

Treatment of Wastewaters from the Olive Mill Industry Wastewaters by Sonication Process at Different Conditions

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Authors' contributions

This work was carried out in collaboration between both authors. Author DTS designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author RÖ managed the analyses of the study. Author DTS Managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

In this study, the effects of increasing sonication time (60 min, 120 and 150 min), increasing temperatures (25°C, 30°C and 60°C), different Dissolved Oxygen (DO) concentrations (2 mg/l, 4 mg/l, 6 and 10 mg/l), different N₂(g) sparging (15 and 30 min) and H₂O₂ concentrations (100 mg/l, 500 and 2000 mg/l) was investigated on Olive Mill Industry wastewaters (OMI ww) by sonication process. The maximum removal efficiencies were 60.91% COD_{dis}, 59.28% TOC, 49.70% color, 58.25% total phenol, 63.27% total aromatic amines (TAAs), 37.51% total fatty acids (TFAs), at 25°C and 150 min, respectively. The maximum removal yields were 66.83% COD_{dis}, 65.92% TOC, 83.77% color, 61.24% total phenol, 70.52% TAAs, 48.84% TFAs, at 60°C and 150 min, respectively. The maximum removal efficiencies were 88.73% COD_{dis}, 93.79% color, 91.38% total phenol, 91.58% TAAs, 74.44% TFAs, at DO=10 mg/l, at 60°C and 150 min, respectively. The maximum removal efficiencies were 84.51% COD_{dis}, 91.88% color, 78.98% total phenol, 74.56% TAAs, 80.18% TFAs, at 30 min N₂(g) sparging, at 60°C and 150 min, respectively. The maximum removal yields were 91.13% COD_{dis}, 93.59% color, 93.65% total phenol, 83.68% TAAs, 90.30%

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TFAs, at 2000 mg/l H₂O₂, at 60°C and 150 min, respectively. Sonication at 35 kHz proved to be a viable tool for the effective removal of COD, TOC, color, total phenol, TAAs and TFAs from OMI ww, providing a cost-effective alternative for destroying and detoxifying the refractory compounds in OMI ww.

Keywords: Hydrogen peroxide; nitrogen gas; olive mill industry wastewater; sonication; titanium dioxide; total aromatic amines; total fatty acids; total phenols.

1. INTRODUCTION

Agro-industrial wastewaters such as olive-oilmill effluent wastewaters (OMW) are among the strongest industrial effluents since they cause considerable environmental problems (coloring of natural waters, a serious threat to aquatic life, pollution of surface and ground waters) particularly in the Mediterranean Sea region due to its high organic chemical oxygen demand (COD), polyphenol and aromatic amines concentration [1].

The organic content of the OMW consists mainly of phenols, polyphenols, polyalcohols, sugars, tannins and pectins at concentrations as high as 200 g COD/l [2]. The concentration of phenolic acids in the OMW may vary from as low as 0.05–0.2 g/l to as high as 10 g/l depending on the type and origin of the effluent [2]. The total aromatic amines (TAAs) in the OMW are known to be carcinogenic and toxic [3,4].

Significant numbers of studies have focused on the efficient treatment of OMWs including various chemical, physical, physicochemical and biological treatments or combinations of them [5]. Usually OMW is inappropriate for direct biological treatment and the alternative treatment technologies mentioned above did not give sufficient yields for phenol byproducts (2-pheyl phenol (2-PHE) and 3-phenyl phenol (3-PHE)) and aromatic amines (aniline, 2, 6-dimethylaniline, durenene, o-toluidine).2,4 Even though all of these methods are practicable and effective, they cannot be used ubiquitously with high efficiency and may generate hazardous by-products [5,6,7,8].

Recently, significant interest has been shown in the application of ultrasound for the degradation of OMWs [9]. Sonochemical reactions are induced by directing sound waves into liquids, there by producing cavitation bubbles [9]. Ultrasonication produces radicals such as hydrogen, hydroxyl and hydroperoxyl radicals (H[•], OH[•], O₂H[•]), respectively, and can be classified as an advanced oxidation process (AOP) [10]. The formation of cavitation bubbles and the extent of bubble collapse depend on the

sonication frequency, power and sound intensity. Preliminary studies showed that as the sonication frequency and power were increased from 8 kHz to 35 kHz and from 110 W to 640 W the COD yields increased, respectively [11]. As the acoustic power is increased the number of cavitation events and consequently the opportunities for free radicals to be generated increase, enhancing sono-degradation. As the intensity is increased the number of collapsing cavities is also increased, thus leading to enhanced degradation rates, as reported by Psillakis et al. [12]. A significant increase in the number of bubbles, close to the emitting surface, was caused by increasing both the sonication power and intensity. An increase in ultrasonic intensity led to greater sonochemical effects in the collapsing bubble. Furthermore, the collapse of bubbles in the reaction cell occurs more rapidly and the number of cavitation bubbles increases thus producing a higher concentration of OH[•] at optimum ultrasonic intensities. These OH[•] react with the pollutants and enhance their yields [13,14,6,15,16,17,18].

The research performed for the sono-degradation of the OMW is limited to a few studies and lower removals were obtained for the pollutants: phenolic compounds such as p-coumaric acid and p-hydroxybenzaldehyde in the OMW were sono-degraded at 150 W sonication power at 19 kHz frequency and at a specific energy of 5.87 kWh/kg COD with a volume of 45 mL throughout 240 min sonication. 45 and 47% sonodegradation yields were observed for these polyphenols while the total phenol removal was 49% [10]. Vassilakis et al. [19] 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 with COD and total phenol yields of around 56 and 60%, respectively. Adrian et al. [20] obtained 56 and 58% COD and phenol yields in a OMW with H₂O₂/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. [9] at 150 W power at 80 kHz after 240 min sonication while the phenol yield decreased to 6% with 10% NaCl. In the study undertaken by Entezari and Petrier [21] 53% phenol yield was observed at 23 kHz after 220 min sonication. In studies investigating the TAAs, color removals in the OMW with sonication are limited with some TAAs and color yields exhibiting low aromatic amines and color yields (44% and 41%, respectively [3,5]. In the study performed by Kallel et al. [22] the results exhibited low aromatic amines yields (45%, 58%) with 190 min sonication at 56 kHz, at 340 W. Electrocoagulation which is one of the advanced treatment methods removed only 69% of COD, 65% of polyphenols and 65% of color present in the OMW [23]. However, the operating cost for decolorization and dephenolization of the OMW using electrocoagulation processes is high due to electrode and specific energy costs [23].

The recent studies performed about the sonication of olive mills was summarized as follows. Uzun et al., [24] found that COD and TSS was removed with yields of 89% and 91%, respectively at 582 kHz frequency after 60 min sonication time. Al-Bsoul et al., [25] found 59% COD removal was achieved within 90 min in the ultrasound at a frequency of 20 kHz. Addition of 1 g/l TiO₂ increased the COD yield to 96% at olive mill wastewater. Zurob et al., [26] investigated the natural deep eutectic solvents from the extraction of hydroxytyrosol and tyrosol from the olive mill wastewater via sonication at 56 kHz frequency after 40 min. di Mauro et al., [27] mentioned that the polyphenolic compounds in olive mill well-known for their beneficial effects on human health, due to their antioxidant, cardioprotective, anticancer, anti-inflammatory, and antimicrobial properties. They are nowadays widely recognized as valuable molecules in pharmaceutical and nutraceutical fields. Therefore, olive mill wastewater represents a really challenging bioresource. They found that hydroxytyrosol is the most abundant biophenol in OMW acts as a free radical-scavenger and metal-chelator, protects against oxidative damage, inhibits the NADPH oxidase, the inducible form of nitric oxide synthase (iNOS), and the proinflammatory enzymes such as 5-lipoxygenase and cyclooxygenase, decreasing the production of nitric oxide, leukotrienes, and prostaglandins. Moreover, hydroxytyrosol is able to modulate the release of tumor necrosis factor- α (TNF- α) and other proinflammatory mediators [27]. Piccolella et al., [28] investigated the nutraceutical effects of olive mill effluents. Some

chronic and degenerative diseases (e.g. cancer, cardiovascular, and neurodegenerative diseases) identify phenols and polyphenols, widespread and mostly copious in dietary plant sources, as beneficial for human health. These compounds, as intrinsically antioxidant, are claimed as nutraceuticals with preventive efficacy in offsetting oxidant species over-generation in normal cells, and with the potential ability to halt or reverse oxidative stress-related diseases (Piccolella et al., [28]. Polyphenols and their complexes were found to exert both anti- and prooxidant activities, suggesting also a promising chemopreventive efficacy. In fact, different evidence further highlights their ability to induce apoptosis, growth arrest, DNA synthesis inhibition and/or modulation of signal transduction pathways. Indeed, a full understanding of the phenolic and polyphenolic compositions can cause to use of OMW as nutraceutical extract sources [28]. Yahyaoui et al., [29] investigated the occurrence of secoiridoid glycosides via degradation of phenolic glucosides which have strong effects on commercial, nutritional, and sensory properties of olive oil wastes. With a high ultrasound frequency of 890 kHz sonication treatment was performed after 10 min.

In this study, the effects of increasing sonication time (60 min, 120 and 150 min), increasing temperatures (25°C, 30°C and 60°C), different DO concentrations (2 mg/l, 4 mg/l, 6 and 10 mg/l), different N₂(g) sparging (15 min and 30 min), different H₂O₂ concentrations (100 mg/l, 500 and 2000 mg/l) and different TiO₂ concentrations (0.1 mg/l, 0.5 mg/l, 10 and 20 mg/l) was investigated on Olive Mill Industry wastewaters (OMI ww) by sonication process at 35 kHz sonication frequency, at 640 W sonication power, at pH=7.0.

2. MATERIALS AND METHODS

2.1 Raw Wastewater

The characterization of raw OMI ww taken from the influent of a olive oil production industry in Izmir, Turkey. This plant is operated with a three phase olive oil extraction process.

2.2 Configuration of Sonicator

A Bandelin Electronic RK510H flat sonicator was used for sonication of the OMI ww samples. Glass serum bottles in a glass reactor were filled to volumes of 5–500 ml with OMI ww and were placed in a water bath. They were then closed

with teflon coated stoppers throughout the measurement of the OMI ww. Recent studies showed that high ultrasound frequencies of 80 and 150 kHz did not increase the yields of the parameters studied [30]. Therefore, they were studied at a sonication frequency of 35 kHz and at a power of 650 W. Increasing the sonication frequency did not increase the number of free radicals, therefore free radicals did not escape from the bubbles and did not produce enough OH ions [30]. Ultrasonic waves for 35 kHz frequency were emitted from the bottom of the reactor through a piezoelectric disc (4 cm diameter) fixed on a pyrex plate (5 cm diameter). The evaporation losses of volatile compounds were estimated to be 0.01% in the reactor and, therefore, assumed to be negligible. The serum bottles were filled with 0.1 ml methanol in order to prevent adsorption on the walls of the bottles and to minimize evaporation. The temperature in the sonicator was monitored continuously and it was adjusted electronically in the sonicator with an automatic heater. The stainless steel sonicator reactor was sealed with a water jacket to maintain the desired temperature and to prevent temperature losses. The schematic configuration of the sonicator used in this study is given in before studies [3]. The schematic configuration of the sonicator used in this study is shown in Fig. 1. Samples were taken after 60 min, 120 and 150 min of sonication and they were analyzed immediately.

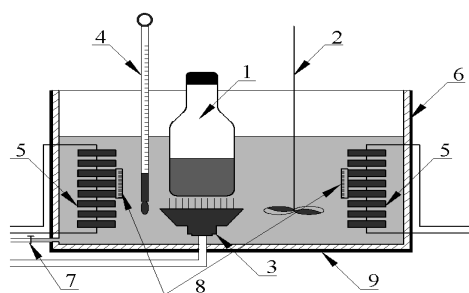


Figure 1: The structural diagram of the sonicator used in this study: (1) glass reactor, (2) stirrer, (3) energy conversion device, (4) thermometer, (5) heater, (6) stainless steel bath, (7) water exit valve, (8) thermostate, (9) teflon cover

2.3 Analytical Methods

BOD₅, and COD were monitored following Standard Methods 5210 B and 5220 D, respectively [31]. Total-N, NH₄-N, NO₃-N, NO₂-N,

total-P and PO₄-P were measured with cell test spectroquant kits (Merck) in a spectroquant NOVA 60 (Merck) spectrophotometer (2003). Oil, Na⁺ and Cl⁻, total suspended solid concentration (TSS), total volatile suspended solid concentration (TVSS), dissolved oxygen (DO), pH, temperature T (°C), and oxydation reduction potential (ORP, mV) were determined with Standard Methods 5520 B, 3550, 2540 C, 2540 E, 2550, 2580, respectively. The measurement of color was carried out following the methods described by Olthof and Eckenfelder, [32]. The color content was determined by measuring the absorbance at three wavelengths (445, 540 and 660 nm), and taking the sum of the absorbances at these wavelengths. In order to identify the TAAs, OMI ww (25 ml) was acidified at pH=2.0 with a few drops of 6 N HCl and extracted three times with 25 ml of ethyl acetate. The pooled organic phases were dehydrated on sodium sulphate, filtered and dried under vacuum. The residue was silylated with bis(trimethylsilyl)trifluoroacetamide (BSTFA) in dimethylformamide and analyzed by GC-MS. Mass spectra were recorded using aVGTs 250 spectrometer equipped with a capillary SE 52 column (0.25 mm ID, 25 m) at 220°C with an isothermal program for 10 min. TAAs were measured using retention times and mass spectra analysis. The total phenol was monitored as follows: 40 ml of OMI ww was acidified to pH=2.0 by the addition of concentrated HCl. Phenols were then extracted with ethyl acetate. The organic phase was concentrated at 40°C to about 1 ml and silylized by the addition of N,O-bis(trimethylsilyl)acetamide (BSA). The resulting trimethylsilyl derivatives were analysed by Gas Chromatography–Mass Spectrometry (GC-MS) (Hewlett-Packard 6980/HP5973MSD).

2.4 Chemical Oxygen Demand (COD) Measurements

COD was determined with Close Reflux Method following the Standard Methods 5220 D [31] using an Aquamate thermo electron corporation UV visible spectrophotometer (2007). First the samples were centrifuged for 10 min at 7000 rpm. Secondly, 2.50 ml volume samples were treated with 1.50 ml 10216 mg/l K₂Cr₂O₇ with 33.30 g/l HgSO₄ and 3.50 ml 18.00 M H₂SO₄ which contains 0.55% (w/w) Ag₂SO₄. Thirdly the closed sample tubes were stored in a 148°C heater (thermoreactor, CR 4200 WTW, 2008) for 2 h. Finally, after cooling, the samples were measured at 600 nm with an Aquamate thermo

electron corporation UV visible spectrophotometer (2007). The Close Reflux Method COD was used to measure the COD in OMI ww before and after sonication experiments

2.5 Total COD (COD_t)

Wastewater samples were used to measure the total COD (COD_t) in OMI ww before and after sonication process.

2.6 Dissolved COD (COD_{dis})

0.45 µm membrane-filtered (Schleicher & Schuell ME 25, Germany) wastewater samples were used to measure the dissolved COD (COD_{dis}) in OMI ww prior and after sonication experiments.

2.7 Total Organic Carbon (TOC) Measurements

TOC was measured following the Standard Methods 5310 [31] with a Rosemount Dohrmann DC-190 high-temperature total organic carbon (TOC) analyzer (1994).

2.8 Color Measurements

In the studies with real colorful OMI ww which is including Methylene Blue (C₁₆H₁₈N₃SCI). The measurement of color was carried out following the approaches described by Olthof and Eckenfelder, [32] and Eckenfelder [33]. According these methods, the color content was determined by measuring the absorbance at three wavelengths (445 nm, 540 nm and 660 nm), and taking the sum of the absorbances at these wavelengths. To convert the absorbance into (m⁻¹) the equation given below Equation (1) was used.

$$\alpha = \left(\frac{A}{d}\right)f \quad (1)$$

where

- a: Color in (m⁻¹) unit,
- A: Measured absorbance value from the spectrophotometer,
- d: Sample length (cell width, 10 mm),
- f: Factor (1000).

Raw wastewater was diluted with deionized H₂O between 100 and 1000 mg/l at ten different concentrations for the calibration graphic and calibration equation of color measurement.

These ten different wastewater concentrations were measured at three different wavelents (445 nm, 540 nm and 660 nm) with an Aquamate thermo electron corporation UV visible spectrophotometer (2007). Results of three different wavelents were illustrated in Table 1, Table 2 and Table 3. Three different calibration in Equations (2), (3) and (4) were obtained for color measurement at three different wavelents (445 nm, 540 nm and 660 nm).

$$y = 1.0068 * X + 2.133 \quad R^2 = 0.9983 \quad (2)$$

$$y = 0.9933 * X + 18.467 \quad R^2 = 0.9968 \quad (3)$$

$$y = 1.0198 * X - 1.2 \quad R^2 = 0.9979 \quad (4)$$

2.9 Polyphenol Measurements

Polyphenol measurement was performed following the Standard Methods 5520 B [31]. Firstly, 5 ml of OMI ww sample was added in 40 ml dark brown color Amber I-cem vial (Catalog number: 98716). Secondly, 5 ml of mixture of siklohexane (50%) and etilacetate (50%) was added on 5 ml of OMI ww sample in 40 ml dark brown color Amber I-cem vial. After, this solutions were mixtured at 15 min. Upper part of mixtured solution was taken with a pasteur pipette in a new 40 ml dark brown color Amber I-cem vial. 0.50 g Na₂SO₄ chemical was added for waterless condition in a new 40 ml dark brown color Amber I-cem vial. After that, this 40 ml dark brown color Amber I-cem vial again was mixtured at 15 min. The upper part of 40 ml dark brown color Amber I-cem vial was taken with a Pasteur pipette in a 1.5 ml of colorless glass vial (Agilent). 1 ml sample was added in a 1.5 ml of colorless glass vial for GC-MS analysis. Polyphenol was analysed with a gas chromatography (Agilent 6890) combined with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30 m, 0.25 mm, 0.25 µm) was used. The initial oven temperature to hold at 50°C for 1 min, to rise to 200°C at 25°C /min and from 200°C to 300°C at 80°C /min and was held for 5.5 min. The injector ion source and quadrupole temperatures were 295°C, 300°C and 180°C, respectively. High purity helium (He) was used as the carrier gas at constant flow mode (1.5 ml/min, 45 cm/s linear velocity). The MSD to run in selected ion-monitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions. Qualification was based on the Internal Standard Calibration Procedure.

Table 1. Standard concentrations (mg/l) versus absorbance (nm) values of color A1:445 nm (λ = 445 nm) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007)

Concentrations (mg/l)	Absorbance (nm)
100	0.098
200	0.199
300	0.296
400	0.412
500	0.534
600	0.591
700	0.705
800	0.816
900	0.910
1000	0.998

Table 2. Standard concentrations (mg/l) versus absorbance (nm) values of color A2:540 nm (λ = 540 nm) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007)

Concentrations (mg/l)	Absorbance (nm)
100	0.102
200	0.214
300	0.313
400	0.428
500	0.507
600	0.653
700	0.711
800	0.826
900	0.900
1000	0.994

Table 3. Standard concentrations (mg/l) versus absorbance (nm) values of color A3:660 nm (λ = 660 nm) using an Aquamate thermo electron corporation UV visible spectrophotometer (2007)

Concentrations (mg/l)	Absorbance (nm)
100	0.091
200	0.197
300	0.302
400	0.401
500	0.523
600	0.630
700	0.724
800	0.812
900	0.927
1000	0.990

2.10 Determination of Total Aromatic Amines (TAAs)

The total aromatic amines (TAAs) were determined colorimetrically at 440 nm after reacting with 4-dimethylaminobenzaldehyde-HCl according to the method described by Oren et al. (1991). 1 g/l benzidine chemical was prepared to a standard solution for using TAAs standard

measurements. TAAs calibration graphic was obtained with benzidine concentrations varying between 100 and 1000 mg benzidine/l from the stock 1 g/l benzidine concentration at 440 nm using an Aquamate thermo electron corporation UV visible spectrophotometer (2007) (Table 4). A calibration equation (Equation 5) was shown as follows.

Firstly, 0.2 ml wastewater sample was added in 14 ml glass test tube. Secondly, 0.8 ml deionized H₂O was appended in 14 ml glass test tube. Thirdly, 0.05 ml HCl (30% purity) solution was affixed in 14 ml glass test tube. After, 3 ml absolute ethanol solution was added in 14 ml glass test tube. Then, 0.5 ml of 5% of p-dimethyleaminobenzaldehyd/ethanol solution was appended in 14 ml glass test tube. After that, 0.5 ml 15.70% of citric acid (C₆H₈O₇) / 6% of NaOH solution was affixed in 14 ml glass test tubes. Afterwards, the glass test tube was closed with a black plastic stopper and was waited for 10 min. Then, 10 min, 2.5 ml deionized H₂O was added in this 14 ml glass test tube. Finally, TAAs concentration was measured at 440 nm in an Aquamate thermo electron corporation UV visible spectrophotometer (2007).

$$y = 0.9958 * X + 15.933 \quad R^2 = 0.9990 \quad (5)$$

2.11 Total Fatty Acid (TFA) Measurements

Bicarbonate (HCO₃) alkalinity and total fatty acid (TFA) concentrations were measured simultaneously using titrimetric method proposed by Anderson and Yang [34]. The test was carried out as follows: firstly the pH of the sample was measured, secondly the sample was titrated with standard H₂SO₄ (0.10 N) through two stages (first to pH=5.10, then from 5.10 to 3.50), and finally the TFA and HCO₃ alkalinity concentrations were calculated with a computer program by solved the Equations (6) and (7):

$$A_1 = \frac{[HCO_3^-] * ([H]_2 - [H]_1)}{[H]_1 + K_C} + \frac{[TFA] * ([H]_2 - [H]_1)}{[H]_2 + K_{TFA}} \quad (6)$$

$$A_2 = \frac{[HCO_3^-] * ([H]_3 - [H]_1)}{[H]_3 + K_C} + \frac{[TFA] * ([H]_3 - [H]_1)}{[H]_3 + K_{TFA}} \quad (7)$$

where;

A₁ and A₂: The molar equivalent of the standard acid consumed to the first and second end points,

[HCO₃⁻]: The bicarbonate concentration (mg HCO₃/l),

[TFA]: The total fatty acid ion concentration (mg/l),

[H]_{1,2,3}: The hydrogen ion concentrations of the original sample and at the first and the second end points,

K_C: The conditional dissociation constant of carbonic acid,

K_{TFA}: The combined dissociation constant of the volatile fatty acids (C₂-C₆), this pair of constants was assumed, being 6.6×10⁻⁷ for bicarbonate and 2.40×10⁻⁵ for volatile acids.

HCO₃ concentrations also were calculated for the wastewater from the **Equations (6) and (7)**. The HCO₃ concentration was not showed in the results since did not discuss through sonication with the exception of section "effect of HCO₃ on sonication".

2.12 Statistical Analysis

ANOVA analysis of variance between experimental data was performed to detect F and P values. Comparison between the actual variation of the experimental data averages and standard deviation is expressed in terms of F ratio. F is equal (found variation of the date averages/expected variation of the date averages). P reports the significance level, d.f indicates the number of degrees of freedom. Regression analysis was applied to the experimental data in order to determine the regression coefficient R². The aforementioned test was performed using Microsoft Excel program [35].

All experiments were carried out three times and the results are given as the means of triplicate samplings. The data relevant to the individual pollutant parameters in OMI ww (COD, color, phenol and TAAs) are given as the mean with standard deviation (SD) values.

3. RESULTS AND DISCUSSION

3.1 Raw Wastewater

The characterization of raw OMW taken from the influent of a olive oil production industry in Izmir, Turkey is given in Table 5. This plant is operated with a three phase olive oil extraction process.

3.2 Effect of Increasing Sonication Frequency on the COD_{dis} Removal in OMI ww at 25°C Ambient Conditions

Three different sonication frequencies (25 kHz, 35 and 132 kHz) was researched under ambient conditions (25°C), at constant sonication power (640 W) and increasing sonication times (for 60 min, 120 and 150 min) to determine the optimum

sonication frequency for maximum PAHs and COD_{dis} removals in PCI ww, OMI ww and TI ww. Among the frequencies used in the sonication process (25 kHz, 35 and 132 kHz) it was found that a sonication frequency of 35 kHz is the optimum frequency for maximum COD_{dis} removals in OMI ww (Table 6).

Increasing the sonication frequency did not increase the number of free radicals, therefore a low number of free radicals did not escape from the bubbles and did not migrate [36]. Explanation of such phenomenon is not yet fully understood, since a more energetic implosion of cavitation

bubbles is expected to occur at low frequency rather than at high frequency because of a larger bubbles radius observed at low frequency [37,38]. According to Minnaert [39], the size of bubbles formed in water, under one atmosphere, is inversely proportional to the frequency of the wave [40,41]. However, the larger the bubble size, the greater the water vapour within the bubble, leading to a more important damping of the collapse at low frequency like 20–40 kHz [36]. This damping induces a decreases in the temperature and pressure within the cavitation bubble at low frequency compared to a medium frequency [40].

Table 4. Standard concentrations versus absorbance values at $\lambda=440$ nm using an Aquamate thermo electron corporation UV visible spectrophotometer (2007)

Concentrations (mg benzidine / l)	Absorbance (nm)
100	0.115
200	0.214
300	0.310
400	0.411
500	0.512
600	0.628
700	0.721
800	0.802
900	0.925
1000	0.998

Table 5. Characterization values of OMI ww (n=3, mean values \pm SD)

Parameters	Values		
	Minimum	Medium	Maximum
pH ₀	4.00 \pm 0.14	4.56 \pm 0.160	4.90 \pm 0.172
DO ₀ (mg/l)	0.01 \pm 0.0004	0.05 \pm 0.002	0.09 \pm 0.003
ORP (mV)	120 \pm 4.20	126 \pm 4.41	132 \pm 4.62
TSS (mg/l)	53.60 \pm 1.876	53.74 \pm 1.881	53.88 \pm 1.886
TVSS (mg/l)	34.80 \pm 1.218	35.6 \pm 1.246	36.42 \pm 1.275
COD _t (mg/l)	98780 \pm 3457	126632 \pm 4432	140560 \pm 4920
COD _d (mg/l)	85400 \pm 2989	109444 \pm 3831	123500 \pm 4323
TOC (mg/l)	58510 \pm 2048	66488 \pm 2327	80450 \pm 2816
BOD ₅ (mg/l)	63800 \pm 2233	81254 \pm 2844	99130 \pm 3470
BOD ₅ / COD _d	0.58 \pm 0.020	0.74 \pm 0.026	0.90 \pm 0.032
Total N (mg/l)	194 \pm 6.79	248 \pm 8.68	300 \pm 10.50
NH ₄ -N (mg/l)	23.40 \pm 0.819	30 \pm 1.050	36.60 \pm 1.281
NO ₃ -N (mg/l)	39 \pm 1.365	50 \pm 1.750	61 \pm 2.135
NO ₂ -N (mg/l)	17.63 \pm 0.617	22.6 \pm 0.791	27.57 \pm 0.965
Total P (mg/l)	492 \pm 17.22	630 \pm 22.05	768.60 \pm 26.901
PO ₄ -P (mg/l)	350 \pm 12.250	448 \pm 15.680	546.20 \pm 19.117
Total phenol (mg/l)	3320 \pm 116.20	4090 \pm 143.15	5150 \pm 180.25
TFAs (mg/l)	4050 \pm 141.75	5200 \pm 182	6344 \pm 222.04
TAAAs (mg benzidine/l)	2340 \pm 81.90	3000 \pm 105	3660 \pm 128.10
Color (m ⁻¹)	99.70 \pm 3.490	99.80 \pm 3.493	99.90 \pm 3.497
Oil (mg/l)	564 \pm 19.74	640 \pm 22.40	775 \pm 27.125

Table 6. Effect of sonication frequency on the COD_{dis} removals in OMI ww at ambient conditions (25°C) (sonication power=640 W, sonication times=60 min, 120 and 150 min, initial COD_{dis} concentration in OMI ww=109444 mg/l, n=3, mean values)

Sonication Frequency (kHz)	COD _{dis} Removal Efficiencies in OMI ww (%)		
	After		
	60 min	120 min	150 min
25	10.67	39.56	56.43
35	12.58	41.74	60.91
132	11.10	40.34	59.85

3.3 Effect of Increasing Sonication Time on the COD_{dis} Removals in OMI ww at 25°C Ambient Conditions

5–10–15–20–25–30–35–40–45–50–55–60–120 and 150 min sonication times was researched under ambient conditions (25°C), at constant sonication frequency (35 kHz) and constant sonication power (640 W) to determine the optimum sonication time for maximum COD_{dis} removals in OMI ww. Among the sonication times used in the sonication process (0–60–120 and 150 min) it was found that 150 min sonication time is the optimum sonication time for maximum COD_{dis} removals in OMI ww (Table 7).

Higher sonication times are needed for complete mineralization. Short sonication times did not provide high degradation yields for refractory PAHs since they were not exposed for a long enough time to ultrasonic irradiation. Moreover, the choice of solvent affected the degradation of

PAHs under sonication which ultimately is expected to alter the effectiveness of ultrasonic extractions at long sonication times. The cavities are more readily formed when using solvents with low viscosity and low surface tension during long sonication times [42,43]. Among the solvents used acetone and hexane have the highest surface tension and viscosity. The preliminary studies showed that solvents with high surface tension and viscosity generally have a higher threshold for cavitation resulting in fewer cavitation bubbles but more harsh conditions once cavitation is established resulting in higher temperatures and pressures upon bubble collapse [44]. Higher vapor pressure leads to more solvent volatilizing into cavitation bubbles which are able to be dissociated by high temperature after 150 min sonication. Hexane and acetone have the highest vapor pressure among solvents. Thus, more hexane molecules migrate into cavitation bubbles leading to more molecules dissociating to generate radicals.

Table 7. Effect of sonication time on the COD_{dis} removals in OMI ww at ambient conditions (25°C) (sonication frequency=35 kHz, sonication power=640 W, initial COD_{dis} concentration in OMI ww=109444 mg/l, n=3, mean values)

Sonication Time (min)	COD _{dis} Rem. Eff. in OMI ww (%)
0	0.00
5	2.17
10	3.75
15	4.33
20	4.79
25	5.01
30	5.54
35	6.25
40	7.01
45	8.66
50	9.73
55	11.08
60	12.58
120	41.74
150	60.91

3.4. Effect of Increasing Sonication Time on the Removals of COD_{dis} and TOC in OMI ww at 25°C Ambient Conditions

OMI ww samples were sonodegraded in a sonicator at increasing sonication times (60 min, 120 and 150 min) in ambient conditions at pH=7.0 and at 25°C. 12.58%, 41.74% and 60.91% COD_{dis} removal efficiencies were observed at an initial COD_{dis} concentration of 109444 mg/l after 60 min, 120 and 150 min, respectively (Table 8, Fig. 2). The maximum COD_{dis} removal efficiency was 60.91% after 150 min at pH=7.0 and at 25°C (Table 8, Fig. 2). A significant linear correlation between COD_{dis} yields and increasing sonication time was observed ($R^2=0.83$, $F=16.38$, $p=0.01$).

Organic compounds may be degraded either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation or in the solution bulk via oxidative degradation by

OH• and H₂O₂ throughout sonication of OMI ww [45]. Preliminary studies showed that the organic pollutants in OMI ww were sonodegraded by hydroxylation reactions [46]. In this study, the effects of H₂O₂ production and the levels of OH• concentrations were not determined in this step since the COD_{dis} removals are low for the sonication performed under ambient conditions (25°C). It was found that low temperature under ambient conditions was not enhanced the COD_{dis} removals even it was studied at long sonication times as 150 min. This probably caused by the insufficient levels of OH• formation. Hence, COD_{dis} are not the ability to attack to the low concentrations of OH•, thus leading to decreased sonodegradation rates of COD_{dis} as reported by Lafi et al. [5]. Furthermore, the high relative concentration of organic by-products generated in the system (without ultimate mineralization) is known to complete for the OH• in solution, slowing the sonodecomposition rates of COD_{dis} (Khokhawala and Gogate, 2010).

Table 8. Effect of increasing sonication time on COD_{dis} removal efficiencies of OMI ww before and after sonication process in ambient conditions at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration of 109444 mg/l, n=3, mean values ±SD)

Parameters	COD _{dis} removal efficiencies (%)			
	25°C			
	0. min	60. min	120. min	150. min
Raw ww	0	12.58	41.74	60.91

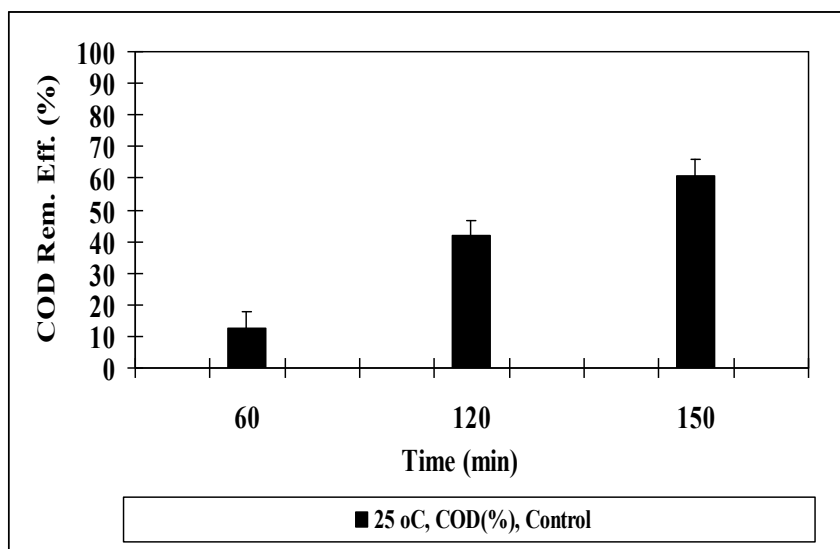


Figure 2. Effect of increasing sonication time on the COD_{dis} removal efficiencies in OMI ww at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values)

12.47%, 40.80% and 59.28% TOC removal efficiencies were observed at an influent TOC concentration of 66488 mg/l after 60 min, 120 and 150 min, respectively, at 25°C and at pH=7.0 (Table 9). The maximum TOC removal efficiency was 59.28% after 150 min at pH=7.0 and at 25°C (Table 9). A significant linear correlation between TOC yields and increasing sonication time was observed ($R^2=0.83$, $F=16.17$, $p=0.01$).

The treatment by sonication converts TOC to much smaller sonodegraded compounds. In such cases, it is obvious that higher sonication times are needed for complete mineralization of TOC in OMI ww since this wastewater contains high COD levels. Short sonication times (60 min) did not provide high degradation yields for refractory COD_{dis} and TOC since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease in the percentage of remaining COD_{dis} and TOC were expected at longer sonication times due to sufficient radical reactions through cavitation. COD_{dis} and TOC were not completely removed under the ultrasonic action even with a long sonication time (150 min) in OMI ww. The reason of this could be explained by the fact that degradation products of COD (pyridine, straight-chain aliphatic compounds) sometimes are recalcitrant toward the sonochemical treatment. This is due to the fact that the intermediate products have very low probabilities of making contact with OH^\bullet , which react mainly at the interface of the bubble. Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency toward COD_{dis} abatement. Canizares-Macias et al. [47] investigated an ultrasound system assisted with Rancimat Method for the determination of the olive oil industry yields. 80% COD removal was found at 20 kHz frequency, and at a power of 400 W, after 60 min. In this study, 60.91% COD_{dis} removal was observed at 25°C after 150 min. This COD_{dis} yield is lower than the yield obtained by Canizares-Macias et al. [47] at 25°C.

In a study performed by Atanassova et al. [9] it was found a COD yield of 45% after 240 min at 150 W, at 80 kHz at 25°C. This COD_{dis} yield is lower than the yield obtained in this study at 25°C as mentioned above. Azzam et al. (2004) tested to the maximum adsorption capacity for activated carbon in OMI ww for less than 4 h at 25°C. The maximum removal of COD is 85%. The COD_{dis} yield found in this study is higher than the yield observed by the present study at 25°C as mentioned above. In an Up-flow

Anaerobic Sludge Blanket (UASB) reactor, 80–85% COD removals was obtained at a HRT=5 days with an influent COD concentration of 40 g/l and organic loading rate (OLR)=8 g/COD l. day (Sabbah et al., 2004) in OMI ww. This yield is higher than the yield obtained by this study at 25°C as mentioned above. Anaerobic Filter (AF) compared with Aerobic Fluidized Bed Fermentor (AFBF) for removal of OMI ww by *Aspergillus niger* [48]. The AFBF removes 57% of the total COD while AF reduces the COD_{total} and COD_{dis} with yields 67% and 68.10%, respectively.

3.5. Effect of Increasing Sonication Time on the Removals of Color, TAAs and TFAs in OMI ww at 25°C Ambient Conditions

3.5.1 Effect of increasing sonication time on the color removal efficiencies in omi ww at 25°C in ambient conditions

36.37%, 47.90% and 49.70% color removal efficiencies were observed at an influent color concentration of 99.80 m^{-1} after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 25°C (Table 10). In this study, it was found that the color removal efficiencies in OMI ww increased from 36.37% up to 49.70% as the sonication time was increased from 60 to 150 min at pH=7.0 and at 25°C. The maximum color removal efficiency was 49.70% after 150 min at pH=7.0 and at 25°C. A significant linear correlation between color yields and increasing sonication time was observed ($R^2=0.83$, $F=17.34$, $p=0.01$) (Table 10). Low color (46%) and phenol removals in OMI effluents showed that low sonication temperature (25°C) is not able to achieve the complete removal of the colorful organics (e.g., lignin, organic acids, etc.) and the phenolic compounds (e.g., tannins, antocyanins, catechins, etc.) [49]. This might be due to the generation of high concentration of intermediate compounds that cannot be further oxidized by OH^\bullet and consequently are accumulated in the system [49]. In this study, 49.70% color removal was found at 25°C after 150 min. The color removal is higher than the yield obtained by Adhoum & Monser [49] 46% at 25°C as mentioned above. Adhoum and Monser [49] investigated the color removal in OMI ww by electrocoagulation with aluminium electrodes at pH=4.0-6.0, at a current density of 75 mA/cm² and 25 min. 95% color removal was found after 25 min, at 25°C. This color yield is higher than the yield obtained in the present study at 25°C.

3.5.2 Effect of increasing sonication time on the total phenol removal efficiencies in omi ww at ambient conditions

26.89%, 54.74% and 58.25% total phenol removal efficiencies were measured at an influent total phenol concentration of 4090 mg/l after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 25°C (Table 11). It was found that the total phenol removal efficiencies in OMI ww increased from 26.89% up to 54.74% as the sonication time was increased from 60 to 120 min. The maximum total phenol removal efficiency was 58.25% after 150 min at pH=7.0 and at 25°C. The contribution of 150 min on the total phenol removals was not significant ($R^2=0.43$, $F=3.78$, $p=0.01$) (Table 11).

Pyrolytic destruction of phenol in the gas phase is negligible; the degradation occurs mainly in the bulk solution. A possible explanation for this is that a considerable increase in the concentration results in the formation of a complex H-bonding network between the phenolic compounds [19]. During sonication low decrease of total phenol concentrations in the effluent samples results in the formation of a complex H-bonding network

between the phenolic compounds after 60 min. It is well known that molecules containing COOH or CHO groups exist as dimers in solution due to the formation of H-bonds between two neighboring molecules. This results in a more robust and stable configuration, thus leading to reduced degradation (Currell et al., 1963). In addition to this, the formation of such a network may impede their diffusion towards the bubble interface and this would also lead to reduced degradation of phenols [9].

Canizares-Macias et al. [47] investigated an Ultrasound-assisted with Rancimat method for the determination of the phenol yields in OMI effluents. 56% phenol removal was found at 20 kHz, and at 400 W, after 60 min at 25°C. In this study, 58.25% total phenol removal was measured at 25°C after 150 min. This study exhibited similar phenol yields with the present study at 25°C. In a study performed by Atanassova et al. [9] it was found 6% - 14% sonodegradation yields for total phenolic compounds after 240 min at power 75 and 150 W, respectively. These yields are significantly lower than the present study at 25°C.

Table 9. Effect of increasing sonication time on TOC removal efficiencies of OMI ww before and after sonication process in ambient conditions at pH=7.0 and at 25°C (sonication power=640 W, sonication frequency=35 kHz, initial TOC concentration of 66488 mg/l, n=3, mean values ±SD)

Parameters	TOC removal efficiencies (%)			
	25°C			
	0. min	60. min	120. min	150. min
Raw ww	0	12.47	40.80	59.28

Table 10. Effect of increasing sonication time on color removal efficiencies in OMI ww before and after sonication experiments at pH=6.98 and at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m⁻¹, n=3, mean values ±SD)

Parameters	Initial Conc.	Removal efficiencies (%)		
		25°C		
		60. min	120. min	150. min
Color	99.80 ± 3.493 m ⁻¹	36.37	47.90	49.70

Table 11. Effect of increasing sonication time on total phenol removal efficiencies in OMI ww before and after sonication experiments at pH=6.98 and at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values ±SD)

Parameters	Initial Conc.	Removal Efficiencies (%)		
		25°C		
		60. min	120. min	150. min
Total phenol	4090 ± 143.15 mg/l	26.89	54.74	58.25

Hydrophilic and less volatile compounds such as phenol and polyphenols e.g., 2-phenyl-phenol (vapor pressure; 3.10×10^{-7} mm Hg at 25°C , soluble in diethyl ether, acetone, ethanol, isopropanol, ethylene glycol, glycoethers, polyglycols and alkali hydroxide solutions. Insoluble in cold and hot water) and 3-phenyl-phenol (vapor pressure; 3.20×10^{-7} mm Hg at 25°C , easily soluble in diethyl ether, soluble in alkalies and most organic solvents, very soluble in alcohol, chloroform and pyrimidine, slightly soluble in petroleum ether, insoluble in cold and hot water) mainly degrade by reacting with OH^{\bullet} at the gas-liquid interface and/or in the bulk liquid and possibly to a much lesser extent by thermal decomposition at the gas-liquid interface [50].

4090 mg/l initial phenol concentration in OMI ww decreased to 2990 mg/l, to 1851 mg/l and to 1708 mg/l after 60 min, 120 and 150 min, respectively, at $\text{pH}=7.0$ and at 25°C . It was found low phenol yields (58.25%) after 150 min. This could be attributed to the studied low temperature under ambient conditions. From 2990 mg/l total phenol 426.34 mg/l 2-phenyl-phenol and 846.03 mg/l 3-phenyl-phenol were produced after 60 min at $\text{pH}=7.0$ and at 25°C . 426.34 mg/l 2-phenyl-phenol reduced to 40.50 mg/l after 150 min at $\text{pH}=7.0$ and at 25°C . 846.03 mg/l 3-phenyl-phenol decreased to 40.76 mg/l after 150 min at $\text{pH}=7.0$ and at 25°C . The phenol metabolites (2-phenyl-phenol and 3-phenyl-phenol) were removed with yields 90.50% and 95.18%, respectively, after 150 min at $\text{pH}=7.0$ and at 25°C . It was found that the total phenol breakdown to 1272.37 mg/l 2-phenyl-phenol and 3-phenyl-phenol. It can be assumed that the remaining total phenol (remaining phenol=4090-1272.37=2817.63 mg/l) could be mineralized, volatilized or cleaved to other phenol metabolites namely, tyrosol, hydroxytyrosol, oleuropein, caffeic acid, quercetin, ferulic acid, catechol, vanillic acid, o-quinone, *p*-coumaric acid, *p*-hydroxybenzaldehyde, etc., throughout sonication.

Some smaller more volatile phenolic by-products were vaporized in OMI ww after sonication experiments [22]. In this reason, these smaller more volatile phenolic intermediates were rapidly removed in OMI ww after a long sonication time (150 min). Therefore, higher removal efficiencies of phenol intermediates (> 93%) were observed in OMI ww after 150 min at 25°C , compared to the total phenol yields (58.25%) in OMI ww after 150 min at $\text{pH}=7.0$ and at 25°C .

In a study performed by Kallel et al. [22] it was found that the polyphenol organics composed of alcohol [4-hydroxyphenylethanol (*tyrosol*), 4-hydroxybenzoic acid, 4-hydroxy-3-methoxyphenethylalcohol (*homovanillyl alcohol*), 4-hydroxy-3-methoxybenzoic acid (*vanillic acid*), 3,4-Dihydroxyphenyl alcohol (*hydroxytyrosol*), 3,4-dihydroxybenzoic acid (*protocatechuic acid*), 3,4-dihydroxyphenylglycol and 3,4-dihydroxycinnamic acid (*caffeic acid*)]. The removal yields of these polyphenolic compounds were 30%, 40%, 50%, 35%, respectively, through sonication of OMI ww at 25°C . In this study, 90.50-95.18% phenol by-products (2-phenyl-phenol and 3-phenyl-phenol) removals were found at 25°C after 150 min. In the present study the phenol by-products yields are higher than the yields obtained by Kallel et al. [22] at 25°C .

Vassilakis et al. [19] 30.00% *p*-coumaric acid (a polyphenolic compound) removal efficiency was found at a 80 kHz frequency with sonication. In this study, 90.50-95.18% phenol by-products (2-phenyl-phenol and 3-phenyl-phenol) removals were observed at 25°C after 150 min. In the present study, the phenol by-products yields are higher than the yield obtained by Vassilakis et al. [19] at 25°C as mentioned above. In a study performed by Andreozzi et al. (1998) showed that total phenols are reduced to about 43% in 3 h by ozonation while the total COD removal remains unvaried in OMI ww. In the present study, the total phenol removal obtained by sonication is higher than the yield obtained by Andreozzi et al. (1998) at 25°C as mentioned above. In this study 88% *p*-coumaric acid and 85% *p*-hydroxybenzaldehyde removal were obtained at 80 kHz, and applied sonication powers varying between 75 and 150 W at 25°C . The phenol by-products removal found in this study are higher than the yield observed by Andreozzi et al. (1998) at 25°C . Adhoum and Monser [49] found 88.00% polyphenol removal by electrocoagulation at 25 min retention time and at 25°C . The phenol by-product yields found by sonication are higher than the data obtained by electrocoagulation at 25°C .

It was reported that the dihydroxy phenols are further converted to organic mineral acids and finally to CO_2 and H_2O under sonication [51] 17% total phenol and 56% dihydroxy phenols removals were obtained after 60 min sonication at 30 kHz frequency and 500 W powers. These results were significantly lower than the yields obtained in the present study. The study

performed by Khoufi et al. [52] showed that fenton reaction followed by an anaerobic biotreatment provided 80% orthobiphenols removals. These data were lower than the yields obtained for 2-phenyl-phenol and 3-phenyl-phenol having the same carbon rings.

3.5.3 Effect of increasing sonication time on the taas removal efficiencies in omi ww at 25°C ambient conditions

33.67%, 48.27% and 63.17% TAAs removal efficiencies were observed at an influent TAAs concentration of 3000 mg benzidine/l after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 25°C (Table 12). The TAAs removal efficiencies in OMI ww increased from 33.67% up to 63.17% as the sonication time was increased from 60 to 150 min. The maximum TAAs removal efficiency was 63.17% after 150 min at pH=7.0 and at 25°C (Table 12). A significant linear correlation between TAAs yields and increasing sonication time was observed ($R^2=0.79$, $F=15.32$, $p=0.01$).

Low TAAs yields at low temperature could be attributed to the modifications of some sonodegraded aliphatic chains to generate condensed aromatic structures containing large proportions of hydroxyl, methoxyl, carboxyl and carbonyl groups (Oussi et al., 1997). The recent studies, showed that the destruction of TAAs from OMI ww are difficult since OMI ww contained some methoxyl groups of aromatic ethers, *N*-substituted aromatic carbons and amide moieties [5].

Fig. 3 shows the theoretical sono-degradation of aromatic amine (AA) namely “4-hydroxybenzoic acid” containing Cl^{-1} , CH_2 , CH_3 and $COOH$ groups with five aromatic benzene rings: In the first metabolic pathway the benzene rings in AAs cleaved with hydroxylation reaction with sonication of OMI ww. In the second metabolic pathway the destruction of carboxyl structure in 4-hydroxybenzoic acid occurred and the ethyl groups with *N* bound cleaved from the AAs in question via *N*-deethylation.

Table 12. Effect of increasing sonication time on TAAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98 and at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values ±SD)

Parameters	Initial Conc.	Removal Efficiencies (%)		
		25°C		
		60. min	120. min	150. min
TAAs	3000 ± 105 mg/l	33.67	48.27	63.17

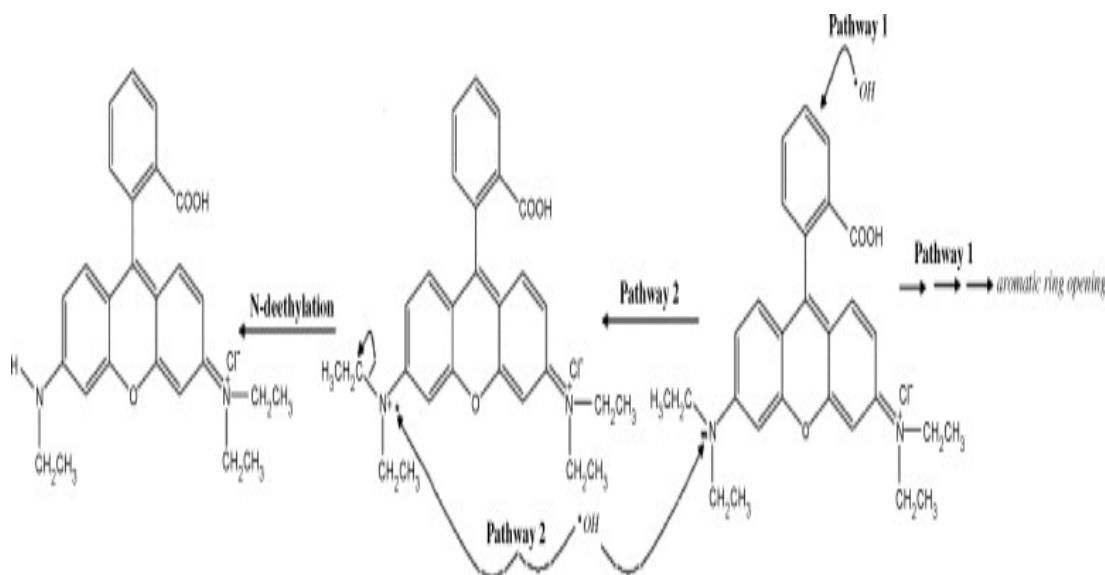


Fig. 3. The sonodegradation mechanism of OMI ww with OH^\bullet via two competitive processes: *N*-Deethylation and destruction of the Aromatic rings

As can be seen in Table 12 the absorption spectra given in absorption band at wavelengths of $\lambda=0.850$ nm, $\lambda=0.680$ nm and $\lambda=0.440$ nm decreased with increasing sonication times and the minimum absorption wavelength shifts was obtained at 150 min at pH=7.0. As a result, 4-hydroxybenzoic acid sonodegraded to benzene and carboxyl groups. Therefore, destruction of carboxyl structure takes place in the AA in question under sonication. The sonodegradation scheme of 4-hydroxybenzoic acid" AA showed spectral changes of *N*-deethylation under sonolysis (Fig. 3).

The absorption decreased with the concomitant high wavelength shift of band to the shorter wavelengths (from 0.683 nm to 0.640 nm, to 0.615 nm and to 0.593 nm). 33.67%, 48.27% and 63.17% absorbance removals for TAAs in OMI ww were observed as the wavelengths decreased from 0.683 nm to 0.640 nm and 0.615 nm, respectively, at pH=7.0 and at 25°C. These results indicate that in the sonication of AAs the cleavage of aromatic chromophore ring structure takes place, but decomposition of aromatic structure is predominant as can be seen in Fig. 3. With increasing the sonication time the poly-aromatic rings are destroyed and the produced aromatic rings and intermetabolites display low absorption levels compared to the initial wavelengths ($\lambda=0.850$ nm, $\lambda=0.680$ nm and $\lambda=0.400$ nm).

Although, in this study it was studied at a temperature as low as 25°C, long sonication time as high as 150 min provided high TAAs removals. At longer sonication times it was reached quickly to the equilibrium and faster rate of TAAs removals was obtained. The high TAAs yields could be attributed to the higher mass transfer and higher surface area produced by the cavitation process [53].

Hydrolysis and pyrolysis are main degradation mechanisms for AAs with ultrasound. The attack of non-volatile compounds in the "bulk water" by

OH[•] destroy the chromophoric system through azo bond cleavage. OH[•] attack leads to hydroxyl amines followed by subsequent oxidation forming aromatic nitroso and nitro compounds. The attack at the carbon atom adjacent to the azo bond, leading to production phenyl derivative radicals. Further degradation pathways are difficult to predict since the fate of the fragments depends on their physical and chemical properties. Further reactions may occur inside the cavity (pyrolysis), in the hypercritical water layer or in the "bulk" water as reported by Reherek et al. [54].

Tang and Isacson [55] found 30% TAAs (toluene, ethyl benzene, m-xylene, p-xylene, o-xylene, 3-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,3,4-tetramethylbenzene) removals in OMI ww after 60 min at 25°C. In this study, 33.67% TAAs removal was observed at 25°C after 60 min. The TAAs removals in both studies exhibited similarities at 25°C. Dungan [56] 27% TAAs (benzene, toluene, xylene, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene) yields obtained after 60 min at 25°C. These TAAs removals were found to be lower than the present study at 25°C after 60 min.

3.5.4 Effect of increasing sonication time on the TFAs removal efficiencies in omi ww at 25°C ambient conditions

12.73%, 18.84% and 37.51% TFAs removal efficiencies were obtained at an influent TFAs concentration of 5200 mg/l after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 25°C (Table 13). The TFAs removal efficiencies in OMI ww increased from 12.78% up to 37.51% as the sonication time was increased from 60 to 150 min. The maximum TFAs removal efficiency was 37.51% after 150 min at pH=7.0 and at 25°C (Table 13). A significant linear correlation between TFAs yields and increasing sonication time was observed ($R^2=0.75$, $F=18.76$, $p=0.01$).

Table 13. Effect of increasing sonication time on TFAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98 and at 25°C ambient conditions (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values \pm SD)

Parameters	Initial Conc.	Removal Efficiencies (%)		
		25°C		
		60. min	120. min	150. min
TFAs	5200 \pm 182 mg/l	12.73	18.84	37.51

In a study performed by Jimenez et al. [57] 43%, 45% and 46% TFAs removals were found in OMI ww in 3 different sonicators with horn probe, cleaning bath and conventional thermal treatment, respectively at 150 W, at 25 kHz for 20 min at temperatures varying between 28°C and 30°C. In the present study, low TFAs yields were obtained compared to the TFAs removals obtained by Jimenez et al. [57].

3.6 Effect of Increasing Temperature on the Removals of COD_{dis} and TOC versus Sonication Times in OMI ww

3.6.1 Effect of increasing sonication time on the removals of COD_{dis} in the OMI ww

At the beginning of the studies the raw OMI ww samples were sonicated at 30°C and at 60°C, at increasing sonication times from 5 min up to 60 min to determine the lowest sonication times for the maximum COD_{dis} removal efficiencies at pH=7.0. The lowest sonication time was determined as 60 min for the maximum COD_{dis} removals at pH=7.0. 15.47%, 42.29% and 62.57% COD_{dis} removals were measured after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 14). An increase of 2.89% and 1.66% in COD_{dis} yields was obtained compared to the control at pH=7.0 and at 25°C after 60 and 150 min, respectively, at 30°C (Table 14). Sonication alone provided 41.74% and 60.91% COD_{dis} removals after 120 and 150 min at pH=7.0 and at 25°C (Table 14). A significant linear correlation between COD_{dis} yields and sonication time was not observed ($R^2=0.41$, $F=2.99$, $p=0.01$).

17.77%, 46.81% and 66.83% COD_{dis} removals were observed after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 14). 5.19%, 5.07% and 5.92% increases in COD_{dis} yields was obtained after 60 min, 120 and 150 min, respectively, at 60°C, compared to the control ($E=60.91\%$ COD_{dis} after 150 min at pH=7.0 and at 25°C) (Table 14). The maximum COD_{dis} removal efficiency was 66.83% after 150 min at pH=7.0 and at 60°C (Table 14). A significant linear correlation between COD_{dis} yields and sonication time was not observed ($R^2=0.47$, $F=3.67$, $p=0.01$). A significant linear correlation between COD_{dis} yields and increasing temperature was not found at all sonication times.

14.34%, 42.42% and 61.62% TOC removals were measured after 60 min, 120 and 150 min,

respectively, at pH=7.0 and at 30°C (Table 15). 1.87%, 1.62% and 2.34% increase in TOC yields was obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C, compared to the control (40.80% and 59.28% TOC removals after 120 and 150 min at pH=7.0 and at 25°C) (Table 15) ($R^2=0.36$, $F=2.78$, $p=0.01$). A significant linear correlation between TOC yields and sonication time was not observed ($R^2=0.40$, $F=2.99$, $p=0.01$).

17.83%, 45.27% and 65.92% TOC removals were obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 15). 5.36%, 4.47% and 6.64% increase in TOC yields was obtained after 60 min, 120 and 150 min, respectively, at 60°C, compared to the control ($E=59.28\%$ TOC removals after 150 min at pH=7.0 and at 25°C) (Table 15). The maximum TOC removal efficiency was 65.92% after 150 min at pH=7.0 and at 60°C (Table 15). A significant linear correlation between TOC yields and sonication time was not observed ($R^2=0.43$, $F=4.56$, $p=0.01$).

It is generally believed that although, increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapor pressure, the sonochemical effect of such bubbles may be reduced. This is due to the fact that bubbles contain more vapor, which cushions the implosion growth as well as use enthalpy for condensation. The increase of aqueous temperature certainly increases the number of cavitation bubbles on sonolysis and thus the rate of production of radicals (OH^\bullet and OOH^\bullet) results in a lowering of the cavitation threshold. Additionally, at low temperature ($< 25^\circ\text{C}$), the vapor pressure of water is lower, and the solubility of gas is higher, hence the cavitation bubbles exhibit a more gaseous nature. As a result, the reaction rates do not decrease with increase in solution temperature between 30°C and 60°C. Therefore, reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement on the rate of reaction of radicals with pollutant [58].

3.6.2 Effect of increasing temperature on the color removal efficiencies in omi ww at increasing sonication times

38.68%, 52.61% and 74.45% color removals were found after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 16).

2.31%, 4.71% and 24.75% increase in color yields was obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C, compared to the control (E=59.70% color after 150 min at pH=7.0 and at 25°C) (Table 16). A significant linear correlation between color yields and temperature was not observed ($R^2=0.37$, $F=3.28$, $p=0.01$).

44.59%, 69.74% and 83.77% color yields were obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 16). The contribution of temperature to the color yields in OMI ww were 8.22%, 21.84% and 34.07% after 60 min, 120 and 150 min, respectively, at 60°C, compared to the control (E=59.70% color at pH=7.0 and at 25°C) (Table 16). The maximum color removal efficiency was 83.77% after 150 min at pH=7.0 and at 60°C (Table 16). A significant linear correlation between color yields and temperature was not obtained in OMI ww ($R^2=0.45$, $F=3.67$, $p=0.01$).

Oxidation and pyrolysis are main degradation mechanisms for decolorization with ultrasound. Reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement of the reaction rate of radicals (H^\bullet , OH^\bullet , O_2H^\bullet) with dye molecules [59]. On the other hand, any increase in temperature will raise the vapor pressure of a medium and so lead to easier cavitation but less violent collapse [60]. Under extreme alkaline conditions, OH^\bullet scavenging effects become more significant [61]. The enhancement of degradation rate at basic conditions may be caused by the change of hydrophobic property of dye [59]. The hydrophilic property of the color originating from the ferric humates, humic materials, potassium chloroplatinate (K_2PtCl_6), MnO_2 , Fe_2O_3 , etc., is mostly degraded outside the cavitation process by the OH^\bullet produced by ultrasound.

The color of OMI ww varied from dark-red to brownish black depending on its age and the extraction procedure. While the monomeric phenols exhibit phytotoxic [62] and antimicrobial activities [48], polymeric phenols have a lignin-like structure as their most recalcitrant fraction and are mainly responsible for the typical color of OMI ww [48,63]. On the other hand, the high-molecular-weight phenolic compounds similar in structure to the lignin gives the characteristics recalcitrant brownish black color in OMI ww [64,65].

Guzman-Duque et al. [66] 53% color removal was measured at 80 kHz after 180 min, at 60°C in OMI ww. In this study 83.77% color removal was found at 60°C. In the present study, high color yields were observed compared to the color removals obtained by Guzman-Duque et al. [66] In the study performed by Svitelska et al. [67] 50% color yield was obtained at 20 kHz, at pH > 10.0 and at 60°C. In this study, 83.77% color removal measured at 60°C after 150 min. In this study, the color yield is higher than the yield obtained by Svitelska et al. [67] at 60°C as mentioned above.

3.6.3 Effect of increasing temperature on the total phenol removal efficiencies in omi ww at increasing sonication times

28.26%, 56% and 59.40% total phenol removals were observed after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 17). The contribution of temperature increase to the total phenol removals were found to be as 1.37%, 1.26% and 1.15% after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C, compared to the control (E=58.25% total phenol after 150 min at pH=7.0 and at 25°C) (Table 17). A significant linear correlation between total phenol yields and temperature was not obtained in OMI ww ($R^2=0.42$, $F=3.99$, $p=0.01$).

30.20%, 57.94% and 61.24% total phenol yields were found after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 17). The contribution of temperature to the total phenol yields were only 3.31%, 3.20% and 2.99% after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C, compared to the control (E=58.25% total phenol after 150 min at pH=7.0 and at 25°C) (Table 17). The maximum total phenol removal efficiency was 61.24% after 150 min at pH=7.0 and at 60°C (Table 17). A significant linear correlation between total phenol yields and temperature was not observed ($R^2=0.32$, $F=2.89$, $p=0.01$).

The sonochemical degradation of actual OMI ww samples is likely to occur through complex reaction pathways involving the formation of numerous intermediates competing for the available sonication energy; moreover, several of these intermediates such as caffeic acid may be of phenolic nature. On the other hand, with caffeic acid as the starting molecule, fewer reactions and intermediates are likely to occur and this would explain the enhanced performance of sonochemical degradation [49].

Table 14. Effect of increasing sonication temperature on COD_{dis} removal efficiencies of OMI ww before and after sonication process at pH=7.0, at 25°C, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, , initial COD_{dis} concentration of 109444 mg/l, n=3, mean values ±SD)

Parameters	COD _{dis} Removal Efficiencies (%)							
	25°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww	0	12.58	41.74	60.91				
	30°C				60°C			
Raw ww	0	15.47	42.29	62.57	0	17.77	46.81	66.83

Table 15. Effect of increasing sonication temperature on TOC removal efficiencies of OMI ww before and after sonication process at pH=7.0, at 25°C, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TOC concentration of 66488 mg/l, n=3, mean values ±SD)

Parameters	TOC Removal Efficiencies (%)							
	25°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww	0	12.47	40.80	59.28				
	30°C				60°C			
Raw ww	0	14.34	42.42	61.62	0	17.83	45.27	65.92

Table 16. Effect of increasing temperature on color removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m⁻¹, n=3, mean values ±SD)

Parameters	Color Removal Efficiencies (%)							
	25°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	36.37	47.90	59.70				
	30°C				60°C			
Raw ww	0	38.68	52.61	74.45	0	44.59	69.74	83.77

Table 17. Effect of increasing temperature on total phenol removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values ±SD)

Parameters	Total Phenol Removal Efficiencies (%)							
	25°C							
	0. min	60. min	120. min	150. min				
Raw ww, control	0	26.89	54.74	58.25				
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww	0	28.26	56.00	59.40	0	30.20	57.94	61.24

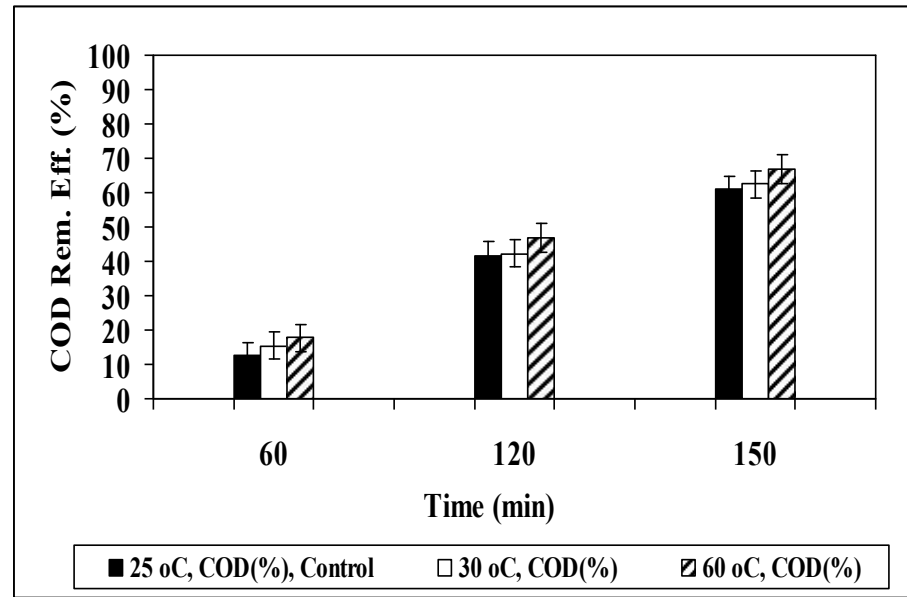


Fig. 4. Effect of increasing temperature on the COD_{dis} removal efficiencies in OMI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values)

The study performed by Kidak and Ince [68] showed that 60% phenol removal could be achieved at acidic pH with sonication at 300 kHz, after 90 min, at 60°C. In this study, 61.24% total phenol removal was observed at 60°C after 150 min. In the present study the total phenol removal is higher than the yield obtained by Kidak and Ince [68]. In a study performed by Entezari and Petrier [21] 50%-60% phenol removal efficiency was measured at 423 kHz, after 45 min, at 60°C. They reported that the OH[•] produced by ultrasound can react with phenol resulting in a dephenolization process. In this study, 61.24% total phenol removal was observed at 60°C after 150 min. The total phenol removal is higher than the yield observed by Kidak and Ince [68] as mentioned above.

The phenol intermediates measured (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww with HPLC at pH=7.0 after 60 min, 120 and 150 min at 30°C and at 60°C. From 4090 mg/l total phenol 501.55 mg/l 2-phenyl-phenol and 899.99 mg/l 3-phenyl-phenol were produced after 60 min at pH=7.0 and at 60°C (Table 18). 501.55 mg/l 2-phenyl-phenol was reduced to 10.98 mg/l after 150 min at pH=7.0 and at 60°C (Table 18). 899.99 mg/l 3-phenyl-phenol decreased to 8.76 mg/l after 150 min at pH=7.0 and at 60°C (Table 18).

The phenol metabolites (2-phenyl-phenol and 3-phenyl-phenol) were removed with yields of 97.81% and 99.03%, respectively, after 150 min at pH=7.0 and at 60°C (Table 18). It was found that 4090 mg/l total phenol sonodegraded to 1401.54 mg/l (2-phenyl-phenol and 3-phenyl-phenol). Since the total phenol yields are high (98.25%) after 150 min at pH=7.0 and at 60°C it can be assumed that the remaining total phenol (remaining phenol=4090-1401.54=2688.46 mg/l) mainly sono-degraded to the end products with high yields and minorly converted to other phenol metabolites which they are not measured in this study (tyrosol, hydroxytyrosol, oleuropein, caffeic acid, quercetin, ferulic acid, catechol, vanillic acid, o-quinone, *p*-coumaric acid, *p*-hydroxybenzaldehyde, etc.) through sonication.

Jahouach-Rabai et al. [69] investigated the removal of OME using a sonicator at 20 kHz, at 750 W and at 30°C. 61% removal efficiencies were obtained for some non-odorous organics (hexanal, hept-2-enal, 2(E)-decadienal, 4(E)-decadienal) and for some phenolic organics. Vassilakis et al. [19] investigated to the sonochemical degradation of some phenolic by-

products namely, *p*-coumaric acid and *p*-hydroxybenzaldehyde in OMI ww at 80 kHz in a horn-type sonicator. 90% phenol removals were found at an initial phenolic compound concentration of 100 mg/l, at between 75 and 150 W and at between 25 and 70°C. 88% degradation yields were obtained for *p*-coumaric acid. The removals of the phenol metabolites mentioned above are lower than the yields of phenol metabolites (2-phenyl-phenol and 3-phenyl-phenol) found after 150 min at 60°C.

3.6.4 Effect of increasing temperature on the taas removal efficiencies in omi ww at increasing sonication times

37.19%, 55.34% and 64.98% TAAs yields were obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 19). 3.52%, 7.07% and 1.81% increase in TAAs removals was obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C, compared to the control (E=63.17% TAAs after 150 min at pH=7.0 and at 25°C) (Table 19). A significant linear correlation between TAAs yields and temperature was not obtained in OMI ww ($R^2=0.38$, $F=4.34$, $p=0.01$).

38.14%, 59.39% and 70.52% TAAs removals were found after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 19). The contribution of temperature to the TAAs yields were 4.47%, 11.12% and 7.35% after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C, compared to the removals obtained in control (E=63.17% TAAs after 150 min at pH=7.0 and at 25°C) (Table 19). The maximum TAAs removal efficiency was 70.52% after 150 min at pH=7.0 and at 60°C (Table 19). A significant linear correlation between TAAs yields and increasing sonication times was observed ($R^2=0.73$, $F=15.87$, $p=0.01$) while the correlation between temperature and TAA yields was not significant ($R^2=0.43$, $F=2.87$, $p=0.01$).

In this study, the TAA content of OMI was measured based on Benzidine as mg/l. The identification of the TAAs was not performed. The recent literature showed that the sonochemical degradation of TAAs predominantly occurs via OH[•] attack; although a thermal reaction occurring in the vicinity of the bubble cannot be completely discounted, its contribution should be small [54]. Degradation proceeds through a series of aromatic and ring cleavage intermediates with OH[•]- mediated reactions being the prevailing mechanism occurred (Oussi et al., 1997).

Benzoic acid, terephthalic acid and isophthalic acid are the main TAAs by-products after the sonodegradation of hydroquinone. 53% benzoic acid, 47% terephthalic acid and 38% isophthalic acid removals were observed at 30 kHz, at 750 W at 75°C (Entezari et al., 2003). In the present study, 70.52% TAAs removal was observed at 60°C after 150 min.

3.6.5 Effect of increasing temperature on the TFAs removal efficiencies in OMI ww at increasing sonication times

15.62%, 22.37% and 45.66% TFAs yields were observed after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 20). 2.89%, 3.53% and 8.15% increase in TFAs removals was observed after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C compared to the control (E=37.51% TFAs after 150 min at pH=7.0 and at 25°C) (Table 20). A significant linear correlation between TFAs yields and increasing sonication times and increasing temperatures was not observed ($R^2=0.37$, $F=3.09$, $p=0.01$; $R^2=0.41$, $F=3.07$, $p=0.01$).

17.33%, 24.77% and 48.84% TFAs removals were found after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 20). The contribution of temperature to the TFAs yields were 4.60%, 5.93% and 11.33% after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C, compared to the control (E=37.51% TFAs after 150 min at pH=7.0 and at 25°C) (Table 20). The maximum TFAs removal efficiency was 48.84% after 150 min at pH=7.0 and at 60°C (Table 20). A significant linear correlation between TFAs yields and increasing temperature was not observed ($R^2=0.33$, $F=2.37$, $p=0.01$).

Chemat et al. [70,71] found that the TFAs in an OMI ww composed of palmitic, stearic, oleic and linoleic acids. The removal yields of these TFAs were 61% in a sonicator at 20 kHz, at 150 W, after 20 min at 50°C. In this study, 48.84% TFAs yields was observed at 60°C after 150 min. This TFAs removal is higher than the yield found by in the present study. Jahouach-Rabai et al. (2008) investigated the removal of olive mill effluents using a sonicator at 20 kHz, at 750 W, at 30°C. In this study, it was found that many volatile compounds are responsible for the flavors originated from the degradation of triacylglycerols, polyunsaturated fatty acids or

phospholipids in OMI. Other odor given compounds are derived from the autoxidation of fatty acids. In fact, a large number of volatiles can be formed during autoxidation of unsaturated acyl lipids. In a study performed by Hachicha et al. [72] it was found that the TFAs fraction of OMI sludge composed of oleic, palmitic and linoleic acids and degraded through sonication with yields varying between 50.40% and 52%. These removals are comparable similar with TFAs yields obtained in the present study.

3.7. Effect of DO Concentrations on the Removals of COD_{dis} in OMI ww

OMI ww samples were oxygenated with increasing DO concentrations (2 mg/l, 4 mg/l, 6 and 10 mg/l) with pure O₂ tubing before the sonication experiments. 62.71%, 71.22%, 74.83% and 79.86% COD_{dis} removals were obtained in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO, respectively, after 150 min, at pH=7.0 and at 30°C (Table 21, Fig. 4). Increasing sonication time and DO concentrations increased the COD_{dis} yields at 30°C. 6-10 mg/l DO concentrations increased the COD_{dis} yields from 62.57% to 74.83% and to 79.86% after 150 min, respectively at pH=7.0 and at 30°C, compared to the control (without DO at pH=7.0 and at 30°C) (Table 21, Fig. 4). Sonication alone provided 15.47%, 42.29% and 62.57% COD_{dis} yields after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 21, Fig. 4). A significant linear correlation between COD_{dis} yields and increasing DO concentrations was observed ($R^2=0.94$, $F=17.37$, $p=0.01$).

73.12%, 79.41%, 84.32% and 88.73% COD_{dis} yields were measured in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO after 150 min, respectively, at pH=7.0 and at 60°C (Table 21, Figure 4). The COD_{dis} removals increased by 22-30% as the DO increased from 2 to 10 mg/l DO after 150 min at pH=7.0 and at 60°C (Table 21, Figure 4). Control reactor provided 17.77%, 46.81% and 66.83% COD_{dis} removals after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 21, Figure 4). 88.73% maximum COD_{dis} removals were obtained at a DO concentration of 10 mg/l after 150 min sonication time at pH=7.0 and at 60°C (Table 21, Figure 4). A significant linear correlation between COD_{dis} yields and increasing DO concentrations was observed ($R^2=0.97$, $F=17.51$, $p=0.01$).

Table 18. The measurements of phenol intermediates (2-phenyl-phenol and 3-phenyl-phenol) in OMI ww with HPLC at pH=7.0 after 60 min, 120 and 150 min at 60°C (initial total phenol concentration=4090 mg/l, n=3, mean values ±SD)

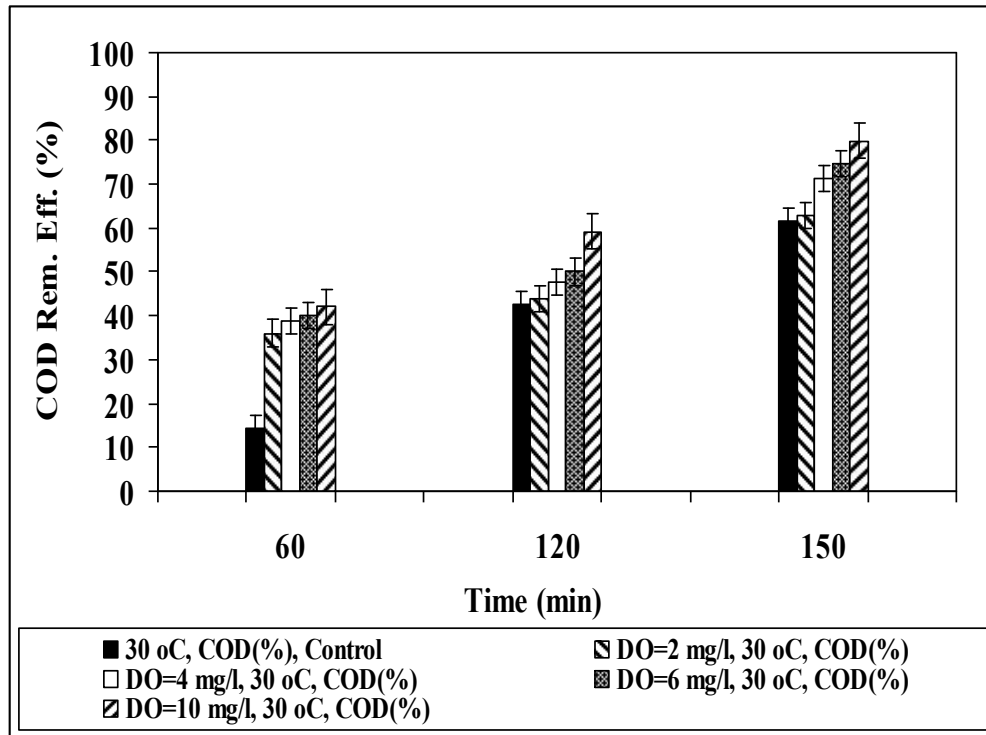
Parameters	Phenol Concentrations (mg/l)				Phenol Intermediates Removal Efficiencies (%)			
	0. min	60. min	120. min	150. min	60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2-phenyl-phenol	4090	501.55	278.4	10.98	0	87.73	93.19	97.81
3-phenyl-phenol	4090	899.99	251.7	8.76	0	77.99	93.85	99.03

Table 19. Effect of increasing temperature on TAAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values ±SD)

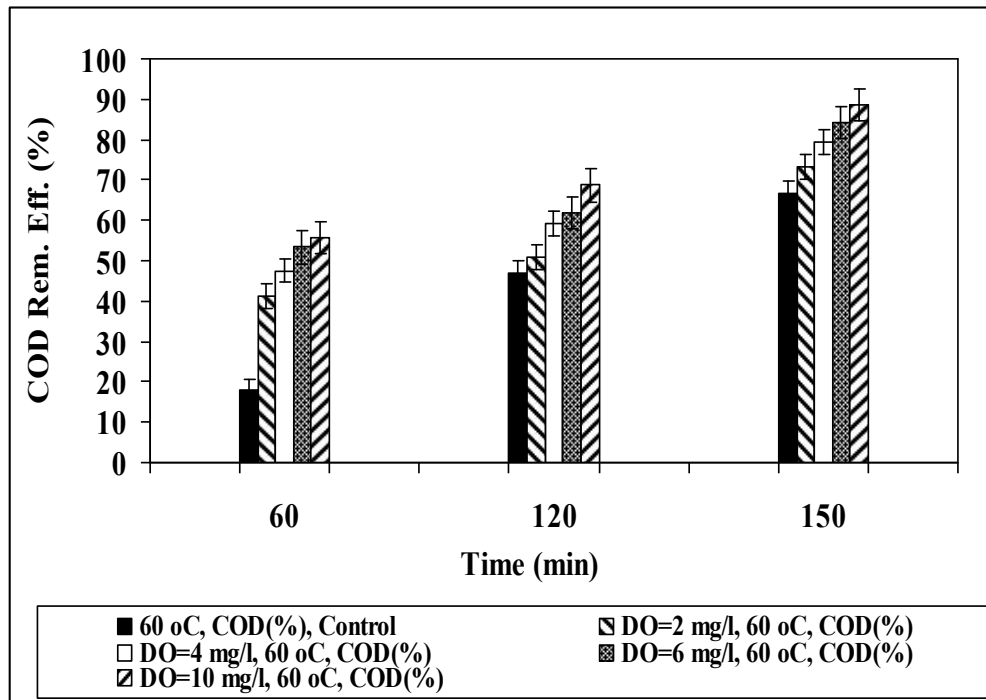
Parameters	TAAs Removal Efficiencies (%)							
	25°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	33.67	48.27	63.17				
Raw ww	0	37.19	55.34	64.98	0	38.14	59.39	70.52

Table 20. Effect of increasing Temperature on TFAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values ±SD)

Parameters	TFAs Removal Efficiencies (%)							
	25°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	12.73	18.84	37.51				
Raw ww	0	15.62	22.37	45.66	0	17.33	24.77	48.84



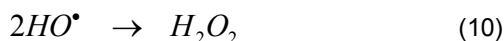
(a)



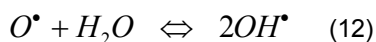
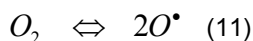
(b)

Fig. 4. Effect of increasing DO concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values)

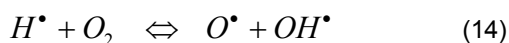
It is clearly shown that the destruction of COD_{dis} increases significantly with an increase of O_2 . This observation may be partially ascribed to the generation of OH^\bullet , resulted from dissociation of molecular O_2 in the bubble, which is likely to recombine to form H_2O_2 at the gas-liquid interface of the bubbles [73] in Equations (8), (9) and (10):



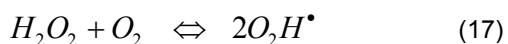
O_2 present in the bubble (in gaseous form) and present in the medium (in dissolved or aqueous form as well as in the form of tiny bubbles suspended in the medium) can scavenge radicals inside the bubble as well as in the bulk medium in several ways. Dissociation of molecular O_2 in the bubble influences the formation of OH^\bullet via **Equations (11) and (12)**:



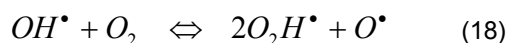
The O_2 in the bubble can also react with H^\bullet formed out of H_2O dissociation to generate OH^\bullet and O_2H^\bullet via Equations (13), (14) and (15):



Equations (14) and (15) can also occur in bulk liquid medium where DO can react with H^\bullet released during transient bubble collapse. In addition to this, the DO in the medium can help revert the loss of oxidation potential due to recombination of OH^\bullet released in the medium by generating O_2H^\bullet species via Equations (16) and (17):



Finally, the DO can also react with OH^\bullet released in the medium to generate additional oxidizing species via Equation (18):



The H_2O_2 measurement during acoustic cavitation, in absence and in the presence of OMI ww, is a suitable method to estimate the radical production rate for specific sonochemical conditions. The initial rate of H_2O_2 formation associated to the COD treatment by sonication in OMI ww decreases with increasing sonication time at 60°C (Table 22). In the absence of OMI ww (in deionized water) the H_2O_2 was accumulated and its concentration was measured as 185 mg/l while the H_2O_2 concentration increased to 98 and 145 mg/l after 30 and 120 min, whereas the H_2O_2 level was only 14.00 mg/l in OMI ww after 150 min in samples containing 10 mg/l DO (Table 22). The OH^\bullet ion concentrations also increased from 10×10^{-62} to 43×10^{-7} mg/l after 150 min in OMI ww. This showed that hydroxylation is the main mechanism for the removal of COD_{dis} . In other words, OH^\bullet is the major process for complete degradation of COD_{dis} . In this study, in OMI ww the most sonogenerated OH^\bullet reacted with 87% maximum COD_{dis} removal and radical recombination to produce H_2O_2 .

In the study carried out Lafi et al. [5] 28.90% COD_t removal efficiency was obtained with UV/ O_3 process in OMI ww. Aerobic biodegradation followed by ozonation provided 80% COD removal in OMI ww at 50°C. In this study, 88.73% COD_{dis} yield was observed at 60°C after 150 min. In this study, the COD_{dis} removal is higher than the yield found by Lafi et al. [5] at 50°C as mentioned above.

3.7.1 Effect of DO concentrations on the color removal efficiencies in omi ww at increasing sonication time and temperature

80.16%, 84.07%, 86.27% and 87.47% color yields were observed in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO after 150 min, respectively, at pH=7.0 and at 30°C (Table 23). 2-10 mg/l DO concentrations increased the color yields from 42.59-68.84% to 54.81-78.06% after 60 and 120 min, respectively, at pH=7.0 and at 30°C, compared to the control (38.68%, 52.61% and 74.45% color removals after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C) (Table 23). A significant linear correlation between color yields and increasing DO concentrations was observed ($R^2=0.91$, $F=19.12$, $p=0.01$).

Table 21. Effect of increasing DO concentrations on COD_{dis} removal efficiencies of OMI ww before and after sonication process at pH=7.0, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration of 109444 mg/l, n=3, mean values ±SD)

Parameters	COD _{dis} Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	15.47	42.29	62.57	0	17.77	46.18	66.83
DO=2 mg/l	0	36.05	43.90	62.71	0	41.16	50.99	73.12
DO=4 mg/l	0	38.88	47.60	71.22	0	47.54	59.21	79.41
DO=6 mg/l	0	40.18	50.01	74.83	0	53.32	61.70	84.32
DO=10 mg/l	0	42.17	59.23	79.86	0	55.56	68.68	88.73

Table 22. Effect of DO=10 mg/l concentration on H₂O₂ and OH[•] ion concentration in OMI ww at 60°C after 30 min, 120 and 150 min (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values)

Conditions	H ₂ O ₂ Conc. (mg/l) (60°C)	OH [•] ion Conc. (mg/l)
H ₂ O ₂ concentration (mg/l) in deionized water (60°C)	185	0
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 30 min sonication	98	10x10 ⁻⁶²
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 120 min sonication	145	2x10 ⁻⁵²
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 150 min sonication	14	43x10 ⁻⁷

Table 23. Effect of increasing DO concentrations on color removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m⁻¹, n=3, mean values ±SD)

Parameters	Color Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	38.68	52.61	74.45	0	44.59	69.74	83.77
DO=2 mg/l	0	42.59	54.81	80.16	0	70.84	75.85	86.87
DO=4 mg/l	0	52.00	77.66	84.07	0	73.75	79.86	89.58
DO=6 mg/l	0	62.42	78.96	86.27	0	74.75	79.96	91.38
DO=10 mg/l	0	68.84	78.06	87.47	0	80.86	84.17	93.79

86.87%, 89.58%, 91.38% and 93.79% color yields were found in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO after 150 min, respectively, at pH=7.0 and at 60°C (Table 23). 2-10 mg/l DO concentrations increased the color yields from 70.84-80.86% to 75.85-84.17% after 60 and 120 min, respectively, at pH=7.0 and at 60°C, compared to the control (44.59%, 69.74% and 83.77% color yield after 60 min, 120 and 150 min at pH=7.0 and at 60°C) (Table 23). The maximum color removal efficiency was 93.79% under DO=10 mg/l after 150 min at pH=7.0 and at 60°C (Table 23). A significant linear correlation between color yields and increasing DO concentrations was observed ($R^2=0.96$, $F=19.20$, $p=0.01$).

Dissolved gas is an important factor that affects aqueous sonochemical processes and it acts as nucleation sites for cavitation [74]. This may improve color removal in combination with ultrasonic irradiation. The efficiency of acoustic cavitation increased in the presence of DO since DO is strongly consumed inside the bubble when the bubble temperature at the bubble collapse is higher such as 60°C after 150 min. However, the presence of dissolved N_2 achieved less decolorization efficiency than that of DO. Thermal conductivities ($\gamma = C_p/C_v$) of the dissolved gases have been inversely correlated to the sonochemistry field. Though, the efficiency of acoustic cavitation under N_2 is almost equal to that under O_2 due to the little difference between their thermal conductivities, oxidants are strongly consumed inside a bubble by oxidizing N_2 when the bubble temperature at the bubble collapse is higher than about 7000°K. In addition, dissolved N_2 present in aqueous solution might scavenge the free radicals and inhibit OH^\bullet oxidation of color [75].

3.7.2 Effect of DO concentrations on the total phenol removal efficiencies in omi ww at increasing sonication times and temperatures

77.20%, 80.04%, 82.92% and 88.02% total phenol removals were found in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO, respectively, after 150 min, at pH=7.0 and at 30°C (Table 24). 2-10 mg/l DO concentrations increased the total phenol yields from 28.26-56% to 43.46-43.98% and to 74.58-81.83% after 60 and 120 min, respectively, at pH=7.0 and at 30°C, compared to the control reactor (28.26%, 56% and 59.40% total phenol yields after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C) (Table 24). A significant linear correlation between total

phenol yields and increasing DO concentrations was observed ($R^2=0.92$, $F=18.11$, $p=0.01$).

85.53%, 88.02%, 89.46% and 91.38% total phenol yields were found in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO, respectively, after 150 min at pH=7.0 and at 60°C (Table 24). 2-10 mg/l DO concentrations increased the total phenol yields from 30.20-57.94%, to 44.06-73.80% and to 79.25-84.66% and to 85.53-91.38% after 60, 120 min and 150 min, respectively, at pH=7.0 and at 60°C, compared to the control (30.20%, 57.94% and 61.24% total phenol yields after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C) (Table 24). The maximum total phenol removal efficiency was 91.38% at DO=10 mg/l after 150 min at 60°C (Table 24). A significant linear correlation between total phenol yields and increasing DO concentrations was observed ($R^2=0.90$, $F=19.68$, $p=0.01$).

A number of studies have shown that ultrasonic treatment can result in successful sonodegradation of phenolic compounds (Entezari et al., 2003) [76,77] Pétrier and Francony, 1997; [78]. In the presence of DO the total phenol were removed due to their interaction with OH^\bullet , produced during thermal base catalyzed decomposition of H_2O_2 . This decomposition was more extended at higher temperatures such as 60°C.

Sonication at higher temperature caused higher total phenol removals. The highest efficiency of total phenol removal in the presence of ultrasound was found at high temperature. It was mentioned that the condensed tannins which are one of the phenolic constituents in OMI ww are polar compounds. Therefore, under sonication total phenol removal takes place in the solution bulk or at the bubble-liquid interface. This means that, during sonication, total phenol are removed by OH^\bullet attack, produced from the H_2O_2 by low frequency ultrasound. The injection of H_2O_2 into the cavity and its cleavage into OH^\bullet during the collapse of the cavitation bubble sono-degraded the phenol (Entezari et al., 2003). Usually high ambient temperatures ($> 90^\circ C$) are not favorable for the majority of sonochemical reactions due to the decrease of dissolved gas and increase of vapor pressure [79,80,81]. Nevertheless, in our study the sonolytic reactions of H_2O_2 production from H_2O , was not affected negatively at a temperature as high as 60°C at low frequency (35 kHz).

O_2 present in the bubble (in gaseous form) and present in the medium (in dissolved or aqueous

form as well as in the form of tiny bubbles suspended in the medium) can scavenge radicals inside the bubble as well as in the bulk medium in several ways. Dissociation of molecular O_2 in the bubble influences the formation of OH^\bullet via Equations (19) and (20):



It should be noted that the second reaction could also occur in the bulk medium where O^\bullet released in the medium with transient collapse of the bubble can react with water molecules to generate additional OH^\bullet . The O_2 in the bubble can also react with H^\bullet formed out of water dissociation to generate OH^\bullet and O_2H^\bullet via Equations (21), (22) and (23):

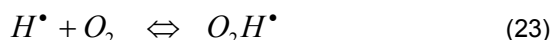
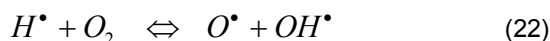
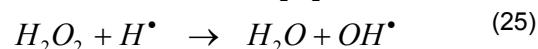
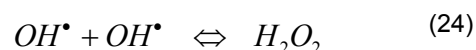


Table 25 shows the effect of 10 mg/l DO on H_2O_2 production, OH^\bullet ion concentrations and phenol yields throughout phenol sonodegradation at 60°C. The OH^\bullet ion concentrations increased from 4×10^{-56} to 10×10^{-6} mg/l after 150 min compared to the deionized water without OMI ww at pH=7.0. The H_2O_2 concentration in deionized water was high (156 mg/l) while it increased from 92 to 135 mg/l as the sonication time increased from 30 to 120 min in OMI ww. The high H_2O_2 production through sonication of OMI ww verified the presence of high OH^\bullet ion concentrations and showed that the main removal mechanism of phenol was the hydroxylation. As the sonication time increased to 150 min the H_2O_2 production decreased to 11 mg/l by ending of sonication with a phenol yield of 93% at 10 mg/l DO concentration (Table 25).

The degradation of phenol occurs in the bulk liquid medium due to hydroxylation reaction induced by OH^\bullet generated from cavitation bubble. This is a consequence of low vapor pressure of phenol (due to which it does not evaporate into the cavitation bubble) and the hydrophilic nature of the phenol molecule. The interaction between radicals and phenol molecules becomes an important factor influencing the overall degradation. The scavenging phenomenon increases the sonodegradation of phenol. Moreover, the

concentration of the radical scavenging species is another important factor affecting the degradation. The formation of OH^\bullet and H_2 derived from sonolysis of H_2O in aqueous solution saturated with O_2 as an endpoint of inertial cavitation was examined.

It should be pointed out that OH^\bullet , formed via H_2O sonolysis, can partly recombine yielding H_2O_2 which in turn reacts with H_2 to regenerate OH^\bullet in Equations (24) and (25):



3.7.3 Effect of DO concentrations on the taas removal efficiencies in omi ww at increasing sonication times and temperatures

68.91%, 69.45%, 73.37% and 77.00% TAAs removals were found in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO, respectively, after 150 min at pH=7.0 and at 30°C (Table 26). 19.05-19.77% and 3.34-9.88% increase in TAAs removals were measured after 60 and 120 min, respectively, at pH=7.0 and at 30°C, compared to the control (37.19%, 55.34% and 64.98% TAAs yields after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C) (Table 26). A significant linear correlation between TAAs yields and increasing DO concentrations was not observed ($R^2=0.30$, $F=2.08$, $p=0.01$).

80.28%, 83.67%, 87.30% and 91.58% TAAs yields were measured in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO, respectively, after 150 min at pH=7.0 and at 60°C (Table 26). The contribution of increasing DO to the TAAs removals were 18.93-29.47% and 5.66-16.37% after 60 and 120 min, respectively, at pH=7.0 and at 60°C, compared to the control (38.14%, 59.39% and 70.52% TAAs removals after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C) (Table 26). The maximum TAAs removal efficiency was 91.58% in DO=10 mg/l after 150 min at pH=7.0 and at 60°C (Table 26). A significant linear correlation between TAAs yields and increasing DO concentrations was observed ($R^2=0.82$, $F=16.71$, $p=0.01$). At longer sonication times and temperatures it was reached high TAAs removals. The high TAAs yields could be attributed to the higher mass transfer and higher surface area produced by the cavitation process [82].

Table 24. Effect of increasing DO concentrations on total phenol removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values ±SD)

Parameters	Total Phenol Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	28.26	56.00	59.40	0	30.20	57.94	61.24
DO=2 mg/l	0	43.46	74.58	77.20	0	44.06	79.25	85.53
DO=4 mg/l	0	43.50	76.89	80.04	0	44.24	79.51	88.02
DO=6 mg/l	0	43.59	76.98	82.92	0	49.35	79.69	89.46
DO=10 mg/l	0	43.98	81.83	88.02	0	73.80	84.66	91.38

Table 25. Effect of 10 mg/l DO concentration on H₂O₂ and OH^{*} ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values)

Conditions	H ₂ O ₂ Conc. (mg/l) (60°C)	OH [*] ion Conc. (mg/l)
H ₂ O ₂ concentration (mg/l) in deionized water (60°C)	156	0
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 30 min sonication	92	4x10 ⁻⁵⁶
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 120 min sonication	135	6x10 ⁻⁴⁸
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 150 min sonication	11	10x10 ⁻⁶

Table 26. Effect of increasing DO concentrations on TAAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values ±SD)

Parameters	TAAs Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	37.19	55.34	64.98	0	38.14	59.39	70.52
DO=2 mg/l	0	56.24	58.68	68.91	0	57.07	65.05	80.28
DO=4 mg/l	0	56.30	61.83	69.45	0	57.31	68.74	83.67
DO=6 mg/l	0	56.42	62.95	73.37	0	64.28	72.31	87.30
DO=10 mg/l	0	56.96	65.22	77.00	0	67.61	75.76	91.58

3.7.4 Effect of DO concentrations on the TFAs removal efficiencies in omi ww at increasing sonication times and temperatures

66.98%, 69.21%, 71.03% and 72.03% TFAs removals were obtained in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 27). 21.48-21.94% and 30.45-37.70% increase in TFAs yields were measured in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO, respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control (15.62%, 22.37% and 45.66% TFAs removals after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C) (Table 27). A significant linear correlation between TFAs yields and increasing DO concentrations was observed ($R^2=0.87$, $F=17.65$, $p=0.01$).

68.19%, 71.18%, 72.74% and 74.44% TFAs yields were found in 2 mg/l, 4 mg/l, 6 and 10 mg/l DO after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 27). The contribution of increasing DO concentrations (from 2 to 10 mg/l) in TFAs removals were found as 22.01-22.76% and 28.46-37.64% after 60 and 120 min, respectively, at pH=7.0 and at 60°C compared to the control reactor (17.33%, 24.77% and 48.84% TFAs yields after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C) (Table 27). The maximum TFAs removal efficiency was 74.44% in DO=10 mg/l after 150 min at pH=7.0 and at 60°C (Table 27). A significant linear correlation between TFAs yields and increasing DO concentrations was observed ($R^2=0.89$, $F=17.96$, $p=0.01$).

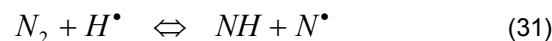
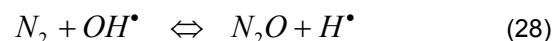
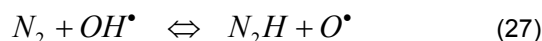
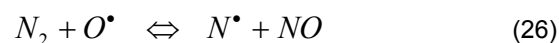
3.8 Effect of N₂(g) on the Removals of COD_{dis} in OMI ww

Pure N₂(g) was sparged in OMI ww before sonication experiments. 28.21%, 42.29% and 70.56% COD_{dis} removals were obtained after 60 min, 120 and 150 min, respectively, under 15 min N₂(g) (3 mg/l N₂) sparging at pH=7.0 and at 30°C (Table 28). 30.39%, 53.46% and 77.36% COD_{dis} removals were measured under 30 min N₂(g) (6 mg/l N₂) sparging after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C (Table 28). 30 min N₂(g) sparging increased the COD_{dis} yields from 42.29% to 53.46% after 120 min sonication time at 30°C, compared to the control [without N₂(g) sparging while E=62.57% COD_{dis} at pH=7.0 after 150 min at pH=7.0 and at 30°C] (Table 28). A significant linear correlation between COD_{dis} yields and increasing N₂(g)

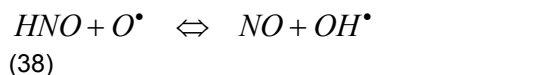
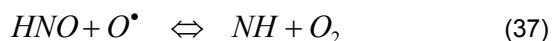
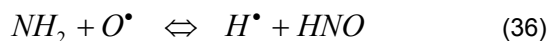
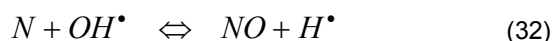
sparging was not observed ($R^2=0.42$, $F=16.34$, $p=0.01$).

37.81%, 60.09% and 79.89% COD_{dis} removals were obtained after 60 min, 120 and 150 min, respectively, under 15 min N₂(g) sparging at pH=7.0 and at 60°C (Table 28). 40.44%, 61.62% and 84.51% COD_{dis} yields were obtained under 30 min N₂(g) sparging after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C (Table 28). No significant differences in COD_{dis} yields was obtained under 15 and 30 min N₂(g) sparging after 120 and 150 min at 60°C. The contribution of the N₂(g) sparging on the COD_{dis} removal efficiency varied between 13.28% and 14.81% under 30 min N₂(g) sparging after 120 min at 60°C compared to the control (E=66.83% COD_{dis} after 150 min at pH=7.0 and at 60°C) (Table 28). The maximum COD_{dis} removal efficiency was 84.51% under 30 min N₂(g) sparging after 150 min at 60°C (Table 28). A significant linear correlation between COD_{dis} yields and increasing N₂(g) sparging was observed ($R^2=0.85$, $F=18.62$, $p=0.01$).

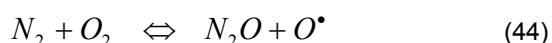
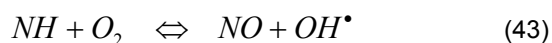
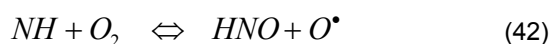
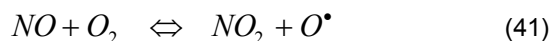
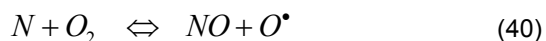
The predominant N₂(g) species produced through sonication are not followed by N₂O, NO₂, HNO and HNO₂. N₂(g) present in the air bubble scavenges H[•], OH[•] and O[•] produced by the dissociation of entrapped water vapor through various reactions. Lindsey and Tarr [83] determined a few representative reactions are given in **Equations (26), (27), (28), (29), (30) and (31)**:



The N₂(g) species produced with the reactions given above also scavenge the radicals through various reactions. Some representative reactions are given in Equations (32), (33), (34), (35), (36), (37), (38) and (39) by Lindsey and Tarr [83]:



It needs to be specifically mentioned that Equations (26), (27), (28), (29), (30), (31), (32), (33), (34), (35), (36), (37), (38) and (39) also occur in the bulk liquid medium due to the reaction of dissolved N_2 with various radicals released into the bulk medium with collapse of cavitation bubble. However, the O_2 present in the bubble reacts concurrently with $N_2(g)$ species to regenerate O^{\bullet} and OH^{\bullet} through the following reactions given in Equations. (40), (41), (42), (43) and (44) in the presence of DO :



3.8.1 Effect of $N_2(g)$ on the color removal efficiencies in omi ww at increasing sonication times and temperatures

82.36% and 89.28% color removals were obtained under 15 and 30 min $N_2(g)$ sparging, respectively, after 150 min at pH=7.0 and at 30°C (Table 29). 37.47-38.88% and 25.05-30.56% increase in color removals were observed under 15 and 30 min $N_2(g)$ sparging, respectively, after

60 and 120 min at pH=7.0 and at 30°C, compared to the control (E=74.45% color after 150 min at pH=7.0 and at 30°C) (Table 29). A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.74$, $F=15.78$, $p=0.01$). 85.87% and 91.88% color yields were measured under 15 and 30 min $N_2(g)$ sparging, respectively, after 150 min at pH=7.0 and at 30°C (Table 29).

The contribution of $N_2(g)$ sparging to the color yield were 33.47-34.67% and 10.62-16.03% under 15 and 30 min $N_2(g)$ sparging, respectively, after 60 and 120 min at pH=7.0 and at 60°C compared to the control (E=83.77% color yield after 150 min at pH=7.0 and at 60°C) (Table 29). The maximum color removal efficiency was 91.88% under 30 min $N_2(g)$ sparging after 150 min at pH=7.0 and at 60°C (Table 29). A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.83$, $F=16.32$, $p=0.01$).

The mechanism affecting the yield of color removals through sonication was explained as follows: $N_2(g)$ sparging changed the temperature within the cavitation site and the variations of chemical properties of the system resulting in high color removals at low temperature such as 30°C and 60°C [84]. Gases with lower thermal conductivity (18.40 mW/mol.K) values such as $N_2(g)$ increased the temperature up to 90°C inside the cavitation bubble upon collapse because they allowed less heat to the surroundings such as 37°C. The ratio of specific heat plays a role in determining the maximum size of the cavitation bubble. The greater the ratio, the greater the radius of the bubble before collapse. Significant changes in the cavitation process, due to changes in the chemical properties of OMI ww occurred due to sparging with $N_2(g)$. The decolorization phenomenon in $N_2(g)$ sparged systems suggests that an O_2 dependent, OH^{\bullet} pathway also exists. This pathway is most likely hydroxylation occurring in the gas-liquid phase (Dewulf et al., 2001). The color removal yields reached in this study was higher than that found by Svitelska et al. (2004) under similar operational and sonication conditions. They observed 80% color removal efficiency for initial 75.30 m^{-1} color level, at 250 W and at 24 kHz under 25 min $N_2(g)$ (5 mg/l N_2) sparging at 60°C after 150 min. In the present study, 91.88% color removal was observed under 30 min $N_2(g)$ (6 mg/l N_2) sparging at 60°C after 150 min. This color yield is higher than the yield obtained by Svitelska et al. (2004) at 60°C as mentioned above.

Table 27. Effect of increasing DO concentrations on TFAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values ±SD)

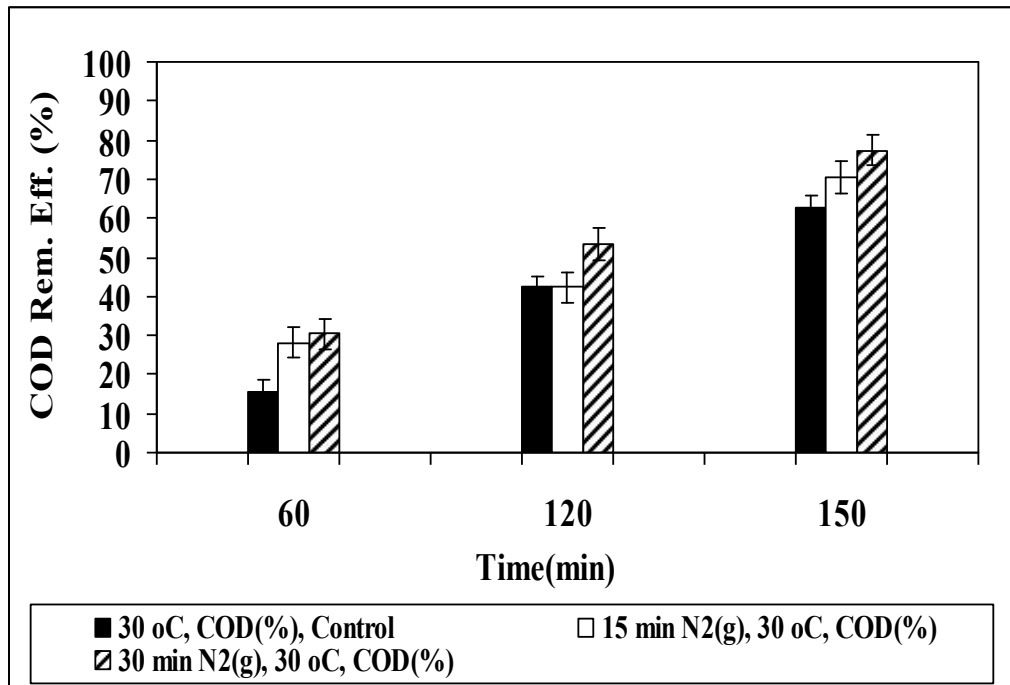
Parameters	TFAs Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0.min	60. min	120.min	150. min
Raw ww, control	0	15.62	22.37	45.66	0	17.33	24.77	48.84
DO=2 mg/l	0	37.10	52.82	66.98	0	37.63	53.23	68.19
DO=4 mg/l	0	37.15	56.01	69.21	0	37.67	57.62	71.18
DO=6 mg/l	0	37.29	58.61	71.03	0	38.33	59.91	72.74
DO=10 mg/l	0	37.56	60.04	72.03	0	38.38	62.41	74.44

Table 28. Effect of increasing N₂(g) sparging on COD_{dis} removal efficiencies of OMI ww before and after sonication process at pH=7.0, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration of 109444 mg/l, n=3, mean values ±SD)

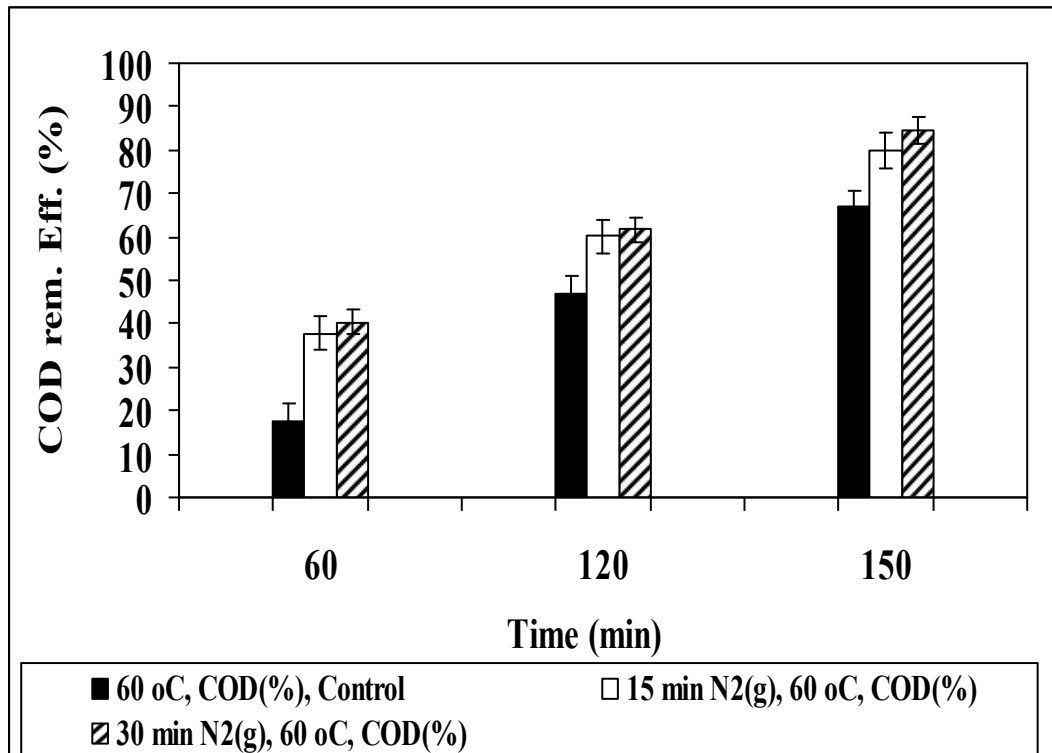
Parameters	COD _{dis} Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	12.76	25.58	32.43	0	17.77	39.51	47.67
15 min N ₂ (g)	0	28.21	42.29	70.56	0	37.81	60.09	79.89
30 min N ₂ (g)	0	30.39	53.46	77.36	0	40.44	61.62	84.51

Table 29. Effect of increasing N₂(g) sparging on color removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m⁻¹, n=3, mean values ±SD)

Parameters	Color Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	38.68	52.61	74.45	0	44.59	69.74	83.77
15 min N ₂ (g)	0	76.15	77.66	82.36	0	78.06	80.36	85.87
30 min N ₂ (g)	0	77.56	83.17	89.28	0	79.26	85.77	91.88



(a)



(b)

Fig. 5. Effect of increasing N₂(g) sparging on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values)

3.8.2 Effect of N₂(g) on the total phenol removal efficiencies in omi ww at increasing sonication times and temperatures

71.16% and 73.99% total phenol removals were found under 15 and 30 min N₂(g) sparging, respectively, after 150 min at pH=7.0 and at 30°C (Table 30). 11.37-12.37% and 11.27-11.78% increase in total phenol yields were measured under 15 and 30 min N₂(g) sparging, respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control (E=59.40% total phenol yield after 150 min at pH=7.0 and at 30°C) (Table 30). A significant linear correlation between total phenol yields and increasing N₂(g) sparging was not observed ($R^2=0.42$, $F=3.78$, $p=0.01$).

74.91% and 78.98% total phenol yields were measured under 15 and 30 min N₂(g) sparging, respectively, after 150 min at pH=7.0 and at 60°C (Table 30). The contribution of increasing N₂(g) sparging were 10.73-11.17% and 9.51-10.27% in total phenol removals under 15 and 30 min N₂(g) sparging, respectively, after 60 and 120 min at pH=7.0 and at 60°C, compared to the control (E=61.24% total phenol after 150 min at pH=7.0 and at 60°C) (Table 30). The maximum total phenol removal efficiency was 78.98% under 30 min N₂(g) sparging after 150 min at pH=7.0 and at 60°C (Table 30). A significant linear correlation between total phenol yields and increasing N₂(g) sparging was not observed ($R^2=0.36$, $F=2.71$, $p=0.01$).

Berlan et al. [51] observed that high dissolved N₂ concentrations present in the solution degassed the medium after an initial period of sonication resulting in a decrease in the amount OH[•] generated. Kidak and Ince [68] found higher phenol yields in the presence of air than that of N₂(g) at pH=7.0, at 35 kHz after 150 min at 60°C. Larger phenol yields in the presence of air despite its lower polytrophic gas ratio is due to the reactions of N₂ with molecular O₂ to yield HNO₃ and radical species such as OH[•], •NO₂, and •NO₃ accelerate the oxidation process.

3.8.2.1 Effect of pH on the Removal of Phenol Removal Efficiencies in OMI ww in the Presence of 30 min N₂(g) (6 mg/l N₂) Sparging after 150 min Sonication at 60°C

In aqueous solutions of phenol the degree of ionization from molecular state to the phenolate ion increases as pH is raised, and at pH > pK_a

(=10) phenolate ion is the major species, which due to repulsive forces are unable to approach the negatively charged cavity bubbles or even the bubble-liquid interface, where uncombined OH[•] concentration is at a maximum. As pH is lowered and the fraction of molecular phenol increases, the probability of solutes approaching the interfacial area also increases, resulting in enhanced rates of phenol removal as reported by Mahamuni and Pandit [75]. In this study, phenol removals versus pH is demonstrated at three different pH at 60°C after 150. The maximum phenol removal was obtained at a pH=4.0. The phenol yields in pH=7.0 and pH=10.0 followed this yield with phenol removals of 79%, 69% and 60%, respectively.

During sonication low decrease of total phenol concentrations in the effluent samples results in the formation of a complex H-bonding network between the phenolic compounds at short sonication times (20-60 min). It is well known that molecules containing COOH or CHO groups exist as dimers in solution due to the formation of H-bonds between two neighboring molecules. This results in a more robust and stable configuration and leading to the reduced degradation. In addition to this, the formation of such a network may impede their diffusion towards the bubble interface and this would also lead to reduced degradation of phenols (Kallel et al., 2009a). In general, hydrophobic and volatile organics tend to partition into the bubbles and degrade mainly by direct thermal decomposition leading to the formation of combustion by-products.

3.8.3 Effect of N₂(g) on the TAAs removal efficiencies in omi ww at increasing sonication times and temperatures

67.43% and 71.18% TAAs removals were observed under 15 and 30 min N₂(g) sparging, respectively, after 150 min at pH=7.0 and at 30°C (Table 31). The contribution of 15 and 30 min N₂(g) sparging was found as 13.83-15.26% and 6.74-10.07% to the TAAs yields, respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C (Table 31). The contribution of 15 and 30 min N₂(g) sparging are not significant to the TAAs yields since sonication alone provided 64.98% TAAs removal efficiencies after 150 min at pH=7.0 and at 30°C (Table 31). A significant linear correlation between TAAs yields and increasing N₂(g) sparging was not observed ($R^2=0.30$, $F=2.64$, $p=0.01$).

72.43% and 74.56% TAAs yields were found under 15 and 30 min N₂(g) sparging after 150 min, respectively, at pH=7.0 and at 60°C (Table 31). 14.66-15.26% and 3.28-7.39% increase in TAAs removals were measured under 15 and 30 min N₂(g) sparging, respectively, after 60 and 120 min, compared to the control at pH=7.0 and at 60°C (Table 31). An increase of 1-4% in TAAs removal was observed under 15 and 30 min N₂(g) sparging, respectively, after 150 min, compared to the control (E=70.52% TAAs at pH=7.0 and at 60°C) (Table 31). The maximum TAAs removal efficiency was 74.56% under 30 min N₂(g) sparging after 150 min at pH=7.0 and at 60°C (Table 31). A significant linear correlation between TAAs yields and increasing N₂(g) sparging was not observed (R²=0.33, F=2.41, p=0.01). The recent literature showed that the sonochemical degradation of aromatic amines namely, 4,4-oxydianiline and aniline predominantly occurs via OH[•] attack; although, a thermal reaction occurring in the vicinity of the bubble cannot be taken into consideration (Cardoso et al., 2010).

3.8.4 Effect of N₂(g) on the TFAs removal efficiencies in omi ww at increasing sonication times and temperatures

76.05% and 78.62% TFAs removals were observed under 15 and 30 min N₂(g) sparging, respectively, after 150 min at pH=7.0 and at 30°C (Table 32). The contribution of N₂(g) sparging on the TFAs removals were 23.28-23.30% and 43.42-47.09% under 15 and 30 min N₂(g) sparging, respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C (Table 32). The contribution of 15 and 30 min N₂(g) sparging on the TFAs removals were significant (R²=0.78, F=17.09, p=0.01). TFAs yields were increased from 45.66% to 76.05% and to 78.62% with 15 and 30 min N₂(g) sparging, respectively, after 150 min at 30°C, compared to the control (E=45.66% TFAs at pH=7.0 and at 30°C) (Table 32). A significant linear correlation between TFAs yields and increasing N₂(g) sparging was observed (R²=0.85, F=16.63, p=0.01).

77.22% and 80.18% TFAs yields were obtained under 15 and 30 min N₂(g) sparging, respectively, after 150 min at pH=7.0 and at 60°C (Table 32). 21.77-21.96% and 41.73-46.09% increase in TFAs yields were found under 15 and 30 min N₂(g) sparging, respectively, after 60 and 120 min at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C (Table 32). The

contribution of 15 and 30 min N₂(g) sparging on the TFAs removals were significant (R²=0.76, F=17.89, p=0.01). TFAs removals increased from 48.84% to 77.22% and to 80.18% with 15 and 30 min N₂(g) sparging, respectively, after 150 min at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs at pH=7.0 and at 60°C) (Table 32). The maximum TFAs removal efficiency was 80.18% under 30 min N₂(g) sparging after 150 min at pH=7.0 and at 60°C (Table 32). A significant linear correlation between TFAs yields and increasing N₂(g) sparging was observed (R²=0.87, F=16.63, p=0.01).

3.9. Effect of H₂O₂ Concentrations on the Removals of COD_{dis} in OMI ww

Increasing H₂O₂ concentrations (100 - 500 and 2000 mg/l) were added in OMI ww before sonication process. 73.87%, 80.80% and 85.61% COD_{dis} removals were obtained in 100 mg/l, 500 and 2000 mg/l H₂O₂, respectively, after 150 min at pH=7.0 and at 30°C (Table 33, Figure 6). 33.69-39.67% and 22.05-30.86% increase in COD_{dis} removals were observed in 100 mg/l, 500 and 2000 mg/l H₂O₂, respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control (without H₂O₂ at pH=7.0 and at 30°C) (Table 33, Figure 6). Control reactor provided 62.57% COD_{dis} yield after 150 min at pH=7.0 and at 30°C (Table 33, Figure 6). The contribution of increasing H₂O₂ concentrations on the COD_{dis} removal were significant (R²=0.89, F=19.09, p=0.01).

89.09%, 91.13% and 93.19% COD_{dis} yields were measured in 100 mg/l, 500 and 2000 mg/l H₂O₂, respectively, after 150 min at pH=7.0 and at 60°C (Table 33, Fig. 6). The contribution of increasing H₂O₂ concentrations were found as 38.34-44.00% and 28.58-32.77% on the COD_{dis} removals in 100, 500 and 2000 mg/l H₂O₂, respectively, after 60 and 120 min at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C (Table 33, Fig. 6). The contribution of increasing H₂O₂ concentrations on the COD_{dis} yield were significant (R²=0.79, F=19.98, p=0.01). Sonication alone provided 66.83% COD_{dis} yield after 150 min at pH=7.0 and at 60°C (Table 33, Fig. 6). The maximum COD_{dis} removal efficiency was 93.19% in H₂O₂=2000 mg/l after 150 min at pH=7.0 and at 60°C (Table 33, Fig. 6). A significant linear correlation between COD_{dis} yields and increasing H₂O₂ concentrations was not observed (R²=0.65, F=3.32, p=0.01). In this study, it was found that the COD_{dis} removal increased with H₂O₂

Table 30. Effect of increasing N₂(g) sparging on total phenol removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values ±SD)

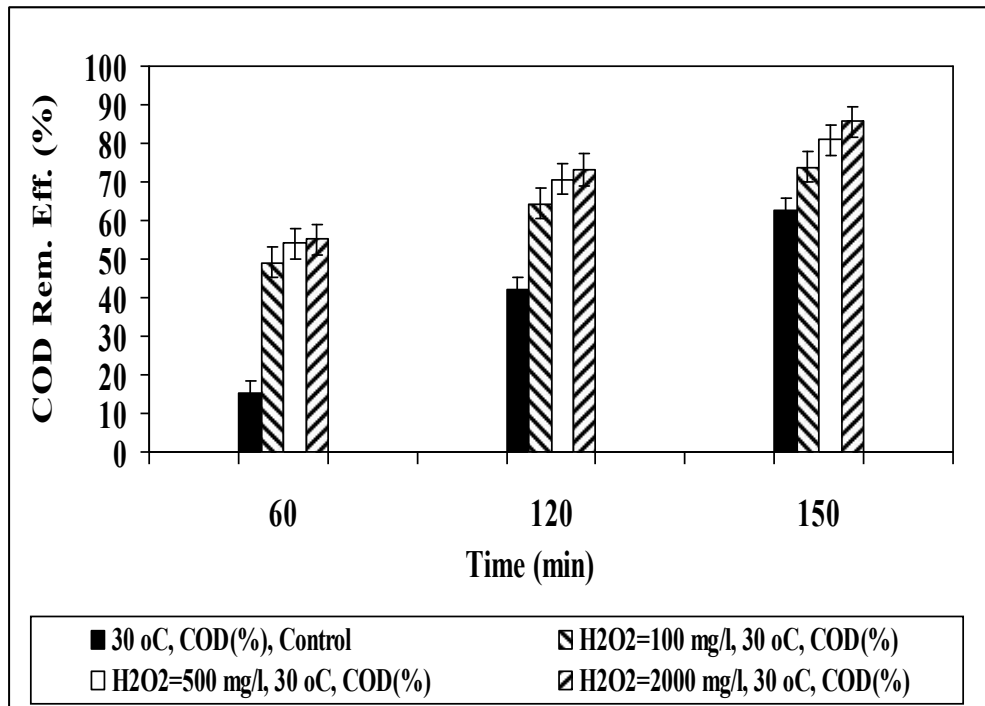
Parameters	Total Phenol Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	28.26	56.00	59.40	0	30.20	57.94	61.24
15 min N ₂ (g)	0	39.63	67.27	71.16	0	40.93	67.45	74.91
30 min N ₂ (g)	0	40.63	67.78	73.99	0	41.37	68.21	78.98

Table 31. Effect of increasing N₂(g) sparging on TAAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values ±SD)

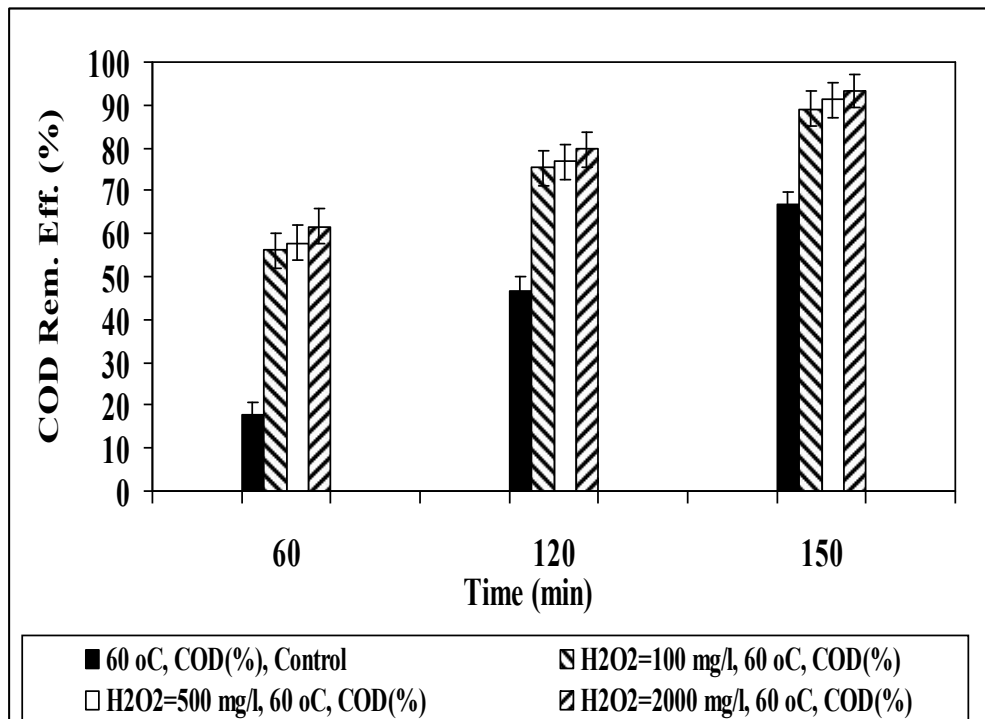
Parameters	TAAs Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	37.19	55.34	64.98	0	38.14	59.39	70.52
15 min N ₂ (g)	0	51.02	62.08	67.43	0	52.80	62.67	72.43
30 min N ₂ (g)	0	52.45	65.41	71.18	0	53.40	66.78	74.56

Table 32. Effect of increasing N₂(g) sparging on TFAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values ±SD)

Parameters	TFAs Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
Raw ww, control	0	15.62	22.37	45.66	0	17.33	24.77	48.84
15 min N ₂ (g)	0	38.90	65.79	76.05	0	39.10	66.50	77.22
30 min N ₂ (g)	0	38.92	69.46	78.62	0	39.29	70.86	80.18



(a)



(b)

Fig. 6. Effect of increasing H₂O₂ concentrations on the COD_{dis} removal efficiencies in OMI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=109444 mg/l, n=3, mean values).

concentration and reached the maximum 93.19% by using 2000 mg/l H_2O_2 . From this, we can evaluate that 0.02 mg/l of H_2O_2 was needed to the removal of 1 mg/l of COD with a COD_{dis} yield of 91.37% after 150 min. Sivasankar and Moholkar [85] estimated that the removal of 1 g of COD needs 2.04 g of H_2O_2 . In this optimized condition, the maximum value of COD removal is at the level of 93% with H_2O_2 oxidation [86]. In this study, it is clear that 2000 mg/l of H_2O_2 is the optimum amount to obtain maximum decrease (93.19%) in COD_{dis} from OMI ww after 150 min at 60°C.

Organic compounds may be degraded either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation or in the solution bulk via oxidative degradation by H_2O_2 in OMI ww (Entezari et al., 2003). Under ultrasound irradiation, water is pyrolyzed, in which process H^\bullet , OH^\bullet , O^\bullet and O_2H^\bullet are produced and then react with organic pollutants measured as COD in the bulk solution or at the interface between the bubbles and the liquid phase [87]. During aqueous ultrasound irradiation, OH^\bullet forms during the thermolytic reactions of H_2O and self-recombine to form H_2O_2 . This showed that the sono-degradation of COD_{dis} in OMI ww occurred via hydroxylation.

In a study performed by Kallel et al. (2009a) a COD removal of 78% was found by sonication at a power of 650 W and at a frequency of 35 kHz in OMI ww. In this study, it was found that for the sono-degradation of 1 g COD 0.06 M of H_2O_2 is needed. In this study, 93.19% COD_{dis} removal was observed for 2000 mg/l H_2O_2 concentration at 60°C after 150 min. In the present study the COD_{dis} yield is higher than the yield obtained by Kallel et al. (2009a) at 60°C.

3.9.1 Effect of H_2O_2 concentrations on the color removal efficiencies in omi ww at increasing sonication times and temperatures

81.96%, 86.07% and 89.88% color removals were observed at 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 30°C (Table 34). The contribution of 100 mg/l, 500 and 2000 mg/l H_2O_2 concentrations to the color removals were 11.82-33.56% and 19.73-30.06% after 60 and 120 min, respectively, at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C (Table 34). The contribution of increasing H_2O_2 concentrations on the color yields were found to be significant ($R^2=0.76$,

$F=15.09$, $p=0.01$). Sonication alone provided 74.45% color removal after 150 min at pH=7.0 and at 30°C (Table 34). A significant linear correlation between color yields and increasing H_2O_2 concentrations was observed ($R^2=0.81$, $F=14.78$, $p=0.01$).

90.58%, 92.48% and 93.59% color yields were measured in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 60°C (Table 34). 19.34-28.76% and 7.51-16.93% increase in color yields were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60 and 120 min at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C (Table 34). Control provided 83.77% color removal after 150 min at pH=7.0 and at 60°C. The maximum color removal efficiency was 93.59% in $H_2O_2=2000$ mg/l after 150 min at pH=7.0 and at 60°C (Table 34). A significant linear correlation between color yields and increasing H_2O_2 concentrations was observed ($R^2=0.83$, $F=15.98$, $p=0.01$).

A non-volatile organic substance is mainly eliminated by OH^\bullet outside the cavitation bubble: a hydrophobic compound at the bubble-solution interface, while hydrophilic substrates into the bulk solution. Tannins and lignins are non-volatile compounds given color in OMI ww. Therefore, these organics cannot enter inside the bubble. Additionally, the positive charge of the nitrogen atoms of the amine groups exhibiting hydrophilic properties to the benzene molecules which are giving the color to the OMI ww. As a consequence, under ultrasonic action, the removal of color must mainly occur through the reaction with OH^\bullet in the bulk solution (Guzman-Duque et al., 2011).

Table 35 shows the effect of 2000 mg/l H_2O_2 addition on H_2O_2 and OH^\bullet ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min throughout color removal in OMI ww. The H_2O_2 concentration increased to 2135 mg/l and accumulated in deionized water. This level increased to 2196 mg/l after 30 min and began to use through sonication since the H_2O_2 level decreased to 1987 mg/l. The sonication process ending after 150 min with decreasing of H_2O_2 concentration to 28 mg/l after 150 min. The OH^\bullet ion concentration increased from 2×10^{-52} up to 5×10^{-5} as the sonication time increased from 30 to 150 min. This showed that color was removed with hydroxylation process in the presence of 2000 mg/l H_2O_2 in OMI ww.

Table 33. Effect of increasing H₂O₂ concentrations on COD_{dis} removal efficiencies of OMI ww before and after sonication process at pH=7.0, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration of 109444 mg/l, n=3, mean values ±SD)

Parameters	COD _{dis} Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	12.76	25.58	32.43	0	17.77	39.51	47.67
H ₂ O ₂ =100 mg/l	0	49.16	64.34	73.87	0	56.11	75.39	89.09
H ₂ O ₂ =500 mg/l	0	53.98	70.65	80.80	0	57.91	76.83	91.13
H ₂ O ₂ =2000 mg/l	0	55.14	73.15	85.61	0	61.77	79.58	93.19

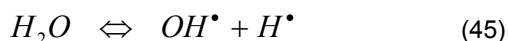
Table 34. Effect of increasing H₂O₂ concentrations on color removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m⁻¹, n=3, mean values ±SD)

Parameters	Color Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	38.68	52.61	74.45	0	44.59	69.74	83.77
H ₂ O ₂ =100 mg/l	0	50.50	72.34	81.96	0	63.93	77.25	90.58
H ₂ O ₂ =500 mg/l	0	65.43	77.05	86.07	0	69.74	80.26	92.48
H ₂ O ₂ =2000 mg/l	0	72.24	82.67	89.88	0	73.35	86.67	93.59

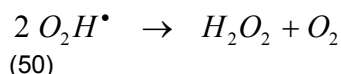
Table 35. Effect of 2000 mg/l H₂O₂ concentration on H₂O₂ and OH[•] ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=99.80 m⁻¹, n=3, mean values)

Conditions	H ₂ O ₂ Conc. (mg/l) (60°C)	OH [•] ion Conc. (mg/l)
Addition of 2000 mg/l H ₂ O ₂ concentration	2000	0
H ₂ O ₂ concentration (mg/l) in deionized water (60°C)	2135	0
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 30 min sonication	2196	2x10 ⁻⁵²
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 120 min sonication	1987	7x10 ⁻¹⁷
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 150 min sonication	28	5x10 ⁻⁵

Under ultrasonic irradiation water sonodegraded to OH^\bullet and H^\bullet . As a result H_2O_2 is produced according to the Equations (45) and (46):



If the solution is saturated with O_2 and $\text{O}_2\text{H}^\bullet$, more OH^\bullet are formed in the gas phase of microbubbles (upon the decomposition of molecular O_2), and the recombination of the former at the cooler sites (bubble–solution interface or the solution bulk) produces additional H_2O_2 [88] in Equations (47), (48), (49) and (50):



3.9.2 Effect of H_2O_2 concentrations on the total phenol removal efficiencies in omi ww at increasing sonication times and temperatures

79.20%, 82.30% and 84.74% total phenol removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 30°C (Table 36). 20.56-21.17% and 21.89-24.73% increase in total phenol yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C (Table 36). Sonication alone provided 59.40% total phenol after 150 min at pH=7.0 and at 30°C (Table 36). The contribution of increasing H_2O_2 concentrations on total phenol removal were significant ($R^2=0.79$, $F=19.66$, $p=0.01$).

85.48%, 90.42% and 93.65% total phenol yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 60°C (Table 36). The contribution of increasing H_2O_2 concentrations were 19.93-45.12% and 20.65-28.38% in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60 and 120 min at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C (Table 36). Control alone provided 61.24% total phenol after 150 min at 60°C (Table 36). The maximum total phenol removal efficiency was 93.65% in $\text{H}_2\text{O}_2=2000$ mg/l after

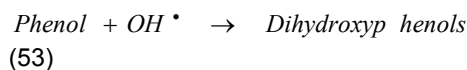
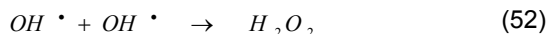
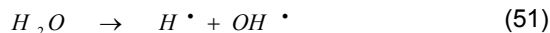
150 min at pH=7.0 and at 60°C (Table 36). A significant linear correlation between total phenol yields and increasing H_2O_2 concentrations was observed ($R^2=0.79$, $F=13.95$, $p=0.01$).

Under ultrasound irradiation, water is pyrolyzed, in which process H^\bullet , OH^\bullet , O^\bullet and $\text{O}_2\text{H}^\bullet$ are produced and water then react with in the bulk solution or at the interface between the bubbles and the liquid phase [89]. During aqueous ultrasound irradiation, OH^\bullet form during the thermolytic reactions of water and self-recombine to form H_2O_2 [50]. Kidak and Ince [68] determined that the controlling mechanism of sonochemical reactors in degradation of phenol is the production of free radicals and their subsequent attack on the pollutant species. It is accepted that H_2O_2 arises from the reactions of OH^\bullet and $\text{O}_2\text{H}^\bullet$ in the liquid phase around the cavitation bubble and hence can be used to quantify the efficacy of reactors in generating the desired cavitation intensity. Sivasankar and Moholkar [88] found that the generation of H_2O_2 increase linearly with time of ultrasonic irradiation without H_2O_2 addition while 66% total phenol removal was found after 100 min at pH=4.8.

In this study it is important to note that in the presence of phenol under acidic conditions (at pH=3.0), the H_2O_2 values in OMI ww are much lower compared to those in distilled water (at a neutral pH=7.0) due to the fact that in the former case many of the OH^\bullet produced by sonication react with phenol before they could combine to form OH^\bullet . In pure water, due to the absence of organic substrates, the H_2O_2 remains as formed. The results for the H_2O_2 generation in deionized water and in OMI ww containing phenol at acidic pH=3.0 is illustrated in Table 37. This table shows the effect of pH=3.0 on H_2O_2 and OH^\bullet ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min. The H_2O_2 concentration increased to 2147 mg/l and accumulated in deionized water. This level increased to 2198 mg/l after 30 min and began to use through sonication since the H_2O_2 level decreased to 1960 mg/l. The sonication process ending after 150 min with decreasing of H_2O_2 concentration to 31 mg/l after 150 min. The OH^\bullet ion concentration increased from 1×10^{-51} up to 3×10^{-5} as the sonication time increased from 30 to 150 min. This showed that the main removal mechanism of phenol degradation in the presence of H_2O_2 is hydroxylation in OMI ww.

In a study performed by Mahamuni and Pandi [73] was found only 7% phenol degradation after

90 min. The attack of OH^\bullet on phenol was confined through sonication. The formation of the hydrophenols through sonication can be explained by the Equations (51), (52) and (53):



In this study, 93.65% total phenol removal was found in 2000 mg/l H_2O_2 at 60°C after 150 min. The total phenol yield is higher than the yield obtained by Mahamuni and Pandit [73] at 60°C as mentioned above.

3.9.3 Effect of H_2O_2 concentrations on the taas removal efficiencies in omi ww at increasing sonication times and temperatures

68.31%, 72.53% and 75.87% TAAs removals were obtained in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 30°C (Table 38). The contribution of increasing H_2O_2 concentrations on TAAs removals were 19.71-20.54% and 11.19-12.39% in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control at pH=7.0 and at 30°C (Table 38). Sonication alone provided 64.98% TAAs yield after 150 min at pH=7.0 and at 30°C (Table 38). A significant linear correlation between TAAs yields and increasing H_2O_2 concentrations was not observed ($R^2=0.44$, $F=3.71$, $p=0.01$).

70.21%, 76.93% and 83.68% TAAs yields were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 60°C (Table 38). The contribution of increasing H_2O_2 concentrations on TAAs removals were 20.54-24.88% and 9.76-15.29% TAAs yields in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60 and 120 min at pH=7.0 and at 60°C, compared to the control at pH=7.0 and at 60°C (Table 38). Control provided 70.52% TAAs yield after 150 min at pH=7.0 and at 60°C. The maximum TAAs removal efficiency was 83.68% in $\text{H}_2\text{O}_2=2000$ mg/l after 150 min at pH=7.0 and at 60°C (Table 38). A significant linear correlation between TAAs yields and increasing H_2O_2 concentrations was not observed ($R^2=0.49$, $F=4.84$, $p=0.01$).

Amir et al. [90] reported that the H_2O_2 formation in OMI ww cannot be inhibited by TAAs. If it is

assumed that the first step of the TAAs degradation results from OH^\bullet reaction in a site close to the surface of the bubble, it should be a competition between reactions. The low TAA yields (48%) throughout sonication could be attributed to the modifications of some sonodegraded aliphatic chains to generate condensed aromatic structures containing large proportions of hydroxyl, methoxyl, carboxyl and carbonyl groups. In this study, 83.68% TAAs removal obtained after 150 min at 60°C. This TAAs yield is higher than the yield observed by Amir et al. [90] at 60°C.

3.9.4 Effect of H_2O_2 concentrations on the tfas removal efficiencies in omi ww at increasing sonication times and temperatures

82.75%, 84.75% and 86.72% TFAs removals were observed in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 30°C (Table 39). The contribution of increasing H_2O_2 concentrations on TFAs removals were 28.38-30.17% and 52.99-58.66% in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60 and 120 min at pH=7.0 and at 30°C, compared to the control reactor at pH=7.0 and at 30°C (Table 39). Sonication alone provided 45.66% TFAs yield after 150 min at pH=7.0 and at 30°C (Table 39). A significant linear correlation between TFAs yields and increasing H_2O_2 concentrations was observed ($R^2=0.74$, $F=15.61$, $p=0.01$).

85.41%, 88.20% and 90.30% TFAs yields were found in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 150 min at pH=7.0 and at 60°C (Table 39). The contribution of increasing H_2O_2 concentrations on TFAs removals were 29.02-31.71%, 53.77-60.96% and 36.57-41.46% in 100 mg/l, 500 and 2000 mg/l H_2O_2 , respectively, after 60, 120 and 150 min at pH=7.0 and at 60°C, compared to the control (E=48.84% TFAs after 150 min at pH=7.0 and at 60°C) (Table 39). The maximum TFAs removal efficiency was 90.30% in $\text{H}_2\text{O}_2=2000$ mg/l after 150 min at pH=7.0 and at 60°C (Table 39). A significant linear correlation between TFAs yields and increasing H_2O_2 concentrations was observed ($R^2=0.82$, $F=16.13$, $p=0.01$).

In a study performed by Jahouach-Rabai et al. (2008) 89% TFAs removal was observed at 20 kHz, at 750 W, after 45 min at 70°C in an OMI ww. By increasing of H_2O_2 concentrations the TFAs concentrations decreased by oxidation of oleic acid and further degradation to hexanal. In this study,

Table 36. Effect of increasing H₂O₂ concentrations on total phenol removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial total phenol concentration=4090 mg/l, n=3, mean values ±SD)

Parameters	Total Phenol Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	28.26	56.00	59.40	0	30.20	57.94	61.24
H ₂ O ₂ =100 mg/l	0	48.82	77.89	79.20	0	50.13	78.59	85.48
H ₂ O ₂ =500 mg/l	0	49.17	78.07	82.30	0	52.49	81.38	90.42
H ₂ O ₂ =2000 mg/l	0	49.43	80.73	84.74	0	75.32	86.32	93.65

Table 37. Effect of 2000 mg/l H₂O₂ concentration at pH=3.0 on H₂O₂ and OH[•] ion concentrations in OMI ww at 60°C after 30 min, 120 and 150 min (sonication power=640 W, sonication frequency=35 kHz, , initial total phenol concentration=4090 mg/l, n=3, mean values)

Conditions	H ₂ O ₂ Conc. (mg/l) (60°C)	OH [•] ion Conc. (mg/l)
Addition of 2000 mg/l H ₂ O ₂ concentration at pH=3.0	2000	0
H ₂ O ₂ concentration (mg/l) in deionized water (60°C) at pH=7.0	2147	0
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 30 min sonication at pH=3.0	2198	1x10 ⁻⁵¹
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 120 min sonication at pH=3.0	1960	4x10 ⁻¹⁵
H ₂ O ₂ concentration (mg/l) in OMI ww (60°C) after 150 min sonication at pH=3.0	31	3x10 ⁻⁵

Table 38. Effect of increasing H₂O₂ concentrations on TAAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=3000 mg benzidine/l, n=3, mean values ±SD)

Parameters	TAAs Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0. min	60. min	120.min	150. min
Raw ww, control	0	37.19	55.34	64.98	0	38.14	59.39	70.52
H ₂ O ₂ =100 mg/l	0	56.90	66.53	68.31	0	58.68	69.15	70.21
H ₂ O ₂ =500 mg/l	0	57.37	67.10	72.53	0	59.22	73.29	76.93
H ₂ O ₂ =2000 mg/l	0	57.73	67.73	75.87	0	63.02	74.68	83.68

Table 39. Effect of increasing H₂O₂ concentrations on TFAs removal efficiencies in OMI ww before and after sonication experiments at pH=6.98, at 30°C and at 60°C (sonication power=640 W, sonication frequency=35 kHz, initial TFAs concentration=5200 mg/l, n=3, mean values ±SD)

Parameters	TFAs Removal Efficiencies (%)							
	30°C				60°C			
	0. min	60. min	120.min	150. min	0.min	60. min	120.min	150. min
Raw ww, control	0	15.62	22.37	45.66	0	17.33	24.77	48.84
H ₂ O ₂ =100 mg/l	0	44.00	75.36	82.75	0	46.35	78.54	85.41
H ₂ O ₂ =500 mg/l	0	45.54	78.22	84.75	0	47.40	82.64	88.20
H ₂ O ₂ =2000 mg/l	0	45.79	81.03	86.72	0	49.04	85.73	90.30

90.30% TFAs removal was observed in $H_2O_2=2000$ mg/l at $60^\circ C$ after 150 min. The TFAs yield is higher than the yield obtained by Jahouach-Rabai et al. (2008) at $70^\circ C$ as mentioned above.

4. CONCLUSIONS

In this study the maximum pollutants yields was detected at a sonication frequency of 35 kHz. It was found that as the temperature, DO and sonication time were increased from $25^\circ C$ to $60^\circ C$, from 2 mg/l to 10 mg/l and from 60 min to 150 min the pollutant yields increased, respectively. The maximum removal efficiencies were 60.91% COD_{dis} , 59.28% TOC, 49.70% color, 58.25% total phenol, 63.27% total aromatic amines (TAAs), 37.51% total fatty acids (TFAs), at $25^\circ C$ and 150 min, respectively. The maximum removal yields were 66.83% COD_{dis} , 65.92% TOC, 83.77% color, 61.24% total phenol, 70.52% TAAs, 48.84% TFAs, under $60^\circ C$ temperature after 150 min, respectively. The maximum removal efficiencies at a DO concentration of 10 mg/l increased to 88.73% for COD_{dis} , to 93.79% for color, to 91.38% for total phenol, to 91.58% for TAAs and to 74.44% for TFAs at $60^\circ C$ and 150 min, respectively. The maximum removal efficiencies increased to 84.51% for COD_{dis} , to 91.88% for color, to 78.98% for total phenol, to 74.56% for TAAs and to 80.18% for TFAs, at 30 min $N_2(g)$ sparging, at $60^\circ C$ and 150 min, respectively. The maximum removal yields increased to 91.13% for COD_{dis} , to 93.59% for color, to 93.65% for total phenol, to 83.68% for TAAs, to 90.30% for TFAs in the presence of 2000 mg/l H_2O_2 , at $60^\circ C$ and 150 min, respectively. With 2000 mg/l H_2O_2 around 94% maximum phenol, TAAa and TFAs yields was detected. Sonication at 35 kHz proved to be a viable tool for the effective removal of COD, TOC, color, total phenol, TAAs and TFAs from OMI ww, by production of enough OH radical production.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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