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

Kyungho Kim a, Eunju Cho a, Binota Thokhom a, Mingcan Cui b, Min Jang b, Jeehyeong Khim a,b,*

a School of Civil, Environmental and Architectural Engineering, Korea University, Seoul 136-701, Republic of Korea
b Department of Civil Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia

ARTICLE INFO
Article history:
Received 23 April 2014
Received in revised form 11 October 2014
Accepted 5 November 2014
Available online 13 November 2014

Keywords:
Sonoelectrochemical treatment
Frequency
Power density
Physicochemical properties
Synergetic effect

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 synergetic 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 (Sw), Henry’s law constant (KH) and water diffusivity (Dw). Among these parameters, Log K ow and Dw were found to have substantial effects on synergy indexes.

© 2014 Elsevier B.V. All rights reserved.

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]

\[ R_{\text{ads}} - ze^- \rightarrow P_{\text{ads}} \]  
(1)

\[ M \rightarrow M(\text{OH}) + H^+ + e^- \]  
(2)

\[ M(\text{OH}) + R \rightarrow M + \text{CO}_2 + H_2O + H^+ + e^- \]  
(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 electrolyte ions through the diffusion layer on electrodes, (2) electrodes activation through continuous cleaning of insoluble fouling, (3) limiting the accumulation of gases 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 synergetic 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 synergetic 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
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 (C₆H₅OH) were purchased from Sigma-Aldrich, Korea and used as received. Sodium sulfate (Na₂SO₄), 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 1260 DAD 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.

![Schematic diagram of experimental set-up. S.S: stainless steel.](image)

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

\[
P_{US} = \frac{dT}{dt} \cdot C_{M}
\]

where \(P_{US}\) is the calorimetric power, \(dT/dt\) is the rate of increase in liquid temperature, \(C_M\) 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, Tepco). 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 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:

\[
dC = k_{EC}\cdot C_{US} \cdot C
\]

\[
Synergy\text{ index} = \frac{k_{EC/US}}{k_{EC} + k_{US}}
\]

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 \(3.2 \times 10^{-3}, 0.9 \times 10^{-3}, 2.4 \times 10^{-3}, 1.6 \times 10^{-3}\) and \(0.2 \times 10^{-2}\) 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>
<thead>
<tr>
<th>Type of power (W/L)</th>
<th>Electric power</th>
<th>Calorimetric power (W/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>11.3</td>
<td>22.5</td>
</tr>
<tr>
<td>50</td>
<td>22.5</td>
<td>31.5</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Measurement of electric powers and corresponding calorimetric powers in US experiments.
while comparing 20 and 500 kHz. Likewise, Shen et al. [17] reported that the sonochemical degradation of PCP was faster at 800 kHz than at 16 kHz. Wang et al. [18] examined the effect of frequencies in a range from 20 to 1040 kHz and the order of kinetic constants was $530 > 800 > 40 > 200 > 1040$ kHz. These previous results are supported by a widely-accepted explanation for the effect of frequency on sonolysis.

In general, the sonochemical destruction of a pollutant has an optimum frequency which is determined by the number of cavitation events and the extent of the violence of each cavitation bubble. At low frequencies, there is a greater chance of more OH production against a single bubble because it produces more violent cavitation leading to more extreme localized conditions such as higher temperatures and pressures. However, as frequency increases, the total number of cavitation bubbles increases leading to more generation of OH. Moreover, a shorter lifetime of bubbles prevents the recombination of OH into H$_2$O$_2$, and facilitates the diffusion of these radicals out of the bubbles. Consequently, an optimum frequency is observed when a wide range of frequency is considered [19].

Although it is widely accepted that there is an optimum frequency around 200–500 kHz as explained above, different results can still be obtained depending on experimental conditions in US. As in the case of the present study, cases in which a lower frequency giving better efficiency can also be found. There are three different conditions applied in the present study which could result in the enhancement of sonolysis at low frequency, thus, inconsistency with a general trend. First, according to Asakura et al. [20], it is possible to achieve higher sonochemical efficiency, indicating the ratio of the number of reacted molecules to the ultrasound energy, at lower frequency with a certain level of liquid height. Second, it should be noted that the existence of electrodes is not negligible in sonolysis. Park et al. [21] investigated the role of stainless steel wire mesh as sonocatalyst and reported the improvement in sonolytic performance at low frequency more than twice as much when the stainless steel wire mesh was installed vertically in the reactor. Third, the use of electrolyte can also enhance the sonolytic performance at low frequency. According to Lin et al. [22], removal efficiency of US at 40 kHz increased significantly with the addition of sulfate ions.

Fig. 2B shows the concentration profile of PCP under EC and EC/US. The kinetic constant of EC was $7.2 \times 10^{-3}$ min$^{-1}$ and those of EC/US at 35, 170, 300, 500 and 700 kHz were $2.0 \times 10^{-2}$, $1.9 \times 10^{-2}$, $1.3 \times 10^{-2}$, $1.1 \times 10^{-2}$ and $0.95 \times 10^{-2}$ min$^{-1}$, respectively. From the above results, it can be clearly seen that the application of ultrasound on electrolysis of PCP enhances the electrolysis of PCP. However, the extent of the enhancement was different depending on the frequency. The highest removal efficiency and enhancement was obtained at 35 kHz followed by 170 kHz while the other three frequencies namely, 300, 500 and 700 kHz, produced only a slight improvement in EC.

Synergy indexes from Fig. 2C show that the enhancement in EC achieved at high frequencies such as 300, 500 and 700 kHz (synergy index: 1.40, 1.26 and 1.28, respectively) could be attributed to the simple sum of individual treatments, whereas the one at low frequencies i.e., 35 and 170 kHz (synergy index: 2.31 and 2.35 respectively) was due to the synergistic effect of ultrasound on EC process.

To investigate the cause for the difference in synergy index depending on frequency, about 1000-fold excess amount of n-butanol (0.01 M) relative to PCP has been added in EC and EC/US as a scavenger for OH. Here, n-butanol has been employed as it has already been proved to be an effective scavenger in previous studies [23,24].

Link to Full-Text Articles: