Sonochemical Degradation of Aromatic Compounds in the Presence of Inorganic Salts

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1. Introduction

Sonication of aqueous solutions provides the formation and collapse of cavitation bubbles. During the collapse high temperatures and pressures are produced (1), leading to the formation of chemical species such as $H\cdot$, $OH\cdot$, $O\cdot$ and H_2O_2 (2-3). These high energy phenomena cause degradation of aromatic pollutants in aqueous solutions. The variety of degradation pathways ensures that many pollutants undergo transformation under sonochemical conditions (4-5).

The purpose of present research is to degrade the aromatic compounds efficiently in the presence of inorganic salts. In addition, we discuss the effects of hydrophobicity of aromatic compounds on the rates of degradation.

2. Experimental procedure
2.1 Chemicals

1-octanol, catechol, resorcinol, phenol, 4-chlorophenol, sodium sulfate, sodium chloride, methanol, sodium nitrate, sodium carbonate, hydrochloric acid were used as received. High purity argon was used. All solutions were prepared with Milli-Q purified water.

2.2 Determination of log P of aromatic compounds

Hydrophobicity is commonly expressed by the logarithm of the octanol-water partition coefficient (referred as log P). The partition coefficient is determined by the following equation: $P = C_{octanol} / C_{water}$. The advanced stir-flask method was used to determine log P: n-octanol, water, and aromatic compound solutions were added to a flat-bottomed flask and then the contents were sealed and stirred continuously. Instrumental parameters were set at the following levels: time 24 hours, 500 rpm and $22\pm1^{o}C$ to achieve mutual saturation of the phases. The contents were allowed to settle to keep on the desk 2/3 hours at the same temperatures. An aliquot of aqueous (hydrophilic) layer was taken and was directly injected in a high performance liquid chromatograph (HPLC) with an ODS column under a mobile phase methanol and water, (V:V = 30:70)% for resorcinol, catechol and phenol, and (V:V = 80:20)% for 4-chlorophenol, flow rate of 0.70 ml min^{-1} and the detection wavelength of 254 nm for resorcinol and catechol, and of 280 nm for phenol and 4-chlorophenol.

2.3 Sonolysis

An ultrasonic generator (Kaijo 4021) and an oscillator of 65 mm inner diameter were used for ultrasonic irradiation and were operated at 200 kHz with an input power of 200 W. A glass vessel with a 60 ml sample solution was used for ultrasonic irradiation. The vessel had a side arm with a silicon rubber septum for argon gas bubbling and sample extracting (every 0, 5, 10, 20 and 30 min) by a glass syringe without exposing the sample to air. The schematic diagram of the experimental setup was described in literature (6). The glass vessel was flat bottomed and 1 mm thick. The vessel was mounted at a constant position (4 mm from the oscillator). The concentrations of the sonicated solutions were determined with a HPLC. The yield of hydrogen peroxide was measured by the method of Korman et al. (7), where the absorbance measurements were performed at 352 nm and room temperature by a UV-Vis spectrophotometer (Shimadzu UV-2450).

3. Results and Discussion

Fig. 1 shows the effects of concentrations of Na_2SO_4 on the sonochemical degradation of a) resorcinol, b) phenol and c) 4-chlorophenol, respectively. Fig. 1 indicates that the initial rate of degradation increases with increasing concentration of Na_2SO_4 for resorcinol, 4-cholorophenol but for phenol the change in the initial rate of degradation is not significant.
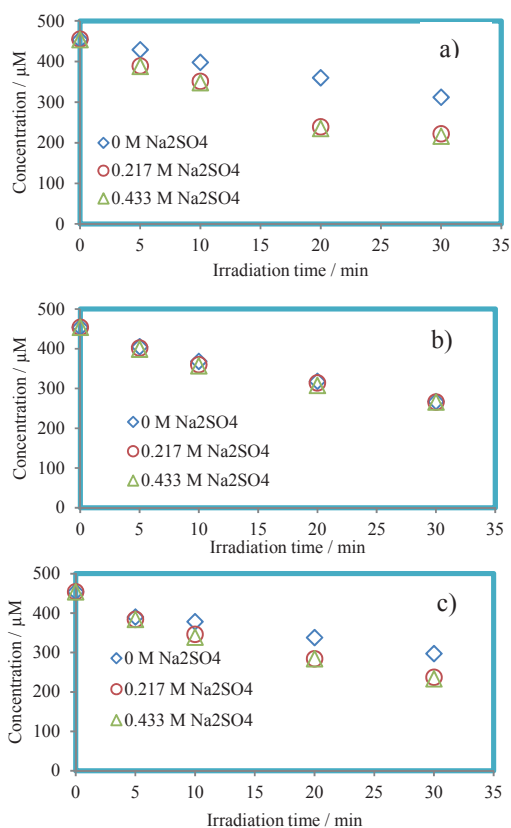
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Fig. 1 Effects of Na₂SO₄ on the degradation of a) resorcinol, b) phenol and c) 4-chlorophenol.

After 30 min sonication, the concentration of resorcinol decreased 50% in the presence of 0.433 M Na_2SO_4 whereas it was 37% without Na_2SO_4. In the presence of the same concentration of Na_2SO_4, the degradation rate constants of resorcinol, catechol, phenol, and 4-chlorophenol were 2.3, 1.2, 1.0, and 1.5 times higher respectively than without Na_2SO_4.

To discuss chemical effects of ultrasound, the yield of H_2O_2 was measured as shown in **Fig. 2**.
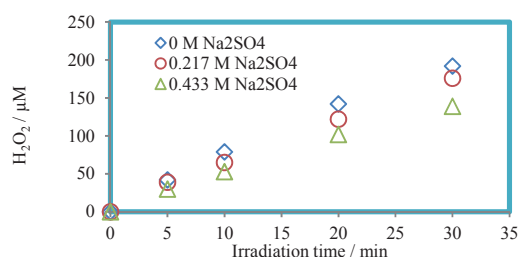

Fig. 2 Hydrogen peroxide produced during sonolysis of water in the absence and presence of Na_2SO_4.

Fig. 2 indicates that the yield of H_2O_2 decreases with increasing concentration of Na_2SO_4. During sonolysis, hydrogen atoms and hydroxyl radicals are formed due to the pyrolytic decomposition of water (8): $H_2O \rightarrow H^. + {}^.OH$. Hydroxyl radicals can recombine to form hydrogen peroxide: $OH + {}^.OH \rightarrow H_2O_2$. Based on these reactions, it is considered that the yield of H_2O_2 corresponds to that of hydroxyl radicals. Therefore, lower yield of H_2O_2 suggests that the formation of cavitation bubbles with high temperatures may be suppressed in the presence of Na_2SO_4.

In spite of lower yield of H_2O_2 in the presence of Na_2SO_4, the results of Fig.1 show that the initial rates of degradation tend to increase or keep constant when the concentration of Na_2SO_4 increases. Since the value of log P increases with increasing concentration of Na_2SO_4, it is suggested that the aromatic compounds more easily accumulate on and/or enter in the cavitation bubbles when the concentration of Na_2SO_4 is high.

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