8,200 mg/L; total phenols 3,800 mg/L) was investigated. FeCl₃ coagulation, Ca(OH)₂ precipitation, electrocoagulation using stainless steel electrodes and the Fenton's reagent were applied as chemical treatment methods. Removal performances were examined in terms of COD, TOC, oil-grease, total phenols, colour, suspended solids and acute toxicity with the photobacterium *Vibrio fischeri*. Significant oil-grease (95%) and suspended solids (96%) accompanied with 58% COD, 43% TOC, 39% total phenols and 80% colour removals were obtained by acid cracking-filtration pretreatment. Among the investigated chemical treatment processes, electrocoagulation and the Fenton's reagent were found more effective after pretreatment, especially in terms of total phenols removal. Total phenols removal increased from 39 to 72% when pretreatment was applied, while no significant additional (≈10–15%) COD and TOC removals were obtained when acid cracking was coupled with chemical treatment. The acute toxicity of the original olive mill wastewater sample increased considerably after pretreatment from 75 to 89% (measured for the 10-fold diluted wastewater sample). An operating cost analysis was also performed for the selected chemical treatment processes.

Key words | acid cracking, acute toxicity, chemical treatment, electrocoagulation, Fenton's reagent, olive mill wastewater (OMW)

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INTRODUCTION

Olive oil production is one of the most traditional agricultural industries in Mediterranean countries and of primary importance to their economies. Olive mill wastewater (OMW) is generated in huge quantities from the milling process in the range of 0.5–1.5 m³ per ton of olives depending on the extraction process (El Abbassi *et al.* 2013). The environmental characterization of OMW is highly variable depending on factors such as olive type, harvesting time, climatic conditions and the olive oil extraction process. OMW is characterized by its typical odour, dark, brownish colour, acidic pH, high salinity and considerably high organic matter content being mainly composed of flavanoids, fatty acids, pectins, tannins and polyphenols (Iamarino *et al.* 2009; Goncalves *et al.* 2012; Azaizeh *et al.* 2012). Its polluting load is typically estimated as 50–100 g/L biochemical oxygen demand (BOD₅), 80–200 g/L chemical oxygen demand (COD), 2–15 g/L TPh and 4.5–5.2 pH, which may

vary according to the olive processing method. The BOD₅ and COD values are typically 200–400 times higher than those of domestic effluent (Ahmadi *et al.* 2005).

Treatment of OMW is a common and serious problem in Mediterranean countries. The difficulties are mainly associated with the high and biologically difficult-to-degrade organic carbon content, seasonal production (typically in the December–March period) and decentralized disposal (10–100 m³/d) of OMW. To date several processes have been studied for the treatment of OMW, such as lagooning, evaporation, co-composting (Moraetis *et al.* 2011), chemical oxidation and coagulation (Yalili-Kilic *et al.* 2013), biological processes including anaerobic, aerobic and fungal treatment (Ntougias *et al.* 2013) as well as membrane technologies (El Abbassi *et al.* 2013). Additionally, advanced oxidation processes (Zorpas & Costa 2010) including catalytic ozonation, Fenton and Photo-Fenton processes have been

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proposed for OMW polishing and/or phenolics removal. More recently, electrochemical processes including electrocoagulation (EC) have been applied for the treatment of complex industrial wastewaters including dairy (Tchamango *et al.* 2010) and textile effluent (Merzouk *et al.* 2011) as well as OMW (Hanafi *et al.* 2011; Yahiaoui *et al.* 2011). In the above listed treatment studies significant drawbacks such as high operating (electric energy) and sludge management costs were evidenced and it was concluded that no single technology was capable of effectively treating OMW to the discharge standards (Erses-Yay *et al.* 2012). OMW treatment is particularly hindered by its heavy suspended organic matter and oil-grease content. These two parameters render chemical treatment of OMW without pretreatment rather difficult. Therefore, elimination of these two parameters from OMW should be an important step in order to increase its treatability. Depending on the characteristics of the wastewater, acid cracking, flotation or gravity settling could be applied as alternative pretreatment processes (Yalili-Kilic *et al.* 2013). Among them, acid cracking has proven to be the most suitable and effective for organic matter removal from OMW associated with oil-grease (Yangin-Gomec *et al.* 2007).

Among chemical treatment processes, coagulation, precipitation, EC and the Fenton's reagent seem to be more promising and feasible for OMW treatment, since these are relatively efficient, well-known and simple in operation. Furthermore, EC involves multiple removal mechanisms and hence could better cope with high-strength, complex wastewater (Li *et al.* 2011; Nieto *et al.* 2011). Fenton's reagent has also proved to be effective and feasible for the treatment of toxic and/or refractory industrial wastewater when compared with other advanced oxidation processes (Vedrenne *et al.* 2012). The target pollutants of the Fenton's reagent are mainly polar and soluble aromatic substances (Wadley & Waite 2004). Hydrophobic compounds and colloids present in OMW are not available to oxidizing agents but could principally be removed during the pH re-adjustment step of Fenton's treatment step; so-called Fenton's coagulation. Suspended and particulate organic matter present in OMW could be eliminated during filtration and coagulation. Hence, pretreatment of OMW is important for oil-grease and particulate organic matter removal to enhance the ultimate chemical treatment performance.

The motivation of the present experimental work was to examine acid cracking coupled with filtration as a pretreatment method to reduce the oil-grease and colloidal/suspended content of OMW prior to chemical treatment applications. For this purpose, the effect of acid cracking +

filtration pretreatment on lime precipitation, ferric chloride coagulation, EC and the Fenton's reagent was examined on the basis of environmental parameters being characteristic for OMW. Within this frame, changes in the major organic carbon components of OMW, namely COD, total organic carbon (TOC), total phenols (TPh), colour (absorbance at 400 nm) and acute toxicity, were investigated. An operating (running) cost analysis was also conducted for the treatability of OMW with acid cracking and the selected chemical processes.

MATERIAL AND METHODS

Characterization of the OMW

OMW was obtained from a three-phase olive mill extraction plant located in Bursa, Turkey and used as received. The characteristics of the OMW are presented in Table 1. From Table 1 it is obvious that the OMW is a high-strength wastewater, referring to its high COD (140,000–155,000 mg/L) and oil-grease (approximately 8,200 mg/L) contents. The corresponding TOC was 35,000–40,000 mg/L. The TPh was in the range of 3,800–4,200 mg/L. Other important parameters including suspended and dissolved solids were also relatively high as compared with most industrial effluents. Moreover, it is known that three-phase extraction mills

Table 1 | Environmental characterization of the studied OMW sample. The data ranges correspond to the standard deviation of average values

Parameter	Unit	Range
Total COD	mg/L	140,000–155,000
Total TOC	mg/L	35,000–40,000
BOD ₅	mg/L	37,000–40,000
TPh	mg/L	3,800–4,200
SS	mg/L	46,000 ± 2,000
VSS	mg/L	44,000 ± 2,000
Oil-grease	mg/L	8,200 ± 1,000
PO ₄ -P	mg/L	320 ± 50
TKN ^a	mg/L	1,064 ± 100
Conductivity	µS/cm	7,000–7,500
Colour ^b	cm ⁻¹	130–145
pH	–	4.8–4.9

^aTotal Kjeldahl Nitrogen.

^bAbsorbance at 400 nm.

create more pollution than two-phase extraction processes (El Abbassi *et al.* 2013).

Pretreatment with acid cracking

Acid cracking of OMW has already been reported in previous related work (Kiril-Mert *et al.* 2010; Yalili-Kilic *et al.* 2013). In the present study, acid cracking was also applied for a pretreatment purpose. The pH of the untreated OMW was adjusted to 2.0 with concentrated (0.13 M) H₂SO₄. Then, the OMW samples were heated to 70 °C and kept at this temperature for 60 min. In order to obtain efficient phase separation, the samples were delivered into a funnel for 30 min. Finally, the acid-cracked samples were filtered through 1,600 nm pore size filters to ensure removal of all colloidal/suspended fractions.

Chemical treatment processes

Pretreated OMW samples were subjected to chemical treatment and the results were compared to pretreatment and chemical treatment only. The experimental conditions of the chemical treatment processes were selected considering preliminary experiments and previously published work (Dogruel *et al.* 2009; Kiril-Mert *et al.* 2010; Yalili-Kilic *et al.* 2013). Coagulation with FeCl₃ (pH = 3.0; dose = 2,500 mg/L) and precipitation with Ca(OH)₂ (pH = 11.0; corresponding dose = 5,800–6,700 mg/L) were selected as the more conventional chemical treatment processes. EC was performed with stainless steel electrodes at pH 2.0, a current density of 50 mA/cm² at a temperature of 65 °C for 120 min. Fenton's reagent was applied at pH 2.0 and 3.0, with 10 and 20 mM Fe²⁺, and 100 and 200 mM H₂O₂ at 20 and 65 °C for 120 min. Fenton's reagent was quenched by increasing the pH of the reaction solution to 7.0–7.5 with 6 N NaOH solution. No residual (unreacted) H₂O₂ remained in the reaction solution after Fenton treatment.

Analytical procedures

All analytical procedures used for conventional wastewater characterization were accomplished in accordance with *Standard Methods* (APHA/AWWA/WPCF 2005), whereas the COD parameter was measured based on the ISO 6060 (1986) procedure. TOC analysis was carried out on a Shimadzu VCPN model carbon analyzer equipped with an autosampler.

The TPh concentration was determined based on the reaction of the samples with the Folin-Ciocalteu reagent

(Fluka) based on a test procedure developed by Box (1983). Colour was measured as absorbance in diluted OMW samples at 400 nm using a Novespec II/Pharmacia LKB colorimeter in 1 cm optical path length reusable glass cells. Acute toxicity of the diluted OMW samples was determined in accordance with the *Vibrio fischeri* bioluminescence inhibition test protocol ISO π 348-3 (2007) for an incubation period of 15 min.

RESULTS AND DISCUSSION

Pretreatment by acid cracking and filtration

As mentioned above, acid cracking was employed for pretreatment purposes, by adjusting the pH to 2.0, raising the temperature to 70 °C, separating the phases by a funnel and filtering the final sample through 1,600 nm-cutoff filters. Removal efficiencies obtained after each treatment step are shown in Figure 1. As is clear from Figure 1, not pH adjustment but thermal treatment had a significant impact on removal efficiencies. By heating the OMW sample to 70 °C, the oil-grease content was decomposed; however, obtained removal efficiencies did not increase due to inefficient phase separation. Therefore it was decided to separate the evolved OMW phases with a funnel. In this way, 54% COD, 38% TOC, 32% TPh, 94% oil-grease and 78% suspended solids could be removed. The filtration step had no significant effect on the studied environmental parameters. In the related scientific literature where OMW was subjected to acid cracking at ambient temperatures, 38, 23 and 99% removal efficiencies were reported for COD, TOC and oil-grease, respectively (Kestioglu *et al.* 2005). In another study, the effect of acid cracking was investigated at pH 2.0 and 46% COD, 37% TPh, 94% oil-grease and 92% suspended solids removals were achieved (Kiril-Mert

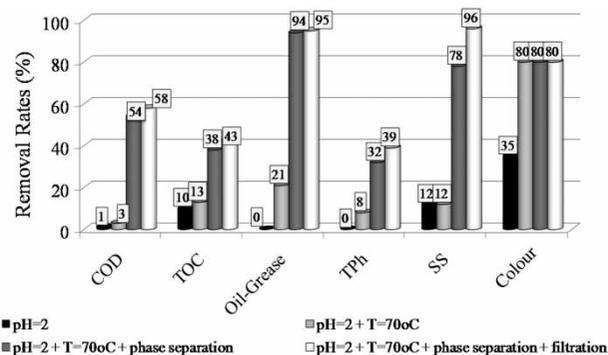


Figure 1 | Percentage removal efficiencies obtained after pretreatment of OMW.

et al. 2010). It was concluded that both acidic pH and elevated temperature were needed for significant organic matter removal during pretreatment with acid cracking.

Chemical treatment processes

Coagulation and precipitation

A dose of 2,500 mg/L FeCl_3 at pH 7.0 was recently found to be the most efficient treatment resulting in 57% COD, 45% TOC and 26% TPh removals (Gursoy-Haksevenler & Arslan-Alaton 2012). Considering the acidic pH (2.0) of the pretreated OMW and related work recently published (Yalili-Kilic *et al.* 2013), the effectiveness of FeCl_3 coagulation was investigated at pH 3.0 instead of pH 7.0 so as to minimize the operating costs associated with pH adjustment. The environmental characterization of OMW obtained after acid cracking pretreatment + FeCl_3 coagulation under varying conditions is summarized in Table 2. From Table 2 it is evident that similar efficiencies were observed for the chemical treatment processes. Removal efficiencies of 62% COD, 48% TOC, 47% TPh and 96% oil-grease were achieved. Consequently, a value of pH 3.0 was found to be appropriate for FeCl_3 coagulation in this study. No significant differences (5–8%) between the individual and combined treatments were observed. The effect of acid cracking on FeCl_3 coagulation of OMW was assessed at room temperature by Kiril-Mert *et al.* (2010). Removal efficiencies increased from 46 to 67% for COD and from 37 to 72% for TPh when the OMW sample was first subjected to acid cracking.

The effects of pretreatment and $\text{Ca}(\text{OH})_2$ precipitation were also examined. For this purpose, 6,700 mg/L $\text{Ca}(\text{OH})_2$ was added to OMW at pH 11.0. $\text{Ca}(\text{OH})_2$ precipitation carried out without acid cracking resulted in 56% COD, 47% TOC, 30% TPh and 95% oil-grease removals, whereas for combined treatment, removal efficiencies were 63% COD,

50% TOC, 47% TPh and 97% oil-grease. These findings indicated that, with the exception of the TPh parameter, no significant additional removals were achieved when the sample was subjected to pretreatment followed by lime precipitation. Moreover, considering the high operation pH and sludge formation rate of lime precipitation, acid cracking followed by lime precipitation was not found to be suitable for OMW treatment.

Electrocoagulation

EC experiments were conducted at the natural pH (5.0) of the sample and, due to the high conductivity of the original OMW (7,000 $\mu\text{S}/\text{cm}$), no external electrolyte addition was necessary for EC. When the current density was raised to 30 mA/cm^2 , reductions of 43% COD, 46% TOC and 21% TPh occurred after 30 min EC. In another study, EC was performed at a current density of 10–40 mA/cm^2 and a pH range of 4.0–9.0 with aluminium and stainless steel plate electrodes (Inan *et al.* 2004). When stainless steel electrodes were employed, 42% COD and 96% colour removals were obtained for OMW, while 52% COD and 96% colour removals were achieved using aluminium electrodes. Belaid *et al.* 2013 investigated the electrochemical treatment of OMW with platinumized titanium electrodes at a current density of 35 mA/cm^2 for 10 h; 55% COD and TOC removals were obtained indicating that significant organic matter removals could be reached with electrochemical treatment of OMW.

In the present study, considering earlier research and our own preliminary optimization experiments, OMW was subjected to EC but this time under relatively harsh operating conditions (pH 2.0; 65 °C; 50 mA/cm^2 and 120 min) after pretreatment. As is obvious from Table 3, EC resulted in 66% COD, 54% TOC and 72% TPh removals. When the removal efficiencies of the single and combined treatment processes are compared, it is obvious that the

Table 2 | Environmental characterization of the OMW obtained after acid cracking (AC), FeCl_3 coagulation and their combinations. Percentage relative removal efficiencies are provided in parentheses

Parameter	Unit	Untreated OMW (pH = 5.0)	FeCl_3 coagulation (pH = 7.0)	AC (pH = 2.0)	AC (pH = 2.0) + FeCl_3 coagulation (pH = 7.0) ^b	AC (pH = 2.0) + FeCl_3 coagulation (pH = 3.0) ^b
COD	mg/L	150,000	65,000 (57%)	63,000 (58%)	58,750 (61%)	57,500 (62%)
TOC	mg/L	40,000	21,820 (45%)	23,000 (43%)	21,250 (47%)	21,000 (48%)
Oil-grease	mg/L	8,200	7,550 (8%)	400 (95%)	367 (96%)	350 (96%)
TPh	mg/L	3,800	2,831 (26%)	2,300 (39%)	2,100 (45%)	2,000 (47%)
Colour ^a	cm^{-1}	131	25 (80%)	25 (80%)	25 (80%)	25 (80%)

^aAbsorbance at 400 nm.

^b FeCl_3 dose = 2,500 mg/L.

Table 3 | Environmental characterization of the OMW obtained after acid cracking (AC), electrocoagulation (EC) and their combinations. Percentage relative removal efficiencies are provided in parentheses

Parameter	Unit	Untreated OMW (pH = 5.0)	EC-1 ^b	AC (pH = 2.0)	AC (pH = 2.0) + EC-2 ^c
COD	mg/L	150,000	84,890 (43%)	63,000 (58%)	51,000 (66%)
TOC	mg/L	40,000	24,000 (46%)	23,000 (43%)	18,500 (54%)
Oil-grease	mg/L	8,200	7,820 (5%)	400 (95%)	325 (96%)
TPh	mg/L	3,800	3,012 (21%)	2,300 (39%)	1,065 (72%)
Colour ^a	cm ⁻¹	131	100 (25%)	25 (80%)	25 (80%)

^aAbsorbance at 400 nm.^bEC-1: pH = 5.0; T = 65 °C; A = 30 mA/cm².^cEC-2: pH = 2.0; T = 65 °C; A = 50 mA/cm².

effect of acid cracking was only significant for the TPh parameter. After applying EC to the acid-cracked OMW, additional removal rates of 8% for COD, 10% for TOC and 33% for TPh were obtained. Speculatively, the organic matter remaining after acid cracking was expected to be more polar and water soluble and hence more resistant to phase transfer-based treatment processes. Obviously, destructive (oxidative) treatment steps were required to remove the remaining, soluble organic matter present in OMW. Organic matter in particular phenolics was more effectively treated when acid cracking was followed by EC which featured several removal mechanisms including adsorption, coagulation, flotation, particle entrapment, as well as redox reactions (Holt *et al.* 2005).

Fenton's reagent

In a previous study (Gursoy-Haksevenler & Arslan-Alaton 2012), Fenton experiments were conducted at the original pH (5.0) of the OMW sample and at pH 3.0, known as the optimum pH of the Fenton's reagent (Chamarro *et al.* 2001). Fenton's reagent was applied at different Fe²⁺ and H₂O₂ concentrations in the range of 5–50 mM and 50–

200 mM, respectively. For OMW treatment with the Fenton's reagent, no differences were obtained in removal efficiencies at Fe²⁺ and H₂O₂ concentrations and pHs. Removal rates always remained below 15% for the parameters under consideration. This is not surprising, since rather poor removal efficiencies were expected during Fenton treatment of high-strength OMW with a significant particulate and high organic matter content.

Without acid cracking, Fe²⁺ and H₂O₂ concentrations were first selected as 10 and 100 mM, respectively (here called Fenton's Reagent-1; FR-1). For combined treatment (AC pretreatment + Fenton's reagent), removal efficiencies were obtained as 61% COD, 50% TOC and 49% TPh. In order to improve these treatment results, the Fenton process was accomplished after acid cracking and at pH 2.0 with 20 mM Fe²⁺ and 200 mM H₂O₂, at T = 65 °C for 120 min (namely, under relatively extreme conditions; here called Fenton's Reagent-2; FR-2). An improvement in removal rates was observed for pretreatment combined with FR-2, resulting which in 63% COD, 50% TOC and 61% TPh; that corresponded to additional removals of 5% COD, 7% TOC and 22% TPh (Table 4). A significant increase in treatment efficiency was obtained in particular for TPh which

Table 4 | Environmental characterization of the OMW obtained after acid cracking (AC), Fenton treatment and their combinations. Percent relative removal efficiencies are provided in parenthesis

Parameter	Unit	Untreated OMW (pH = 5.0)	Fenton's Reagent (pH = 3.0)	AC (pH = 2.0)	AC (pH = 2.0) + FR-1 ^b	AC (pH = 2.0) + FR-2 ^c
COD	mg/L	150,000	130,000 (13%)	63,000 (58%)	58,000 (61%)	56,000 (63%)
TOC	mg/L	40,000	36,000 (10%)	23,000 (43%)	20,000 (50%)	20,000 (50%)
Oil-grease	mg/L	8,200	8,000 (2%)	400 (95%)	320 (96%)	320 (96%)
TPh	mg/L	3,800	3,500 (8%)	2,300 (39%)	1,950 (49%)	1,480 (61%)
Colour ^a	cm ⁻¹	130	100 (25%)	25 (80%)	25 (80%)	25 (80%)

^aAbsorbance at 400 nm.^bFenton's Reagent-1: pH = 2.0; T = 25 °C; Fe²⁺ = 10 mM; H₂O₂ = 100 mM.^cFenton's Reagent-2: pH = 2.0; T = 25 °C; Fe²⁺ = 20 mM; H₂O₂ = 200 mM.

might be due to the improvement of the Fenton's oxidation that caused additional soluble organics removal (phenols, aromatic acids, etc.) present in the OMW after pretreatment. The effect on the Photo-Fenton process of coagulation using ferrous sulfate as the coagulant and an anionic polyelectrolyte as the flocculent was also examined by Papaphilippou *et al.* (2013). Photo-Fenton treatment was applied to coagulated samples for 240 min using 3.5 mM Fe^{2+} and 147 mM H_2O_2 at pH 3.0 under UV light radiation. The COD and TPh content of the coagulated sample could be reduced by an additional 73% COD and 40% TPh in that study. Similarly, COD removal efficiencies increased from 46 to 90% and TPh removals from 37 to 91% after applying Fenton's reagent to acid-cracked OMW in a study conducted by Kiril-Mert *et al.* (2010).

The COD, TOC, TPh and colour profiles for combined treatment of OMW are comparatively displayed in Figure 2. According to Figure 2, the major removal occurred in the pretreatment step with 58% COD and 43% TOC abatements, associated with the removal of the oil-grease and particulate organics present in the OMW. As mentioned above, the chemical treatment processes had no positive effect on COD and TOC removals, since only 5–10% additional removals could be achieved. Overall COD and TOC removals achieved were 66 and 54%, respectively, after application of EC and Fenton's reagent which could be attributed to the OMW characteristics and differences in the removal mechanisms of the selected treatment process. Only for the TPh parameter did removal efficiencies increase considerably: from 39 to 61% and 72% when the pretreated (acid-cracked) OMW was additionally subjected to Fenton treatment and EC, respectively.

The colour of the OMW sample was mainly removed in the pretreatment step (80%), revealing that this parameter was mostly observed in the suspended/particulate form

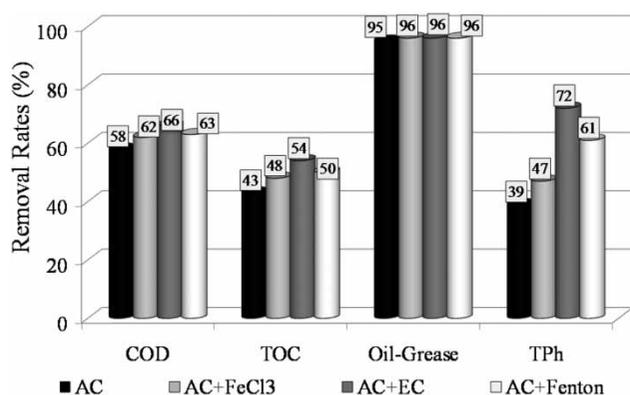


Figure 2 | Percent removal efficiencies obtained for pretreated and chemically treated OMW. (AC = acid cracking; EC = electrocoagulation.)

and no further removal could hence be observed when the acid-cracked OMW was additionally treated by the selected chemical processes.

Changes in acute toxicity

According to the acute toxicity tests carried out with the photobacterium *V. fischeri*, the inhibitory effect of the original OMW was 75% in the 10-fold diluted sample indicating the presence of toxic ingredients. After FeCl_3 coagulation, EC and Fenton treatment, a decrease to 67, 62 and 60% inhibition was observed, respectively (Figure 3). However, when the OMW was first subjected to acid cracking pretreatment, the inhibitory effect increased from 75 to 89%. This observation could speculatively be due to structural (physico-chemical) changes brought about in OMW during acid cracking. Currently, experiments are in progress to explain the negative effect of acid cracking on the toxicity results.

Operating cost analysis

While comparing the performance and efficiency of the selected treatment processes, operating (running) costs should also be evaluated to meet all the economic aspects for their successful implementation. Operating costs for the studied chemical treatment processes (acid cracking, FeCl_3 coagulation, $\text{Ca}(\text{OH})_2$ precipitation, EC and the Fenton's reagent) are comparatively summarized in Table 5 in $\text{€}/\text{m}^3$. Cost calculations were based on average prices of technical grade chemicals used for pH adjustment (NaOH and H_2SO_4), coagulation (FeCl_3), precipitation with $\text{Ca}(\text{OH})_2$ and the Fenton's reagent (FeSO_4 and H_2O_2). For EC, operating cost analysis comprised three main items,

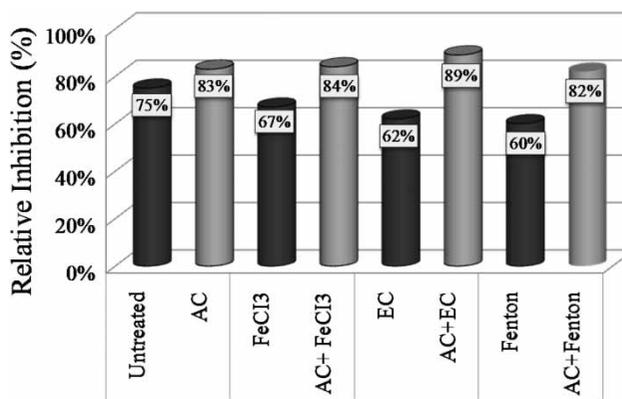


Figure 3 | Percent relative inhibition values measured for untreated, pretreated and chemically treated OMW. Bioassay conditions: The test organism was the photobacterium *V. fischeri* and the incubation period was 15 min. (AC = acid cracking; EC = electrocoagulation.)

Table 5 | Operating costs for the studied pretreatment and chemical treatment processes

Treatment process	Treatment conditions	Operating costs (€/m ³)
Acid Cracking (AC)	pH = 2; T = 70 °C; 60 min	4.7
AC + FeCl ₃ Coagulation	pH = 3; FeCl ₃ = 2,500 mg/L	7.9
AC + Ca(OH) ₂ Precipitation	pH = 11; Ca(OH) ₂ = 6,700 mg/L	8.2
AC + Electrocoagulation	pH = 2; T = 65 °C; A = 50 mA/cm ² ; 120 min	28.1
AC + Fenton's Reagent	pH = 2; T = 65 °C; 20 mM Fe ²⁺ ; 200 mM H ₂ O ₂ , 120 min	15.5

AC = Acid cracking.

namely electric energy consumption, electrode (stainless steel anode) material consumption, as well as sludge (Ca(OH)₂ and Fe(OH)₃) handling and disposal costs. The following equation was considered for this assessment (Bayramoglu *et al.* 2007)

$$\text{Operating cost (EC)} = a \times C_{\text{energy}} + b \times C_{\text{electrode}} + c \times C_{\text{sludge}} \quad (1)$$

where C_{energy} (kWh/m³) and $C_{\text{electrode}}$ (kg electrode/m³) are the quantities of consumed electricity and electrode material, respectively, while C_{sludge} (kg/m³) is the amount of chemical sludge generated during EC. The constants represented by the letters a , b , and c in Equation (1) are unit prices used in the present work, namely 0.07 €/kWh for electricity (TEDAS 2013), 1.4 €/kg for the electrode material (Bayramoglu *et al.* 2007) and 0.04 €/kg for costs associated with sludge handling and disposal (Olmez-Hanci *et al.* 2012), respectively. The electric energy consumption (in kWh/m³) was calculated by monitoring the cell voltage U (in V), and the applied current I (in A) of the wastewater for 120 min in $V = 1,000$ mL OMW during EC, whereas electrode material consumption (in kg/m³) was calculated according to Faraday's Law by considering the amount of Fe²⁺ delivered to the reaction solution during EC (Bayramoglu *et al.* 2007) under the selected reaction conditions. As can be seen from Table 5, EC exhibits the highest operating cost, while AC appears to be the most attractive in terms of operating expenses. From the obtained cost analysis it is evident that, for real-scale implementation of the chemical process to treat OMW, further investigations will be needed to reduce operating costs.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions could be drawn from this paper:

- (i) It was possible to remove oil-grease and suspended organic matter from the wastewater by acid cracking + filtration pretreatment. Acid cracking pretreatment at 70 °C and pH 2.0 resulted in 95% oil-grease and 96% suspended matter (96%) reduction. The corresponding COD, TOC, total phenols and colour removals obtained were 58, 43, 39 and 80%, respectively.
- (ii) Following acid cracking pretreatment, EC and the Fenton's reagent in particular were more effective in the removal of the total phenols parameter. This might be attributed to the fact that the soluble phenolics content of the remaining wastewater could only be removed appreciably by an oxidative treatment mechanism.
- (iii) On the other hand, no significant additional COD and TOC removals (<10–15%) were obtained when the samples were pretreated before chemical treatment processes were applied.
- (iv) The inhibitory effect (*V. fischeri* acute toxicity) of the olive mill wastewater increased considerably from 75 to 89% in the 10-fold diluted sample after acid cracking. This toxicity increase was not observed after direct chemical treatment and is thought to be a consequence of structural changes brought about during acid cracking.
- (v) The operating cost analysis implied that electrocoagulation appeared to be the most expensive chemical treatment process due to intensive anode material and electricity consumption, whereas acid cracking appeared to be more attractive in terms of running costs.

The above results obviously demonstrate that olive mill wastewater treatment remains a difficult task due to its high strength and complex nature. Before deciding on the economically and technically most feasible process combination for olive mill wastewater treatment, toxicological studies also need to be undertaken to decide on the environmentally safest treatment option.

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