

Removals of Polycyclic Aromatics Hydrocarbons and Acute Toxicity with Sonication in a Petrochemical Industry Wastewater during Increasing Ferrous and Ferric Ions Concentrations

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Abstract

The effects of ambient conditions (25oC), increasing sonication time (0–150 min), temperature (30oC and 60oC), Ferrous ions (Fe^{+2}) (2 mg/l, 8 mg/l and 20 mg/l) and Ferric ions (Fe^{+3}) (10 mg/l, 20 mg/l and 50 mg/l) concentrations on the removal of polycyclic aromatic hydrocarbon (PAH) and destruction of toxicity in a petrochemical industry wastewater (PCI ww) in Izmir (Turkey) were investigated. The maximum PAH removals were 80.2%, 91%, 98.56% and 96.76% at 25oC, at 60oC, at $Fe^{+2}=20$ mg/l and at $Fe^{+3}=50$ mg/l, respectively, after 150 min sonication time. Sonication alone provides PAH removals varying between 90.11% and 96.90% without Fe^{+2} and Fe^{+3} at 30oC and 60oC after 150 min sonication time. The *Daphnia magna* acute toxicity decreased significantly from EC=342.6 mg/l to EC=50 mg/l, to EC=32 mg/l and to EC=15 mg/l, respectively, as the temperature, the Fe^{+2} and Fe^{+3} concentrations were increased. The matrix for the maximum *Daphnia magna* acute toxicity removals (100%) was 80% *Daphnia magna* acute toxicity yield for $Fe^{+2}=20$ mg/l and 70% *Daphnia magna* acute toxicity yield for $Fe^{+3}=10$ mg/l, respectively, at 60oC after 150 min sonication time, respectively. The *Daphnia magna* acute toxicity measurement procedure was successfully applied to seventeen PAHs removals during sonication process in the PCI ww with the addition of different Fe^{+2} and Fe^{+3} ions concentrations, respectively. The PAH sonodegradation appeared to be Pseudo first order in PAHs naphthalene (NAP), acenaphthylene (ACL), phenanthrene (PHE), pyrene (PY) and benz[b] fluoranthene (BbF) ($k=0.026$ 1/min, $k=0.024$ 1/min, $k=0.017$ 1/min, $k=0.015$ 1/min and $k=0.011$ 1/min, respectively). The main mechanism of PAH sonodegradation appears to be pyrolysis.

Keywords: retroperitoneal hernia; posterior approach; hernia; spine surgery; postoperative complications

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 [6] 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 mg/l of acenaphthalene (ACT), PHE and NAP at a power of 300W and frequency of 24 kHz. Benabdallah El-Hadj et al. [5] found 57% NAP, 40% PY and 45% total COD removal efficiencies in a sonicator at 70 W sonication power and at 20 kHz sonication frequency. Taylor et al. [8] investigated the sonication of PAHs, namely ANT, PHE and PY. 46%, 20% and 50% removal

efficiencies, respectively, were found at 600 W and at 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 N₂(g) purges were increased from 1 mg/l to 5 mg/l and from 2 ml/min to 4 ml/min and from 3 ml/min to 6 ml/min, respectively.

When sonolysis of water occurs, it leads to the formation of the non-specific oxidative species OH[•]. 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[•] [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) [5, 7, 12, 13]. No study was found investigating the effects of operational conditions such as sonication time, temperature, Fe⁺² and Fe⁺³ on the sonication of a PCI ww. Furthermore, the effects of the operational conditions on the removal of acute toxicity has not been determined for a PCI ww. 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), increasing sonication temperatures (25°C, 30°C and 60°C), increasing Fe⁺² ion (2 mg/l, 8 mg/l and 20 mg/l) and Fe⁺³ ion (10 mg/l, 20 mg/l and 50 mg/l) concentrations on the sonodegradation of seventeen PAHs. The effects of these operational conditions on the acute toxicity of *Daphnia magna* microorganisms were determined. Furthermore, the reaction kinetics of five representative PAHs and the mechanism of PAH sonodegradation were investigated.

Materials And Methods

Sonicator and Operational Conditions

A BANDELIN Electronic RK510 H sonicator was used for sonication of the PCI ww samples. The wastewater was not pre-treated before sonication since the solids was disintegrated through sonication. Glass serum bottles in a glass reactor were filled to a volume of 100 ml with PCI ww after the dosing of oxygen (O₂) and hydrogen peroxide (H₂O₂). 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 (CH₃OH) 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 at 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 cm², and a maximum input power of 650 W. Four sonication intensities (16 W/m², 37 W/m², 23.02 W/m² and 51.75 W/m²) 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 O₂(g) was provided to the samples before sonication. Dissolved oxygen (DO) 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 (monitored by a rotameter), and then stopped. H₂O₂ solutions were slurried in the reaction

mixture with a pressured pump 20 min prior to sonication at a flow rate of 100 ml/min and then stopped.

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 seventeen 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[ghi]perylene (BghiP), respectively, 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 and from 200°C to 300°C at 8°C/min, 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, 45 cm/s 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 NAP, p-hydroxybenzoic acid by-products and FLN 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 CH₄, CO₂ and H₂S gas analysis was performed following Standard Methods [15]. pH, temperature, oxidation-reduction potential (ORP), COD and TOC concentrations were monitored following the Standard Methods 2550, 2580, 5220 D and 5310 [15]. H₂O₂ was quantified with a colorimetric method following the Standard Methods 3550 [15]. DO, 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 SO₄ were monitored following the Standard Methods [15].

Daphnia magna Acute Toxicity Test

To test toxicity 24 h old *Daphnia 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 7.0–8.0 pH, providing a minimum DO concentration of 6 mg/l at an ambient temperature of 20–25°C. Young *Daphnia magna* were used in the test (≤ 24 h old). A 24 h exposure is generally accepted as standard for a *Daphnia magna* 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.

Statistical Analysis

Multiple regression analysis between y and x variables was performed using the Excell in Windows. The linear correlation was assessed with R². The significance of the correlations between data was determined using the ANOVA Test Statistics.

Results And Discussion

Raw Wastewater

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

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	1380 ± 7

a: All concentrations (except pH) in mg/l; b: mV.

Table 1: Characterization of raw PCI ww taken from the influent of the aeration unit of a PCI ww treatment plant (n = 3, mean values ± SD).

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 Therefore, they were studied at a sonication frequency of 35 kHz. Increasing the sonication frequency decrease the number 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/m², 37 W/m², 23 W/m² and 51.8 W/m²) in this study the most effective sonication intensity was found to be 51.8 W/m² [16]. The degradation of PAHs increased with increasing applied power. Therefore, in this study the power of the sonicator was adjusted to be 640 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• radicals at higher ultrasonic intensities. These OH• 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.

Sonication Experiments

Effect of Increasing Sonication Time on the PAH Removal Efficiencies in Ambient Conditions

Raw PCI ww 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 time, respectively, at an influent total PAH concentration of 1380 mg/l (Figure 1).

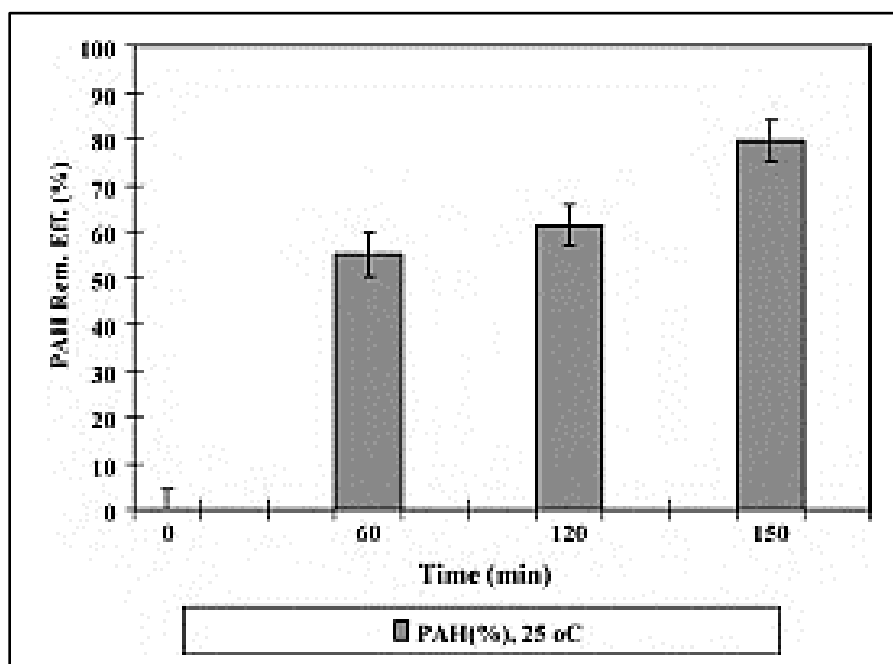


Figure 1: Effect of sonication time on the total PAH removals at ambient conditions (T=25°C) (n = 3, mean values ± SD)

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 sonication time, 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 (Figure 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 and BbF, respectively, at 25°C after 150 min sonication time.

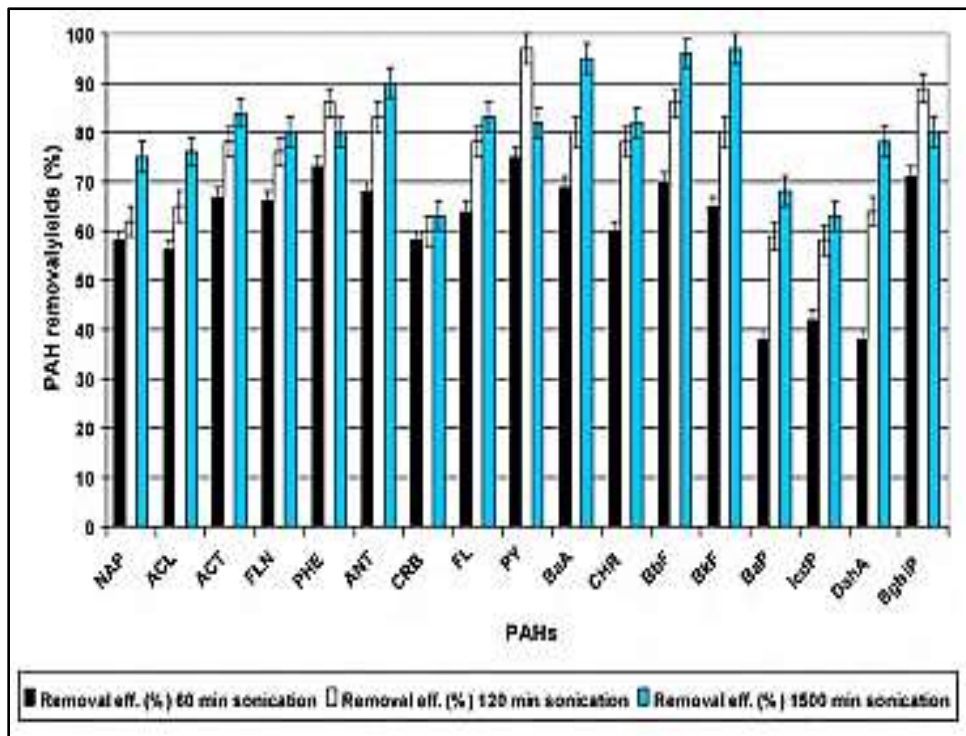


Figure 2: Effect of increasing sonication time on PAH removal efficiencies in ambient temperature ($T=25^{\circ}\text{C}$) ($n = 3$, mean values \pm SD).

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. 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 PHE from by-products such as fluorene. A decrease of the percentage remaining PHE was expected at longer sonication times due to high temperature and radical reactions from cavitation. A radical mechanism proposed by David [6] 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.

The PAH removals found in our study were high in comparison to the study performed by David [6]. They found 74%, 72% and 76% PHE, NAP and ACL degradation rates, respectively, at 40°C after 150 min sonication time [19]. Similarly, in a study performed by Litlee et al. [20] it was found that 0.6 mg/l PHE was removed with low yields (32%) at 22°C after 20 min sonication time. However, increasing the sonication time to 135 min led to about 56% removal in a sonicator with at 30 kHz and at 320 W.

Effect of Increasing Temperature on the Removal of PAHs at Increasing Sonication Times

Raw PCI ww samples were sonicated in a sonicator at 30°C and 60°C for 0 min, 60 min, 120 and 150 min sonication time. No influence of temperature increase on PAH removals at ambient temperatures from 25°C to 30°C and 60°C after 60 min sonication time was observed (Figure 3).

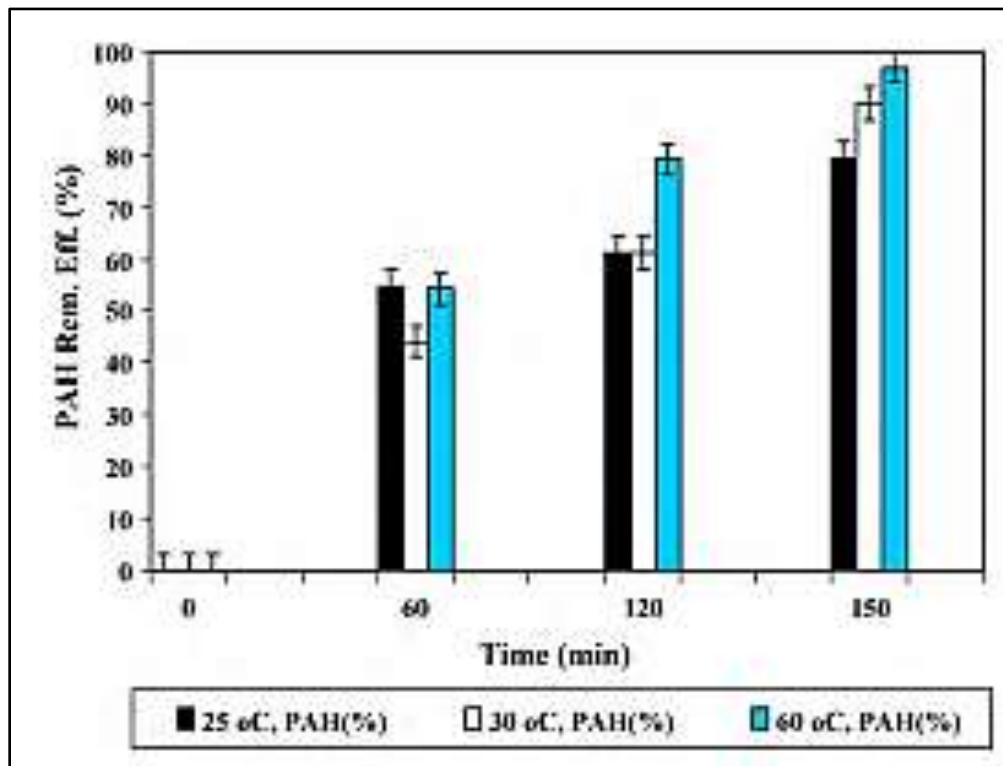


Figure 3: Effect of increasing temperature on the total PAH removal efficiencies at increasing sonication times ($n = 3$, mean values \pm SD).

As the temperature was increased from 25°C to 30°C the total PAH removal did not change after 60 min 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 sonication time. Temperature increase from 30°C to 60°C elevated the total PAH removal up to 88%–91%, respectively, after 150 min sonication time. The removal efficiencies for PAHs with 3, 4, 5 and 6 benzene rings were > 87% at 60°C after 150 min sonication time (Table 2).

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

Table 2: Influent and effluent PAH concentrations and maximum PAH removal efficiencies in the sonication experiments at DO=6 mg/l and 30°C after 150 min sonication time ($n = 3$, mean values \pm SD).

The individual PAH removal efficiencies versus increasing temperature are given in Figure 4 for 60 min, 120 min and 150 min sonication time, at 60°C.

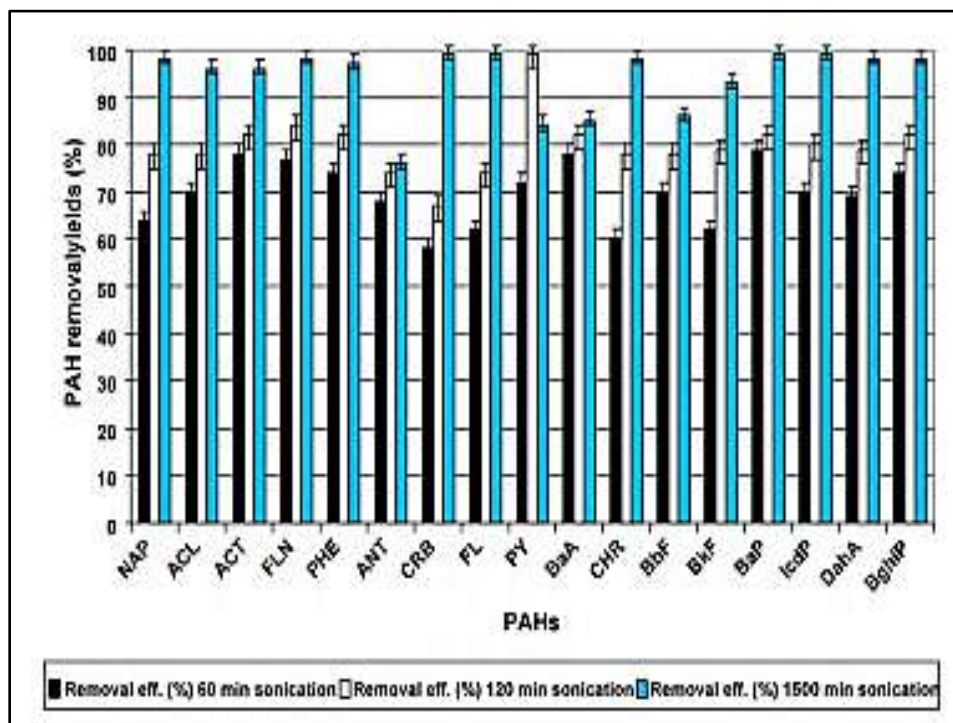


Figure 4: Maximum PAH removal efficiencies at increasing sonication times at 60°C (n = 3, mean values ± SD).

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 determined at 60°C after 150 min sonication time. 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 [6, 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 (Equation 1):

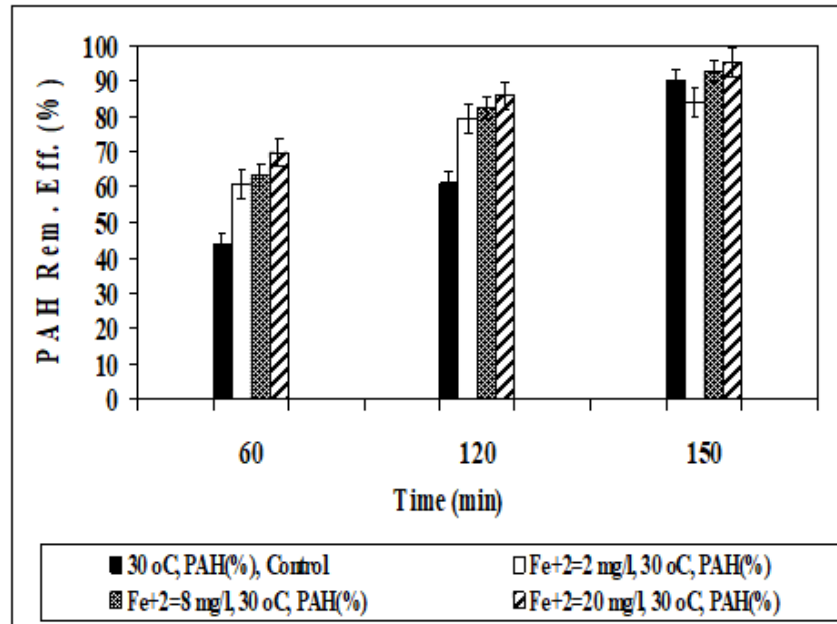
$$T_{max} = T_0 \frac{P}{P_0} (\gamma - 1) \quad (1)$$

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 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 mg/l NAP, 55 mg/l ACL and 52 mg/l

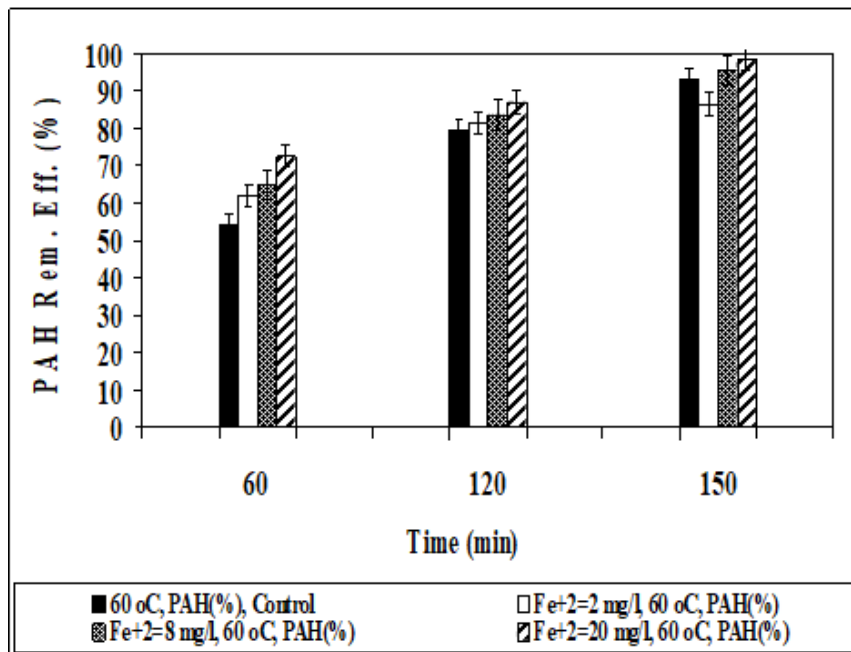
PHE) in water after 120 min sonication time, at 40°C, at 150 W and at 24 kHz, respectively. Benabdallah El-Hadj et al. [5] found 31%–34% and 44%–50% PAH removal efficiencies in mesophilic (35°C) and thermophilic (55°C) conditions for NAP and PY by a sonicator, at 20 kHz and at 70 W, after 110 min sonication time, before anaerobic digestion.

Effect of Fe⁺² Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

2 mg/l, 8 mg/l and 20 mg/l Fe⁺² ions (from FeCl₂·4H₂O) were added to the PCI ww before the sonication experiments. 83.27%, 92.62% and 95.12% total PAHs removals were obtained in 2 mg/l, 8 mg/l and 20 mg/l Fe⁺², respectively, after 150 min sonication time, at pH=7.0 and at 30°C (Figure 5a). No significant increase in PAHs yields was obtained from 8 mg/l to 20 mg/l Fe⁺² after 150 min sonication time, at pH=7.0 and at 30°C, compared to the control (without Fe⁺² while E=90.11% for total PAHs at pH=7.0 and at 30°C). A significant linear correlation between total PAHs yields and increasing sonication time was not observed (R²=0.30, F=0.28, p=0.01) (Figure 5a).



(a)



(b)

Figure 5: Effect of increasing Fe⁺² concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (at 640 W and at 35 kHz).

86.28%, 95.27% and 98.56% total PAHs yields were observed in 2 mg/l, 8 mg/l and 20 mg/l Fe^{+2} , respectively, after 150 min sonication time, at pH=7.0 and at 60°C (Figure 5b). No significant increase in total PAHs yields were obtained by increasing the Fe^{+2} concentrations compared to the control after 120 min and 150 min sonication time, at pH=7.0 and at

60°C. Sonication alone provided 96.90% total PAHs yield after 150 min sonication time, at pH=7.0 and at 60°C. The maximum total PAHs removal efficiency was 98.56% after 150 min sonication time, at $Fe^{+2}=20$

mg/l, at pH=7.0 and at 60°C. A significant linear correlation between total PAHs yields and increasing Fe^{+2} concentrations was not observed ($R^2=0.32$, $F=0.31$, $p=0.01$) (Figure 5b).

The individual PAHs removal for seventeen PAHs are given in Table 3 in 20 mg/l Fe^{+2} after 150 min sonication time, at pH=7.0 and at 60°C. The removal efficiencies of all seventeen PAHs were above 90% after 150 min sonication time. The PAHs containing four (CHR, BaA), five (BkF, BaP) and six benzene (DahA, BghiP) rings were removed with high efficiencies at 60°C after 150 min sonication time, at pH=7.0 (Table 3).

PAHs	Inf. ^(A) T=0 min PAHs (mg/l) ± SD	Eff. ^(B) T=150 min PAHs (mg/l) ± SD	T=60 min PAHs (%)	T=120 min PAHs (%)	T=150 min PAHs (%)
NAP	1884.52 ± 65.96	448.59 ± 15.70	38.99	76.87	98.94
ACL	52.34 ± 1.83	1.28 ± 0.05	69.57	83.63	97.99
ACT	70.61 ± 2.47	1.45 ± 0.05	68.64	82.51	95.93
FLN	58.20 ± 2.04	1.30 ± 0.05	69.27	83.27	97.21
PHE	138.98 ± 4.96	4.58 ± 0.16	65.55	78.79	97.44
ANT	7.52 ± 0.26	0.11 ± 0.004	71.08	86.65	94.22
CRB	14.36 ± 0.50	0.26 ± 0.009	70.68	86.16	98.50
FL	19.68 ± 0.70	0.33 ± 0.012	69.37	85.78	96.80
PY	15.75 ± 0.55	0.26 ± 0.009	71.59	86.06	96.99
BaA	0.55 ± 0.02	0.01 ± 0.0004	72.51	87.15	94.59
CHR	2.69 ± 0.09	0.04 ± 0.001	73.38	86.78	96.76
BbF	0.80 ± 0.03	0.01 ± 0.0004	70.49	84.14	90.37
BkF	0.80 ± 0.03	0.01 ± 0.0004	72.49	88.14	95.23
BaP	0.07 ± 0.003	0.001 ± 0.00004	75.54	89.19	98.45
IcdP	1.09 ± 0.04	0.02 ± 0.0007	72.47	87.12	98.59
DahA	4.60 ± 0.16	0.07 ± 0.003	72.26	86.86	97.63
BghiP	0.51 ± 0.02	0.01 ± 0.0004	70.51	82.16	97.52

^(A) Inf.= influent, ^(B) Eff. = effluent.

Table 3: Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in $Fe^{+2}=20$ mg/l, after 60 min, 120 min and 150 min sonication time, at 60°C (at 640 W, at 35 kHz, initial $COD_{dis} = 1027.43$ mg/l, initial TOC = 620.81 mg/l, initial total PAHs = 1378.77 mg/l, n=3, mean values ± SD).

These high removals in PAHs with high molecular weights could be attributed to effective sonication at 35 kHz with 20 mg/l Fe^{+2} . The findings of the study demonstrate that sonication enhanced with 20 mg/l Fe^{+2} can be used to improve the mass transport of poorly soluble PAHs in PCI ww and alleviate limiting steps of removal of hydrophobic refractory PAHs after 150 min sonication time, at 60°C. Furthermore, the reaction of Fe^{+2} with H_2O_2 form OH^\bullet ion. This phenomenon leading to the destruction of benzene rings of hydrophobic and hydrophilic PAHs. Some of the recent studies showed that there is a highly significant relationship between the average removal percentages and the hydrophobicity of PAHs, indicated as the octanol water partition coefficient is shown [18, 21]. It becomes evident that a larger hydrophobicity resulted in smaller removal of the PAHs. However, in this study, the 4-ring, 5-ring and 6-ring PAHs, in contrast to the relationship mentioned above, exhibiting

higher removals than expected from their log K_{ow} at 60°C after 150 min sonication time. No significant correlation was observed between PAHs yields, water solubility, vapor pressure, C number in benzene rings, Henry's law constant through sonication assisted 20 mg/l Fe^{+2} at 60°C after 150 min sonication time ($R^2=0.43$, $F=3.56$, $p=0.001$) (Table 4).

On the other hand, it was found that the coefficient of the correlation between the PAHs yields and the residual concentrations was strong and significant ($R^2=0.83$, $F=13.16$, $p < 0.001$) at 60°C after 150 min sonication time (Figure 6). Similar PAHs removal in PAHs with low and high benzene rings could be attributed to the remaining PAHs percentages varying between 0.04% and 10% after 150 min sonication time since the hydrophobic PAHs can easily diffuse near cavitation bubbles under pyrolytic destruction.

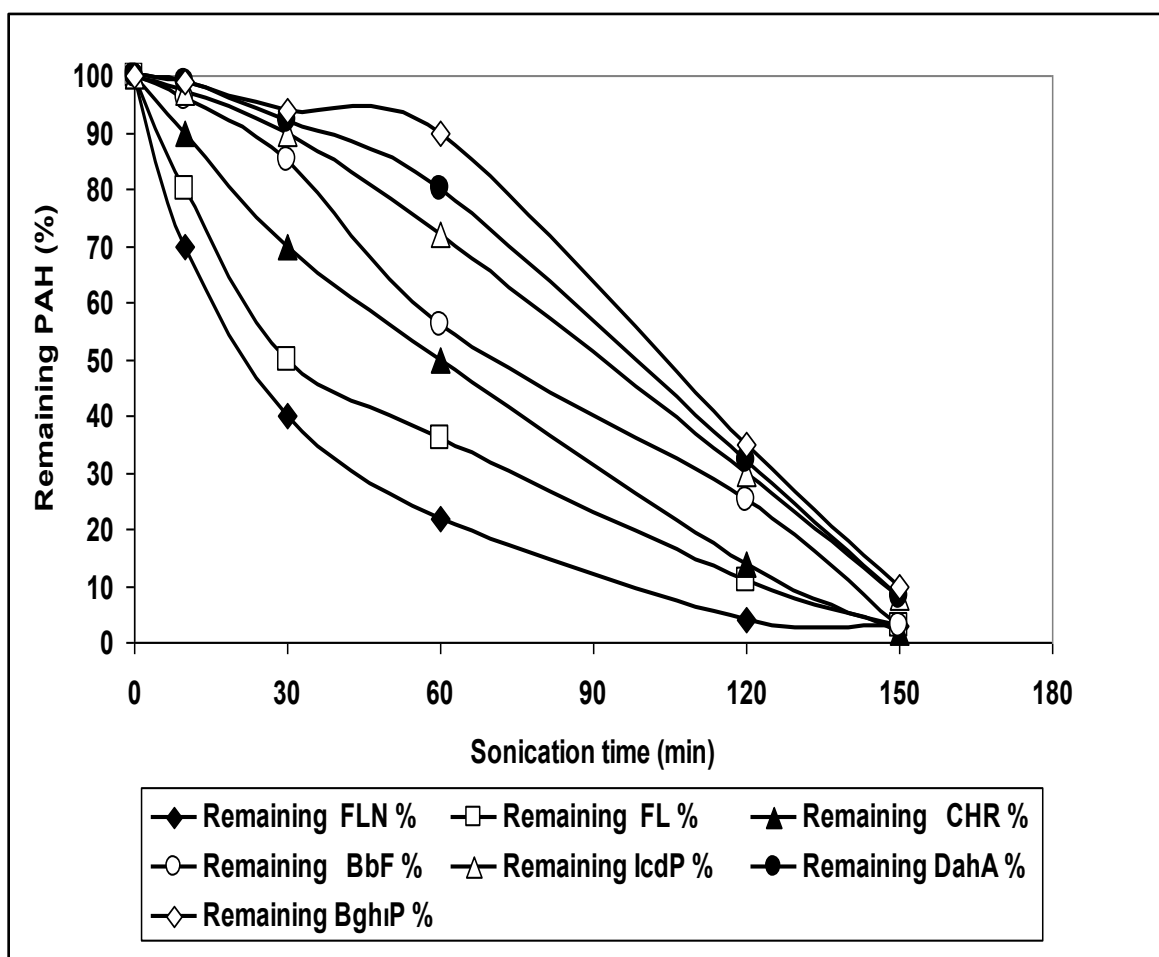


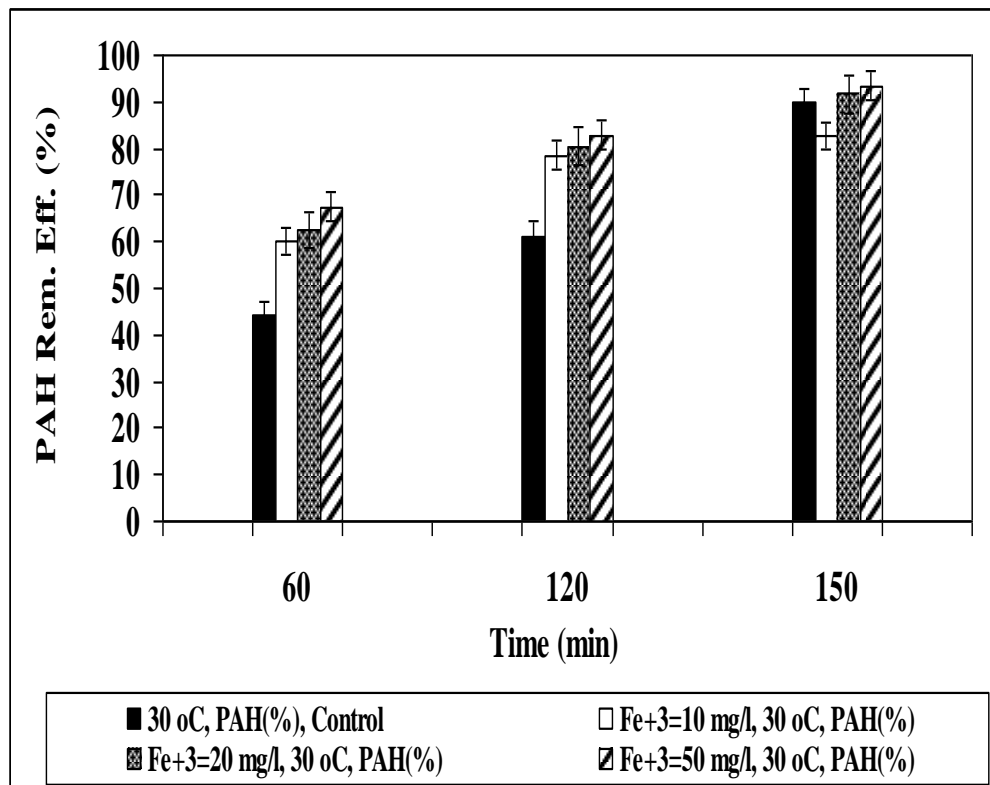
Figure 6: The remaining (untreated) PAHs percentages versus sonication time in pseudo first order reaction kinetic (at 640 W and at 35 kHz).

As reported by Lindsey and Tarr [14] a possible explanation of the positive effect of Fe^{+2} on the sonication of PAHs could be the reaction of Fe^{+2} with H_2O_2 to form OH^\bullet at 34 kHz and at 450 W after 125 min sonication time, at 60°C. As this reaction proceeds, the concentration of Fe^{+2} declines, and consequently the rate of H_2O_2 consumption and OH^\bullet formation decline. The loss of Fe^{+2} is eventually balanced by the formation of Fe^{+2} through reduction of Fe^{+3} by reaction with H_2O_2 or $\text{O}_2\text{H}^\bullet$, and a steady state Fe^{+2} concentration is reached. At this point (> 60 s), pseudo first order loss of H_2O_2 is observed. This explanation is also supported by evidence that the OH^\bullet formation rate is significantly higher in the first 60 s. Psillakis et al. [7] studied the sono-removal of 150 $\mu\text{g/l}$ total initial concentration of PAHs mixture (NAP, ACT, PHE) in an aqueous solution. 92.20% of NAP, 96.25% of ACT and 89.80% of PHE removal efficiencies were found with $\text{Fe}^{+2}=14$ mg/l, in a sonicator with at 150 W, at 80 kHz, at 20°C, after 150 min irradiation. In our study the removal efficiencies for the aforementioned PAHs were found to be higher ($E_{\text{NAP}}=99\%$, $E_{\text{ACT}}=98.25\%$ and $E_{\text{PHE}}=98.11\%$) at 35°C for the same sonication time. Beckett and Hua [22] and Beckett and Hua [23] also found that the addition of 0.02-1.00 mg/l Fe^{+2} concentrations improved the 1,4-dioxane decomposition rate and mineralization efficiency at 30 kHz and at 590 W after 115 min sonication time. During aqueous ultrasonic irradiation, OH^\bullet

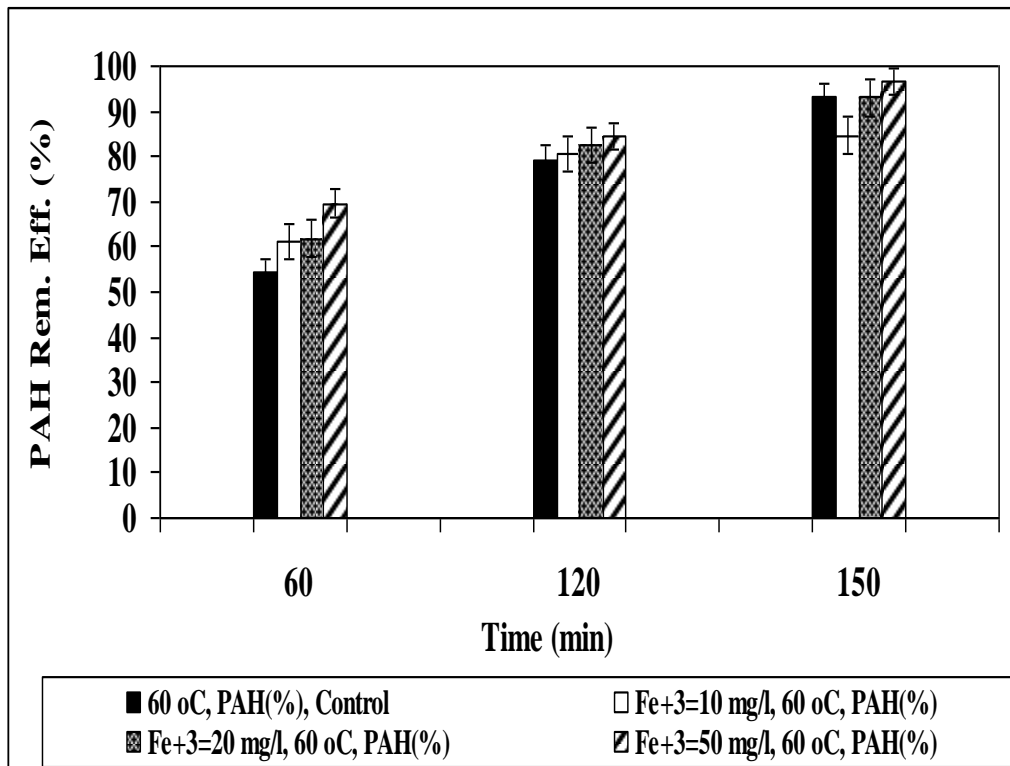
formed during the thermolytic reactions of H_2O recombine to form H_2O_2 that tends to accumulate in the solution and does not usually play an important role in oxidizing organic species. However, the reaction between H_2O_2 and Fe^{+2} is known to produce OH^\bullet and is commonly referred to as the Fenton process [21].

Effect of Fe^{+3} Concentrations on the Removal of PAHs in PCI ww at Increasing Sonication Times and Temperatures

Increasing Fe^{+3} concentrations (10 mg/l, 20 mg/l and 50 mg/l) were added to the PCI ww before sonication process. 82.92%, 91.72% and 93.58% total PAHs removals were measured in 10 mg/l, 20 mg/l and 50 mg/l Fe^{+3} , respectively, after 150 min sonication time, at pH=7.0 and at 30°C (Figure 7a). An increase of 14.66%-22.28% and 16.21%-20.55% in total PAHs yields were measured for after 60 min and 120 min sonication time, compared to the control (without Fe^{+3}) at pH=7.0 and at 30°C. Although, a correlation between PAHs removal efficiencies and Fe^{+3} concentrations were obtained this relationship was not significant ($R^2=0.76$, $F=2.56$, $p=0.01$). Control provided 90.11% total PAHs yield after 150 min sonication time, at pH=7.0 and at 30°C (Figure 7a).



(a)



(b)

Figure 7: Effect of increasing Fe³⁺ concentrations on the total PAHs removal efficiencies in PCI ww at (a) 30°C and (b) 60°C versus increasing sonication times (at 640 W and at 35 kHz).

84.61%, 93% and 96.76% total PAHs yields were observed in 10 mg/l, 20 mg/l and 50 mg/l Fe^{+3} , respectively, after 150 min sonication time, at pH=7.0 and at 60°C (Figure 7b). The contribution of increasing Fe^{+3} on the total PAHs removal was only 7.06%-15.41% and 1.25%-5.04% compared to the control after 60 min and 120 min sonication time, at pH=7.0 and at 60°C. The maximum total PAHs removal efficiency was 96.76% after 150 min sonication time in $Fe^{+3}=50$ mg/l at pH=7.0 and at 60°C. However, this contribution of Fe^{+3} was no significant ($R^2=0.66$, $F=9.86$, $p=0.01$). Similarly, increasing the Fe^{+3} concentrations did not significantly affect the PAHs yields compared to the control after 120 min

and 150 min sonication time, at pH=7.0 and at 60°C ($R^2=0.52-0.56$, $F=8.34-9.91$, $p=0.01$) (Figure 7b).

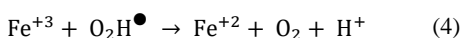
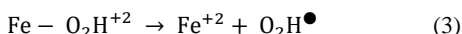
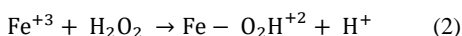
95.80% BbF, 90.29% BkF, 96.84% BaP, 97.13% IcdP, 95.18% DahA and 94.95% BghiP maximum removal yields were obtained for PAHs with four, five and six benzene rings after 150 min sonication time, at 60°C in 50 mg/l Fe^{+3} (Table 4). The yields found in this study were not dependent to the physicochemical properties of the PAHs. Therefore, a significant correlation between the PAHs removals and the high octanol-air coefficient and the octanol-water coefficient of the heavily PAHs was not observed ($R^2=0.39$, $F=3.91$, $p=0.01$).

PAHs	Inf. ^(A) T=0 min PAHs (mg/l) ± SD	Eff. ^(B) T=150 min PAHs (mg/l) ± SD	T=60 min PAHs (%)	T=120 min PAHs (%)	T=150 min PAHs (%)
NAP	1896.53 ± 66.38	472.83 ± 16.55	47.18	75.05	97.84
ACL	52.37 ± 1.83	2.20 ± 0.08	66.74	80.85	95.91
ACT	70.67 ± 2.47	2.67 ± 0.09	65.83	79.76	91.71
FLN	58.23 ± 2.04	2.31 ± 0.08	66.44	80.50	94.32
PHE	139.17 ± 4.87	6.88 ± 0.24	62.83	76.12	94.80
ANT	7.53 ± 0.26	0.25 ± 0.009	69.18	83.81	94.40
CRB	14.36 ± 0.50	0.52 ± 0.02	68.78	83.33	96.94
FL	19.69 ± 0.70	0.68 ± 0.02	67.48	82.97	93.48
PY	15.75 ± 0.55	0.54 ± 0.02	68.70	83.24	93.88
BaA	0.55 ± 0.02	0.02 ± 0.0007	69.59	84.31	94.58
CHR	2.69 ± 0.09	0.09 ± 0.003	67.46	82.16	93.40
BbF	0.80 ± 0.03	0.03 ± 0.001	70.57	84.29	95.80
BkF	0.80 ± 0.03	0.03 ± 0.001	69.57	80.29	90.29
BaP	0.07 ± 0.003	0.002 ± 0.0001	72.62	87.34	96.84
IcdP	1.09 ± 0.04	0.04 ± 0.001	67.56	84.27	97.13
DahA	4.60 ± 0.16	0.15 ± 0.005	69.35	81.02	95.18
BghiP	0.51 ± 0.02	0.02 ± 0.0007	62.59	80.31	94.95

^(A) Inf.= influent, ^(B) Eff. = effluent.

Table 4: Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments in $Fe^{+3}=50$ mg/l after 60 min, 120 min and 150 min sonication time, at 60°C (at 640 W, at 35 kHz, initial $COD_{dis} = 1027.43$ mg/l, initial TOC = 620.81 mg/l, initial total PAHs = 1378.77 mg/l, n=3, mean values ± SD).

In the presence of Fe^{+3} , the sonolytic degradation of less hydrophobic PAHs was enhanced by the increase in OH^\bullet induced from the decomposition of the recombined H_2O_2 [24]. Under these conditions, it can be expected that $Fe-O_2H^{+2}$ as an intermediate produced from the reaction of Fe^{+3} with H_2O_2 and it may be partitioned as Fe^{+2} and O_2H^\bullet by the ultrasonic irradiation in Equation (2) and Equation (3) [24]. The regenerated Fe^{+2} also catalyze the decomposition of H_2O_2 in Equation (3). These results suggest that in the presence of Fe^{+3} , the sonolytic degradation of less hydrophobic PAHs was enhanced by the increase in OH^\bullet [24] in Equation (4).



A large fraction of Fe^{+3} formed from the reaction Fe^{+2} with H_2O_2 would mainly exist in the form of $Fe^{+3}-O_2H$ or $Fe^{+3}-OH$ complexes. Fe^{+3} /ultrasound it can be expected that $Fe-O_2H$ as an intermediate produced from the reaction of Fe^{+3} with H_2O_2 may be partitioned as Fe^{+2} and O_2H^\bullet by the ultrasonic irradiation. It was found that the Fe^{+3} /ultrasound system

under O_2 is more effective for mineralization than the Fe^{+2} /ultrasound system and ultrasound only [14]. For Fe^{+3} , the overall degradation of

organic compounds by oxidation is slower, but the mineralization process is successfully achieved. The degradation of organic compounds by the attack of OH^\bullet can be enhanced.

PAH Degradation Kinetics

The sonic degradation of 17 PAHs in the raw PCI ww was found to be pseudo first order with respect to PAH concentrations at a frequency of 35 kHz and 60°C (Equation 5).

$$-\frac{d[PAH]}{dt} = k[PAH]_t \quad (5)$$

The degradation rates for all PAHs were deduced from the slopes of the curves given by (Equation 6);

$$\ln \frac{[PAH]_t}{[PAH]_0} = k[PAH] \times t \quad (6)$$

where, $k[PAH]$ is the rate constant at 35 kHz, $[PAH]_0$ the initial PAH concentration and $[PAH]_t$ 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 5.

PAHs	k_{PAH/HO^\bullet} ^a	k_{pf} ^b	$[HO^\bullet]_{ss}$ ^c	V_{PAH/HO^\bullet} ^d	$V_{PAH/US}$ ^e	$V_{PAH/HO^\bullet} / V_{PAH/US}$ ^f
NAP	2.8×1018	0.026	9.28×10^{-21}	0.0029	0.52	0.05
ACL	2.6×1018	0.024	9.23×10^{-21}	0.023	0.48	0.04
PHE	2.3×1018	0.017	4.34×10^{-21}	0.009	0.06	0.15
PY	1.5×1018	0.015	1.44×10^{-21}	0.003	0.04	0.07
BhP	0.9×1018	0.011	1.22×10^{-21}	0.001	0.04	0.02

a: PAH oxidation rate (ng/ml.s); b: Experimental pseudo first order reaction of PAH (1/min); c: Steady-state $[HO^\bullet]$ concentrations (mg/l); d: PAH oxidation rate (mg/l.min); e: Experimental rate of PAH sonodegradation (mg/l.min); f: The percentage of PAH oxidation with HO^\bullet ratio to conventional sonodegradation.

Table 5: 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 time, at 35 kHz and at 60°C (n = 3, mean values).

The pseudo first order rate constants ranged between $k=0.011$ 1/min and $k=0.026$ 1/min. The pseudo first order kinetic rate constants obtained in this study agree with the literature data of low frequencies (20 kHz and 32 kHz) [5, 8, 12]. 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 [6]. 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 [6] 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 5). 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 time (Figure 8). Therefore, the removal efficiencies for all PAHs were > 95% after 150 min sonication time (Figure 8).

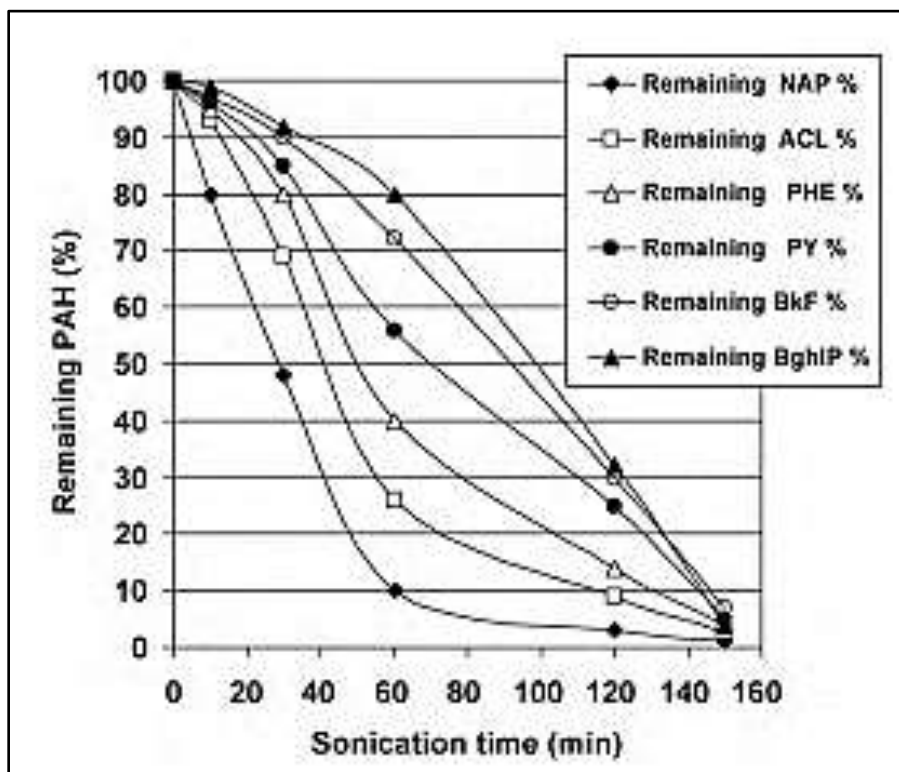


Figure 8: Effects of sonication time on the residual PAH percentages (n = 3, mean values).

A more energetic implosion of cavitation bubbles is expected to occur at low frequency because a larger bubble radius is observed in that range [25, 26]. 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 kHz – 30 kHz [6]. This contributes

to enhancing the penetration of water containing PAHs into the bubbles. Suslick [27] showed that non-linear bubble implosions play a significant role on the degradation of chemicals at low frequency. De Visscher et al. [25] 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 (CO₂, CH₄ and H₂S) 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• as reported by Dewulf et al. [26] since the formation of these products arises from a possible OH•-driven oxidation.

Mechanisms of PAH Sonication

Some studies suggested that PAHs for example (PHE are degraded by a free radical mechanism with OH•, since hydroxylated compounds like phenanthrenediols have been detected [6]. 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 [28]. The contribution of the oxidation pathway of PAHs through ultrasonic degradation can be determined. If we assume that OH• is the main species leading to sonodegradation of PAHs, the oxidation rate $V_{PAH/OH\bullet}$ can be calculated using (Equation 7):

$$V_{PAH/OH\bullet} = - \left(\frac{d[PAH]}{dt} \right)_{OH\bullet} = k_{PAH/OH\bullet} [PAH][OH\bullet]_{ss} \quad (7)$$

where; $k_{PAH/OH\bullet}$ is the second order reaction kinetic rate constant, $[OH\bullet]$ is the steady-state OH• concentration in PCI ww under ultrasound and

$[PAH]$ is the PAH concentration. The experimental rate of PAH sonodegradation $V_{PAH/US}$ is given with Equation (8) and Equation (9):

$$V_{PAH/US} = \{d[PAH]/dt\}_{US} = k_{pf}[PAH] \quad (8)$$

Therefore,

$$k_{pf} = k_{PAH/OH\bullet} [OH]_{ss} \quad (9)$$

where; k_{pf} is the experimental pseudo first order reaction kinetic rate constant. It is assumed that the sonication process is 100% controlled by oxidation of PAHs with $[OH\bullet]$ at 35 kHz. $[OH\bullet]_{ss}$ is the calculated the steady-state concentrations in PCI ww during sonication of 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 [13] (Table 5). The calculated values of $[OH\bullet]_{ss}$ concentrations are in good agreement with the studies performed by David [6] and Destailats et al. [29]. A comparison of calculated oxidation rates of OH• with Equation (6) for the experimental sonodegradation rates is given in Table 5 for at 35 kHz for five PAHs.

Since the sonooxidation of NAP, ACL, PHE, PY and BbF PAHs comprised 0.05%, 0.04%, 0.15%, 0.07% and 0.02%, respectively, of the

total sonodegradation process, OH• is not the major process for complete degradation of these PAHs (Table 5). In this study, the contribution of OH• is minor for the ultimate sonodegradation of PAHs. The formation of by-products (hydroxylated compounds namely phenanthrenediols) for possible OH• 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 pyrolytic mechanism of PAH degradation a synthetic saturated solution of a mixture of 16 PAHs (1 mg/l) was prepared to detect the gaseous by-products in the headspace of the sonication reactor (David, 2009). 67% CO₂ and 56% CH₄ were measured after 30 min sonication time. This could be explained by the rapid formation of the aforementioned two gases as PAHs penetrate the cavitation bubbles in order to be pyrolyzed, as reported by David [6].

Effect of Sonolysis Operating Parameters on the Acute Toxicity Removal

The *Daphnia magna* test is accepted as an acute toxicity test. Toxicity was estimated in terms of EC₅₀, defined as the concentration of the toxicant causing 50% reduction in activity of the water flea. Table 6 shows the acute toxicity test results obtained from the *Daphnia magna* test through sonication with increasing temperatures, Fe⁺² and Fe⁺³ concentrations.

The test samples containing an initial total PAH concentration of 1380 mg/l 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 6; SET 1, the initial EC₅₀ values in control samples containing no Fe⁺² and Fe⁺³ were measured as 342.60 mg/l at 25°C. After 120 min and 150 min of sonication the EC₅₀ values decreased to EC₄₀ and EC₃₅ at 25°C. The toxicity decreased approximately to the ratios 2/5 and 4/5 respectively. The EC₄₀ and the EC₃₅ values were measured as 325 mg/l and 182 mg/l, respectively, at 25°C (Table 6; SET 1). This showed that the PAHs were degraded to less toxic by-products via sonication. The toxicity removal efficiencies were 46% and 70% after 120 min and 150 min of sonication, respectively, in control samples at 25°C (Table 6; SET 1). This indicates a significant lowering of the acute toxicity in the control samples at 25°C. The GL (dilution ratio) value was found as 0.16 and 0.05 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).

Set	Conditions	EC ₅₀ (mg/l)				* EC (mg/l) values			
		25 (°C)				25 (°C)			
		0 ^a	60 ^a	120 ^a	150 ^a	0 ^a	60 ^a	120 ^a	150 ^a
1	Control	618	EC ₄₅ =425	EC ₄₀ =325	EC ₃₅ =182				
Set	Conditions	EC ₅₀ (mg/l)				EC (mg/l) values			
		30(°C)				60(°C)			
		0 ^a	60 ^a	120 ^a	150 ^a	0 ^a	60 ^a	120 ^a	150 ^a
2	Control	618	EC ₄₀ =510	EC ₃₅ =340	EC ₃₀ =85	618	EC ₄₀ =425	EC ₃₀ =190	EC ₂₅ =32
3	Fe ⁺² =2 ^b	618	EC ₄₀ =360	EC ₃₀ =180	EC ₂₀ =125	618	EC ₃₅ =350	EC ₂₅ =170	EC ₁₅ =110
	Fe ⁺² =8 ^b	618	EC ₃₅ =340	EC ₂₅ =160	EC ₁₅ =65	618	EC ₃₀ =310	EC ₂₀ =150	EC ₁₀ =47
	Fe ⁺² =20 ^b	618	EC ₄₅ =300	EC ₃₅ =150	EC ₂₅ =50	618	EC ₃₅ =275	EC ₃₀ =130	EC ₂₀ =15

4	Fe ⁺³ =10 ^b	618	EC ₄₀ = 350	EC ₃₀ = 210	EC ₂₀ = 160	618	EC ₃₅ = 390	EC ₂₅ = 170	EC ₁₅ = 130
	Fe ⁺³ =20 ^b	618	EC ₃₅ = 360	EC ₂₅ = 175	EC ₁₅ = 70	618	EC ₃₀ = 355	EC ₂₀ = 180	EC ₁₀ = 60
	Fe ⁺³ =50 ^b	618	EC ₄₅ = 460	EC ₄₀ = 180	EC ₂₅ = 65	618	EC ₄₀ = 300	EC ₃₀ = 160	EC ₂₀ = 32

a: Sonication time (min), b: Concentration (mg/l). * EC values were calculated based on COD (mg/l).

Table 6: Effect of sonication on the *Daphnia magna* acute toxicity (EC₅₀) removal efficiencies under different operational conditions [T(°C)= 25–60°C; T(min)= 60–150 min; Fe⁺²: 2–20 mg/l; Fe⁺³: 10–50 mg/l, n = 3, mean values].

The EC₅₀ values decreased to EC₃₀ to EC₂₀ and to EC₁₀ after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺²=8 mg/l at 60°C (Table 6; SET 3). The EC₃₀, the EC₂₀ and the EC₁₀ values were measured as 310 mg/l, 150 mg/l and 47 mg/l, respectively, in Fe⁺²=8 mg/l at 60°C. The toxicity removal efficiencies were 40%, 60% and 80% after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺²=8 mg/l at 60°C. 80% maximum *Daphnia magna* acute toxicity removal was measured in Fe⁺²=8 mg/l after 150 min sonication time, at 60°C (Table 6; SET 3).

The EC₅₀ values decreased to EC₄₀=360 mg/l to EC₃₀=180 and to EC₂₀=125 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺²=2 mg/l at 30°C (Table 6; SET 3). The EC₅₀ values decreased to EC₄₅=300 mg/l to EC₃₅=150 mg/l and to EC₂₅=50 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺²=20 mg/l at 30°C. The toxicity removal efficiencies were 60% and 50% in 2 mg/l Fe⁺² and 20 mg/l Fe⁺², respectively, after 150 min sonication time, at 30°C. It was obtained an inhibition effect of Fe⁺²=20 mg/l to *Daphnia magna* after 150 min sonication time, at 30°C (Table 6; SET 3).

The EC₅₀ values decreased to EC₃₅=350 mg/l to EC₂₅=170mg/l and to EC₁₅=110 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺²=2 mg/l at 60°C (Table 6; SET 3). The EC₅₀ values decreased to EC₃₅=275 mg/l to EC₃₀=130 mg/l and to EC₂₀=15 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺²=20 mg/l at 60°C. The toxicity removal efficiencies were 70% and 60% in 2 mg/l Fe⁺² and 20 mg/l Fe⁺², respectively, after 150 min sonication time, at 60°C. It was observed an inhibition effect of Fe⁺²=20 mg/l to *Daphnia magna* after 150 min sonication time, at 60°C (Table 6; SET 3).

The acute toxicity decreased from an initial 618 mg/l to EC₁₀=47 mg/l at Fe⁺²=8 mg/l, at 60°C after 150 min sonication time (Table 6; SET 3). The maximum acute toxicity removal was nearly 80% in the samples containing at Fe⁺²=8 mg/l, at 60°C after 150 min sonication time. The acute toxicity removal decreased at Fe⁺² concentrations above 8 mg/l (Table 6; SET 3).

The initial EC₅₀ values were observed as 618 mg/l at 25°C (Table 6; SET 1). After 60 min, 120 min and 150 min of sonication the EC₅₀ values decreased to EC₃₅=360 mg/l to EC₂₅=175 mg/l and to EC₁₅=70 mg/l in Fe⁺³=20 mg/l at 30°C. The toxicity removal efficiencies were 30%, 50% and 70% after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=20 mg/l, at 30°C (Table 6; SET 4).

The EC₅₀ values decreased to EC₃₀ to EC₂₀ and to EC₁₀ after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=20 mg/l, at 60°C (Table 6; SET 4). The EC₃₀, the EC₂₀ and the EC₁₀ values were measured as 355 mg/l, 180 mg/l and 60 mg/l, respectively, in Fe⁺³=20 mg/l at 60°C. The toxicity removal efficiencies were 40%, 60% and 80% after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=20 mg/l at 60°C. 80% maximum *Daphnia magna* acute toxicity removal was obtained in Fe⁺³=20 mg/l after 150 min sonication time, at 60°C (Table 6; SET 4).

The EC₅₀ values decreased to EC₄₀=350 mg/l to EC₃₀=210 mg/l and to EC₂₀=160 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=10 mg/l at 30°C (Table 6; SET 4). The EC₅₀ values decreased to EC₄₅=460 mg/l to EC₄₀=180 mg/l and to EC₂₅=65 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=50 mg/l at 30°C. The toxicity removal efficiencies were 60% and 50% in Fe⁺³=10 mg/l and Fe⁺³=50 mg/l, respectively, after 150 min sonication time, at 30°C. It was obtained an inhibition effect of Fe⁺³=50 mg/l to *Daphnia magna* after 150 min sonication time, at 30°C (Table 6; SET 4).

The EC₅₀ values decreased to EC₃₅=390 mg/l to EC₂₅=170 mg/l and to EC₁₅=130 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=10 mg/l at 60°C (Table 6; SET 4). The EC₅₀ values decreased to EC₄₀=300 mg/l to EC₃₀=160 mg/l and to EC₂₀=32 mg/l after 60 min, 120 min and 150 min sonication time, respectively, in Fe⁺³=50 mg/l at 60°C. The toxicity removal efficiencies were 70% and 60% in 10 mg/l Fe⁺³ and 50 mg/l Fe⁺³, respectively, after 150 min sonication time, at 60°C. It was observed an inhibition effect of Fe⁺³=50 mg/l to *Daphnia magna* after 150 min sonication time, at 60°C (Table 6; SET 4).

Conclusions

The results of this study show that PAHs in PCI ww could be treated efficiently with low-frequency sonication. Although, the degradation efficiency of PAHs in PCI ww was affected by the time, temperature, Fe⁺² and Fe⁺³ sonication alone could provide 90.11%-96.90% PAH removals at 30°C and 60°C after 150 min sonication time. The optimum operational conditions for maximum PAH removals at 25°C and 60°C were Fe⁺²=20 mg/l and Fe⁺³=50 mg/l, respectively, after 150 min sonication time. All the PAHs were removed with treatment efficiencies above 87% (up to 99%) after 150 min sonication time, at 60°C.

The matrix for the maximum *Daphnia magna* acute toxicity removals (100%) was 80% *Daphnia magna* acute toxicity yield for Fe⁺²=20 mg/l and 70% *Daphnia magna* acute toxicity yield for Fe⁺³=10 mg/l, respectively, at 60°C after 150 min sonication time, respectively. The *Daphnia magna* acute toxicity measurement procedure was successfully applied to seventeen PAHs removals during sonication process in the PCI ww with the addition of different Ferrous ions and Ferric ions concentrations, respectively.

The PAH sonodegradation appeared to be Pseudo first-order rate constants in PAHs NAP, ACL, PHE, PY and BbF (k = 0.026 1/min, k=0.024 1/min, k=0.017 1/min, k=0.015 1/min and k=0.011 1/min, respectively). The main PAH degradation mechanism during ultrasonic irradiation is pyrolysis.

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