



Effects of Na₂SO₄ or NaCl on sonochemical degradation of phenolic compounds in an aqueous solution under Ar: Positive and negative effects induced by the presence of salts



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ABSTRACT

Sonochemical degradation of 4-chlorophenol, phenol, catechol and resorcinol was studied under Ar at 200 kHz in the absence and presence of Na₂SO₄ or NaCl. The rates of sonochemical degradation in the absence of salts decreased in the order 4-chlorophenol > phenol > catechol > resorcinol and this order was in good agreement with the order of log *P* (partition coefficient) value of each phenolic compound. The effects of salts on the rates of sonochemical degradation consisted of no effect or slight negative or positive effects. We discussed these unclear results based on two viewpoints: one was based on the changes in pseudo hydrophobicity and/or diffusion behavior of phenolic compounds and the other was based on the changes in solubility of Ar gas. The measured log *P* value of each phenolic compound slightly increased with increasing salt concentration. In addition, the dynamic surface tension for 4-chlorophenol aqueous solution in the absence and presence of Na₂SO₄ or NaCl suggested that phenolic compounds more easily accumulated at the interface region of bubbles at higher salt concentration. These results indicated that the rates of sonochemical degradation should be enhanced by the addition of salts. On the other hand, the calculated Ar gas solubility was confirmed to decrease with increasing salt concentration. The yield of H₂O₂ formed in the presence of Na₂SO₄ or NaCl decreased with increasing salt concentration. These results suggested that sonochemical efficiency decreased with decreasing gas amount in aqueous solution: a negative effect of salts was observed. Because negative and positive effects were induced simultaneously, we concluded that the effects of salts on the rates of sonochemical degradation of phenolic compounds became unclear. The products formed from sonochemical degradation of 4-chlorophenol were also characterized by HPLC analysis. The formation of phenol and 4-chloro-1,3-dihydroxy benzene was confirmed and these concentrations were affected by the presence of salts.

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1. Introduction

Phenol and substituted phenols are important organic intermediates for the products of industry and agriculture. However, they are high toxic and create serious problems to human health and aquatic species. The conventional methods to deal with such phenolic compounds include activated carbon adsorption, biological treatment, and chemical oxidation [1–5], however, the application of these methods has its limitations and disadvantages. Actually, high toxicity and stability of phenolic compounds hamper the treatments of wastewater.

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Advanced oxidation processes (AOPs) have been developed to degrade organic pollutants in water. AOPs include ozonation, UV/photocatalysis, UV/H₂O₂, Fenton reaction, radiolysis, sonolysis and their combinations [6–19]. When a solution containing organic pollutants is irradiated by ultrasound, organic pollutants are degraded by OH radicals and/or direct pyrolysis reactions during acoustic cavitation. Although unique reaction conditions consisting of extremely high temperatures and pressures, rapid cooling, shock waves, micro-jets, etc. are generated in an aqueous solution [20,21], the rate of sonochemical degradation of organic pollutants is still slow for practical use.

Therefore, a new technique has to be developed to enhance the rate of sonochemical degradation. So far, effects of various types of salts on sonochemical degradation of organic compounds have

been investigated, where NaCl or Na₂SO₄ are often used. However, it seems that the experimental results observed often conflict each other. For example, it was reported that the rates of sonochemical degradation of chlorobenzene, p-ethylphenol and phenol were enhanced by the addition of NaCl under 20 kHz ultrasound irradiation [14,16,17]: a positive effect of NaCl was observed. On the other hand, Chen and Smirniotis reported that the rates of sonochemical degradation of phenol decreased by the addition of NaCl or Na₂SO₄ under 20 kHz ultrasound irradiation [13]. The effects of NaCl or Na₂SO₄ on the rates of sonochemical degradation of Rhodamin B [22,23], malachite green [24] and crystal violet [25] have been investigated, but all cases showed no effect of NaCl or Na₂SO₄.

In this study, we investigated the effects of Na₂SO₄ or NaCl on sonochemical degradation of several phenolic compounds by using a standing wave type 200 kHz ultrasound irradiation system under Ar atmosphere. We chose phenolic compounds as probe compounds because they are the most common and recalcitrant pollutants present in industrial wastewaters.

2. Experimental section

2.1. Experimental procedure

2.1.1. Chemicals

1-Octanol (purity > 99.5%) was purchased from Tokyo Chemical Industries. Catechol (purity 99.0%), resorcinol (purity 99.0%), phenol (purity 99.0%), 4-chlorophenol (purity 98%), Na₂SO₄ (purity 99%), NaCl (purity 99.5%), and methanol (purity 99.7%) were purchased from Wako Pure Chemical Industries. All the chemicals were reagent grade and used as received. Ar (purity 99.999%) was purchased from Osaka Sanso. All solutions were prepared with Milli-Q purified water (resistivity of 18.2 MΩ cm at 25 °C).

2.1.2. Measurement of log *P*

Hydrophobicity is commonly expressed by log *P*, where *P* is the octanol–water partition coefficient. *P* is determined by $C_{\text{octanol}}/C_{\text{water}}$, where C_{octanol} and C_{water} are the concentrations of a target organic solute in octanol and water, respectively. The stir-flask method [26] improved was used to measure *P*: 1-octanol (5 ml), aqueous solution with or without salt (4 ml), and 0.45 mM phenolic solution (1 ml) were added to a flat-bottomed flask. The contents were sealed and stirred at 500 rpm for 24 hours at room temperature (22 ± 1 °C). The contents were settled on the desk for 2–3 h at room temperature. 50 μl of aqueous layer was injected in a high performance liquid chromatograph (HPLC, Shimadzu LC-20ATvp with a VP-ODS C-18 reversed phase column (4.6 × 250 mm)) for analysis. A mobile phase of methanol and water (volume ratio = 30:70) was used for resorcinol, catechol and phenol, and methanol and water (volume ratio = 80:20) was used for 4-chlorophenol at flow rate of 0.70 ml min⁻¹ where the detection wavelength of 254 nm was used for resorcinol and catechol, and of 280 nm for phenol and 4-chlorophenol.

2.1.3. Measurement of surface tension

When the concentration of 4-chlorophenol was less than 1.0 mM, the change in surface tension was too small to monitor the change in surface tension. Therefore, as a sample solution for surface tension measurements, 20 mM 4-chlorophenol aqueous solution was chosen. The changes in the surface tension of the sample solution in the absence and presence of 0.50 M Na₂SO₄ or 0.45 M NaCl were measured in the time range from 0 to 1800 s by using a Young–Laplace method for a pendant drop with an interfacial tension meter (Kyowa Interface Science DM-501), where

the surface tension was monitored at 1 s interval. Three or five experimental runs were performed and the average data were used in figure, where the standard deviation was 0.4 (no salt), 0.4 (0.50 M Na₂SO₄) and 1.3 (0.45 M NaCl) at 1000 s, respectively.

2.1.4. Sonolysis

An ultrasonic generator (Kaijo 4021, Lot No. 1033) and an oscillator (Kaijo 4611, MFG. No. 34C3) of 65 mm diameter were used for ultrasonic irradiation and were operated at 200 kHz with a nominal power of 200 W (calorimetric power for 60 ml sample solution: 16 W) at 20 °C. A glass vessel with 60 ml sample solution was used for ultrasonic irradiation under Ar atmosphere, where the vessel was mounted at a constant position (4 mm from the oscillator). The vessel had flat bottom with 1 mm thick and a side arm with a silicon rubber septum for Ar gas bubbling and sample extracting by glass syringe (1 ml) without exposing the sample to air. The schematic diagram of the experimental setup was described in the literature [27]. The sonication was performed up to 30 min to understand the initial degradation behavior of phenolic compounds. When the degradation products were analyzed, the sonication was performed up to 60 min. The sonicated solutions were analyzed by a HPLC. The analysis conditions for resorcinol, catechol, phenol and 4-chlorophenol were the same as the measurement of log *P*. For determination of products formed from sonochemical degradation of 4-chlorophenol, a mobile phase of methanol and water (volume ratio = 40:60) was used at flow rate of 0.70 ml min⁻¹, where the detection wavelength of 224 nm was used. The changes in UV–vis spectra of the sample solutions were measured by a UV–vis spectrophotometer (Shimadzu UV-2450). The concentration of H₂O₂ formed in the sonolysis of aqueous solution with and without salts under Ar was measured by a KI method [28], where the absorbance at 352 nm was measured.

3. Results and discussion

Sonochemical degradation of 4-chlorophenol, phenol, catechol and resorcinol was investigated in the absence and presence of Na₂SO₄ or NaCl under Ar. The rate of degradation of phenolic compounds obeyed a pseudo first order rate constant as seen in Figs. S1–S3 in Supplementary data. Therefore, we analyzed the pseudo rate constant as a rate of degradation in this study. The result obtained in the absence and presence of Na₂SO₄ is shown in Fig. 1(a). The rate constant for sonochemical degradation of 4-chlorophenol in the absence of salt was determined by three times sonication experiments as shown in Fig. S1. The average value was plotted in Fig. 1(a), where the error bar corresponds to the standard deviation. Figs. 1(a) and S2 indicate that no effect or a slight positive effect of Na₂SO₄ were observed. We also investigated the effects of NaCl on the rate constant for sonochemical degradation. The result is shown in Figs. 1(b) and S3. Even in the case of NaCl addition, no effect for chlorophenol ($k = 0.0214 \text{ min}^{-1}$ at no salt, 0.0209 min^{-1} at 0.023 M NaCl, 0.0217 min^{-1} at 0.45 M NaCl), a slight negative effect for phenol ($k = 0.0180 \text{ min}^{-1}$ at no salt, 0.0168 min^{-1} at 0.023 M NaCl, 0.0160 min^{-1} at 0.045 M NaCl), or slight positive effects for catechol ($k = 0.0125 \text{ min}^{-1}$ at no salt, 0.0143 min^{-1} at 0.023 M NaCl, 0.0142 min^{-1} at 0.045 M NaCl) and for resorcinol ($k = 0.00977 \text{ min}^{-1}$ at no salt, 0.0128 min^{-1} at 0.023 M NaCl, 0.0134 min^{-1} at 0.045 M NaCl) were observed.

In the absence of salt, the results showed that the rate constants for sonochemical degradation decreased in the order 4-chlorophenol > phenol > catechol > resorcinol. It has been reported that the hydrophobicity of an organic solute is one of the most important parameters for the rate of sonochemical degradation, because highly hydrophobic compounds tend to accumulate

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