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Synergistic sonoelectrochemical removal of substituted phenols: Implications of ultrasonic parameters and physicochemical properties

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ABSTRACT

The effects of ultrasonic conditions and physicochemical properties on the synergistic degradation in synthetic solution were investigated. A wide range of ultrasound frequencies, including 35, 170, 300, 500 and 700 kHz, and ultrasonic power densities, including 11.3, 22.5 and 31.5 W/L were used. It was revealed that the physical effect of ultrasound plays a major role in synergistic mechanism and 35 kHz was found to be the most effective frequency due to its more vigorous physical effect induced by high implosive energy released from collapse of cavitation bubbles. The highest ultrasonic power density (31.5 W/L) showed the highest synergy index as it increases the number of cavitation bubbles and the energy released when they collapse. The synergy indexes of various substituted phenols under identical condition were investigated. These results were correlated with physicochemical properties, namely octanol–water partition coefficient (Log K_{OW}), water solubility (S_W), Henry's law constant (K_H) and water diffusivity (D_W). Among these parameters, Log K_{OW} and D_W were found to have substantial effects on synergy indexes.

1. Introduction

Electrochemical treatment (EC) is an oxidative water treatment which utilizes electrical potential as a generative force to trigger both direct and indirect oxidative reactions. In direct oxidation process, organic pollutants are oxidized by losing their electrons at the surface of the anode without involving any other extra reagent (Eq. (1)) [1]. During indirect oxidation process, water molecules are discharged and form ·OH at the anode (Eq. (2)), which then attacks the pollutants adsorbed on the anodic surface (Eq. (3)) [2]

$$R_{ads} - ze^- \rightarrow P_{ads} \quad (1)$$

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \quad (2)$$

$$M(\cdot OH) + R \rightarrow M + CO_2 + H_2O + H^+ + e^- \quad (3)$$

where M and R denote anodic electrode material and organic pollutant.

Since the oxidative reaction area in EC is restricted to the surface of electrodes, the reaction kinetics are significantly governed by a mass transfer [3]. Thus, the irradiation of ultrasound (US) has been adopted to enhance the performance of EC in several ways: (1) uniform transport of electrolytic ions through the diffusion layer on electrodes, (2) electrodes activation through continuous cleaning of insoluble fouling, (3) limiting the accumulation of gasses on the electrode surface, (4) enhancing mass transfer by reducing the diffusion layer thickness and preventing the depletion of electro-active species at the electrode-liquid interface [4].

The application of the combined electrochemical and sonochemical treatment (EC/US) has already been investigated extensively by various researchers through the degradation of different pollutants. However, these studies concluded discretely on the extent of the enhancement or synergistic effect [2,5–10]. Moreover, some researchers reported unanticipated results that under certain conditions the influence of US was found to be negligible or even to have a negative effect on EC [11–13]. Therefore, these controversial results can be considered to imply that the synergistic degradation of a pollutant by EC/US can considerably alter depending on the experimental conditions.

Even though various evaluations at different ultrasonic frequencies have been published, there are still limits in giving a firm conclusion based on collective analysis due to different experimental conditions. Moreover, previous studies dealing with frequency effects are limited to either a few frequencies [6,14] or a very restricted range [2]. In the case of ultrasonic power density, significantly conflicting results reported from previous researches can be

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observed [4,7,15]. Besides, based on the comparison of previous results on different pollutants showing a significant difference in synergy index under similar experimental condition [7,8], it can be assumed that the physicochemical properties of pollutant may affect synergy index. In short, there has been no attempt to study EC/US process strictly focusing on evaluating its synergistic effect quantitatively depending on various conditions.

Therefore, considering the essential role of ultrasound, the effect of an extensive range of frequencies (35, 170, 300, 500, 700 kHz) and power densities (11.3, 22.5, and 31.5 W/L) is examined with pentachlorophenol (PCP) as a model pollutant. Furthermore, to check the possibility of influence of physicochemical properties on the synergistic mechanisms of EC/US, additional substituted phenols were used to further investigate the effect of physicochemical properties for the first time.

2. Materials and methods

2.1. Chemicals

All the model pollutants and *n*-butanol (C_4H_9OH) were purchased from Sigma–Aldrich, Korea and used as received. Sodium sulfate (Na_2SO_4), used as a supporting electrolyte, was purchased from Samchun Pure Chemical Co., Ltd. All aqueous solutions were prepared at room temperature with deionized water obtained from Millipore Milli-Q. The initial concentration of model pollutants and electrolyte for the entire experimental sets was 2 and 100 ppm, respectively.

2.2. Analytical methods

The concentrations of substituted phenols were analyzed using HPLC (Agilent 1260 Infinity) equipped with ZORBAX SB-C18 (4.6 × 150 mm, 5 μm) and a G4212B 1260DAD Detector (λ = 222 μm). The temperature of the column was kept constant at 25 °C. The mobile phase was a combination of 0.01 M phosphoric acid and acetonitrile (ACN) in a volumetric ratio of 80:20 with a gradient of 80% ACN in 2 min and a flow rate of 1.5 mL min^{-1}. The retention times were varied, including an 1 min post-time depending on the pollutant species.

2.3. Experimental set-up

The experimental set-up is described schematically in Fig. 1. A sealed cylindrical reactor was made of stainless steel and surrounded by a water jacket (diameter: 10 cm, height: 15 cm and solution volume: 1 L) was employed throughout the experiments.

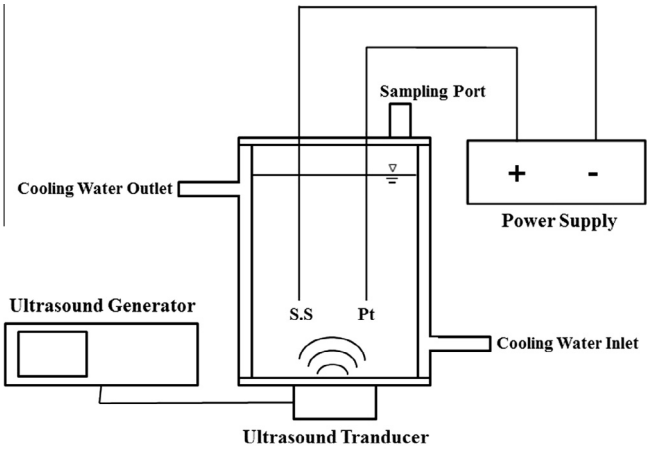

Fig. 1. Schematic diagram of experimental set-up. S.S: stainless steel.

In the US experiment, ultrasonic waves were generated through a transducer installed at the bottom of the reactor. It was powered by an ultrasound generator (Flexonic 4, Mirae Ultrasonic Tech). Calorimetric power was measured to evaluate the actual ultrasonic power transferred to the liquid following the equation shown below

$$P_{US} = \frac{dT}{dt} C_P M \quad (4)$$

where P_{US} is the calorimetric power, dT/dt is the rate of increase in liquid temperature, C_p is the specific heat capacity of the liquid (4.2 J/g K for water), and M is the mass of the liquid. The temperature of the liquid was measured using a thermometer (DTM-318, Tecpel). Table 1 shows the electric powers and corresponding transferred calorimetric powers.

For the EC experiment, a Pt anode (coated on Ti, mesh type, width: 6 cm, height: 7 cm) and a stainless steel cathode (mesh type, width: 8 cm, height: 7 cm) were used. A regulated DC power supply from PNCYS (EP-3010) was used to a apply voltage (30 V in potentiostat mode) to the electrodes.

2.4. Data analysis

The synergy index was calculated with the assumption that all the degradation reactions of US, EC and EC/US process followed a pseudo first order as given below:

$$\frac{dC}{dt} = k_{EC,US,EC/US} C \quad (5)$$

$$\text{Synergy index} = \frac{k_{EC/US}}{k_{EC} + k_{US}} \quad (6)$$

where k denotes the degradation kinetic constant and each subscript designates each treatment process. All experiments were duplicated.

3. Results and discussion

3.1. The effect of ultrasonic frequency

Three different sets of pentachlorophenol (PCP) degradation experiments (EC, US and EC/US) were performed to investigate the effect of frequency on synergy index. Various frequencies (35, 170, 300, 500, and 700 kHz) with a fixed ultrasonic power density (22.5 W/L) were used for US and EC/US experiments. For accurate analysis of a contribution of US to EC/US, the electrodes were placed and sulfate ions were added during US.

As shown in Fig. 2A, at all of the frequencies examined, sonolysis was found to be ineffective for the decontamination of PCP. Only less than 20 % of PCP degradations were achieved within an hour at all frequencies. Kinetic constants at 35, 170, 300, 500 and 700 kHz in US were 3.2×10^{-3}, 0.9×10^{-3}, 2.4×10^{-3}, 1.6×10^{-3} and 0.2×10^{-3} min^{-1}, respectively. Sonolysis at 35 kHz was the most effective in degrading PCP, which was not a usual observation in sonolysis.

Sonolysis of PCP has been studied by several researchers. Petrier et al. [16] has reported an efficient treatment at a higher frequency

Table 1
Measurement of electric powers and corresponding calorimetric powers in US experiments.

Type of power	Measured value		
Electric power (W/L)	35	50	70
Calorimetric power (W/L)	11.3	22.5	31.5