Degradation of polycyclic aromatic hydrocarbons in aqueous solutions by ultrasonic irradiation

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Abstract

The effect of various operating conditions (initial concentration, liquid phase temperature, applied power, ultrasound frequency) and of the presence of matrix components (1-butanol, NaCl and $FeSO_4$) on the sonochemical degradation of naphthalene, acenaphthylene and phenanthrene in water has been studied. A horn-type sonicator was used to deliver the ultrasound energy, while immersion sampling solid-phase microextraction (SPME) coupled with GC–MS was employed to follow concentration–time profiles of the chosen PAHs. At the operating conditions in question (initial concentrations of 150, 300 and 450 μg/l, temperatures of 20 and 40 °C, applied power of 45, 75 and 150 W and ultrasound frequencies of 24 and 80 kHz), all PAHs were susceptible to sonochemical treatment and, in most cases, complete degradation could be achieved in up to 120 min of treatment. Conversion was found to decrease with increasing initial concentration and temperature and decreasing power and frequency as well as in the presence of an excess of dissolved salts. Addition of 1-butanol, a known hydroxyl radical scavenger, substantially suppressed degradation throughout the course of the reaction, thus highlighting the role of oxidation reactions in PAHs degradation. In contrast, addition of Fe^{2+} ions at a low concentration enhanced degradation through a Fenton-like reaction.
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1. Introduction

Over the past few decades, advanced and thermochemical oxidation processes have received increasing attention for the destruction of various organic pollutants commonly found in waters and wastewaters. Although processes such as UV irradiation, hydrogen peroxide oxidation, ozonation, wet air oxidation, electrochemical oxidation have been comprehensively investigated and employed in water remediation, relatively few studies report the use of ultrasound as a potential treatment technology. Sonochemical destruction of pollutants in aqueous phase generally occurs as the result of imploding cavitation bubbles and involves several reaction pathways and zones such as pyrolysis inside the bubble and/or at the bubble–liquid interface and hydroxyl radical-induced reactions at the bubble–liquid interface and/or in the liquid bulk [1]. As has been reported in a recent review [2], the process is capable of effectively degrading several target compounds including, amongst others, phenol, chlorophenols, nitrophenols, polychlorinated biphenyls, chloroaromatics, pesticides, dyes, CFCs, polycyclic aromatic hydrocarbons and surfactants, present in relatively dilute solutions typically in the micro- to milli-molar range. So far, the use of ultrasound in industrial wastewater treatment applications is limited given that the process is relatively inefficient and burdened with high operational costs since almost half of the supplied energy for ultrasound generation is dissipated as heat. Nonetheless, operating costs appear to be less severe than would be required by conventional thermochemical methods (e.g. wet air oxidation) requiring high temperatures and pressures [1]. Furthermore, the process does not require the use of extra chemicals (e.g. oxidants and catalysts) commonly employed in several advanced oxidation processes (e.g. ozonation, Fenton's reagent), thus avoiding the respective costs as well as the need to remove the excess of toxic compounds prior to discharge.

It is notable that relatively few studies report the sonochemical degradation of polycyclic aromatic hydrocarbons (PAHs) which are known toxic and hazardous pollutants.

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PAHs, a class of environmental pollutants mainly derived from the incomplete combustion of fossil fuels, enter groundwaters and surface waters through leaching processes. While their solubility is generally quite low and usually decreases with increasing molecular weight, their hazard potential can be relatively high, thus making their presence in the water cycle an acute and chronic risk to human health and environmental quality. Wheat and Tumeo [3] studied the sonochemical degradation of phenanthrene and biphenyl in aerated aqueous solutions in the presence of Fe^{3+} ions. In further studies, Taylor et al. [4] and Laughrey et al. [5] studied the sonochemical degradation of anthracene, phenanthrene and pyrene at 20 kHz with emphasis on the effect of matrix components (i.e. fulvic and benzoic acids, pentanol, pentane and sodium dodecyl sulfate) and purging gases (i.e. nitrogen and oxygen) on the kinetics of PAHs degradation. Park et al. [6] studied the effect of various operating conditions (i.e. pH value, ultrasound intensity, water:ethanol ratio) and of the presence of matrix components (i.e. hydrogen peroxide) and purging gases (i.e. argon) on the sonochemical degradation of phenanthrene, anthracene, pyrene, coronene, 1-methylnaphthalene and 1,12-benzoperylene at 20 kHz in water:ethanol mixtures. Little et al. [7] studied the sonochemical degradation of phenanthrene at 30 kHz monitoring the influence of parameters such as applied power, liquid phase temperature and light. In an attempt to investigate ultrasonically assisted extraction of PAHs from soil, Leonhardt and Stahl [8] sonicated soil samples in solutions containing equal volumes of an organic solvent (dichloromethane, cyclohexane or toluene) and water and reported the decomposition of acenaphthylene by ultrasonic irradiation. The authors concluded that the presence of chlorinated solvent during sonication results in the formation of solvent radicals, which react with PAHs leading to the built-up of chloro-PAHs by-products.

The scope of this work is to study the sonochemical degradation of three reference lower molecular weight PAHs (namely, naphthalene, acenaphthylene and phenanthrene) either in mixture or in single-component aqueous solutions with emphasis given on the effect of various operating conditions (initial concentration, temperature, applied power, ultrasound frequency) and of the presence of matrix components (1-butanol, NaCl and $FeSO_4$) on the extent of degradation.

2. Experimental and analytical

2.1. Materials

Stock solutions containing naphthalene, acenaphthylene or phenanthrene at a concentration of 500 µg/ml in acetonitrile (>99% purity purchased from Aldrich-Chemie GmbH & Co., Steinheim, Germany) were used for the preparation of aqueous spiked solutions containing either equal concentrations of all three PAHs (at a concentration of 50 or 100 µg/l each) or each PAH alone (at concentrations of 150 or 450 µg/l). A 500 µg/ml acetone solution of acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}, purchased from Supelco (Sigma-Aldrich Chemie) was used as internal standard solution. The deionised water used for sample preparation was obtained from a water purification system supplied by Barnstead/Thermolyne Corporation (EASYpure® RF). 1-Butanol, $FeSO_4 \cdot 7H_2O$ and NaCl used as matrix species during sonochemical degradation experiments were purchased from LabScan, Lancaster and Merck, respectively. All organic solvents were Suprasolv quality and were purchased from Merck.

2.2. Sonication experiments

Most of the experiments were carried out at an ultrasound frequency of 80 kHz; in this case, an Ultrason 250 (LabPlant Ltd., UK) horn-type generator capable of operating either continuously or in a pulse mode at a variable electric power output up to 150 W was used for sonication experiments. For those experiments carried out at a frequency of 24 kHz, a UP 400S (Dr. Hielscher GmbH, Germany) horn-type generator capable of operating either continuously or in a pulse mode at a variable electric power output up to 300 W was used. In either case, a titanium probe with 7 mm diameter tip was used to deliver the ultrasound energy to the liquid medium. Reactions were carried out in a 200 ml cylindrical all-glass reaction vessel with the titanium horn sitting on top of the reaction vessel and sealed using O-rings and a Teflon valve. The vessel was immersed in a water bath which was connected to a temperature control unit (Polystat cc2, Huber, Germany). To avoid any photochemical reactions the vessel was covered with aluminium foil. A schematic diagram of the experimental setup is given in Fig. 1.

2.3. Analytical method

Samples periodically drawn from the vessel were analysed with respect to the PAHs concentration by means of immersion solid-phase microextraction (SPME) sampling coupled with gas chromatography–mass spectrometry (GC–MS). We have recently reported an optimised SPME/GC–MS protocol capable of monitoring trace levels of PAHs in water, while minimising both the overall sample preparation time and the use of toxic organic solvents. With this protocol which is described in detail elsewhere [9], limits of detection are 0.01 µg/l for acenaphthylene and phenanthrene and 0.02 µg/l for naphthalene. Repeatability expressed as the relative standard deviation (RSD) of five consecutive replicates was found to be 9% for naphthalene, 14% for acenaphthylene and 4% for phenanthrene [9]. It should be mentioned here that according to the European Community directive 80/778/EEC, the maximum levels for PAHs (when considering fluoranthene, benzo[α]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and indeno[1,2,3-
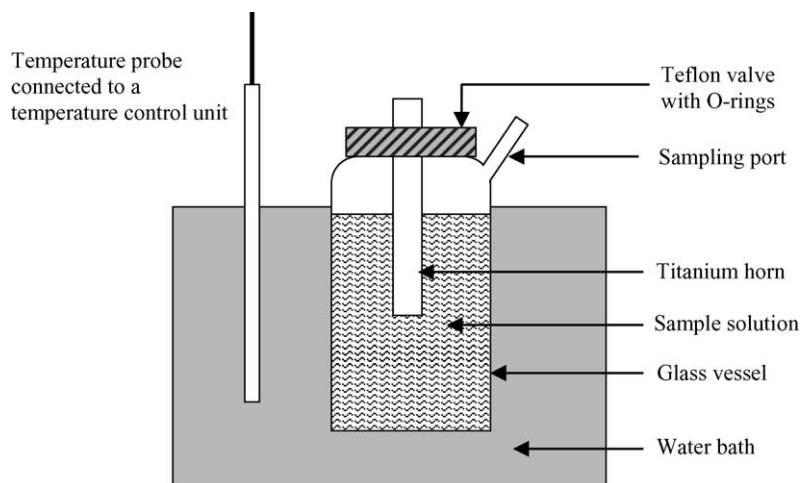
Fig. 1. Schematic diagram of the reactor setup.

cd]pyrene as reference compounds) in drinking water is 0.2 μg/l whilst their sum can reach 1 μg/l in surface waters depending on the surface water treatment process [10].

3. Results and discussion

3.1. Effect of operating conditions

Fig. 2 shows concentration changes of the three PAHs in mixture as a function of the sonication time at 80 kHz, 150 W, 20 °C and at 50 and 100 μg/l initial concentrations for each individual solute (150 and 300 μg/l total initial concentrations, respectively). Mean values of three experiments are quoted as results with the reproducibility (expressed as RSD) ranging between 6 and 16%. Given that these values

are only marginally greater than the RSD values obtained for the repeatability of the SPME/GC–MS method (intra-day measurements), it can be concluded that the main parameter introducing error is the analytical method used here. This is also in accordance with other recently reported results [11].

As seen, all PAHs easily degrade at the conditions in question and complete removal can be achieved within 60–120 min of sonication. In general, the sonochemical degradation of chemical compounds can occur through two distinct pathways, namely, oxidation by hydroxyl radicals and pyrolytic decomposition [2]. Hydrophobic and volatile compounds tend to migrate towards the bubble and predominantly degrade via hydroxyl radical and pyrolytic reactions occurring at the bubble–liquid interfacial region and inside the bubble, while hydrophilic and non-volatile compounds tend to accumulate in the liquid phase, where they degrade
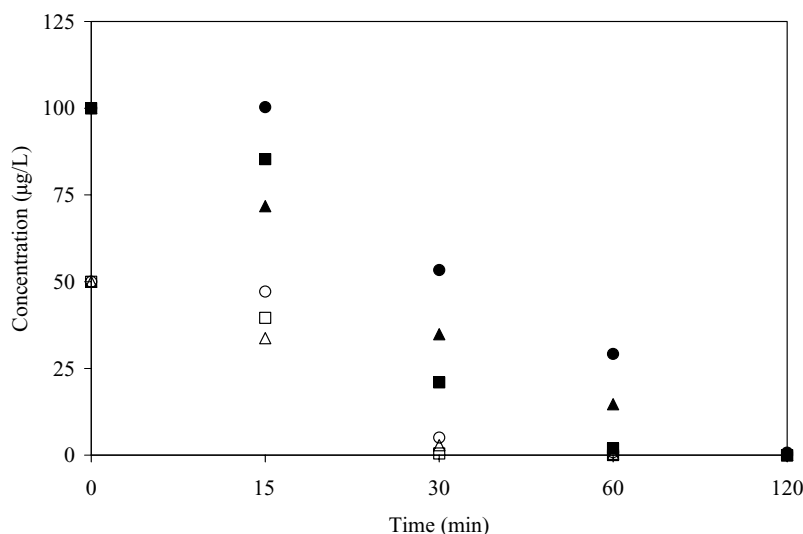

Fig. 2. Effect of initial solute concentration on the sonochemical degradation at 80 kHz, 150 W, 20 °C of aqueous solutions containing a mixture of all target compounds. (△, ▲) naphthalene, (□, ■) acenaphthylene, (○, ●) phenanthrene. Open symbols: 50 μg/l of each PAH (150 μg/l total initial concentration); closed symbols: 100 μg/l of each PAH (300 μg/l total initial concentration).

via hydroxyl radical reactions. As all PAHs employed in this study are hydrophobic and semi-volatile [10], it is reasonable to assume that they partly degrade through thermal reactions occurring inside the bubble [5].

Furthermore, the amount of degraded PAHs appears to increase with increasing initial concentration and this is more pronounced during the early stages of the process. As seen, sonicating the reaction mixture initially containing 50 μg/l of each target PAH (150 μg/l total initial concentration) for 15 min resulted in 33% naphthalene and 21% acenaphthylene degradation. For the experiment using a reaction mixture initially containing 100 μg/l of each target PAH (300 μg/l total initial concentration) the extent of degradation was 28 and 15% for naphthalene and acenaphthylene, respectively. However, the amount of naphthalene and acenaphthylene degraded after 15 min at 100 μg/l of each target PAH is as much as about 1.7 and 1.4 times, respectively, greater than that degraded at 50 μg/l. Regarding the more recalcitrant solute, phenanthrene, the same conclusion is more pronounced when comparing results at prolonged sonication times. For instance, 60 min sonication of the reaction mixture initially containing 50 μg/l of each target PAH resulted in 98% phenanthrene degradation, whereas the respective value for the solution containing 100 μg/l of each target PAH was 71%. Nonetheless, in the latter case the amount of phenanthrene degraded is 1.4 times greater than that in the reaction mixture initially containing 50 μg/l of each PAH.

It should be mentioned here that, at the experimental and analytical conditions in question (i.e. level of contamination, type of SPME fibre, SPME methodology and analytical equipment), identification of potential PAHs degradation by-products was not possible. One of the major advantages of SPME over other extraction methods is its high degree of selectivity, enabling the development of more sensitive and discriminating analytical methods which have the ability to identify and quantify analytes with less interference from matrix components. Although selectivity is required in any modern sample preparation method, removing unwanted analytes restricts or even hinders the identification of

by-products formed during sonochemical degradation. Similar observations, while using the SPME/GC–MS approach to monitor the sonochemical degradation of phthalates, have been previously published [11].

Table 1 shows the effect of power output and ultrasound frequency on the degradation of PAHs in mixture at 20 °C and 50 μg/l of each target PAH (150 μg/l of total initial concentration). As seen, conversion increases with increasing applied power and ultrasound frequency. The beneficial effect of power on degradation rates is believed to be due to increased cavitational activity occurring at higher levels of power. As power increases, the number of collapsing cavities also increases, thus leading to enhanced degradation rates. These results are in line with those reported by Park et al. [6] who found that the degree of pyrene degradation after 60 min of sonication at 20 kHz and 25 °C nearly doubled increasing the power intensity from 50 to 600 W. At the conditions employed in this study, increasing ultrasound frequency from 24 to 80 kHz exerts a positive effect on PAHs degradation. Although the effect of frequency is a complex issue associated with the dynamics of bubble formation, it is generally believed that higher frequency ultrasound may actually increase the number of free radicals in the system because, although cavitation is less violent, there are more cavitational events and thus more opportunities for free radicals to be generated [1]. Moreover, as bubble lifetime is shorter at higher frequencies, free radicals have a greater chance to escape from the bubble and migrate towards the liquid bulk prior to undergoing any recombination reactions [12].

Fig. 3 shows the conversion of PAHs in mixture as a function of the sonication time at 80 kHz, 150 W, 40 °C and 50 μg/l of each target PAH (150 μg/l of total initial concentration). Although complete PAHs degradation can be achieved after about 60 min at 40 °C, initial rates (i.e. within the first 15 min) appear to decrease with increasing temperature. This phenomenon is believed to be associated with the effect of temperature on both the bubble formation energy threshold and the intensity of bubble implosion as discussed

Table 1
Effect of power output and ultrasound frequency on the conversion of PAHs in mixture during sonochemical degradation at 20 °C and 150 μg/l of total initial concentration

Experimental conditions			Naphthalene conversion (%)	Acenaphthylene conversion (%)	Phenanthrene conversion (%)
Power (W)	Frequency (kHz)	Sonication time (min)			
150	80	30	94.2	99.0	89.8
150	80	60	99.2	>99.9[a]	98.2
75	80	30	60.6	91.6	57.6
75	80	60	92.2	>99.9[a]	>99.9[a]
45	80	30	39.4	53.2	7.4
45	80	60	52.8	77.2	58.6
150	24	30	77.6	80.7	73.8
150	24	60	84.4	96.6	83.0
75	24	30	55.7	77.4	32.7
75	24	60	83.4	87.8	59.9

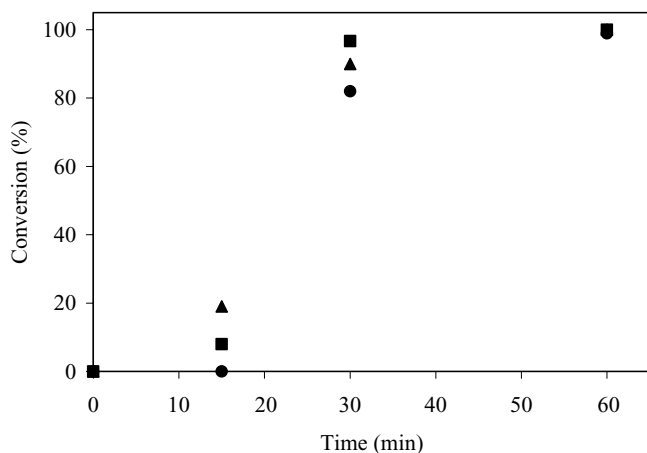[a] Values below quantification limit.

Fig. 3. Effect of temperature on the sonochemical degradation at 80 kHz, 150 W, 40 °C of an aqueous PAHs mixture containing 50 μg/l of each target analyte (150 μg/l total initial concentration). (▲) Naphthalene, (■) acenaphthylene, (●) phenanthrene.
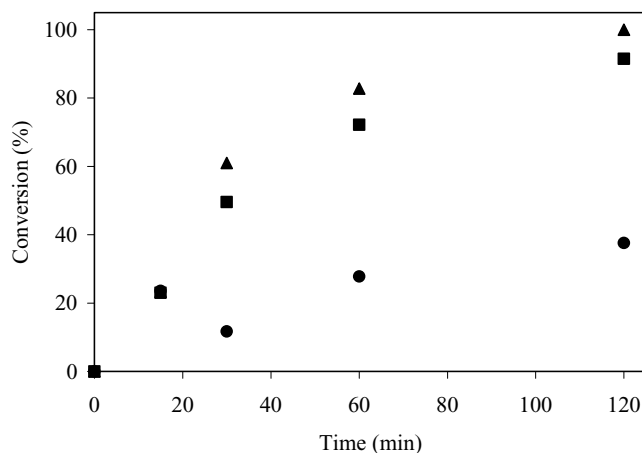

Fig. 4. Effect of radical scavenger (320 μg/l 1-butanol) on the sonochemical degradation at 80 kHz, 150 W, 20 °C of an aqueous PAHs mixture containing 50 μg/l of each target analyte (150 μg/l total initial concentration). (▲) Naphthalene, (■) acenaphthylene, (●) phenanthrene.

in detail elsewhere [1]. In brief, increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapour pressure; nevertheless, this beneficial effect is compensated by the fact that bubbles contain more vapour which cushions bubble implosion and consequently reduces the maximum temperature obtained during bubble collapse. In addition to this, increased temperatures are likely to favour degassing of the liquid phase, thus reducing the number of gas nuclei available for bubble formation. In a recent study [7], the sonochemical degradation of an aqueous solution of phenanthrene (100 ml) was studied at 30 kHz of ultrasound frequency (delivered through a horn-type sonicator), 32.5 W of power output and 600 μg/l of initial concentration. Phenanthrene was found to be recalcitrant to sonochemical degradation at 20 °C; however, increasing the liquid bulk temperature to 40 °C led to about 80% removal. It should be pointed out that the effect of temperature on sonochemical degradation is a relatively complex issue closely related to the properties and reaction conditions of each specific system in question; therefore, it is not surprising that several investigators have reported contradictory findings regarding the temperature effect [1,2]. In certain reaction systems, for instance, the net effect of an increase in liquid bulk temperature and consequently in maximum collapse temperature is an increase in degradation rates. This occurs up to the point at which the cushioning effect of the vapour begins to dominate the system and further increases in liquid temperature result in reduced reaction rates.

3.2. Degradation in the presence of matrix components

Addition of radical reaction inhibitors (radical scavengers) often confirms the presence of a radical chain mechanism. Degradation rates of target contaminants have to be considerably reduced in the presence of these scavengers to conclude that a free radical chain reaction is involved. It is possible to obtain information about the sonochemical reaction zones by controlling the type of radical scavenger in which the free radicals are located or produced. For example, 1-butanol is a known scavenger for the gaseous region and/or interfacial region of the collapsing bubble, whereas inorganic salts, such as potassium iodide or bromide, reside on the bulk liquid region or possibly at the interfacial region of the cavitation bubble [13]. In further experiments, the effect of 1-butanol on the degradation of PAHs was investigated. Fig. 4 shows the conversion of PAHs in mixture as a function of the sonication time at 80 kHz, 150 W, 20 °C, 50 μg/l of each target PAH (150 μg/l of total initial concentration) and in the presence of 320 μg/l of 1-butanol. As clearly seen from Figs. 2 and 4, addition of 1-butanol leads to decreased conversion although, at the conditions in question, complete inhibition of PAHs degradation was not observed. The data indicates that although liquid phase reactions predominate PAHs degradation, gas phase reactions also occur. This is in accordance with the work of Laughrey et al. [5] who studied the sonochemical degradation of pyrene, anthracene and phenanthrene in the presence of various radical scavengers (including humic and benzoic acids, pentane and pentanol amongst others) and reported a similar trend in their data.

During aqueous ultrasonic irradiation, hydroxyl radicals formed due to the thermolytic reactions of water recombine to form hydrogen peroxide [1] that tends to accumulate in the solution and, in its molecular form, does not usually play an important role in oxidising organic species. To enhance degradation efficiency, a more effective utilisation of hydrogen peroxide is desirable; this can be achieved with the addition of ferrous ion, thus simulating a Fenton-like reaction. The synergy between iron and the ultrasound has been demonstrated in several recent studies regarding the sonochemical degradation of alkylphenols [14], 1,4-dioxane [15],
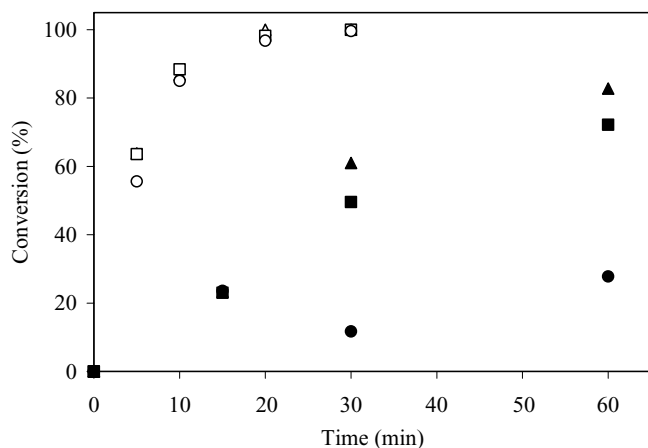
Fig. 5. Effect of different Fe^{2+} concentrations on the sonochemical degradation at 80 kHz, 150 W, 20 °C of an aqueous PAHs mixture containing 50 μg/l of each target analyte (150 μg/l total initial concentration). (△, ▲) Naphthalene, (□, ■) acenaphthylene, (○, ●) phenanthrene. Open symbols: 75 mg/l $FeSO_4 \cdot 7H_2O$; closed symbols: 100 g/l $FeSO_4 \cdot 7H_2O$.

MTBE [16] and chlorophenols [17]. Fig. 5 shows the conversion of PAHs in mixture as a function of the sonication time at 80 kHz, 150 W, 20 °C, 50 μg/l of each target PAH (150 μg/l of total initial concentration) and in the presence of Fe^{2+} ions. As clearly seen from Figs. 2 and 5, addition of $FeSO_4 \cdot 7H_2O$ at a concentration of 75 mg/l considerably enhances PAHs degradation with nearly complete conversion being achieved after about 20 min of sonication. On the contrary, addition of $FeSO_4 \cdot 7H_2O$ at a concentration of 100 g/l, although does not inhibit complete PAHs removal, has a detrimental effect on initial degradation rates; this is possibly due to the fact that an excessive amount of iron acts as a scavenger for the hydroxyl radicals. Yim et al. [14] and Nagata et al. [17] who studied the sonochemical degradation of 4-*n*-nonylphenol and 3-chlorophenol, respectively, at various concentrations of Fe^{2+} reported that there was an

optimum iron concentration beyond which degradation was found to decrease.

In further experiments, PAHs sonochemical degradation was studied at 80 kHz, 150 W, 20 °C, 50 μg/l of each target PAH (150 μg/l of total initial concentration) and in the presence of 100 g/l NaCl (10%, w:v) and the results are shown in Fig. 6. Depending on the nature of contaminants, addition of salt to the solution can decrease their solubility and consequently increase their hydrophobicity due to the salting-out effect. This is expected to enhance diffusion of solutes from the bulk solution to the bubble–liquid interface, thus leading to increased degradation rates. Seymour and Gupta [18] who studied the sonochemical degradation of chlorobenzene, *p*-ethylphenol and phenol at 20 kHz reported that NaCl addition improved substantially degradation rates. This was attributed to the salting-out effect, while the role of chloride radicals in enhancing oxidation was thought to be insignificant. As seen from Figs. 2 and 6, addition of NaCl restricted initial PAHs degradation (i.e. within the first 15–30 min of reaction). A possible explanation would be that adding salt to the reaction mixture results in reduced vapour pressure and increased surface tension, both of which tend to reduce the number of bubbles formed. This hypothesis is supported by the work of Chen and Smirniotis [19] who also found that addition of NaCl or Na_2SO_4 had a detrimental effect on the sonochemical degradation of phenol at 20 kHz.

It should be mentioned here that altering matrix composition of the reaction mixture influences the partitioning of analytes between the sample matrix and the SPME fibre during SPME extraction and consequently extraction conditions are likely to differ from the ones used during the internal standard calibration procedure. Furthermore, in the case of 1-butanol, the radical scavenger is consumed during the sonication of the reaction mixture and as a result the composition of the matrix is continually altered throughout the experiment; this is why its initial concentration had to be kept to a minimum. However, these effects are
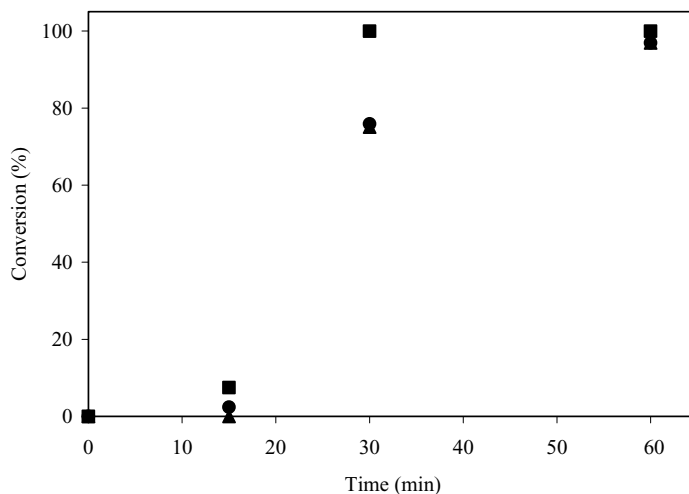

Fig. 6. Effect of NaCl (100 g/l) on the sonochemical degradation at 80 kHz, 150 W, 20 °C of an aqueous PAHs mixture containing 50 μg/l of each target analyte (150 μg/l total initial concentration). (▲) Naphthalene, (■) acenaphthylene, (●) phenanthrene.
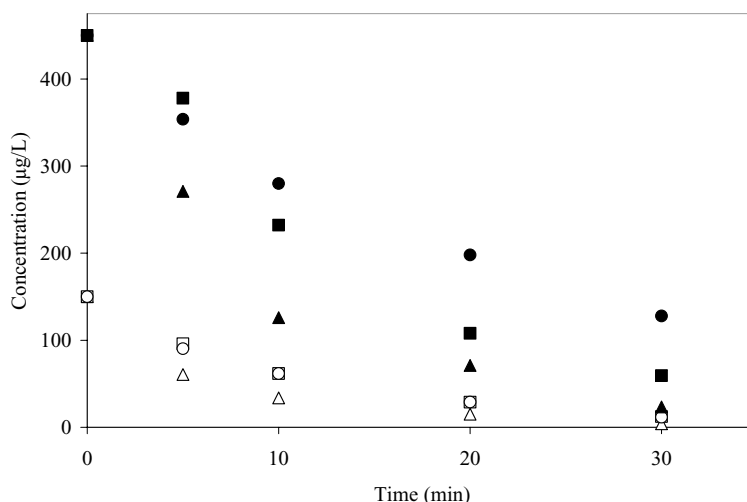
Fig. 7. Concentration–time profiles of PAHs in single-component solutions during sonochemical degradation at 80 kHz, 150 W, 20 °C and various initial concentrations. ($\triangle$, $\blacktriangle$) naphthalene, ($\square$, $\blacksquare$) acenaphthylene, ($\bigcirc$, $\bullet$) phenanthrene. Open symbols: 150 µg/l; closed symbols: 450 µg/l.

counteracted sufficiently using internal standards closely related to the analytes of interest as well as quoting results in the form of normalised concentrations.

3.3. Kinetics of degradation

In further experiments, solutions containing each PAH alone were subject to ultrasonic irradiation at 80 kHz, 150 W, 20 °C and initial concentrations of 150 and 450 µg/l and the results are shown in Fig. 7. Like the experiments with mixtures of PAHs, the amount of degraded contaminant increases with increasing initial concentration. In the case of naphthalene, for example, the amount of naphthalene degraded following sonication for 10 min at an initial concentration of 450 µg/l is as much as 2.8 times greater than that at an initial concentration of 150 µg/l.

Furthermore, it appears that sonolysis of the reaction mixture containing all three PAHs behaves like the average of the three solutions containing each PAH alone. This conclusion can be deduced comparing PAHs conversions based on molar rather than mass concentrations. The molar concentration corresponding to 150 µg/l of each PAH is 1.172 µmol/l for naphthalene, 0.987 µmol/l for acenaphthylene and 0.843 µmol/l for phenanthrene (resulting in an average value of 1.001 µmol/l). Following sonication of each PAH alone for 30 min, the remaining molar concentrations are 0.033 µmol/l for naphthalene, 0.081 µmol/l for acenaphthylene and 0.066 µmol/l for phenanthrene, yielding an average value of 0.060 µmol/l. In the case of the reaction mixture initially containing 50 µg/l of each target PAH, the sum of the initial molar concentrations is 1.009 µmol/l (i.e. 0.391 µmol/l for naphthalene, 0.329 µmol/l for acenaphthylene and 0.289 µmol/l for phenanthrene). After sonication for 30 min there are 0.022 µmol/l of naphthalene, 0.003 µmol/l of acenaphthylene and 0.029 µmol/l of phenanthrene left in the reaction mixture, the sum of which

is 0.055 µmol/l; this sum is comparable to the average value of the molar concentrations obtained for the three separate solutions (0.060 µmol/l) implying that co-degradation of PAHs does not substantially differ from the degradation of each individual PAH.

In previous studies, the sonochemical degradation of several PAHs such as phenanthrene, anthracene and pyrene [4–6] as well as 1-methylnaphthalene, 1,12-benzoperylene and coronene [6], was found to be first order with respect to PAH concentration, i.e.

$$-\frac{dC_i}{dt} = kC_i \tag{1}$$

Rearranging and integrating Eq. (1) yields:

$$\ln\left(\frac{C_{i,0}}{C_i}\right) = kt \tag{2}$$

where k is an apparent reaction rate constant, and C_0 and C_i is PAH concentration at time zero and t, respectively. If data is plotted in the form of Eq. (2) rate constants can be calculated from the slopes of the respective straight lines. Table 2 summarises the rate constants of the sonochemical degradation of PAHs during the experiments described in Fig. 7; indeed, degradation appears to be first order regarding PAH concentration. It should be pointed out that no attempt was made to compute rate constants from data of experiments with mixtures of PAHs because no samples were taken during the early stages (i.e. first 5–10 min) of the reaction, thus making the analysis inaccurate. Rate constant values of phenanthrene degradation reported in the literature are also included in Table 2; these values are considerably different from the ones reported in our study as well as from each other and this is presumably due to the different experimental conditions employed in each study. No information regarding naphthalene and acenaphthylene sonochemical degradation rate constants is available in the literature.

Table 2
First-order rate constants ($1/\mathrm{min} \times 10^{-3}$) for the sonochemical degradation of PAHs in single-component solutions

Source	Naphthalene	Acenaphthylene	Phenanthrene
This work (150 μg/l)[a]	121.7 (0.9759)	84.6 (0.9990)	83.6 (0.9971)
This work (450 μg/l)[a]	98.9 (0.9817)	67.8 (0.9888)	42.2 (0.9956)
Ref. [4][b]	na	na	354 ± 18
Ref. [5][c]	na	na	660 ± 120
Ref. [6][d]	na	na	2.07

Numbers in brackets show correlation coefficient (r^2) values for the linear regression of the logarithm of concentration versus time. na: not available.

[a] Frequency: 80 kHz; power: 150 W; bulk temperature: 20 °C; liquid volume: 200 ml; initial concentration: 150 or 450 μg/l; sonication mode: continuous; liquid medium: water.

[b] Frequency: 20 kHz; power: 600 W; bulk temperature: 20 °C; liquid volume: 50–100 ml; initial concentration: 20–100 μg/l; sonication mode: pulse (1 s on, 9 s off or 1 s on, 4 s off); liquid medium: water.

[c] Frequency: 20 kHz; power: 600 W; bulk temperature: 20 °C; liquid volume: 50–70 ml; initial concentration: 20–100 μg/l; sonication mode: pulse (1 s on, 4 s off); liquid medium: water.

[d] Frequency: 20 kHz; power: 50 W; bulk temperature: 25 °C; liquid volume: 16 ml; initial concentration: 40×10^3 μg/l; sonication mode: continuous; liquid medium: water:ethanol (70:30).

4. Conclusions

Low frequency ultrasonic irradiation proved to be a viable tool for the effective degradation of PAHs in aqueous solutions. SPME coupled with GC–MS enabled monitoring of the low-level concentration transients. The extent of degradation is a function of sonication time and operating conditions such as ultrasound intensity and frequency, temperature and initial concentration, and also depends on the presence of matrix species. The latter may have either a beneficial or detrimental impact on degradation depending on their type and function i.e. whether they act as radical promoters or scavengers. Furthermore, their presence may alter the physicochemical properties of the reaction mixture and consequently affect the cavitation process and associated reaction mechanisms and pathways.

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