The Removal of Pollutants by Sonication using Nitrogen Gas in Textile Industry Wastewater: Comparison of Energy Consumption and Cost Analysis with Other Advanced Oxidation Processes

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Abstract: - In this study, the effects of ambient conditions, the effects of increasing sonication time (60 min, 120 and 150 min), increasing temperatures (25° C, 30°C and 60°C), different nitrogen gas sparging {15 min [3 mg/l $N_2(g)$] and 30 min [6 mg/l $N_2(g)$]} on sonication at a textile industry wastewater (TI ww) treatment plant in Izmir (Turkey) containing toxic and resistant pollutants was investigated in 500 ml glass reactor, at 640 W sonication power, at 35 kHz sonication frequency has been researched. The maximum removal yields were measured to 98.23% chemical oxygen demand-dissolved (COD_{dis}), 95.30% color and 68.08% total aromatic amines (TAAs), at 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging after 150 min sonication time, at pH=7.0 and at 60°C in TI ww, respectively. In the final stage of this study, the energy and costs used for the sonication process were compared in detail with the other Advanced Oxidation Process (AOPs) methods. Statistical analysis was also investigated for operational conditions. Finally, sonication at 35 kHz proved to be a viable tool for the effective removal of COD_{dis}, color and TAAs from TI ww, providing a cost-effective alternative for destroying and detoxifying the refractory compounds in TI ww, respectively. Also, this study showed that the energy requirements of the sonication process is lower than the other AOPs.

Key-Words: - Advanced oxidation processes (AOPs); Comparion of energy consumption; Cost analysis; Hydroxyl radicals ($OH^{\bullet}$); Nitrogen (N_2) gas sparging; Textile industry wastewater (TI ww); Sonication; Statistical analysis (ANOVA); Ultrasound (US); Ultraviolet (UV).

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1 Introduction

Textile industries generate a number of pollutants, which they discharge to the surrounding environment without any further treatment, [1]. These pollutants not only add color to water but also cause extensive toxicity to aquatic and other forms of life, [2]. About 10%–15% of the total dyes from various textile and other industries get discharged in wastewater causing extensive pollution, [1], [2]. Therefore, the treatment of industrial effluents containing polyaromatic and polyphenolic compounds becomes necessary prior to their final discharge to the environment. Conventional methods for the effective removal of phenols, polyphenols, aromatic amines and dyes are outdated due to certain inherent limitations that they have, [3]. The recalcitrant nature of textile effluents largely containing high concentrations of dyestuffs, salts, acids, bases, surfactants, dispersants, humectants, oxidants and detergents renders these waters aesthetically unacceptable and unusable. Textile dyes are well-known mutagens and carcinogens posing risks to various ecosystems, animals' health and agriculture, [4]. Therefore, the treatment of these high volumes of wastewater becomes crucial. Available techniques such as physical and biological adsorption, membrane filtration, oxidation, ozonation and microbial biodegradation are generally employed for remediation of dye containing effluents. These treatment and removal practices are not always followed as per the governing standards and thus ultimately cause serious pollution. These approaches are expensive and unaffordable for small-scale industries and processors, [5].

It was shown that the complex structures of amino-azo benzene dyes and their various derivatives may lead to mutagenesis, which is a major cause of cancer, [6]. The International Agency for Research on Cancer (IARC) has declared benzidine-like dyes to be extremely powerful carcinogens to many mammals and, alarmingly, human beings, [7]. Experiments on Swiss albino rats as model organisms have shown the toxicity of TI ww to animals, [8]. TI ww effluents are characterized by alkaline reaction, significant salinity, intensive color and toxicity, [9]. As a result, colored wastewater is emitted to the aquatic environment, where it creates problems for photosynthetic aquatic plants and algae, [10], [11], [12]. Some of them or their degradation products are toxic, mutagenic or cytotoxic, [13], [14], [15].

The textile industries use enormous amounts of H_2O and chemicals for the wet processing of textiles and also use various types of dyes to impart attractive colors of commercial importance. The wastewater let out by the textile industries generally contain about 10% of dyes used for the textile coloration, [16]. These dye stuff include various types like acidic, basic, azo, reactive, anthroquinone-based compounds and among these azo dyes are widely used by the industries. Further, azo dyes contribute about 60–70% of the total dyestuff produced, [17]. The application of ultrasound as an alternative to the removal of dyes in waters has become of increasing interest in recent years, [18, 19]. This technique is considered as an AOP that generates hydroxyl radicals ($OH^\bullet$) through acoustic cavitation, which can be defined as the cyclic formation, growth and collapse of microbubbles. Fast collapse of bubbles compressed adiabatically entrapped gas and vapors which leads to short and local hot spots, [20]. In the final stage of the collapse, the temperature inside the residual bubble or in the surrounding liquid is thought to be above 5000ºC. The $OH^\bullet$ and hydroperoxyl radicals ($O_2H^\bullet$) can be generated from H_2O and O_2, [21]. The sonochemical activity arises mainly from acoustic cavitation in liquid media. The acoustic cavitation occurring near a solid surface will generate microjets which will facilitate the liquid to move with a higher velocity resulting in increased diffusion of solute inside the pores of the TI ww, [22], [23]. In the case of sonication, localized temperature raised and swelling effects due to ultrasound may also improve the diffusion. The stable cavitation bubbles oscillate which is responsible for the enhanced molecular motion and stirring effect of ultrasound. In case of cotton dyeing TI ww, the effects produced due to stable cavitation may be realized at the interface of fabric and colored solution. Mass transport intensification using a conventional approach such as very high elevated temperatures (> 500ºC), is not always feasible, due to undesired side-effects such as fabric damage. About 87% and 81% COD_{dis} yields were achieved using 40 min and 50 min ultrasound time, respectively, while compared to only 48% and 28.9% COD_{dis} removals in the absence of ultrasound in TI ww at 25ºC, [24].

Aerobic, anaerobic and sequential anaerobic–aerobic reactors were used for aromatic amine removals, [25], [26], [27]. Moreover, biological treatment with chemical physical processes such as adsorption on waste sludge and activated carbon, photochemical oxidation and membrane nanofiltration can be used, although the cost is high, [27], [28], [29], [30], [31].

In recent years, AOPs have emerged as potentially powerful methods that are capable of transforming the pollutants into harmless substances, [32], and that almost all rely on the generation of very reactive free radicals, such as the $OH^\bullet$, [33]. AOPs, generally involving H_2O_2, O_3 or Fenton's reagent as oxidative species for the destruction of contaminants, are alternative techniques for eliminating dyes and other organics in wastewater, [34], [35], [36], [37], [38]. Semiconductor photocatalysis has emerged as a promising AOP that provides solutions to many environmental pollution problems, [35], [36], [37], [38].

The operating costs appear to be less severe than would be required by conventional thermochemical methods (e.g. wet air oxidation), which require high temperatures and pressures, [39], [40]. Furthermore, the sonication process does not require the use of extra chemicals (e.g. oxidants and catalysts) commonly employed in several AOPs (e.g. ozonation, Fenton's reagent), thus avoiding the respective costs as well as the need to remove the excess of toxic compounds prior to discharge. Among them, ultrasonic treatment has been used widely because of its relatively low processing cost and high efficiency of reduction. Studies have shown that polyaromatic amines and color in water and wastewaters are degraded with ultrasonic treatment with stronger irradiation intensity and longer irradiation time.

In this study, the effects of ambient conditions, the effects of increasing sonication time (60 min, 120 min and 150 min), increasing temperatures (30ºC and 60ºC), different nitrogen gas [$N_2(g)$] sparging {15 min [3 mg/l $N_2(g)$] and 30 min [6 mg/l $N_2(g)$]} on sonication at a TI ww treatment plant in Izmir (Turkey) containing toxic and resistant pollutants was investigated in 500 ml glass reactor, at 640 W sonication power, at 35 kHz sonication frequency, respectively. In the final stage of this study, the energy and costs used for the sonication process were compared in detail with other AOPs methods. Statistical analysis was also investigated for operational conditions.

2 Materials and Methods

2.1 Raw Wastewater

The TI ww used in this study contains color (> 70.90 1/m), TAAs (> 1296 mg benzidine/l), COD (> 770 mg/l) and high BOD_5 (> 251 mg/l) concentrations and a BOD_5/COD ratio of 0.33, respectively. The characterization of TI ww was shown in Table 1 for minimum, medium and maximum values, respectively. All measurements were carried out three times and the results are given as the means of the triplicate samplings with standard deviation (SD) values.

Table 1. Characterization values of TI ww (n=3, mean values ± SD).

Parameters	Values		
	Minimum	Medium	Maximum
pH	5±0.18	5.27 ± 0.19	6 ± 0.21
DO (mg/l)	1.3 ± 0.05	1.40 ± 0.05	1.5 ± 0.05
ORP (mV)	85 ± 2.98	106 ± 3.71	128 ± 4.48
TSS (mg/l)	285 ± 9.98	356 ± 12.46	430 ± 15.05
TVSS (mg/l)	192 ± 6.72	240 ± 8.40	290 ± 10.15
COD_{total} (mg/l)	931.7 ± 32.61	1164.6 ±40.76	1409.2 ± 49.32
$COD_{dissolved}$ (mg/l)	770.4 ± 26.96	962.99 ±33.71	1165.22 ± 40.78
TOC (mg/l)	462.4 ± 16.18	578 ± 20.23	700 ± 24.50
BOD_5 (mg/l)	251.5 ± 8.8	314.36 ± 11	380.38 ± 13.31
BOD_5/COD_{dis}	0.26 ± 0.01	0.33 ± 0.012	0.4 ± 0.014
Total N (mg/l)	24.8 ± 0.87	31 ± 1.09	37.51 ± 1.31
NH_4-N (mg/l)	1.76 ± 0.06	2.2 ± 0.08	2.66 ± 0.09
NO_3-N (mg/l)	8 ± 0.28	10 ± 0.35	12.1 ± 0.42
NO_2-N (mg/l)	0.13 ± 0.05	0.16 ± 0.06	0.19 ± 0.07
Total P (mg/l)	8.8 ± 0.31	11 ± 0.39	13.3 ± 0.47
PO_4-P (mg/l)	6.4 ± 0.22	8 ± 0.28	9.68 ± 0.34
Total phenol (mg/l)	29.6 ± 1.04	37 ± 1.3	44.8 ± 1.57
SO_4^{-2} (mg/l)	1248 ± 43.7	1560 ± 54.6	1888 ±66.1
Color (1/m)	70.9 ± 2.48	88.56 ± 3.1	107.2±3.75
TAAs (mg benzidine/l)	1296 ± 45.36	1620 ± 56.7	1960± 68.6

2.2 Configuration of Sonicator

A Bandelin Electronic RK510 H (Bandelin, Berlin, Germany) sonicator was used for sonication of the TI ww samples. The sonication frequency and sonication power were 35 kHz and 640 W, respectively. Glass serum bottles in a glass reactor were filled to 500 ml with raw ww and closed with teflon-coated stoppers for the measurement of volatile compounds (evaporation) of the raw ww. The evaporation losses of samples were estimated to be 0.01% in the reactor and, therefore, assumed to be negligible. The serum bottles were filled with 0.1 ml of methanol in order to prevent adsorption on the walls of the bottles and to minimize evaporation. Ultrasonic waves for 35 kHz sonication 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 matter; It was electronically regulated in two thermostatically heated sonicators at 30°C and 60°C temperatures. The stainless steel sonicator was equipped with a teflon holder to prevent temperature losses. In recent studies, have shown that high ultrasound frequencies of 80 kHz and 150 kHz; It has been shown that the investigated parameters and the studied parameters do not increase their efficiencies, [41]. Therefore, It was studied at a sonication frequency of 35 kHz and at a sonication power of 640 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, [41], [42].

2.3 Operational Conditions

The effects of ambient conditions (25°C), increasing sonication time (60 min, 120 min and 150 min), sonication temperature (30°C and 60°C) on the sonication of wastewater from TI ww treatment plant in Izmir, Turkey was investigated. 5 minutes before the start of the ultrasound, the TI ww was pH=5.4. Sonicated samples were taken at 60th, 120th and 150th min of sonication time and were kept in a refrigerator with a temperature of +4°C for experimental analysis. Deionized pure H_2O (R ¼ 18 MΩ/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 cm^2, 13.84 cm^2, 17.34 cm^2, 26.4 cm^2 and 40.69 cm^2, with diameters of 3.98 cm, 4.41 cm, 4.7 cm, 5.8 cm and 7.2 cm, with input ultrasound powers of 120 W, 350 W, 640 W, 3000 W and 5000 W, with ultrasound frequencies of 25 kHz, 35 kHz, 132 kHz, 170 kHz and 350 kHz, with ultrasound intensities of

15.7 W/cm^2, 24.2 W/cm^2, 36.9 W/cm^2, 46.2 W/cm^2 and 51.4 W/cm^2, with power densities of 0.1 W/ml, 0.9 W/ml, 1.65 W/ml, 1.9 W/ml, 2.14 W/ml, with specific energies of 2.4 kWh/kg.COD$_{influent}$, 3.1 kWh/kg.COD$_{influent}$, 4.1 kWh/kg.COD$_{influent}$, 5.1 kWh/kg.COD$_{influent}$ and 11.5 kWh/kg.COD$_{influent}$, respectively. It was chosen to identify for maximum removal of pollutant parameters (COD$_{dis}$, color and total aromatic amines) in the TI ww at the bottom of the reactor through a piezoelectric disc (4-cm diameter) fixed on a pyrex plate (5-cm diameter).

2.4 Analytical Methods

pH, temperature [T(°C)], oxidation reduction potential [ORP (mV)], total suspended solids (TSS), total volatile suspended solids (TVSS), dissolved oxygen (DO), biological oxygen demand 5-days (BOD$_5$), total chemical oxygen demand (COD$_{total}$), dissolved chemical oxygen demand (COD$_{dis}$), total organic carbon (TOC) were monitored according to Standard Methods 2550, 2580, 2540 C, 2540 E, 5210 B, 5220 D, 5310, 5520 B, respectively, [43]. Total nitrogen (Total-N), ammonium nitrogen (NH$_4$-N), nitrate nitrogen (NO$_3$-N), nitrite nitrogen (NO$_2$-N), total phosphorus (Total-P), phosphate phosphorus (PO$_4$-P), total phenol and sulfate ion (SO$_4^{-2}$) were measured with cell test spectroquant kits (Merck, Germany) at a spectroquant NOVA 60 (Merck, Germany) spectrophotometer (2003). The characterization of TI ww was shown in Table 1 for minimum, medium and maximum values. The measurement of color was carried out following the approaches described by Olthof and Eckenfelder, [44], and Eckenfelder, [45]. 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. In order to identify the TAAs, TI ww (25 ml) was acidified at pH=2.0 with a few drops of 6 N hydrochloric acid (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 gas chromatography-mass spectrometry-mass spectrometry (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.

2.5 Statistical Analysis

ANOVA analysis of variance between experimental data was performed to detect F and *P* values. The ANOVA test was used to test the differences between dependent and independent groups, [46]. 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, and d.f indicates the number of degrees of freedom. Regression analysis was applied to the experimental data in order to determine the regression coefficient R^2, [47]. The aforementioned test was performed using Microsoft Excel Program.

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 are given as the mean with standard deviation (SD) values.

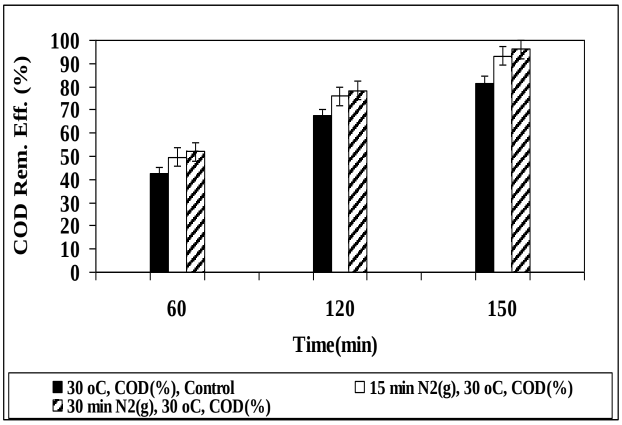
3 Results and Discussions

3.1 Effect of N$_2$(g) on the Removals of COD$_{dis}$ in TI ww

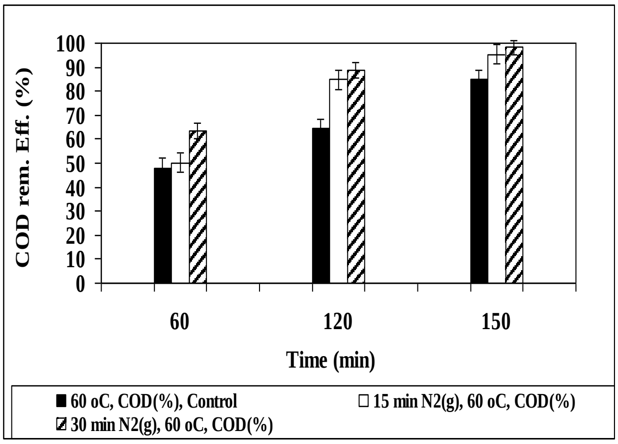
93.10% and 96.21% COD$_{dis}$ removals were observed under 15 min N$_2$(g) [3 mg/l N$_2$(g)] and 30 min N$_2$(g) [6 mg/l N$_2$(g)] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 30°C, respectively (Fig. 1a). 11.53% and 14.68% increase in COD$_{dis}$ removals were obtained under 15 min N$_2$(g) [3 mg/l N$_2$(g)] and 30 min N$_2$(g) [6 mg/l N$_2$(g)] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 30°C, respectively, and compared to the control (without N$_2$(g) sparging, E=74.27% COD$_{dis}$ at pH=7.0 and at 30°C, respectively). A significant linear correlation between COD$_{dis}$ yields and increasing N$_2$(g) sparging was observed (R^2=0.91, F=18.11, p=0.01) (Fig. 1a).

95.22% and 98.23% COD$_{dis}$ yields were found under 15 min N$_2$(g) [3 mg/l N$_2$(g)] and 30 min N$_2$(g) [6 mg/l N$_2$(g)] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 60°C, respectively (Fig. 1b). The contribution of N$_2$(g) sparging on COD$_{dis}$ removals were 10.30% and 13.31% under 15 min N$_2$(g) [3 mg/l N$_2$(g)] and 30 min N$_2$(g) [6 mg/l N$_2$(g)] sparging, respectively, after 150 min sonication time, at pH=7.0 at 60°C, respectively, and compared to the control (E=84.92% COD$_{dis}$ at pH=7.0 and at 60°C, respectively). The maximum COD$_{dis}$ removal efficiency was 98.23% at 30 min N$_2$(g) [6 mg/l N$_2$(g)] sparging after 150 min sonication time, at pH=7.0 and at 60°C, respectively.

A significant linear correlation between COD_{dis} yields and increasing $N_2(g)$ sparging was observed ($R^2=0.92$, F=18.12, p=0.01) (Fig. 1b).



(a)



(b)

Fig. 1: Effect of increasing $N_2(g)$ sparging on the COD_{dis} removal efficiencies in TI 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=962.99 mg/l, n=3, mean values).

In principle, $N_2(g)$ sparging enhances sonochemical activity as gases act as nucleation sites for cavitation. There are three properties of gases that can affect sonochemical activity, namely: (i) The polytropic ratio since the maximum temperatures and pressures achieved upon bubble collapse increase with increasing polytropic ratio, [48, 49], (ii) gas thermal conductivity. Although, bubble collapse is modeled as adiabatic, there is always a small amount of heat dissipated upon collapse; therefore, gases with low thermal conductivities should reduce heat dissipation, thus favoring increased collapse temperatures and consequently increasing sonochemical activity, (iii) gas solubility. As solubility increases, more nucleation sites become available, thus facilitating cavitation. $N_2(g)$ has a greater polytropic ratio (i.e. 1.67 against 1.4), lower thermal conductivity (17.90 against 26.30 mW/m.K at 27°C) and is slightly more soluble (5.60 against 4.90 ml/100 ml H_2O) than O_2 and all these would explain the increased reactivity observed with $N_2(g)$, [50].

In a study performed by Kritikos et al., [50], 97% COD removal was accomplished in a TI ww containing 120 mg/l Reactive Black 5, at 80 kHz, at 135 W, under N_2=4.20 mg/l.min, after 90 min sonication time, at 30°C and at pH=5.8, respectively. In this study, 96.21% COD_{dis} removal was found under 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging after 150 min sonication time, at 30°C, respectively. In this study, similar results were found to the COD_{dis} yield obtained by Kritikos et al., [50], at 30°C as mentioned above.

3.2 Effect of $N_2(g)$ on the Color Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

86.02% and 90.48% color removals were observed under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 30°C, respectively (Table 2). 7.76% and 12.22% increase in the color removals were obtained under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 30°C, respectively, and compared to the control (E=78.26% color at pH=7.0 and at 30°C). A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.79$, F=14.28, p=0.01) (Table 2).

92.24% and 95.30% color removal yields were found under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 60°C, respectively (Table 2). The contribution of $N_2(g)$ sparging on color removals were 4.58% and 7.64% for 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 60°C, respectively, and compared to the control (E=87.66% color at pH=7.0 and at 60°C). The maximum color removal efficiency was 95.30% at 30 min $N_2(g)$ [6 mg/l $N_2)(g)$] sparging after 150 min sonication time, at pH=7.0 and at 60°C, respectively. A significant linear correlation between color yields and increasing $N_2(g)$ sparging was observed ($R^2=0.82$, F=17.06, p=0.01) (Table 2).

Table 2. Effect of increasing $N_2(g)$ sparging on the color removal efficiencies in TI ww at 30°C and at 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial color concentration=88.56 1/m, n=3, mean values).

Parameters	**Color Removal Efficiencies (%)**					
	30°C			**60°C**		
	60. min	**120. min**	**150. min**	**60. min**	**120. min**	**150. min**
Raw ww, control	52.29	76.38	78.26	79.32	83.20	87.66
15 min $N_2(g)$ [3 mg/l $N_2(g)$]	54.76	77.20	86.02	80.96	85.08	92.24
30 min $N_2(g)$ [6 mg/l $N_2(g)$]	56.40	83.67	90.48	83.90	88.37	95.30

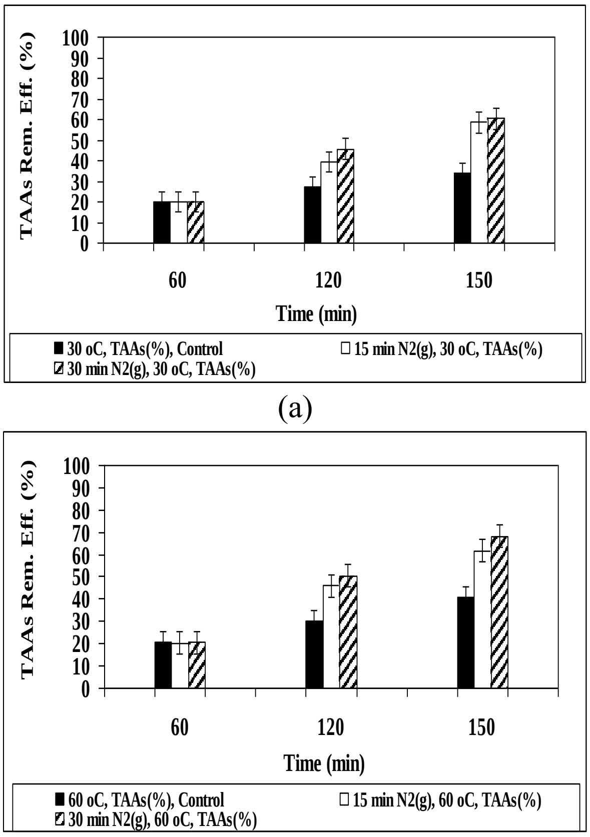
For decolorization under $N_2(g)$ sparging, reactions inside or in the vicinity of the bubble (where fast thermal decomposition and increased concentrations of radicals exist) are unlikely to occur to an appreciable extent. Therefore, its degradation will be driven by $OH^{\bullet}$-mediated secondary activity in the liquid bulk. This may explain the discrepancies in the reactivity of dyestuff between sonochemical. Because the latter involves the participation of a more diverse range of reactive species (i.e. radicals, holes and electrons) than the former. In addition to, the physicochemical properties of the substrate in question that are likely to dictate the dominant reaction site(s) for sonochemical activity and, consequently, degradation efficiency, sonochemical reactions are also sensitive to several other operating parameters such as ultrasound frequency and intensity, reactor geometry, mode of ultrasound irradiation (i.e. continuous or pulsed), solution temperature and the water matrix, [48]. For instance, different ranges of ultrasound frequency are suitable for hydrophilic and hydrophobic organics, while increased reaction temperatures may cause a decrease in degradation, [48]. In some cases, ultrasound irradiation in an ‘‘on-off’’ mode may be more beneficial than the ultrasound irradiation in continuous mode, which results in more effective use of $OH^{\bullet}$ and a better temperature control, [51].

Kritikos et al., [50], found 80% decolorization in a TI ww containing 120 mg/l Reactive Black 5, at 80 kHz, at 135 W, N_2=4.20 mg/l.min, after 90 min sonication time, at 30°C and at pH=5.8, respectively. In this study, 90.48% color removal was measured under 30 min N_2 (g) [6 mg/l $N_2(g)$] sparging after 150 min sonication time, at 30°C, respectively. The color yield in the present study is higher than the yield obtained by Kritikos et al., [50], at 30°C as mentioned above.

3.3 Effect of $N_2(g)$ on the TAAs Removal Efficiencies in TI ww at Increasing Sonication Times and Temperatures

58.56% and 60.41% TAAs removals were observed under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 30°C, respectively (Fig. 2a). 24.67% and 26.52% increase in TAAs removals were obtained under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 30°C, respectively, and compared to the control (E=33.89% TAAs at pH=7.0 and at 30°C). A significant linear correlation between TAAs yields and increasing $N_2(g)$ sparging was not observed (R^2=0.62, F=3.21, p=0.01) (Fig. 2a).

61.79% and 68.08% TAAs yields were found under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 60°C, respectively (Fig. 2b). The contribution of $N_2(g)$ sparging on TAAs removals were 21.17% and 27.46% under 15 min $N_2(g)$ [3 mg/l $N_2(g)$] and 30 min $N_2(g)$ [6 mg/l $N_2(g)$] sparging, respectively, after 150 min sonication time, at pH=7.0 and at 60°C, respectively, and compared to the control (E=40.62% TAAs at pH=7.0 and at 60°C). The maximum TAAs removal efficiency was 68.08% at 30 min $N_2(g)$ [6 mg/l $N_2)(g)$] sparging after 150 min sonication time, at pH=7.0 and at 60°C, respectively. A significant linear correlation between TAAs yields and increasing $N_2(g)$ sparging was not observed (R^2=0.31, F=3.90, p=0.01) (Fig. 2b).



(a)

(b)

Fig. 2: Effect of increasing $N_2(g)$ sparging on the TAAs removal efficiencies in TI ww at (a) 30°C and (b) 60°C versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial TAAs concentration=1620 mg benzidine/l, n=3, mean values).

3.4 Cost and Specific Energy Estimation

3.4.1 Cost Estimation Methodology

A very simple methodology was developed to arrive at the treatment costs of the various AOPs processes studied. First of all, data were collected from the published literature for all the AOPs involving the use of ultrasound and some standard commercial AOPs. Table 3 shows the various studies considered for this investigation along with their operating conditions. From this data, the kinetics of pollutant removal was found. If the kinetics is reported then it was taken from the literature as such; otherwise it was calculated from the data given in the literature using standard methods of finding kinetics, [52, 53].

*Table 3 can be found in Appendix section

By kinetics, we mean the order of degradation and the rate constant. Table 4 depicts the kinetic data collected from these studies. These rate constants were then used to calculate the time required for 90% degradation of the pollutant from its initial concentration. This time was assumed as the residence time for the reactor for wastewater treatment using the given AOP. The cost estimation was done for the assumed flow rate of 1000 l/min. The reactor capacity was calculated by multiplying the residence time with the design flow rate (1000 l/min). From the treatability study in the literature, the energy consumption data was then collected as energy dissipated per unit volume (W/ml). The total amount of energy required to treat the wastewater at the designed flow rate for a given residence time was then calculated. From the quotations, which we had invited from manufacturers, we knew the amount of energy supplied by one commercial unit. Hence, the number of such commercial units required for dissipating the required energy was calculated. From the number of commercial units required, the capital cost of the wastewater treatment unit was calculated (AOP unit cost). This AOP unit cost was used to calculate the total capital cost using certain standard assumptions. These assumptions are described in the next section. Similarly, total annual operating and maintenance cost was also calculated. The total capital cost was amortized at a rate of 7% over a period of 30 years to arrive at total amortized annual capital cost. Sum of the annual operating and maintenance cost and annual capital cost gave the total annual operating cost. Dividing this cost with the amount of liters of wastewater treated in a year gave us the cost of wastewater treatment per 3.79 l of water treated. It was assumed that the plant is running throughout the year continuously.

For the elimination of phenol and reactive dyes; Cost estimation of various ultrasonic AOPs was done on the basis of rate constants. Since the rate of degradation changes significantly with the experimental system, the reactor configuration and the operating conditions such as pH, UV intensity or US intensity etc., a limited number of sources having similar operating conditions were considered. Kinetic data was collected from a limited number of sources in the literature (Table 4). Five sources were considered for phenol and three sources were considered for reactive dyes. The collected data was then compared with the kinetic data available for a number of other similar treatability studies in the literature to make sure that it is comparable with the reported values.

Table 4. Rate constants of various AOPs throughout sonodegradation.

Wastewater	Item	Removed Parameter	k (1/min)	References
TI ww	UV (254 nm)	color	No degradation observed	Tezcanli-Güyer and Ince (2004)
TI ww	O_3 (12.40 mg/l)	color	$11.08x10^{-3}$	Tezcanli-Güyer and Ince (2004)
TI ww	US	COD_{dis}	$1.50x10^{-4}$	In this study
TI ww	US	TOC	$1.33x10^{-4}$	In this study
TI ww	US	color	$1.00x10^{-4}$	In this study
TI ww	US	TAAs	$3.33x10^{-5}$	In this study

Adewuyi, [48], has summarized results of a number of studies of wastewater treatment using ultrasonic processes. They have reported the rates of degradation for phenol, reactive dyes and a number of other hazardous compounds, [48]. Kidak and Ince, [54], have recently reviewed the subject of phenol degradation using ultrasonic processes. Beckett et al., [55], have described the degradation of phenols and chlorinated compounds and their mixtures using ultrasonic cavitation. Destaillats et al., [56], and Destaillats et al., [57], have reported the scale up of sonochemical reactors for TI ww treatment. They have also reported the rates of degradation for reactive dyes; it lies in the range of 0.002–0.045 1/min, [56, 57]. Lesko et al., [58], have reported the rates of degradation of phenol using a pilot station sonochemical reactor. The authors found that the rate of phenol degradation was in the range of 0.0011–0.063 1/min, [58]. Zheng et al., [59], have reported the rates of sonochemical degradation of phenol in the range of 0.014–0.061 1/min. Lesko et al., [58], have reported the rate of phenol degradation in the presence of ozone (O_3) and ultrasound to be in the range of 0.137 1/min. One can observe from Table 4 that the reported rates of degradation of phenol and reactive dyes are in the same range as are considered in this study. Hence, it can safely be said that the results of cost estimation of this study can at least provide an order of magnitude glimpse of the economics involved in the wastewater treatment using ultrasonic processes.

3.4.2 The Calculation of Energy Requirement in Sonication Reactor

From the referred publications or calculations from the data in the publications (energy density, ε), the total energy requirement in the AOP reactor is given by X ε watt, [53]. From the manufacturer quotations, the energy supplied by a single unit of AOP = E watt was defined, [53]. The number of such standard commercial units required is given in Equation (1), [53];

$$N = X(W) / E(W) \tag{1}$$

where;
N: The number of such standard commercial units
X: The total energy requirement in the AOP reactor (W),
E: The energy supplied by single unit of AOP

Total cost of N units was given in Equation (2):

Total cost of N units = Cost of AOP reactor =

$$P = N / C(\$) \tag{2}$$

where;
C: Cost of each unit from the manufacturer=1000 $
P: Cost of AOP reactor ($)=1000 $

3.4.2.1. The Calculation of Energy Requirement in Sonication Reactor Capacity for TI ww

X=640 W=0.64 kW
E=640 W=0.64 kW
N=(640 W) / (640 W)=1 units
P=Total cost of 1 units=Cost of AOP reactor=1000 $

The total hourly electrical cost=0.165454 TL/kWh * 0.64 kWh=0.07 $/h.

3.4.3 General Calculation of Capital Cost in Sonication Reactor

The general calculation of capital cost for TI ww during sonication process are presented in Table 5. The capital cost is amortized over a span of years at given amortization rate. Amortized capital cost (A) is given by following formula, [60], in Equation (3):

$$A = \frac{1.2S*r}{1-\left(\frac{1}{1+r}\right)^{n}} \tag{3}$$

where;
A: Amortized annual capital cost
r: Annual discount rate (assumption = 7%)
1.2S: Total capital cost
n: Life of project (assumption = 30 years) EE/O is kWh/m^3/order

The total capital cost of ultrasound system=Cost of ultrasound System=1000 \$/year

Using Equation (3);
Amortized capital cost (A)=[(1500 Tl * 0.07) / {1-$(1/(1+0.07))^{30}$}]=80 \$/year

Total amortized capital cost=A + Cost of ultrasound system=120 TL + 1500 TL=1080 \$/year

r=7%=0.07
1.2S=5 N/ C=2.2 P
n=30 year
A=[(2.2 P * 0.07) / {1-$(1/(1+0.07))^{30}$}]=0.18 P=180 \$

Table 5. General calculation of capital cost in this study.

Item	TI ww Capital Cost			
	TI ww	Cost (TL)	Cost (\$)	Cost (€)
AOP reactor	P	1500	1000	789.47
Piping, valves, electrical (30%)	0.30 P	450	300	236.84
Site work (10%)	0.10 P	150	100	78.95
Subtotal	1.40 P = Q	2100	1400	1105.26
Contractor O&P (15%)	0.15 Q	315	210	165.79
Subtotal	1.15 Q = R	2415	1610	1271.05
Engineering (15%)	0.15 R	362.25	241.50	190.66
Subtotal	1.15 R = S	2777.25	1851.50	1461.71
Contingency (20%)	0.20 S	555.45	370.30	292.34
Total capital	1.20 S=2.2P	3332.70	2221.80	1754.05

P: Total cost of one unit or cost of AOP reactor; Q: Subtotal of labor cost; R: Subtotal of contractor cost; S: Subtotal of part replacement cost.

3.4.4 The Comparison of Cost for AOPs in Different Literatures Studies

Table 6 summarizes the cost estimation of some literature data performed with AOPs and sonication including the cost results for TI ww.

*Table 6 can be found in Appendix section

3.4.5 Capital Cost Calculations for Ultrasound System

Capital cost estimation (\$) of various AOPs for degradation given in Table 7.

1.5 TL=1 \$ (was assumed).

The total capital cost of ultrasound system=Cost of ultrasound system=1000 \$/year

Using Equation (3); Amortized capital cost (A)=80 \$/year

Total amortized capital cost=A + Cost of ultrasound system=120 TL + 1500 TL=1620 TL/year=1080 \$/year

Table 7 summarizes the capital cost estimation in different AOPs and in TI ww throughout sonication process.

*Table 7 can be found in Appendix section

3.4.6 Operating and Maintenance (O & M) Cost Calculations for Sonication Process

The O&M (operating and maintenance cost) consists of labor costs, analytical costs, chemical costs, energy (electrical) costs and part replacement costs.

Total O&M cost=labor cost + analytical cost + chemical cost + energy (electrical) cost + part replacement cost

3.4.6.1 Labor Cost for Sonication Process

The labor costs consisted of water sampling cost, general and specific system O&M costs. System specific operation and maintenance consisted of inspection, replacement and repair based on hours of service life. General O&M annual labor consists of general system oversight and maintenance such as pressure gauges, control panels, leakages etc.

For ultrasonic systems, it was assumed that sampling frequency (Sf)=2 samples/week; sampling time (St)=2 min/sample=0.033 h/sample or 1 h/week and time required for O&M=17.16 h/year. Breakdown of labor costs (\$) of various AOPs for degradation determined in Table 8.

Ultrasound systems, the sampling frequency was taking 2 samples/day. It was assumed to be 52 weeks in a year. The sampling period was 2 min/sample=(2 min/sample) * (2 samples/day)=4 min/day=(4 min/day) * (1 h/60 min)=0.067 h/day=(0.067 h/day) * (5 days/week) =0.335 h/week

Annual sampling labor=1 h/week * 52 weeks/year=52 h/year

Sampling labor hours=1 h/week
Ultrasound system O & M=1 h/week * 52 weeks/year=52 h/year.
Total annual labor hours=52 h/year + 52 h/year=104 h/year

The sample analysis labor cost is 30 TL/h.
Total annual labor cost=104 h/year * 30 TL/h=3120 TL/year=2080 $/year

Table 8 summarizes the labor cost estimation in different AOPs and in TI ww throughout sonication process.

*Table 8 can be found in Appendix section

3.4.6.2 Analytical Costs for Sonication Process

Analytical costs were based upon sampling frequency, the labor required to do the analysis of the samples and the cost of chemicals required for analysis. These costs were considered at a rate of 200 $/h, [61]. Analytical costs ($) of various AOPs for degradation shown in Table 9.

The sample analysis labor cost is 30 TL/h.
Annual analysis labor=1 h/week * 52 week/year=52 h/year
Total annual labor hours=52 h/year.

Total annual analysis labor hours=Annual analysis labor + Total annual labor hours=52 h/year + 52 h/year=104 h/year

Total annual analysis labor cost=104 h/year * 30 TL/h=3120 TL/year=2080 $/year

Table 9 summarizes the analytical cost estimation in different AOPs and in TI ww throughout sonication process.

*Table 9 can be found in Appendix section

3.4.6.3 Chemical Costs for Sonication Process

The chemical costs include the costs of consumables such as N_2(g). These prices were obtained from standard industrial suppliers such as International Construction Information Society (ICIS) Pricing and Inframat Advanced Materials, [62]. Chemical costs ($) of various AOPs for degradation indicated in Table 10.

500 ml reactor volume was used during sonication process.
For 500 ml sonication reactor=(1.00 TL/100 ml at 1 h) * 5=5 TL/500 ml at 1 h
For annual labor cost =52 h/year

The annual chemical cost for N_2(g) during ultrasound system=5 TL/h * 52 h/year=260 TL/500 ml bottle for 1 year=173.33 $/500 ml wastewater in bottle for 1 year

Table 10 summarizes the chemical cost estimation in different AOPs and in TI ww throughout sonication.

*Table 10 can be found in Appendix section

3.4.6.4. Electrical Cost for Ultrasound System

Electrical costs were based on the power consumption by a given AOP. The electricity cost was calculated at a rate of 0.11 $/kWh. Power consumption was calculated for each AOP based upon the power consumed in a year multiplied by the electricity rate. Electrical costs ($) of various AOPs is demonstrated in Table 11.

Power consumption in the ultrasound system=The sum of power consumed by ultrasound system in an hour=640 W/h=0.64 kW/h

Power consumption in the ultrasound system=The sum of power consumed by ultrasound system in a day=640 W/h * 5 h/day=3200 W/day= 3.20 kW/day

Power consumption in the ultrasound system=The sum of power consumed by ultrasound system in a week=640 W/h * 5 h/day * 5 days/week=16000 W/week=16 kW/week

Power consumption in the ultrasound system=The sum of power consumed by ultrasound system in a month=640 W/h * 5 h/day * 5 days/week * 4 weeks/month=64000 W/month=64 kW/month

Power consumption in the ultrasound system=The sum of power consumed by ultrasound system in a year=640 W/h * 5 h/day * 5 days/week * 52 weeks/year=832000 W/year =832 kW/year.

1 kWh=3.60x10^6 j=3.60x10^3 kj and electrical energy consumed index constant per hour is 1.083 kW/h.

Total energy consumed in an hour=(1.083 kW/h) * 0.64 kW/h=0.69 kW/h

Total energy consumed in a day=(1.083 kWh) * 3.20 kW/day * (24 h/day)=83.17 kWh/day

Total energy consumed in a week=(1.083 kWh) * 16 kW/week * (5 days/week) * 5 h/day=433.20 kWh/week

Total energy consumed in a month=(1.083 kWh) * 64.00 kW/month * (4 weeks/month) * (5 days/week) * (5 h/day)=6931.20 kWh/month

Total energy consumed in a year=(1.083 kWh) * (832 kW/year) * (52 weeks/year) * (5 day/week) * (5 h/day)=1171372.80 kWh/year

Rate of electricity=0.11 $/kWh

The total hourly electrical cost=0.165454 TL/kWh * 0.69 kWh=0.114 TL/h=0.076 $/h.

The total daily electrical cost=0.165454 TL/kWh * 83.17 kWh=13.761 TL/day=9.174 $/day

The total weekly electrical cost=0.165454 TL/kWh * 433.20 kWh=71.675 TL/week=47.78 $/week

The total monthly electrical cost=0.165454 TL/kWh * 6931.20 kWh=1146.80 TL/month
=764.53 $/month

The total annual electrical cost=0.165454 TL/kWh * 1171372.80 kWh
=193808.32 TL/year
=129205.55 $/year

Table 11 summarizes the electrical cost estimation in different AOPs and in TI ww throughout sonication process.

*Table 11 can be found in Appendix section

3.4.6.5 Part Replacement Cost for Sonication Process

Part replacement cost may include bulb replacements for UV systems, O_3 generator parts for O_3 system, catalyst holder replacements for catalytic systems, tip replacements or electronic circuit replacements or transducer element replacements for ultrasound systems. The part replacement costs were assumed to be 0.5% of the capital cost, [61, 63]. For UV systems, the part replacement costs were assumed to be 45% of the annual electrical power consumption costs, [64, 65]. For O_3 systems, the annual part replacement cost was assumed to be 1.5% of the capital cost, [61]. Part replacement cost ($) of various AOPs is shown in Table 12.

Part replacement cost=0.5% of capital cost of ultrasound system
=0.005 * 1500 TL/year=7.5 TL/year=5 $/year

Table 12 summarizes the part replacement cost estimation in different AOPs and in TI ww throughout sonication process.

*Table 12 can be found in Appendix section

Total O&M cost= total annual labor cost + total annual analytical cost + total annual chemical cost + total annual electrical cost + total annual part replacement cost

Total O&M cost=3120 TL + 3120 TL + 3380 TL + 193808.32 TL + 7.50 TL
=203435.82 TL/year=135623.88 $/year

Total annual operating cost for ultrasound system=Total amortized annual capital cost + annual O&M cost=1620 TL + 203435.82 TL/year=205055.82 TL/year=136703.88 $/year

Annual operating and maintenance (O&M) cost estimation ($) of various AOPs for degradation of some parameters are shown in Table 13.

The total annual cost = total annual labor cost + total annual analytical cost + total annual chemical cost + total annual electrical cost + total annual capital cost + total annual part replacement cost

Total annual cost=3120 TL + 3120 TL + 3380 TL + 193808.32 TL + 1500 TL + 7.50 TL=204935.82 TL/year=136623.88 $/year

*Table 13 can be found in Appendix section

3.4.7 General Procedure for Calculation of Electric Energy per Order (EE/O) or Electrical Energy per Unit Mass (EE/M)

3.4.7.1. EE/O Calculation for US System

Electric energy per order (EE/O) is the electric energy in kilowatt hours [kWh] required to degrade a contaminant by one order of magnitude in a unit volume (e.g., 1 m^3 = 1000 l) of contaminated water or air, [66]. This figure-of-merit is best used for situations where final concentration, (C_A, mg/l) is low (i.e., cases that are overall first-order in concentration of pollutant) because the amount of electric energy required to bring about a reduction by one order of magnitude in concentration is independent of (C_A). Thus, it would take the same amount of electric energy to reduce the contaminant concentration from 10 mg/l to 1 mg/l in a given volume as it would to reduce it from 10 µg/l to 1 µg/l. EE/O is, in general, a measure of operating cost. It allows for easy and accurate scale up to a full-scale design and costs. EE/O is defined by Bolton et al., [66], as Equation (4).

$$EE/O = \frac{P_{elec} * t * 1000}{V * 60 * \log\left(\frac{C_{AO}}{C_A}\right)} \quad (4)$$

where;

EE/O: Electric energy per order (kWh/m^3/order)
P_{elec}: The input power (kW) to the AOP system
t: The irradiation time (min)
V: The volume in liter of water in the reactor (l)
C_{AO}: Initial concentration in ppm (mg/l)
C_A: Final concentration in ppm (mg/l)

for TI ww at 25°C;
Sonication power=640 W
Sonication time=150 min
Sonication volume=V=500 ml=0.50 l
COD_0=$COD_{influent}$=962.99 mg/l
$COD_{effluent}$=247.75 mg/l

EE/O=[0.64 kW * 150 min * 1000] / [0.50 l * 60 * log (962.99/247.75)]
=5427.33 kWh/m^3/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 5427.33 kWh/m^3/order COD_{dis}
=897.97 TL/m^3/order COD_{dis}=598.65 $/ m^3/order COD_{dis}

3.4.7.2 EE/M Calculation for US System

For zero order degradations, EE/M (electrical energy per unit mass) is used instead of EE/O. EE/M is defined as Equation (5):

$$EE/M = \frac{P_{elec} * t * 1000}{V * M * 60 * (C_{AO} - C_A)} \quad (5)$$

where;

EE/M: Electrical energy per unit mass (kWh/kg/order)
M: Mass (kg)
P_{elec}: The input power (kW) to the AOP system
t: The irradiation time (min)
V: The volume in liter of water in the reactor
C_{AO}: Initial concentration in ppm (mg/l)
C_A: Final concentration in ppm (mg/l)

For TI ww at 25°C;
Sonication power=640 W
Sonication time=150 min
Sonication volume=V=500 ml=0.50 l
COD_0=$COD_{influent}$=962.99 mg/l
$COD_{effluent}$=247.75 mg/l

EE/M=[0.64 kW * 150 min * 1000] / [0.50 l * 0.001 kg/g * 60 * (962.99-247.75)]
=4474.02 kWh/kg/order COD_{dis}

The electrical cost=0.165454 TL/kWh * 4474.02 kWh/kg/order COD_{dis}
=740.25 TL/kg/order COD_{dis}=493.50 $/ kg/order COD_{dis}

3.4.8 Specific Energy Calculations for Ultrasound System

The specific energy was calculated according to Equation (6):

$$E_s\ (kWh/kg\ COD_0) = \frac{Sonicator\ \ power(W) * Time(h) * (1\ kj/1000\ j)}{V(l) * COD_0\,(g/l) * (1\ kg/1000g)} \quad (6)$$

where;

E_s: The specific energy for the maximum COD_{dis} removal after sonication process (kWh/kg COD_0),
Sonicator power: The input power of sonicator during sonication experiments (W),
Time: The sonication time during sonication process (h),
(1 kj/1000 j): The equation of transformation from 1 kilojoule to 1 joule,
V: The sample volume during sonication process (l),

COD_0: Initial COD_{dis} concentration before sonication process (g/l),
(1 kg/1000 g): the equation of transformation from 1 kilogram to 1 gram.

For TI ww at 25°C;
Sonication power=640 W
Sonication time=150 min=2.50 h
Sonication volume=V=500 ml=0.50 l
COD_0=962.99 mg/l=0.96299 g/l

$$E_s = \{[(640\ W * 2.50\ h * 1\ kj/1000\ j)] / [(0.50\ l * 0.96299\ g/l * 1\ kg/1000g)]\}$$
$$=3322.98\ Wh / kg\ COD_0=3.32\ kWh / kg\ COD_0$$

$$\text{The electrical cost}=0.165454\ TL/kWh * 3.32\ kWh/ kg\ COD_0$$
$$=0.55\ TL/kg\ COD_0=0.37\ \$/ kg\ COD_0$$

3.4.9 The Cost Comparison of Anaerobic, Aerobic, UV, O_3 and Sonication Treatment

In this study, the annual chemical cost of N_2(g) sparged were calculated as 260 TL/year (136.84 €/year), respectively. For N_2(g) sparged systems the annual chemical cost was calculated as 40 Euro/year (76 TL/year), respectively, [61, 63]. In this study, the total annual chemical cost of N_2(g) sparged is higher than the total annual chemical cost obtained by Melin, [61], and Mahamuni and Adewuyi, [63], as mentioned above.

Table 14 summarizes the cost comparison of anaerobic, aerobic, UV, O_3 and sonication treatment, respectively. The electrical energy requirements of conventional activated sludge process reported by Eckenfelder et al., [67], between 250 and 1000 kWh/m^3 water (75–300 TL m^3/h=655200–2620800 TL m^3/year=436800–1747200 \$/year) with mechanic mixing and recycle pump equipment (1 kWh/m^3 electric energy=0.3 TL m^3/h) was assumed. In this study, 193808.32 TL/year (=129205.55 \$/year) total annual electrical cost was observed for sonication process in TI ww. In this study, the total annual electrical cost is lower than the total annual electrical cost obtained by Eckenfelder et al., [67], as mentioned above.

Table 14. The cost comparison of Anaerobic, Aerobic, UV, O_3 and Sonication treatment processes, [67].

Parameters	**Anaerobic Treatment**	**Aerobic Treatment**	**UV Treatment**	**O_3 Treatment**	**Sonication Treatment**
Energy requirements	Low	High	High	Medium	Low
Nutrient requirements	Low	High (for certain industrial wastes)	No	No	No
Alkalinity requirements	High (for certain industrial wastes)	Low	No	No	Low
Chemicals costs	High	Medium	No	No	Low
Reactor requirement	High	Medium	High	High	Low
Part replacement cost (generator, piping, pumps, valves, etc).	High	High	High	High	Low
Analytical cost	High	Medium	Medium	High	Low
CH_4 production cost	High	No	No	No	No
Natural gas (biogas) production cost (electric energy requirement in anaerobic digester)	Yes (net benefit is contingent on the need for reactor heating)	No	No	No	No
Sludge production (mechanic mixing, recycle pump, etc.)	Low	High	No	No	No
Site work	Low	High	Medium	Medium	Very low

Site / area requirement	Low	High	Medium	Medium	Very low
Labor costs	High	High	High	High	Very low
Engineering costs	High	High	High	High	Very low
Contractor costs	High	High	High	High	Very low
Contingency costs	High	High	High	High	Low
Cleaning costs	High	High	Low	Low	Very low
Capital cost	High	High	High	Medium	Low

UV: ultrasound

Tchobanoglous and Burton, [68], the electrical energy requirements of CH_4(g) gas production in an anaerobic digester; 60 to 100 kWh/m^3 water (18–30 TL m^3/h=157248–262080 TL m^3/year=104832–174720 \$/year). In the present study, 193808.32 TL/year (=129205.55 \$/year) total annual electrical cost was measured for sonication process in TI ww. In this study, the total annual electrical cost is lower than the total annual electrical cost found by Tchobanoglous and Burton, [68], as mentioned above.

The electrical energy requirement of sonication process in a sonicator; only 1–10 kWh/m^3 water (0.3–3 TL m^3/h=2620.80-26208 TL m^3/year=1747.20–17472 \$/year) was found by Zhang et al., [69]. In this study, 193808.32 TL/year (=129205.55 \$/year) total annual electrical cost was measured for sonication process in TI ww. In this study, the total annual electrical cost is higher than the total annual electrical cost obtained by Zhang et al., [69], as mentioned above.

The electrical energy consumption of natural gas (biogas, etc) production in an anaerobic digester was higher than 110 kWh/m^3 water (33 TL m^3/h=288288 TL m^3/year=192192 \$/year) was reported by Tchobanoglous and Burton, [68]. In this study, 193808.32 TL/year (=129205.55 \$/year) total annual electrical cost was calculated for sonication process in TI ww. In this study, the total annual electrical cost is lower than the total annual electrical cost observed by Tchobanoglous and Burton, [68], as mentioned above.

The sonication process does not require the use of extra chemicals (e.g. oxidants and catalysts) commonly used in several AOPs (e.g. ozonation, Fenton reagent), thus eliminating the need to pre-discharge excess toxic compounds as well as the associated costs, [40]. The operating and maintenance (O&M) cost in sonication systems consists of labor costs, analytical costs, chemical costs, electrical costs and part replacement costs.

For ultrasonic systems, the annual analysis labor time is 52 h/year (sampling frequency is 2 samples/week), sampling time (1 h/week) while the total annual labor cost is 3120 TL/year (=2080 \$/year).

The total annual analytical cost was calculated as 3120 TL/year (=2080 \$/year) with sonication process in TI ww at 35 kHz, at 640 W, at 500 ml after 150 min sonication time, respectively.

The capital cost and the part replacement costs were 1500 TL/year (=1000 \$/year) and 7.5 TL/year (=5 \$/year), respectively.

The total energy consumed was measured as 3.2 kW/day to obtain 71% COD_{dis} removal without additives at 35 kHz, at 640 W, at 500 ml, after 150 min sonication time, at 25°C, respectively. The annual total energy utilization was 832 kWh/year while the annual total energy cost was 193808.32 TL/year =129205.55 \$/year. The electricity cost was calculated at a rate of electricity of 0.17 TL/kWh (=0.11 \$/kWh).

5427.33 kW/m^3/order COD electric energy per order (EE/O) values calculated in TI ww, at 35 kHz, at 640 W, at 500 ml, without additives, after 150 min sonication time, at 25°C, respectively. 897.97 TL/m^3/order COD electrical costs were obtained in TI ww for EE/O values during sonication process.

4474.02 kWh/kg/order COD electrical energy per unit mass (EE/M) values were measured in TI ww, respectively, at 35 kHz, at 640 W, at 500 ml, without additives, after 150 min sonication time, at 25°C, respectively. 740.25 TL/kg/order COD electrical costs were calculated in TI ww for EE/M values during sonication process.

3.32 kWh / kg COD_0 specific energy (E_S) values were calculated in TI ww, at 35 kHz, at 640 W, at 500 ml, without additives, after 150 min sonication time, at 25°C, respectively. 0.55 TL/kg COD_0 electrical costs were observed in TI ww for E_s values during sonication process.

Finally, sonication process is cheaper than that the anaerobic, aerobic treatment processes and the other AOPs processes. Sonication process is a cost-effective AOP for the treatment of toxic and recalcitrant compounds in TI ww, compared to the anaerobic, aerobic, UV and O_3 treatment processes (Table 14).

4 Conclusion

The results of this study showed that sonodegradation is a very useful process in the removal of toxic and refractory compounds in TI ww. Low frequency (35 kHz) sonication proved to be a viable tool for the effective degradation of refractory compounds in TI ww. The removals increased after 60 min, 120 min and 150 min sonication time, at 30°C and at 60°C. The sonication process could prove to be less land-intensive, less expensive and require less maintenance than traditional biological treatment processes and other AOPs processes. Sonication technology can provide a cost-effective alternative for destroying and detoxifying refractory compounds in TI ww.

4.1 The Removal of Toxic and Refractory Compounds in TI ww during Sonication with only Sonication

COD_{dis}, color and TAAs yields in TI ww were measured during sonication process with only sonication. The effects of only sonication to the yields of the parameters given above were investigated. Toxic and refractory compounds removal efficiencies were determined in TI ww after 60 min, 120 min and 150 min sonication time, at 30°C and at 60°C with only sonication process. The maximum COD_{dis} (E=84.92%), color (E=87.66%), TAAs (E=34.12%) yields in TI ww were measured at 60°C after 150 min sonication time only with sonication process.

4.2 The Removal of Toxic and Refractory Compounds in TI ww during Sonication with the Addition of N_2(g) sparging

COD_{dis}, Color and TAAs yields in TI ww were measured during sonication process with the addition of N_2(g) sparging. The removal yields in the parameters given above were investigated in TI ww after 60 min, 120 min and 150 min sonication time, at 30°C and at 60°C with the addition of N_2(g) sparging. The maximum COD_{dis} (E=98.23%), color (E=95.30%), TAAs (E=68.08%) removals in TI ww were observed with 30 min N_2(g) [6 mg/l N_2(g)] sparging at 60°C after 150 min sonication time.

The initial rate of H_2O_2 formation associated to the toxic and refractory pollutants (COD_{dis}, color and TAAs) treatments by sonication process in TI ww decreases with increasing sonication time (60 min, 120 min and 150 min) at 60°C. The high H_2O_2 production through sonication of TI ww verified the presence of high $OH^\bullet$ ion concentrations. The high $OH^\bullet$ ion concentration is the major process for complete degradation of toxic and refractory pollutants (COD_{dis}, color and TAAs) in TI ww. This showed that hydroxylation is the main mechanism for the removal of the toxic and refractory pollutants (COD_{dis}, color and TAAs) in TI ww by sonication process.

4.3 The Evaluation of Specific Energies in COD_{dis} (E_s), Electric Energy per Unit Volume in COD_{dis} (EE/O) and Electrical Energy per Unit Mass in COD_{dis} (EE/M) Values in TI ww during only Sonication

The specific energy in COD_{dis} (E_s) parameter was calculated 3.32 kWh / kg COD_{dis} in TI ww at 35 kHz, at 640 W, at 500 ml after 150 min sonication time, at 25°C with only sonication process. The cost of this specific energy for COD_{dis} (E_s) parameter was found 0.55 TL/kg COD_{dis} in TI ww at 35 kHz, at 640 W, at 500 ml, after 150 min sonication time, at 25°C, with only sonication process.

The electric energy per unit volume in COD_{dis} (EE/O) parameter was calculated as 5427.33 $kW/m^3/COD_{dis}$ in TI ww at 35 kHz, at 640 W, at 500 ml after 150 min sonication time, at 25°C with only sonication process. The cost of this electric energy per unit volume for COD_{dis} (EE/O) parameter was measured 897.97 $TL/m^3/COD_{dis}$ in TI ww at 35 kHz, at 640 W, at 500 ml after 150 min sonication time, at 25°C, with only sonication process.

The electric energy per unit mass in COD_{dis} (EE/M) parameter was calculated 4474.02 $kWh/kg/COD_{dis}$ in TI ww at 35 kHz, at 640 W, at 500 ml, after 150 min sonication time, at 25°C with only sonication process. The cost of this electric energy per unit mass for COD_{dis} (EE/M) parameter was measured 740.25 $TL/kg/COD_{dis}$ in TI ww at 35 kHz, at 640 W, at 500 ml after 150 min sonication time, at 25°C, with only sonication process.

4.4 The Evaluation of Costs in TI ww during Sonication Process with only Sonication and with the Addition of N_2(g) sparging

The evaluation of costs in TI ww during sonication process with only sonication and with the addition of some chemicals were calculated for annual, monthly, weekly, daily and hourly time periods. 3120, 3120, 193808.32, 7.50, 200055.82, 120, 1500, 1620, 201675.82 and 201555.82 TL/year was calculated for total annual labor cost, total annual analysis cost, total annual electrical cost, total annual part replacement cost, total annual O&M cost, amortized capital cost, total annual capital cost, total annual amortized capital cost, total annual operating cost and total annual cost, respectively, for TI ww with only sonication process. The total annual cost with only sonication was calculated as 201555.82 TL/year (=134370.55 \$/year) including the annual labor costs, the annual analytical costs, the annual chemical costs, the annual energy (electrical) costs, the annual capital costs and the annual part replacement costs.

The evaluation of costs in TI ww during sonication process with the addition of N_2(g) sparging were calculated for annual, monthly, weekly, daily and hourly time periods. 3120, 3120, 650, 193808.32, 7.50, 200705.82, 120, 1500, 1620, 202325.82 and 202205.82 TL/year was calculated for total annual labor cost, total annual analysis cost, total annual N_2(g) chemical cost, total annual electrical cost, total annual part replacement cost, total annual O&M cost, amortized capital cost, total annual capital cost, total annual amortized capital cost, total annual operating cost and total annual cost, respectively, for TI ww with the addition of N_2(g) sparging during sonication process. The total annual cost with N_2(g) sparging was calculated as 202205.82 TL/year (=134803.88 \$/year) including the annual labor costs, the annual analytical costs, the annual chemical costs, the annual energy (electrical) costs, the annual capital costs and the annual part replacement costs.

4.5 The Discussions of Specific Energy and Cost in TI ww during Sonication Process with only Sonication and with the Addition of N_2(g) Sparging

Less specific energy (3.32 kWh / kg COD_{dis}) is required to derive a better sonication treatment and cost savings for TI ww treatment plants with only sonication and with the addition of N_2(g) sparging compared to the other AOPs processes.

4.6 The Comparison of Anaerobic, Aerobic, Ultraviolet (UV), Ozone (O_3) and Sonication Treatment Processes

Anaerobic pretreatment is most effectively applied to wastewaters with high concentrations of readily degradable organic constituents. The cost-effectiveness of anaerobic pretreatment is specific to each wastewater and associated parameters (for example, ability to use biogas, power costs, sludge disposal costs).

For the operating and maintenance (O&M) cost components, off-site sludge disposal costs and macro-nutrients costs are linear functions of the wastewater strength for both treatment methods; however, absolute costs for the aerobic option are much higher. The energy requirement for aerobic treatment increases rapidly with wastewater strength, since aeration comprises most of the energy needs. For anaerobic systems, the electricity consumption is much lower and virtually constant for the influent strength range, since only pumping costs are incurred. Maintenance costs for both systems are considered aa function of capital costs in this analysis. Alkalinity requirements for anaerobic treatment are higher than for aerobic treatment and increase proportionately with influent strength. This is a consequence of the sensitivity of anaerobic processes to low pH upsets and the necessity to buffer volatile acids generated during the initial reaction step. Labor requirements for both treatment options are not a function of wastewater strength for the plant sizes considered. Heating is specific for anaerobic treatment only. Since heating is mostly a function of the wastewater flow (reactor volume), it does not increase with wastewater strength in the range considered. O&M costs of the anaerobic plant are credited with the biogas generated during the treatment, and the credits are proportional to the mass of organic matter removed (wastewater strength).

Though high energy requirement and high removal efficiencies observed with UV treatment methods in many industrial wastewaters, however, high capital and high operating area are required for the UV treatment process. Energy requirement, startup time, operation time and capital cost of UV treatment are higher than sonication treatment for many industrial wastewaters.

Although, high removal efficiencies provided with O_3 treatment process in many industrial wastewater, high capital cost and medium operating area are required for O_3 treatment process. Energy requirement, startup time, operation time and capital cost of O_3 treatment are higher than Sonication treatment for many industrial wastewaters.

The TI ww have been treated using biological treatment, physical-chemical treatment and their combinations. On the other hand, the TI ww was treated using aerobic biological processes, physico/chemical processes and their modifications. The most commonly employed biological processes are conventional and extended activated sludge system. Nevertheless, these processes cannot be degraded the dyes, COD_{dis} in TI ww ultimately. Therefore, sonication process easily removed the COD_{dis} color and TAAs from TI ww.

The extent of sonodegradation is a function of sonication time and operating conditions such as ultrasound intensity, ultrasonic frequency, sonication power, sonication temperature and initial concentration, and also depends on the presence of matrix species. These can produce more cavities and free radicals. They may have either a beneficial or detrimental impact on degradation depending on their type and function i.e. whether they act as radical promoters or scavengers. Furthermore, their presence may alter the physicochemical properties of the reaction mixture and consequently affect the cavitation process and associated reaction mechanisms and pathways. Sonication is economical for effectively degrading and destroying way fort the all pollutant parameters and some intermediates in TI ww.

Sonication process works on the principle of generating free radicals and their subsequent attack on the contaminant molecules with the aim of either, completely mineralizing the contaminants or converting it into less harmful or lower chain compounds which cannot be efficiently treated by biological processes.

The sonolysis process can be removed the toxicity and can be increased the biodegradability of pollutant compounds. The chemicals are mineralized or degraded to smaller molecules with improved biodegradability or lower toxicity. The intensification of the organic matter solubilization induced by the ultrasonic action, can lead to an increase of the bioavailability of some micropollutants to the degrader consortium.

The combination of ultrasonic treatment with some additives and biodegradation represents a promising new technique in the field of environmental engineering. Toxic compounds inhibiting the microbial degradation processes can be removed by ultrasounds.

The sonication process could prove to be less land-intensive, less expensive and require less maintenance and undergo lesser inhibition by the anions than other treatment processes in TI ww with only sonication and the addition of N_2(g) sparging. Sonication process is recommended for the treatment of TI ww containing toxic and refractory compounds. Sonication process can be applied as a pre-treatment or post-treatment in combination with other water purification processes.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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APPENDIX

Table 3. Operating conditions for different wastewaters and different AOPs.

Process	**Waste water**	**Pollutant Parameter**	**Removed Parameter**	**Reaction Volume**	**Initial Concentration**	**UV Source**	**US Source**	**O_3 Source**	**Oxidant**	**Catalyst**	**References**
For reactive azo dye UV, US, O_3, UV+US US + O_3, UV+O_3, US + UV + O_3	TI ww	COD, color	color	1200 ml	19.95 mg/l	254 nm, Philips, PL-L 18WT UV two lamps	520 kHz, Undatim Ultrasonics, 600W	Ozonelab OL-100 model, 36W at 0.25 l/min	O_3 40 mg/l	-	Tezcanli-Güyer & Ince (2004)
US	TI ww	**(a)**	**(a)**	500 ml	962.99 mg/l	-	35 kHz, 640 W	-	**(b)**		In this study
(a): COD_{dis}, TOC, color and TAAs; (b) $N_2(g)$; US: ultrasound; UV: ultraviolet; O_3: ozone											

Table 6. Summary of cost estimation of various AOPs for degradation of some parameters

Waste water	**Item**	**Removed Parameter**	**k (1/min)**	**P_{elec} (kW)**	**t (min)**	**V (liter)**	**C_0 (COD_{dis})**	**C (COD_{dis})**	**Energy Density (W/ml)**	**Specific Energy (kWh / kg COD_0**	**EE/O or EE/M**	**Cost $/3790 liters**	**References**
TI ww	UV (254 nm)	color	No	0.036	60	1.2	20	20	0.03	-	$1.38x10^9$	-	Tezcanli-Güyer and Ince (2004)
TI ww	O_3 (12.40 mg/l)	color	0.01108	0.036	207.814	1.2	20	2	0.03	-	103.91	4.0839	Tezcanli-Güyer and Ince (2004)
TI ww	US	**(a)**	0.00015	0.64	150	0.5	962.99	247.75	1.28	3.32	5423.73	1000	In this study
(a): COD_{dis}, TOC, color and TAAs; US: ultrasound													

Table 7. Capital cost estimation ($) for various AOPs for degradation of some parameters.

Item	**Removed Parameter**	**AOP Reactor ($)**	**Piping, Valves, Electrical (30 %) ($)**	**Site Work (10 %)**	**Subtotal ($)**	**Contractor O&P (15 %)**	**Subtotal ($)**	**Engineering (15 %)**	**Subtotal ($)**	**Contingency (20 %)**	**Total Capital ($)**	**Amortized Annual Capital Cost ($)**	**References**
UV	phenol	$2.47x10^{8}$	$7.4x10^{7}$	$2.47x10^{7}$	$3.46x10^{8}$	$5.18x10^{7}$	$3.97x10^{8}$	$5.96x10^{7}$	$4.57x10^{8}$	$9.14x10^{7}$	$5.48x10^{8}$	$4.42x10^{7}$	Kidak and Ince (2007)
US	phenol	$9x10^{9}$	$2.7x10^{9}$	$9x10^{8}$	$1.26x10^{10}$	$1.89x10^{9}$	$1.45x10^{10}$	$2.17x10^{9}$	$1.67x10^{10}$	$3.33x10^{9}$	$2x10^{10}$	$1.61x10^{9}$	Kidak & Ince (2007)
O_3	phenol	$3.4x10^{4}$	$1.02x10^{4}$	$3.4x10^{3}$	$4.76x10^{4}$	$7.14x10^{3}$	$5.47x10^{4}$	$8.21x10^{3}$	$6.30x10^{4}$	$1.26x10^{4}$	$7.55x10^{4}$	$7.55x10^{4}$ [a]	Entezari et al. (2003)
US+ Fenton	phenol	$7.14x10^{7}$	$2.14x10^{7}$	$7.14x10^{6}$	$1.00x10^{8}$	$1.50x10^{7}$	$1.15x10^{8}$	$1.72x10^{7}$	$1.32x10^{8}$	$2.64x10^{7}$	$1.59x10^{8}$	$1.28x10^{7}$	Entezari et al. (2003)
UV	color	-	-	-	-	-	-	-	-	-	-	-	Tezcanli-Guyer & Ince (2004)
O_3	color	$2.04x10^{5}$	$6.12x10^{4}$	$2.04x10^{4}$	$2.86x10^{5}$	$4.28x10^{4}$	$3.28x10^{5}$	$4.93x10^{4}$	$3.78x10^{5}$	$7.55x10^{4}$	$4.53x10^{5}$	$4.53x10^{5}$ [a]	Tezcanli-Guyer & Ince (2004)
US, TI ww	**(a)**	$1x10^{3}$	-	-	-	-	-	-	$8x10^{1}$	-	$1x10^{3}$	$1.08x10^{3}$	In this study
(a): COD_{dis}, TOC, color and TAAs; UV: ultraviolet; US: ultrasound.													

Table 8. Labor costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Sampling Frequency (Samples/Week)**	**Sampling Annual Labor (h) [a]**	**AOP System O&M (h/year)**	**General O&M whole Treatment Plant (h/year)**	**Total Annual Labor (h)**	**Total Annual Labor Cost ($)**	**References**
TI ww	UV	color	-	-	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	color	4	208	48	312	568	45440	Tezcanli-Güyer & Ince (2004)
TI ww	US	**(a)**	2	52	52	-	104	2080	In this study
(a): COD_{dis}, TOC, color and TAAs; UV: ultraviolet; US: ultrasound.									

Table 9. Analytical costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Sampling Frequency (samples/week)**	**Analysis Annual Labor (hours/year)**	**Total Annual Analytical Cost ($)** [a]	**References**
TI ww	UV	Color	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	Color	4	208	41600 [a]	Tezcanli-Güyer & Ince (2004)
TI ww	US	**(a)**	2	104	20800 [a]	In this study
(a): COD_{dis}, TOC, color and TAAs; UV: ultraviolet; US: ultrasound.						

Table 10. Chemical costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Chemicals**	**Amount of Chemicals Consumed (g)**	**Cost of Chemicals ($)**	**Total Cost of Chemicals ($)**	**References**
TI ww	UV	color	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3	color	-	-	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	US	color	$N_2(g)$	$5x10^2$	$1.73x10^2$	$1.73x10^2$	In this study
UV: ultraviolet; US: ultrasound.							

Table 11. Electrical costs ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Removal Efficiencies (%) (at 60°C)**	**Power Consumed (kW/year)**	**Total Annual Power Consumed (kWh/year)**	**Power Cost ($)** [a]	**References**
TI ww	US	color	-	$1.88x10^4$	$1.65x10^8$	$1.35x10^7$	Drijvers et al. (1999)
TI ww	O_3	color	-	34.98	$3.06x10^7$	$2.45x10^6$	Tezcanli-Guyer & Ince (2004)
TI ww	US	**(a)**	84.92% COD_{dis}	832	$1.17x10^6$	$1.29x10^5$	In this study
(a): COD_{dis}, TOC, color and TAAs; US: ultrasound							

Table 12. Part replacement cost ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Removal Efficiencies (%) (at 60ºC)**	**Part Replacement Cost ($/year)**	**References**
TI ww	UV (45% of electrical cost)	color	-	-	Tezcanli-Güyer & Ince (2004)
TI ww	O_3 (1.5% of capital cost)	color	-	3.06x10^3	Tezcanli -Güyer & Ince (2004)
TI ww	US	**(a)**	84.92% COd$_{dis}$	5	In this study
(a): COD$_{dis}$, TOC, color and TAAs; UV: ultraviolet; US:ultrasound.					

Table 13. Annual O&M cost estimation ($) of various AOPs for degradation of some parameters and sonication process used in this study.

Wastewater	**Item**	**Removed Parameter**	**Removal Efficiencies (%) (at 60ºC)**	**Part Replacement Cost ($/y)**	**Labor Cost ($/y)**	**Analytical Cost ($/y)**	**Chemical Cost ($/y)**	**Electrical Cost ($/y)**	**Total Annual O&M Cost ($/y)**	**References**
TI ww	UV	color	-	-	-	-	-	-	-	Tezcanli -Güyer & Ince (2004)
TI ww	O_3	color	-	3.06x10^4	4.54x10^5	4.16x10^5	-	2.45x10^5	1.15x10^6	T.-Güyer & Ince (2004)
TI ww	US	**(a)**	84.92% COD$_{dis}$	5	2.08x10^3	2.08x10^3	2.25x10^3	1.29x10^5	1.35x10^5	In this study
(a): COD$_{dis}$, TOC, color and TAAs; UV: ultraviolet; US: ultrasound.										