Science and Technology Publishing (SCI & TECH)
ISSN: 2632-1017
Vol. 5 Issue 2, February - 2021

Remediation of Olive Mill Industry Wastewater With Titanium Dioxide (TiO_2), Silisium Dioxide (SiO_2) And Zinc Oxide (ZnO) Using Ultrasound

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***Abstract* — The effects of nano-sized metal oxides namely titanium dioxide (TiO_2), silisium dioxide (SiO_2) and zinc oxide (ZnO) on the ultrasound of olive mill effluent wastewater (OMW) in Turkey were investigated. 150 min ultrasound alone provided 61%, 50%, 61% and 66% dissolved chemical oxygen demand (COD_{dis}), color, total phenol and total aromatic amines (TAAs) removals, respectively, at 25°C. The maximum TAAs (90%), total phenol (97%), color (94%) and COD_{dis} (97%) removals were obtained with 5 mg/l nano-sized ZnO, 4 mg/l nano-sized TiO_2, 4 mg/l nano-sized TiO_2 and 4 mg/l nano-sized TiO_2, respectively, throughuot ultrasound.**

Keywords* —- *Nano-sized metal oxides; olive mill effluent; silisium dioxide; titanium dioxide; ultrasound; zinc oxide.

I. INTRODUCTION

Agro-industrial wastewaters such as olive-oil mill effluent wastewaters (OMW) are among the strongest industrial effluents and increasing concern has been expressed about their treatment and safe disposal, since they cause considerable environmental problems (coloring of natural waters, a serious threat to aquatic life, pollution in surface and ground waters, alterations in soil quality, phytotoxicity and odor nuisance) particularly in the Mediterranean Sea region due to its high organic chemical oxygen demand (COD), polyphenol, aromatic amines concentration, and organic content [1]. The concentration of phenolic compounds 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 TAAs in the OMW are known to be carcinogenic and toxic. Some aromatic amines containing the azo bonds (–N═N–) have complex structure and are resistant to biodegradation under aerobic conditions [2, 3].

Significant numbers of studies were focused on the efficient treatment of the OMW including various chemical, physical, physicochemical and biological treatments or combinations of them [1, 4]. Usually, the OMW is inappropriate for direct biological treatment and the alternative treatment technologies mentioned above did not give sufficient removals for pollution parameters (COD_{dis}, total phenol, color and aromatic amines). Recently, significant interest has been shown in the application of ultrasound for the degradation of the OMW [5]. Hydrophobic compounds with high volatility are easily and directly destroyed inside the cavitation bubbles [6]. Hydrophilic organic compounds are indirectly decomposed mainly through the reaction with hydroxyl radicals ($OH^•$) that is produced during cavitation process. The highly reactive $OH^•$ could diffuse from the cavitation bubbles to the interfacial region and bulk solution when large temperature gradient exist [6]. There are three potential reaction zones in sonochemistry; i.e. inside of the cavitation bubble, interfacial liquid region between cavitation bubbles and bulk liquid, and in the bulk solution [6]. The collapse of cavitation bubbles near the micro-particle surface will generate high-speed microjets of liquid in the order of 100 m/s [6]. This will subsequently produce ultrasonic asymmetric shock wave upon implosion of cavitation bubbles which may cause direct erosion (damage) on the particle's surface and de-aggregation of particles to hinder agglomeration. Consequently, it will experience a decrease in particle size and an increase in reactive surface area available for the subsequent reaction. The nano-particles with the size less than that of cavitation bubbles have higher cavitation erosion resistant and are easier to approach the interfacial region (bubbles surface) during the expansion cycles of ultrasound [6]. It was observed synergetic effects with the addition of various metal oxides with ultrasound to enhance the rate of degradation efficiency of organic pollutants via increasing the $OH^•$. This increasing the rate of degradation of the organic compouns in wastewaters. The sonication of organic pollutants in the present of some metal oxides (this reaction could be named as heterogenous sonication) can easily ocur in the interfacial region where very high concentration of $OH^\bullet$ is achieved after the bubbles collapse [6]. Ultrasound (US) will induce the splitting of water molecules with the presence of dissolved oxygen [6]. In these reactions, ‘)))’ denotes the ultrasonic irradiation. Thermal dissociation of water and dissolved oxygen molecules in the cavities will convert them into reactive species such as $OH^\bullet$, hydrogen atoms ($H^\bullet$), $O^\bullet$ atoms and hydroperoxyl radicals ($O_2H^\bullet$) in a cavitation bubble reactions [6].

Previously, the sonocatalytic degradation of some organic pollutants in aqueous solution adopting nano-sized metal oxides powder (TiO_2 and ZnO) has been reported [6]. The nano-sized TiO_2 and nano-sized ZnO as photocatalyst have been widely used with ultraviolet (UV) radiation in the degradation of organic dyes due to their stability of the chemical structure, non-toxicity, optical and electrical properties. Although, these nano-sized metal oxides are non-toxic, stable, and cheap the utilization of UV increase the cost of the treatment. However, to date, the use of nano-sized metal oxides namely, TiO_2, ZnO and SiO_2 in the ultrasound of the OMW for the removal of pollutants from this wastewater was not studied yet.

In İzmir Turkey the OMW treatment plants consisting of a combined chemical and biological process could not provide efective treatment removals. Therefore, in the peresent study, the effects of increasing ultrasound times (60, 120 and 150 min) and ultrasound temperature (30°C and 60°C) on the removals of COD_{dis}, total phenol, color and TAAs were investigated. The main ultrasound mechanisms for the pollution parameters given above were investigated. The poly-phenols were identified and their metabolites were detected. The effects of some nano-sized metal oxides (TiO_2, SiO_2 and ZnO) on the removals of COD_{dis}, color, total phenol and TAAs in the OMW were investigated in a sonicator with a power of 640 W and a frequency of 35 kHz.

II. MATERIALS AND METHODS

A. *Raw Wastewater*

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

TABLE I. Characterization of the OMW at pH=5.4 (n=3, mean values ± standard deviation).

Parameters	Values		
	Minimum	Medium	Maximum
pH_0	4 ± 0.1	4.5 ± 0.1	4.9 ± 0.1
DO_0 (mg/l)	0.01 ± 0.0004	0.05 ± 0.002	0.09 ± 0.003
ORP (mV)	120 ± 4.2	126.0 ± 4.4	132 ± 4.6
TSS (mg/l)	53.6 ± 1.87	53.7 ± 1.8	53.8 ± 1.8
TVSS (mg/l)	34.8 ± 1.2	35.6 ± 1.2	36.4 ± 1.2
COD_t (mg/l)	98780 ± 3457	116632 ± 4432	121560 ± 4920
COD_{dis} (mg/l)	85400 ± 2989	109444 ± 3831	113500 ± 4323
TOC (mg/l)	58510 ± 2048	66488 ± 2327	80450 ± 2816
BOD_5 (mg/l)	63800 ± 2233	81254 ± 2844	99130 ± 3470
BOD_5 / COD_{dis}	0.5 ± 0.02	0.7 ± 0.026	0.9 ± 0.032
Total N (mg/l)	194 ± 6.7	248 ± 8.6	300 ± 10.5
NH_4-N (mg/l)	23.4 ± 0.8	30 ± 1.05	36.6 ± 1.2
NO_3-N (mg/l)	39 ± 1.3	50 ± 1.7	61 ± 2.1
NO_2-N (mg/l)	17.6 ± 0.6	22.6 ± 0.7	27.5 ± 0.9
Total P (mg/l)	492 ± 17	630 ± 22.05	768.6 ± 26.9
PO_4-P (mg/l)	350 ± 12.2	448 ± 16	546.2 ± 19.1
Total phenol (mg/l)	1332 ± 117	2990 ± 143	3250 ± 180.2
Phenol metabolites			
Cathecol	2	23	26
Tyrosol	7	42	45
Quercetin	9	21	28
Caffeic acid	19	30	42
4- methyl catechol	9	15	29
2-PHE	2	4	6
3-PHE	2	9	14
TFAs (mg/l)	3050 ± 141	3900 ± 182	4344 ± 222
TAAs (mg/l)	1190 ± 82	1990 ± 105	2200 ± 128
İndividual TAAs (mg/l)			
2,4,6 trimetylalanin	47	125	187
Aniline	43	83	163
o-toluidine	29	110	156
o-ansidine	45	110	129
Dimethylalanine	13	68	87
Ethylbenzene	21	110	116
Durene [1,2,4,5-tetramethylbenzene]	34	100	123
Color (1/m)	99.7 ± 3	99.8 ± 3.4	99.9 ± 3.4
Oil (mg/l)	564 ± 19	640 ± 22.4	775 ± 27.1

B. *Configuration of Sonicator*

A BANDELIN Electronic RK510 H sonicator was used for ultrasound of the OMW samples. Glass serum bottles in a glass reactor were filled to volumes of 5-500 mL with OMW and were placed in a water bath. They were then closed with teflon coated stoppers throughout the measurement of the OMW. 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 (CH_3OH) in order to prevent adsorption on the walls of the bottles and 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 the temperature losses. The schematic configuration of the sonicator used in this study was given elsewhere [7].

C. Operational Conditions

Fresh solutions of nano-sized metal oxides TiO_2 (2, 4 and 8 mg/l), SiO_2 (3, 6 and 9 mg/l) and ZnO (1, 3 and 5 mg/l) were added to the OMW by an peristaltic pump (Watson-Marlow Bredel pumps, USA) with a flow rate of 0.1 ml/min through 5 min before ultrasound was begun at pH=5.4. Sonicated samples were taken at 60th, 120th and 150th min of ultrasound time and were kept in refrigerator with a temperature of +4°C for experimental analysis. Deionized pure water (R ¼ 18 MΩ 1/cm) was obtained through a SESA Ultrapure water system.

All experiments were in batch mode by using an ultrasonic transducer (horn-type), which has five adjustable active acoustical vibration areas of 12.43, 13.84, 17.34, 26.4 and 40.69 cm^2, with diameters 3.98, 4.41, 4.7, 5.8 and 7.2 cm, respectively, and a maximum input power of 640 W. Five ultrasound intensities (15.7, 24.2, 36.9, 46.2 and 51.4 W $1/cm^2$) were chosen to identify the optimum intensity for maximum removal of pollutant parameters (COD_{dis}, color, total phenol and TAAs) in the OMW while the sonicator power was 640 W. Samples were taken after 60, 120 and 150 min of ultrasound time and they were analyzed immediately as mentioned in the recent studies [7].

Nano-sized metal oxides TiO_2, SiO_2 and ZnO were purchased from Merck (Germany), while reagent grade perfluorohexane (C_6F_{14}) was taken from Fluka (Germany). Aniline (99%), 2-PHE (99%), 3-PHE (99%), 2, 4, 6 trimetylaniline (99%), dimethylaniline (99%) and o-toluidine (99%) was purchased from Aldrich (USA).

D. Analytical Methods

BOD_5 and COD were monitored following Standard Methods 5210 B and 5220 D, respectively [8]. Total-N, NH_4-N, NO_3-N, NO_2-N, total-P and PO_4-P were measured with cell test spectroquant kits (Merck) in a spectroquant NOVA 60 (Merck) spectrophotometer (2003). Oil, Na^{+1} and Cl^{-1}, 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 following Standard Methods 5520 B, 3550, 2540 C, 2540 E, 2550, 2580, respectively [8]. The measurement of color was carried out following the methods described by Olthof and Eckenfelder [9]. In order to identify the TAAs, OMW (25 ml) was acidified at pH=2 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 sylilated with bis(trimethylsylil)trifluoroacetamide (BSTFA) in dimethylformamide and analyzed by GC-MS. Mass spectra were recorded using a VGTS 250 spectrometer equippedwith 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 OMW was acidified to pH=2 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 GC-MS (Hewlett-Packard 6980/HP5973MSD). 2-PHE and 3-PHE concentrations were determined with Shimadzu CLASS-VPV6.14SP2 with Phenomenex Hyperclone 125 mm x 4.6 mm x 5 µm HPLC column using an ultraviolet (UV) method [10]. Aniline, 2,4,6 trimetylaniline and dimethylaniline measurements were carried out using a high pressure liquid chromatograph (HPLC) (Agilent-1100) with a C-18 reverse phase HPLC column (25 cm x 4.6 mm, 5 µm (Ace 5C-18)) following the method developed by EPA [11]. Detection was performed at 280, 214 and 216 nm wavelengths using a UV detector for aniline, 2,4,6 trimetylaniline and dimethylaniline, respectively. *o*-toluidine was determined using a HPLC (Agilent-1100) with a Spectra system model SN4000 pump and Asahipak ODP-506D column (150 mm x 6 mm x 5 µm). o-anisidine was measured in a HPLC (Agilent -1100) with UV detector at a mobile phase of 35% acetonitrile/65% H_2O at a flow rate of 1.2 ml/min. The column was 50 cm x 2 mm ID stainless steel packed with µ-Bondapak C-18. Ethylbenzene and durene (1,2,4,5-tetramethylbenzene) measurements were performed with a GC-MS (GC-MS Agilent Technologies, 7890A (G3440A) GC System, 5975C Inert MSD7683B Series Injector) containing inlet split/splitless ratio of 50:1 with a HP-1 polymethylsiloxane 30 m x 0.32 mm x ID 0.25 µm film thickness column (Hewlett-Packard) at 240°C. The carrier was helium (He) with a flowrate of 1.4 ml/min and column 60 m x 0.25 m x ID 0.25 µm. The steady-state OH ion concentration $[OH^\bullet]$ throughout sonication was calculated following the method proposed by Villeneuve et al. [11] while the second-order reaction kinetics of aromatic amines and phenols were found by Silva et al. [10] and Bertin et al.[12].

III. RESULTS AND DISCUSSION

A. Role of Ultrasound Frequency, Ultrasound Power, Ultrasound Intensity and Power Density on

the Removals of COD$_{dis}$, Color, Total Phenol and TAAs Removals in OMW

Five different ultrasound frequencies (25, 35, 132, 170 and 350 kHz) was researched under ambient conditions (25°C), at constant ultrasound power (640 W) to determine the optimum ultrasound frequency for maximum COD$_{dis}$ removals in the OMW (Table II). Among the frequencies used in the ultrasound process (25, 35, 132, 170 and 350 kHz) it was found that an ultrasound frequency of 35 kHz is the optimum frequency for maximum COD$_{dis}$ removal (61%) in the OMW after 150 min ultrasound at 25°C (Table II). Increasing the ultrasound frequencies > 35 kHz did not increase the number of OH$^{\bullet}$ radicals [13]. 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 [13]. the size of bubbles formed in H_2O, is inversely proportional to the frequency of the wave. 120, 350, 640 and 3000 W ultrasound powers was researched under ambient conditions (at 25°C), at constant ultrasound frequency (35 kHz) to determine the optimum ultrasound power for maximum COD$_{dis}$ removals in the OMW (Table II). Among the powers used it was found that a ultrasound power of 640 W is the optimum power for maximum COD$_{dis}$ removals (61%) in the OMW after 150 min ultrasound at 25°C (Table II). In general, when ultrasonic irradiation is used, the degradation ratio gradually becomes higher when the output power of the ultrasound is increased from 120 to 640 W. The sono-degradation of pollutants increased with increasing applied power. As the power increased, the number of collapsing cavities also increased, thus leading to enhanced degradation rates, thus resulting in high OH$^{\bullet}$ production and COD$_{dis}$ removal. Because the formation of cavitation bubbles and the extent of bubble collapse depends on the sound intensity, various ultrasound intensities were compared for their impacts on the COD$_{dis}$ removals. In this study, the optimum cavitation threshold was 51.4 W/cm^2 for the maximum removals of COD$_{dis}$ (61%) at 25°C after 150 min ultrasound time (Table II). For the maximum COD$_{dis}$ removal, the specific energy was 11.5 kWh/kg COD$_{dis}$ in the influent (Table II).

TABLE II. Sonicational parameters and corresponding values of sonication process in this study at pH=5.4 after 150 min ultrasound time for maximum COD$_{dis}$ yields under ambient conditions (at 25°C).

Ultrasound parameters	Values				
Ultrasound frequency (kHz)	25	35	132	170	350
Ultrasound power (W)	120	640	350	3000	5000
Power density (W/ml)	0.1	2.14	0.9	1.65	1.9
Ultrasound intensity (W/cm^2)	15.7	51.4	24.2	36.9	46.2
Specific energy (kWh/kg COD$_{influent}$)	2.4	11.5	3.1	4.1	5.1
COD removal efficiency (%)	45	61	47	53	58

B. Effect of increasing ultrasound time and temperature on the COD$_{dis}$, total phenol, color and totatal aromatic amine (TAA) removal efficiencies in the OMW

The OMW samples were sonicated at 30°C and at 60°C during 60, 120 and 150 min ultrasound times (Table III). Increasing the ultrasound time from 60 to 120 min enhanced the COD$_{dis}$ removals under ambient conditions (at 25°C). The maximum COD$_{dis}$ removal was 61% after 150 min ultrasound time, at 25°C and at pH=5.4 (Table III). 16%, 42% and 63% COD$_{dis}$ removals were measured after 60, 120 and 150 min ultrasound time, respectively, at pH=5.4 and at 30°C (Table III). The maximum COD$_{dis}$ removal was 67% after 150 min ultrasound time, at pH=5.4 and at 60°C (Table III). An initial increase in solution temperature increase the rate of reaction leading to a greater fraction of OH ion production and volatile compounds partitioning into the cavity. A further increase in solution temperature leads to a decrease in the rate of reaction [7]. The treatment by ultrasound converts COD$_{dis}$ in the OMW to much smaller sonodegraded compounds. Short ultrasound times (60 min) did not provide high degradation removals for refractory COD throughout ultrasonic irradiation. COD$_{dis}$ was not completely removed under the ultrasonic action even with a long ultrasound time (150 min) in OMW. This was probably caused by insufficient levels of OH$^{\bullet}$ formation. Hence, COD$_{dis}$ do not have the ability to attack to the low concentrations of OH$^{\bullet}$, thus leading to decreased sonodegradation rates of COD$_{dis}$ as reported by David [13].

TABLE III. Effect of increasing ultrasound time (60, 120 and 150 min) and increasing temperature (at 25°C, at 30°C and at 60°C) on the COD$_{dis}$, total phenol, color and TAAs removal efficiencies in OMW, at an initial COD$_{dis}$ concentration=109444 mg/l, at an initial total phenol concentration=2990 mg/l, at an initial color concentration=99.8 1/m, at an initial TAAs concentration=1990 mg benzidine/l, at ultrasound power=640 W, at ultrasound frequency=35 kHz and at pH=5.4 (n=3, mean values).

SET	Parameters	Removal Efficiencies (%)								
		25°C (Control)			30°C			60°C		
		60. min	120. min	150. min	60. min	120. min	150. min	60. min	120. min	150. min
1	COD$_{dis}$	13	42	61	16	42	63	18	47	67
2	Total phenol	30	57	61	45	62	80	48	70	88
3	Color	36	48	50	39	53	75	45	70	84
4	TAAs	41	52	66	47	56	69	62	71	79

The COD$_{dis}$ removals obtained in the OMW were higher than those of the recent studies obtained at 25°C with ultrasound: Canizares-Macias et al. [14]

56% COD_{dis} removal found at 20 kHz frequency, and at a power of 400 W, after 60 min ultrasound time by an ultrasound system assisted with Rancimat Method. In a study performed by Atanassova et al. [15] a COD_{dis} removal of 45% was found after 240 min ultrasound time at a power of 150 W and a frequency of 80 kHz at 25^{o}C. 40% COD_{dis} removal was provided in the OMW containing 10 mg/l alpechin at 40 kHz frequency, at 700 W power, after 15 min ultrasound time, at 50^{o}C [16]. In this study, the COD_{dis} removal (61%) is higher than the data obtained by Benedito et al. [16] and by Canizares-Macias et al. [14] mentioned above. In this study, it was found that the total phenol removal efficiencies in the OMW increased from 30% up to 57% as the ultrasound time was increased from 60 to 120 min at 25^{o}C at pH=5.4. The maximum total phenol removal efficiency was 61% after 150 min ultrasound time, at pH=5.4 and at 25^{o}C (Table III, SET 2). 48%, 70% and 88% total phenol removals were found after 60, 120 and 150 min ultrasound time, respectively, at pH=5.4 and at 60^{o}C (Table III, SET 2). The maximum total phenol removal was 88% after 150 min ultrasound time, at pH=5.4 and at 60^{o}C (Table III, SET 2). The Kruskal–Wallis test statistics showed that the effects of increasing ultrasound time (from 60 up to 120 and 150 min) and temperature (from 25^{o}C to 30 and 60^{o}C) on the total phenol removals are not differed and these differences are not significant (Mann–Whitney *U*-test statistic=2.98, $p < 0.10$) after 60 and 120 min at all increasing temperatures. Although, the increase in ultrasound times increase the total phenol removals, the temperature increse from 25 up to 60^{o}C did not contribute to total phenol removals after 60 and 120 min ultrasound time. However, the increase in temperature contributed to the total phenol removals after 150 min ultrasound time. The total phenol removals is significantly differed (Mann–Whitney *U*-test statistic=11.02, $p < 0.1$).

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. Higher ultrasound times are needed for complete mineralization of phenol. Short ultrasound times (60 min) did not provide high degradation removals for refractory part of phenolic organics throughout ultrasonic irradiation since the $OH^\bullet$ can not have enough time to binding to the phenol. Phenol was not completely removed under the ultrasonic action even with a long ultrasound time (150 min) in the OMW.

Around 36, 48 and 50% color removals were obtained at 60 and 150 min ultrasound time, respectively, at an initial color level of 99.8 1/min in the OMW at ambient conditions (at 25^{o}C) (Table III). 39%, 53% and 75% color removals were found after 60, 120 and 150 min ultrasound time, respectivley, at pH=5.4 and at 30^{o}C. 45%, 70% and 84% color removals were observed after 60, 120 and 150 min ultrasound time, respectively, at pH=5.4 and at 60^{o}C (Table III). The maximum color removal was 84% after 150 min ultrasound time, at pH=5.4 and at 60^{o}C.

Although, the color yields increased as the ultrasound time were increased from 60 to 120 min, the contribution of low temperature on the color yields was found to be not significant. Kruskal–Wallis test statistics showed that the color removals are not differed significantly after 60 and 120 min ultrasound times, at 30^{o}C (Mann–Whitney *U*-test statistic=2.38, *p*=0.05) Low color removals in the OMW effluents showed that low ultrasound temperature (25^{o}C) is not able to achieve the complete removal of the colored organics (e.g. lignin, organic acids, etc.) and the phenolic compounds (e.g. tannins, antocyanins, catechins, etc.). 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. It was found that high temperature such as 60^{o}C increased significantly the color yields after 150 min ultrasound time. The Kruskal–Wallis test statistics showed that the color removals are differed after 150 min ultrasound time at a temperature of 60^{o}C and these differences are significant (Mann–Whitney *U*-test statistic=12.63, *p*=0.05). The increasing of temperature is likely to facilitate the buble formation due to an increase of vapour pressure of a medium and so lead to easier cavitation with less violent collapse.

41%, 52% and 66% TAAs removal efficiencies were observed at an influent TAAs concentration of 1990 mg/l after 60, 120 and 150 min ultrasound time, respectively, at pH=5.4 and at 25^{o}C (Table III). As the temperature increased to 30^{o}C the TAAs removals increased to 47%, 56% and 69% after 60, 120 and 150 min ultrasound time, respectively, at pH=5.4 (Table III). 62%, 71% and 79% TAAs removal efficiencies were found after 60, 120 and 150 min ultrasound time, respectively, at pH=5.4 and at 60^{o}C (Table III). The maximum TAAs removal efficiency was 79% after 150 min ultrasound time, respectively, at pH=5.4 at 60^{o}C (Table III).

Although, the increasing of ultrasound time contribute to the TAAs removals the Kruskal–Wallis test statistics showed that the TAAs removals are not differed significantly after 60 min ultrasound time, at 30 and at 60^{o}C (Mann–Whitney *U*-test statistic=1.09, *p*=0.05). The increasing of temperature and ultrasound time from 25 to 30 and to 60^{o}C and from 120 to 150 min ultrasound time, respectively, increased the TAAs removals. The Kruskal–Wallis test statistics showed that the TAAs removals are differed after 150 min ultrasound time versus increasing temperature and these differences are significant (Mann–Whitney *U*-test statistic=13.88, *p*=0.05).

C. Removal Mechanisms of COD_{dis} , Total Phenol, Color and Total Aromatic Amines (TAAs) in the OMW throughout Ultrasound

The H_2O_2 measurements were performed in the absence and in the presence of OMW throughout ultrasound of TAAs, color, total phenol and COD_{dis} at 30°C after 150 min ultrasound time, in order to detect the ultrasound mechanisms of the parameters in suspension. In the absence of OMW (in deionized water) the H_2O_2 was accumulated (176 mg/l). Similarly the H_2O_2 concentration remains as formed after 150 min ultrasound time (Table IV). The initial rate of H_2O_2 formation associated with the COD_{dis} treatment by ultrasound in the OMW decreased significantly with increasing ultrasound time at 60°C (Table IV). The H_2O_2 concentration was 34 mg/l at the beginning of the ultrasound in the OMW then increased to 156 mg/l with the production of $OH^{\bullet}$ ion since H_2O_2 is formed by the recombination of $OH^{\bullet}$ throughout sonolysis. Afterwards, the H_2O_2 concentrations decreased to 92 and 11 mg/l with the $OH^{\bullet}$ ion increase. The $OH^{\bullet}$ ion concentrations increased from $10 * 10^{-62}$ to $16 * 10^{-7}$ mg/l after 150 min ultrasound time in the OMW. This showed that hydroxylation is the main mechanism for the removal of COD_{dis}.

TABLE IV. H_2O_2 and $OH^{\bullet}$ ion concentrations in the OMW at 60°C, after 30, 120 and 150 min ultrasound time, at an initial COD_{dis} concentration=109444 mg/l, at an initial color concentration=99.8 1/m and at an initial TAAs concentration=1990 mg/l, respectively, at pH=5.4 at ultrasound power=640 W and ultrasound frequency=35 kHz (n=3, mean values).

Conditions	**COD_{dis} removal**		**Color removal**		**Aromatic amines removal**		**Phenol removal**	
	H_2O_2[a]	**$OH^{\bullet}$**[a]	**H_2O_2**[a]	**$OH^{\bullet}$**[a]	**H_2O_2**[a]	**$OH^{\bullet}$**[a]	**H_2O_2**[a]	**$OH^{\bullet}$**[a]
H_2O_2 concentration (mg/l) in deionized water (60°C) at pH=7 at the beginning	177	0	177	0	0	0	209	0
H_2O_2 concentration (mg/l) in deionized water (60°C) at pH=7 after 150 min ultrasound time	176	0	176	0	0	0	198	0
H_2O_2 concentration (mg/l) in OMW (60°C) at pH=5.4 at the beginning	34	$1 * 10^{-92}$	49	$1 * 10^{-82}$	175	$1 * 10^{-272}$	98	$25 * 10^{-82}$
H_2O_2 concentration (mg/l) in OMW (60°C) after 30 min ultrasound time at pH=5.4	156	$10 * 10^{-62}$	160	$1 * 10^{-52}$	174	$1 * 10^{-262}$	185	$10 * 10^{-62}$
H_2O_2 concentration (mg/l) in OMW (60°C) after 120 min ultrasound time at pH=5.4	92	$13 * 10^{-15}$	73	$9 * 10^{-12}$	174	$1 * 10^{-252}$	145	$2 * 10^{-52}$
H_2O_2 concentration (mg/l) in OMW (60°C) after 150 min ultrasound time at pH=5.4	11	$16 * 10^{-7}$	5	$9 * 10^{-5}$	173	$1 * 10^{-242}$	14	$43 * 10^{-7}$

[a] Concentration (mg/l)

In the absence of the OMW (in deionized water) the H_2O_2 concentration was measured as 209 mg/l at pH=7.0 while the H_2O_2 concentration decreased sligtly and remained around 198 mg/l after 150 min ultrasound time, at pH=5.4 throughout ultrasound of phenols (Table IV). The H_2O_2 concentration was 98 mg/l at the beginning of the ultrasound in the OMW and then increased to 185 mg/l after 30 min ultrasound time with the production of $OH^{\bullet}$ ion since H_2O_2 is formed by the recombination of $OH^{\bullet}$ throughout sonolysis. Afterwards, the H_2O_2 concentrations decreased to 145 and 14 mg/l with the $OH^{\bullet}$ ion increase in the OMW after 120 and 150 min ultrasound time, respectively. The H_2O_2 values in the OMW are much lower compared to those in deionized water (at a neutral pH=7.0) due to the fact that in the former case many of the $OH^{\bullet}$ produced by ultrasound reacted with phenol before they could combine to form $OH^{\bullet}$. The $OH^{\bullet}$ ion concentrations reached $25 * 10^{-82}$ mg/l from $43 * 10^{-7}$ mg/l after 150 min ultrasound time in the OMW. This showed that hydroxylation is the main mechanism for the removal of phenol. In this study, in the OMW the most sonogenerated $OH^{\bullet}$ reacted with 93% maximum total phenol removal and radical recombination to produce H_2O_2 after 150 min ultrasound time. Different phenol removal mechanisms and metabolites were reported throughout ultrasound: Pétrier et al. [17] investigated the sonolysis of phenol in aqueous solution and found hydroquinone, catechol, and benzoquinone as reaction products. These reaction products are attributed to the attack of the $OH^{\bullet}$ on phenol. Similarly, Anju et al. [18] showed that the $OH^{\bullet}$ was involved in the degradation pathways of phenol. They reported that $OH^{\bullet}$ generated from the dissosiation of H_2O during ultrasonic irradiation process. very high concentration of $OH^{\bullet}$ is achieved after the bubbles collapse. The concentration that could be reached is estimated to be as high as 4 mM. However, Currell et al. [19] found that the ultrasound of phenol was sono-degraded partially by pyrolysis in the bubble phase. This could be due to the reactor configuration and geometry, to the wastewater characteristics, to the ultrasound intensity, frequency and the presence of matrix components in the wastewater researched.

Throughout ultrasound of the colored organics and phenols in the OMW, the H_2O_2 production decreased while the $OH^\bullet$ ion concentration increased. Since the sonooxidation of the COD_{dis} and the colored organic substances comprised 63% and 75% of the total sonodegradation process at 30°C after 150 min ultrasound time, $OH^\bullet$ is the major process for complete degradation of these parameters. Throughout the sonodegradation of the TAAs the rate of $OH^\bullet$ production was zero. This accomplished with H_2O_2 concentration as low as $1 * 10^{-272}$ mg/l (Table IV). Therefore, it can be seen that $OH^\bullet$ is not the major process for complete degradation of the aromatic amines. In other words, in this study, the contribution of $OH^\bullet$ was minor for the ultimate sonodegradation of aromatic amines. The formation of by-products (aniline, o–toluidine, anisidine, dimethylaniline and dimethylaniline) for possible $OH^\bullet$ oxidation was not observed in HPLC. Similar results were obtained in the studies performed by Wu and Ondruschka [20]. The contribution of the pyrolysis to the destruction of TAAs is significant. The occupation of the heart and/or the surrounding shell of the bubble by TAA molecules, limiting the sonolysis of H_2O and the formation of $OH^\bullet$. This indicates that the main process for the destruction of TAAs is pyrolysis. The addition of 600 mg/l 1-butanol to the OMW very slightly affected (4%) the TAAs removals by the $OH^\bullet$ scavenger (data not shown) while about 67-59% inhibition was observed for COD_{dis} and color removal (data not shown). Throughout ultrasound of TAAs some gaseous by-products were observed in the headspace of the ultrasound reactor. 31.2-41.11% CO_2 and 16-18.32% NH_3 were measured after 10 min ultrasound time in the headspace of the sonicator reactor (data not shown). It can be assumed that these gases are primarily formed as soon as TAAs penetrate the cavitation bubbles in order to be pyrolyzed. The oxidation of TAAs with $OH^\bullet$ appears to be of relatively minor importance, because of the low inhibition of the sono-degradation by means of 1-butanol and since the expected steady-state $OH^\bullet$ concentration in the interfacial region of the cavitation bubble, where TAAs accumulate, is lower and not sufficient for a complete degradation of TAAs. The TAAs are then expected to be mainly localized in the heart and/or in the surrounding shell of the bubble, inhibiting the production of $OH^\bullet$ and hence the oxidation pathway.

In this study, the ultrasound mechanism of the AAs in the OMW are attributable to the priority of cleavage of azo links by pyrolysis. Throughout pyrolysis, $OH^\bullet$ initially diffuse into their long-lived cavity bubbles to undergo pyrolytic destruction inside the collapsing bubble then the cleavage of azo groups open the $N{=}N$ bonds. The cleavage of methyl, ethyl and C-H-O bonds can destroyed the aromatic structures in TAAs namely o-toluidine, dimethylaniline, ethylbenzene and durene.

D. Effects of Nano-sized Metal Oxides (TiO_2, SiO_2 and ZnO) on the Sonodegradation of COD_{dis} , Total Phenol, Color and TAAs in the OMW

Keeping the conditions of 35 kHz, 640 W and 21°C, ultrasonic degradation of COD_{dis}, TAAs, total phenol and color in the OMW were investigated in the presence of nano-sized metal oxides TiO_2, NiO and ZnO. Table V shows the effect of nano-sized metal oxides on the removal of the pollutant parameters given above in the OMW samples. The contribution of nano-sized TiO_2 on COD_{dis}, TAAs, total phenol and color yields was found to be significant. Although, 2 mg/l nano-sized TiO_2 increase significantly the COD_{dis} (92%), TAAs (86%), total phenol (90%) and color (85%) (Table V). The maximum COD_{dis} (97%), TAAs (88%), total phenol (97%) and color (94%) yields were obtained at 4 mg/l nano-sized TiO_2 concentration. The increasing of nano-sized TiO_2 to 8 mg/l decreased the removals in the aforementioned pullution parameters. Nano-sized TiO_2 particles provides more chances for the organic compounds (COD_{dis}) phenol and TAAs) to adsorb on the surface of the nano-sized TiO_2 particles to be directly composed by holes. Throughout ultrasound of the OMW with semiconductor nano-sized TiO_2, firstly, the formation of the light at wavelentgh below 375 nm occurred. Under these conditions the ligth can excite the semiconductor nano-sized TiO_2 acting as a photocatalyst and $OH^\bullet$ with oxidative performance activate the surface of the nano-sized TiO_2. Secondly, the temperatrure of hot spot produced by ultrasonic cavitation in the sonicator can achieve high temperatures such as 102 and 104°C. As a result, temperatures as high as 104°C bring many holes producing $OH^\bullet$ on the surface of the nano-sized TiO_2. Throughout ultrasound the steps of treatment of the OMW include the following steps: (i) the mass transfer of the polutants (COD_{dis}, phenol, TAAs and color giving organics) from the bulk solution to the surface of nano-sized TiO_2, (ii) adsorption of pollutants onto the nano-sized TiO_2 surface (iii) chemical reactions ($OH^\bullet$ and other radical productions) on the surface of nano-sized TiO_2. Desorption of the products from the nano-sized TiO_2 surface during oscillation and mass transfer of the product from the nano-sized TiO_2 surface to the bulk solution of the OMW in the sonicator [5]. At low nano-sized TiO_2 concentrations the adsorbed pollutant molecules on nano-sized TiO_2 surfaces decrease in the OMW. Therefore, the degradatıon ratio of the pollutants decreased since the organics did not find enough holes in the surface of the nano-sized TiO_2 nano-particles. Thus it reduces the formatıon rate and number of $OH^\bullet$ and inhibits the generation of $OH^\bullet$. At high nano-sized TiO_2 concentrations the COD_{dis}, total phenol, TAAs and color removals decreased. This could be attributed to the aggregation of nano-sized TiO_2 particles at high concentrations, causing a decrease in the number of active surface sites, and this decrease in the passage of sonic waves through sonication of the OMW samples. Wang et al. [21] also reported that high nano-sized TiO_2 concentrations (≥ 6-12 mg/l) decrease the COD_{dis} removals. The increase in sono-destruction of polutants at 4 mg/l nano-sized TiO_2 may be explained by the cavitation process which produces higher surface area. The ultrasonic waves not only destroy the phenol compounds through cavitation process but also could increases the adsorption process by increasing the surface area of the nano-sized TiO_2 catalyst as reported by Laxmi et al. [22]. During the ultrasound of the OMW with nano-sized TiO_2, more active free radicals, such as $OH^\bullet$ and $O_2H^\bullet$ were produced from the dissociation of the H_2O and H_2O_2 [22]. In this study, the maximum TAAs removal (88%) observed in 4 mg/l nano-sized TiO_2 at 30^oC, was higher than the removal obtained by Cardoso et al. [23] for 4,4–oxydianiline aromatic amine removal (81%) with 5 mg/l nano-sized TiO_2 after 150 min ultrasound. In a study performed by Khochawala and Gogate [24] it was observed that 2 g/l nano-sized TiO_2 is the optimum concentration for maximum phenol (78%) removal. The removals obtained in our study are comparable higher than that the literatures mentioned above. Among the nano-sized ZnO doses used in this study the maximum COD_{dis} (92%), TAAs (90%), total phenol (93%) and color (93%) were obtained at a nano-sized ZnO concentration of 5 mg/l (Table V). At low nano-sized ZnO doses the removal efficiencies of the pollution parameters given above decreased. Nano-sized ZnO particles have been used to bind to the pollution parameters in wastewaters throughout ultrasound due to their surface properties, porosity, size distribution, density and surface charges. Throughout ultrasound of the OMW in the presence of nano-sized ZnO particles ultrasound acted as a deaggregator by microstreaming and causing microbubble collapse, which induced surface cleaning of the nano-sized ZnO particles; (i) US acted as a deaggregator by microstreaming and causing microbubble collapse, which induced surface cleaning of the ZnO particles; (ii) the presence of an additional liquid–solid interface in the liquid bulk promotes cavitation, and (iii) ultrasound (US)-accelerated mass transfer occurs between the solution phase and the nano-sized ZnO surface [18, 25]. The nano-sized ZnO nanoparticles help to break up the microbubbles created by ultrasound into smaller ones, thus increasing the number of regions of high temperature and pressure [25]. This leads to increase in the number of $OH^\bullet$ which will interact with the organic molecules present in H_2O and oxidise them, resulting in eventual mineralization. The increase in degradation removals of COD_{dis}, phenol rate can be attributed to the increase in the number of active cavitation bubbles and consequent generation of more $OH^\bullet$. At high nano-sized ZnO concentration (> 10 mg/l) the aggregation of nano-sized ZnO nanoparticles cause decreasing in surface holes [21]. This leads to decrease in the formation of $OH^\bullet$, resulting in low sonolytic efficiency. Beyond the optimum nano-sized ZnO concentration (3 mg/l), the degradation slows down and thereafter remains more or less steady or even decreases. The enhanced degradation efficiency is probably due to increased number of $OH^\bullet$ and their interactions. Another reason may be the aggregation of nano-sized ZnO particles causing decrease in the number of available nano-sized ZnO surface sites for binding of $OH^\bullet$. The particles cannot be fully and effectively suspended beyond a particular loading in the sonicator. Anju et al. [18] found 63%, 62% and 73% phenol yields in the present of 10 mg/l nano-sized ZnO under US, UV and combination of UV and US irradiation conditions after 2 h of exposure time. In another study by Drijvers et al. [26], the decomposition of phenol and COD_{dis} were investigated using nano-sized metal oxides Al_2O_3 and ZnO under the combined effect of sonolysis at 520 kHz and chemical oxidation with H_2O_2, 67%, 68% and 70% phenol yields was obtained with the metal oxides mentioned above. These COD_{dis} and phenol yields in these studies were lower than that our data. This could be attibuted to the differences of the wastewater, nano-sized ZnO concentrations and sonicational operational conditions. pH affects the nano-sized ZnO surface properties, phenol, TAAs dissociation and $OH^\bullet$ formation [21]. Hydroxyl anions (OH^-) in alkaline solution typically act as scavenger of holes on the surface of nano-sized ZnO particles and become $OH^\bullet$ with strong oxidation ability after they lose one electron. Consequently, the probability of generating $OH^\bullet$ increases with pH [21]. Nano-sized ZnO is known to be an effective oxidation catalyst as it could promote the formation of reactive radicals to oxidize organic compounds to lower carbon organic compounds and even to CO_2 and H_2O [18].

TABLE V. Effects of some nano-sized metal oxides on the removal of COD_{dis}, total phenol, TAAs and color at 25^oC, after 150 min ultrasound time, at a frequency of 35 kHz, at a power of 640 W and at pH=5.4 (n=3, mean values).

Nano-sized metal oxides and their concentrations	**Sonodegradation removals (%)**			
	COD_{dis}	**Phenol**	**TAAs**	**Color**
Control without nano-sized metal oxides	61	61	66	50
TiO_2 = 2 mg/l	92	90	86	85
TiO_2 = 4 mg/l	97	97	88	94
TiO_2 = 8 mg/l	90	94	83	90
SiO_2 = 3 mg/l	66	84	84	83
SiO_2 = 6 mg/l	89	91	88	88
SiO_2 = 9 mg/l	85	88	85	90
ZnO = 1 mg/l	64	86	74	80
ZnO = 3 mg/l	72	90	89	88
ZnO = 5 mg/l	92	93	90	93

In this study, the maximum COD_{dis} (89%), TAAs (88%), total phenol (91%) and color (88%) yields were obtained at a nano-sized SiO_2 concentration of 6 mg/l (Table V). At low (3 mg/l) and high (9 mg/l) nano-sized SiO_2 doses the removal efficiencies of the pollution parameters given above decreased (Table V). Dissociation of water in the cavitation bubbles throughout ultrasound will convert it into reactive species such as $OH^{\bullet}$, $H^{\bullet}$ and $O_2H^{\bullet}$ [7]. H_2O_2 will be formed outside the hot bubbles or at the cooler interface as a consequence of $OH^{\bullet}$ and $O_2H^{\bullet}$ recombination. On the other hand, the $H^{\bullet}$ and $OH^{\bullet}$ species may further react with H_2O_2. The presence of 6 mg/l nano-sized SiO_2 increase the number of free radicals generated, thereby increasing the rate of degradation of the COD_{dis}, phenol and TAAs in the OMW. The nano-sized SiO_2 nano-particles with the size less than that of cavitation bubbles have higher cavitation erosion resistant and are easier to approach the interfacial region (bubbles surface) during the expansion cycles of ultrasound [27]. Throughout ultrasound for the removals of pollutans from the OMW contained; mass transfer of the polutants from the bulk solution to the surface of nano-sized SiO_2, adsorption of pollutants onto the nano-sized SiO_2 surface during oscillation, chemical reactions ($OH^{\bullet}$ and other radical productions) on the surface of nano-sized SiO_2, Desorption of the products from the nano-sized SiO_2 surface during oscillation and mass transfer of the product from the nano-sized SiO_2 surface to the bulk solution steps. A nano-sized SiO_2 system was used as a catalyst for low-temperature oxidation of phenol [27]. Nano-sized SiO_2 is also being used as a catalyst for the oxidation of CO [27]. The catalytic properties of nano-sized SiO_2 depend on the number of factors such as the particle size and surface area, as well the catalyst structure. The maximum conversion of cyclohexane has been observed when nano-sized SiO_2 was used as a catalyst [27]. The utilization of the nano-sized SiO_2 in the treatment of wastewater are limited only with the utilization of this oxide as adsorbent fo the removal of dyes from the OMW.

E. Variation of Poly-phenols in the OMW in the Presence of Nano-sized Metal Oxides

The treatment by ultrasound converts the poly-phenols in the OMW to much smaller sonodegraded compounds such as tyrosol, hydroxytyrosol, caffeic acid, quercetin, ferulic acid, catechol, vanillic acid, o-quinone, *p*-coumaric acid, *p*-hydroxybenzaldehyde, 4-methyl catechol, 2-PHE and 3-PHE [21]. Table VI shows the measured phenol intermediates and their removals in this study (cathecol, tyrosol, quercetin, caffeic acid, 4-methyl catechol, 2-PHE and 3-PHE) in the OMW defined with HPLC before ultrasound at t=0 and after 150 min ultrasound times, at pH=5.4 at increasing concentrations of nano-sized metal oxides TiO_2 (2, 4 and 8 mg/l), SiO_2 (3, 6 and 9 mg/l) and ZnO (1, 3 and 5 mg/l) at 25°C.

TABLE VI. Measurements of phenol metabolites (catechol, 4-methyl catechol, tyrosol, quercetin, caffeic acid, 2-PHE and 3-PHE) in the OMW with the addition of some nano-sized TiO_2, SiO_2 and ZnO oxides with HPLC after 150 min ultrasound time at pH=5.4, at an initial total phenol concentration=2990 mg/l, at ultrasound power=640 W, at ultrasound frequency=35 kHz and at 25°C (n=3, mean values).

Time (min)	PHE$_0$ [d]	TiO_2=2 mg/l [a] ; TiO_2=4 mg/l [b] ; TiO_2=8 mg/l [c]							
			Initial phenol metabolites concentrations [d]						
		Control	2-PHE [d]	3-PHE [d]	Catechol [d]	4 – methyl catechol [d]	Tyrosol [d]	Quercetin [d]	Caffeic acid [d]
0	2990	2990	4	9	23	15	42	21	30
Time (min)	PHE$_0$ [d]	PHER [e]	Phenol degradation metabolites						
			2-PHE [e]	3-PHE [e]	Catechol [e]	4 – methyl catechol [e]	Tyrosol [e]	Quercetin [e]	Caffeic acid [e]
150 [a]	299	90	64	68	62	63	61	68	64
150 [b]	90	97	84	83	84	84	83	82	85
150 [c]	179	94	72	69	78	77	79	76	75
Time (min)	PHE$_0$ [d]	SiO_2=3 mg/l [f] ; SiO_2=6 mg/l [g] ; SiO_2=9 mg/l [h]							
		PHER [e]	Phenol degradation metabolites						
			2-PHE [e]	3-PHE [e]	Catechol [e]	4 – methyl catechol [e]	Tyrosol [e]	Quercetin [e]	Caffeic acid [e]
150 [f]	478	84	61	63	59	60	56	64	61
150 [g]	269	91	81	78	82	81	80	78	82
150 [h]	359	88	69	64	70	73	76	72	71
Time (min)	PHE$_0$ [d]	ZnO=1 mg/l [j] ; ZnO=3 mg/l [k] ; ZnO=5 mg/l [m]							
		PHER [e]	Phenol degradation metabolites						
			2-PHE [e]	3-PHE [e]	Catechol [e]	4 – methyl catechol [e]	Tyrosol [e]	Quercetin [e]	Caffeic acid [e]
150 [j]	419	86	62	65	60	61	58	65	62
150 [k]	209	93	82	80	83	82	81	80	84
150 [m]	299	90	70	66	72	75	77	74	73

PHE_0: Initial total phenol concentration (mg/l).
PHER: Total phenol removal efficiency (%).
2-PHE (%): 2-phenyl-phenol removal efficiency (%).
3-PHE (%): 3-phenyl-phenol removal efficiency (%).
[a] TiO_2=2 mg/l.
[b] TiO_2=4 mg/l.
[c] TiO_2=8 mg/l.
[d] Concentration (mg/l).
[e] Removal efficiency (%).
[f] SiO_2=3 mg/l.
[g] SiO_2=6 mg/l.
[h] SiO_2=9 mg/l.
[j] ZnO=1 mg/l.
[k] ZnO=3 mg/l.
[m] ZnO=5 mg/l.

As shown in Table VI, 2990 mg/l total phenol in the raw wastewater consisted of 23 mg/l catechol, 42 mg/l tyrosol, 21 mg/l quercetin, 30 mg/l caffeic acid, 15 mg/l 4-methyl catechol, 4 mg/l 2-PHE and 9 mg/l 3-PHE before ultrasound at t=0. The phenol metabolite concentrations mentioned above increased to 600 mg/l, 388 mg/l, 350 mg/l, 345 mg/l, 395 mg/l, 247 mg/l and to 268 mg/l with 2 mg/l nano-sized TiO_2 after 120 min ultrasound time, at pH=5.4 at 30°C (data not shown). Catechol, tyrosol, quercetin, caffeic acid, 4-methyl catechol, 2-PHE and 3-PHE reduced to 280, 220, 190, 185, 195, 123 and 99 mg/l after 150 min ultrasound time, at pH=5.4 and at 30°C (data not shown). These phenol metabolites were removed with yields of 62, 61, 68, 64, 63, 64 and 68%, respectively, at a nano-sized TiO_2 concentration of 2 mg/l after 150 min ultrasound time, at pH=5.4 and at 25°C while 299 mg/l total phenol remained in the sonicator reactor. The catechol, tyrosol, quercetin, caffeic acid, 4-methyl catechol, 2-PHE and 3-PHE removals were 84, 83, 82, 85, 84, 84 and 83%, respectively, at nano-sized TiO_2=4 mg/l after 150 min ultrasound time, at 25°C and pH=5.4 with an effluent total phenol concentration of 90 mg/l. The yields of the aforementioned phenol metabolites decreased to 78, 79, 76, 75, 77, 72 and 69%, respectively, as the nano-sized TiO_2 concentration was decreased from 4 to 8 mg/l after 150 min ultrasound time, at pH=5.4 and at 25°C (Table VI). Anju et al. [18] showed that the primary degradation products of phenol were hydroquinone, catechol, and benzoquinone. The differences in the phenol metaboloites can be attributed to the differences in wastewater composition, to the operational conditions and to the nano-sized TiO_2 concentration.

Throughout the simultaneous ultrasound in the presence of nano-sized TiO_2 in the OMW, the bonds in nano-sized TiO_2 could be easily attacked by $OH^{\bullet}$ and H^+ cations that originate from H_2O_2 and H_2O molecules, respectively, to subsequently form O Ti^+— O^-— $OH^{\bullet}$ and O Ti^+— $OH^{\bullet}$ ions. These ions would combine with each other on the surface of original nano-sized TiO_2 particles. The generation of $OH^{\bullet}$ from the pyrolysis of H_2O during ultrasonic irradiation of phenol was shown in Eq. (1):

$$C_6H_5-OH+OH^{\bullet} \rightarrow C_6H_5(OH)_2+phenol\,metabolites \rightarrow CO_2+H_2O \quad (1)$$

The phenol metabolite concentrations increased after 60 and 120 min ultrasound time with 3 mg/l nano-sized SiO_2 addition. 550 mg/l catechol, 377 mg/l tyrosol, 330 mg/l quercetin, 314 mg/l caffeic acid, 344 mg/l 4-methyl catechol, 226 mg/l 2-PHE and 251 mg/l 3-PHE were produced with the addition of nano-sized SiO_2=3 mg/l after 60 min ultrasound time, at pH=5.4 at 25°C. These phenol metabolites were removed with yields of 59, 56, 64, 61, 60, 61 and 63%, respectively, at the aforementioned nano-sized SiO_2 concentration after 150 min ultrasound time, at pH=5.4 and at 25°C while 478 mg/l total phenol remained in the sonicator reactor. The catechol, tyrosol, quercetin, caffeic acid, 4-methyl catechol, 2-PHE and 3-PHE removal efficiencies increased to 82, 80, 78, 82, 81, 81 and 78% as the nano-sized SiO_2 concentration was increased from 3 mg/l to 6 mg/l after 150 min ultrasound time, at pH=5.4 and at 25°C. The metabolite yields decreased to 70, 76, 72, 71, 73, 69 and 64%, at nano-sized SiO_2=9 mg/l after 150 min ultrasound time, at 30°C and pH=5.4 (Table VI). The increase in degradation yields of phenol metabolites at a 3 mg/l nano-sized SiO_2 concentration can be attributed to the increase in the number of active cavitation bubbles and consequent generation of more $OH^{\bullet}$ with simultaneous adsorption of metabolites to the aforementioned nano-sized metal oxides.

Catechol, tyrosol, quercetin, caffeic acid, 4-methyl catechol, 2-PHE and 3-PHE were removed with yields of 60, 58, 65, 62, 61, 62 and 65%, respectively, in nano-sized ZnO=1 mg/l after 150 min ultrasound time, at pH=5.4 and at 30°C while 419 mg L^{-1} total phenol remained in the sonicator reactor. The removal yields in the phenol metatabolites increased to 83, 81, 80, 84, 82, 82 and 80% removals were respectively, in nano-sized ZnO=3 mg/l after 150 min ultrasound time, at 25°C and at pH=5.4. The removal efficiencies decreased to 72, 77, 74, 73, 75, 70 and 66%, respectively, as the nano-sized ZnO concentration was increased from 3 mg/l to 5 mg/l after 150 min ultrasound time, at pH=5.4 and at 30°C (Table VI). Throughout ultrasound the highly excited holes on on the surface of nano-sized ZnO not only directly decompose the phenol to their metabolites but also phenol molecules adsorbed on the surface of nano-sized ZnO nano-particles, but also oxidize the H_2O to produce $OH^{\bullet}$ with high activity and indirectly degrade the phenols molecules to their metabolites in the OMW.

It can be assumed that the total phenol concentrations of 90, 269 and 209 mg/l remaining from the ultrasound at nano-sized TiO_2=4 mg/l (Table VI), at nano-sized SiO_2=6 mg/l and at nano-sized ZnO=3 mg/l, respectively, at 30°C, after 150 min ultrasound time and at pH=5.4 could not be cleaved to other phenol metabolites namely, hydroxytyrosol, o-quinone, *p*-coumaric acid and *p*-hydroxybenzaldehyde throughout ultrasound since their concentrations were detected as zero. Probably the phenol remaining from the ultrasound can be the phenol which was not converted to corresponding metabolites given above and to the other metabolites not measured in this study (oleurapein, quercetin, ferrulic acid, and vanillic acid) through ultrasound. In the study by Khoufi et al. [5] 45% catechol, 52% tyrosol, 42% quercetin, 49% caffeic acid and 30% 2-PHE removal efficiencies were found at a 80 kHz frequency with 140 min ultrasound time. The higher phenol and phenol metabolites removals found in our study could be originated from the composition of the OMW, from the operarational conditions such as the ultrasound power, ultrasound intensity, ultrasound frequency and ultrasound temperature.

IV. CONCLUSIONS

The maximum COD_{dis}, color, TAAs and total phenol yields were > 90% with 4 nano sized mg/l TiO_2 and 5 mg/l ZnO and 4 mg/l TiO_2. The combination of ultrasound and nano-sized metal oxides appears to have a positive synergistic effect on the reduction of COD_{dis}, total phenol, color, TAAs and phenol metabolites from the the OMW. COD_{dis}, phenol by-products and color are mainly eliminated by $OH^{\bullet}$ while the dominant TAAs degradation mechanism is high temperature pyrolysis in ultrasonic cavities rather than free radical oxidation.

Sonication at 35 kHz proved to be a viable tool for the effective removal of COD, color, total phenol, TAAs and toxicity from OMW, providing a cost-effective alternative for destroying and detoxifying the refractory compounds in OMW.

ACKNOWLEDGEMENTS

This research study was undertaken in the Environmental Microbiology Laboratory at Dokuz Eylül University Engineering Faculty Environmental Engineering Department, Izmir, Turkey. The authors would like to thank this body for providing financial support.

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