Sonophotolytic degradation of phthalate acid esters in water and wastewater: Influence of compound properties and degradation mechanisms
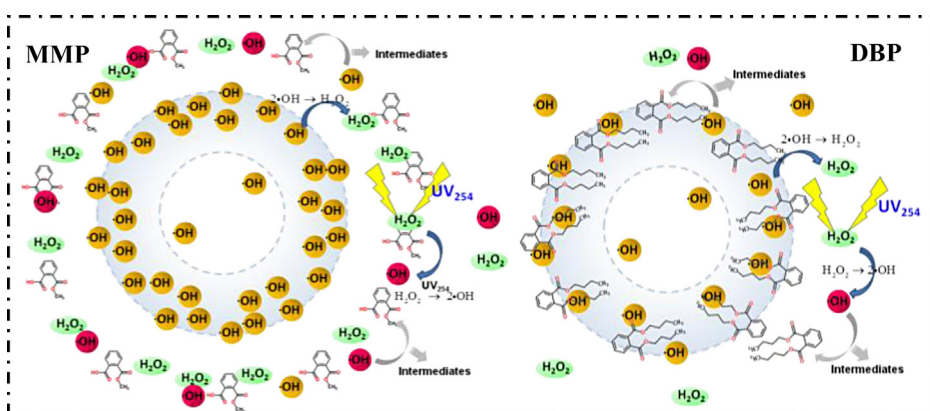
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HIGHLIGHTS

- Hydrophobicity of PAEs can influence their sonolysis and sonophotolysis efficiency.
- More hydrophobic PAEs exhibited stronger competitiveness in sonolytic degradation.
- More hydrophobic PAEs obtained less synergistic effect in sonophotolytic degradation.
- More hydrophobic PAEs experienced less inhibition in real wastewater environment.
- The US/UV process showed the highest efficiency in mineralizing DBP.

GRAPHICAL ABSTRACT

ABSTRACT

The influence of physicochemical properties on the sonolytic and sonophotolytic degradation of a group of short-chain phthalate acid esters (PAEs) was investigated in this study. A 400 kHz ultrasonic system and a photolytic system at 253.7 nm were employed separately and together, and both pure water and secondary effluent were used as the water matrices. It was found that PAEs with greater hydrophobicity demonstrated more rapid sonolysis and exhibited greater competitiveness in sonochemical reactions in the presence of other compounds. However, although a greater compound hydrophobicity is beneficial for the sonochemical degradation of PAEs, the observed synergy between ultrasound and UV in the sonophotolytic process is reduced owing to the lower accumulation of H_2O_2 in the aqueous phase. For the sonophotolysis of PAEs in secondary effluent, it was found that PAEs with greater hydrophobicity experienced less inhibition or competition from the background organic substances (expressed as TOC). Identification of prominent degradation intermediates of di-n-butyl phthalate (DBP), as a representative PAE, indicated that hydroxylation of the aromatic ring and butyl-scission of the aliphatic chain are the principal degradation mechanisms. The combined process of US/UV produced a greater degree of DBP mineralization than either US or UV alone (17% TOC reduction within 90 min).

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1. Introduction

The sonochemical oxidation process has been proposed and investigated as a promising technology for the degradation of

refractory organic contaminants, such as bisphenol A [1], phenolic compounds [2], phthalates [3] among other compounds [4,5]. Significant advantages of this technique compared to other advanced oxidation technologies (AOTs) (e.g., photocatalysis, ozonation, UV/H_2O_2) are safety, cleanness, high penetrability in water medium, and the avoidance of secondary pollutant generation [6]. So far, the "hot spot" theory is the most commonly adopted description of the sonochemical reaction which assumes a heterogeneous process in gas and liquid phases, in which the reactive species (e.g., $H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H$, ${}^{\bullet}OH + {}^{\bullet}H \rightarrow H_2O$, $2{}^{\bullet}OH \rightarrow H_2O_2$, $2{}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O$, $2{}^{\bullet}H \rightarrow H_2$) and heat are produced from the cavitation bubbles [7,8]. Organic compounds with different physicochemical properties are presumed to have different driving forces toward the bubble-liquid interfaces, where the reactive radicals are concentrated, and different tendencies to pass into the gaseous phase within the bubbles, leading to different degradation efficiencies.

Some previous studies have evaluated the influence of several physicochemical properties of compounds on their sonochemical degradation, such as the octanol–water partition coefficient (K_{ow}), water solubility (S_w), vapor pressure (V_p), and Henry's law constant (K_H) [2,3,5,9,10]. However, these studies were limited to investigating the influence of the properties within the ultrasonic process (US) alone. In practice, the sonochemical process can be combined with other processes (hybrid AOTs) to improve the performance and cost-effectiveness, and the physicochemical properties of the target compounds may be critical in determining their degradation. Compared to the hybrid AOTs using chemicals (e.g., US/HSO_5^- [11], US/catalyst [12], US/Fe^{2+} [13]), the combination of ultraviolet irradiation (UV) and US may be regarded as a more environmentally-acceptable alternative through the absence of chemical addition. Previously we reported a synergistic effect in the sonophotolytic process (US/UV) which involved the photo-dissociation of ultrasonically produced H_2O_2 ($H_2O_2 + UV_{254nm} \rightarrow 2{}^{\bullet}OH$) [14]. To date, however, no studies have examined the relationship between physicochemical properties of target compounds and their degradation performance in the US/UV process.

Furthermore, most of the previous investigations were conducted under pure water mediated conditions in the absence of any background solutes. AOTs, however, are particularly suited as tertiary wastewater treatment processes (for organic micro-pollutant removal) following secondary biological treatment. Thus, it is necessary to evaluate the proposed AOTs using real wastewater as the matrix in order to consider the role of the background TOC in the effluent in the degradation of compounds with different physicochemical properties.

A group of phthalate acid esters (PAEs) with relatively short alkyl chains and high water solubility were selected as the probe compounds, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP) and monomethyl phthalate (MMP). The PAEs are widely used industrial chemicals, serving as important additives which impart flexibility in various resins [15]. Because of the large quantities of production and various losses/releases during manufacture, usage and disposal, PAEs are considered ubiquitous pollutants of the aquatic environment [15,16]. Many studies have been conducted concerning the degradation of individual PAEs using AOT methods [13,14,17–21], and a few studies have also compared the degradation performance of a group of PAEs [3,16,22,23]. Although the physicochemical properties of different PAEs are sometimes used to describe their degradation performances, little systematic investigation has been conducted to relate the properties to the degradation performance, and particular for the US or US/UV processes.

In view of the above, the sonolytic and sonophotolytic degradation of four PAEs (DMP, DEP, DBP, MMP) were investigated. The

influence of the physicochemical properties of compounds was evaluated using both pure water and real secondary effluent as water matrices. From the results obtained the degradation pathways of DBP were proposed based on the intermediates identified in the reactions.

2. Methodology

2.1. Chemicals and samples

DMP (>99%), DEP (99.5%), and DBP (>99%) were purchased from Sigma–Aldrich Inc., USA; and MMP (>98%) was purchased from Dr. Ehrenstorfer GmbH, Germany. Both deionized-distilled water (DDW) and wastewater secondary effluent were used as the water matrices. The DDW was prepared from a Millipore Waters Milli-Q water purification system with a resistivity of 18.2 $M\Omega$ cm, and the effluent was obtained from Tai Po Wastewater Treatment Works, Hong Kong, and filtered by 0.45 μm glass fiber membrane papers before use.

2.2. Apparatus and experimental conditions

Sonolytic experiments were conducted using a 400 kHz ultrasound, and the power density was determined to be 0.03 W mL^{-1} by a calorimetric method [24]. The photolytic experiments were conducted using phosphor-coated low pressure mercury lamps emitting 253.7 nm monochromatic UV lights. Six lamps were employed in this study, corresponding to an approximate incident light intensity of 1.03×10^{-5} Einstein L^{-1} s^{-1} (as cited by the lamp manufacturer, Southern New England Ultraviolet Co., USA). The specific descriptions and the schematic diagrams of the ultrasound, UV reactors and the sonophotolytic apparatus have been provided in previous publications [14,21]. The ultrasound reactor without cover was used as the unique reactor for all experiments.

Solutions of the PAEs with an initial compound concentration of 0.01 mM and 250 mL total reaction volume were used for all the experiments. The initial pH of the unbuffered (without adjustment) PAE solutions was 6.5 ± 0.2 in water background and 7.5 ± 0.2 in effluent background. A convoluted cooling finger was submerged in the tested water to keep the solution temperature constant at 28 ± 2 °C. All the experiments were duplicated and values shown in the figure were the arithmetic averages.

2.3. Analytical method

The concentration of PAEs was determined by high performance liquid chromatography (Waters 717) equipped with a Brava C18-BDS column (5 μm, 25 × 0.46 cm) and a Waters 2489 UV detector. The wavelength of 230 nm was selected for detection of all PAEs. The mobile phase of 60%, 90%, and 35% acetonitrile (ACN) water solution containing 0.1% phosphoric acid was used for DMP/DEP, DBP, and MMP determination, respectively, at a flow rate of 1.0 mL min^{-1}. The UV absorption spectra were obtained by Biochrom Libra S35 UV–vis Spectrophotometer. The concentration of hydrogen peroxide was determined by measuring the absorbance of TiO2 + 2 at 405 nm, which is formed via the reaction between H_2O_2 and Ti^{4+} [25]. The lowest detection limit of H_2O_2 was determined to be 0.025 mg (7.4×10^{-4} mM) with the correlation coefficient higher than 0.9993 in the concentration range of $7.4 \times 10^{-4} \sim 0.015$ mM. Total organic carbon (TOC) and total nitrogen (TN) were analyzed by Shimadzu TOC-L analyzer. Intermediates were identified using a LC/ESI–MS system equipped with Bruker amaZon SL ion trap mass analyzer and Dionex UltiMate 3000 Ultra Performance Liquid Chromatography (UPLC). The Thermo Hypersil GOLD column (1.9 μm, 50 × 2.1 mm) was used for UPLC. Positive ion mode was used for DBP detection and both negative and positive