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Degradation of PAHs by high frequency ultrasound

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic compounds, which have been reported in the literature to efficiently degrade at low (e.g. 20 kHz) and moderate (e.g. 506 kHz) ultrasound frequencies. The present study focuses on degradation of naphthalene, phenanthrene, and pyrene by ultrasound at three different relatively high frequencies (i.e. 582, 862, and 1142 kHz). The experimental results indicate that for all three frequencies and power inputs $\geq$133 W phenanthrene degrades to concentrations lower than our experimental detection limit (<1 μg/L). Phenanthrene degrades significantly faster at 582 kHz than at 862 and 1142 kHz. For all three frequencies, the degradation rates per unit mass are similar for naphthalene and phenanthrene and lower for pyrene. Furthermore, naphthalene degradation requires less energy than phenanthrene, which requires less energy than pyrene under the same conditions. No hexane-extractable metabolites were identified in the solutions.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread in the environment. PAHs often accumulate in various environmental systems including coastal estuaries and marine sediments (Daskalakis and O'Connor, 1995; Karapanagioti et al., 2009) as well as in drinking water supplies (Yang and Silverman, 1988; Kim Oahn et al., 2002). PAHs generally occur as complex mixtures and not as single compounds. Although their concentration in environmental systems is very low due to their low solubility (~μg/L), they are of great importance because they are listed as priority pollutants (Callahan et al., 1979; EEC, 1980). The European drinking water standard for the sum of four PAHs is 0.1 μg/L (EC, 1988).

PAHs can originate from various sources by thermal combustion processes (i.e. coal burning, cooking and heating oils), vehicular emissions (i.e. automobiles), and biomass burning (Simoneit, 1984; Stein et al., 2006). Combustion-derived PAHs present in the atmosphere can enter the water supply by gaseous exchange in the air–water interface, dry deposition of particulate matter, wet deposition (rainfall), and urban runoff (Chen et al., 2004). The PAH loading pathways to coastal waters in highly urbanized areas are mainly via storm water runoff, tributary inflow, wastewater treatment plant effluent, atmospheric deposition, and dredged material disposal (Chrysikopoulos et al., 1992; Oros et al., 2007). Concentrations of PAHs are generally higher in samples from urban streams and in combined overflow sewers than in effluents of wastewater treatment plants (Bergqvist et al., 2006; Phillips and Chalmers, 2009; Roswell et al., 2010). PAHs are removed in wastewater treatment plants by absorption onto the generated sludge (Jiries et al., 2000).

During the past several years, ultrasound has been effectively employed as an emerging advanced oxidation process (AOP) for a wide variety of micropollutants (Virkutyte and

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Rokhina, 2010; Adewuyi, 2001, 2005; Kotronarou et al., 1991; Hoffmann et al., 1996; Taylor et al., 1999; Lifka et al., 2003; Matouq et al., 2008; David, 2009). Biological treatment can be inhibited by toxic or persistent pollutants, it is very sensitive to several environmental factors, and it is slow, therefore uneconomical for high concentrations of micropollutants (Adewuyi, 2005). Mahamuni and Adewuyi (2010) reported that the cost of ultrasound treatment of various contaminants is higher compared to other AOPs, and combination of ultrasound with different AOPs is economically more attractive than the use of ultrasound alone. Acoustic cavitation in aqueous solutions results in the formation of micro bubbles producing local areas of high energy. Within these localized high energy regions, chemical transformations occur including the cleavage of chemical bonds, oxidation, pyrolysis and/or combustion of organic compounds (Suslick, 1990). Temperature and pressure can reach levels of 3000–5000 K and 500–10,000 atm, respectively (Riesz et al., 1985; Suslick, 1990). In the region of cavitation, three reaction zones exist: (a) the gas phase, (b) the gas–liquid interface, and (c) the liquid surrounding the cavitation bubble (Riesz et al., 1985). Various studies suggest that the sonodegradation of PAHs occurs via: (i) oxidation by $HO^{\cdot}$ in the solution phase, (ii) pyrolytic processes within the bubble, and (iii) combination of oxidation by $HO^{\cdot}$ and pyrolytic processes (Wheat and Tumeo, 1997; Taylor et al., 1999; Laughrey et al., 2001; David and Riguier, 2002; Little et al., 2002; Psillakis et al., 2004). David (2009) concluded that because of their properties, PAHs are expected to be mainly localized in the center and/or in the surrounding shell of the bubble inhibiting the production of hydroxyl radicals and hence the oxidation pathway, and that they are mainly pyrolyzed within the bubble.

Most studies so far are focused on low ultrasound frequencies (20–80 kHz) and volumes treated ranging from 50 to 200 mL. The power and frequency of ultrasound are reported to affect the degradation rate of PAHs. The mean bubble diameter increases with increasing acoustic power and decreases with increasing ultrasound frequency. At 1056 kHz the mean diameter of active bubbles have been observed to reach a limiting value of about 4.5 μm, and for acoustic power greater than 6 W the bubble size is unaffected (Brothie et al., 2009). The acoustic power enhances the degradation rate of PAHs (Psillakis et al., 2004). The increase of input power intensity from 50 to 600 W results in higher degradation efficiency of pyrene after 60 min sonication at 20 kHz and 20 °C (Park et al., 2000). The effect of frequency is associated with the dynamics of bubble formation. Generally, higher ultrasound frequencies may increase the number of free radicals because there are more cavitational events that consequently lead to increased degradation of PAHs (Psillakis et al., 2004). David (2009) reported that high frequency (506 kHz) is more efficient than low frequencies.

The degradation of PAHs is affected positively or negatively by the presence of matrix compounds, and the predominant mechanism for the decomposition of PAHs is known to involve oxygen derived chemicals (Laughrey et al., 2001). Furthermore, chemical alteration of PAHs can occur in aqueous solutions exposed to high intensity ultrasound (Wheat and Tumeo, 1997; Park et al., 2000; Little et al., 2002). The sonochemical degradation of hydrophobic pollutants can also be significantly reduced by the presence of additional dissolved species, which may inhibit PAH access to the cavitation sites (Taylor et al., 1999; Laughrey et al., 2001).

The objective of this work is to evaluate the effectiveness of ultrasound waves at relatively high frequencies (i.e. 582, 862 and 1142 kHz) to degrade three PAH molecules of varying sizes (naphthalene, phenanthrene and pyrene) in pure aqueous solutions. Furthermore, the effect of input power on PAH degradation, the degradation kinetics as well as the presence of hexane-extractable metabolites are examined. To our knowledge, PAHs sonodegradation results at 582, 862 and 1142 kHz have never been reported in the literature. In addition, the present study employs a system able to treat higher volume solutions (500 and 1000 mL) than those reported in the literature (50–200 mL). Finally, a correlation between the energy required to degrade a compound and its molecular weight is determined.

2. Materials and methods

2.1. Test system

An ultrasonic system (Meinhardt Ultraschalltechnik, Leipzig, Germany) composed of a 75-mm diameter titanium transducer operating at 582, 862, and 1142 kHz, a function generator, and an amplifier was employed in this study (see Fig. 1). The transducer was mounted at the bottom of a cylindrical 2-L glass laboratory reactor with double walls to allow water circulation for cooling. PAH aquatic solutions with volume 500 or 1000 mL were poured into the ultrasonic reactor. A sample solution was used to measure and record the initial PAH concentration. During each experiment, 4 mL samples were taken at 5, 10, 15, 30, 60, 90, and 120 min. Samples were collected with a glass pipette and stored in glass vials. All samples were analyzed at the end of each experiment and the PAH concentrations were compared to the initial concentration. The temperature of the reactor liquid was measured with a digital thermometer equipped with a thermistor (Oakton Temp 5 Acorn Series, Eutech Instruments Ltd., Singapore). The electric power of the system could be adjusted to any level up to 200 W.

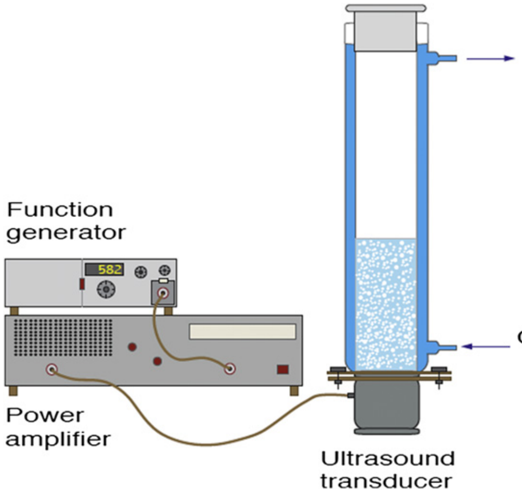

Fig. 1 – Experimental setup arrangement.

2.2. Analytical methods

Naphthalene, phenanthrene, and pyrene with two, three, and four ring chemical structure, respectively, were used in this study as model PAH compounds. Naphthalene (99.8% Dr. Ehrenstorfer GmbH, Germany), phenanthrene (>97% FLUKA Chemika, Switzerland), and pyrene (98% Aldrich Chemicals, Milwaukee, WI) were dissolved in methanol (>99.8% Merck) to yield a 12.5, 1.0, and 0.1 g/L stock solutions, respectively, which were kept in the dark at 4 °C. Aquatic solutions of 3000, 100, and 10 μg/L were prepared for naphthalene, phenanthrene, and pyrene. The pH of each PAH solution was 6.5.

Aqueous PAH concentrations were measured by a cuvette mode fluorescence spectrophotometer (Cary Eclipse, Varian Australia PTY LTD, Australia) using a quartz cuvette and excitation/emission wavelengths of 278/324 for naphthalene, 249/347 for phenanthrene, and 272/373 for pyrene. The conditions of the various experiments conducted in this study are listed in Table 1. Selected experiments were performed in duplicates or triplicates. All experiments were performed at 25 °C. A temperature control system was used and the highest temperature increase was less than 5 °C for all experiments.

To determine whether PAH hexane-extractable metabolites were produced during sonication, selected naphthalene and pyrene solutions (500 mL) were analyzed before and after sonication. The solutions were extracted with Pestiscan grade hexane (10 mL) in separatory funnels that were shaken for 10 min (modified from USEPA, 1999). After the hexane phase was separated from the aqueous phase, it was condensed to about 300 μL using a gentle stream of nitrogen gas and then, was cleaned through microcolumns containing glass wool, copper, and anhydrous sodium sulfate. Subsequently, a 2 μL sample was injected in a gas chromatograph with mass spectrometer (Shimadzu QP2000 GC–MS, with a 30 m Quadrex column). The detection limit of this analysis is about 1 μg/L. Fluorescence spectra of the three PAHs at various sonication times with ultrasound frequency of 582 kHz and an electric power of 133 W were examined for possible formation of aromatic byproducts. Excitation wavelengths in the UV range are generally used for the excitation of aromatic compounds (Little et al., 2002).

Table 1 – Experimental conditions.

Run number	f_a (kHz)	Power input (W)	Solution volume (mL)	PAH
1	582	67	500	Phenanthrene
2	582	100	500	Phenanthrene
3	582	133	500	Naphthalene
4	582	133	500	Phenanthrene
5	582	133	1000	Pyrene
6	582	133	1000	Phenanthrene
7	582	166	500	Phenanthrene
8	862	100	500	Phenanthrene
9	862	133	500	Naphthalene
10	862	133	500	Phenanthrene
11	862	133	500	Pyrene
12	1142	100	500	Phenanthrene
13	1142	133	500	Naphthalene
14	1142	133	500	Phenanthrene
15	1142	133	1000	Pyrene
16	1142	133	1000	Phenanthrene
17	1142	166	1000	Phenanthrene

2.3. Data analysis

Experimental data plotted as logarithmic normalized concentrations vs time (not shown here) suggested that the degradation process follows a first-order kinetic equation:

$$\ln\left[\frac{C}{C_0}\right] = -k_1 t \tag{1}$$

where C [μg/L] is the PAH aqueous concentration measured at a given time, C_0 [μg/L] is the initial PAH aqueous concentration, k_1 [1/min] is the first-order reaction constant, and t [min] is time. The half-life of PAH degradation reaction ($t_{1/2}$) [min] was calculated by the following equation:

$$t_{1/2} = \frac{0.693}{k_1} \tag{2}$$

The bubble radii as a function of ultrasound frequency employed were calculated from the following empirical expression (Brothie et al., 2009):

$$\log_{10}[r_b] = -\log_{10}[f_a] + 3.5 \tag{3}$$

where r_b [μm] is the bubble radius, and f_a [kHz] is the acoustic frequency. The bubble radius for a given frequency does not change for acoustic power higher than 8 W (Brothie et al., 2009). In this study, the acoustic power in all experiments was higher than 8 W. Therefore, the bubble radius is assumed to be similar for all experiments performed at the same frequency regardless of the acoustic power used.

The calorimetric power of the system, P_{cal} [W], was determined by recording the temperature fluctuation of the liquid during the initial 30 s of each experiment and using the following equation (Kimura et al., 1996):

$$P_{\mathrm{cal}} = \frac{\Delta T}{\Delta t} c_p M_w \tag{4}$$

where ΔT [K] is the temperature difference, $c_p = 4.2$ [J/g·K] is the heat capacity of the water, and M_w [g] is the water mass in the reactor.

The acoustic pressure, P_a, was calculated using the following equation (Mason and Lorimer, 2002):

$$P_a = \sqrt{2\rho c I_A} \tag{5}$$

where $\rho = 1000$ (kg/m^3) is the density of water, $c = 1500$ (m/s) is the speed of sound in water, $I_A = P_{\mathrm{cal}}/A_p$ (W/m^2) is the intensity, which is defined as the amount of energy flowing per unit area, A_p [cm^2] is the plate surface area, and P_a is measured in [N/m^2]. The plate diameter was 75 mm and thus, the plate surface area was $A_p = 44 \times 10^{-4}$ m^2.

The void fraction was calculated based on scarce experimental results found in the literature (Burdin et al., 1999) and the extrapolation method used by David (2009). The void fraction at $f_a = 20$ kHz and $P_a = 3.2$ bar was reported as 10^{-4} and at $f_a = 308$ kHz and $P_a = 0.2$ bar was reported as 3×10^{-4}. Through linear extrapolations among frequencies and acoustic pressures, the void fraction for each experimental condition was predicted. The bubble number per liter is the void fraction divided by the bubble volume calculated based on the bubble radius (David, 2009). Note that the void fraction value of 5×10^{-3} used by Servant et al. (2000) at $f_a = 477$ kHz and high acoustic pressure is in line with the results of this study, and supports the assumption of a linear relationship between acoustic frequencies and void fraction. Although the bubbles were not uniform in size and shape (David, 2009), our simplified calculations provided a means to compare the different experimental systems employed in this study (i.e. various frequencies and power inputs).

3. Results and discussion

3.1. *Effect of input power and frequency on PAHs concentration*

Fig. 2 presents the experimental data of the normalized phenanthrene concentration with time at $f_a = 582$ kHz and at varying power inputs. Determination of the optimum input power (resulting in faster degradation rate with the least input power) is necessary in order to operate the instrument in a cost effective mode. For power inputs $P \geq 133$ W, phenanthrene degraded to concentrations lower than the detection limit (<1 μg/L) within 100 min. Similar trends for varying power inputs were observed for the other two frequencies tested (862 and 1142 kHz). In Fig. 2, a delay of 10–15 min for the phenanthrene removal from the solution is observed for $P = 100$ W. Note that at $P = 167$ W there was a slight increase in concentration during the initial period. This degradation delay is probably attributed to the formation of a dense cloud around the probe at high powers, which blocks the energy transmitted from the probe to the fluid (Thompson and Doraiswamy, 1999).

It was reported that doubling the power from 75 to 150 W, phenanthrene degradation in a mixture of PAHs at $f_a = 24$ kHz increased from 60 to 83% after 60 min of sonication and at $f_a = 80$ kHz increased from 58 to 90% after 30 min of sonication (Psillakis et al., 2004). For naphthalene, increasing P from 75 to 150 W resulted in slightly higher degradation of naphthalene; (83–84%) at $f_a = 24$ kHz and (92–99%) at $f_a = 80$ kHz. Park et al. (2000) reported that at $f_a = 20$ kHz and increasing P from 50 to 600 W, the degree of pyrene degradation doubled after 60 min of sonication. In the present study at $f_a = 582$ kHz, by progressively increasing the input power from 67–100 to 133–167 W, phenanthrene degradation increased from 3–54 to 84–84%, respectively, after 60 min of sonication. The above results show that increasing P improved degradation in a nonlinear fashion. Worthy to note is that the reaction rate reaches a maximum value and a subsequent power increase does not alter reaction rates.

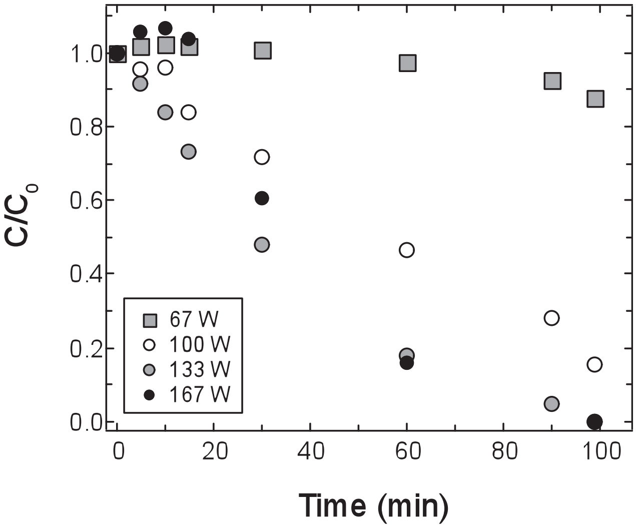

Fig. 2 – Phenanthrene degradation as a function of time at four different input power levels (67, 100, 133, and 167 W) with $f_a = 582$ kHz.

Fig. 3 presents the experimental data of the normalized PAH concentrations with time at one power input (133 W) and at three acoustic frequencies (582, 862, and 1142 kHz). Phenanthrene and pyrene degraded to concentrations lower than 10% of C_0 in around 100 min for all three frequencies employed. Naphthalene degraded to concentrations lower than 15% of C_0 in 100 min at 582 kHz, and lower than 25% of C_0 at 862 and 1142 kHz. Note that at $f_a = 582$ kHz, the degradation of all three PAHs examined was significantly faster than at the other two frequencies (862 and 1142 kHz). Also, the degradation behavior of all three PAHs examined at $f_a = 862$ and 1142 kHz was similar.

The properties of the bubbles generated at each of the three acoustic frequencies employed in this study are presented in Table 2. Bubble size decreased with increasing frequency. The void fraction and number of bubbles per volume considerably increased with increasing P. Whereas for the same P, the number of bubbles per volume increased by a factor of 4 by increasing f_a from 582 to 862 kHz and another factor of 4 by increasing f_a from 862 to 1142 kHz. No correlation was observed between the properties of the bubbles and the sonodegradation results. The results of the present study and those reported by David (2009) suggest that possibly at $f_a \sim 500$ kHz bubbles with optimum radius are formed that lead to better degradation. Although higher frequencies were expected to yield better activity because they result in more void volume (cavitation bubbles created per unit of time), at the same time higher frequencies result in smaller bubbles that might not be as active as bubbles at $f_a \sim 500$ kHz.

David (2009) reported that f_a from 20 kHz to 506 kHz resulted in higher rate constants for five PAHs examined. It was reported that the main mechanisms of PAH degradation was their pyrolysis in the heart of the bubble, and oxidation by hydroxyl radicals was a minor pathway. David and Riguier (2002) also studied the degradation of anthracene in aqueous suspensions adsorbed on silica at low (20 kHz) and high (506 kHz) acoustic frequencies and observed that the degradation rate was higher at the high f_a. The oxidation pathway by hydroxyl radicals was ruled out. As it is demonstrated in the present study, the degradation rates did not significantly increase for increasing f_a in the range 582–1142 kHz. On the contrary, the degradation rates were lower for increasing f_a in the range 582–1142 kHz.

3.2. *Degradation kinetics*

Table 3 presents the $t_{1/2}$ of the three PAHs examined in this study for the different experiments performed. In all cases,

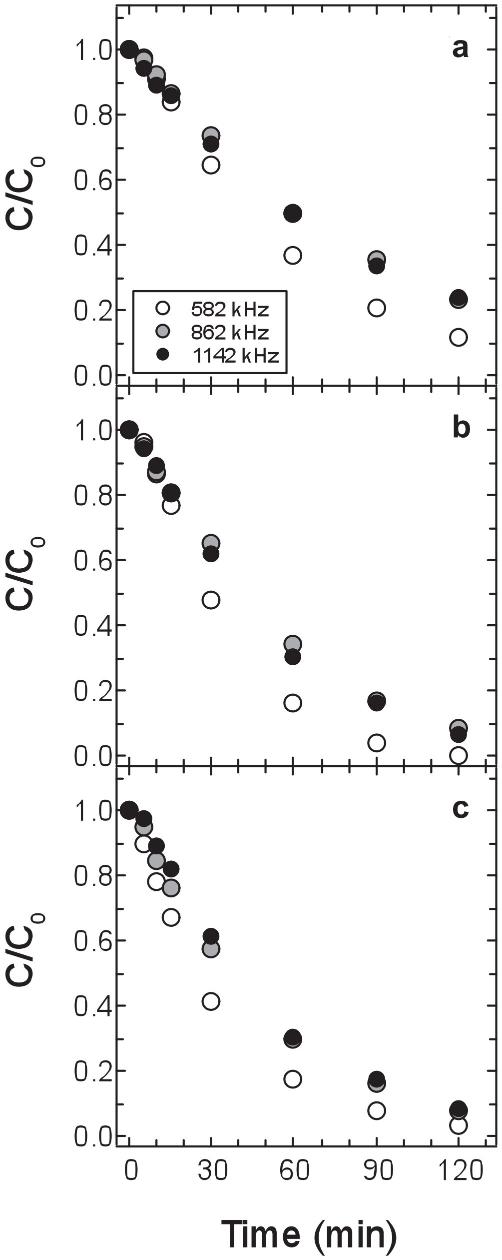

Fig. 3 – Degradation of (a) naphthalene, (b) phenanthrene, and (c) pyrene as a function of time at three different acoustic frequencies (582, 862, and 1142 kHz).

Table 2 – Bubble properties for different experimental conditions.

P (W)	r_b[a] (μm)	P_{cal} (W)	P_a (bar)	Void fraction (–)	No of bubbles (number/L)
$f_a = 582$ kHz					
67		13	0.92	2.6×10^{-3}	4.7×10^{9}
100	5.1	21	1.2	3.4×10^{-3}	6.1×10^{9}
133		37	1.6	4.5×10^{-3}	8.1×10^{9}
167		48	1.8	5.1×10^{-3}	9.2×10^{9}
$f_a = 862$ kHz					
133	3.5	37	1.6	6.6×10^{-3}	3.7×10^{10}
$f_a = 1142$ kHz					
133	2.6	37	1.6	8.8×10^{-3}	1.2×10^{11}

a Calculated from Equation (3).

faster degradation was observed at $f_a = 582$ kHz and $P \geq 133$W. For initial concentrations of the three PAHs at 10% of their aqueous solubility, the faster degradation was observed at $f_a = 582$ kHz and $P \geq 133$W for phenanthrene and pyrene. Degradation rates per unit mass were similar for naphthalene and phenanthrene and lower for pyrene.

For phenanthrene, the lower $t_{1/2} = 23 \pm 2$ min was observed for 500 mL at $f_a = 582$ kHz and $P \geq 133$W. Similar results have been observed by other researchers at lower frequencies (e.g. at 20 kHz, Taylor et al., 1999; 24 and 80 kHz, Psillakis et al., 2004; 20 and 506 kHz, David, 2009). However, these results were obtained by treating lower solution volumes compared to the volumes treated in the present study. The highest solution volume treated by other investigators was 200 mL (Psillakis et al., 2004). Once aqueous solution volume was increased to 1 L, longer times were necessary for phenanthrene to degrade ($t_{1/2} = 45$ min). Decreasing the volume by half also decreased the half-life time by half. For this reason, the 500 mL volume was chosen for further study. The values of the first-rate constants for the three PAHs tested are given in Table 4, together with the corresponding values obtained from literature.

No obvious correlation between compound size, hydrophobicity, and degradation rates was observed. Such correlations have been reported in the literature for monocyclic aromatic compounds (Nanzai et al., 2008). However, there exists a positive correlation between the treated PAH compound size and the required energy, $E = P \times \text{time}$ [W × h]. Naphthalene degradation required almost 1.5 orders of magnitude less energy than phenanthrene, which required one order of magnitude less energy than pyrene. The energy required for the degradation of phenanthrene at different input power levels is presented in Fig. 4. Note that less energy was required when operating at high P. The degradation of naphthalene with a molecular weight (MW) of 128 required 0.22 Wh/μg, almost 1.5 orders of magnitude less energy than phenanthrene (MW = 178) that required 5.1 Wh/μg, which is one order of magnitude less energy than the 57 Wh/μg required by pyrene (MW = 202) (see Fig. 5).

Table 3 – Estimated $t_{1/2}$ (min).

P(W)	Sample volume (mL)	f_a (kHz) 582	862	1142
Naphthalene ($C_0 = 3000$ μg/L)				
133	500	$38^{a} \pm 3.3$	57	57
Phenanthrene ($C_0 = 100$ μg/L)				
67	500	580	–	–
100	500	51	47	65
133	500	23 ± 2.0	32 ± 4.0	31 ± 1.4
133	1000	45	–	–
166	500	21	–	–
166	1000	–	–	87
Pyrene ($C_0 = 10$ μg/L)				
133	500	24 ± 4.2	32 ± 1.2	33 ± 1.4

a Mean ± standard deviation of triplicate or duplicate experiments.

Table 4 – Estimated sonodegradation first-order rate (k_1) values of various PAH.

PAH	P (W)	Sonicated volume (mL)	C_0 (μg/L)	f_a (kHz)	k_1 (1/min)	Reference
Acenaphthylene	150	200	150	80	0.0846	Psillakis et al. (2004)
Acenaphthylene	150	200	450	80	0.0678	Psillakis et al. (2004)
Anthracene	600	50–100	18	20	0.9 ± 0.36	Taylor et al. (1999)
Anthracene	150–180	50–70	18–89	20	1.6 ± 0.018	Laughrey et al. (2001)
Anthracene	30	150	110	20	0.040 ± 0.003	David (2009)
Anthracene	30	150	110	506	0.093 ± 0.006	David (2009)
Benzo(k)fluoranthene	30	150	12	20	0.008 ± 0.001	David (2009)
Benzo(k)fluoranthene	30	150	12	506	0.028 ± 0.001	David (2009)
Naphthalene	150	200	150	80	0.1217	Psillakis et al. (2004)
Naphthalene	150	200	450	80	0.0989	Psillakis et al. (2004)
Naphthalene	200	150	227	20	0.12 ± 0.01	David (2009)
Naphthalene	200	150	227	506	0.27 ± 0.01	David (2009)
Naphthalene	133	500	3000	582	0.018 ± 0.002	This study
Naphthalene	133	500	3000	862	0.012	This study
Naphthalene	133	500	3000	1142	0.012	This study
Phenanthrene	600	50–100	18	20	0.354 ± 0.018	Taylor et al. (1999)
Phenanthrene	150–180	50–70	18–89	20	0.66 ± 0.12	Laughrey et al. (2001)
Phenanthrene	150	200	150	80	0.0836	Psillakis et al. (2004)
Phenanthrene	150	200	450	80	0.0422	Psillakis et al. (2004)
Phenanthrene	200	150	97	20	0.047 ± 0.003	David (2009)
Phenanthrene	200	150	97	506	0.17 ± 0.01	David (2009)
Phenanthrene	133	500	100	582	0.030 ± 0.003	This study
Phenanthrene	133	500	100	862	0.022 ± 0.002	This study
Phenanthrene	133	500	100	1142	0.023 ± 0.0001	This study
Pyrene	600	50–100	20	20	0.36 ± 0.18	Taylor et al. (1999)
Pyrene	150–180	50–70	20–100	20	0.624 ± 0.054	Laughrey et al. (2001)
Pyrene	200	150	118	20	0.029 ± 0.002	David (2009)
Pyrene	200	150	118	506	0.067 ± 0.003	David (2009)
Pyrene	133	500	10	582	0.030 ± 0.005	This study
Pyrene	133	500	10	862	0.021 ± 0.0008	This study
Pyrene	133	500	10	1142	0.021 ± 0.0009	This study

3.3. *Intermediate products*

Naphthalene and pyrene solutions were analyzed for hexane-extractable metabolites using liquid–liquid extraction and GC–MS. Naphthalene solutions at two concentrations (3 and

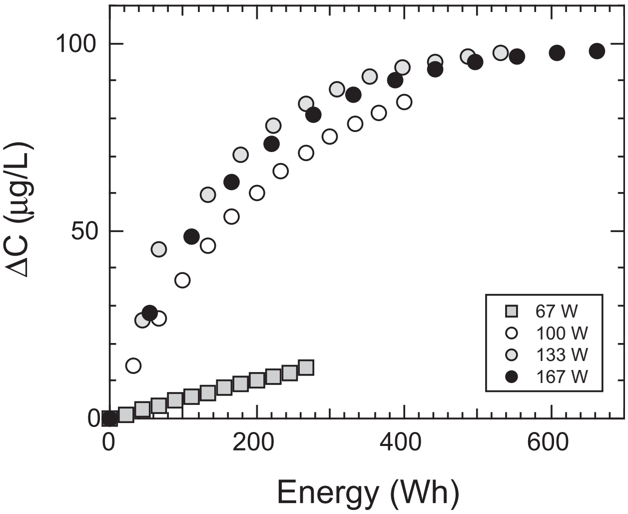

Fig. 4 – Phenanthrene degradation as a function of energy required at different input power levels (67, 100, 133, and 167 W) with f_a = 582 kHz.

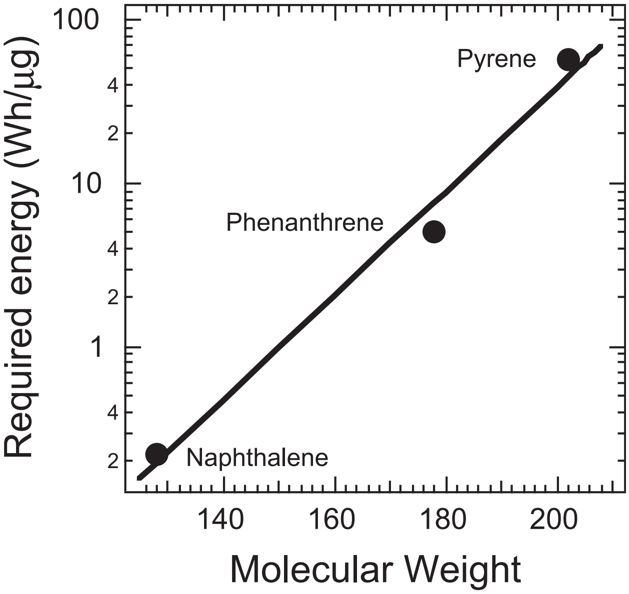

Fig. 5 – Energy required for the three PAHs examined in this study as a function of the molecular weight at an input power level of 133 W with f_a = 582 kHz (experimental data are presented with solid circles and the correlation curve is presented with a line; Required energy = 0.0318 • MW − 4.784, R^2 = 0.985).

0.3 mg/L) were analyzed before and after sonication. For both cases considered, naphthalene was detected in the solution before and after sonication. Also, a 10 μg/L pyrene solution was analyzed before and after sonication. Pyrene was only detected in the solution before sonication but was not detected in the solution after sonication. No additional peaks from other ions present in the hexane extract were observed in the chromatograms obtained by using GC–MS in the SCAN mode. Also, no additional peaks were observed even when the GC–MS was operated in the SIM mode, searching for specific ion masses of possible byproducts such as 1,2 dihydrohynaphthalene, salicylaldehyde, salicylate, gentisate, catechol, etc. Little et al. (2002) identified phenanthrene byproducts in solutions sonicated at $f_a = 30$ kHz. A possible explanation could be that the sonication mechanism is different at higher frequencies or the byproducts were present at concentrations lower than the detection limit (~1 μg/L). High frequencies result in shorter bubble life times and production of free radicals. Also, at high frequencies the amount of free radicals which are able to escape from the cavitation site to the bulk volume may increase and facilitate the bulk reaction (Thompson and Doraiswamy, 1999). Wheat and Tumeo (1997) found phenanthrene-diol as an intermediate product after sonication of the phenanthrene. Taylor et al. (1999) did not observe oxidized compounds after the sonication of phenanthrene and anthracene. Finally, Park et al. (2000) reported that after 1 h ultrasonic irradiation of pyrene, the major products were tetrahydro-2,5-dimethyl-furan, tetrahydro-2-methyl-2-furanol, 2,2-dimethyl-3-propyl-oxirane, 3,4-dihydro-6-methyl-2H-pyran, and 1,2-benzedicarboxylic acid.

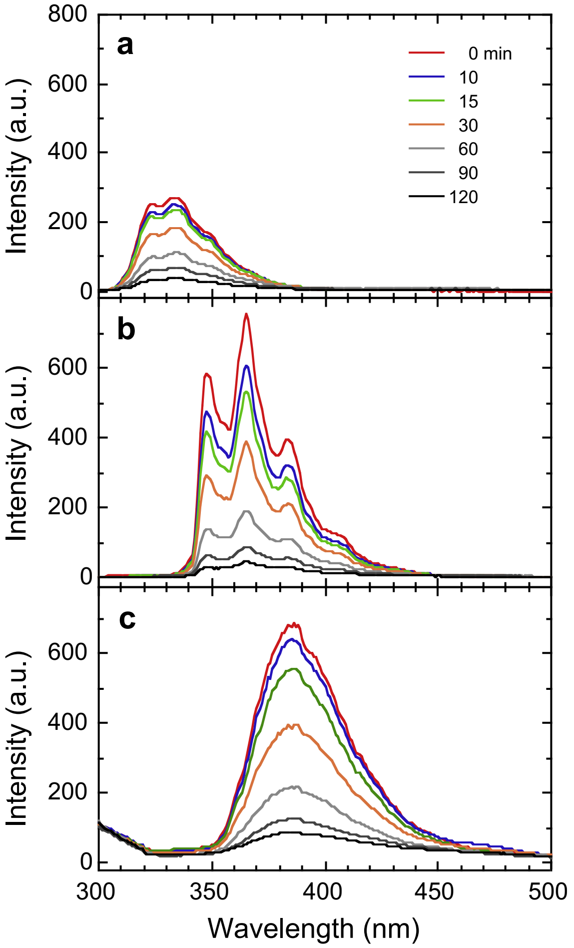

Fig. 6 – Fluorescence spectra at various times for: (a) naphthalene, (b) phenanthrene, and (c) pyrene.

The fluorescence spectra at various sonication times for naphthalene, phenanthrene, and pyrene at $f_a = 582$ kHz and $P = 133$ W are presented in Fig. 6. A decrease in the fluorescence intensity with increasing time was observed without any significant change in the spectral shape. This observation indicated that there were no fluorescent interferences by other intermediate compounds with the excitation and emission wavelengths used. Similar results have been reported in the literature for the sonication of anthracene, phenanthrene and pyrene at $f_a = 20$ kHz (Taylor et al., 1999; Laughrey et al., 2001).

4. Conclusions

High frequency ultrasounds (i.e. 582, 862, and 1142 kHz) were tested to degrade three PAH molecules of varying sizes (naphthalene, phenanthrene and pyrene) in pure aqueous solutions. Phenanthrene and pyrene degraded to concentrations lower than 10% of C_0 in about 100 min for all three frequencies employed. Naphthalene degraded to concentrations lower than 15% of C_0 in 100 min at 582 kHz, and lower than 25% of C_0 at 862 and 1142 kHz. Degradation rates per unit mass were similar for naphthalene and phenanthrene and lower for pyrene. A positive correlation was observed between the treated PAH compound size and the required energy.

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