Effects of ultrasound on electrochemical oxidation mechanisms of $p$-substituted phenols at BDD and PbO$_2$ anodes

Xiuping Zhu$^a$, Jinren Ni$^a$,* , Hongna Li$^a$, Yi Jiang$^a$, Xuan Xing$^a$, Alistair G.L. Borthwick$^b$

$^a$Department of Environmental Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, China
$^b$Department of Engineering Science, Oxford University, Parks Rd, Oxford OX1 3PJ, UK

**Abstract**

The effects of low-frequency (40kHz) ultrasound are investigated with regard to the effectiveness and mechanisms of electrochemical oxidation of $p$-substituted phenols ($p$-nitrophenol, $p$-hydroxybenzaldehyde, phenol, $p$-cresol, and $p$-methoxyphenol) at BDD (boron-doped diamond) and PbO$_2$ anodes. Although ultrasound improved the disappearance rates of $p$-substituted phenols at both the BDD and PbO$_2$ anodes, the degree of enhancement varied according to the type of $p$-substituted phenol and type of anode under consideration. At the BDD anode, the %Increase values were in the range 73–83% for $p$-substituted phenol disappearance and in the range 60–70% for COD removal. However, at the PbO$_2$ anode, the corresponding %Increase values were in the range 50–70% for disappearance of $p$-substituted phenols and only 5–25% for COD removal, much lower values than obtained at the BDD anode. Further investigations on the influence of ultrasound on the electrochemical oxidation mechanisms at BDD and PbO$_2$ anodes revealed that the different increase extent were due to the specialized electrochemical oxidation mechanisms at these two anodes. The hydroxyl radicals were mainly free at the BDD electrodes with a larger reaction zone, but adsorbed at the PbO$_2$ electrodes with a smaller reaction zone. Therefore, the enhancement due to ultrasound was greater at the BDD anode than at the PbO$_2$ anode.

**1. Introduction**

Phenols are typical organic pollutants. They are toxic and biorefractory. Many industrial processes generate effluents containing phenol compounds; for example, the production of pesticides, herbicides, dyes, pharmaceuticals, paper, plastics, and detergents [1–3]. Conventional biological methods have not proven very effective at treating industrial wastewaters containing phenol compounds. Electrochemical oxidation offers a promising technological solution to the treatment of bio-refractory wastewaters, because it is environmentally clean, efficient at organic degradation, easy to control, and simple in structure [4].

Anode materials play an important part in electrochemical oxidation technology. Different anode materials lead to different electrochemical oxidation mechanisms, effectiveness and efficiencies. In general, at active anodes, such as Pt, IrO$_2$, and RuO$_2$, the hydroxyl radicals produced by water decomposition interact with the oxide anode and are transferred to the lattice of the oxide anode to form chemisorbed “active oxygen” (oxygen in the oxide lattice, MO$_{x+1}$). This oxidant MO$_{x+1}$ has weak oxidation ability, and thus the active anodes have low reactivity regarding organic oxidation [5–9]. On the contrary, hydroxyl radicals do not react with non-active anodes, such as PbO$_2$, SnO$_2$, and BDD (boron-doped diamond), and thus the organic compounds instead react with hydroxyl radicals (·OH) at non-active anodes. Because the hydroxyl radical is a strong oxidant, the PbO$_2$, SnO$_2$, and BDD anodes exhibit high oxidation capability for organic pollutants [10–22]. However, compared to PbO$_2$ and SnO$_2$ anodes, BDD electrodes appear to have much higher oxidation ability [23–26]. Recent studies [3,27] demonstrate that the different oxidation capabilities may be due to the existence of different types of hydroxyl radicals at PbO$_2$, SnO$_2$, and BDD electrodes. At BDD anodes, the hydroxyl radicals mainly exist as free hydroxyl radicals, which react effectively with organic pollutants. At PbO$_2$ anodes, adsorbed hydroxyl radicals dominate, and are not very effective for the oxidation of organic compounds. At SnO$_2$ anodes, the organic compounds reacted with both adsorbed hydroxyl radicals and free hydroxyl radicals.

Under normal operating conditions, electrochemical oxidation processes are under mass-transport control [28,29]. As a result, the enhancement of mass transport would appear to be a very important factor in optimizing the electrochemical oxidation processes. Ultrasound with low frequency, which usually is in the range of 20–40 kHz due to their ease of implementation and use [30,31], can clean electrode surface and improve mass transport. It produces cavitation in liquid media. When cavitation bubbles undergo asymmetrical implosion near a solid surface, it results in a strong...
microjet of liquid and violent shock wave towards the solid surface. Consequently, the solid–liquid mass transfer between the electrodes and the solution is strongly enhanced and the anode fouling is reduced [32–35]. It therefore seems reasonable that the combination of electrochemical oxidation and ultrasound could be particularly useful.

Several studies [36–38] have demonstrated that enhanced electrochemical oxidation of phenol and 2,4-dihydroxybenzoic acid at Pt and BDD electrodes can be attributed to improved mass transfer due to the effect of ultrasound. However, to the authors’ knowledge no published studies have investigated the influence of ultrasound on electrochemical oxidation mechanisms. There is presently confusion as to which reactions are enhanced and which are weakened by the presence of ultrasound during electrochemical oxidation. The present study investigates the effect of ultrasound on electrochemical oxidation mechanisms at BDD and PbO2 anodes, with the aim of gaining a better understanding of the reaction mechanisms.

2. Experimental

2.1. Bulk electrolysis

Electrochemical oxidation of p-substituted phenols (p-nitrophenol, p-hydroxybenzaldehyde, phenol, p-cresol, and p-methoxyphenol) was performed at constant current density (20 mA cm⁻²) and room temperature (25 °C). The volume of electrolyte (1 mM substrate + 0.2 M Na₂SO₄) was 250 mL. In the absence of ultrasound, the electrolyte was stirred by a magnetic stirring bar during the electrolysis process. In the presence of ultrasound, the cell without the stirring bar was put into an ultrasound rinse slot (40 kHz, 150 W). To keep the room temperature constant, tap water continuously flowed through the rinse slot.

The anode comprised either a BDD or a PbO₂ electrode, with an exposed geometric area of 4 cm². The BDD electrode was bought from CONDIAS GmbH, Germany. The PbO₂ electrode was prepared by electrodeposition technique [39]. A stainless steel sheet of the same size was used as the cathode. The electrode gap was 10 mm. Samples were collected from the cell at prescribed intervals for chemical analysis.

The concentration of p-substituted phenols was measured using Agilent HP1100 HPLC with a ZORBAX SB-C18 column and a DAD detector. The mobile phase was methanol/water (50/50) with a flow rate of 1.0 mL min⁻¹. The UV detector was set at 314 nm for p-nitrophenol, and 280 nm for other p-substituted phenols. Chemical oxygen demand (COD) was measured by a titrimetric method using dichromate as the oxidant in acidic solution at 150 °C for 2 h (Hachi, USA).

2.2. Electrochemical measurement

The electrochemical measurements were performed using a CHI 760B electrochemical workstation (Shanghai Chenhua, China). The working electrode was the BDD or PbO₂ electrode. A platinum plate was used as the auxiliary electrode, while a saturated calomel electrode (SCE) was used as the reference electrode in a separate compartment connected to the reactor by a salt bridge (all potentials are quoted against SCE).

2.3. Detection of electrogenerated oxidants

I⁻/I₃⁻ assays were performed to measure electrogenerated oxidants [1,27]. Electrolysis was carried out in 0.2 M Na₂SO₄ solution of 250 mL volume. Every 0.5 h, a 5 mL sample was collected from the electrolysis cell. 10 mL 0.01 M KI and 5 mL HCl (1:1) were then immediately added to the sample, which was then stored in the dark for 5 min. Finally, 1 mM Na₂S₂O₃ was used to titrate the amount of produced I₂ in the presence of starch. The concentration of electrogenerated oxidants (CETO, in mM O₂) was calculated...
Table 1

Rate constants of p-substituted phenols and COD removal at the BDD and PbO₂ anodes in the absence of ultrasound (k_{elec}) and presence (k_{sonel}) of ultrasound (in h⁻¹).

<table>
<thead>
<tr>
<th>Phenols</th>
<th>BDD anode removal</th>
<th>PbO₂ anode removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-N₂O₂</td>
<td>k_{elec}</td>
<td>k_{sonel}</td>
</tr>
<tr>
<td>p-CHO</td>
<td>0.653</td>
<td>1.900</td>
</tr>
<tr>
<td>p-H</td>
<td>0.276</td>
<td>1.154</td>
</tr>
<tr>
<td>p-Ch₃</td>
<td>0.205</td>
<td>1.215</td>
</tr>
<tr>
<td>p-OCH₃</td>
<td>0.193</td>
<td>0.710</td>
</tr>
</tbody>
</table>

Using the following equation:

\[
C_{EO} = \frac{VC}{4V_s} \tag{1}
\]

where \( V \) is the volume of Na₂S₂O₃ solution used for titration (in mL), \( C \) is the concentration of Na₂S₂O₃ solution (in mM), \( V_s \) is the volume of collected sample (in mL), and 4 is a factor for charge conservation (1 mol O₂ mol⁻¹ e⁻¹ 14 mol S₂O₃²⁻ mol⁻¹ e⁻¹).

2.4. Detection of hydroxyl radicals

According to references [27,40], N,N-dimethyl-p-nitrosoaniline (RNO) was used for spin trapping the hydroxyl radicals. Electrolysis was performed in a 250-mL phosphate buffer (pH 7.1) solution containing 20 µM RNO. The bleaching of the yellow color (RNO) during electrolysis process was measured at 440 nm using UV–visible spectrophotometer (Specord 200, Analytikjena).

2.5. Mass transfer measurement

The mass transfer coefficient was obtained by electrochemical measurement [36,41,42]. The electrochemical system comprised a ferro/ferricyanide redox couple (5 mmol L⁻¹ K₃[FeIII(CN)₆] and 5 mmol L⁻¹ K₃[FeII(CN)₆]) in alkaline media (NaOH 0.5 mol L⁻¹). In the absence of ultrasound, the solution was stirred by a magnetic stirring bar. In the presence of ultrasound, the cell without the stirring bar was put into the ultrasound rinse slot. When the potential of the working electrode was controlled at −0.1 V vs. SCE, in the plateau zone of the ferricyanide reduction, the resulting reduction current was diffusion controlled and related to:

\[
k_l = \frac{nFSD_{OX,C_{OX,S}}}{\delta} \tag{2}
\]

where \( k_l \) is the diffusion current (in A), \( n \) is the number of exchanged electrons per anion (n=1), \( F \) is the Faraday constant (96487 C mol⁻¹), \( S \) is the electrode surface area (4 × 10⁻⁴ m²), \( D_{OX} \) is the diffusion coefficient of ferricyanide (0.9 × 10⁻⁹ m² s⁻¹), \( C_{OX,S} \) is the bulk solution concentration of ferricyanide (5 mol m⁻³), and \( \delta \) is the diffusion layer thickness (in m).

Then, the mass transfer coefficient (k_d) and the diffusion layer thickness (\( \delta \)) can be calculated by:

\[
k_d = \frac{D_{OX} \delta}{nFSC_{OX,S}} \tag{3}
\]

The mass transfer coefficients were estimated as follows: 2.00 × 10⁻⁵ m s⁻¹ (\( \delta = 4.50 \mu m \)) without ultrasound and 4.99 × 10⁻⁵ m s⁻¹ (\( \delta = 1.84 \mu m \)) with ultrasound at the BDD anode; and 1.02 × 10⁻⁴ m s⁻¹ (\( \delta = 0.88 \mu m \)) without ultrasound and 1.31 × 10⁻⁴ m s⁻¹ (\( \delta = 0.69 \mu m \)) with ultrasound at the PbO₂ anode. The bigger mass transfer coefficients at the PbO₂ electrode relative to those at the BDD electrode might be attributed to the larger specific area because of their surface roughness, which resulted in the larger total active area of PbO₂ electrodes. For both types of anode, the increase of mass transfer coefficients was similar (−2.9 × 10⁻⁵ m s⁻¹) in the presence of ultrasound, indicating that the influence of ultrasound on mass transfer was the same.

3. Results and discussion

3.1. Bulk electrolysis in the absence and presence of ultrasound

Electrochemical oxidation of p-substituted phenols (p-nitrophenol, p-hydroxybenzaldehyde, phenol, p-cresol, and p-methoxyphenol) at the BDD and PbO₂ anodes was performed in the absence and presence of ultrasound, respectively. Fig. 1 shows the evolution of substrate concentration and COD during the bulk electrolysis. It can be observed that the disappearance rates of...
Fig. 3. Cyclic voltammograms of 1 mM $p$-substituted phenols in 0.2 M Na$_2$SO$_4$ media at the BDD and PbO$_2$ electrodes in the absence (dashed line) and presence (solid line) of ultrasound: (A) $p$-nitrophenol, (B) $p$-hydroxybenzaldehyde, (C) phenol, (D) $p$-cresol, and (E) $p$-methoxyphenol at the BDD electrode; (F) $p$-nitrophenol, (G) $p$-hydroxybenzaldehyde, (H) phenol, (I) $p$-cresol, and (J) $p$-methoxyphenol at the PbO$_2$ electrode. Dotted line: blank (0.2 M Na$_2$SO$_4$). Scan rate: 100 mV s$^{-1}$. Auxiliary electrode: Pt. Reference electrode: SCE.
the substrates and COD were improved by ultrasound. However, the enhancements varied according to the particular choice of \( p \)-substituted phenol and specialized anode. Table 1 lists the rate constants of \( p \)-substituted phenol and COD disappearance at the BDD and PbO\(_2\) anodes in the absence \((k_{\text{elec}})\) and presence \((k_{\text{sonel}})\) of ultrasound, obtained by fitting the concentration data to the following pseudo-first order kinetic equation \((\text{Eq. (4)})\) \[ C(t) = C_0 \exp(-kt) \] where \(C(t)\) is the concentration at time \(t\) (in h), \(C_0\) is the initial concentration, and \(k\) is the rate constant (in \(h^{-1}\)).

Under the conditions in the present study, the ultrasound did not itself degrade the \( p \)-substituted phenols (see supporting information Fig. S1), which might be due to the relative low frequency and small power intensity of used ultrasound. Therefore, the improvement of substrate disappearance was mainly attributed to the mass transfer enhancement by ultrasound. We estimated the increasing extent using the following equation:

\[
\%\text{Increase} = \left( \frac{k_{\text{sonel}} - k_{\text{elec}}}{k_{\text{sonel}}} \right) \times 100
\] (5)

Fig. 2 is a histogram showing the \%Increase levels obtained for the five \( p \)-substituted phenols in terms of \( p \)-substituted phenol disappearance and COD decrease at the BDD and PbO\(_2\) anodes. At the BDD anode, the values of \%Increase were in the range 73–83\% for \( p \)-substituted phenols disappearance and 60–70\% for COD removal. Compared to the BDD electrode, the values of \%Increase obtained for the PbO\(_2\) anode were much lower: 50–70\% for \( p \)-substituted phenol disappearance and only 5–25\% for COD removal. The \%Increase values for COD removal were lower than those for \( p \)-substituted phenol disappearance at both the BDD and PbO\(_2\) anodes, due to the formation of intermediate chemicals. The differences in \%Increase values obtained for the same \( p \)-substituted phenol at the BDD and PbO\(_2\) anodes are due to the different electrochemical oxidation mechanisms at these two anodes. In the next section, we carry out a thorough investigation into the effects of ultrasound on the electrochemical oxidation mechanisms at BDD and PbO\(_2\) anodes.

3.2. Effects of ultrasound on electrochemical oxidation mechanisms

The electrochemical oxidation mechanisms could be \([1,27]\): (1) direct electrochemical oxidation on the anode surface, (2) indirect electrochemical oxidation mediated by electrogenerated oxidants, such as peroxodisulfates \((\text{in the presence of } \text{SO}_4^{2-})\) and active chlorine \((\text{in the presence of } \text{Cl}^-)\), and (3) indirect electrochemical oxidation mediated by hydroxyl radicals. In order to elucidate the influences of ultrasound on these electrochemical reactions, electrochemical measurements, detection of electrogenerated oxidants, and detection of hydroxyl radicals were performed in the absence and presence of ultrasound at BDD and PbO\(_2\) electrodes, respectively.

Electrochemical measurements were performed to investigate the direct electrochemical oxidation. Fig. 3 shows the cyclic voltammograms of the five \( p \)-substituted phenols at the BDD and the PbO\(_2\) electrodes, in the absence and the presence of ultrasound. For the BDD electrode, the oxidation current of all \( p \)-substituted phenols substantially increased in the presence of ultrasound, indicating that the direct electrochemical oxidation of the \( p \)-substituted phenols would be greatly improved by ultrasound. However, the ascending order of the phenols with regard to oxidation current \((\text{Ph}^-\text{OCH}_3 > \text{Ph}^-\text{CH}_3 > \text{Ph}^-\text{OH} > \text{Ph}^-\text{CHO} > \text{Ph}^-\text{NO}_2)\) was opposite to their ascending order in terms of disappearance rate during bulk electrolysis \((\text{Ph}^-\text{NO}_2 > \text{Ph}^-\text{CHO} > \text{Ph}^-\text{OH} > \text{Ph}^-\text{CH}_3 > \text{Ph}^-\text{OCH}_3)\) in the presence of ultrasound. Hence, it was deduced that the enhancement of \( p \)-substituted phenol disappearance rates during bulk electrolysis mainly was not due to improvement of direct electrochemical oxidation by ultrasound. This was most likely because direct electrochemical oxidation was not the main reaction during electrolysis processes, as also observed in previous studies. For the PbO\(_2\) electrode, the oxidation current and hence direct electrochemical oxidations of \( p \)-substituted phenols were hardly enhanced in the presence of ultrasound except for \( p \)-nitrophenol and \( p \)-methoxyphenol. This implies that the raised \( p \)-substituted phenol disappearance rates during bulk electrolysis at the PbO\(_2\) anode also mainly were not due to the increased direct electrochemical oxidation by ultrasound, which was most likely because direct electrochemical oxidation was not the main reaction during electrolysis processes at PbO\(_2\) electrodes.

In the presence of sulfates \((\text{SO}_4^{2-})\), peroxodisulfates \((\text{SO}_5\text{O}_2^{2-})\) form, of which a proportion decomposes to hydrogen peroxide and other oxidants at BDD anodes. In the present investigation, \(1^-/I_2\) assays were performed to measure the electrogenerated oxidants. Fig. 4 shows the evolution of electrogenerated oxidant concentration at the BDD and PbO\(_2\) electrodes in the absence and presence of ultrasound. More electrogenerated oxidants were generated at the BDD electrode than at the PbO\(_2\) electrode. However, the electrogenerated oxidant concentration in the presence of ultrasound was lower than that in the absence of ultrasound at both electrodes, which might be due to the lower stability of electrogenerated oxidants in the presence of ultrasound. These results indicate that enhancement of \( p \)-substituted phenol disappearance rates during bulk electrolysis was not due to better indirect electrochemical oxidation mediated by electrogenerated oxidants. It also confirmed that indirect electrochemical oxidation mediated by electrogenerated oxidant was not the main reaction at the BDD and PbO\(_2\) anodes, consistent with the previous study.

Therefore, it can be deduced that indirect electrochemical oxidation mediated by hydroxyl radicals was the main reaction at BDD and PbO\(_2\) anodes, and the improvement of \( p \)-substituted phenol disappearance could be mainly attributed to enhancement of this mechanism by ultrasound. Fig. 5 plots the time-evolution of the hydroxyl radical concentrations at the BDD and PbO\(_2\) anodes in the absence and the presence of ultrasound. It can be observed that hydroxyl radical concentration was higher in the presence than absence of ultrasound at both BDD and PbO\(_2\) electrodes, but the raise of hydroxyl radical concentration at the BDD anode was more obvious than at the PbO\(_2\) anode. The different increases of hydroxyl radical concentration obtained at the BDD and PbO\(_2\) anodes in the presence of ultrasound may be attributed to the effect of different types of hydroxyl radicals. At BDD electrodes, hydroxyl radicals mainly exist as free hydroxyl radicals due to their weak adsorption properties. Such hydroxyl radicals were present...
in the vicinity of BDD anode with a larger reaction zone. In the presence of ultrasound, RNO (trapping reagent of hydroxyl radicals) and phenols were quickly transported into the larger reaction zone to react with hydroxyl radicals due to the enhancement of mass transfer. Hence, ultrasound led to a larger increase of detected hydroxyl radical concentration and thus more rapid disappearance of \( \text{p-substituted phenols at BDD anode than at PbO}_2 \text{ anode. Instead, hydroxyl radicals at PbO}_2 \text{ electrodes exist in an adsorbed state since such electrodes have strong adsorption properties [12,14,26,27]. Such hydroxyl radicals were restricted on the anode surface with a smaller reaction zone. Although mass transfer was also greatly improved by ultrasound, the increase of detected hydroxyl radical concentration at PbO}_2 \text{ anode was lower and the enhancement of p-substituted phenol oxidation was not so obvious due to the smaller reaction zone.}

The above finding was further confirmed by the increasing linear relationship observed between the rate constant \( k \) of \( \text{p-substituted phenols and Hammett's constant (} \sigma \text{) at the BDD electrode (Fig. 6A), and between the rate constant (} k \text{) of p-substituted phenols and the initial surface concentration (} \Gamma \text{) at the PbO}_2 \text{ anode (Fig. 6C). Hammett's constant represents the effect of different substituents on the electronic character of a given aromatic system. A positive value of Hammett's constant indicates an electron-withdrawing group, while a negative value indicates an electron-donating group. They are obtained from the literature [47]. The initial surface concentration indicates the capacity of phenols to be adsorbed to the electrode surface, which was obtained from the linear sweep voltammograms of \( \text{p-substituted phenols at BDD and PbO}_2 \text{ electrodes at various potential scan rates (see [27] for more details).}

At the BDD electrodes, the hydroxyl radicals mainly exist as free hydroxyl radicals, which directly attack the substrates. Under the attack of hydroxyl radicals, the removal of \( \text{p-substituted groups from the aromatic ring was the rate-limiting step. Since electron-withdrawing groups are easily released, p-substituted phenols within these groups are degraded faster than those within electron-donating groups. Therefore, the disappearance rate of \( \text{p-substituted phenol increased monotonically with Hammett's constant (} Fig. 6A \text{) rather than with the initial surface concentration (} Fig. 6B \text{). In the presence of ultrasound, the already enhanced \( \text{p-substituted phenol disappearance rate was still increased with increasing Hammett's constant (} Fig. 6A \text{) rather than with increasing initial surface concentration (} Fig. 6B \text{). This implies that indirect electrochemical oxidation mediated by free hydroxyl radicals was significantly improved by ultrasound at the BDD anode.}

Fig. 6. Relationships (A) between rate constant \( k \) of \( \text{p-substituted phenol and Hammett's constant (} \sigma \text{), and (B) between rate constant (} k \text{) of \( \text{p-substituted phenol and the initial surface concentration (} \Gamma \text{) at the BDD electrode, (C) between rate constant (} k \text{) of p-substituted phenol and the initial surface concentration (} \Gamma \text{), and (D) between rate constant (} k \text{) of \( \text{p-substituted phenol and Hammett's constant (} \sigma \text{) at the PbO}_2 \text{ anode, in the absence (●) and the presence (○) of ultrasound.}
On the other hand, at the PbO$_2$ anode, hydroxyl radicals mainly existed as adsorbed hydroxyl radicals, and these adsorbed hydroxyl radicals reacted with $p$-substituted phenols on the anode surface. Hence, the disappearance rate of $p$-substituted phenol increased with the increase of initial surface concentration (Fig. 6C) rather than with the increase of Hammett’s constant (Fig. 6D). In the presence of ultrasound, the disappearance rate of $p$-substituted phenol was improved, and the disappearance rate still increased with the increase of initial surface concentration (Fig. 6C) rather than with the increase of Hammett’s constant (Fig. 6D), thus demonstrating that indirect electrochemical oxidation mediated by adsorbed hydroxyl radicals was improved by ultrasound at the PbO$_2$ anode.

Fig. 6 also shows that the increase in $p$-substituted phenol disappearance at the BDD anode was larger than that at the PbO$_2$ anode in the presence of ultrasound, confirming that ultrasound was more beneficial to indirect electrochemical oxidation mediated by free hydroxyl radicals than by adsorbed hydroxyl radicals. In addition, the higher gradient of the linear slope fitted to the data obtained in the presence of ultrasound at both BDD and PbO$_2$ anodes indicates the easier reaction was improved more obviously by ultrasound.

4. Conclusions

Electrochemical oxidation of $p$-substituted phenols was significantly improved by ultrasound at both the BDD and PbO$_2$ anodes. Moreover, it was found that the degree of enhancement was more obvious at BDD anodes than at PbO$_2$ anodes. At the BDD anode, the %Increase values were in the range 73–83% for $p$-substituted phenol disappearance and in the range 60–70% for COD removal. However, at the PbO$_2$ anode, the corresponding %Increase values were in the range 50–70% for disappearance of $p$-substituted phenols and only 5–25% for COD removal. Investigations on the influence of ultrasound on the electrochemical oxidation mechanisms at BDD and PbO$_2$ anodes revealed that the different enhancement extent mainly were due to the diverse effects of ultrasound on specialized types of hydroxyl radicals. Because hydroxyl radicals were mainly free at the BDD electrodes with a larger reaction zone and otherwise adsorbed at the PbO$_2$ electrodes with a smaller reaction zone, the enhancement by ultrasound was greater at the BDD anode than at the PbO$_2$ anode.

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Appendix A. Supplementary data


References