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Removals of PAHs and acute toxicity via sonication in a petrochemical industry wastewater

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ABSTRACT

The effects of ambient conditions (25 °C), increasing sonication time (0–150 min), temperature (30–60 °C), dissolved oxygen (DO, 2–10 mg L^{-1}) and hydrogen peroxide (H_2O_2, 100–2000 mg L^{-1}) concentrations on the removal of polycyclic aromatic hydrocarbon (PAH) and destruction of toxicity in a petrochemical industry wastewater in Izmir (Turkey) were investigated. The maximum PAH removals were 80.2%, 91%, 98.5% and 98% at 25 °C, 60 °C, DO concentration of 6 mg L^{-1} and H_2O_2 concentration of 2000 mg L^{-1}, respectively, after 150 min sonication. Sonication alone provides PAH removals varying between 88% and 92% without DO and H_2O_2 at 30 °C and 60 °C after 150 min sonication. The *Daphnia magna* acute toxicity decreased significantly from 342.6 ng mL^{-1} to 5.4 ng mL^{-1}, to 0.7 ng mL^{-1}, and to 0.4 ng mL^{-1}, respectively, as the temperature, the DO and the H_2O_2 concentrations were increased. The PAH sonodegradation appeared to be pseudo first order in PAHs naphthalene (NAP), acenaphthylene (ACL), phenanthrene (PHE), pyrene (PY) and benz[*b*] fluoranthene (BbF) ($k = 0.026$ min^{-1}, 0.024 min^{-1}, 0.017 min^{-1}, 0.015 min^{-1} and 0.011 min^{-1}, respectively). The main mechanism of PAH sonodegradation appears to be pyrolysis.

1. Introduction

PAHs are listed as US-EPA and EU priority pollutants, and their concentrations, therefore, need to be controlled in treated wastewater effluents [1,2]. Due to their toxic, mutagenic and carcinogenic properties the US-EPA classifies 16 of these PAHs as priority pollutants [1,2]. Recent studies have shown that sonication may be a useful tool for degrading the aqueous pollutants [3–6]. The sonication process is capable of effectively degrading target compounds including chlorophenols, chloroaromatics and PAHs present in dilute solutions, typically in the micro and nano ranges. The process does not require the use of additional chemicals commonly employed in several oxidation processes, thus again reducing costs.

David [5] found that naphthalene (NAP), phenanthrene (PHE), anthracene (ANT) and pyrene (PY) removal efficiencies varied between 93% and 95%, after a sonication time of 90 min in a sonicator with a power of 400 W and a frequency of 20 kHz. Psillakis et al. [7] reported a 99% removal efficiency for 0.01 μg L^{-1} of acenaphthalene (ACT), PHE and NAP at a power of 300 W and frequency of 24 kHz. Benabdallah El-Hadj et al. [4] found 57% NAP, 40% PY and 45% total COD removal efficiencies in a sonicator with a power of 70 W and frequency of 20 kHz. Taylor et al. [8] investigated the sonication of PAHs, namely ANT, PHE and PY. 46%, 20% and 50% removal efficiencies, respectively, were found at a power of 600 W and a frequency of 20 kHz. Laughrey et al. [9] investigated the effects of DO, air on the sonication of PHE, PY and ANT. They found removals of these PAHs as high as 80–90% as the DO concentration, air and N_2(g) purges were increased from 1 mg L^{-1} to 5 mg L^{-1} and from 2, 4 mL min^{-1} up to 3, 6 mL min^{-1}.

When sonolysis of water occurs, it leads to the formation of the non-specific oxidative species $OH^{\bullet}$. The ultrasonic degradation of hydrophobic organics such as PAHs can occur when they penetrate to the surrounding of the hot heart of the cavitation bubble being pyrolyzed, burnt and/or ionized in the plasma core [10,11]. The literature data concerning the sonodegradation of PAHs is scarce and the results are contradictory. Two mechanisms have been proposed to account for sonolytic degradation: (i) oxidation by $OH^{\bullet}$ [8,9] and (ii) pyrolytic decomposition [7].

In Izmir, Turkey, petrochemical plant wastewaters are treated with conventional activated sludge systems. Since such systems are unable to completely remove the main PAHs present (ca. 17) these are released into receiving bodies. Although some studies aimed at increasing the degradation of some PAHs (NAP, PHE, ANT, PY and ACT) with sonication have appeared, these have been limited to only a few of those generally present (3–5) [4,7,12,13]. No study was found investigating the effects of operational conditions such as sonication time, temperature, DO and H_2O_2 on the sonication of a petrochemical industry wastewater. Furthermore, the effects of the operational conditions on the removal of acute toxicity has not been determined for a petrochemical industry wastew-

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ater. Thus, in this study our aim was to determine the effects of ambient conditions, increasing sonication time (0 min, 60 min, 120 min and 150 min), sonication temperatures (25 °C, 30 °C and 60 °C), DO (2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1} and 10 mg L^{-1}) and H_2O_2 (100 mg L^{-1}, 500 mg L^{-1} and 2000 mg L^{-1}) on the sonodegradation of 17 PAHs. The effects of these operational conditions on the acute toxicity of *Daphnia magna* were determined. Furthermore, the reaction kinetics of five representative PAHs and the mechanism of PAH sonodegradation were investigated.

2. Materials and methods

2.1. Sonicator and operational conditions

A BANDELIN Electronic RK510 H sonicator was used for sonication of the petrochemical industry wastewater samples. The wastewater was not pre-treated before sonication since the solids was disentegrated through sonication. Glass serum bottles in a glass reactor were filled to a volume of 100 mL with petrochemical wastewater after the dosing of oxygen and hydrogen peroxide. They were then closed with teflon coated stoppers for the measurement of volatile compounds (evaporation) of the petrochemical wastewater. The evaporation losses of PAHs were estimated to be 0.01% in the reactor and therefore, assumed to be negligible. The serum bottles were filled with 0.1 mL methanol in order to prevent adsorption on the walls of the bottles and minimize evaporation. The temperature in the sonicator was monitored continuously and was maintained constant at 30 °C and 60 °C. For ambient conditions the sonicator was not heated – it was used at 25 °C. All experiments were in batch mode using an ultrasonic transducer (horn type), which has an active acoustical vibration area of 19.6 cm^2, and a maximum input power of 650 W. Four sonication intensities (16 W m^{-2}, 37 W m^{-2}, 23.02 W m^{-2} and 51.75 W m^{-2}) were chosen to identify the optimum intensity for maximum PAH removal. Samples were taken after 60 min, 120 min and 150 min of sonication and were kept for a maximum of 15 min in a refrigerator at a temperature of +4 °C until the sonication experiments were begun.

Air enriched with oxygen was provided to the samples before sonication. Dissolved oxygen was sparged into the liquid samples with a pump under a pressure of 0.5 atm for 10 min at a flow rate of 5 mL min^{-1} (monitored by a rotameter), and then stopped. H_2O_2 solutions were slurried in the reaction mixture with a pressured pump 20 min prior to sonication at a flow rate of 100 mL min^{-1} and then stopped.

2.2. Analytical methods

For PAHs and some metabolites (phenanthrenediol, naphthalene and p-hydroxybenzoic acid by-products and fluorene) analyses the samples were first filtered through a glass fiber filter (47-mm diameter) to collect the particle-phase in series with a resin column (∼10 g XAD-2) and to collect dissolved-phase polybrominated diphenyl ethers. Resin and water filters were ultrasonically extracted for 60 min with a mixture of 1:1 acetone:hexane. All extracts were analyzed for 17 PAHs including naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[*a*]anthracene (BaA), chrysene (CHR), benz[*b*] fluoranthene (BbF), benz[*k*]fluoranthene (BkF), benz[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenz[*a*,*h*]anthracene (DahA), and benzo[*g*,*h*,*i*]perylene (BghiP) gas chromatographically (Agilent 6890N GC) equipped with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-MS, 30 m, 0.25 mm, 0.25 μm) was used. The initial oven temperature was kept at 50 °C for 1 min, then raised to 200 °C at 25 °C min^{-1} and from 200 °C to 300 °C at 8 °C min^{-1}, and then maintained for 5.5 min. High purity He(g) was used as the carrier gas at constant flow mode (1.5 mL min^{-1}, 45 cm s^{-1} linear velocity). PAHs and their metabolites were identified on the basis of their retention times, target and qualifier ions and were quantified using the internal standard calibration procedure. The Phenanthrenediol analysis was performed using a high-pressure liquid chromatography (HPLC) (Agilent-1100) with a method developed by Lindsey and Tarr [14]. The chromatographic conditions for the phenanthrenediol determination were as follows: C-18 reverse phase HPLC column (Ace 5C18; 25 cm × 4.6 mm, 5 μm, mobile phase: 50/50 (v/v) methanol/organic-free reagent water). The naphthalene, p-hydroxybenzoic acid by-products and fluorene were measured in the aforementioned HPLC by using C-8 column (Ace 8; 15 cm × 2.6 mm, 3 μm, mobile phase: 70/30 (v/v) methanol/organic-free reagent water). The CH_4, CO_2 and H_2S gas analysis was performed following Standard Methods [13]. pH, temperature, oxidation-reduction potential (ORP), COD and TOC concentrations were monitored following the Standard Methods 2550, 2580, 5220 D and 5310 [15]. Hydrogen peroxide was quantified with a colorimetric method following the Standard Methods 3550 [15]. DO, and pH were measured in a WTW dissolved oxygen meter and pH meter the ORP was measured using a WTW redox meter. TSS, TVSS, inorganic nitrogen compounds, Total-P, oil and SO_4 were monitored following the Standard Methods [15].

2.3. D. magna toxicity test

To test toxicity 24 h old *D. magna* were used as described in Standard Methods [15]. After preparing the test solution, experiments were carried out using 5 or 10 *daphnids* introduced into the test vessels. These vessels had 100 mL of effective volume at 7–8 pH, providing a minimum DO concentration of 6 mg L^{-1} at an ambient temperature of 20–25 °C. Young *D. magna* were used in the test (≤24 h old). A 24 h exposure is generally accepted as standard for a *Daphnia* acute toxicity test. The results were expressed as mortality percentage of the *Daphnids*. Immobile animals were reported as dead *Daphnids*.

All experiments were carried out three times and the results given as the means of triplicate samplings. Individual PAH concentrations are given as the mean with standard deviation (SD) values.

2.4. Statistical analysis

Multiple regression analysis between *y* and *x* variables was performed using the Excell in Windows. The linear correlation was assessed with R^2. The significance of the correlations between data was determined using the ANOVA test statistics.

3. Results and discussion

3.1. Raw wastewater

Characterization of raw petrochemical wastewater taken from the influent of the aeration unit of a petrochemical wastewater treatment plant was performed. The results are given as the mean value of triplicate samplings (Table 1).

3.2. Effect of sonication frequency on the removal of PAHs

Preliminary studies showed that high ultrasound frequencies of 80 kHz and 150 kHz did not increase the results of the parameters studied. Therefore, they were studied at a sonication frequency of 35 kHz. Increasing the sonication frequency decrease the num-