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Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction

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Abstract

The sonochemical degradation of aqueous solutions containing low concentrations of six phthalate esters at an ultrasonic frequency of 80 kHz has been investigated. Ultrasonic treatment was found capable of removing the four higher molecular mass phthalates (di-*n*-butyl phthalate, butylbenzyl phthalate, di-(2-ethylhexyl) phthalate and di-*n*-octyl phthalate) within 30–60 min of irradiation. The rest (dimethyl phthalate and diethyl phthalate) were more recalcitrant and nearly complete removal could be achieved only after prolonged irradiation times. The relative reactivity of phthalates was explained in terms of their hydrophobicity. Experiments were carried out at an overall initial phthalate concentration of 240 $\mu\text{g l}^{-1}$, values of electric power of 75 and 150 W, temperatures of 21 and 50 °C and in the presence of NaCl to study the effect of various operating conditions on degradation. Solid-phase microextraction (SPME) coupled with GC–MS proved to be a powerful analytical tool to monitor the sonochemical degradation of phthalate esters at low $\mu\text{g l}^{-1}$ concentration levels, minimising the risk of secondary contamination during sample preparation, a major parameter to consider during phthalates analysis. The advantages as well as disadvantages of using SPME are also highlighted.

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Keywords: SPME; Phthalates; Ultrasound; Sonolysis; Water samples

1. Introduction

Phthalate acid esters (phthalates) have a wide variety of industrial, agricultural and domestic applications, but by far the most important is their use as plasticisers that improve the flexibility and workability of polymeric materials. The physical rather than chemical incorporation of phthalates in the polymeric matrix ensures that they are widespread contaminants. Penetration of phthalates into the ecosystem or in wastewater effluents occurs during the production phase and via leaching and volatilisation from plastic products during their usage and/

or after disposal (Staples et al., 1997). The level of contamination is usually in the low $\mu\text{g l}^{-1}$ due to their hydrophobic nature.

In recent years, phthalates have attracted much attention because even at low concentration levels they are suspected of interfering with reproductive and behavioral health in humans and wildlife, through disturbance of the endocrine system (Petrović et al., 2001). As a result several regulatory bodies, such as the US Environmental Protection Agency (US EPA, 1991) and the European Union (1993) classified phthalates in their top priority lists for risk assessment, mandating the reduction and elimination of phthalate pollution. Current research efforts are directed towards the development of simple and sensitive analytical methods, capable to accurately monitor the removal of trace quantities of phthalates by using innovative treatment technologies.

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Solid-phase microextraction (SPME), developed by Arthur and Pawliszyn (1990), addressed the need for simple and rapid sample preparation. The commercially available SPME unit consists of a short length of narrow diameter fused-silica optical fibre externally coated with a thin film of a polymeric stationary phase. The coated fibre is immersed in the solution where analytes preferentially partition by adsorption or absorption (depending on the fibre type) from the solution to the stationary phase and are concentrated. After sampling for a well-defined period of time, the fibre is withdrawn and transferred to the heated injection port of a gas chromatograph (GC) or to a modified high-performance liquid-phase (HPLC) rheodyne valve (Eisert and Pawliszyn, 1997). SPME rapidly gained wide acceptance incorporating sampling, extraction, concentration and sample introduction into a single solventless step improving method's detection limits and saving preparation time. SPME has been successfully applied to a wide variety of compounds in the gas, liquid and solid phase for the extraction of volatile and semi-volatile organic compounds from environmental, food and biological samples (Lord and Pawliszyn, 2000; Kataoka, 2002). Recently, the possibility of using SPME as a viable tool to monitor trace quantities of phthalates in water samples has been demonstrated (Luks-Betlej et al., 2001; Peñalver et al., 2001; Prokúpková et al., 2002; Psillakis and Kalogerakis, 2003).

In recent years, considerable interest has been shown on the application of ultrasound as an advanced oxidation process (AOP) for the treatment of chemical contaminants in water. Ultrasonic irradiation of aqueous solutions induces acoustic cavitation, which can be defined as the cyclic formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small intervals of time and releasing large quantities of energy over a small location (Gogate, 2002). Thus, cavitation serves as a means of concentrating the diffuse energy of ultrasound into microreactors. The heat from the cavity implosion decomposes water into extremely reactive hydrogen atoms and hydroxyl radicals, which may recombine during the cooling phase to form hydrogen peroxide and molecular hydrogen (Ince et al., 2001). This environment often leads to enhanced chemical reactivity whereby organic compounds are decomposed and inorganic complexes are oxidised or reduced (Seymour and Gupta, 1997). Various investigations report successful removal of a wide range of organic pollutants from aqueous solution and it appears that the applications of this novel means of reaction in environmental remediation and pollution prevention is unlimited (Adewuyi, 2001).

The aim of the present studies is to investigate sonolysis of phthalates in aqueous solutions under a variety of operating conditions and in the presence of different matrix components. Although a previous report (Yim

et al., 2002) dealt with the sonochemical degradation of the three lower molecular weight phthalates, namely dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-*n*-butyl phthalate (DBP) at relatively high concentrations (in the mg l^{-1} level), this is the first investigation dealing with the successful sonochemical removal of all six phthalates at levels similar to the ones found in water systems (low $\mu\text{g l}^{-1}$ level). The use of SPME enabled monitoring of low phthalates concentrations minimising the risk of secondary contamination during sample preparation, a major parameter to consider during phthalate analysis. The present studies also include for the first time di-(2-ethylhexyl) phthalate (DEHP), one of the most important phthalates, accounting for nearly 90% of European plasticiser use.

2. Experimental

2.1. Chemicals

DMP, DEP, DBP, butylbenzyl phthalate (BBP), DEHP, and di-*n*-octyl phthalate (DOP) were purchased from Supelco (Bellefonte, PA, USA) in the form of a standard methanolic stock solution containing 2000 mg l^{-1} of each target phthalate. From this solution, working mixtures in methanol (100 mg l^{-1}) were prepared weekly. All solutions were stored at 4 °C in the dark. The solvents (methanol and acetonitrile) were Suprasolv quality and were obtained from Merck (Darmstadt, Germany). *n*-Butanol was purchased from Lab-Scan Analytical Sciences (Dublin, Ireland). Deionized water used for sample preparation was prepared on a water purification system (EASYpureRF) supplied by Barnstead/Thermolyne (Dubuque, IO, USA). Sodium chloride (>99.5% pure) was obtained from Merck and potassium bromide (>99.5% pure) from Fluka (Sigma-Aldrich, Steinheim, Germany). All laboratory glassware and glass vials used were washed prior to analysis several times with acetone for analysis (Sigma-Aldrich, Germany) and finally with Suprasolv-quality acetonitrile. Some of the properties of the phthalates used in this study are summarised in Table 1.

2.2. Sonication experiments

A fixed-frequency (80 kHz) and of variable electric power output (up to 150 W) ultrasound generator (Ultrason 250, LabPlant, UK) connected to a titanium-made horn was used for all sonication experiments. Reactions were carried out in a cylindrical all-glass reaction vessel, which was closed during ultrasonic irradiation. The vessel was immersed in a water bath and the temperature was monitored with a Pt100 temperature sensor housed inside the water bath and connected to a temperature control unit (Polystat cc2 model, Huber,

Table 1
Selected physical properties of the phthalates used in this study

Phthalate	Molecular weight	Vapour pressure (mm Hg)	Water solubility (mg l ⁻¹)	log K_{ow} ^a
DMP	194.2	2.0×10^{-3}	4200	1.61
DEP	222.2	1.0×10^{-3}	1100	2.38
DBP	278.4	2.7×10^{-5}	11.2	4.45
BBP	312.4	5.0×10^{-6}	2.7	4.59
DEHP	390.6	1.0×10^{-7}	3×10^{-3}	7.50
DOP	390.6	1.0×10^{-7}	5×10^{-4}	8.06

Values taken from Staples et al. (1997).

^a Recommended values based on available evidence (Staples et al., 1997).

Germany). To avoid any photochemical reactions the vessel was covered with aluminium foil. In all cases, 195 ml of an aqueous solution containing 40 µg l⁻¹ of each target contaminant were prepared daily and were subject to ultrasonic irradiation. Depending on the runs, experiments were carried out at an electric power output of 75 or 150 W. Unless otherwise stated the water bath temperature was kept constant at 21 °C. Experiments were discontinued periodically to remove 5 ml samples that were analysed by means of SPME/GC–MS.

2.3. SPME procedure

For SPME, a 5 ml aqueous sample, withdrawn from the reaction vessel, was added in a 7 ml clear glass vial (Supelco), fitted with aluminium foil and screw caps with hole (Supelco). Extraction was performed at room temperature and under intensive magnetic stirring (1000 rpm) using a glass-coated mini-impeller (8 mm × 3 mm). The 65-µm polydimethylsiloxane-divinylbenzene (PDMS-DVB) SPME fibre type and SPME fibre holder assembly (all purchased from Supelco) were used for extraction. Before the first usage, the fibre was conditioned according to the manufacturer's recommendations. Three blank runs were run to verify the absence of impurities and phthalate peaks on the SPME fibre. Each day and prior to extracting any samples, the fibre was immersed for few minutes in a stirred acetonitrile solution, and a blank analysis was then run as to ensure that the fibre was free of contaminants. For extraction, the SPME fibre holder assembly was clamped and allowed to sit on top of the 7-ml glass vials containing the 5-ml samples. The SPME fibre was exposed to the aqueous phase and after sampling for 35 min at room temperature, the fibre was retracted and transferred to the heated injection port of the GC–MS for desorption, where it remained for 5 min.

2.4. GC–MS analysis

Phthalates were analysed using a Shimadzu GC-17A (Version 3) QP-5050A gas chromatograph–mass spec-

trometer system. The split/splitless injector operated at 260 °C with the split closed for 5 min. Helium (>99.999% pure) was used as the carrier gas at a flow-rate of 1.2 ml min⁻¹. The instrument was equipped with a 30 m × 0.25 mm, 0.25 µm HP-5MS capillary column (Agilent Technologies). The column oven was programmed as follows: 60 °C for 1 min and then to 300 °C at a rate of 10 °C min⁻¹, where it was held for 5 min. A 5 min solvent delay time was used. The interface temperature was set at 310 °C and the detector voltage at 1.40 kV. The ionization mode was electron impact (70 eV). Data was acquired in the full-scan detection mode from 50 to 465 amu at rate of 0.5 scans s⁻¹. Quantification was based on the GC–MS peak areas found for the base peaks of each analyte (i.e. *m/z* DMP: 163, DEP: 149, DBP: 149, BBP: 149, DEHP: 167, 149, DOP: 149).

Calibration was performed by extracting water samples spiked in the concentration range from 1 to 100 µg l⁻¹ for most analytes (apart for DEHP and DOP where the concentration range was from 5 to 100 µg l⁻¹). A very good linear correlation coefficient (r^2) was found for most target contaminants, ranging between 0.9983 and 0.9992. DEHP and DOP had r^2 values of 0.9455 and 0.9432 respectively. The limits of detection (LOD) ranged between 0.24 and 0.93 µg l⁻¹ and were calculated from the calibration curves by considering the value of the Winefordner and Long criterion according which the LOD for each target analyte is three times the standard error of the independent term of the regression divided by the value of the slope of the calibration curve (Long and Winefordner, 1983). Repeatability expressed as the relative standard deviation (RSD) of five consecutive replicates ranged between 4% and 16%.

2.5. Practical considerations during SPME/GC–MS

It is noteworthy that the reported values for solubility and octanol–water partitioning vary by several orders of magnitude reflecting the difficulties in obtaining reliable data for phthalates. Problems arising when analysing trace quantities of these hydrophobic

contaminants include the ease of sample contamination during sample preparation and experimental artefacts arising from the tendency of undissolved phthalates to form stable, homogenous dispersions in water and surface films at the air–water interface (Staples et al., 1997).

To minimise the effect of drawbacks associated with the analysis of trace quantities of phthalates a number of measures were taken. All glassware and accessories used in the experiments were washed several times with Suprasolv quality organic solvents. A glass-coated mini-impeller was used as a stirrer and aluminium foil replaced Teflon septa. Furthermore, the thick protector needle of the SPME fibre irreversibly damaged the thermo-resistant Thermogreen LB-2 septa (Supelco, Sigma–Aldrich Chemie GmbH) used in the GC instrument. Such damages typically resulted in carrier gas leaks, extraneous peaks and phthalate contamination due to small polymer septa pieces introduced into the inlet liner of the GC injector. Pre-drilling the septa prior to using them and replacing them on a daily basis avoided such damages (Psillakis and Kalogerakis, 2003). Between runs a clean-up procedure for the SPME fibre eliminated the possibility of analyte carry-over between analyses (Lord and Pawliszyn, 2000; Psillakis and Kalogerakis, 2003), a major drawback of SPME during phthalates analysis (Prokúpková et al., 2002). Accordingly, after desorption, the SPME fibre was immersed in a stirred solvent solution for 5 min and was subsequently transferred to the heated injection port (260 °C) of another GC until the next extraction. Moreover, blanks were run periodically during experiments to confirm the absence of contaminants.

The combination of SPME with GC–MS enables trace-level detection of phthalates in water samples. Comparison between several types of absorption and adsorption SPME fibres revealed that the highest extraction efficiency was achieved with adsorption-type fibres containing a DVB phase (Luks-Betlej et al., 2001; Peñalver et al., 2001). In view of these results the PDMS–DVB SPME fibre was chosen for the present analyses. Fibre to fibre variation in coating character may influence the fibre's response or absolute amount extracted with a given sample leading to invalid results (Lord and Pawliszyn, 2000). It is important to monitor fibre response on a regular basis. A previous investigation evaluating the repeatability of measurements for different SPME fibres during phthalates analysis concluded that PDMS–DVB yielded high relative standard deviation values (Luks-Betlej et al., 2001). During the present experiments several PDMS–DVB fibres were used and it was observed that the absolute amount of DEHP and DOP extracted could vary from fibre to fibre. In order to eliminate the fibre from being a source of unacceptable method imprecision, fibres with substantially different response factors were discarded.

3. Results and discussion

3.1. Sonochemical degradation of phthalates

An aqueous solution containing 40 $\mu\text{g l}^{-1}$ of each phthalate (i.e. an initial overall concentration of 240 $\mu\text{g l}^{-1}$) was subject to continuous ultrasonic irradiation for 240 min at a constant electric power output of 150 W and a constant water bath temperature 21 °C. Direct comparison between the total ion chromatograms (Fig. 1) obtained by means of SPME/GC–MS at the beginning (time zero) and at the end (after 240 min of sonication) of the experiment, reveals that all peaks corresponding to the six phthalates are essentially gone

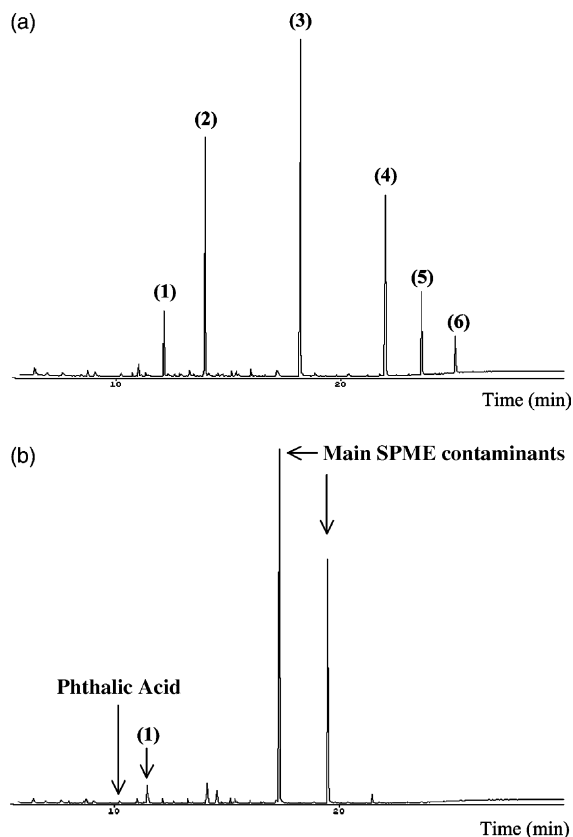


Fig. 1. Total ion chromatograms obtained with SPME/GC–MS of (a) the reaction mixture at time zero containing 40 $\mu\text{g l}^{-1}$ of each phthalate (i.e. initial overall phthalates concentration of 240 $\mu\text{g l}^{-1}$) where (1) DMP, (2) DEP, (3) DBP, (4) BBP, (5) DEHP and (6) DOP; and (b) after 240 min of sonication. The two extra peaks assigned as SPME contaminants originate from the partial loss of the SPME coating due to increased usage. The extra eluting peak assigned as phthalic acid is the only degradation product which could be detected with a certain degree of confidence. Other experimental conditions: 80 kHz of ultrasound frequency, 150 W of electric power output, 21 °C water bath temperature.

by the end of the experiment. The strong eluting peaks appearing after 240 min of sonication correspond to contaminants originating from the partial loss of the SPME fibre coating due to increased usage.

Fig. 2 shows the normalised concentration–time profiles of all six phthalates during sonochemical degradation. The data shown in the graph represent the mean values obtained after running the same set of experiments in triplicate with the reproducibility (expressed in terms of RSD) ranging between 6% and 17%. The relative reactivity of the compounds present in the aqueous mixture can be explained in terms of their physicochemical properties in conjunction with the reaction pathways and mechanisms typically occurring during sonochemical reactions. It is generally believed that there are three potential sites for chemical reactions in ultrasonically irradiated aqueous solutions (Thompson and Doraiswamy, 1999), namely: (a) the bubble itself where pyrolysis of volatile solutes takes place in the gas phase, while water decomposes thermally to form hydrogen and hydroxyl radicals, (b) the interface between the bubble and the surrounding liquid where the temperature is lower than that in the bubble but is still high enough to cause thermal decomposition. Moreover, reactive radicals formed through water decomposition in the bubble accumulate at high concentrations in this site and may mediate free radical decomposition reactions, and (c) the solution bulk, where reactions of hydrogen or hydroxyl radicals, which escape from the interface, may occur. Organic compounds may be destroyed either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation, or in the solution bulk via oxidative degradation by hydroxyl radicals and hydrogen peroxide (Ince et al., 2001). The relative importance of the various mechanisms depends on the localization of the solute which, in turn, depends on its

physicochemical properties (i.e. hydrophobicity, volatility, octanol–water partition coefficient) as well as on the operating conditions employed (ultrasound frequency, power density, presence of saturating gases and/or co-solutes, reactor configuration and geometry, initial solute concentration, ionic strength and pH value of the liquid phase) (Gonze et al., 1999; Dewulf et al., 2001; Jiang et al., 2002; Psillakis et al., 2003). In general, low-frequency ultrasound is expected to induce destructive effects only 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 (Ince et al., 2001). Given that all phthalates used in this study are relatively non-volatile (Table 1), 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 DBP, BBP, DEHP and DOP are all readily susceptible to sonochemical degradation and nearly complete removal is achieved within 30–60 min of irradiation at the conditions under consideration. Conversely, the less hydrophobic DMP and DEP are more recalcitrant and complete degradation can be achieved only after prolonged ultrasonic irradiation.

In a recent report, Yim et al. (2002) investigated the sonochemical degradation of DMP, DEP and DBP. At the conditions employed in their study (i.e. plate-type sonicator operating at 200 kHz, 20 °C of temperature, 150 ml of liquid volume and 100 µM of initial solute concentration corresponding to about 20–30 mg l⁻¹ depending on the phthalate in question), the relative reactivity was found to decrease in the order: DEP > DMP ≈ DBP. They also reported that DEP degradation primarily occurred at the bubble–liquid interface via hydroxyl radical reactions and, to a lesser extent, via thermal and hydrolysis reactions.

3.2. Effect of NaCl addition on the sonochemical degradation of phthalates

In order to examine in more detail the importance of hydrophobicity on degradation rates, an experiment was carried out in the presence of salt. In general, depending on the nature of the contaminants, addition of salt to the sample solution can decrease their solubility and consequently increase their hydrophobicity. This is due to the salting-out effect where fewer water molecules are available for dissolving the analyte molecules, preferably forming hydration spheres around the salt ions (Lord and Pawliszyn, 2000).

Fig. 3 shows the effect of NaCl addition (10% w/v) on phthalates removal. It appears that changes in the salinity of the reaction mixture may have several effects on the degradation rates of target pollutants. For the more polar DMP, DEP, DBP and BBP, the presence of salt

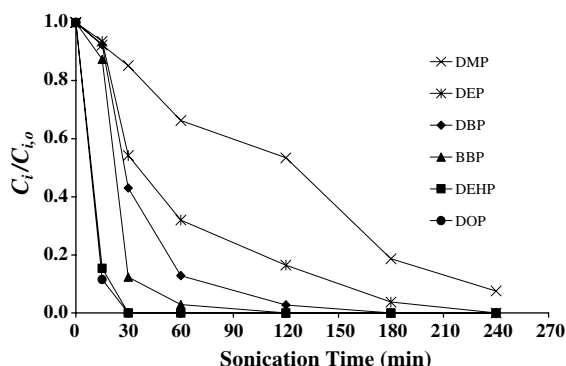


Fig. 2. Normalised concentration–time profiles during sonication (80 kHz of ultrasound frequency, 150 W of electric power output, 21 °C water bath temperature) of a 195 ml aqueous solution containing 40 µg l⁻¹ of each phthalate (i.e. the initial overall phthalate concentration is 240 µg l⁻¹).

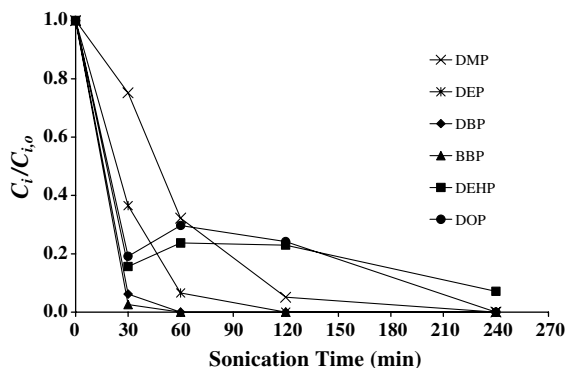


Fig. 3. Normalised concentration–time profiles during sonication of a 195 ml aqueous solution containing 10% NaCl (w/v) and $40 \mu\text{g l}^{-1}$ of each phthalate (i.e. the initial overall phthalate concentration is $240 \mu\text{g l}^{-1}$). Other experimental conditions: 80 kHz of ultrasound frequency, 150 W of electric power output, 21°C water bath temperature.

enhanced their removal. This may be explained in terms of the dynamics of solute accumulation in the bubble–water interface. The apparent decrease in solubility due to the addition of salt in the reaction mixture enhanced diffusion of solutes from the bulk solution to the bubble–water interface facilitated their accumulation in the interfacial sheath, thus leading to increased degradation rates. This observation is in agreement with the work carried out by Seymour and Gupta (1997) that studied the sonochemical degradation of chlorobenzene, *p*-ethylphenol and phenol at 20 kHz and reported that NaCl addition improved substantially degradation rates. In their report enhancement of removal rates was attributed to the salting-out effect, while the role of chloride radicals in enhancing oxidation was thought to be insignificant. It should be mentioned here that under the present experimental conditions the presence of chloro-products was not confirmed.

Regarding the non-polar DEHP and DOP, it appears that the presence of salt restricted their removal rates. Next to the partitioning effect, adding salt to a sonicated reaction mixture results in reduced vapour pressure and increased surface tension (Seymour and Gupta, 1997). Although the latter two parameters tend to promote a more violent collapse of the cavitation bubbles, they also tend to reduce the number of formed bubbles (Chen and Smirniotis, 2002). Accordingly, despite the apparent decrease in solubility, these two solutes have to overcome several barriers (including less vacant sites and reduced number of formed bubbles) in order to accumulate in the interfacial region. This means that with increased salt concentrations diffusion of these non-polar analytes towards the interface becomes more and more difficult and they tend to be back-diffused into the bulk solution, increasing the overall time required for

their sonochemical removal. This hypothesis is supported by the work of Chen and Smirniotis (2002) who found that addition of NaCl or Na_2SO_4 had an adverse effect on the sonochemical degradation of phenol at 20 kHz and in the presence of TiO_2 . They suggested that a possible explanation for this observation might be associated with the change in vapour pressure and the number of cavities generated in the same acoustic power.

3.3. Effect of electric power on the sonochemical degradation of phthalates

To investigate the effect of applied power on the sonochemical degradation of phthalates an additional run at a reduced electric power (75 W) was carried out and the results are shown in Fig. 4. Comparison of Figs. 2 and 4 shows that the overall irradiation time required for complete sonochemical removal of DBP, BBP, DEHP and DOP is increased from 30–60 min at 150 W to 60–120 min at 75 W. The reduced power had also a detrimental effect for the more recalcitrant DMP and DEP and irradiation times had to be prolonged for complete removal of these contaminants. The beneficial effect of power on removal rates is believed to be due to increased cavitation activity occurring at higher levels of power: as power increases, the number of collapsing bubbles also increases, thus leading to enhanced degradation rates (Thompson and Doraiswamy, 1999; Jiang et al., 2002).

3.4. Effect of temperature on the sonochemical degradation of phthalates

In further experiments the effect of temperature on the sonochemical degradation of phthalates was studied

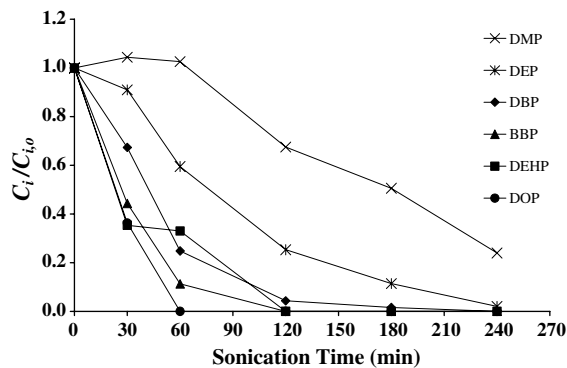


Fig. 4. Normalised concentration–time profile during sonication at reduced electric power output (75 W) of a 195 ml aqueous solution containing $40 \mu\text{g l}^{-1}$ of each phthalate (i.e. the initial overall phthalate concentration is $240 \mu\text{g l}^{-1}$). Other experimental conditions: 80 kHz of ultrasound frequency, 21°C water bath temperature.

and the results are summarised in Table 2. In one set the experiments sonolysis was carried out at a constant temperature of 50 °C, and in another one the reaction temperature was left uncontrolled and gradually increased from 21 °C (time zero) to 39.3 °C (after 60 min of sonication) to 49.4 °C (after 120 min of sonication) and finally to 50.9 °C (after 180 min of sonication) due to heat dissipation. The respective data of the experiment carried out at 21 °C is also given in Table 2 to allow for an easy comparison.

As can be seen, an increase in the reaction temperature has a detrimental effect on the degradation of phthalates and this is more pronounced during sonolysis at 50 °C. This effect 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 in detail elsewhere (Thompson and Doraiswamy, 1999). 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 is expected to cushion bubble implosion. 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. Gondrexon et al. (1993) reported that the extent of 2-chlorophenol removal (after 30 min at 530 kHz) decreased from 50% to 35% with increasing liquid bulk temperature from 25 to 50 °C. In further studies, Goskonda et al. (2002) found that a temperature increase from 12.5 to 30 °C had practically no effect (within experimental error) on the rate of 2,4-dichlorophenol degradation at 20 kHz. Conversely, the extent of 2,4,6-trichlorophenol removal (after 300 min at 22 kHz and in the presence of TiO₂ as a heterogeneous catalyst) was found to increase from 10% to about 25% with increasing temperature from 30 to 45 °C (Shirgaonkar and Pandit, 1998). Sehgal and Wang (1981) reported that the degradation rate of thymine at 1000 kHz increased with

increasing temperature from 15 to 30 °C and then remained constant as temperature increased to 50 °C. Nevertheless, a temperature increase beyond 50 °C led to decreased degradation rates. These different observations reported in the literature are believed to be due to the fact that the dependence of sonochemical degradation on the liquid bulk temperature is a complex issue closely related to the properties and reaction conditions of each specific system in question (Sehgal and Wang, 1981; Thompson and Doraiswamy, 1999).

3.5. Identification of degradation products

In general, one of the major advantages of SPME over other extraction methods is its high degree of selectivity. Selectivity enables the development of more sensitive and discriminating analytical methods that have the ability to identify and quantify analytes with less interference from matrix components (Lord and Pawliszyn, 2000). Today, there are several types of commercially available SPME fibres, as the method's selectivity towards classes of compounds depends on the polarity and film thickness of the extraction phase. Although, selectivity is required in any modern sample preparation method, removing unwanted analytes restricts the number of identified byproducts formed during sonochemical degradation. As such, under the present experimental conditions (level of contamination, type of SPME fibre, SPME methodology and analytical equipment), only one degradation product could be detected with a certain degree of confidence. The mass spectrum of this extra product (peak shown in Fig. 1) in the full-scan mode corresponded with a 0.90 match factor to phthalic acid. Phthalates can undergo two hydrolytic steps, producing first the mono-ester and one free alcohol and a second hydrolytic step, forming phthalic acid and a second alcohol (Staples et al., 1997).

The formation of mono-ester as a primary degradation byproduct has been reported by Yim et al. (2002)

Table 2

Normalised phthalates concentration ($C_i/C_{i,0}$) during sonochemical degradation at 21, 50 °C and without temperature control (no control)

Temperature	Sonication time	DMP	DEP	DBP	BBP	DEHP	DOP
21 °C	60 min	0.663	0.320	0.129	0.029	nd	nd
50 °C	60 min	0.933	0.730	0.404	0.396	0.233	0.151
No control ^a	60 min	0.674	0.417	0.268	0.145	nd	nd
21 °C	120 min	0.534	0.165	0.028	nd	nd	nd
50 °C	120 min	0.927	0.409	0.039	nd	nd	nd
No control ^b	120 min	0.630	0.182	0.182	nd	nd	nd

Other experimental conditions: 80 kHz of ultrasound frequency, 150 W of electric power output, 40 µg l⁻¹ of each compound (i.e. initial overall phthalates concentration of 240 µg l⁻¹). nd (not detected) corresponds to phthalate concentration levels (C_i) below the limits of detection.

^a After 60 min of sonication the temperature was 39.3 °C.

^b After 120 min of sonication the temperature was 49.4 °C.

who studied the degradation pathways of DEP (100 M of initial aqueous concentration) as a function of pH during sonolysis at 200 kHz. In their report they concluded that at pH=4–11 sonolysis occurred predominantly due to OH radical reactions and to some extent via the thermal reaction and hydrolysis degradation pathways. At pH>11 the proportion of OH radical reaction decreased whereas the contribution of the hydrolysis reaction pathway to DEP degradation appreciably increased. At the conditions employed in the present studies none of the mono-esters of the phthalates in question was identified. This may be due to (a) the small contribution of hydrolysis during sonication at neutral pH, and (b) the fact that the trace quantities of phthalates examined here possibly result in the formation of mono-esters below the detection limit of the present analytical procedure.

In general, the role of hydroxyl radical reactions can be confirmed by sonicating aqueous phthalates mixtures in the presence of radical reaction inhibitors (radical scavengers). In the case where the predominant degradation pathway is via OH radical reactions removal rates are expected to be suppressed by the addition of radical scavengers, thus verifying the contribution of radical reactions towards phthalates degradation. In an attempt to identify the role of radical reactions in phthalates sonochemical degradation, it was decided to investigate sonolysis in the presence of radical scavengers such as potassium bromide and *n*-butanol. In a separate set of experiments attempts were made to monitor the effect of KBr on the sonochemical degradation of phthalates. It was concluded that the presence of KBr irreversibly damaged the specific type of SPME fibre used here which had to be discarded after coming into direct contact with the sample solutions initially containing 10% w/v of KBr.

In general, adding radical scavengers, such as KBr or *n*-butanol, to the reaction mixture alters matrix composition and consequently the partitioning of analytes between the sample matrix and the SPME fibre during extraction. This means that extraction conditions will differ from the ones used during the external calibration procedure and results are expected to be invalid. This phenomenon can be compensated and this was the case for NaCl, where during the same set of experiments the amount of salt present in the reaction mixture remained the same thought sonolysis. With increased sonication time however radical scavengers are consumed and consequently the composition of the matrix can be no longer normalised.

Furthermore, adding *n*-butanol to the reaction mixture substantially reduces the amount of extracted analytes since adsorption of organic compounds onto the fibre is suppressed. Thus, it is imperative to minimise the amount of *n*-butanol present in the reaction mixture when using the SPME approach. In an attempt to

monitor the effect of *n*-butanol on the removal rates of phthalates a separate set of sonication experiments was run in the presence of *n*-butanol (400 µl), but all measured concentrations lead to spurious results confirming all the above-mentioned reservations. Overall, no safe conclusions could be withdrawn from these series of experiments since both scavengers heavily interfered with SPME analysis.

4. Conclusions

Overall, ultrasonic irradiation proved to be a viable tool for effectively degrading phthalates in low aqueous concentrations. Emphasis was given on the effect of electric power and temperature on degradation rates. The relative reactivity of phthalates was explained in terms of hydrophobicity. Addition of salt to the reaction mixture accelerated the removal of the more polar phthalates and this was attributed to the salting-out effect. During the present studies, SPME proved to be a powerful tool for monitoring trace quantities of phthalates in water samples minimising the risk of phthalate contamination during sample preparation. However, the selectivity of the SPME fibres as well as the restrictions regarding the composition of the matrix may obstruct studies on identification of degradation pathways and mechanisms.

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