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Removals of PAHs and acute toxicity via sonication in a petrochemical industry wastewater

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ABSTRACT

The effects of ambient conditions (25 °C), increasing sonication time (0–150 min), temperature (30–60 °C), dissolved oxygen (DO, 2–10 mg L^{-1}) and hydrogen peroxide (H_2O_2, 100–2000 mg L^{-1}) concentrations on the removal of polycyclic aromatic hydrocarbon (PAH) and destruction of toxicity in a petrochemical industry wastewater in Izmir (Turkey) were investigated. The maximum PAH removals were 80.2%, 91%, 98.5% and 98% at 25 °C, 60 °C, DO concentration of 6 mg L^{-1} and H_2O_2 concentration of 2000 mg L^{-1}, respectively, after 150 min sonication. Sonication alone provides PAH removals varying between 88% and 92% without DO and H_2O_2 at 30 °C and 60 °C after 150 min sonication. The *Daphnia magna* acute toxicity decreased significantly from 342.6 ng mL^{-1} to 5.4 ng mL^{-1}, to 0.7 ng mL^{-1}, and to 0.4 ng mL^{-1}, respectively, as the temperature, the DO and the H_2O_2 concentrations were increased. The PAH sonodegradation appeared to be pseudo first order in PAHs naphthalene (NAP), acenaphthylene (ACL), phenanthrene (PHE), pyrene (PY) and benz[*b*] fluoranthene (BbF) ($k = 0.026\ \text{min}^{-1}$, $0.024\ \text{min}^{-1}$, $0.017\ \text{min}^{-1}$, $0.015\ \text{min}^{-1}$ and $0.011\ \text{min}^{-1}$, respectively). The main mechanism of PAH sonodegradation appears to be pyrolysis.

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1. Introduction

PAHs are listed as US-EPA and EU priority pollutants, and their concentrations, therefore, need to be controlled in treated wastewater effluents [1,2]. Due to their toxic, mutagenic and carcinogenic properties the US-EPA classifies 16 of these PAHs as priority pollutants [1,2]. Recent studies have shown that sonication may be a useful tool for degrading the aqueous pollutants [3–6]. The sonication process is capable of effectively degrading target compounds including chlorophenols, chloroaromatics and PAHs present in dilute solutions, typically in the micro and nano ranges. The process does not require the use of additional chemicals commonly employed in several oxidation processes, thus again reducing costs.

David [5] 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. Psillakis et al. [7] reported a 99% removal efficiency for 0.01 μg L^{-1} of acenaphthalene (ACT), PHE and NAP at a power of 300 W and frequency of 24 kHz. Benabdallah El-Hadj et al. [4] found 57% NAP, 40% PY and 45% total COD removal efficiencies in a sonicator with a power of 70 W and frequency of 20 kHz. Taylor et al. [8] investigated the sonication of PAHs, namely ANT, PHE and PY. 46%, 20% and 50% removal efficiencies, respectively, were found at a power of 600 W and a frequency of 20 kHz. Laughrey et al. [9] investigated the effects of DO, air on the sonication of PHE, PY and ANT. They found removals of these PAHs as high as 80–90% as the DO concentration, air and N_2(g) purges were increased from 1 mg L^{-1} to 5 mg L^{-1} and from 2, 4 mL min^{-1} up to 3, 6 mL min^{-1}.

When sonolysis of water occurs, it leads to the formation of the non-specific oxidative species $OH^{\bullet}$. The ultrasonic degradation of hydrophobic organics such as PAHs can occur when they penetrate to the surrounding of the hot heart of the cavitation bubble being pyrolyzed, burnt and/or ionized in the plasma core [10,11]. The literature data concerning the sonodegradation of PAHs is scarce and the results are contradictory. Two mechanisms have been proposed to account for sonolytic degradation: (i) oxidation by $OH^{\bullet}$ [8,9] and (ii) pyrolytic decomposition [7].

In Izmir, Turkey, petrochemical plant wastewaters are treated with conventional activated sludge systems. Since such systems are unable to completely remove the main PAHs present (ca. 17) these are released into receiving bodies. Although some studies aimed at increasing the degradation of some PAHs (NAP, PHE, ANT, PY and ACT) with sonication have appeared, these have been limited to only a few of those generally present (3–5) [4,7,12,13]. No study was found investigating the effects of operational conditions such as sonication time, temperature, DO and H_2O_2 on the sonication of a petrochemical industry wastewater. Furthermore, the effects of the operational conditions on the removal of acute toxicity has not been determined for a petrochemical industry wastew-

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ater. Thus, in this study our aim was to determine the effects of ambient conditions, increasing sonication time (0 min, 60 min, 120 min and 150 min), sonication temperatures (25 °C, 30 °C and 60 °C), DO (2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1} and 10 mg L^{-1}) and H_2O_2 (100 mg L^{-1}, 500 mg L^{-1} and 2000 mg L^{-1}) on the sonodegradation of 17 PAHs. The effects of these operational conditions on the acute toxicity of *Daphnia magna* were determined. Furthermore, the reaction kinetics of five representative PAHs and the mechanism of PAH sonodegradation were investigated.

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. The wastewater was not pre-treated before sonication since the solids was disentegrated through sonication. Glass serum bottles in a glass reactor were filled to a volume of 100 mL with petrochemical wastewater after the dosing of 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 constant at 30 °C 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. 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 min, 120 min 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.

Air enriched with oxygen was provided to the samples before sonication. Dissolved oxygen was sparged into the liquid samples with a pump under a pressure of 0.5 atm for 10 min at a flow rate of 5 mL min^{-1} (monitored by a rotameter), and then stopped. H_2O_2 solutions were slurried in the reaction mixture with a pressured pump 20 min prior to sonication at a flow rate of 100 mL min^{-1} and then stopped.

2.2. Analytical methods

For PAHs and some metabolites (phenanthrenediol, naphthalene and p-hydroxybenzoic acid by-products and fluorene) analyses the samples were first filtered through a glass fiber filter (47-mm diameter) to collect the particle-phase in series with a resin column (∼10 g XAD-2) and to collect dissolved-phase polybrominated diphenyl ethers. Resin and water filters were ultrasonically extracted 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), fluorene (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), dibenz[*a*,*h*]anthracene (DahA), and benzo[*g*,*h*,*i*]perylene (BghiP) gas chromatographically (Agilent 6890N GC) equipped with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30 m, 0.25 mm, 0.25 μm) was used. The initial oven temperature was kept at 50 °C for 1 min, then raised to 200 °C at 25 °C min^{-1} and from 200 °C to 300 °C at 8 °C min^{-1}, and then maintained for 5.5 min. High purity He(g) was used as the carrier gas at constant flow mode (1.5 mL min^{-1}, 45 cm s^{-1} linear velocity). PAHs and their metabolites were identified on the basis of their retention times, target and qualifier ions and were quantified using the internal standard calibration procedure. The Phenanthrenediol analysis was performed using a high-pressure liquid chromatography (HPLC) (Agilent-1100) with a method developed by Lindsey and Tarr [14]. The chromatographic conditions for the phenanthrenediol determination were as follows: C-18 reverse phase HPLC column (Ace 5C18; 25 cm × 4.6 mm, 5 μm, mobile phase: 50/50 (v/v) methanol/organic-free reagent water). The naphthalene, p-hydroxybenzoic acid by-products and fluorene were measured in the aforementioned HPLC by using C-8 column (Ace 8; 15 cm × 2.6 mm, 3 μm, mobile phase: 70/30 (v/v) methanol/organic-free reagent water). The CH_4, CO_2 and H_2S gas analysis was performed following Standard Methods [13]. pH, temperature, oxidation-reduction potential (ORP), COD and TOC concentrations were monitored following the Standard Methods 2550, 2580, 5220 D and 5310 [15]. Hydrogen peroxide was quantified with a colorimetric method following the Standard Methods 3550 [15]. DO, and pH were measured in a WTW dissolved oxygen meter and pH meter the ORP was measured using a WTW redox meter. TSS, TVSS, inorganic nitrogen compounds, Total-P, oil and SO_4 were monitored following the Standard Methods [15].

2.3. D. magna toxicity test

To test toxicity 24 h old *D. magna* were used as described in Standard Methods [15]. After preparing the test solution, experiments were carried out using 5 or 10 *daphnids* introduced into the test vessels. These vessels had 100 mL of effective volume at 7–8 pH, providing a minimum DO concentration of 6 mg L^{-1} at an ambient temperature of 20–25 °C. Young *D. magna* were used in the test (≤24 h old). A 24 h exposure is generally accepted as standard for a *Daphnia* acute toxicity test. The results were expressed as mortality percentage of the *Daphnids*. Immobile animals were reported as dead *Daphnids*.

All experiments were carried out three times and the results given as the means of triplicate samplings. Individual PAH concentrations are given as the mean with standard deviation (SD) values.

2.4. Statistical analysis

Multiple regression analysis between *y* and *x* variables was performed using the Excell in Windows. The linear correlation was assessed with R^2. The significance of the correlations between data was determined using the ANOVA test statistics.

3. Results and discussion

3.1. Raw wastewater

Characterization of raw petrochemical wastewater taken from the influent of the aeration unit of a petrochemical wastewater treatment plant was performed. The results are given as the mean value of triplicate samplings (Table 1).

3.2. Effect of sonication frequency on the removal of PAHs

Preliminary studies showed that high ultrasound frequencies of 80 kHz and 150 kHz did not increase the results of the parameters studied. Therefore, they were studied at a sonication frequency of 35 kHz. Increasing the sonication frequency decrease the num-

Table 1
Characterization of raw petrochemical industry wastewater taken from the influent of the aeration unit of a petrochemical industry wastewater treatment plant ($n = 3$, mean values ± SD).

Parameters	Values[a]	Parameters	Values[a]
pH	7.2 ± 0.5	Total-N	15.4 ± 2
ORP[b]	28.2 ± 1	NH_4-N	2.2 ± 1
TSS	310.3 ± 6	NO_3-N	1.8 ± 0.3
TVSS	250.6 ± 4	NO_2-N	0.1 ± 0.01
DO	1.8 ± 0.1	Total-P	10.6 ± 2
BOD_5	584 ± 9	PO_4-P	6.8 ± 1
COD_{total}	1475 ± 13	Oil	206 ± 7
$COD_{dissolved}$	1127 ± 12	SO_4	9 ± 2
TOC	876 ± 9	PAH[c]	1380 ± 7

[a] All concentrations (except pH) in mg L^{-1}.
[b] mV.
[c] ng mL^{-1}.

ber of free radicals, therefore they did not escape from the bubbles and did not migrate [16]. Among the sonication intensities applied to the sonication process (16 W m^{-2}, 37 W m^{-2}, 23 W m^{-2} and 51.8 W m^{-2}) in this study the most effective sonication intensity was found to be 51.8 W m^{-2} [16]. The degradation of PAHs increased with increasing applied power. Therefore, in this study the power of the sonicator was adjusted to be 650 W. As the power increased, the number of collapsing cavities also increased, thus leading to enhanced degradation rates, as reported by Psillakis et al. [7] and Papadaki et al. [17]. It has been shown that increasing the ultrasonic intensity improves the degradation rate of organic compounds [17]. Furthermore, collapse of bubbles in the reaction cell of the sonicator occur more rapidly and the number of cavitation bubbles increases. Thus, produces higher concentration of $OH^\bullet$ radicals at higher ultrasonic intensities. These $OH^\bullet$ radicals react with PAHs in the solution. Therefore, the increased degradation of PAHs noted on increasing the ultrasonic power arises from the enhancement of radical yields.

3.3. Sonication experiments

3.3.1. Effect of increasing sonication time on the PAH removal efficiencies in ambient conditions

Raw petrochemical wastewater samples were sonicated at an ambient temperature of 25 °C at increasing sonication time (60 min, 120 min and 150 min). The results of the study showed that as the sonication time was elevated the total PAH removals increased. 54.9%, 61.3% and 79.6% maximum total PAH removal efficiencies were observed after 60 min, 120 min and 150 min sonication times, respectively, at an influent total PAH concentration of 1380 ng mL^{-1} (Fig. 1). Much of the PAH decomposition was accomplished in the initial 60 min of sonication and the efficiency of this decomposition increased approximately 10% and 25% by increasing the time from 60 min to 120 min and 150 min, respectively. The effect of sonication time on the total PAH removal was significant ($p < 0.01$). Treatment by sonication converts PAHs with multiple benzene rings to much smaller compounds. In such cases it is obvious that higher sonication times are needed for complete mineralization. Therefore, experiments at three ultrasonic irradiation times were conducted monitoring the 17 individual PAHs concentrations to examine the effect of sonication time on their degradation. For example 89% BkF, 66% BaP, 63% IcdP and 78% DahA removal yields were obtained for PAHs with five and six benzene rings after 150 min sonication time at 25 °C (Fig. 2). 72.4%, 87.3%, 90.3%, 90.1%, 83.5% and 94.2% removal yields were obtained for PAHs with three and four benzene rings, namely, NAP, ACT, BaA, CHR

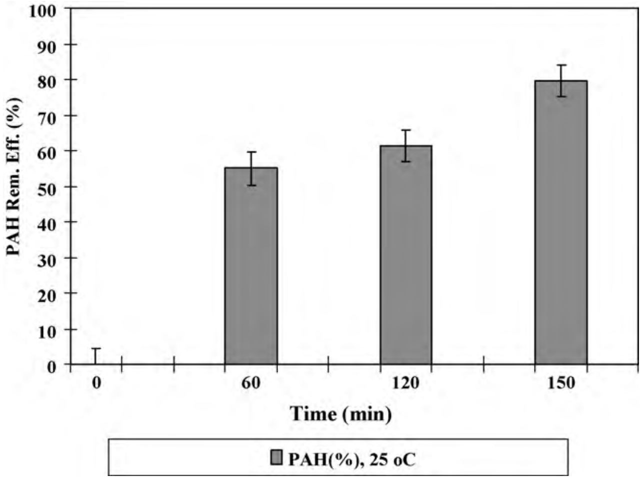

Fig. 1. Effect of sonication time on the total PAH removals at ambient conditions (25 °C) ($n = 3$, mean values ± SD).

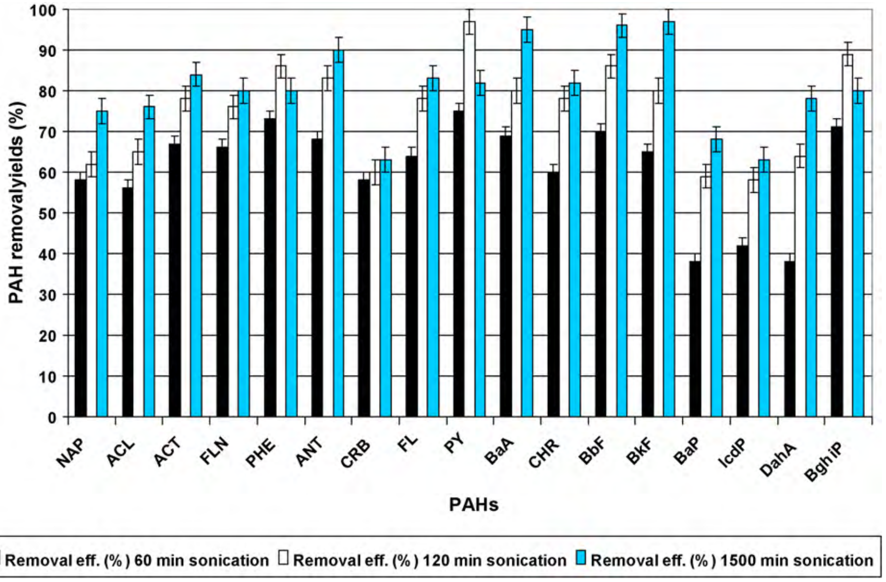

Fig. 2. Effect of increasing sonication time on PAH removal efficiencies in ambient temperature (25 °C) ($n = 3$, mean values ± SD).

and BbF, respectively, at 25 °C after a sonication time of 150 min. Although the total PAH removals increased at increasing sonication times among the PAHs studied it was found that PHE, BghiP and PY concentrations decreased as the sonication time increased from 60 min to 120 min while the concentration of these PAHs increased after 150 min of sonication time. With the increase of sonication time, the amount of naphthalene and p-hydroxybenzoic acid by-products and fluorene first increased and then decreased, after 60 min and 120 min throughout sonication of PHE, respectively, suggesting formation and decomposition reactions of these by-products (data not shown). Since the percentage of PHE remaining decreased for 60 min and 120 min and then increased after 150 min with increasing sonication time we suspected that the increase of PHE with longer sonication may be due to the formation of phenanthrene from by-products such as fluorene. A decrease of the percentange remaining PHE was expected at longer sonication times due to high temperature and radical reactions from cavitation. A radical mechanism proposed by David [5] showed PHE formation from pyrolysis of 9,9-dimethylfluorene at high temperatures by a free radical ring expansion process. Thus, fluorene formed during the sonication of PHE may be attacked by methyl radicals from hexane and acetone dissociation to regenerate PHE. In addition, different types of radicals (e.g., methyl, ethyl) were produced from the dissociation of solvents. Cyclization reactions of these radicals with methyl or ethyl naphthalene may also contribute to the reformation of phenanthrene. Wu and Ondruschka [18] also reported NAP and benzene formation during PHE pyrolysis (<900 °C). Furthermore, Wen et al. [19] studied PHE pyrolysis at 700 °C and 850 °C and reported NAP as one of the pyrolysis products. Therefore, the methylated-NAP by-products detected may be direct pyrolysis products of PHE or products of NAP reacting with methyl radicals generated from the dissociation of solvent.

The PAH removals found in our study were high in comparison to the study performed by David [5]. They found 74%, 72% and 76% PHE, NAP and ACL degradation rates, respectively, at a temperature of 40 °C after 150 min of sonication time. Similarly, in a study performed by Litlee et al. [20] it was found that 0.6 ng mL^{-1} PHE was removed with low yields (32%) at 22 °C after 20 min of sonication time. However, increasing the sonication time to 135 min led to about 56% removal in a sonicator with an ultrasound frequency of 30 kHz and a power of 320 W.

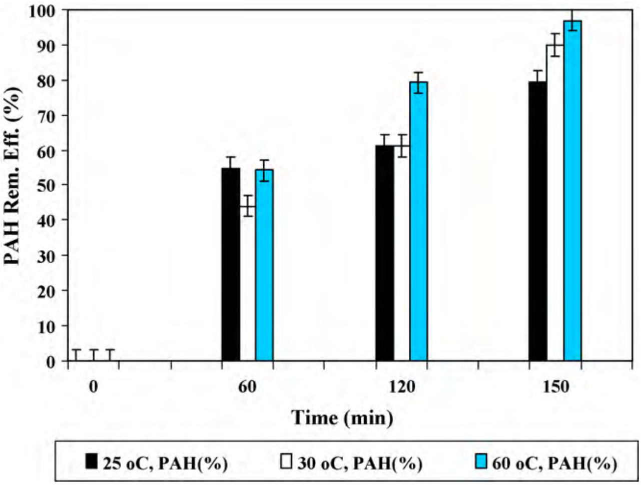

Fig. 3. Effect of increasing temperature on the total PAH removal efficiencies at increasing sonication times ($n = 3$, mean values ± SD).

3.3.2. *Effect of increasing temperature on the removal of PAHs at increasing sonication times*

Raw petrochemical industry wastewater samples were sonicated in a sonicator at 30 °C and 60 °C for 0 min, 60 min, 120 min and 150 min. No influence of temperature increase on PAH removals at ambient temperatures from 25 °C to 30 °C and 60 °C after 60 min of sonication time, was observed (Fig. 3). As the temperature was increased from 25 °C to 30 °C the total PAH removal did not change after 60 min of sonication time and remained between 46% and 50% compared to the control (the sonicator was operated under ambient temperature of 25 °C). The total PAH removal efficiency raised from 58.1% to 78.3% at 60 °C after 120 min of sonication time. Temperature increase from 30 °C to 60 °C elevated the total PAH removal up to 88–91%, respectively, after 150 min of sonication.

The individual PAH removal efficiencies versus increasing temperature are given in Fig. 4 for 60 min, 120 min and 150 min of sonication at 60 °C. The removal efficiencies for PAHs with 3, 4, 5 and 6 benzene rings were >87% at 60 °C after 150 min of sonication (Table 2). The maximum removals for PAHs with one ring (NAP 98.2%, and ACL 97.2%), three rings (CRB 97.9%, CHR 95.1) four and five rings (BaP 97.3%, IcdP 98.2% and BghiP 96.3%) were deter-

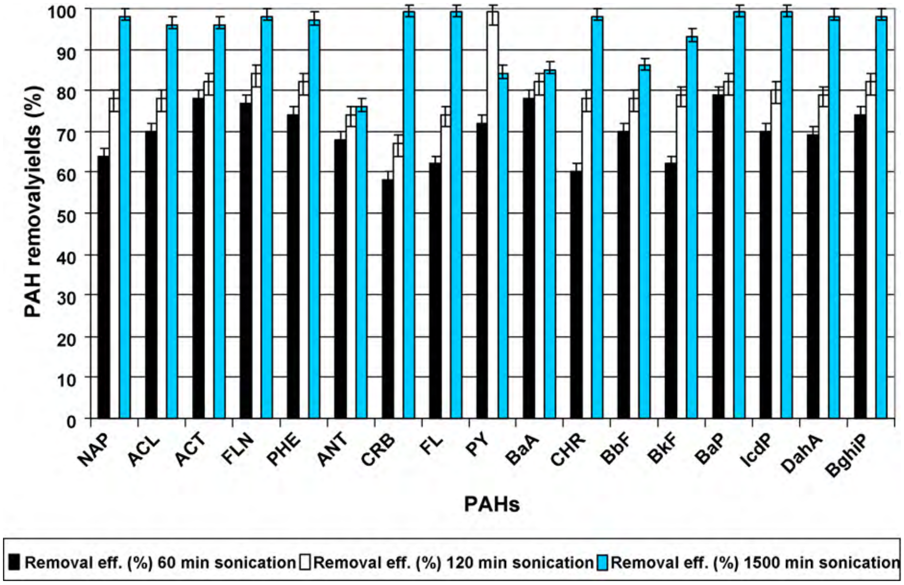

Fig. 4. Maximum PAH removal efficiencies at increasing sonication times at 60 °C ($n = 3$, mean values ± SD).

Table 2
Influent and effluent PAH concentrations and maximum PAH removal efficiencies in the sonication experiments at DO 6 mg L^{-1} and 30 °C after 150 min (n = 3, mean values ± SD).

PAHs	Influent T = 0 minPAH (ng mL^{-1})	Effluent T = 150 minPAH (ng mL^{-1})	Max. PAH removal (%)
NAP	2159.1 ± 29.2	32.5 ± 0.4	98.5
ACL	56.4 ± 7.6	1.6 ± 0.2	97.1
ACT	37.1 ± 5.0	2.2 ± 0.3	94.2
FLN	45.0 ± 6.1	1.8 ± 0.2	96.1
PHE	111.0 ± 15.0	4.1 ± 0.5	96.4
ANT	2.9 ± 0.4	0.2 ± 0.03	91.8
CRB	21.3 ± 2.9	0.5 ± 0.1	97.9
FL	13.7 ± 1.8	0.6 ± 0.1	95.5
PY	11.7 ± 1.6	0.5 ± 0.1	95.7
BaA	0.2 ± 0.03	0.02 ± 0.002	92.3
CHR	1.9 ± 0.3	0.09 ± 0.01	95.4
BbF	0.2 ± 0.03	0.03 ± 0.004	86.3
BkF	0.4 ± 0.1	0.03 ± 0.003	93.2
BaP	0.1 ± 0.01	0.002 ± 0.0003	97.8
IcdP	1.8 ± 0.2	0.04 ± 0.01	98.0
DahA	4.4 ± 0.6	0.2 ± 0.02	96.6
BghiP	0.5 ± 0.1	0.02 ± 0.002	96.5
Total	2467.5 ± 33.3	44.3 ± 0.6	
Mean			95.3

mined at 60 °C after 150 min of sonication. Among the PAHs studied, only in the case of PY temperature increase did not influence its removal. The yield of PY decreased slightly on temperature rose from 120 °C to 150 °C while the removals of PHE, BghiP and the rest of the PAHs elevated. The slight decrease in degradation rate observed for PY may be due to the increased solution temperature. For PY, an elevated solution temperature might imply a slightly higher adsorption on the air–water interface and an improved diffusivity. These factors act to affect the slight accumulation of PY on the interface in different ways. As the temperature increased, the raised diffusivity may contribute to more available PY at the subsurface for adsorption. Thus, a slight increment in removal efficiency was observed from 25 °C to 60 °C. The decrease in removal efficiency at 150 °C may be due to less favorable adsorption resulting in reduced accumulation on the interface.

Although the effects of raising temperature on the sonolytic removal efficiencies were also examined for all PAHs, in this section only PHE and BghiP PAHs are discussed. The removal yields of PHE and BghiP improved with increasing temperature. For partitioning into the bubble, the elevated solution temperature will allow PHE and BghiP molecules to more easily enter the cavitation bubble (i.e., increase diffusivity). At higher temperatures this effect will be enhanced and this may be the cause of the improve in removal rates for PHE and BghiP at 150 °C.

Different suggestions were presented to explain the effect of temperature on the sonochemical degradation of PAHs since it is a relatively complex issue closely related to the properties and reaction conditions of each specific system in question. As the temperature elevates the collapse temperature of the cavitation bubble should decrease [5,9]. However, other studies have shown that after an initial increase in solution temperature the rate of reaction increases leading to a greater fraction of volatile compounds partitioning into the cavity. A further increase in solution temperature leads to a decrease in the rate of reaction [7]. Therefore, it is not surprising that several investigators have reported contradictory findings regarding the temperature effect. In certain reaction systems for instance, the net effect of an increment in T_0 and consequently $T_{\max}$, is an increase in degradation rates. This occurs up to the point at which the cushioning effect of the vapour begins to dominate the system and further increases in liquid temperature result in reduced reaction rates. The fact that removal decreases with raising liquid temperature is believed to be associated with the effect of temperature on both the bubble formation energy threshold and the intensity of bubble implosion. The maximum temperature ($T_{\max}$) obtained during the bubble collapse is given as follows:

$$T_{\max} = T_0 \frac{P}{P_0}(\gamma - 1) \tag{1}$$

where T_0 is the liquid bulk temperature, P_0 is the vapour pressure of the solution, P is the liquid pressure during the collapse and γ is the specific heat ratio (i.e. the ratio of constant pressure to constant volume heat capacities). Increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapour pressure; nevertheless, this beneficial effect is compensated by the fact that bubbles contain more vapour which cushions bubble implosion and consequently reduces $T_{\max}$. In addition to this, increased temperatures are likely to favour degassing of the liquid phase, thus reducing the number of gas nuclei available for bubble formation [7]. It was observed that the PAHs with multiple benzene rings were also degradable with high yields, even though some studies demonstrated that sonication is not effective for PAHs with a large number of benzene rings [7]. The PAHs removal yields obtained in our study are high in comparison to the removal performances of PAHs by the studies given below. In the study by Laughrey et al. [9] 77% PAH removal efficiency was observed for the sonochemical degradation of a PAHs mixture [50 μg L^{-1} NAP, 55 μg L^{-1} ACL and 52 μg L^{-1} PHE] in water after a sonication time of 120 min, at a temperature of 40 °C, a power of 150 W and an ultrasound frequency of 24 kHz. Benabdallah El-Hadj et al. [4] found 31–34% and 44–50% PAH removal effiencies in mesophilic (35 °C) and thermophilic (55 °C) conditions for NAP and PY by a sonicator with a frequency of 20 kHz, and an ultrasonic power of 70 W, after 110 min sonication time, before anaerobic digestion.

3.3.3. *Effect of dissolved oxygen (DO) concentration on the removal of PAH at increasing sonication time and temperature*

The raw petrochemical wastewater samples were oxygenated with increasing DO concentrations (2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1} and 10 mg L^{-1}) with pure O_2 before the sonication experiments. 90%, 92%, 94% and 95% total PAH removal efficiencies were measured for 2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1} and 10 mg L^{-1} DO concentrations, respectively, after 150 min of sonication time at 30 °C (Fig. 5a). Only 4 mg L^{-1}, 6 mg L^{-1} and 10 mg L^{-1} DO concentrations increased the total PAH removal efficiencies from 90% to 92–93% in comparison to the non-oxygenated samples (control, total PAH removal efficiency = 90%) at a temperature of 30 °C and a sonication time of 150 min. In other words, the effect of increasing DO

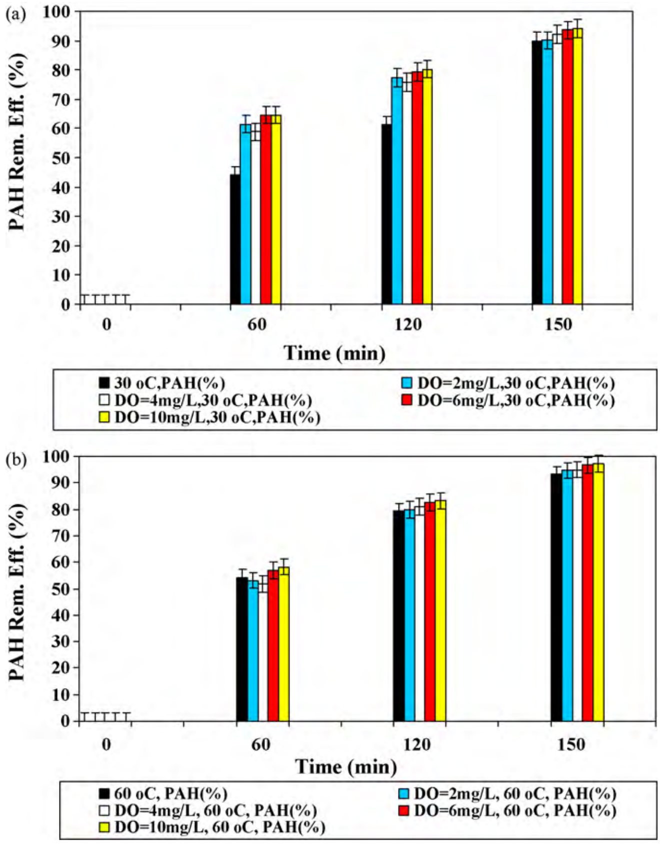

Fig. 5. Effects of DO at (a) 30 °C and (b) 60 °C on the total PAH removal efficiencies ($n = 3$, mean values ± SD).

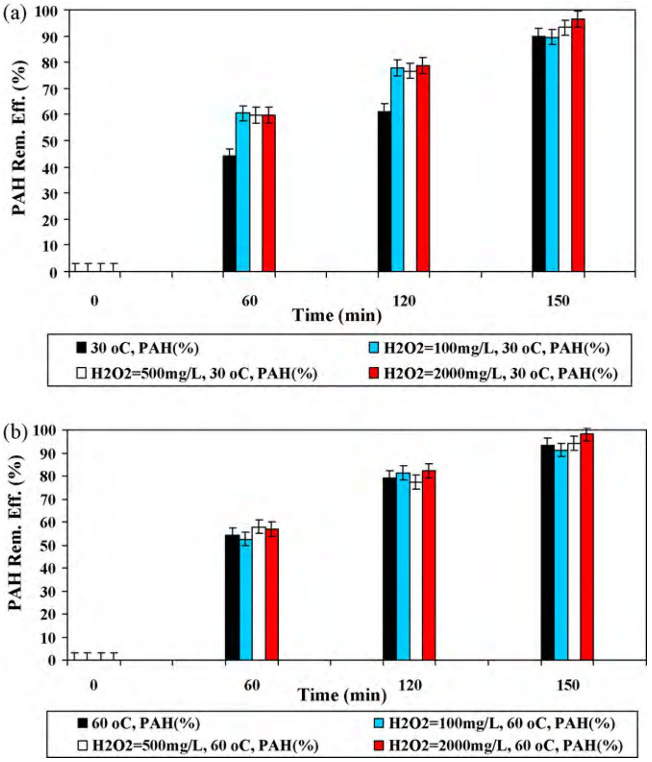

Fig. 6. Effects of H_2O_2 at (a) 30 °C and (b) 60 °C on the total PAH removal efficiencies ($n = 3$, mean values ± SD).

concentrations on the total PAH removals was found to be insignificant at a temperature of 30 °C and a sonication time of 150 min. The total PAH yields also increased significantly (from 40% to 65% and from 60% to 80%) after 60 min and 120 min sonication, respectively, compared to the control at all DO concentrations for the same temperature. The yield of 2 and 3-ring PAH removals was almost 96% for FLN and PHE PAHs, respectively, in raw petrochemical industry wastewater samples containing 6 mg L^{-1} DO at 30 °C after 150 min of sonication (Table 2). The removal efficiencies of four ring PAHs (CHR, BkF, BaP and IcdP) were also higher (efficiency varied between 92% and 96%) in the samples oxygenated with 6 mg L^{-1} DO at 30 °C in comparison to the PAHs containing few benzene rings after 150 min sonication. Similarly, around 96–97% removal efficiencies were obtained for PAHs with five rings (DahA and BghiP).

95.2%, 95.5%, 98.5% and 95.8% total PAH removal efficiencies were obtained for 2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1} and 10 mg L^{-1} DO concentrations at 60 °C after 150 min sonication (Fig. 5b). As shown, the total PAH removal efficiencies increased as the sonication time increased. However, the PAH yields did not show a significant increase at increasing DO concentrations compared to the control. Increasing the temperature also did not increase the total PAH removal efficiencies at increasing DO concentrations. The maximum total PAH removal efficiencies obtained were 98% at 6 mg L^{-1} DO concentration after 150 min sonication time and a temperature of 30 °C.

Oxygen mediates the rate of mineralization of PAHs. The higher DO content of petrochemical wastewater resulted in faster rates of phenanthrene degradation through sonication, supporting the hypothesis that increased oxygenation was largely responsible for the enhanced PAHs degradation. Although oxygen exposure is an important factor in PAH degradation it was reported that saturating the solutions causes decreases in $HO_2^{\bullet}$ production resulting in low PAH yields. In the presence of O_2, reactive radicals such as $O^{\bullet}$, $OH^{\bullet}$ and $HOO^{\bullet}$ will be produced by a series of reactions and may participate in the decomposition reaction of the PAHs with sonication. Although O_2 and air have similar ratios of specific heats and thermal conductivity, the highest formation rate of H_2O_2, which was induced from the recombination of reactive radicals ($OH^{\bullet}$ and $OOH^{\bullet}$) was observed under oxygen [21]. In aerated solutions, the hydroperoxyl radicals ($HO_2^{\bullet}$) formed by;

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{2}$$

will decay with generation of H_2O_2. However, the production of the $HO_2^{\bullet}$ increases the oxidation process due to further formation of H_2O_2 by its recombination reaction [21];

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{3}$$

3.3.4. Effect of hydrogen peroxide (H_2O_2) concentration on the removal of PAH at increasing sonication times and temperature

100 mg L^{-1}, 500 mg L^{-1} and 2000 mg L^{-1} H_2O_2 were added to the raw petrochemical wastewater samples before the sonication experiments. This increased the total PAH removals from 52% (in the control reactor containing no H_2O_2 at ambient temperature) to 59–60% and to 60–78% after 60 and 120 min of sonication times, respectively, at 30 °C. However, it is important to note that the total PAH removals were the same (around 58% and 76%) at all increasing H_2O_2 concentrations after 60 min and 120 min sonication times at 30 °C (Fig. 6a). Similarly, no significant changes in total PAH removals were obtained after 150 min of sonication time by the addition of H_2O_2. An increase of 5% and 6% was obtained for total PAH yields compared to the control for 500 mg L^{-1} and 2000 mg L^{-1} H_2O_2 concentrations at 30 °C (Fig. 6a).

As the sonication time was increased from 120 min to 150 min at 60 °C no significant increases in total PAH removals were observed compared to control at all H_2O_2 concentrations. The total PAH

Table 3

Calculated steady-state $[HO^\bullet]_{ss}$ concentrations for five PaHs, comparison of PAH oxidation rates of $OH^\bullet$ and experimental PAH removal rates after 150 min sonication at 35 kHz frequency and 60 °C ($n = 3$, mean values).

PAHs	$k_{PAH/HO^\bullet}$ [a]	k_{pf} [b]	$[HO^\bullet]_{ss}$ [c]	$V_{PAH/HO^\bullet}$ [d]	$V_{PAH/US}$ [e]	$V_{PAH/HO}/V_{PAH/US}$ [f]
NAP	2.8×10^{18}	0.026	9.28×10^{-21}	0.029	0.52	0.05
ACL	2.6×10^{18}	0.024	9.23×10^{-21}	0.023	0.48	0.04
PHE	2.3×10^{18}	0.017	4.34×10^{-21}	0.009	0.06	0.15
PY	1.5×10^{18}	0.015	1.44×10^{-21}	0.003	0,04	0.07
BhP	0.9×10^{18}	0.011	1.22×10^{-21}	0.001	0,04	0.02

[a] PAH oxidation rate, ng mL^{-1} s^{-1}.
[b] Experimental pseudo first order reaction of PAH, min^{-1}.
[c] Steady-state $[HO^\bullet]$ concentrations, ng mL^{-1}.
[d] PAH oxidation rate, ng mL^{-1} min^{-1}.
[e] Experimental rate of PAH sonodegradation, ng mL^{-1} min^{-1}.
[f] The percentage of PAH oxidation with $HO^\bullet$ ratio to conventional sonodegradation.

yields increased from 92% to 98% at a H_2O_2 concentration of 2000 mg L^{-1} compared to control after 150 min at 60 °C (Fig. 6b). The removal yields of all 17 PAHs were above 95%. In other words, the PAHs containing one, two, three, four and five benzene rings were removed with efficiencies varying between 95% and 99% (data not shown). It was reported that this oxidant elevates the extent of PAH removal through acustic cavitation [22]. The similar degradation degree in the control and in the presence of H_2O_2 may be attributed to the increased level of $OH^\bullet$ scavenging by the PAHs and by H_2O_2 itself. During the sonolysis of aqueous solutions, $OH^\bullet$ and $H^\bullet$ are generated by the thermolysis of water in the solution medium and can scavenge hydroxyl radicals produced. As the concentration of H_2O_2 in the solution is increased, its $OH^\bullet$ scavenging effect increases causing decrease in degradation of PAHs. It was reported that at very high H_2O_2 concentrations detrimental effects are observed, since the recombination reaction of $OH^\bullet$ is more predominant and H_2O_2 acts as a scavenger for $OH^\bullet$ [22]. The scavenging of free $OH^\bullet$ becomes the dominant process at high H_2O_2 concentrations in the system, thereby lowering the ability of $OH^\bullet$ to degrade PAHs. A similar trend has been reported in the sonolytic destruction of 5,5-dimethyl-1-pyrroline-N-oxide and oxalic acid using H_2O_2 [23].

3.3.5. PAH degradation kinetics

The sonic degradation of 17 PAHs in the raw petrochemical wastewater was found to be pseudo first order with respect to PAH concentrations at a frequency of 35 kHz and 60 °C (Eq. (4)).

$$-\frac{d[\mathrm{PAH}]}{dt} = k[\mathrm{PAH}]_t \qquad (4)$$

The degradation rates for all PAHs were deduced from the slopes of the curves given by:

$$\ln\frac{[\mathrm{PAH}]_t}{[\mathrm{PAH}]_0} = k[\mathrm{PAH}] \times t \qquad (5)$$

where $k[\mathrm{PAH}]$ is the rate constant at 35 kHz frequency, $[\mathrm{PAH}]_0$ the initial PAH concentration and $[\mathrm{PAH}]_t$ its value at time t. In this study, the rate constants of sonodegradation are given for only five PAHs. These rate constants are tabulated in Table 3. The pseudo first order rate constants ranged between 0.011 min^{-1} and 0.026 min^{-1}.The pseudo first order kinetic rate constants obtained in this study agree with the literature data of low frequencies (20 kHz and 32 kHz) [4,8,13]. The biodegradation rate constants of the PAHs depend on their properties, such as the benzene ring numbers, the vapour pressure, the water solubility and Henry's law constant, as reported by David [5]. The biodegradation rate constants increased as the vapour pressure, the water solubility and the Henry's law constants increased and the number of benzene rings of PAHs decreased. The most hydrophobic PAHs, with four and five benzene rings (BkF, BaP, IcdP, DahA, BghiP) (low water solubility and Henry's law constant) have the lowest degradation constants compared to one, two and three ring PAHs (NAP, ACL, ACT, FLN, PHE, ANT) with high water solubility and Henry's law constants. The data obtained in this study are in good agreement with the rate constants obtained by David [5] and Wu and Ondruschka [18].

The pseudo first order rate constants decreased from PAHs with one benzene ring to PAHs with five rings at low sonication times such as 60 min (Table 3). However, the untreated percentages of PAHs with four and five rings at a sonication time of 150 min reached the same levels as PAHs with low ring numbers after 150 min sonication (Fig. 7). Therefore, the removal efficiencies for all PAHs were >95% after 150 min sonication time (Fig. 7).

A more energetic implosion of cavitation bubbles is expected to occur at low frequency because a larger bubble radius is observed in that range [24,25]. The larger the bubble size, the greater the amount of water vapour within the bubble, leading to a more important damping of the collapse at low frequencies such as 20–30 kHz [5]. This contributes to enhancing the penetration of water containing PAHs into the bubbles. Suslick [26] showed that non-linear bubble implosions play a significant role on the degradation of chemicals at low frequency. De Visscher et al. [24] demonstrated that the equilibrium time of a partitioning process between the liquid and the bubble phases is 560 times longer at low frequencies such as 20 kHz and 30 kHz. During the PAH sonication gaseous by-products (CO_2, CH_4, and H_2S) were detected in the headspace of the reactor. No hydroxylated by-products such as phenanthrenediols were detected in HPLC, similar to the process involving $OH^\bullet$ as reported by Dewulf et al. [25] since the

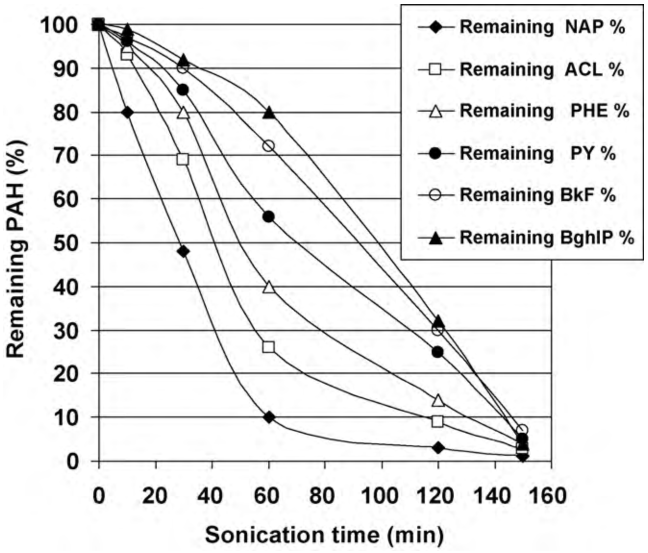

Fig. 7. Effects of sonication time on the residual PAH percentages ($n = 3$, mean values).

Table 4
Effect of sonication on the acute toxicity (EC_{50}) removal efficiencies under different operational conditions (temperature: 25–60 °C; sonication time: 60–150 min; DO: 2–10 mg L^{-1}; H_2O_2: 100–2000 mg L^{-1}) ($n = 3$, mean values).

# of set	Conditions	EC_{50} (ng mL^{-1})		EC (ng mL^{-1}) values	
		25 (°C)			
		0^a	60^a	120^a	150^a
1	Control	342.60	$EC_{45} = 70.80$	$EC_{28} = 65.10$	$EC_{13} = 11.60$

# of set	Conditions	EC_{50} (ng mL^{-1})				EC (ng mL^{-1}) values			
		30 (°C)				60 (°C)			
		EC_{50}		EC		EC_{50}		EC	
		0^a	60^a	120^a	150^a	0^a	60^a	120^a	150^a
2	$DO = 2^b$	342.60	$EC_{30} = 74.10$	$EC_{22} = 33.90$	$EC_{4} = 15.90$	342.60	$EC_{40} = 77.10$	$EC_{32} = 33.00$	$EC_{18} = 11.70$
3	$DO = 4^b$	342.60	$EC_{32} = 82.00$	$EC_{27} = 28.30$	$EC_{12} = 1.60$	342.60	$EC_{11} = 112.60$	$EC_{3} = 30.20$	$EC_{2} = 6.90$
4	$DO = 6^b$	342.60	$EC_{28} = 130.70$	$EC_{17} = 25.30$	$EC_{2} = 0.70$	342.60	$EC_{50} = 87.00$	$EC_{40} = 14.50$	$EC_{5} = 5.50$
5	$DO = 10^b$	342.60	$EC_{18} = 120.00$	$EC_{11} = 40.20$	$EC_{8} = 18.30$	342.60	$EC_{50} = 84.90$	$EC_{45} = 19.00$	$EC_{2} = 12.60$
6	$H_2O_2 = 100^b$	342.60	$EC_{18} = 74.6$	$EC_{10} = 37.20$	$EC_{3} = 1.20$	342.60	$EC_{11} = 75.10$	$EC_{5} = 29.70$	$EC_{2} = 0.40$
7	$H_2O_2 = 500^b$	342.60	$EC_{22} = 47.20$	$EC_{10} = 22.70$	$EC_{4} = 4.30$	342.60	$EC_{23} = 68.20$	$EC_{10} = 79.10$	$EC_{8} = 18.80$
8	$H_2O_2 = 2000^b$	342.60	$EC_{50} = 168.50$	$EC_{50} = 80.60$	$EC_{50} = 12.40$	342.60	$EC_{50} = 259.90$	$EC_{50} = 92.70$	$EC_{50} = 19.30$

[a] Sonication time (min).
[b] Concentration (mg L^{-1}).

formation of these products arises from a possible $OH^\bullet$-driven oxidation.

3.3.6. *Mechanisms of PAH sonication*

Some studies suggested that PAHs for example (PHE are degraded by a free radical mechanism with $OH^\bullet$, since hydroxylated compounds like phenanthrenediols have been detected [5]. On the other hand, some recent research has shown that plasma allows the ionization of organics like PAHs. This can lead to oxidized by-products [23].

The contribution of the oxidation pathway of PAHs through ultrasonic degradation can be determined. If we assume that $HO^\bullet$ is the main species leading to sonodegradation of PAHs, the oxidation rate $V_{PAH/HO^\bullet}$ can be calculated using Eq. (6)

$$V_{PAH/OH^\bullet} = -\left\{\frac{d[PAH]}{dt}\right\}_{OH^\bullet} = k_{PAH/OH^\bullet}[PAH][OH^\bullet]_{ss} \tag{6}$$

where $k_{PAH/HO^\bullet}$ is the second order reaction kinetic rate constant, $[HO^\bullet]$ is the steady-state $OH^\bullet$ concentration in petrochemical industry wastewater under ultrasound and [PAH] is the PAH concentration. The experimental rate of PAH sonodegradation $V_{PAH/US}$ is given with Eq. (7).

$$V_{PAH/US} = \left\{\frac{d[PAH]}{dt}\right\}_{US} = k_{pf}[PAH] \tag{7}$$

Therefore,

$$k_{pf} = k_{PAH/OH^\bullet}[OH]_{ss} \tag{8}$$

where k_{pf} is the experimental pseudo first order reaction linetic rate constant. It is assumed that the sonication process is 100% controlled by oxidation of PAHs with $[HO^\bullet]$ at a frequency of 35 kHz. $[HO^\bullet]_{ss}$ is the calculated the steady-state concentrations in petrochemical industry wastewater during sonication of naphthalene NAP, ACL, PHE, PY and BbF PAHs. The second order reaction kinetic rate constants for NAP, ACL, PHE, PY and BbF PAHs were taken from the study performed by Lindsey and Tarr [12] (Table 3). The calculated values of $[HO^\bullet]_{ss}$ concentrations are in good agreement with the studies performed by David [5] and Destaillats et al. [27]. A comparison of calculated oxidation rates of $OH^\bullet$ with Eq. (6) for the experimental sonodegradation rates is given in Table 3 for a frequency of 35 kHz for five PAHs.

Since the sonooxidation of NAP, acenaphthylene ACL, PHE, PY and BbF PAHs comprised 0.05%, 0.04% and 0.15%, 0.07% and 0.02% of the total sonodegradation process, $OH^\bullet$ is not the major process for complete degradation of these PAHs (Table 3). In this study, the contribution of $OH^\bullet$ is minor for the ultimate sonodegradation of PAHs. The formation of by-products (hydroxylated compounds namely phenanthrenediols) for possible $OH^\bullet$ oxidation was not observed in HPLC. Similar results were obtained in the studies performed by Lindsey and Tarr [14] and Wen et al. [19].

In order to determine the pyrolitic mechanism of PAH degradation a synthetic saturated solution of a mixture of 16 PAHs (1 mg L^{-1}) was prepared to detect the gaseous by-products in the headspace of the sonication reactor. 67% CO_2 and 56% CH_4 were measured after 30 min of sonication time. This could be explained by the rapid formation of the aforementioned two gases as PAHs penetrate the cavitation bubles in order to be pyrolized, as reported by David [5].

3.3.7. *Effect of sonolysis operating parameters on the acute toxicity removal*

The *D. magna* test is accepted as an acute toxicity test. Toxicity was estimated in terms of EC_{50}, defined as the concentration of the toxicant causing 50% reduction in activity of the water flea. Table 4 shows the acute toxicity test results obtained from the *D. magna* test through sonication with increasing temperatures, DO and H_2O_2 concentrations.

The test samples containing an initial total PAH concentration of 1380 ng/mL were diluted at 1/1, 1/2, 1/8, 1/16 and 1/24 ratios after sonication experiments. 10 young *Daphnids* (<24 h old) were added to each test vessel at the initiation time ($t = 0$). After 24 h of exposure, the EC values of total PAH concentrations were calculated. As seen in Table 4 (Set 1), the initial EC_{50} values in control samples containing no DO and H_2O_2 were measured as 342.60 ng mL^{-1} at 25 °C. After 120 and 150 min of sonication the EC_{50} values decreased to EC_{28} and EC_{13} at 25 °C. The toxicity decreased approximately to the ratios 2/5 and 4/5 respectively. The EC_{28} and the EC_{13} values were measured as 65.10 ng mL^{-1} and 11.60 ng mL^{-1}, respectively, at 25 °C (Table 4, Set 1). This showed that the PAHs were degraded to less toxic by-products via sonication. The toxicity removal efficiencies were 89% and 96% after 120 min and 150 min of sonication, respectively, in control samples at 25 °C. This indicates a significant lowering of the acute toxicity in the control samples at 25 °C. The G_L (dilution ratio) value was found as 0.17 and 0.06 in the samples diluted 1:2 and 1:8 times after 120 min and 150 min sonicated control samples, which were used in the calculation of the EC values (data not shown).

The EC_{50} values decreased as the DO concentration increased from 2 mg L^{-1} to 6 mg L^{-1} in Sets 2, 3 and 4 (Table 4) at 30 °C after 120 min and 150 min of sonication. Increasing the H_2O_2 concentration to 10 mg L^{-1} had no positive effect on the decrease of EC values. The acute toxicity (EC_{50}) decreased from 342.60 ng mL^{-1} to EC_2 = 0.70 ng mL^{-1} after 150 min of sonication at a DO concentration of 6 mg L^{-1} at 30 °C. The acute toxicity removal efficiency was 100% at this DO concentration. The G_L value was found as 0.14 and 0.006 in the samples diluted 1:2 and 1:8 times after 120 min and 150 min in sonicated wastewater samples (data not shown).

Similarly, the EC_{50} values decreased as the DO concentration increased from 2 mg L^{-1} to 6 mg L^{-1} in Sets 2, 3 and 4 at 60 °C after 120 min and 150 min of sonication (Table 4). Although increasing the DO concentration to 10 mg L^{-1} decreased the acute toxicity (EC_{50}) from initially 342.60 ng mL^{-1} to EC_5 = 5.50 ng mL^{-1} the maximum toxicity removal efficiencies were 99% and 99.2% at DO concentrations of 4 mg L^{-1} and 6 mg L^{-1}, respectively, after 150 min of sonication at 60 °C. The results showed that the maximum acute toxicity removal was obtained as 100% at a DO concentration of 6 mg L^{-1} after 150 min sonication at a temperature of 30 °C.

The acute toxicity decreased from an initial value of 342.60 ng mL^{-1} to EC_3 = 1.20 ng mL^{-1} at a H_2O_2 concentration of 100 mg L^{-1} at 30 °C after a sonication time of 150 min. Increasing the H_2O_2 concentration did not contribute to acute toxicity removal (Table 4, Sets 6–8). H_2O_2 concentrations above 100 mg L^{-1} increased the acute toxicities in *D. magna*. In other words, the maximum acute toxicity removal was obtained in the samples containing 100 mg L^{-1} H_2O_2 concentration at a temperature of 60 °C after 150 min of sonication. The acute toxicity decreased from 342.60 ng mL^{-1} initially to EC_2 = 0.40 ng mL^{-1}. This corresponds to an acute toxicity removal efficiency of 100% at a temperature of 60 °C after 150 min of sonication (Table 4).

4. Conclusions

The results of this study show that PAHs in petrochemical industry wastewater could be treated efficiently with low-frequency sonication. Although the degradation efficiency of PAHs in petrochemical wastewater was affected by the time, temperature, DO and H_2O_2 sonication alone could provide 88–92% PAH removals at 30 °C and 60 °C after 150 min sonicaton. The optimum operational conditions for maximum PAH removals at 25 °C and 60 °C were DO concentration of 6 mg L^{-1} and H_2O_2 concentration of 2000 mg L^{-1}, respectively, after 150 min sonication. All the PAHs were removed with treatment efficiencies above 87% (up to 99%) after 150 min of sonication at 60 °C. The matrix for the maximum acute toxicity removals (100%) was 6 mg L^{-1} and 100 mg L^{-1} DO and H_2O_2 concentrations, respectively, at a temperature of 30 °C and a sonication time of 150 min. The main PAH degradation mechanism during ultrasonic irradiation is pyrolysis.

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