Research Article

Treatment of Textile Industry Wastewaters with Sonication

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Abstract

In this study, the effects of ambient conditions (25°C), increasing sonication time (60, 120 and 150 min), sonication temperature (30°C and 60°C), on the sonication of wastewater from textile industry wastewater (TI ww) treatment plant in Izmir, Turkey was investigated in a sonicator with a power of 640 W, a frequency of 35 kHz and a sonication time of 150 min for the treatments of Methylene Blue (MB) and Rhodamine B (RhB) dyestuffs. Dissolved chemical oxygen demand (COD_{dis}), color and three polyphenols [4-methyl phenol (C_7H_8O) (4-MP), 4-hydroxyanisole ($C_7H_8O_2$) (4-H), 2-methyl-4-hydroxyanisole ($C_8H_{10}O_2$) (2-M-4-H)] removal efficiencies were observed during sonication experiments. 99.37% COD_{dis}, 98.07% color, 96% total phenol (PHE R), 93% 4-MP, 88% 4-H and 85% 2-M-4-H maximum removal efficiencies were found after 150 min sonication time and at 60°C.

Keywords: Methylene Blue; Polyphenols; Rhodamine B; Sonication; Textile industry wastewater

Introduction

The textile industries use enormous amount 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 [13]. 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 [14].

The application of ultrasound as an alternative to the removal of dyes in waters has become of increasing interest in recent years [24,43]. This technique is considered as an Advanced Oxidation Process (AOP) that generates hydroxyl radicals (OH•) through acoustic cavitation, which can be defined as the cyclic formation, growth and collapse of microbubbles. Fast collapse of bubbles compresses adiabatically entrapped gas and vapours which leads to short and local hot spots [6]. In the final stage of the collapse, the temperature inside the residual bubble or in the surrounding liquid is thought to be above 5000°C. The OH• and hydroperoxyl radicals (O_2H•) can be generated from H_2O and O_2 [20]. 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 [16,17]. In the case of sonication, localized temperature raise 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 (> 500°C), is not always feasible, due to

undesired side-effects such as fabric damage. About 87% and 81% COD_{dis} yields was achieved using 40 and 50 min ultrasounds while compared to only 48% and 28.9% COD_{dis} removals in the absence of ultrasound in TI ww at 25°C [44].

The influence of bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) ions on sonolytic degradation of cationic dye, Rhodamine B (RhB), in water was investigated [22]. As a consequence of ultrasonic cavitation that generates OH•, carbonate radicals (•CO3) were secondary products of water sonochemistry when it contains dissolved HCO_3^- or CO_3^{-2}. The results clearly demonstrated the significant intensification of sonolytic destruction of RhB in the presence of HCO_3^- and CO_3^{-2}, especially at lower dye concentrations. Degradation intensification occurs because •CO_3 sonochemically formed undergo radical-radical recombination at a lesser extent than OH•. The generated •CO_3 are likely able to migrate far from the cavitation bubbles towards the solution bulk and are suitable for the degradation of RhB [22]. Therefore, at low dye concentrations, •CO_3 presents a more selective reactivity towards RhB molecules than OH•. In the presence of HCO_3^-, degradation rate reached a maximum at 3 g L^{-1} HCO_3^-, but subsequent addition retards the destruction process. In RhB solutions containing CO_3^{-2}, the oxidation rate gradually increased with increasing CO_3^{-2} concentration up to 10 g L^{-1} and slightly decreased afterward. •CO_3 sonochemically generated are suitable for total removal of COD of sonicated RhB solutions [22].

In a study performed by Entezari and Sharif Al-Hoseini [12] 98% color removal was accomplished in a TI ww containing 50 mg L^{-1} MB, at 20 kHz frequency, at 120 W power, after 30 min sonication time at 30°C with 700 rpm agitation. In this study, 78.26% color removal was observed after 150 min sonication time at 30°C at not agitated conditions. The color yield in the present study is lower than the yield obtained by Entezari and Sharif Al-Hoseini [12] at 30°C as mentioned above. This could be attributed to the differentiations in dyes present

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})	1.30 ± 0.05	1.40 ± 0.05	1.50 ± 0.05
ORP (mV)	85 ± 2.98	106 ± 3.71	128 ± 4.48
TSS (mg L^{-1})	285 ± 9.98	356 ± 12.46	430 ± 15.05
TVSS (mg L^{-1})	192 ± 6.72	240 ± 8.40	290 ± 10.15
CODtotal (mg L^{-1})	931.70 ± 32.61	1164.60 ± 40.76	1409.20 ± 49.32
CODdissolved (mg L^{-1})	770.40 ± 26.96	962.99 ± 33.71	1165.22 ± 40.78
TOC (mg L^{-1})	462.40 ± 16.18	578 ± 20.23	700 ± 24.50
BOD5 (mg L^{-1})	251.50 ± 8.80	314.36 ± 11	380.38 ± 13.31
BOD5/CODdis	0.26 ± 0.01	0.33 ± 0.012	0.40 ± 0.014
Total N (mg L^{-1})	24.80 ± 0.87	31 ± 1.09	37.51 ± 1.31
NH$_4$-N (mg L^{-1})	1.76 ± 0.06	2.20 ± 0.08	2.66 ± 0.09
NO$_3$-N (mg L^{-1})	8 ± 0.28	10 ± 0.35	12.10 ± 0.42
NO$_2$-N (mg L^{-1})	0.13 ± 0.05	0.16 ± 0.06	0.19 ± 0.07
Total P (mg L^{-1})	8.80 ± 0.31	11 ± 0.39	13.30 ± 0.47
PO$_4$-P (mg L^{-1})	6.40 ± 0.22	8 ± 0.28	9.68 ± 0.34
Total phenol (mg L^{-1})	29.60 ± 1.04	37 ± 1.30	44.80 ± 1.57
SO$_4$-2 (mg L^{-1})	1248 ± 43.70	1560 ± 54.60	1888 ± 66.10
Color (m^{-1})	70.90 ± 2.48	88.56 ± 3.10	107.20 ± 3.75
TAAs (mg benzidine L^{-1})	1296 ± 45.36	1620 ± 56.70	1960 ± 68.60

in TI ww to the operational conditions such as sonication duration, sonication frequency and to not stirred conditions of sonicated wastewater. Banerjee et al. [3] has been investigated the sonochemical decolorization of wastewater containing a basic dye, Rhodamine 6G (Rh 6G) and the effect of initial concentration, pH and use of different additives, such as CCl_4, H_2O_2, air and UV light in combination with ultrasound on the extent of decolorization. 77.8% maximum Rh 6G decolorization was observed for the use of H_2O_2 with sonication.

In the persent study, the effects of ambient conditions (25ºC), increasing sonication time (60, 120 and 150 min), sonication temperature (30ºC and 60ºC) on the sonication of wastewater from textile industry wastewater (TI ww) treatment plant in Izmir, Turkey was investigated in a sonicator with a power of 640 W, a frequency of 35 kHz and a sonication time of 150 min for the treatments of MB and RhB dyestuffs. COD$_{dis}$, color and three polyphenols [4-methyl phenol (C_7H_8O) (4-MP), 4-hydroxyanisole ($C_7H_8O_2$) (4-H), 2-methyl-4-hydroxyanisole ($C_8H_{10}O_2$) (2-M-4-H)] removal efficiencies were observed during sonication experiments. 99.37% COD$_{dis}$, 98.07% color, 96% total phenol (PHE R), 93% 4-MP, 88% 4-H and 85% 2-M-4-H maximum removal efficiencies were found after 150 min sonication time and at 60ºC.

Materials and Methods

Raw wastewater

The TI ww used in this study contains color (> 70.9 m^{-1}), total phenol (> 37 mg L^{-1}), COD$_{dis}$ (> 770 mg L^{-1}) and high biological oxygen demand 5-days (BOD$_5$) (> 251 mg L^{-1}) concentrations with a

BOD$_5$/COD$_{dis}$ ratio of 0.33. The characterization of TI ww was shown in Table 1 for minimum, medium and maximum values.

Configuration of sonicator

A Bandelin Electronic RK510 H sonicator was used for sonication of the TI ww samples. The sonication frequency and the sonication power were 35 kHz and 640 W, respectively. Glass serum bottles in a glass reactor were filled to a volume of 100 mL with raw TI ww and they were closed with teflon coated closers for the measurement of volatile compounds (evaporation) of the raw TI ww. The evaporation losses of volatile compounds were estimated to be 0.01% in the reactor and, therefore, assumed to be negligible. The serum bottles were filled with 0.1 mL methanol in order to prevent adsorption on the walls of the bottles and minimize evaporation. 25ºC, 30ºC and 60ºC temperatures were adjusted electronically in the sonicator with two thermostatic heaters. The stainless steel sonicator was equipped with a teflon holder to prevent temperature losses. The shematic configuration of the sonicator used in this study is shown in Figure 1.

Operational conditions

The effects of ambient conditions (25ºC), increasing sonication time (60, 120 and 150 min), sonication temperature (30ºC and 60ºC) on the sonication of wastewater from textile industry wastewater (TI ww) treatment plant in Izmir, Turkey was investigated. Through 5 min before ultrasound was begun at 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 +4ºC for experimental analysis. Deionized pure H_2O (R ¼ 18 MΩ cm^{-1}) 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 cm2, with diameters 3.98, 4.41, 4.7, 5.8 and 7.2 cm, with input ultrasound powers of 120, 350, 640, 3000 and 5000 W, with ultrasound frequencies of 25, 35, 132, 170 and 350 kHz, with US intensities of 15.7, 24.2, 36.9, 46.2 and 51.4 W cm^{-2}, with power densities of 0.1, 0.9, 1.65, 1.9, 2.14 W mL^{-1}, with specific energies of 2.4, 3.1, 4.1, 5.1, 11.5 kWh kg^{-1} COD$_{influent}$$^{-1}$, respectively, were chosen to identify for maximum removal of pollutant parameters (COD$_{dis}$, color, total phenol and polyphenols) 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) (Table 2).
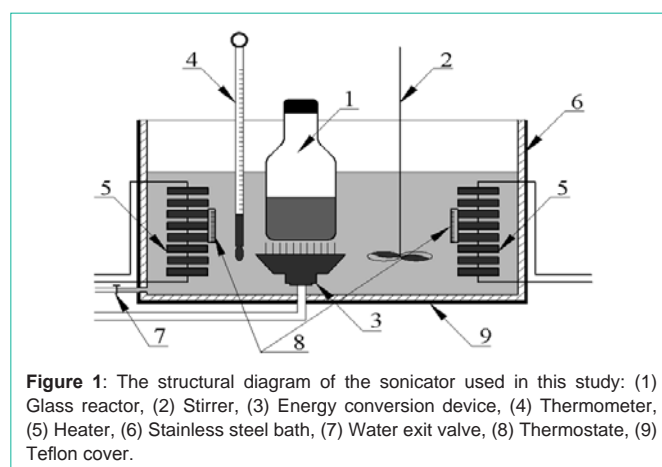

Figure 1: The structural diagram of the sonicator used in this study: (1) Glass reactor, (2) Stirrer, (3) Energy conversion device, (4) Thermometer, (5) Heater, (6) Stainless steel bath, (7) Water exit valve, (8) Thermostate, (9) Teflon cover.

Samples were taken after 120th and 150th min of ultrasound time and they were analyzed immediately.

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).

Analytical methods

pH, temperature [T(^{o}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 Oxygen Demand (COD_{dis}), Total Organic Carbon (TOC), oil were monitored following Standard Methods 2550, 2580, 2540 C, 2540 E, 5210 B, 5220 D, 5310, 5520 B, respectively [10]. 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 [23] and Eckenfelder [11]. According these methods, the color content was determined by measuring the absorbance at three wavelengths (445, 540 and 660 nm), and taking the sum of the absorbances at these wavelengths.

In order to identify the TAAs, 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 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. Polyphenols measurement was performed following the Standard Methods 5520 B (Eaton et al., 2005) with a gas chromatography-mass spectrometry (GC-MS) (Hewlett-Packard 6980/HP5973MSD). Mass spectra were recorded using a VGTS 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. The total phenol was monitored as follows: 40 mL of TI ww was acidified to pH=2.0 by the addition of concentrated HCl. Phenols were then extracted with ethyl acetate. The organic phase was concentrated at 40°C to about 1 mL and silylized by the addition of N,O-Bis(trimethylsilyl)Acetamide (BSA). The resulting trimethylsilyl derivatives were analysed by GC-MS (Hewlett-Packard 6980/HP5973MSD).

Statistical analysis

Analysis of Variance (ANOVA) of experimental data was performed to determine the F and P values, i.e. the ANOVA test was used to test the differences between dependent and independent groups [48]. Comparison between the actual variation in experimental data averages and standard deviation was expressed in terms of F

Table 2: Sonicational parameters and corresponding values of sonication process in this study at pH=5.4 after 150 min sonication time for maximum CODdis yields under ambient conditions (at 25°C), at initial COD_{dis} concentration=962,99 mg L^{-1}, at sonication power=640 W and at sonication frequency=35 kHz (n=3, mean values).

Ultrasound parameters	Values				
Ultrasound frequency (kHz)	25	35	132	170	350
Ultrasound power (W)	120	640	350	3000	5000
Power density (W mL^{-1})	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^{-1} CODinfluent-1)	2.4	11.5	3.1	4.1	5.1
Active acoustical vibration area (cm^2)	12.43	40.69	13.84	17.34	26.4
Reactor diameters (cm)	3.98	7.2	4.41	4.7	5.8
COD removal efficiency (%)	45	61	47	53	58

ratio. F was equal to 'found variation of the data averages/expected variation of the data averages'. P reports the significance level. Regression analysis was applied to the experimental data to determine the regression coefficient (R2) [38].

All experiments were carried out three times and the results given as the means of triplicate samplings. Individual TI ww concentrations are given as the mean with Standard Deviation (SD) values.

Results and Discussion

Effect of sonication frequency and power on the degradation of TI ww

The effect of the ultrasonic frequency on the degradation ratio of COD_{dis} was also considered in the range from 35 kHz to 150 kHz. Increasing the sonication frequency did not increase the number of free radicals, therefore, a low number of free radicals did not escape from the bubbles and did not migrate as reported by David [8]. The optimum time to reach equilibrium and the faster rate of removal in the presence of ultrasound was attributed to the higher mass transfer and higher surface area produced by the cavitation process [30]. The phenomenon responsible for removal of COD_{dis} is the formation of OH$^\cdot$ during sonication of aqueous solution by the cavitation process. This process consists of the formation, growth and collapse by violent implosions to release extreme temperatures and pressures at local hot spots in the liquid (Suslick, 1986). 61% maximum COD_{dis} removal was observed after 150 min sonication time, at 25°C, at 35 kHz ultrasound frequency, at 640 W sonication power, at 2.14 W mL^{-1} power density, at 51.4 W cm^{-2} ultrasound intensity, at 11.5 kWh kg^{-1} $COD_{influent}^{-1}$ specific energy, at 40.69 cm^2 active acoustical vibration area and at 7.2 cm reactor diameters, respectively. The maximum COD_{dis} removal efficiency of our other studies such as petrochemical industry wastewaters (PCI ww) and Olive Mill industry Wastewaters (OMW) was obtained at the same operational conditions at 25°C, after 150 min sonication time, at 35 kHz ultrasound frequency, at 640 W sonication power, at 2.14 W mL^{-1} power density, at 51.4 W cm^{-2} ultrasound intensity, at 11.5 kWh kg^{-1} $COD_{influent}^{-1}$ specific energy, at 40.69 cm^2 active acoustical vibration area and at 7.2 cm reactor diameters, respectively [34-39]. As the power increased, the number of collapsing cavities also increased, thus leading to enhanced degradation rates, as reported by Papadaki, et al. and Psillakis, et al. [25,27].

Table 3: COD_{dis} removal efficiencies of TI ww before and after sonication at initial COD_{dis} concentrations=962,99 mg L^{-1}, at sonication power=640 W and at sonication frequency=35 kHz (n=3, mean values).

Time (min)	CODdis Removal Efficiencies (%)		
	25°C, control	30°C	60°C
0. min	0	0	0
60. min	30.43	42.39	48.08
120. min	53.69	67.34	68.48
150. min	74.27	81.53	84.92

Table 4: Color removal efficiencies of TI ww before and after sonication at initial color concentrations=88.56 m^{-1}, at sonication power=640 W and at sonication frequency=35 kHz (n=3, mean values).

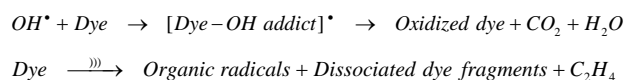| Time (min)	Color Removal Efficiencies (%)		
	25°C, control	30°C	60°C
0. min	0	0	0
60. min	12.37	52.29	79.32
120. min	53.47	76.38	83.2
150. min	57.09	78.26	87.66

Effect of increasing sonication time on the COD_{dis}, color and polyphenols removal efficiencies in ambient conditions (25°C)

TI ww samples were treated with sonicator at different sonication times (60, 120 and 150 min) at 25°C ambient conditions (Figure 2a; Table 3, SET 1). 30.43%, 53.69% and 74.27% COD_{dis} removals were observed at 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 25oC (Figure 2a; Table 3, SET 1). The maximum COD_{dis} removals was 74.27% after 150 min sonication time, at pH=7.0 and at 25°C. As the sonication time was increased the COD_{dis} removal efficiency in TI ww was enhanced. A significant linear correlation between COD_{dis} yields and sonication time was observed (R^2=0.74, F=11.90, p=0.01) (Figure 2a; Table 3, SET 1). The optimum time to reach equilibrium and the faster rate of removal in the presence of ultrasound was attributed to the higher mass transfer and higher surface area produced by the cavitation process (Sivakumar and Pandit, 2001). The phenomenon responsible for removals of COD_{dis} is the formation of $OH^•$ during sonication of aqueous solution by the cavitation process (Suslick, 1986). This process consists of the formation, growth and collapse by violent implosions to release extreme temperatures and pressures at local hot spots in the liquid (Suslick, 1986). Under these critical conditions, the entrapped molecules of H_2O in the bubble dissociate into very reactive $OH^•$ and hydrogen radicals ($H^•$) [12].

8 70% COD removal found in a TI ww containing 20 mg L^{-1} C.I. Reactive Blue 19, at 20 kHz, at 176 W, at 176 W L^{-1}, after 30 min sonication time, at 30°C and at pH=8.0. In this study, 74.27% CODdis removal was observed after 150 min sonication time and at 25°C. The COD_{dis} yield in the present study is higher than the yield obtained by He et al. [18] at 30°C and at a pH of 8.0. Behnajady et al. (2008a) 67% COD_{dis} removal was achieved in a TI ww containing 10 mg L^{-1} RhB concentration at an initial CODdis concentration of 12 mg L^{-1} at 35 kHz frequency, at 170 W power and at a power density of 0.163 W/ml after 180 min sonication time at 25°C. In this study, 74.27% COD_{dis} removal was observed after 150 min sonication time at 25°C.

The COD_{dis} yield found in the present study is higher than the yield obtained by Behnajady, et al. [4] at 25°C. This could be attributed to the differences between sonication power and sonication frequency applied to the TI wws. Yachmenev et al. [46] found 88.00% COD removal in a TI ww containing 20.00 mg/l Reactive Blue 9, at 20 kHz frequency, after 60 min sonication time at 25°C and at pH=8.0. In this study, 74.27% COD_{dis} removal was observed after 150 min sonication time at 25oC. The COD_{dis} yield found in this study is lower than the yield obtained by Yachmenev et al. [49] at 25°C.

12.37%, 53.47% and 57.09% color removals were found after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 25oC (Figure 2b; Table 4, SET 1). The maximum color removal efficiency was 57.09% after 150 min sonication time, at pH=7.0 and at 25°C. A significant linear correlation between color yields and sonication time was obtained (R^2=0.83, F=10.92, p=0.01) (Figure 2b; Table 4, SET 1). The main reaction pathway for TI ww containing azo dye solutions is the oxidation by $OH^•$ attack in the bulk liquid via sonication in (Equation 1), while thermal reactions may occur at the bubble-liquid interface for some dye molecules to approach gaseous bubble surfaces as reported by Ince and Tezcanli-Guyer [19] in (Equation 2):

$$OH^• + Dye \quad \rightarrow \quad [Dye - OH\ addict]^• \quad \rightarrow \quad Oxidized\ dye + CO_2 + H_2O$$

$$Dye \quad \xrightarrow{\hspace{0.3cm})))\hspace{0.3cm}} \quad Organic\ radicals + Dissociated\ dye\ fragments + C_2H_4$$

MB and RhB dyestuffs were selected for our study. It is expected that the sonolytic degradation of MB and RhB dyestuffs would mainly occur by $OH^•$ attack [41,42]. In order to investigate the dependence of the $OH^•$ during the degradation of MB and RhB dyestuffs by ultrasonic irradiation, the sonolytic degradation of MB and RhB in the presence of radical scavengers (such as $H^•$, $OH^•$, $O2H^•$, $O2^•$), known as an effective $OH^•$ scavenger, was performed and was to scavenge $OH^•$ in the bubble and prevent the accumulation of $OH^•$ at the interface of the bubble (Tauber et al., 1999a, b). After the decolorization, the process could shift progressively from the bulk solution to the surface of the catalysts and cleavage of the carbon (C), hydrogen (H_2) and oxygen (O_2) rings was mainly attributed to the radical scavengers ($H^•$, $OH^•$, $O2H^•$, $O2^•$) reactions. The organic dyes (acid, basic, direct, reactive, vat, etc.) are totally mineralized to simple inorganic species such as CO_3^-, Cl^- and NO_3^- [49]. [44] found that the ultrasonic waves can reduce the concentration of MB up to 10% in 30 min sonication time and at 30°C. In this study, 57.09% color removal was observed after 150 min sonication time and at 25°C. The color yield in the present study is higher than the yield obtained by Vankar and Shanker (2008) at 30°C. The color yields obtained in this study are lower than the decolorization efficiencies obtained by Destaillats et al. [9] (80%) and Sun et al. [39] (89%) in TI wws containing 10 mg L^{-1} Methyl Orange and 10 mg L^{-1} Acidic Black^{-1} at 500 kHz frequency, at 50 W power and at 2 W cm^{-2} power intensity after 60 min sonication time at 45°C. This could be attributed to the differences in dyestuff properties, to the dyestuff concentrations in TI ww and to the some operational conditions such as sonication at high frequency. In a study performed by Singla et al. [29] 80% color removal was obtained in a TI ww containing 15 mg L^{-1} Martius Yellow dye at 355 kHz frequency, at 30 W power, at power densities varying between 0.049 and 1.16 W L^{-1}, after 240 min sonication time at 25°C. In this study, 57.09% color removal was observed after 150 min sonication time at 30oC. The color yield found in this study is lower than the yield

Table 5: Measurements of total phenols and three polyphenols (4-methyl phenol, 4-hydorxyanisole and 2-methyl-4-hyroxyanisole) in TI ww with GC-MS after 120 and 150 min sonication time, at pH=7.0, at increasing temperatures, at initial total phenol concentration=37 mg L^{-1}, at sonication power=640 W and at sonication frequency=35 kHz (n=3, mean values).

Time (min)	PHE0 (mg L^{-1})	PHE R (%)	4-MP (mg L-1)	4-MP R (%)	4-H (mg L^{-1})	4-H R (%)	2-M-4-H (mg L^{-1})	2-M-4-H R (%)
		25°C, control						
0	37	0	0	0	0	0	0	0
120	16.65	55	5.2	45	8.52	42	10.11	40
150	11.1	70	3.31	65	5.29	64	6.74	60
		30oC						
0	37	0	0	0	0	0	0	0
120	15.17	59	5	50	8.4	48	9.78	46
150	8.14	78	2.5	75	4.85	70	6.34	65
		60oC						
0	37	0	0	0	0	0	0	0
120	12.58	66	4.85	55	8.2	51	8.54	49
150	5.55	85	2.26	79	4.35	74	4.69	72

PHE0: Initial total phenol concentration (mg L^{-1}), PHE R: Total phenol removal efficiency (%), 4-MP: 4-methyl phenol concentration after sonication (mg L^{-1}), 4-MP R: 4-methyl phenol removal efficiency (%), 4-H: 4-hydorxyanisole concentration after sonication (mg L^{-1}), 4-H R: 4-hydorxyanisole removal efficiency (%), 2-M-4-H: 2-methyl-4-hyroxyanisole concentration after sonication (mg L^{-1}), 2-M-4-H R: 2-methyl-4-hyroxyanisole removal efficiency (%).

obtained by Singla et al. [29] at 30°C. This could be attributed to the low ambient temperature and to the high frequency used throughout sonication and to the high dye concentrations.

Total phenol (PHE R) and three polyphenols [4-methyl phenol (C_7H_8O) (4-MP), 4-hydroxyanisole ($C_7H_8O_2$) (4-H), 2-methyl-4-hydroxyanisole ($C_8H_{10}O_2$) (2-M-4-H)] were measured in TI ww during sonication process after 120 and 150 min sonication time. 55% PHE R, 45% 4-MP, 42% 4-H and 40% 2-M-4-H polyphenols removals were measured after 120 min sonication time, respectively, at pH=7.0 and at 25°C (Table 5). 70% PHE R, 65% 4-MP, 64% 4-H and 60% 2-M-4-H polyphenols removals were observed after 150 min sonication time, respectively, at pH=7.0 and at 25oC. The maximum polyphenols removals were 70% PHE R, 65% 4-MP, 64% 4-H and 60% 2-M-4-H after 150 min sonication time, respectively, at pH=7.0 and at 25°C. A significant linear correlation between polyphenols removals and sonication time was observed (R^2=0.88, F=15.64, p=0.01) (Table 5). Pyrolytic destruction of the polyphenols in the gas phase is negligible; the degradation occurs mainly in the bulk solution. A possible explanation for this is that a considerable increase in the concentration results in the formation of a complex H-bonding network between the polyphenolic compounds [45]. During sonication low decrease of total phenol concentrations in the effluent samples results in the formation of a complex H-bonding network between the polyphenolic compounds after 60 min sonication time. It is well known that molecules containing COOH or CHO groups exist as dimmers in solution due to the formation of H-bonds between two neighboring molecules. This results in a more robust and stable configuration, thus leading to reduced degradation [7]. In addition to this, the formation of such a network may impede their diffusion towards the bubble interface and this would also lead to reduced degradation of polyphenols [2].

Table 6: Measurements of total phenols and three polyphenols (4-methyl phenol, 4-hydroxyanisole and 2-methyl-4-hyroxyanisole) in TI ww with GC-MS after 120 and 150 min sonication time, at pH=7.0, at increasing temperatures (25, 30 and 60°C), at initial total phenol concentration=37 mg L^{-1}, at sonication power=640 W and at sonication frequency=35 kHz (n=3, mean values).

T (°C)	Polyphenols Names	Polyphenols Removal Efficiencies (%)	
		120 min	150 min
25	PHE R	59	73
	4-MP R	48	68
	4-H R	44	66
	2-M-4-H R	41	61
30	PHE R	64	83
	4-MP R	54	79
	4-H R	51	73
	2-M-4-H R	48	67
60	PHE R	72	91
	4-MP R	60	84
	4-H R	55	78
	2-M-4-H R	52	75

PHE R: Total phenol removal efficiency (%), 4-MP R: 4-methyl phenol removal efficiency (%), 4-H R: 4-hydroxyanisole removal efficiency (%), 2-M-4-H R: 2-methyl-4-hyroxyanisole removal efficiency (%).

Effect of increasing temperature on the removal of CODdis, color and polyphenols versus sonication time

42.39%, 67.34% and 81.53% COD_{dis} removals were observed after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 30°C (Figure 2a; Table 3, SET 2). 11.96%, 13.65% and 7.26%
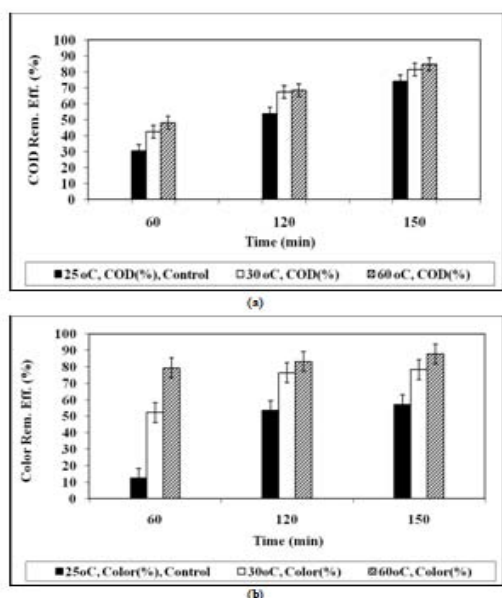
Figure 2: Effect of increasing temperature on the a) COD_{dis} and b) Color removal efficiencies in TI ww versus increasing sonication times (sonication power=640 W, sonication frequency=35 kHz, initial COD_{dis} concentration=962.99 mg L^{-1}, initial color concentration=88.56 m^{-1}, n=3, mean values).

increase in COD_{dis} removals were obtained after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 30°C, compared to the control (E=74.27% CODdis after 150 min sonication time at pH=7.0 and at 25°C). A significant linear correlation between CODdis yields and temperature was not observed (R^2=0.33, F=2.88, p=0.01) (Figure 2a; Table 3, SET 2). 48.08%, 68.48% and 84.92% CODdis yields were found after 120 and 150 min sonication time, respectively, at pH=7.0 and at 60°C (Figure 2a; Table 3, SET 2). The contribution of temperature on COD_{dis} removals were 17.65%, 10.79% and 10.65% after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 60°C, compared to the control (E=74.27% COD_{dis} after 150 min sonication time, at pH=7.0 and at 25°C). The maximum COD_{dis} removal was 84.92% after 150 min sonication time at pH=7.0 and at 60oC. A significant linear correlation between COD_{dis} yields and temperature was observed (R^2=0.71, F=13.92, p=0.01) (Figure 2a; Table 3, SET 2). The optimum time to reach equilibrium and the faster rate of removal in the presence of ultrasound was attributed to the higher mass transfer and higher surface area produced by the cavitation process [30]. The phenomenon responsible for removals of COD_{dis} is the formation of OH· during sonication of aqueous solution by the cavitation process. This process consists of the formation, growth and collapse by violent implosions to release extreme temperatures and pressures at local hot spots in the liquid [39]. Under these critical conditions, the entrapped molecules of H_2O in the bubble dissociate into very reactive OH· and H· [12]. With an increase in the temperature, the initial sono-degradation rate was increased in TI ww [22]. This could be explained by the hydrophilic property of the pollutant which is mostly degraded outside the cavitation process by the OH· produced by ultrasound in TI ww [22]. Therefore, reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at

higher temperatures and this leads to an enhancement of the reaction rate of radicals with COD molecule [15]. On the other hand, any increase in temperature will raise the vapor pressure of a medium and so lead to easier cavitation [4,5].

In a study performed by Arslan et al. [1] 80% COD removal was achieved at 30 kHz frequency, at 640 W power, 22 W m^{-2} power intensity after 80 min sonication time at 30°C in TI ww. In this study, 81.53% COD_{dis} removal was observed after 150 min sonication time at 30°C. The COD_{dis} yield found in the present study is higher than the yield obtained by Arslan et al. [1] at 30°C as mentioned above. Yavuz et al. (2009) accomplished 98.30% COD removal in a TI ww containing 20 mg L^{-1} Basic Red 29 at 40 kHz frequency, at 25 W power and at 0.25 W mL^{-1} power density after 30 min sonication time at 40°C. In this study, 84.92% COD_{dis} removal was observed after 150 min sonication time at 60°C. The COD_{dis} yield in the present study is lower than the yield obtained by Yavuz et al. [47] at 40°C as mentioned above. This could be attributed to the differentiations in the organic content of the TI ww studied.

52.29%, 76.38% and 78.26% color removals were observed after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 30°C (Figure 2b; Table 4, SET 2). 39.92%, 22.91% and 21.17% increase in the color removals were obtained after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 30oC, compared to the control (E=12.37%, E=53.47% and E=57.09% color after 120 and 150 min sonication time, respectively, at pH=7.0 and at 25°C). A significant linear correlation between color yields and temperature was not observed (R^2=0.46, F=4.51, p=0.01) (Figure 2b; Table 4, SET 2). 79.32%, 83.20% and 87.66% color yields were found after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 60oC (Figure 2b; Table 4, SET 2). The contribution of temperatures on color removals were 66.95%, 29.73% and 30.57% after 60, 120 and 150 min sonication time, respectively, at pH=7.0 and at 60°C, compared to the control (E=12.37%, E=53.47% and E=57.09% color after 120 and 150 min sonication time, respecvtively, at pH=7.0 and at 25°C). The maximum color removal was 87.66% after 150 min sonication time at pH=7.0 and at 60°C. A significant linear correlation between color yields and temperature was not observed (R^2=0.51, F=3.09, p=0.01) (Figure 2b; Table 4, SET 2). [28] reported 80.62% color removal in a TI ww containing 1000 mg L^{-1} Rifacion Yellow HE4R with ultrasound and combined ultrasound/activated carbon at 850 kHz, at 140 W, after 120 min sonication time and at 30°C. In this study, 78.26% color removal was observed after 150 min sonication time and at 30oC. In this study, similar yields were observed with the yields obtained by Sayan [28] at 30°C as mentioned above. [44] found that the ultrasonic waves can reduce the concentration of MB up to 10% in 30 min sonication time at 30°C. In this study, 78.26% color removal was observed after 150 min sonication time at 30°C. The color yield in the present study is higher than the yield obtained by Vankar and Shanker [47] at 30°C. In a study performed by Entezari and Sharif Al-Hoseini [12] 98% color removal was accomplished in a TI ww containing 50 mg L^{-1} MB, at 20 kHz frequency, at 120 W power, after 30 min sonication time at 30°C with 700 rpm agitation. In this study, 78.26% color removal was observed after 150 min sonication time at 30°C at not agitated conditions. The color yield in the present study is lower than the yield obtained by Entezari and Sharif Al-Hoseini [12] at 30°C as mentioned above. This could be attributed to

the differentiations in dyes present in TI to the operational conditions such as sonication duration, sonication frequency and to non stirred conditions of sonicated wastewater.

78% PHE R, 75% 4-MP, 70% 4-H and 65% 2-M-4-H polyphenols removals were observed after 150 min sonication time, respectively, at pH=7.0 and at 30°C (Table 5). 8% PHE R, 10% 4-MP, 6% 4-H and 5% 2-M-4-H increase in polyphenols removals were obtained after 150 min sonication time, respectively, at pH=7.0 and at 30°C, compared to the control (E=70% PHE R, E=65% 4-MP, E=64% 4-H, E=60% 2-M-4-H polyphenols after 150 min sonication time, at pH=6.98 and at 25°C). A significant linear correlation between polyphenols yields and temperature was observed (R2=0.83, F=13.95, p=0.01) (Table 5). 85% PHE R, 79% 4-MP, 74% 4-H and 72% 2-M-4-H polyphenols yields were found after 150 min sonication time, respectively, at pH=7.0 and at 60°C (Table 5). The contribution of temperatures on polyphenols removals were 15%, 14%, 10% and 12% for PHE R, 4-MP, 4-H and 2-M-4-H, respectively, after 150 min sonication time, respectively, at pH=7.0 and at 60°C, compared to the control (E=70% PHE R, E=65% 4-MP, E=64% 4-H, E=60% 2-M-4-H polyphenols after 150 min sonication time, at pH=6.98 and at 25°C). The maximum polyphenols removals were 85% PHE R, 79% 4-MP, 74% 4-H and 72% 2-M-4-H after 150 min sonication time, respectively, at pH=7.0 and at 60°C. A significant linear correlation between polyphenols removals and temperature was obtained (R2=0.87, F=14.70, p=0.01) (Table 5). The degradation of phenol occurs in the bulk liquid medium due to hydroxylation reaction induced by OH$^\bullet$ generated from cavitation bubble [23]. This is a consequence of low vapor pressure of phenol (due to which it does not evaporate into the cavitation bubble) and the hydrophilic nature of the phenol molecule. The interaction between radicals and phenol molecules becomes an important factor influencing the overall degradation. The scavenging phenomenon increases the sonodegradation of phenol. Moreover, the concentration of the radical scavenging species is another important factor affecting the degradation. The formation of OH$^\bullet$ and H_2 derived from sonolysis of H_2O in aqueous solution saturated with O_2 as an endpoint of inertial cavitation was examined. It should be pointed out that OH$^\bullet$, formed via H_2O sonolysis, can partly recombine yielding H_2O_2 which in turn reacts with H_2 to regenerate OH$^\bullet$ in (Equation 3,4) [23]:

$$OH^\bullet + OH^\bullet \quad \Leftrightarrow \quad H_2O_2$$

$$H_2O_2 + H^\bullet \quad \rightarrow \quad H_2O + OH^\bullet$$
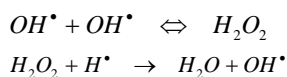
[40] found that ultrasound-assisted the hydroxylation of phenolic compounds, such as phenol, 4-methyl phenol, 4-hydroxyanisole, 2-naphthol, catechol, resorcinol, 3-t-butyl-4-hydroxyanisole, 3-methyl-4-hydroxyanisole, in aqueous solution in 12-18 h, at 200 kHz. In the present study, we agree with the results of Takizawa et al. (1996) in TI ww.

Conclusions

Low frequency (35 kHz) sonication proved to be a viable tool for the effective of COD$_{dis}$, color, polyphenols removals in TI ww. 96.70% COD$_{dis}$, 95.06% color, 94% PHE R, 89% 4-MP, 83% 4-H and 80% 2-M-4-H maximum removals were observed after 150 min sonication time and at 60oC. 98.13% COD$_{dis}$, 96.24% color, 95% PHE R, 92% 4-MP, 85% 4-H and 81% 2-M-4-H maximum yields were obtained

after 150 min sonication time and at 60oC. 99.37% COD$_{dis}$, 98.07% color, 96% PHE R, 93% 4-MP, 88% 4-H and 85% 2-M-4-H maximum removals were obtained after 150 min sonication time and at 60oC. Also, increasing temperature was positively effected in TI ww at sonication time.

The sonication process could prove to be less land-intensive, less expensive and require less maintenance than traditional biological treatment processes and other AOPs. Sonication technology can provide a cost-effective alternative for destroying and detoxifying refractory compounds in TI ww.

Acknowledgements

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