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Effect of sonication on the treatment of polycyclic aromatic hydrocarbons (PAHs) in a petrochemical industry wastewater and toxicity evaluations

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ABSTRACT

The effects of temperature, sparging of N_2(g) (15 and 30 min), H_2O_2 (100 mg/l, 500 and 2000 mg/l) and TiO_2 (0.1 mg/l, 0.5 mg/l, 10 and 20 mg/l) concentrations on the sonication of the petrochemical industry wastewater taken from the influent of the aeration tank in a petrochemical industry treatment plant was investigated. Experiments were performed at a sonication frequency of 35 kHz, at a power of 650 W, and at temperatures increasing from 25 °C to 30 °C and 60 °C. Increasing the temperature from 25 °C to 60 °C did not contribute to the total COD, poly aromatic hydrocarbons (PAHs) and TOC removals after 60 min of sonication time while a temperature of 60 °C increased the removals of the aforementioned parameters from 54% to 72% and 92% after 120 and 150 min of sonication times. 15 and 30 min N_2 sparging increased the PAH removals at short sonication times while no significant increases in PAH removals were observed after 150 min of sonication time at low temperatures. Similary, N_2 sparging did not significantly affect the PAH removals at high temperatures for all sonication times. Increasing the TiO_2 and H_2O_2 concentrations did not contribute to the PAH removals at 60 °C at all sonication times. Sonication alone without TiO_2 and H_2O_2 could provide higher PAH removals (92–98%) at 60 °C after 150 min sonication. The toxicity test performed with *Daphnia magna* showed that acute toxicity decreased significantly by 92–96% at the lowest TiO_2 concentration of 0.1 mg/l and at H_2O_2 and TiO_2 concentrations ≤ 100 and ≤ 0.1 mg/l, respectively.

Keywords: *Daphnia magna* toxicity assay; Petrochemical industry; Polycyclic aromatic hydrocarbons (PAHs); Sonication; N_2; H_2O_2; TiO_2

1. Introduction

Poly aromatic hydrocarbons (PAHs) are organic compounds widely distributed in the environment, formed by the incomplete combustion of organic materials during natural or antropogenic processes. They comprise a large group of compounds with two or more fused benzene rings that are less soluble in H_2O and less volatile with increasing molecular weigths. PAHs are highly hydrophobic, with low biodegradability in wastewater treatment plants [1–12]. PAHs are listed as US-EPA and EU priority pollutants, and their concentrations therefore need to be controlled in treated wastewater effluents [13]. Due to their toxic, mutagenic and carcinogenic properties the US-EPA classifies sixteen PAHs as priority pollutants [14].

Studies in recent literature showed that sonication may be a useful tool in degrading recalcitrant pollutants like PAHs. Sonochemical destruction of PAHs in the aqueous phase generally occurs as the result of imploding cavitation bubbles and involves several reaction pathways such as pyrolysis inside the bubble and/or

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at the bubble–liquid interface and hydroxyl radical-induced reactions at the bubble–liquid interface and/or in the liquid bulk [2–12,15,16]. David, found that naphthalene (NAP), phenanthrene (PHE), anthracene (ANT) and pyrene (PY) removal efficiencies varied between 93 and 95%, after a sonication time of 90 min in a sonicator with a power of 400 W and a frequency of 20 kHz [8]. Psillakis et al. found 99% removal efficiency for 0.01 μg/l of acenaphthalene (ACL), PHE and NAP at a power of 300 W and frequency of 24 kHz [17]. Laughrey et al. investigated the effects of DO, air and N_2(g) on the sonication of PHE, PY and ANT [12]. Maximum PAH removals were reached at the lowest DO (2 mg/l) air (2 l/h) and N_2(g) sparging (15 min) at 60 °C after 150 min of sonication time in a sonicator with a power of 300 W and a frequency of 20 kHz.

In Izmir-Turkey, the conventional technologies used in wastewater treatment systems do not completely remove the petrochemical residues which are then released, via treated effluent, into the environment. PAH residues have been frequently detected in rivers and lakes that receive sewage and industrial effluents supplied by those surface waters. Aerobic activated treatment systems are not equipped for PAH removal.

The recalcitrance of PAHs may play an important role in decreasing the COD removal efficiency in affected treatment systems. The literature survey indicated that no experimental studies have been done investigating the treatability and the toxicity of seventeen PAHs in a real petrochemical industry wastewater. Although, some studies aimed at increasing the biodegradation of some PAHs [NAP, PHE, ANT, PY and acenaphthalene (ACT)] with sonication have appeared, these have been limited to only a few of those generally present [3–5,9,17,18]. No study was found investigating the effects of experimental conditions [sonication time, temperature, N_2(g), H_2O_2 and TiO_2] on the sonication and toxicities of all the PAHs typically present in petrochemical industry wastewaters.

In this study, it was aimed to investigate the effects of temperature (30 °C and 60 °C), sparging of N_2(g) (for 15 and 30 min), H_2O_2 (100, 500 and 2000 mg/l) and TiO_2 (0.1, 0.5, 10 and 20 mg/l) concentrations on sonodegradation of seventeen PAHs, COD and TOC in a petrochemical industry wastewater. Furthermore, the acute toxicity was evaluated with *D. magna*.

2. Materials and methods

2.1. Sonicator and operational conditions

A Bandelin Electronic RK510 H sonicator was used for sonication of the petrochemical industry wastewater samples. Glass serum bottles in a glass reactor were filled to a volume of 50 ml with petrochemical wastewater after dosing with oxygen and hydrogen peroxide. They were then closed with teflon coated stoppers for the measurement of volatile compounds (evaporation) of the petrochemical wastewater. The evaporation losses of PAHs 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. The temperature in the sonicator was monitored continuously and was maintained at A constant of 30 and 60 °C. For ambient conditions the sonicator was not heated—it was used at 25 °C. All experiments were in batch mode using an ultrasonic transducer (horn type), which has an active acoustical vibration area of 19.6 cm^2, and a maximum input power of 650 W and a frequency of 35 kHz. Four sonication intensities (16 W/m^2, 37 W/m^2, 23.02 W/m^2 and 51.75 W/m^2) were chosen to identify the optimum intensity for maximum PAH removal. Samples were taken after 60, 120 and 150 min of sonication and were kept for a maximum of 15 min in a refrigerator at a temperature of +4 °C until the sonication experiments were begun.

H_2O_2 solutions were slurried in the reaction mixture with a pressured pump 10 min prior to sonication at a flow rate of 100 ml/min, and then stopped. The TiO_2 catalyst used in this study supplied by Degussa consisting of 78% anatase and 22% rutile which is low cost and is a relatively stable material. N_2(g) has a purity of 99% and was sparged to the samples prior the sonication for 15 and 30 min.

H_2O_2 and TiO_2 were used as OH radical scavengers for sonication. The amount of N_2(g), H_2O_2 and TiO_2 used in this study was chosen by taken into considerations the literature data [19,20] and the results of the preliminary studies [21–25]. The N_2(g) sparging, H_2O_2 and TiO_2 concentrations were adjusted as 15 and 30 min; as 100 mg/l, 500 and 2000 mg/l; 0.1 mg/l, 0.5 mg/l, 10 and 20 mg/l.

2.1.1. Source of the petrochemical wastewater

The petrochemical industry wastewater used in the sonication experiments was taken from the influent of the aeration tank of a petrochemical industry wastewater treatment plant. The samples were kept in a refrigerator at a temperature of +4 °C until tranferred to labora tory and experiments were begun.

2.2. Analytical methods

2.2.1. PAHs sample preparation and analysis

Samples to were filtered through a glass fiber filter (47 mm diameter) to collect particle-phase in series with a resin column (~10 g XAD-2) to collect dissolved-phase poylbrominated diphenyl ethers. Resin and H_2O filters were used ultrasonically extract the samples for 60 min with a mixture of 1/1 acetone/hexane. All extracts were analyzed for 17 PAHs including naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), flourene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[*a*]anthracene (BaA), chrysene (CHR), benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA) and benzo[*g,h,i*]perylene (BghiP) with a gas chromatograph (GC) (Agilent 6890 N) equipped with a mass selective detector (Agilent 5973 inert MSD) and a capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 mm) [17]. The physical and chemical properties of the PAHs studied were given in Table 1. The PAHs were identified on the basis of their retention times, target and qualifier ions and were quantified using the internal standard calibration procedure.

2.2.2. Limit of quantification and limit of detection of PAHs

The signal/noisy (S/N) values were taken into consideration for every PAHs compound in their lowest concentrations. The measured S/N ratios varied between 64 and 559. Limit of quantification (LOQ) is defined as the standard PAH concentration which is equal to 10 while the limit of detection was detected with the standard PAH concentration which is equal to 10. The LOD and LOQ data varied at between 0.909 and 1.908 and at between 1.175 and 5.201, respectively.

2.2.3. Experimental measurements

pH, T(°C), ORP, DO, BOD_5, COD_{total}, $COD_{dissolved}$, TSS, TVSS, Total-N, NH_3-N, NO_3-N, NO_2-N, Total-P, oil and TOC measurements were monitored following the Standard Methods 2550, 2580 and 5210 B, 5220 D, 2540 C, 2540 D, 4500-N, 4500-NH_3, 4500-NO_3, 4500-NO_2, 4500-P, 5520 and 5310 [26]. TOC was measured with Rosemount Dohrmann DC−190 high-temperature total organic carbon analyzer, Part #: 915–262, Serial #: 98176005, (Dohrmann Division Rosemount Analytical Inc). CA 95052−8007, 1994 [26].

2.2.4. D. magna *toxicity test*

Toxicity was tested using 24 h born *D. magna* as described in Standard Methods [26]. The analysis was carried out using 5 or 10 daphnids (<24 h old) introduced into the test vessel. A 24 h exposure is generally accepted as Standard for a *Daphnia* acute toxicity test. Test vessels were diluted (10, 30, 50, 75, 100%) with dilution water containing 10 mg/l KCl, 192 mg/l $NaHCO_3$,

Table 1
Physical and chemical properties of the PAHs studied in this work

PAHs	CAS-no	Molecular formula	MW (g/mol)	T_M (°C)	T_B (°C)	S_w (25°C) (mg/l)	VP (25 °C) (mm Hg)	H (25 °C) (atm m^3/mol)	log K_{OA} (25 °C)	log K_{OW}
NAP	91-20-3	$C_{10} H_8$	128	80	218	31	8.50 E-02	4.40 E-04	–	3.36
ACL	208-96-8	$C_{12} H_8$	152	93	280	16.1	6.68 E-03	1.14 E-04	6.34	3.94
ACT	83-32-9	$C_{12} H_{10}$	154	93	279	3.9	2.15 E-03	1.84 E-04	6.52	3.92
FLN	86-73-7	$C_{13} H_{10}$	166	115	295	1.69	6.00 E-04	9.62 E-05	6.9	4.18
PHE	85-01-8	$C_{14} H_{10}$	178	99	340	1.15	1.21 E-04	3.35 E-05	7.68[b]	4.46
ANT	120-12-7	$C_{14} H_{10}$	178	215	340	0.0434	2.67 E-06	5.56 E-05	7.71	4.45
CRB	86-74-8	$C_{12} H_{9N}$	167	246	355	1.8	7.50 E-07	1.16 E-07	8.03	3.72
FL	206-44-0	$C_{16} H_{10}$	202	108	384	0.26	9.22 E-06	8.86 E-06	8.76	5.16
PY	129-00-0	$C_{16} H_{10}$	202	151	404	0.135	4.50 E-06	1.19 E-05	8.81	4.88
BaA	56-55-3	$C_{18} H_{12}$	228	84	438	0.0094	2.10 E-07	1.20 E-05	10.28	5.76
CHR	218-01-9	$C_{18} H_{12}$	228	258	448	0.002	6.23 E−09	5.23 E-06	10.30	5.81
BbF	205-99-2	$C_{20} H_{12}$	252	168	–	0.0015	5.00 E-07	6.57 E-07	11.34	5.78
BkF	207-08-9	$C_{20} H_{12}$	252	217	480	0.0008	9.70 E-10	5.84 E-07	11.37	6.11
BaP	50-32-8	$C_{20} H_{12}$	252	177	495	0.00162	5.49 E-09	4.57 E-07	11.56	6.13
IcdP	193-39-5	$C_{22} H_{12}$	276	164	536	0.00019	1.25 E-10	3.48 E-07	12.43	6.7
DahA	53-70-3	$C_{22} H_{14}$	278	270	524	0.00249	1.00 E-10	1.23 E-07	12.59	6.75
BghiP	191-24-2	$C_{22} H_{12}$	276	278	>500	0.00026	1.00 E-10	3.31 E-07	12.55	6.63

Naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), flourene (FLN), phenanthrene (PHE), anthracene (ANT), carbozole (CRB), fluoranthene (FL), pyrene (PY), benz[*a*]anthracene (BaA), chrysene (CHR), benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP).

MW: Molecular weight, T_M: Melting point, T_B: Boiling point, S_w: Solubility in water, VP: Vapor pressure, H: Henry's law constant, log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient

53 mg/l $MgSO_4$ and 183 mg/l $CaSO_4 \cdot 2H_2O$. Results were expressed as the mortality percentage of the *Daphnids.* Immobile animals were determined as dead *daphnids.*

2.2.5. Statistical analysis

The regression analysis between *y* (dependent) and *x* (independent) variables was carried out using Windows Excel data analysis. An ANOVA test was performed in order to determine the statistical significance between *x* and *y* variables.

3. Results and discussion

3.1. Raw wastewater

Characterization of raw petrochemical industry wastewater taken from the influent of the aeration unit of the petrochemical industry wastewater reatment plant is given as the mean value of triplicate samplings: pH, ORP were recorded as 7.21 and 28.20 mV. DO, BOD_5, COD_{total}, $COD_{dissolved}$, Total-N, NH_3-N, NO_3-N, NO_2-N, Total-P, TSS, TVSS and oil concentrations were (mg/l); 1.78, 584, 1475, 1127, 15.40, 2.20, 1.80, 0.05, 10.60, 6.80, 310.3, 250.6 and 206, respectively, while the mean total PAH concentration was 1378 ng/ml.

3.2. Sonication experiments

Among the sonication intensities applied to the sonication process (16 W/m^2, 37 W/m^2, 23.02 W/m^2 and 51.75 W/m^2) in this study the most effective sonication intensity was found to be 51.75 W/m^2 (data not shown). The degradation of PAHs increased with increasing applied power. As the power increased, the number of collapsing cavities also increased, thus leading to enhanced degradation rates. Low frequency ultrasound was used in this study (35 kHz) because at this frequency the cavitation bubbles act like mechanical shredders by the formation of waters jets in the solution. The volume of the solution should be kept as small as possible, depending on the affective volume of sonicator in order to keep the solution in homogeneous turbulence while the ultrasound is on.

3.2.1. Effect of increasing temperature on removal of PAH, COD and TOC versus sonication time

Maximum 55.16%, 70.60% and 95.51% COD (Fig. 1 a), 55.65%, 80.94% and 92.90% total PAH (Fig. 1b), 54.37%, 70.01% and 92.3% TOC (Fig. 1c) removal efficiencies were observed at initial PAH, COD and TOC concentrations of 1378.77 ng/ml, 1027.43 mg/l and 620.81 mg/l, respectively, after 60, 120 and 150 min of sonication times. In this study, it was found that, generally, an increase in COD, PAH and TOC removal efficiencies was obtained as the sonication times increased from 60 to 150 min at all temperatures. Similar COD removals were obtained at 25°C (Control), 30°C and 60°C temperatures after 60 min of sonication time (Fig. 1a). Increasing the temperature did not contribute to the COD removals after 60 min sonication. A significant correlation between COD removals and increasing temperatures was not observed after 60 min (R^2 = 0.56, F = 4.56, p = 0.001). Similar COD removals (60%) were obtained at 25°C and 30°C while the COD removal increased up to 80% at 60°C after 120 min of sonication time. A significant correlation between COD removals and increasing temperatures was not observed after 120 min (R^2 = 0.34, F = 6.97, p = 0.001). 30°C and 60°C temperatures increased the COD removal efficiencies from 79% up to 88% and 95% after 150 min of sonication time (Fig. 1a). A strong correlation between COD removals and temperature was observed after 150 min sonication (R^2 = 0.88, F = 1.99, p = 0.001). It was found that total PAH concentrations decreased from initial 1378.77 to 138.68 ng/ml and from 1378.77 to 42.78 ng/ml at 30°C and 60°C, respectively, after 150 min of sonication time (Fig 1b). Increasing the temperature did not rise the PAH yields after 60 min sonication time while a temperature of 60°C increased the PAH removals from 54% to 72% after 120 min compared to the control at 25°C (Fig. 1b). The correlation between PAH removals and temperature increase was not significant for 60 and 120 min sonication with the exception of 60°C after 120 min sonication. The correlation between PAH yields and temperature is strong and significant for 150 min sonication time (R^2 = 0.79, F = 2.12, p = 0.001). The maximum TOC removal efficiencies were 78%, 88% and 92% in the control and in the samples at 30°C and 60°C, respectively, after 150 min of sonication time (Fig. 1c). The increasing of temperature did not affect the TOC removal after 60 min of sonication time while long sonication times such as 120 and 150 min increased the TOC removals. The effect of temperature is significant on the TOC removals at long sonication times (R^2 = 0.83, F = 2.92, p = 0.001). It can be concluded that increased temperatures raised the sonication yields at long sonication times. Increased temperatures most likely facilitated the bubble formation and consequently reduced the maximum temperature obtained during bubble collapse which lead to high PAH removals at long sonication times. For partitioning into the bubble, increased solution temperature allows PAH molecules to move faster into the cavitation bubble (i.e., increase diffusivity). At higher temperatures more molecules will benefit from the temperature enhanced diffusivity and this may result in increase in removal rates for PAHs at long sonication times.

The total COD and PAH removals found in this study were higher than the data obtained by Benabdallah

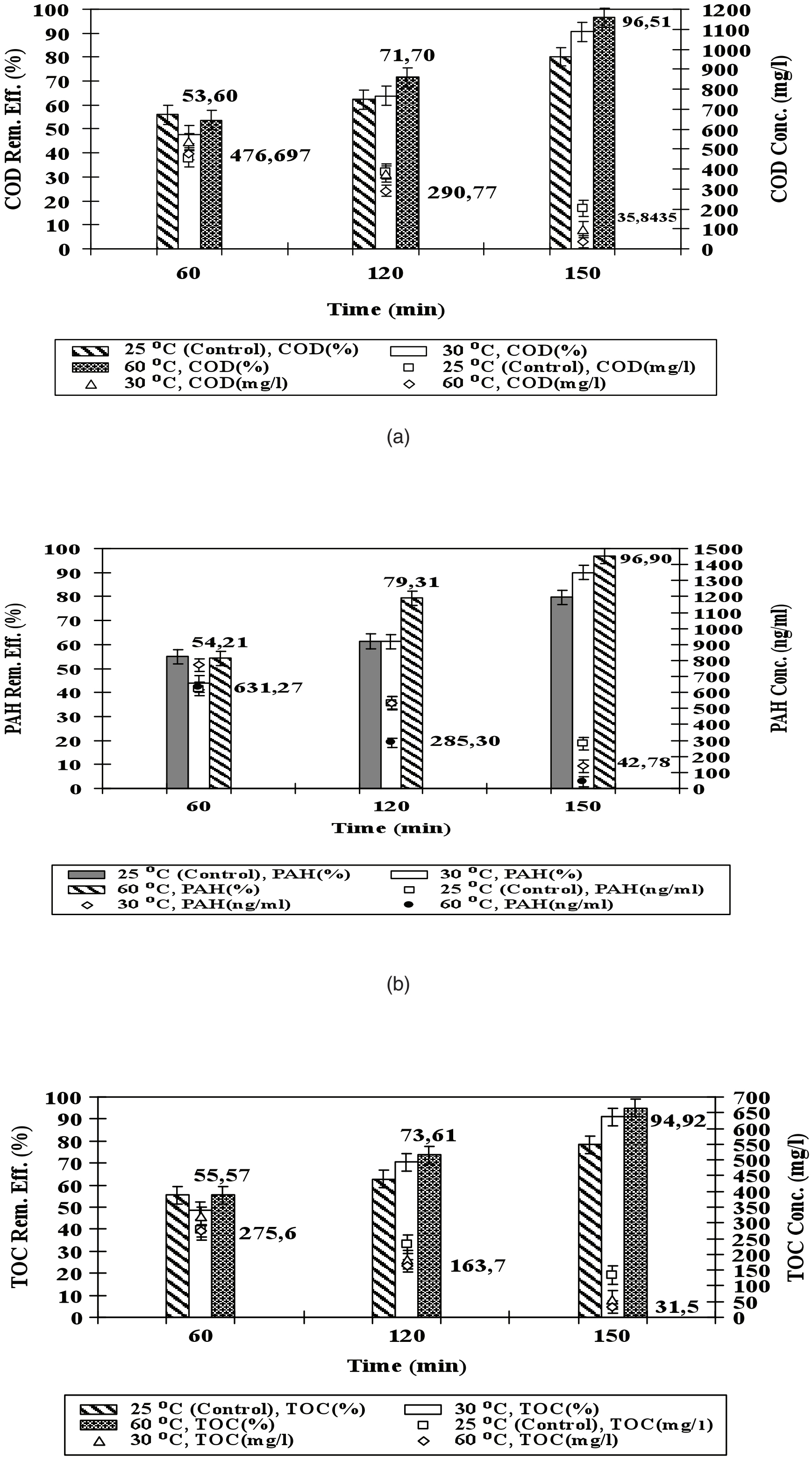
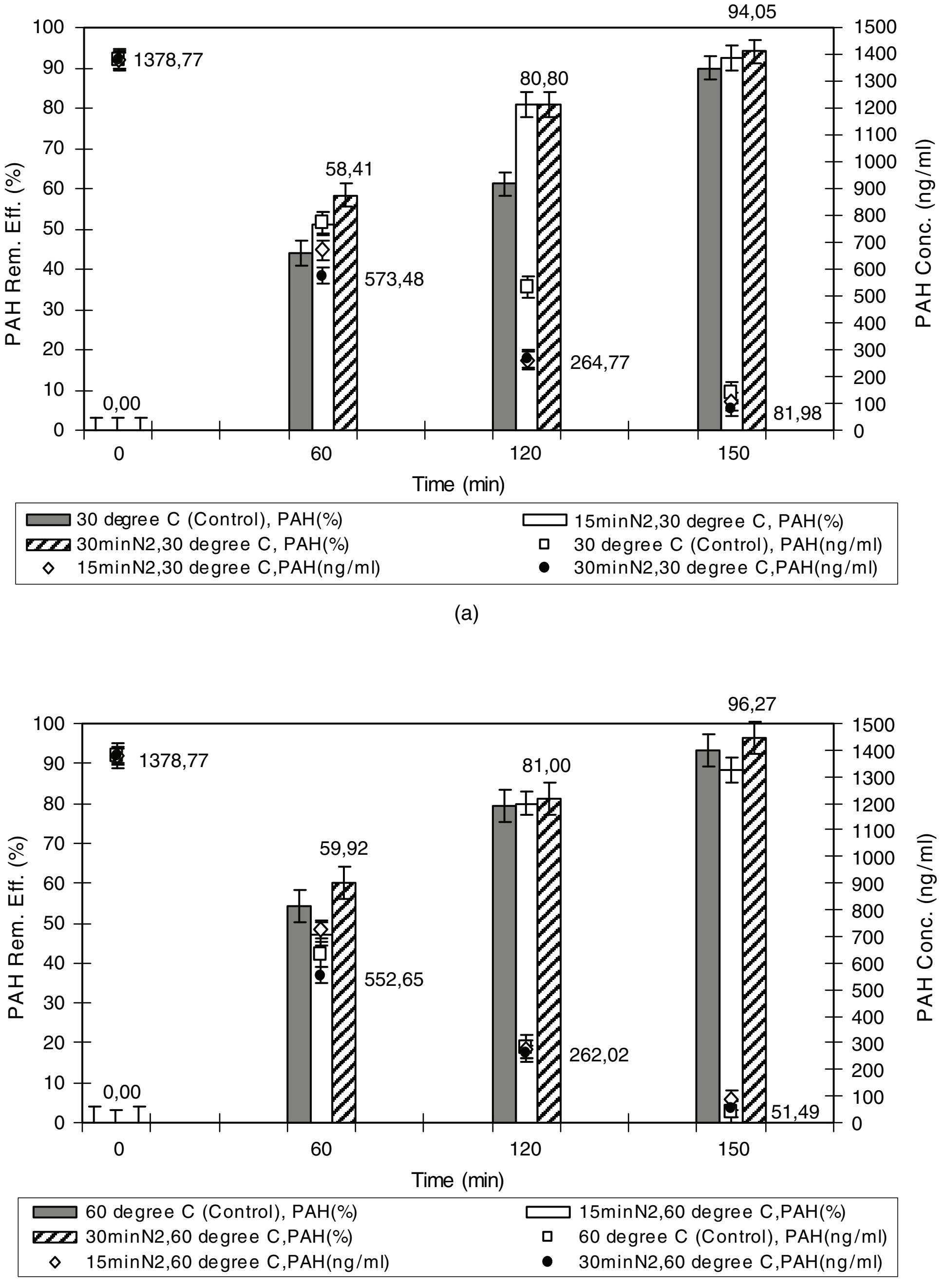


Fig. 1. Effect of increasing temperature on the (a) COD, (b) PAH and (c) TOC removal efficiencies in sonication time (frequency: 35 kHz, power: 650 W, $n = 3$, mean ± y error bar).



(a)

(b)

Fig. 2. Effects of 15 and 30 min N_2(g) sparging on the PAH removal efficiencies at (a) 30 °C and (b) 60 °C (frequency: 35 kHz, power: 650 W) ($n = 3$, mean ± y error bar).

El-Hadj et al. [9] and Laughrey et al. [12]. 86% COD and 31–50% total PAH removal efficiencies were found at an initial PAH concentration of 50 µg/l at 40 °C and 55 °C at ultrasonic powers of 70 and 150 W and ultrasound frequencies of 24 and 80 kHz, respectively, after 120 min of sonication time. On the other hand, in this study, the high PAH removals obtained at 60 °C after 150 min of sonication time were comparable with the PAH removals found by Psillakis et al. (E PAH = 91%) at 45 °C and at initial PAH concentrations varying between 150 and 450 µg/l after 120 min of sonication time [17].

3.2.2. Effect of $N_2(g)$ on the total PAH removal efficiencies versus sonication time and temperature

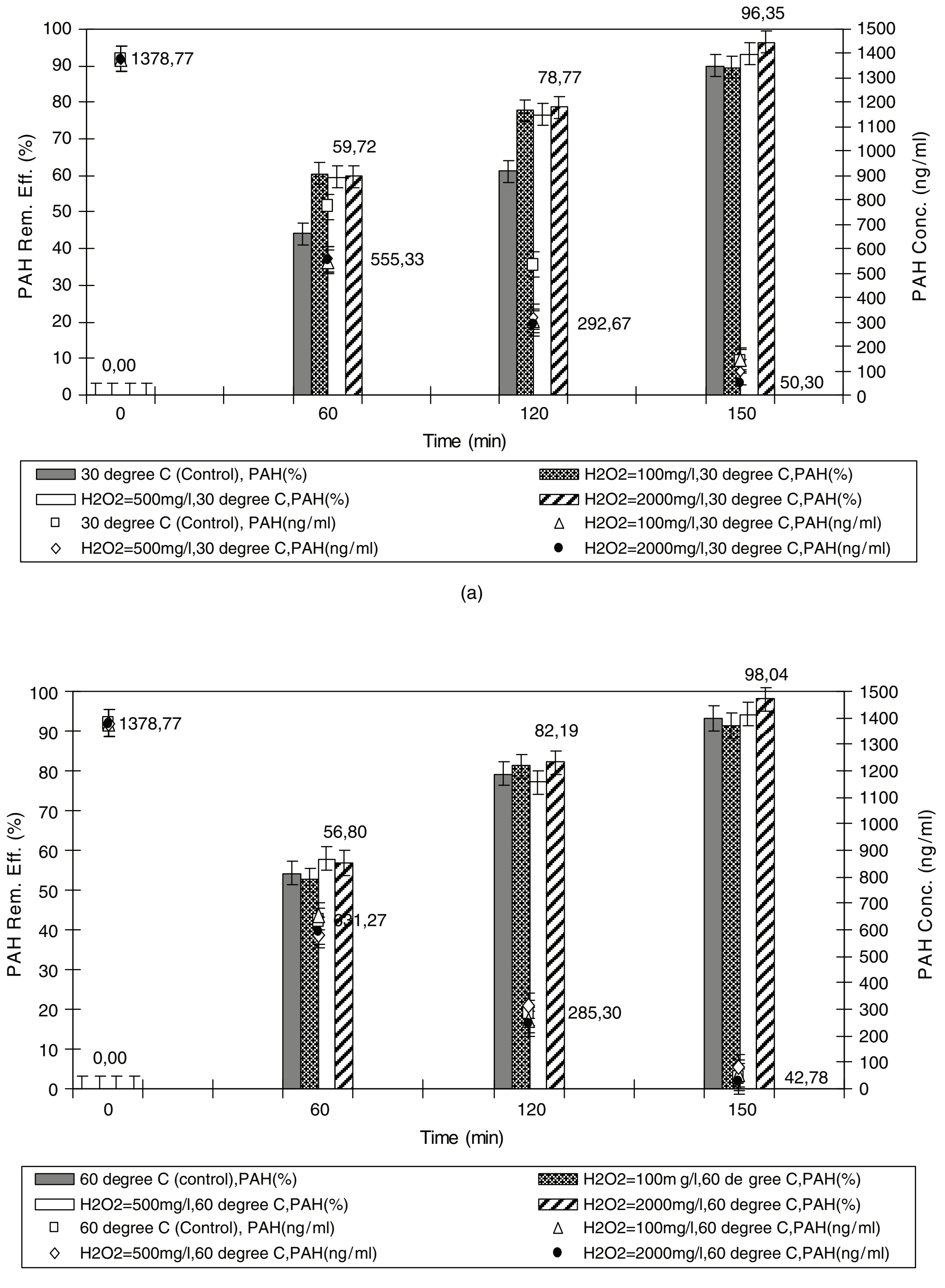
Maximum 88.33%, 91.27% and 88% and 93% total PAH removal efficiencies were found for 15 and 30 min of $N_2(g)$ sparging at 30 °C and 60 °C, respectively, after 150 min of sonication time (Fig 2b). 15 and 30 min N_2 sparging increased the PAH removals from 40% to 55% and from 60 up to 78% after 60 and 120 min of sonication times while no significant increases in PAH removals were observed after 150 min of sonication time compared to control at 30 °C (Fig. 2a). The contribution of 15 and 30 min $N_2(g)$ sparging on the PAH removals are significant at low sonication times (60 and 120 min) and temperature (30 °C) ($R^2 = 0.84$, $F = 1.09$, $p = 0.001$). 88% PAH removals were obtained in the control samples without N_2 sparging at 30 °C. Similary, N_2 sparging did not significantly affect the PAH removals compared to the control at 60 °C at all sonication times (Fig. 2 b). Therefore, the correlation between PAH removals and $N_2(g)$ sparging is not significant at all sonication times at 60 °C ($R^2 = 0.32$, $F = 14.34$, $p = 0.001$). The benefit of $N_2(g)$ sparging in enhancing the sonochemical activity is reported [12,27]. Sparging of N_2 changed the temperature within the cavitation site and the variations of chemical properties of the system resulting in high PAH removals [12]. On the other hand, it was reported that $N_2(g)$ act as nucleation sites for cavitation during sonication process The ultrasonic degradation of PAHs in aqueous solution is strongly affected by the average specific heat ratio of the gas dissolved in the solution, since the degradation is considered to proceed in local hot-spots formed by adiabatic collapsing bubbles [28]. In particular, it was reported that more effective decomposition occurs in Ar and O_2 compared with that of N_2, since the specific heat ratio of Ar and O_2 are the highest. However, it is considered that the initial decomposition of PAHs hardly occurs by direct pyrolysis in the cavitation bubble or near the interface of cavitation bubble [29]. This is due to dissociation of PAHs in water and low volatility of PAHs, which is considered to be scarcely concentrated near the interface of cavitation bubble. In N_2 sparging, the reaction of PAHs with hydroxyl and hydrogen radicals generated by pyrolysis of H_2O molecules is supposed to be predominant, leading to the decomposition of PAHs as reported by Psillakis et al. [17]. On the other hand, even though the maximum temperature and pressure in the cavitation bubble are lower in reactors containing N_2 than those in reactors containing Ar and O_2, many oxidants such as oxygen radical and hydroxyl radical are formed by pyrolysis of O_2 [30]. Similar to the results of Kojima et al. [28] 15 and 30 min N_2 sparging did not contribute to the PAH removals at 60 and 120 min sonication at a temperature of 60 °C with the exception of 15 and 30 min sonication after 120 min at 30 °C temperature. This could be attributed to the to benzene ring-opening reactions of PAHs and other intermediates as well as the degradation of by-products throughout N_2 sparging at low temperature.

In this study, high total PAH removals were found with $N_2(g)$ sparging in comparison with the other literature data. For example, in Laughrey et. al. 80% total PAH removal efficiencies were found at 20 °C for 30 min of $N_2(g)$ sparging at a sonication frequency of 20 kHz, and an ultrasonic power of 70 W, after 120 min of sonication time [12].

3.2.3. Effect of H_2O_2 concentration on the removal of PAH versus sonication time and temperature

Maximum 89.52%, 93.17% and 96.35% total PAH removal efficiencies were found at 30 °C for 100, 500 and 2000 mg/l H_2O_2 concentrations after 150 min of sonication time (Fig 3 a). Maximum 91.33%, 94.19% and 97.04% total PAH removal efficiencies were obtained at 60 °C for the same H_2O_2 concentrations, respectively (Fig. 3b). Increasing the H_2O_2 concentrations from 100 up to 2000 mg/l raised the PAH removals at the same ranges at all sonication times at 30 °C. 100, 500 and 2000 mg/l H_2O_2 concentrations increased the PAH removals from 42% (control, without H_2O_2) up to 69% and from 59% (control) up to 74% after 60 and 120 min, respectively, at 30 °C (Fig 3a). Although a correlation between PAH removals and H_2O_2 concentrations is observed, this relathionship is not significant at 30 °C after 60 and 120 min sonication ($R^2 = 0.80$, $F = 9.87$, $p = 0.001$). The PAH removals were similar (89–91%) in the control-without H_2O_2 and in the samples containing different doses of H_2O_2 after 150 min of sonication time at 30 °C (Fig 3a). Increasing the H_2O_2 concentrations from 100 mg/l up to 2000 mg/l did not significantly affect the PAH removals at 60 °C at all sonication times compared to the control (Fig 3b). The effect of increasing H_2O_2 concentrations on PAH removals is not significant at 60 °C ($R^2 = 0.40$, $F = 11.87$, $p = 0.001$). It can be concluded that the sonication alone could be used effectively to treat the PAHs from petrochemical industry wastewater at 30 and 60 °C after 150 min sonication. As the sonication time increased from 60 to 150 min the PAH removals increased from 52% to 91% at 60 °C in the control reactor.

H_2O_2 is an oxidizing agent and increases the extent of PAH removal through acustic cavitation [10,12]. The similar degradation degree in the control and in the presence of H_2O_2 may be attributed to the increased level of OH^o scavenging by the PAHs and by H_2O_2 itself. During the sonolysis of aqueous solutions, OH^o and H^o are generated by the thermolysis of water in the solution medium and can scavenge hydroxyl radicals produced. As concentration of H_2O_2 in the solution is increased, its OH^o scavenging effect increases causing decrease in degradation of PAHs. It was reported that at very high



(a)

(b)

Fig. 3. Effects of H_2O_2 cncentrations (100, 500 and 2000 mg/l) on the PAH removal efficiencies at (a) 30 °C and (b) 60 °C (frequency: 35 kHz, power: 650 W) ($n = 3$, mean ± y error bar).

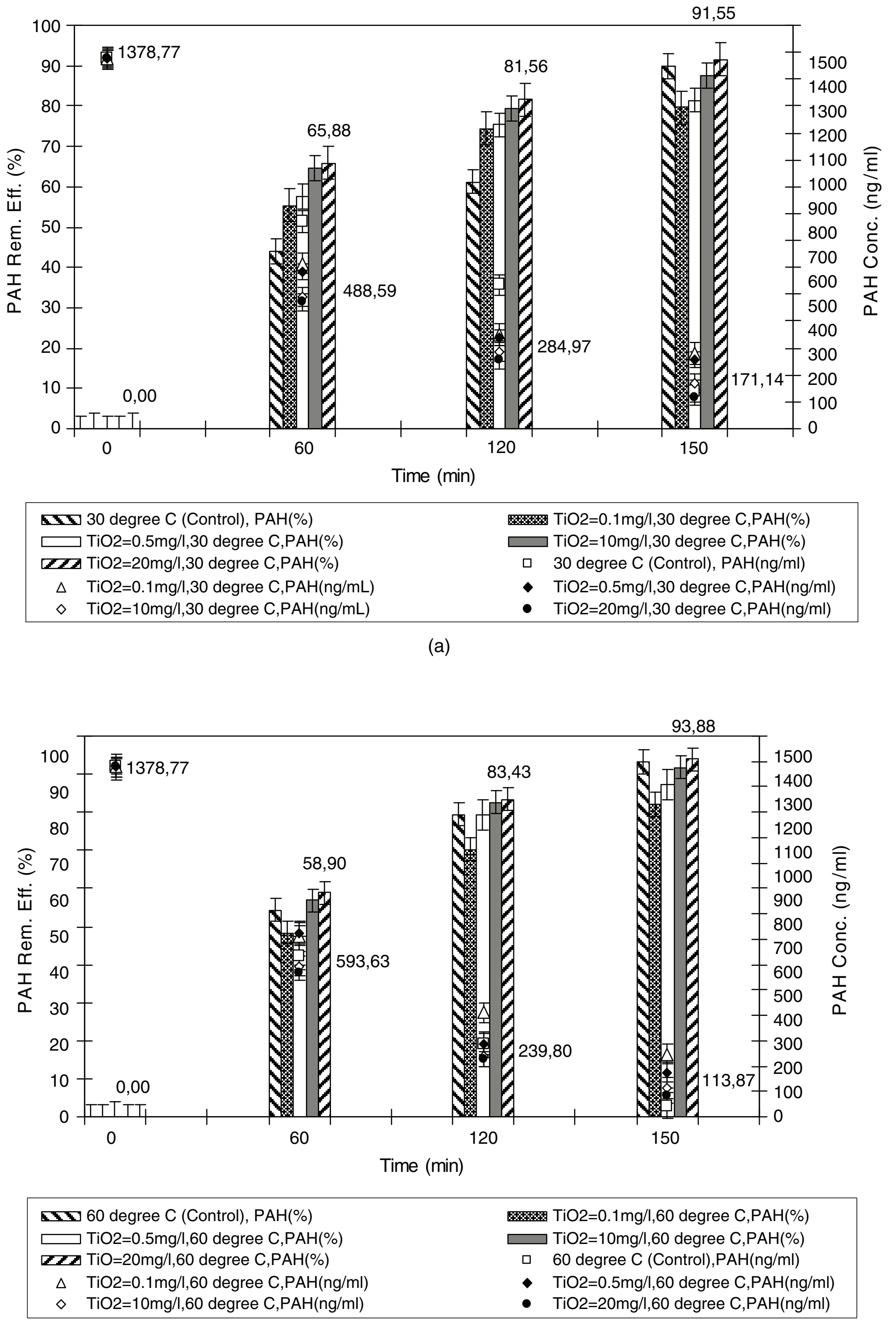


Fig. 4. Effects TiO_2 concentrations (0.1, 0.5, 10 and 20 mg/l) on the PAH removal efficiencies at (a) 30 °C and (b) 60 °C (frequency: 35 kHz, power: 650 W) (*n* = 3, mean ± y error bar).

H_2O_2 concentrations detrimental effects are observed, since the recombination reaction of OH° is more predominant and H_2O_2 acts as a scavenger for OH° [10,12]. The scavenging of free OH° becomes the dominant process at high H_2O_2 concentrations in the system, thereby lowering the ability of OH° to degrade PAHs.

3.2.4. Effect of TiO_2 concentration on the total PAH removal efficiencies versus sonication time and temperature

Maximum 79.58%, 81.47%, 87.59% and 91.55% total PAH removal efficiencies were measured at 30 °C for 0.1, 0.5, 10 and 20 mg/l TiO_2, respectively, after 150 min (Fig. 4a) while maximum 82.06%, 87.34%, 91.74% and 93.88% total PAH yields were obtained at 60 °C, respectively, after 150 min (Fig. 4b). Increasing the TiO_2 concentrations from 0.1 to 20 mg/l increased step-wise the PAH removals from 40% to 62% and from 58% up to 82% after 60 and 120 min, respectively, at 30 °C compared to the control without TiO_2 (Fig. 4a). A significant correlation between PAH yields and increasing TiO_2 concentrations was observed at low sonication times (60 and 120 min) and temperature (30 °C) (R^2 = 0.89, F = 2.02, p = 0.001). Similar PAH yields were obtained in the control-without TiO_2 and in the samples containing different TiO_2 concentrations after 150 min of sonication time at 30 °C (Fig 4a). The contribution of increasing TiO_2 concentrations on PAH removals was not significant at long sonication times (R^2 = 0.38, F = 11.78, p = 0.001). The PAH yields were similar in the control and in samples containing TiO_2 at all sonication times studied at 60 °C (Fig. 4b). The PAH removals were at between 51–52%, 77–78% and at between 87–90% after 60, 120 and 150 min of sonication times, respectively, at 60 °C. Although increasing of TiO_2 raised the PAH yields the contribution of increasing TiO_2 concentrations on the PAH destructions was not significant at high temperature in all sonication times (60 °C) (R^2 = 0.45, F = 9.55, p = 0.001). Sonication alone provided approximately 96% PAH removals at 30 and 60 °C after long sonication time (150 min).

The TiO_2 particules acting as sonocatalyst and shock waves of sonication induce some oxygen atoms of its surface via holes, resulting in decomposition of PAHs in petrochemical industry wastewaters. The increase of TiO_2 catalyst did not further decompose the PAHs in aqueous solution. Excessive TiO_2 particles sometimes result in mutual screens among TiO_2 particles, which not only destruct the PAHs molecules, but also reduce the sonocatalytic activity of TiO_2.

In this study, the identification of seventeen PAHs was performed. The maximum removal efficiencies obtained for each individual PAH are shown in Table 2. The PAHs with all kind of benzene rings exhibited high removal yields at long sonication times. PAHs with low benzene rings (FLN, CRB and FL) and PAHs with high benzene rings (BaP, IcdP and BghıP) exhibited high removal efficiencies (90%, 82% and 80% for PAHs with 3–4 rings; 77%, 78% and 73 for PAHs with 5–6 rings) at 25 °C under ambient conditions after 150 min of sonication (Table 2). The yields for the same PAHs were 90%, 80% and 82% (low benzene rings) and 90%, 85% and 91 (high benzene rings) respectively, at 30 °C after 150 min. The degradation percentages of the all PAHs increased to 91–92% at 60 °C after 150 min. Increasing the temperature improved the yields of the all PAHs. In this study, it was found that the efficiency for the removal of PAHs is not in relation to the number of aromatic rings contrarily to the findings of Laugrey et al. and Pathak et al. [12,14]. They found that PAHs with lower weights were biodegraded more rapidly than the PAHs with high weights. In our study, the PAH removals was not decreased from the PAHs with high benzene rings to the PAHs with low benzene rings. It was found that the sonolytic degradation of PAHs is not depending on the length of the carbon chain. The heavily PAHs are sono-degraded as high as the lower PAHs. The ANOVA test statistics showed that a weak correlation between PAH yields and the molecular weights and this correlation was not significant (R^2 = 0.39, F = 11.34, p = 0.001).

Although, sparging of N_2 for 30 min did not contribute to the yields of FLN, CRB, FL BaP, IcdP and BghıP PAHs after 60 and 120 min of sonication time at 60 °C, the removals of these PAHs increased significantly after 150 min of sonication time (Tables 1 and 2). These removals increased from 51–59% up to 94–97% after sonication time as long as 150 min. A significant correlation between PAH removals and long sonication time was observed when 30 min N_2 is sparged at 60 °C (R^2 = 0.86, F = 1.98, p = 0.001). It is important to note that the PAHs aforementioned were removed with high yields (95–96%) in the control-without N_2 at 60 °C after 150 min. Some physicochemical properties such as low solubility and Henry's Law constant and high octanol-water coefficient in PAHs with high benzene rings did not affect inversely the sonodegradation of these compounds (Tables 1 and 2). Contrarily to the findings of Psillakis et al. [15] in this study the PAHs with high molecular weights and octanol-air coefficients did not exhibit low yields with sonication process at 60 °C after 150 min. Furthermore, low solubility and high octanol-air coefficients of PAHs with long benzene rings such as IcdP, DahA and BghiP removed with high yieds as successufully as the PAHs with low benzene rings. This showed that the sono-degradation of all kind of PAHs are independent from their physicochemical properties. The ANOVA test statistics showed that the correlation between PAH yields and physichechemical properties is weak and not significant (R^2 = 0.29, F = 13.49, p = 0.001). On the other hand in this study it was found

Table 2
Maximum removal efficiencies in seventeen PAHs in the effluent of the sonication experiments at 30°C, 60°C for N_2(g) sparging and increasing H_2O_2 and TiO_2 concentrations (frequency: 35 kHz, power: 650 W, n = 3, mean ± y error bar)

PAHs	Maximum PAH Removal Efficiencies (%)														
	Ambient 25°C	Temperature (°C)			N_2(g) (min)				H_2O_2 (mg/l)				TiO_2 (mg/l)		
		30°C	60°C	60°C[a]	N_2 – 30			60°C[b]	H_2O_2 – 2000			60°C[c]	TiO_2 – 20		
	t-150	*t*-150	*t*-150	*t*-150	*t*-60	*t*-120	*t*-150	*t*-150	*t*-60	*t*-120	*t*-150	*t*-150	*t*-60	*t*-120	*t*-150
NAP	87.04	87.37	92.48	98.48	26.25	65.48	98.12	98.48	30.28	73.82	99.08	97.98	31.88	75.16	96.99
ACL	81.09	90.11	91.12	97.12	56.34	76.15	96.43	98.12	54.44	78.77	98.26	97.12	56.52	80.07	94.30
ACT	79.35	86.05	90.16	93.16	55.24	74.68	92.77	94.16	53.70	77.70	96.48	94.16	55.78	79.01	95.47
FLN	90.86	90.44	90.00	96.00	55.98	75.67	95.04	96.00	54.19	78.42	97.59	96.00	52.28	78.72	92.08
PHE	64.86	88.24	90.34	96.34	51.69	79.88	95.46	96.34	51.24	74.14	97.79	96.34	53.30	75.50	92.75
ANT	83.52	80.20	91.72	91.72	59.35	70.24	89.74	92.72	59.43	81.66	95.00	91.72	58.53	82.91	94.88
CRB	82.46	80.85	90.85	97.85	58.86	79.57	97.33	97.85	58.11	81.19	98.70	97.85	58.21	82.45	95.74
FL	80.25	82.03	90.41	95.41	58.48	76.06	94.31	95.41	55.86	80.84	97.23	95.41	53.96	80.10	90.92
PY	83.73	83.69	90.69	95.69	58.76	79.43	94.66	94.69	56.04	81.10	97.40	95.69	59.14	82.36	91.47
BaA	82.52	81.46	90.24	92.24	59.87	80.94	90.39	92.24	54.77	82.15	95.32	92.24	58.87	78.39	94.99
CHR	88.94	84.89	90.35	95.35	59.71	81.72	94.24	96.35	59.67	83.00	97.19	95.35	58.77	80.25	94.32
BbF	66.03	67.03	86.21	86.21	59.86	80.91	82.91	86.21	56.76	82.13	91.68	86.21	53.86	83.38	95.80
BkF	62.62	83.66	88.17	93.17	59.86	82.91	91.53	93.17	53.76	78.13	95.87	93.17	60.86	84.38	92.92
BaP	77.74	84.68	91.77	97.77	59.91	80.99	97.24	98.77	56.79	83.18	98.66	97.77	58.89	83.43	95.59
IcdP	78.72	90.16	91.98	97.98	59.83	78.88	97.49	97.18	57.74	82.11	98.78	97.98	55.84	81.36	96.00
DahA	50.2	86.88	96.60	96.60	59.57	80.53	95.79	96.60	56.57	84.87	97.95	96.60	50.67	81.11	93.28
BghıP	73.77	85.50	91.45	96.45	59.88	80.94	95.60	96.45	56.77	80.15	97.85	96.45	48.87	83.40	92.97
MEAN	78.60	88.54	91.21	95.21	56.44	77.94	94.06	95.21	54.48	80.20	97.11	95.21	54.48	80.70	94.15

t-60 ; *t*-120 ; *t*-150 = PAH removal efficiencies after 60, 120 and 150 min sonication (%); N_2 – 30 = 30 min N_2(g) sparging at 60°C; H_2O_2 – 2000 = 2000 mg/l H_2O_2 concentration at 60°C; TiO_2 – 20 = 20 mg/l TiO_2 concentration at 60°C; a, b, c: Control samples at 60°C.

that the sonication alone provided high removals both in PAHs with high and low benzene rings at 60 °C after 150 min. A strong correlation between PAH removals in the samples with N_2 and without N_2 (control) was obtained at 60 °C after 150 min sonication ($R^2 = 0.82$, $F = 2.09$, $p = 0.001$).

Although, the yields for ACL, ANT, BkF and DahA PAHs were maximum (95–97%) at a H_2O_2 concentration of 2000 mg/l, the PAH yields obtained in the control reactor without $H_2O_{2\,,}$ were similar (92–98%) at 60 °C after 150 min sonication (Table 2). The ANOVA test statiscs showed that the correlation between the PAH yields in control and in the samples containing H_2O_2 is weak and not significant ($R^2 = 0.32$, $F = 12.07$, $p = 0.001$). On the other hand a weak correlation between PAHs with low and high nenzene rings was observed and this correlation was not significant ($R^2 = 0.46$, $F = 7.99$, $p = 0.001$). The results of this study showed that the PAHs with low and high benzene rings were sono-degraded successfully at long sonication times (150 min) although some literatures stated that sonication process is only usefull to treat the PAHs with low benzene rings [12,15].

Although, 20 mg/l TiO_2 concentration did not contribute to the PAH removals after 60 and 120 min, a long sonication time (150 min) increased all the individual PAH yield to 92–93% at 60 °C. A significant correlation between PAH yields and long sonication time (150 min) was obtained in the samples containing 20 mg/l TiO_2 ($R^2 = 0.96$, $F = 0.94$, $p = 0.001$). The physicochemical properties of PAHs with high benzene rings did not affect the removal efficiencies through sonication ($R^2 = 0.26$, $F = 13.68$, $p = 0.001$) (See Tables 1 and 2). High PAH removals was obtained in more hydrophobic PAHs such as BkF, BaP, IcdP, DahA and BghiP although they have low solubility, vapor pressure and low Henry's law constants. The individual PAH yields in the control reactor were also comparably higher (86–98%) with 20 mg/l TiO_2 after 150 min sonication at 60 °C.

The PAH yields obtained in this study agree with the data obtained by Psillakis et al. (2004) for the PAHs NAP (E = 92.2%), ACL (E = 93.9%) and PHE (E = 92.9%) after 120 min sonication time [15]. The removal efficiencies obtained for PY, PHE and ANT PAH also were higher than the results found by Laughrey et. al. (79% for PY, 90% for PHE and 91% for ANT) after 160 min at 60 °C [12].

3.3. Specific energy (SE) and cost evaluation

Economic efficiency and energy balance calculations are important tools for performing the cost-benefit analysis of a sonication process. The COD removal efficiency during sonication was a good indicator of sonicator yield. Since the reaction time and the applied sonic power are the major parameters influencing the sonication process, it was defined an energy parameter which is called the specific energy and it is obtained by dividing the energy given into the heterogeneous system by the mass of total COD initially present. The specific energy (SE) input into the system should be sufficient to guarantee a good COD removal improvement. Theefore, the energetic calculation was based on the total energy requirement for COD removal yield achieved by sonication. SE was determined for each treatment by using input power (P), treatment time (t), sample volume (V) and initial COD concentrations (S_0) in Eq. (1) [9].

$$\text{SE (kJ/kg COD}^1) = \{[P_{(w)} \times t_{(s)}]/[V_{(L)} \times \text{COD}_0\ (\text{g/l})]\} \quad (1)$$

The SE required to remove 1 kg of COD was calculated as 0.32 kJ / kg COD for sonication by assuming the operational conditions (P, t, V and So concentrations) as 560 W, 150 min, 50 ml and 1200 mg/l,respectively. With this SE it is possible to achieve a PAH removal efficiency as high as 95% in control reactor without $N_{2,}$ H_2O_2 and TiO_2 additions. The SE and energy consumption were equal to 0.09 kWh/kg COD and to 0.009 kWh /m^3 water, respectively. The total cost of consumed energy during the sonication was investigated by considering that the price of electricity was € 0.57 per kWh for Turkey in 2010. Therefore, the corresponding energy cost is around € 0.051 kg /COD in a m^3 water. In fact, a wide variety of parameters may interfere with economic efficiency. Some of the examples considered may be investment costs, personnel costs, operating and maintenance costs. However, most of the above mentioned parameters were not considered in this study because we focused on the exploitation costs. In this regard, it must be pointed out that these results are obtained with the laboratory scale devices with low energetic performances with respect to the full scale module applications. For a full-scale system, the costs strongly depend on the flow rate of the wastewater on the configuration of the sonicator (frequency, power, sonication intensity) as well as the nature of the effluent. In this study, the costs of reagents (1 m^3 N_2 = € 0.25; 1 kg H_2O_2 = € 0.11 and 1 kg TiO_2= € 0.56) was € 2.95 /m^3 water for the same COD removals (E = 96%) found by the control sonicator without reagents. Therefore, if sonication alone is used to destructe the PAHs the energy cost is around € 0.051 kg/COD to treat 1 m^3 of petrochemical industry wastewater.

3.3.1. The effect of the sonication process on the acute toxicity removal efficiencies

After sonication experiments, the acute toxicity measurements were conducted with *D. magna* (Table 3). The EC50 values (the effective concentrations caused

Table 3
Acute toxicity values [EC_{50}] of the petrochemical industry wastewater after sonication performed with *Daphnia magna* (frequency: 35 kHz, power: 650 W, $n = 3$, mean ± y error bar, 99% confidence limits: SD = 0.99 – 1.22; $\alpha = 0.05$; T values: 0.01 – 0.04)

Sets	Conditions	25 (°C)							
		EC_{50}	EC	EC					
		0 min		60 min.		120 min		150 min	
1	Ambient (25 °C)	342.56		EC_{45} = 70.76		EC_{28} = 65.08		EC_{13} = 11.60	
		30 (°C)				60 (°C)			
		EC_{50}	EC			EC_{50}	EC		
		a	b	c	d	a	b	c	d
2	Raw wastewater	342.56	EC_{45} = 53.76	EC_{28} = 67.08	EC_{13} = 11.60	342.56	EC_{46} = 71.51	EC_{29} = 14.54	EC_{4} = 5.38
3	15 min N_2(g)	342.56	EC_{38} = 60.41	EC_{24} = 20.21	EC_{12} = 12.21	342.56	EC_{24} = 60.41	EC_{12} = 17.95	EC_{7} = 12.60
	30 min N_2(g)	342.56	EC_{27} = 41.05	EC_{11} = 17.37	EC_{3} = 12.23	342.56	EC_{18} = 47.47	EC_{7} = 27.01	EC_{3} = 0.30
4	H_2O_2 = 100^e	342.56	EC_{18} = 74.61	EC_{10} = 37.20	EC_{3} = 1.19	342.56	EC_{11} = 75.09	EC_{5} = 29.66	EC_{2} = 0.43
	H_2O_2 = 500^e	342.56	EC_{22} = 47.15	EC_{10} = 22.70	EC_{4} = 1.33	342.56	EC_{23} = 68.20	EC_{10} = 79.07	EC_{8} = 18.81
	H_2O_2 = 2000^e	342.56	EC_{50} = 168.53	EC_{50} = 80.56	EC_{50} = 12.43	342.56	EC_{50} = 259.94	EC_{50} = 92.74	EC_{50} = 7.26
5	TiO_2 = 0.1^e	342.56	EC_{23} = 43.18	EC_{10} = 46.95	EC_{4} = 9.88	342.56	EC_{23} = 77.06	EC_{16} = 64.94	EC_{10} = 53.50
	TiO_2 = 0.5^e	342.56	EC_{45} = 101.85	EC_{32} = 30.74	EC_{20} = 21.36	342.56	EC_{45} = 127.94	EC_{40} = 36.27	EC_{30} = 18.46
	TiO_2 = 10^e	342.56	EC_{50} = 49.01	EC_{48} = 35.73	EC_{22} = 17.17	342.56	EC_{48} = 92.12	EC_{45} = 51.68	EC_{32} = 9.82
	TiO_2 = 20^e	342.56	EC_{50} = 30.80	EC_{42} = 20.81	EC_{40} = 13.35	342.56	EC_{50} = 49.12	EC_{48} = 31.68	EC_{50} = 10.96

EC_{50} = (ng/ml) PAH concentration affecting the half of the *Daphnia magna* number; EC = (ng/ml) PAH concentration affecting the certain amount of *Daphnia magna* number;
a, b, c, d = 0, 60, 120 and 150 min sonication times; e: concentration (mg/l).

decreases of 50% in *D. magna* number) of the petrochemical industry wastewaters decreased from initial EC_{50} = 342.56 ng/ml to EC_{13} = 11.60 ng/ml at 25 °C in the control samples after 150 min of sonication time (Table 3). This reduction is the maximum acute toxicity removal (E = 74%) obtained when sonication was used alone without other additives in ambient conditions. EC_{50} = (ng/ml) PAH concentration affecting the half of the *D. magna* number; EC = (ng/ml) PAH concentration affecting the certain amount of D. magna number; *a*, *b*, *c* , *d* = 0, 60, 120 and 150 min sonication times; *e* : concentration (mg/l)

The maximum acute toxicity removals were 74% and 92% at 30 °C and 60 °C, respectively, after 150 min sonication. The EC_{50} values decreased from 342.56 ng/ml to EC_3 = 12.23 ng/ml and EC_3 = 0.30 ng/ml when the samples was sparged with N_2 for 30 min at 30 °C and 60 °C after 150 min of sonication time (Table 3). The reason for the decrease in EC values after sonication can be explained by the decrease of PAH toxicity to the *D. magna* after sonication. The EC_{50} value (the PAH concentration affecting the half of the *D. magna* number) decreased after sonication since the PAHs was removed by this process and the remaining PAHs at low concentrations affect less number of *D. magna* ($\alpha = 0.05$; T values: 0.01–0.04). For example the EC_{50} value decreased from 342.56 mg/l value to EC_3 = 0.30 mg/l after 30 min N_2 sparging at 60 °C and 150 min sonication. The acute toxicity was decreased 16 times after sonication. Therefore, the low PAH concentrations in petrochemical wastewater caused low mortality and inhibitions in *D. magnas*. The maximum acute toxicity removals were approximately 92% at the lowest TiO_2 concentration of 0.1 mg/l at 30 °C after 150 min of sonication. H_2O_2 and TiO_2 concentrations >100 and >0.1 mg/l decreased the acute toxicity removals by hindering the sonication process.

4. Conclusions

Low frequency (35 kHz) sonication proved to be a viable tool for the effective degradation of PAHs in aqueous solutions. High removals were obtained in PAHs with high benzene rings. High temperatures such as 30 °C and 60 °C increased the COD removals from 79% to 88% and to 95% after 150 min compared to the control (25 °C). The control without H_2O_2 and samples containing H_2O_2 exhibited similar PAH removals (89–91%) after 150 min at 30 °C. Sonication alone could be used to treat the PAH removals at 30 °C and 60 °C after 150 min resulting in maximum total PAH removals of 89–92%. As the temperature increased to 60 °C the acute toxicity removal increased. 30 min N_2 sparging increased the acute toxicity removal. Increasing the H_2O_2 concentration did not contribute to acute toxicity removal. The maximum acute toxicity removal was obtained at the lowest H_2O_2 concentration at 60 °C with long sonication times. The matrix for the maximum acute toxicity removal was N_2 sparging for 30 min, 100 mg/l H_2O_2 and 0.1 mg/l of TiO_2 concentrations at 30 and 60 °C, respectively for >150 min sonication times.

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