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Sonication of Petrochemical Industry Wastewaters

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Authors' contributions

This work was carried out in collaboration between both authors. Authors RO and DTS designed the study, performed the laboratory studies and instruments analysis, wrote the protocol and wrote the first draft of the manuscript. Author DTS managed the analyses of the study and the control of the all study. Authors RO and DTS managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

The objective of the study was the treatment of the pollutants (dissolved chemical oxygen demand (COD_{dis}), total organic carbon (TOC) and total and individual polycyclic aromatic hydrocarbons (PAH)) present in the petrochemical industry wastewater (PCI) by sonication. The effects of increasing sonication times (0 min, 60 min, 120 and 150 min), sonication temperatures (25°C, 30°C and 60°C), on the COD_{dis}, TOC and (PAH) removal efficiencies were researched at a sonication frequency of 35 kHz and a sonication power of 640. All the PAHs and their metabolites were measured by an gas chromatography (Agilent 6890 NC) equipped with a mass selective detector (Agilent 5973 inert MSD) with a capillary column (HP5-MS, 30 m, 0.25mm, 0.25µm)). The CH_4, CO_2 and H_2 gas analysis, COD_{dis}, TOC and the other pollutants were measured according to Standard Methods. As the sonication time and temperature were increased from 60 to 120 and 150 min, and from 25°C to 30°C and to 60°C, the COD_{dis}, total PAH and TOC yields increased from 80.16% to 92.15%, from 78.37% to 94.23% and from 79.65% to 96.90%, respectively. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid, naphthalene, p–hydroxybenzoic acid, fluorene, di–hydroxy pyrene, pyrene di–hydrodiol were sonodegraded with yields of 92.11%, 95.23%,

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98.42%, 97.34%, 99.44%, 96.30%, 99.36%, 97.17%, 99.63% and 99.98% respectively, after 150 min, at 25°C. The presence of CH_4, H_2 and CO_2 gases during sonication showed that the degradation mechanism of the PAHs is ‘‘pyrolysis”.

Keywords: Chemical oxygen demand; petrochemical industry wastewater; polycyclic aromatic hydrocarbons intermediates; pyrolysis; sonication; total organic carbon.

1. INTRODUCTION

A great amount of waste containing high concentration of petroleum hydrocarbons (PHCs) is produced through petroleum production, storage, transportations and refining. Highly toxic waste not only causes irreparable pollution to the environment but also poses threat to human health, and is not legally allowed to be discharged without treatment. Increasing use of fossil fuels leads to the increase of polyaromatics waste products, thus imposing a burden on treatment facilities [1]. Ultrasound shows great promise for both upstream and downstream of the petroleum industry due to its cleanliness, low cost and high efficiency [2]. Especially, power ultrasound (20–100 kHz) not only has favorable penetration in PAH/water media, but can also generate and transmit high energy specific density (10–1000 $W\cdot cm^{-2}$). When the cavitation bubble implodes, it induces high temperature of about 5000 K and high pressure of about 2000 atmospheres, accompanied with shock waves and micro-jets [3]. Such cavitation effects can break long chains of PAH molecules. In addition, the ultrasonic technique meets the requirements of sustainable development since it operates under moderate conditions and produces no volatile organic chemicals (VOCs). However, complicated physical and chemical characteristics of acoustic cavitation hinder our understanding of the mechanism of power ultrasound for various applications, which is required in order to optimize the operating parameters and increase efficiency. Nonetheless, few reviews comprehensively discuss the mechanism and applications of acoustic cavitation for petroleum industry. Petrochemical indutry contains trace-level toxic organic chemicals such as PAHs and polychlorinated dibenzo-*p*-dioxins and furans [4]. These trace pollutants are an important issue for recycling of the wastewater. Although various technologies for petrochemical treatment have been investigated: biological treatment acid and surfactant treatment, ultrasonic treatment, ozone treatment, electrochemical treatment and electro-flotation [5,6]. Among them, ultrasonic treatment has been used widely because of its relatively low processing cost and high efficiency of reduction. Studies have shown that PAHs in water and wastewaters are degraded with ultrasonic treatment with stronger irradiation intensity and longer irradiation time. However, these studies did not investigate the degradation of PAHs in sludge [6].

PAHs are listed as US-EPA and EU priority pollutants, and their concentrations, therefore, need to be controlled in treated wastewater effluents [7,8]. Due to their toxic, mutagenic and carcinogenic properties the US-EPA classifies 16 of these PAHs as priority pollutants [7,8]. Recent studies have shown that sonication may be a useful tool for degrading the aqueous pollutants [9-12]. 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 [12] found that naphthalene (NAP), phenanthrene (PHE), anthracene (ANT) and pyrene (PY) removal efficiencies varied between 93% and 95%, after 90 min in a sonicator with at 400 W and at 20 kHz. Psillakis et al. [13] reported a 99% removal efficiency for 0.01 µg/l of acenaphthalene (ACT), PHE and NAP at 300 W and at 24 kHz. Benabdallah El-Hadj et al. [11] found 57% NAP, 40% PY and 45% total COD removal efficiencies in a sonicator with at 70 W and at 20 kHz. Taylor et al. [14] 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. [15] 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 to 5 mg/l and from 2.4 ml/min up to 3.6 ml/min.

When sonolysis of water occurs, it leads to the formation of the non-specific oxidative species hydroxyl radicals ($OH^\bullet$). 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 [16,17]. 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 $OH^{\bullet}$ [14,15] and (ii) pyrolytic decomposition [13].

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) [11,13,18-20]. No study was found investigating the effects of operational conditions such as sonication time, temperature, PAHs metabolites (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3 thiadiazole–4–carboxylic acid, naphthalene, p-hydroxybenzoic acid, fluorene, di-hydroxy pyrene, pyrene di-hydrodiol) on the sonication of a petrochemical industry wastewater. Furthermore, Furthermore, the mechanism of PAH sonodegradation were investigated for a petrochemical industry wastewater.

Thus, in this study our aim was to determine the effects of ambient conditions, increasing sonication time (0min, 60 min, 120 min and 150 min), sonication temperatures (25ºC, 30ºC and 60ºC), on the sonodegradation of seventeen PAHs. The effects of these operational conditions on the PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3 thiadiazole–4–carboxylic acid, naphthalene, p-hydroxybenzoic acid, fluorene, di-hydroxy pyrene, pyrene di-hydrodiol) in PCI ww were determined. Furthermore, the mechanism of PAH sonodegradation was 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 30ºC and 60ºC. For ambient conditions the sonicator was not heated – it was used at 25ºC. 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 640 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 +4ºC until the sonication experiments were begun. The studies performed during this study was summarized in four step (Picture 1).

2.2 Wastewater Source

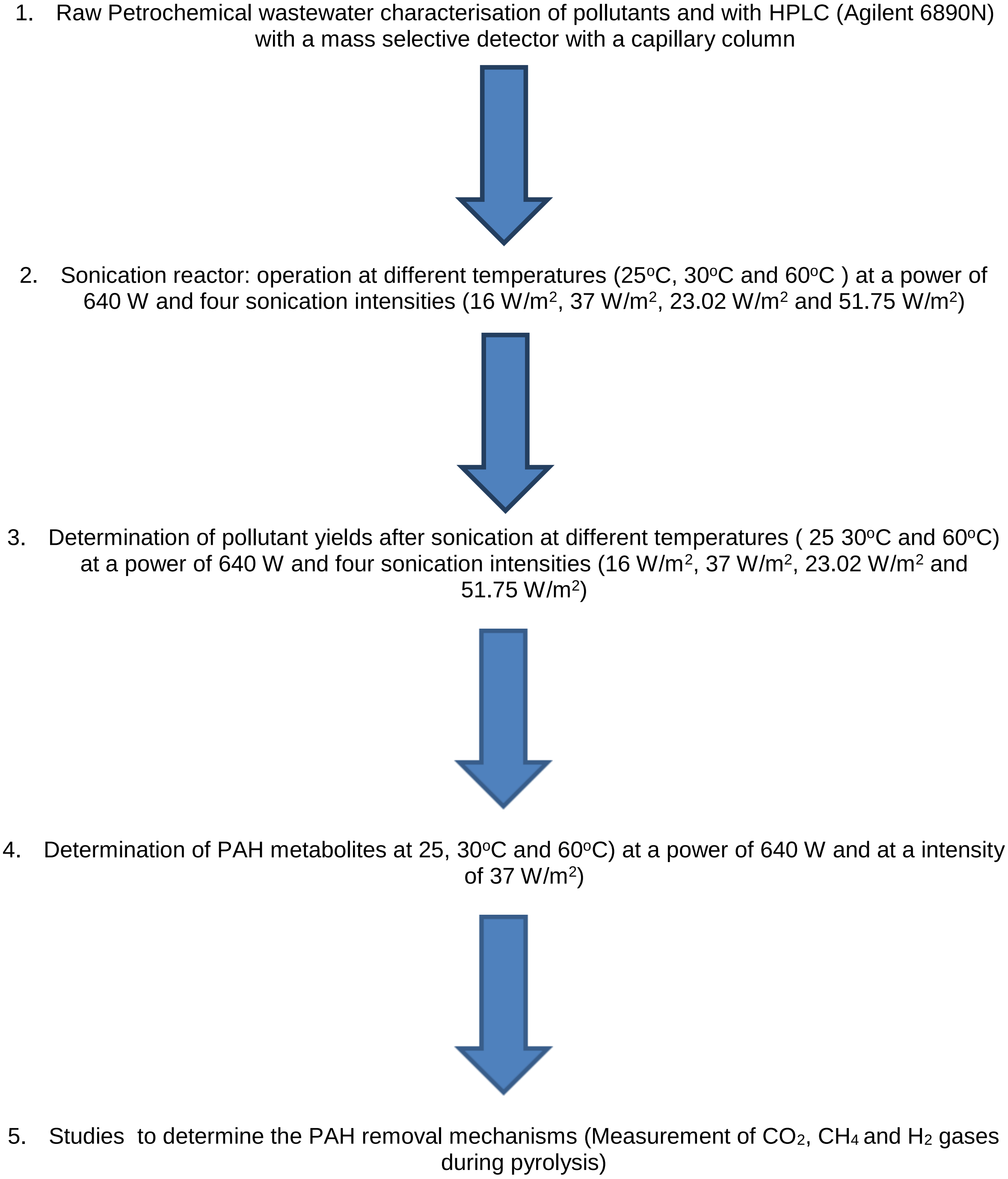
The petrochemical industry wastewater used in this study was taken from the influent of the aerobic activated sludge reactor following the mechanical treatmet of the petrochemical industry wastewater treatment plant in ˙Izmir, Turkey.

2.3 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).

2.4 Characterization of the Petrochemical Industry Wastewater used in this Study

Characterization of raw petrochemical industry wastewater taken from the influent of the aeration unit of the petrochemical industry wastewater treatment plant is given as the mean value of triplicate samplings: pH, ORP were recorded as 7.21 and 28.20 mV. DO, BOD_5, COD_{total}, COD_{dis}, Total-N, NH_4-N, NO_3-N, NO_2-N, Total-P, TSS, TVSS and oil concentrations were (mg/l); 1.78, 584, 1475, 1127, 15.4, 2.2, 1.8, 0.05, 10.6, 6.8, 310.3, 250.6 and 206, respectively, while the mean total PAH concentration was 1378 mg/l.



1. Raw Petrochemical wastewater characterisation of pollutants and with HPLC (Agilent 6890N) with a mass selective detector with a capillary column
2. Sonication reactor: operation at different temperatures (25°C, 30°C and 60°C) at a power of 640 W and four sonication intensities (16 W/m^2, 37 W/m^2, 23.02 W/m^2 and 51.75 W/m^2)
3. Determination of pollutant yields after sonication at different temperatures (25 30°C and 60°C) at a power of 640 W and four sonication intensities (16 W/m^2, 37 W/m^2, 23.02 W/m^2 and 51.75 W/m^2)
4. Determination of PAH metabolites at 25, 30°C and 60°C) at a power of 640 W and at a intensity of 37 W/m^2)
5. Studies to determine the PAH removal mechanisms (Measurement of CO_2, CH_4 and H_2 gases during pyrolysis)

Picture 1. The studies performed during the treatment of pterochemical industry wastewater

Table 1. Characterization of raw petrochemical industry wastewater taken from the influent of the aeration unit of a PCI ww 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
BOD5	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; [b] mV; [c] mg/l

2.5 Chemicals

Seventeen PAH standards including NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR, BbF, BkF, BaP, IcdP, DahA and BghiP and all solvents (acetone and hexane) used in this study were GC grade and had 99% purities. They were purchased from Sigma-Aldrich (USA). The reagents (methanol, ethanol) used in this study are analytical grade with 99% purity (Merck, Germany). All solutions used were prepared daily with water purified by Milli-Q Gradient water purification system.

2.6 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, 0.25mm, 0.25µm) 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 [19]. The chromatographic conditions for the phenanthrenediol determination were as follows: C-18 reverse phase HPLC column (Ace 5C18; 25 cm×4.6 mm, 5µm, 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, 3µm, mobile phase: 70/30 (v/v) methanol/organic-free reagent water). The CH_4, CO_2 and H_2 gas analysis was performed following Standard Methods [18]. pH, temperature, oxidation-reduction potential (ORP), COD and TOC concentrations were monitored following the Standard Methods 2550, 2580, 5220 D and 5310 [21].

2.7 Statistical Analysis

The regression analysis between *y* (dependent) and *x* (independent) variables was carried out using Windows Excel data analysis. An ANOVA test was performed to determine the statistical significance between *x* and *y* variables. The differences between trials and the regression coefficients in HCO^{3-} test were performed using the Microsoft Excel program. All experiments were carried out 3 times and the results given as the means of triplicate samplings.

2.8 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 number of free radicals, therefore they did not escape from the bubbles and did not migrate [22]. 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 [22]. 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. [13] and Papadaki et al. [23]. It has been shown that increasing the ultrasonic intensity improves the degradation rate of organic compounds [23]. 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.

3. RESULTS AND DISCUSSION

3.1 Sonication of PCI ww

Raw wastewaters taken from the influent of the aeration unit of a PCI ww treatment plant in Izmir were analyzed. The characterization of PCI ww was shown in Table 2 for minimum, medium and maximum values. All measurements were carried out three times and the results given as the means of triplicate samplings with standard deviation (SD) values.

3.1.1 Effect of increasing sonication times on the removals of COD_{dis} and TOC in PCI ww

56.05%, 62.30% and 80.16% COD_{dis} removals were found at an initial COD_{dis} concentration of 1027.43 mg/l after 60 min, 120 and 150 min, respectively, at 25°C ambient conditions, at 35 kHz, at 640 W, at pH=7.0 (Table 3).

Table 2. Characterization values of PCI ww (n=3, mean values ± SD)

Parameters	Values		
	Minimum	Medium	Maximum
pH	6.00 ± 0.21	6.80 ± 0.24	7.50 ± 0.26
DO (mg/l)	1.57 ± 0.06	1.78 ± 0.06	2.18 ± 0.08
ORP (mV)	24.82 ± 0.87	28.20± 0.99	34.12 ± 1.20
TSS (mg/l)	273.06 ± 9.56	310.30 ± 10.86	375.47 ± 13.14
TVSS (mg/l)	220.53 ± 7.72	250.60 ± 8.78	303.23 ± 10.61
COD_{total} (mg/l)	1298.12 ± 45.43	1475.20 ± 51.63	1785.36 ± 62.48
COD_{dis} (mg/l)	904.54 ± 31.64	1027.43 ± 35.95	1243.78 ± 43.51
BOD_5 (mg/l)	514.26 ± 17.99	584.09 ± 20.44	707.80 ± 24.80
BOD_5/COD_{dis}	0.46 ± 0.02	0.57 ± 0.02	0.70 ± 0.03
TOC (mg/l)	547.54 ± 19.15	620.81 ± 21.74	751.43 ± 26.30
Total N (mg/l)	13.60 ± 0.48	15.40 ± 0.54	18.60 ± 0.65
NH_4-N (mg/l)	1.90 ± 0.07	2.20 ± 0.08	2.70 ± 0.10
NO_3-N (mg/l)	1.60 ± 0.06	1.80 ± 0.06	2.20 ± 0.08
NO_2-N (mg/l)	0.040 ± 0.001	0.046 ± 0.001	0.056 ± 0.002
Total P (mg/l)	9.30 ± 0.33	10.60 ± 0.37	12.80 ± 0.45
PO_4-P (mg/l)	6.10 ± 0.21	6.80 ± 0.24	8.30 ± 0.29
Oil (mg/l)	181.80 ± 6.36	206.50 ± 7.23	250.32 ± 8.75
Influent PAHs (ng/ml)	1378.77 ± 48.26	1816.40 ± 63.57	2250.21 ± 78.76

Table 3. COD_{dis} removal efficiencies of PCI ww prior and after sonication experiments

No	Parameters	COD_{dis} Removal Efficiencies (%)							
		25°C							
		0. min		60. min		120. min		150. min	
1	Raw ww, control	0		56.05		62.30		80.16	
		30°C				60°C			
		0. min	60. min	120. min	150. min	0. min	60. min	120. min	150. min
2	Raw ww, control	0	44.05	61.22	89.94	0	46.50	67.37	92.48

The maximum COD_{dis} removal efficiency was 80.16% after 150 min at pH=7.0 and at 25°C. A significant linear correlation between COD_{dis} yields and increasing sonication time was observed ($R^2=0.81$, F=16.30, p=0.01). The treatment by sonication converts COD_{dis} to much smaller sonodegraded compounds. In such cases it is obvious that higher sonication times are needed for complete mineralization. Short sonication times (60 min) did not provide high degradation yields for refractory COD since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease in the percentage of remaining COD_{dis} was expected at longer sonication times due to sufficient radical reactions through cavitation. The formation of hydroxylated by products is observed under ultrasonic irradiation; it is suggested that $OH^\bullet$ is an important species for sonodegradation of PCI ww at 35 kHz and at 640 W. COD_{dis} was not completely removed under the ultrasonic action even with a long sonication time (150 min). These results underline the fact that degradation products of COD are recalcitrant toward sonochemical treatment. This is due to the fact that the intermediate products have very low probabilities of making contact with $OH^\bullet$, which react mainly at the interface of the bubble. Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency toward COD_{dis} abatement.

55.39%, 62.74% and 78.37% TOC yields were observed at an initial TOC concentration of 620.81 mg/l after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 25°C (Table 4).

The maximum TOC removal efficiency was 78.37% after 150 min at pH=7.0 and at 25°C (Table 4). A significant linear correlation between TOC yields and increasing sonication time was observed ($R^2=0.80$, F=14.21, p=0.01). TOC removals have similar properties with COD_{dis} removal at sonication process. The treatment by sonication converts TOC to much smaller sonodegraded compounds. Short sonication time (e.g., 60 min) did not provide high degradation yields for TOC since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease in the percentage of remaining TOC was attended at longer sonication times (i.e., 150 min) due to sufficient radical reactions through cavitation.

3.1.2 Effect of increasing sonication times on the PAHs removal efficiencies in PCI ww at 25°C ambient conditions

Raw PCI ww samples were sonicated at an ambient temperature of 25°C and at pH=7.0 and at increasing sonication times (60 min, 120 and 150 min). 54.92%, 61.33% and 79.65% total PAHs removals were observed in 1378.77 mg/l influent total PAHs concentration after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 25°C (Table 5). The maximum total PAHs removal efficiency was 79.65% after 150 min at pH=7.0 and at 25°C. A significant linear correlation between PAHs yields and increasing sonication time was observed ($R^2=0.71$, F=11.34, p=0.01).

Seventeen PAHs (NAP, ACL, ACT, FLN, PHE, ANT, CRB, FL, PY, BaA, CHR, BbF, BkF, BaP, IcdP, DahA and BghiP) in PCI ww were determined with GC-MS in raw ww before sonication experiments at 25°C. High removal efficiencies were found for PAHs with high benzene rings. 88.94% BkF, 66.03% BaP, 62.62% IcdP, 77.74% DahA and 78.72% BghiP yields were obtained for PAHs with 4 and 5 benzene rings after 150 min at 25°C. 70.21% NAP, 87.04% ACT, 90.25% BaA, 83.73% CHR and 94.52% BbF removals were observed for PAHs with one and three benzene rings, respectively, at 25°C after 150 min (Table 6). In this study, no significant difference in yields between PAHs with three (ANT, FL, PY), five (BbF, BkF) and six rings (DahA, BghiP) was observed, although, PAHs with more benzene rings became increasingly less soluble in water with increasing number of benzenoid rings and molecular weight, and with decreasing Henry's law constants at short sonication times (R^2=0.96, F=14.36 p=0.001) (Table 6).

Removal efficiencies in seventeen PAHs were measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min, at 30°C (Table 7). As seen in Table 7, all the removal yields of individual PAHs increased as the sonication time increased from 60 min to 150 min, at 60°C. The yields for all individual PAHs were above 91% except for BbF (86.21%) after 150 min, at 60°C (Table 7). This showed that sonication at high temperature increased the yields in all PAHs species.

Table 4. TOC removal efficiencies of PCI ww before and after sonication process

No	**Parameters**	**TOC Removal Efficiencies (%)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
1	Raw ww, control	0		55.39		62.74		78.37	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
2	Raw ww, control	0	47.70	63.38	90.89	0	49.50	70.00	94.23

Table 5. Total PAHs removal efficiencies of PCI ww before and after sonication process

No	**Parameters**	**Total PAHs Removal Efficiencies (%)**							
		25°C							
		0. min		**60. min**		**120. min**		**150. min**	
1	Raw ww, control	0		54.92		61.33		79.65	
		30°C				**60°C**			
		0. min	**60. min**	**120. min**	**150. min**	**0. min**	**60. min**	**120. min**	**150. min**
2	Raw ww, control	0	45.34	62.40	90.11	0	54.21	79.31	96.90

Table 6. Maximum removal efficiencies in seventeen PAHs measured after sonication experiments at 25°C at a power of 640 W and at afrequency of 35 kHz

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	1012.93 ± 35.45	206.20 ± 7.22	27.30	30.49	70.21
ACL	50.20 ± 1.76	10.22 ± 0.36	52.29	58.40	73.77
ACT	66.82 ± 2.34	13.60 ± 0.48	51.48	57.49	87.04
FLN	55.57 ± 1.95	11.31 ± 0.40	52.03	58.11	81.09
PHE	125.58 ± 4.40	25.56 ± 0.90	48.80	54.50	79.35
ANT	7.48 ± 0.26	1.52 ± 0.05	54.51	60.87	90.86
CRB	14.20 ± 0.50	2.89 ± 0.10	54.15	60.47	64.86
FL	19.36 ± 0.68	3.94 ± 0.14	53.87	60.17	83.52
PY	15.54 ± 0.54	3.16 ± 0.11	54.08	60.39	72.46
BaA	0.55 ± 0.02	0.11 ± 0.004	54.89	61.30	90.25
CHR	2.68 ± 0.09	0.55 ± 0.02	54.77	61.17	83.73
BbF	0.80 ± 0.03	0.16 ± 0.006	54.87	61.28	94.52
BkF	0.80 ± 0.03	0.16 ± 0.006	54.87	61.28	88.94
BaP	0.07 ± 0.003	0.02 ± 0.0007	54.91	61.32	66.03
IcdP	1.09 ± 0.04	0.22 ± 0.008	54.86	61.26	62.62
DahA	4.58 ± 0.16	0.93 ± 0.03	54.67	61.05	77.74
BghiP	0.51 ± 0.02	0.10 ± 0.004	54.89	61.30	78.72

[(A)]Inf.= influent, [(B)]Eff. = effluent.

Table 7. Maximum removal efficiencies in seventeen PAHs measured in the influent and in the effluent of the sonication experiments at 60ºC at a power of 640 W and a frequency of at 35 kHz

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	2164.51 ± 75.76	614.16 ± 21.50	21.76	61.53	98.48
ACL	53.02 ± 1.86	2.76 ± 0.10	44.02	73.77	97.12
ACT	71.83 ± 2.51	3.34 ± 0.12	43.25	72.67	94.16
FLN	59.04 ± 2.07	2.89 ± 0.10	43.77	73.41	96.00
PHE	143.28 ± 5.02	8.71 ± 0.31	40.75	79.04	96.34
ANT	7.54 ± 0.26	0.31 ± 0.01	46.11	76.80	91.72
CRB	14.41 ± 0.50	0.65 ± 0.02	45.77	76.31	97.85
FL	19.78 ± 0.69	0.85 ± 0.03	60.51	75.93	95.41
PY	15.81 ± 0.55	0.67 ± 0.02	60.70	74.21	70.69
BaA	0.55 ± 0.02	0.02 ± 0.0007	46.47	67.32	92.24
CHR	2.69 ± 0.09	0.11 ± 0.004	46.36	77.16	95.35
BbF	0.80 ± 0.03	0.03 ± 0.001	46.46	67.31	86.21
BkF	0.80 ± 0.03	0.03 ± 0.001	46.46	79.30	93.17
BaP	0.07 ± 0.003	0.003 ± 0.0001	46.49	71.36	97.77
IcdP	1.09 ± 0.04	0.04 ± 0.001	46.44	67.28	97.98
DahA	4.60 ± 0.16	0.19 ± 0.007	46.26	67.02	96.60
BghiP	0.51 ± 0.02	0.02 ± 0.0007	46.47	61.33	96.45

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

The results of the study showed that as the sonication time was increased the yields of BghiP, CHR, ANT and BbF increased while the destruction yields of DahA, PHE and PY decreased after 150 min. The effect of sonication time on the BghiP, CHR, ANT and BbF removals was significant for 150 min, at 60ºC (R^2=0.98, F=14.56, p < 0.01). No significant correlation was found between the DahA, PHE and PY yields and 150 min at 60ºC (R^2=0.58, F=6.39, p < 0.01). The 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. Short sonication times (60 min) did not provide high degradation yields for refractory PAHs since they were not exposed for a long enough time to ultrasonic irradiation.

Although, Park et al. [24] reported that lower molecular weight (2-, 3- and 4-ring) PAHs were found to be degraded more rapidly than the heavier (5-6 ring) compounds in this study high removal efficiencies were found for PAHs with high benzene rings after long sonication time (150 min) at 25ºC. In other words, although DahA and BghiP were the most hydrophobic types of PAHs with low Henry's law constants, vapor pressures, solubilities and high octanol-water coefficients, a significant correlation was not observed between the removal percentages of the these PAHs and their physicochemical properties aforementioned after long sonication times and at low temperatures such as 25ºC. Treatment by sonication converts PAHs with multiple benzene rings to much smaller compounds. It is obvious that higher sonication times are needed for complete mineralization. Short sonication times did not provide high degradation yields for refractory PAHs since they were not exposed for a long enough time to ultrasonic irradiation. Therefore, a decrease of the percent remaining PAHs was expected at longer sonication times due to high temperature and radical reactions from cavitation.

Although, ANT and PHE contained similar benzene rings (3) the PHE have higher removal yields than ANT at high sonication times. This could be attributed to higher solubility, water pressure, Henry's law constant and low octanol / water partition coefficient of PHE compared to ANT. This is contrast to the study performed by David [12] which reported that the geometry of the chemical structure of PAHs affected the degradation efficiency of PAHs with a straight structure ANT which was more easily degraded than one with a branched structured PHE. Moreover, the choice of solvent affected the degradation of PAHs under sonication which ultimately is expected to alter the effectiveness of ultrasonic extractions at long sonication times. High PHE yields compared to ANT could be attributed to the type of solvent used. The cavities are more readily formed when using solvents with low viscosity and low surface tension during long sonication times [25,26]. The preliminary studies showed that solvents with high surface tension and viscosity generally have a higher threshold for cavitation resulting in fewer cavitation bubbles but more harsh conditions once cavitation is established resulting in higher temperatures and pressures upon bubble collapse. In this study, among the solvents used acetone and hexane have the highest surface tension and viscosity. Higher cavitation bubbles resulting in fiercer cavitation conditions, was a reason for less PHE remaining with acetone after 150 min. The vapor pressure of the solvent is another important factor affecting the cavitation [27]. Higher vapor pressure leads to more solvent volatilizing into cavitation bubbles which are able to be dissociated by high temperature after 150 min. Hexane and acetone have the highest vapor pressure among solvents [28]. Thus, more hexane molecules migrate into cavitation bubbles leading to more molecules dissociating to generate radicals. As a result, more radical reactions of PHE occurred resulting in a lower percent remaining with hexane after 150 min.

The results found in this study were stronger in comparison with the study performed by Psillakis et al. [13]. They found 74%, 72% and 76% PHE, NAP and ACL removal rates, respectively, at 40°C, at 450 W and at 28 kHz after 98 min. Similarly, in a study performed by Little et al. [29]. 0.60 mg/l PHE was found to be recalcitrant to sonochemical removal at 22°C at 30 kHz and at 320 W after 135 min. However, increasing the liquid bulk temperature to 40°C led to about 56% removal at the same operational conditions. In this study, 79.65% total PAHs removal was observed at 25°C after 150 min. The total PAHs yield is higher than the yield obtained by 56% at 22°C as mentioned above.

In order to detect the effect of increasing sonication time on the yields of less hydrophobic PAHs with low benzene rings (PHE, ANT, CHR, BbF and PY) and more hydrophobic PAHs with high benzene yields (DahA and BghiP) the raw PCI ww samples were sonicated at 60°C at increasing sonication times (from 60 to 120 min and 150 min) (Table 7). The increase in temperature to 60°C will increase the kinetic reaction to a point at which the cushioning effect of the vapor in the bubble begins to dominate the system. Since the PAHs are relatively non-volatile, the degradation reaction took place in the gas-liquid film between the cavitating bubble and the bulk liquid mixture. As the reaction temperature increased, the rate of diffusion of PAHs from the bulk liquid phase to the reaction zone was accelerated. An increase in temperature up to 60°C improved the intensity of the cavitation, thus increasing the amount of free radicals produced within the bubble. It was suggested that these free radicals were required for the degradation reaction to occur and that they diffuse from the vapor cavity to the gas-liquid film where reaction ensues. As the rates of the counter diffusing reactants became comparable, a further increase in temperature (up to 80–90°C) had little or no effect on the reaction (i.e. the percent change in PAHs concentration reached a plateau as a function of temperature).

3.1.2.1 PAH metabolites

The PAHs intermediates (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid, naphthalene, p-hydroxybenzoic acid, fluorene, di-hydroxy pyrene, pyrene di-hydrodiol) in PCI ww were measured with HPLC after 120 min, at 25°C and after 150 min, at 25°C (Table 8).

The initial total PAHs concentration of 1378.77 mg/l decreased to 533.18 mg/l after 120 min at 25°C. From 1378.77 mg/l initial PAHs concentration 320.24 mg/l 1–methylnaphthalene, 205.85 mg/l 9–hydroxyfluorene, 78.16 mg/l 9,10–phenanthrenequione, 174.57 mg/l benzoic acid, 77.58 mg/l 1,2,3–thiadiazole–4–carboxylic acid, 301.39 mg/l naphthalene, 271.20 mg/l p–hydroxybenzoic acid, 288.71 mg/l fluorine, 242.39 mg/l di–hydroxy pyrene, 341.94 mg/l pyrene di–hydrodiol were produced after 120 min, at 25°C. It was found that the initial PAHs cleaved to the inter-metabolites mentioned above. After 120 min the remaining PAHs concentration was found to be high (522.37 mg/l). The low removal efficiency of the total PAHs (61.33%) could be attributed to the studied low temperature (25°C). From 1378.77 mg/l total PAH 855 mg/l total PAHs intermetabolites were produced after 120 min at 25°C. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid, naphthalene, p–hydroxybenzoic acid, fluorene, di–hydroxy pyrene, pyrene di–hydrodiol were sonodegraded with yields of 76.77%, 85.07%, 94.33%, 87.34%, 94.37%, 78.14%, 80.33%, 79.06%, 82.42% and 75.20% respectively, after 120 min at 25°C. The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid, naphthalene, p–hydroxybenzoic acid, fluorene, di–hydroxy pyrene, pyrene di–hydrodiol) in PCI ww after 120 min, at 25°C.

From 1378.77 mg/l initial PAHs concentration 108.78 mg/l 1–methylnaphthalene, 65.77 mg/l 9–hydroxyfluorene, 21.79 mg/l 9,10–phenanthrenequione, 36.68 mg/l benzoic acid, 7.72 mg/l 1,2,3–thiadiazole–4–carboxylic acid, 51 mg/l naphthalene, 8.90 mg/l p–hydroxybenzoic acid, 39 mg/l fluorene, 5.10 mg/l di–hydroxy pyrene, 0.32 mg/l pyrene di–hydrodiol were produced after 150 min, at 25°C. It was found that the initial PAHs cleaved to the inter-metabolites mentioned above. The PAHs intermediates namely, 1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid, naphthalene, p–hydroxybenzoic acid, fluorene, di–hydroxy pyrene, pyrene di–hydrodiol were sonodegraded with yields of 92.11%, 95.23%, 98.42%, 97.34%, 99.44%, 96.30%, 99.36%, 97.17%, 99.63% and 99.98% respectively, after 150 min, at 25°C. The HPLC chromatogram of PAHs by-products (1–methylnaphthalene, 9–hydroxyfluorene, 9,10–phenanthrenequione, benzoic acid, 1,2,3–thiadiazole–4–carboxylic acid, naphthalene, p–hydroxybenzoic acid, fluorene, di–hydroxy pyrene, pyrene di–hydrodiol) in PCI ww after 150 min at 25°C.

3.1.3 Effect of increasing sonication temperature on the removals of COD_{dis} and TOC in PCI ww

At the beginning of the studies the raw PCI ww samples were sonicated at 30°C and 60°C at a pH=7.0 at increasing sonication times from 5 min up to 60 min to determine the lowest sonication time for maximum COD_{dis} removal efficiencies. The lowest sonication time was determined as 60 min for the maximum COD_{dis} removals (Table 9).

44.05%, 61.22% and 89.94% COD_{dis} removals were obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C. An increase of 9.78% in COD_{dis} yield was obtained after 150 min at 30°C, compared to the control (E=80.16% COD_{dis} at pH=7.0 and at 25°C). 46.50%, 67.37% and 92.48% COD_{dis} removals were obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C. The contribution of 60°C temperature on COD_{dis} removals were 5.07% and 12.32% after 120 and 150 min, respectively, compared to the control (E=62.30% and E=80.16% COD_{dis} after 120 and 150 min at pH=7.0 at 25°C). The maximum COD_{dis} removal was 92.48% after 150 min at pH=7.0 and at 60°C. A significant linear correlation between COD_{dis} yields and increasing sonication temperature was observed (R^2=0.93, F=15.43, p=0.01). Increasing temperatures (from 25°C to 30°C and to 60°C) increased the COD_{dis} removal of PCI ww after sonication process since sonodegradation reaction rates in cavitation process increased with increasing temperature during sonication at increasing sonication times. As a result, increasing temperature increased the COD_{dis} removal efficiency in PCI ww after sonication experiments.

47.70%, 63.38% and 90.89% TOC removals were measured after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 30°C. An increase of 12.52% in TOC removal was found after 150 min at 30°C, compared to the control (E=78.37% TOC at pH=7.0 and at 25°C). A significant linear correlation between TOC yields and increasing sonication temperature was observed (R^2=0.95, F=17.78, p=0.01). 49.50%, 70% and 94.23% TOC removals were obtained after 60 min, 120 and 150 min, respectively, at pH=7.0 and at 60°C. The contribution of 60°C temperature to the TOC removals were 7.26% and 15.86% after 120 and 150 min, respectively, compared to the control (E=62.74% and 78.37% TOC after 120 and 150 min at pH=7.0 and at 25°C). The maximum TOC removal efficiency was 94.23% after 150 min at pH=7.0 and at 60°C. A significant linear correlation between TOC yields and increasing sonication temperature was observed (R^2=0.94, F=17.11, p=0.01). Increasing temperatures (30°C and 60°C) increased the TOC removals in PCI ww after sonication process. Sonodegradation reaction in cavitation process was rapidly performed with increasing temperatures at long sonication times such as 150 min. The treatment by sonication converts COD_{dis} and TOC to much smaller sonodegraded compounds. Low sonication temperature (25°C) did not provide high degradation yields for COD_{dis} and TOC.

3.1.4 Effect of increasing temperature on the removal of PAHs in PCI ww at increasing sonication times

Raw PCI ww samples were sonicated in a sonicator at 30°C and 60°C during 60 min, 120 and 150 min at pH=7.0. Similar total PAH removal yields were found at 25°C (E=54.92% total PAHs at pH=7.0) and 60°C (E=54.21% total PAHs at pH=7.0) after 60 min (Table 10).

In other words, increasing the temperature from 25°C to 30°C and 60°C did not contribute to the PAHs removal after 60 min. The total PAHs removal decreased slightly at 30°C with the same sonication time. Similarly, the total PAHs removals at 30°C remained at the same level as 25°C after 120 min. Increasing the temperature from 25°C to 60°C increased the total PAHs removal efficiency after 120 and 150 min. In general, as the sonication time increased from 60 min to 150 min, the total PAHs removal increased. The maximum total PAHs removal efficiency was 96.90% after 150 min at pH=7.0 and at 60°C. A significant linear correlation between total PAHs yields and increasing sonication temperature was observed (R^2=0.83, F=10.41, p=0.01).

Removal efficiencies in seventeen PAHs were measured in the influent and in the effluent of the sonication experiments after 60 min, 120 and 150 min, at 30°C (Table 10). As seen in Table 10, all the removal yields of individual PAHs increased as the sonication time increased from 60 min to 150 min at 60°C. The yields for all individual PAHs were above 91% except for BbF (86.21%) after 150 min, at 60°C (Table 10). This showed that sonication at high temperature increased the yields in all PAHs species.

The results of this study showed that the PAHs removal was not dependent on the ring numbers of benzene for the individual PAHs species. Therefore, it can be concluded that a correlation between the removal of the PAHs and water solubility, Henry's law constants and vapor pressure, was not observed at 60°C and the difference is not significant (R^2=0.54, F=3.34, P=0.001). It was found that the PAHs degradation is a function of long sonication time (150 min) and high temperature (60°C). A high correlation was found between PAHs yields, time and temperature (R^2=0.97). This correlation is also significant (F=17.78 p=0.001). The two experimental conditions (at 640 W and at 35 kHz) employed in this study influenced the important physical parameters related to cavitation bubbles such as the extent of radical production from the bubble, the thickness of the liquid shell surrounding the bubble, the concentration of the PAHs in the interfacial region and extent of radical scavenging in the medium [25,26]. For this reason, most probably, a significant difference was not observed between the lower molecular weight PAHs (e.g. those with two, three or four aromatic rings) and the higher molecular weight, more hydrophobic PAHs for their individual removals (R^2=0.82, F=13.67, p=0.001) at 60°C. On the other hand, low-frequency ultrasound is expected to induce destructive effects for hydrophobic solutes, since they can easily diffuse near cavitation bubbles and undergo pyrolytic destruction inside the collapsing bubble or hydroxylation and thermal decomposition at its interfacial sheath [25-27].

Given that all PAHs with high molecular used in this study are relatively non-volatile, their ability to migrate towards the bubble and rapidly decompose at the interface is likely to be dictated by their hydrophobicity. It appears that the more hydrophobic PAHs are all readily susceptible to sonochemical degradation and high removal yields (86-98%) is achieved within 150 min of irradiation with the conditions under consideration (Table 10).

Among the PAHs studied, only in the case of PY increasing the temperature did not influence its removal (Table 10). The yield of PY decreased slightly as increasing the temperature from 120°C to 150°C while the removals of PHE, BghiP and the rest of the PAHs increased. The slight decrease in degradation rate observed for PY may be due to the increased solution temperature. For PY, an increased solution temperature might imply a slightly higher adsorption on the air-water interface and an increased diffusivity. These factors act to affect the slight accumulation of PY on the interface in different ways. As the temperature increased, the increased diffusivity may contribute to more available PY at the subsurface for adsorption. Thus, a slight increase in PY removal efficiency was observed from 25°C to 60°C (Table 10). 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 increasing temperature on the sonolytic removal efficiencies were also examined for all PAHs, in this section only PHE and BghiP are discussed.

Table 8. Measurements of PAHs intermediates in PCI ww with HPLC after 120 and 150 min, at 25^{o}C at 640 W power and at a frequency of 35 kHz

PAHs Intermediates	PAH_0 (mg/l)	120 min		150 min	
		PAH (mg/l)	PAHR (%)	PAHI (mg/l)	PAHIR (%)
1–methylnaphthalene	1378.77	320.24	76.77	108.78	92.11
9–hydroxyfluorene	1378.77	205.85	85.07	65.77	95.23
9,10–phenanthrenequione	1378.77	78.16	94.33	21.79	98.42
benzoic acid	1378.77	174.57	87.34	36.68	97.34
1,2,3–thiadiazole–4–carboxylic acid	1378.77	77.58	94.37	7.72	99.44
naphthalene	1378.77	301.39	78.14	51.00	96.30
p–hydroxybenzoic acid	1378.77	271.20	80.33	8.90	99.36
fluorene	1378.77	288.71	79.06	39.00	97.17
di–hydroxy pyrene	1378.77	242.39	82.42	5.10	99.63
pyrene di–hydrodiol	1378.77	341.94	75.20	0.32	99.98

PAH_0: Initial total PAHs concentration (mg/l), PAH: Total PAHs concentration (mg/l) after 120 min sonication time, PAHR: Total PAHs removal efficiency (%) after 120 min sonication time, PAHI: PAHs intermediates concentration (mg/l) after 120 min sonication time, PAHIR: removal of PAHs intermediates (%) after 150 min sonication time

Table 9. Effect of sonication time on the COD_{dis} removals in PCI ww at 640 W and at a frequency of 35 kHz

Time (min)	30^{o}C		60^{o}C	
	COD_{dis} (mg/l)	Rem. Eff. (%)	COD_{dis} (mg/l)	Rem. Eff. (%)
0	1027.43 ± 35.96	0.00	1027.43 ± 35.96	0.00
5	950.20 ± 33.26	7.52	932.83 ± 32.65	9.21
10	818.95 ± 28.66	20.29	831.45 ± 29.10	19.07
15	772.48 ± 27.04	24.81	808.75 ± 28.31	21.28
20	738.96 ± 25.86	28.08	746.27 ± 26.12	27.37
25	731.95 ± 25.62	28.76	720.68 ± 25.22	29.86
30	694.78 ± 24.32	32.38	685.60 ± 24.00	33.27
35	668.42 ± 23.40	34.94	665.98 ± 23.31	35.18
40	635.13 ± 22.23	38.18	645.92 ± 22.61	37.13
45	624.08 ± 21.84	39.26	640.29 ± 22.41	37.68
50	597.06 ± 20.90	41.89	548.35 ± 19.20	46.63
55	568.27 ± 19.89	44.69	526.80 ± 18.44	48.73
60	537.64 ± 18.82	47.67	476.70 ± 16.70	53.60

The removal yields of PHE and BghiP increased with increasing temperature. For partitioning into the bubble, the increased 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 increase in removal rates for PHE and BghiP at 150^{o}C.

The results of this study showed that although a strict correlation between the remaining percentage of the aforementioned PAHs and physicochemical properties was observed after 30 min, 60 and 120 min (R^2=0.89, P=4.89, p=0.001), a significant correlation was not observed between the remaining percentages of PAHs and their properties after 150 min (R^2=0.45, p=16.56, P=0.01) and over 90% removal rates of the all PAHs was achieved. Furthermore, it becomes evident that a larger hydrophobicity resulted in smaller reaction kinetic constants of the PAHs. Low initial PAHs concentrations led to low reaction rates and also to smaller residual concentrations. The coefficient of the correlation between the residual concentration and the total initial concentration of the single PAHs was strong and highly significant (R^2=0.85, $p < 0.001$).

Several investigators have reported contradictory findings regarding the temperature effect. In certain reaction systems for instance, the net effect of an increase in T_o and consequently T_{max}, is an increase in degradation rates. This occurs up to the point at which the cushioning effect of the vapor begins to dominate the system and further increases in liquid temperature result in reduced reaction rates. The fact that removal decreases with increasing 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 Eq. (1):

$$T_{\max} = T_o \left(\frac{P}{P_o}\right)(\gamma - 1) \qquad (1)$$

where, T_o is the liquid bulk temperature, P_o is the vapor 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 vapor pressure; nevertheless, this beneficial effect is compensated by the fact that bubbles contain more vapor which cushions bubble implosion and consequently reduces $T_{max.}$ In addition to this, increased temperatures are likely to favor degassing of the liquid phase, thus reducing the number of gas nuclei available for bubble formation [13].

Therefore, a decrease in the percentage of remaining PAHs was expected at longer sonication times due to sufficient radical reactions through cavitation. It was found that the yields in PAHs with high benzene rings (DahA and BghiP; E=90–92%) were as high as the PAHs with lower benzene rings (BbF, CHR, PHE, PY and ANT; E=92–95%). In order to explain this, it is important to mention some of the physical/chemical properties of these compounds. Table 11 shows the Henry’s law constant, the pseudo second-order reaction rate constant for reaction with $OH^{\bullet}$ ($k_{OH^{\bullet}}$), the solubility and the octanol–water partitioning coefficient (K_{OW}) of these seven PAHs. The solubilities of DahA and BghiP are approximately 15 times lower than for CHR and BbF, 100 times lower than for ANT and 10000 times lower than for PHE (Table 11).

Moreover, the Henry’s law constant of DahA and BghiP are also lower than ANT, PY, BbF and CHR. Given the lower solubilities and the low Henry’s law constant of DahA and BghiP and following the studies on non-volatile, hydrophobic compounds [11,30], we would expect lower degradation yields for DahA and BbF compared to ANT and CHR. However, there are two possible explanations for the enhancement in the yields for DahA and BghiP: (1) They have high removals as the ANT, PY, BbF and CHR, via the $OH^{\bullet}$ pathway (hydroxylation) and/or (2) DahA and BghiP accumulate at the interface of the liquid gas phase to a greater degree than the other PAHs by a subsequent entrapment of the pollutant vapor in the cavitation bubble (pyrolysis). Reported second order reaction rate constants for the DahA and BghiP listed in Table 11, are lower than those of the other PAHs. Therefore, suggestion (1) can be ignored. The thickness of the liquid shell surrounding the bubble, in which temperature rises, is higher for hydrophobic organics like PAHs. In this shell, in principle, the thermal penetration depth in the bulk medium varies directly with the bubble size and the thickness of liquid layer around the bubble that gets heated up is larger for saturated medium. Finally, the extent of pyrolysis in the liquid shell depends on the thickness of this shell and concentration of the pollutant molecules in it.

If the pollutant is hydrophobic in nature, characterized by low solubility in water, it tends to partition between the bulk medium and bubble interface [30]. The bubble–bulk interface also has a hydrophobic character, and hence, the concentration of the hydrophobic pollutant molecules in this region is much higher than the bulk. Therefore, hydrophobic PAHs concentrations were high in the interfacial region between bubble and bulk. The PAHs transfer process from the PCI ww to the cavitational bubbles and the removal of PAHs are jointly controlled by the hydrophobicity of PAHs. Increasing hydrophobicity by low Henry’s law constants induces destructive effects for hydrophobic PAHs, since they can easily diffuse near the cavitation bubbles and undergo pyrolytic destruction inside the collapsing bubble [31]. Given that PAHs with high molecular weights (Table 11) in PCI ww have the ability to migrate towards the bubble, rapid decomposition at the interface is likely to be dictated by their hydrophobicity. It appears that the more hydrophobic DahA is readily susceptible to sonochemical degradation and nearly complete removal (99%) is achieved within 150 min, at 60°C (Fig. 1).

On the other hand, the hydrophobicity of an organic compound can be described fairly well by its octanol–water partition coefficient and water solubility. The higher octanol–water partition coefficient of hydrophobic PAHs results in higher PAHs removal although there are a few exceptional cases. In the exceptional cases, such as the yields of CHR and BbF, the vapor pressure and/or the reactivity of PAHs with intermediates (i.e. free radicals, atoms and active molecules) generated in situ in bulk liquid, play a simultaneous role, at least to a certain extent. Although, the BbF is more hydrophobic (having higher octanol–water partition coefficient) than that of CHR its removal efficiency is lower than that of CHR. This could be explained as follows: the hydrophobicity of BbF is higher with low Henry's law constant (log P_{OW}=5.98 at 25ºC) compared to CHR with high Henry's law constant (log P_{OW}=5.71 at 25ºC), but its vapor pressure (V_P, 5.00x10^{-7} mm Hg at 25ºC) is low compared to CHR (V_P, 6.23x10^{-9} mm Hg at 25ºC) (Table 11). Hence, the yield of BbF is lower compared to CHR after 150 min. A significant linear relationship was found between the hydrophobic PAHs yields and the Henry's law constants and the solubilities of these PAHs (R^2=0.96, F=14.67, p=0.001) while the relationship between vapor pressure and the PAHs removals was not significant (R^2=0.65, F=7.95, p=0.001).

Table 10. Maximum removal efficiencies in seventeen PAHs at 640 W, at 35 kHz

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	2164.51 ± 75.76	614.16 ± 21.50	21.76	61.53	98.48
ACL	53.02 ± 1.86	2.76 ± 0.10	44.02	73.77	97.12
ACT	71.83 ± 2.51	3.34 ± 0.12	43.25	72.67	94.16
FLN	59.04 ± 2.07	2.89 ± 0.10	43.77	73.41	96.00
PHE	143.28 ± 5.02	8.71 ± 0.31	40.75	79.04	96.34
ANT	7.54 ± 0.26	0.31 ± 0.01	46.11	76.80	91.72
CRB	14.41 ± 0.50	0.65 ± 0.02	45.77	76.31	97.85
FL	19.78 ± 0.69	0.85 ± 0.03	60.51	75.93	95.41
PY	15.81 ± 0.55	0.67 ± 0.02	60.70	74.21	70.69
BaA	0.55 ± 0.02	0.02 ± 0.0007	46.47	67.32	92.24
CHR	2.69 ± 0.09	0.11 ± 0.004	46.36	77.16	95.35
BbF	0.80 ± 0.03	0.03 ± 0.001	46.46	67.31	86.21
BkF	0.80 ± 0.03	0.03 ± 0.001	46.46	79.30	93.17
BaP	0.07 ± 0.003	0.003 ± 0.0001	46.49	71.36	97.77
IcdP	1.09 ± 0.04	0.04 ± 0.001	46.44	67.28	97.98
DahA	4.60 ± 0.16	0.19 ± 0.007	46.26	67.02	96.60
BghiP	0.51 ± 0.02	0.02 ± 0.0007	46.47	61.33	96.45

$^{(A)}$*Inf.= influent,* $^{(B)}$*Eff. = effluent.*

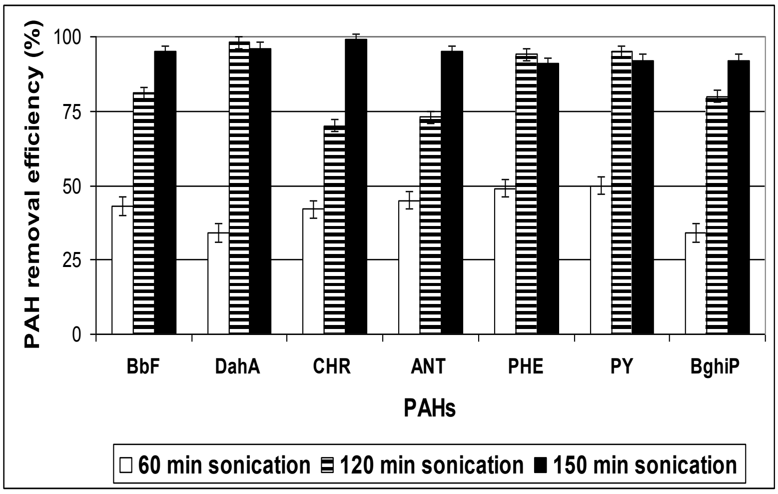


Fig. 1. Effect of increasing sonication time on PAHs removal efficiencies at 60ºC (at 640 W, at 35 kHz)

Table 11. Physical and chemical properties of the PAHs studied in this work

PAHs	**CAS-No**	**MF**	**MW**	**T_M**	**T_B**	**S_W**	**V_P (25ºC)**	**H (25ºC)**	**log K_{OA} (25ºC)**	**Log K_{OW}**	**SORKC**	**IPC**
PHE	85-01-8	$C_{14}H_{10}$	178	99	340	1.15	$1.21x10^{-4}$	$3.35x10^{-5}$	7.68	4.46	23.40	125.58
ANT	120-12-7	$C_{14}H_{10}$	178	215	340	$4.34x10^{-2}$	$2.67x10^{-6}$	$5.56x10^{-5}$	7.71	4.45	28.20	3.63
PY	129-00-0	$C_{16}H_{10}$	202	151	404	$1.35x10^{-1}$	$4.50x10^{-6}$	$1.19x10^{-5}$	8.81	4.88	15.60	14.49
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	$2.00x10^{-3}$	$6.23x10^{-9}$	$5.23x10^{-6}$	10.30	5.81	12.50	2.32
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	$1.50x10^{-3}$	$5.00x10^{-7}$	$6.57x10^{-7}$	11.34	5.78	9.50	0.23
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	$2.49x10^{-3}$	$1.00x10^{-10}$	$1.23x10^{-7}$	12.59	6.75	7.60	5.42
BghiP	191-24-2	$C_{22}H_{12}$	276	278	> 500	$2.60x10^{-4}$	$1.00x10^{-10}$	$3.31x10^{-7}$	12.55	6.63	6.90	0.58

Phenanthrene (PHE), anthracene (ANT), pyrene (PY), chrysene (CHR), benz[b]fluoranthene (BbF), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP).

MF: Molecular formula, MW: Molecular weight (g / mol), T_M: Melting point (ºC), T_B: Boiling point (ºC), S_W: Solubility in water (mg / l), V_P: Vapor pressure (mm Hg), H: Henry's law constant (atm m^3 / mol), log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient; SORKC: Second order reaction kinetic constant (mg/l.s); IPC: Initial PAH concentration (mean, mg / l).

Although, the BbF, DahA, CHR and ANT removals increased at increasing sonication times among the PAHs studied it was found that PHE, PY and BghiP concentrations decreased as the sonication time increased from 60 to 120 min while the concentration of these PAHs increased after 150 min. The reason of this could be explained by the ultimate destruction of these PAHs after 120 min. This sonication time could be accepted as the optimum time for the maximum degradation of PHE, PY and BghiP to the inter-metabolites.

3.1.5 Sonication mechanisms of PAHs

Free radical and pyrolysis reactions produce different products, with relative abundances depending on the nature of the solute and its concentration. For example, Adewuyi [32-34] found that FLN and benzoic acid are the sonication metabolites of PHE and methyl radicals ($CH_3^\bullet$) formed from the pyrolysis of solvent-hexane. Dewulf et al. [35] found that sonolysis of simple hydrocarbons creates the same kind of products associated with very high-temperature pyrolysis. $CH_3^\bullet$ and ethyl ($CH_3CH_2^\bullet$) radicals are expected to be formed when hexane is decomposed sonochemically as a solvent [31]. $CH_3^\bullet$ has also been shown to form during the pyrolysis of acetone molecules. These alkyl radicals then react with PHE to form different types of methyl- and ethyl-phenanthrene by-products. In our study, although $CH_3^\bullet$ and $CH_3CH_2^\bullet$ were not measured the metabolites found from the sonication of PHE (FL, NAP and benzoic acid) agree with the results found by older and more recent research as reported by Rae et al. [31] (Table 8). The mechanism of pyrolysis of PHE had two pathways: (1) Loss of one carbon in PHE and yielding CH_4 and FLN and (2) fragmentation resulting in a four carbon fragment and NAP. Therefore, FLN is an indication of a pyrolysis by-product formed from the PHE due to high-temperature reactions in or near a cavitation bubble as reported by Adewuyi [32]. In our study, CH_4, H_2 and CO_2 gases were identified in the headspace of the sonicator reactor. The GC spectra of these gases are illustrated in (Fig. 2).

The increasing of PAHs concentrations after 150 min could be attributed to the re-formation of the PHE, PY and BghiP from the by-products. We suspected that the increase of PHE with longer sonication time may be due to the re-formation of PHE from the by-products mentioned above and from the FLN. The FLN formed during the sonication of PHE may be attacked by $CH_3^\bullet$ to regenerate PHE as reported by Adewuyi [32]. Cyclization reactions of PHE with methyl- or ethyl-naphthalene may also contribute to the re-formation of PHE. A radical mechanism proposed by David [12] showed PHE formation from pyrolysis of 9,9–dimethyl–fluorene at 800°C by a free radical ring expansion process. Wu and Ondruschka [36] also reported NAP and benzene formation during PHE pyrolysis at < 900°C. Furthermore, Little et al. [29] studied PHE pyrolysis at 700 and 850°C and reported that NAP is one of the pyrolysis products of PHE. Therefore, the NAP by-product detected in this study may be direct pyrolysis products of PHE. Similarly, PY yields increased after 120 min since the PY degraded to di–hydroxy pyrene and to benzoic acid (Table 8). Then we suspected that PY reproduced from the hydroxy-pyrene since the PY yields decreased. Similarly, the yield of BghiP increased after 120 min with sonodegradation to its by-products namely, benzoic acid and pyrene di-hydrodiol at 63°C (Table 8). However, the yields of the BghiP decreased after 150 min. This could be explained by the re-formation of BghiP from pyrene di-hydrodiol and benzoic acid (Table 8).

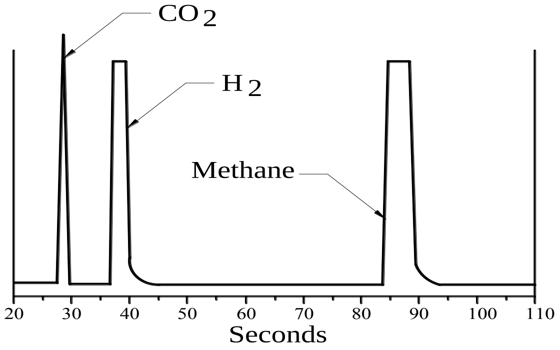


Fig. 2. CH_4(g), H_2(g) and CO_2(g) spectra measured in the headspace of the sonicator by GC (640 W, 35 kHz)

In this study, the presence of CH_4, H_2 and CO_2 gases indicated not only the destruction of the PAHs but also confirmed the mechanism ‘‘pyrolysis” with degassing of the medium throughout sonication. The results given above are consistent with our results. When PHE is sonicated in an organic solvent, it is expected that a certain number of PHE molecules will migrate into the gaseous cavitation bubbles. Then PHE molecules are available to migrate towards the cavitation bubble interfaces or volatilize into the cavitation bubbles to react under pyrolysis thus leading to a lower percentage remaining [32]. In addition, at higher concentrations of PHE, the solute is more likely to compete for reaction with $CH_3^{\bullet}$, which could also contribute to the loss of PHE [29].

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 [13]. The PAHs yields obtained in our study are high in comparison to the removal performances of PAHs in the studies given below. In the study by Laughrey et al. [15] 77% PAHs removal efficiency was observed for the sonochemical degradation of 50 μg/l of initial PAHs mixture concentration (NAP, ACL and PHE) in water after 120 min, at 40ºC, at 150 W and at 24 kHz. Benabdallah El-Hadj et al. [11] found 31-34% and 44-50% PAHs removals in mesophilic (35ºC) and thermophilic (55ºC) conditions for NAP and PY at 20 kHz and at 70 W, after 110 min, before anaerobic digestion. Manoli and Samara [6] found that the PAH removals with 6 and 7 benzene rings ranged between 58 and 67% with 15 min sonication at 340 W at a frequancy of 20 kHz while the PAHs with benzene ring greather than 9 removed with yields as high as 34%. Significant positive relationships were observed for removal efficiencies and the log K_{ow} of PAHs and the log K_H of PAHs in a petrochemical industry wastewater. Zheng [3] found 67% BbF, DahA, CHR and ANT PAH removals after 60 min sonication at 560 W power at a frequency of 80 kHz while 78% PHE, PY and BghiP yields obtained after sonication with the same operational conditions.

The yields obtained in the aforementioned studies are low in comparison to the removal performances of PAHs found in this study. It was observed that the PAHs with high benzene rings were also degradable with high yields, even though some studies demonstrated that sonication is not effective for PAHs with high benzene rings [15].

4. CONCLUSIONS

Low frequency (35 kHz) sonication proved to be a viable tool for the effective degradation of TOC, COD_{dis} and total PAH in PCI ww. The degradation of PAHs, TOC and COD_{dis} were a function of sonication time, frequency, T (ºC). As the temperature increased from 25 ºC to 30ºC and 60ºC, the total PAHs and COD_{dis} removals increased.

The maximum yields was observed to 92.15% COD_{dis}, 94.23% TOC and 96.90% total PAHs removals after 150 min, at 60ºC in the PCI ww during sonication process.

The maximum removal efficiencies of PAHs intermediates were 92.11% 1–methylnaphthalene, 95.23% 9–hydroxyfluorene, 98.42% 9,10–phenanthrenequione, 97.34% benzoic acid, 99.44% 1,2,3–thiadiazole–4–carboxylic acid, 96.30% naphthalene, 99.36% p–hydroxybenzoic acid, 97.17% fluorene, 99.63% di–hydroxy pyrene and 99.98% pyrene di–hydrodiol, respectively, after 150 min, at 25ºC.

Sonication technology can provide an effective alternative for destroying and detoxifying the pollutants present in PCI ww. It could be used as a direct treatment at step to treat the pollutants in PCI ww instead of biological treatment plants in Izmir (Turkey).

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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