Degradation of Ibuprofen by the Electro/Fe$^{3+}$/Peroxydisulfate Process: Reactive Kinetics, Degradation Products and Mechanism

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Abstract: Ibuprofen (IBU), a nonsteroidal anti-inflammatory drug, is one of the most widely used and frequently detected pharmaceuticals and personal care products in water bodies. This study examined the IBU degradation in aquatic solutions via ferric ion activated peroxydisulfate (PDS) coupled with electro-oxidation (EC/Fe$^{3+}$/PDS). The degradation mechanisms involved three synergistic reactions in the EC/Fe$^{3+}$/PDS system, including: (1) the electro-oxidation; (2) SO$_4^{•−}$ generated from the activation of PDS by ferrous ions formed via cathodic reduction; (3) SO$_4^{•−}$ generated from the electron transfer reaction. The radical scavenging experiments indicated that SO$_4^{•−}$ and •OH dominated the oxidation process. The effects of the applied current density, PDS concentration, Fe$^{3+}$ dosage, initial IBU concentration and initial pH as well as inorganic anions and humic acid on the degradation efficiency, were studied, and the degradation process of IBU followed the pseudo-first-order kinetic model. About 99.37% of IBU was removed in 60 min ((Fe$^{3+}$ concentration) = 2.0 mM, (PDS concentration) = 12 mM, (initial IBU concentration) = 30 mg/L, current density = 15 mA/cm$^2$, initial pH = 3). Finally, seven intermediate compounds were identified and probable IBU degradation pathways in the EC/Fe$^{3+}$/PDS system were speculated.

Keywords: sulfate radicals; hydroxyl radicals; electro-oxidation; mechanism; degradation

1. Introduction

Ibuprofen (IBU), a non-steroidal anti-inflammatory drug, is extensively used to treat fever and pain, including muscle aches, tooth aches, headache pain and arthritis pain [1,2]. The annual global production of IBU was more than 30 kilotons due to its widespread utilization in aquaculture, domestic, hospitals and pharmaceutical industries [3]. IBU has been frequently found in municipal and hospital wastewater with concentrations of up to 83 µg/L [4]. Conventional wastewater treatment technologies (e.g., activated sludge, coagulation and filtration) are usually not effective to remove IBU, resulting in the relatively high concentration of IBU in wastewater treatment plants (WWTPs) effluents [5–7]. Constant discharge of IBU into the aquatic environment may pose threat to human health and affect the safety and balance of the aquatic ecosystem [8,9]. For instance, IBU could change the intestinal microbial composition of humans via long-term consumption [10] and the endocrine system could be altered by IBU, inducing compensated hypogonadism in men [11]. Moreover, apoptosis and a decrease in proliferating cells of humans might occur after exposure to 10–100 µmol/L of IBU [12]. As reported, IBU may pose acute toxicity to the reproduction of some aquatic organisms, for example, Japanese medaka and zebrafish [10,13]. Additionally, IBU could promote cyanobacteria and reduce the eukaryotic algae biomass, resulting in algal blooms in freshwaters [14]. IBU also had an adverse
impact on the reproduction and the survival of *Oryzias latipes* as well as the growth of algae *Synechocystis* sp. [15]. Therefore, the development of suitable technologies for removing the IBU efficiently from water is of great urgency.

Recently, advanced oxidation methods, involving the generation of hydroxyl radical (•OH), sulfate radical (SO4•−), were considered as effective technologies for the treatment of IBU [16–18]. Compared with •OH (E0 = 2.8 V), SO4•− also exhibits strong oxidizing ability (E0 = 2.5–3.1 V) [19–21]. Furthermore, SO4•− has longer lifetimes (1 µs for •OH vs. 30–40 µs for SO4•−), higher selectivity, as well as a broad operative range of pH. Generally, SO4•− is produced by activating peroxymonosulfate (PMS) or peroxydisulfate (PDS) with transition metals, heat, UV, electrochemical and ultrasound. Parallel to other transition metals, Fe2+ has been commonly used for the activation of PDS (Equation (1)) since it is inexpensive, effective and environmentally friendly [22].

$$\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2−} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{•−} + \text{SO}_4^{2−}$$ (1)

However, some drawbacks of the Fe2+/PDS process hinder its application [23]. Firstly, Fe2+ could not be regenerated after transformation to Fe3+, leading to a high Fe2+ dosage requirement to maintain the reaction. As a result, the process produces a larger amount of iron sludge [24]. Secondly, excessive Fe2+ would act as a scavenger for SO4•− (Equation (2)). Finally, Fe2+ is readily converted to Fe3+ in the existence of oxygen in the air. The above drawbacks could be solved by the coupling of the Fe3+/PDS system with the electrochemical system (EC/Fe3+/PDS). In the EC/Fe3+/PDS system, Fe2+ could be regenerated from Fe3+ reduction at the cathode (Equation (3)), reducing the addition of the Fe concentration. Moreover, SO4•− could be generated in the electrochemical system by an electron transfer reaction of PDS (Equation (4)). Meanwhile, •OH could be produced on the surface of the dimensionally stable anode (DSA) (Equation (5)), enhancing the degradation process [25].

$$\text{SO}_4^{•−} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2−}$$ (2)

$$\text{Fe}^{3+} + \text{e}^{−} \rightarrow \text{Fe}^{2+}$$ (3)

$$\text{S}_2\text{O}_8^{2−} + \text{e}^{−} \rightarrow \text{SO}_4^{•−} + \text{SO}_4^{2−}$$ (4)

$$\text{M(H}_2\text{O}) \rightarrow \text{M(•OH)} + \text{H}^{+} + \text{e}^{−}$$ (5)

Previous studies have demonstrated IBU removal in the Fe/PS system or in the electro-oxidation system [26–28]. However, to the best of our knowledge, the system of electro-oxidation combined with Fe/PDS has never been applied to the degradation of IBU. It is expected that the coupling system would overcome the disadvantages of the Fe/PDS system, and reduce the reaction time of electro-oxidation, leading to lower energy consumption. Noteworthy, abundant inorganic anions (HCO3−, Cl−, NO3−, H2PO4−) and humic acids (HA) as natural organic matter (NOM) exist in water and waste water. Nevertheless, the effect of these co-existing substances on IBU removal in the processes based on the electrochemical technology, especially in the EC/Fe3+/PDS system, was rarely mentioned in the previous literature, limiting their application in the aquatic environment.

Therefore, the objective of this study was to supplement the knowledge gaps as aforementioned. Firstly, the feasibility of IBU degradation using the EC/Fe3+/PDS system was determined and the influencing factors of current density, PDS concentration, Fe3+ concentration, initial IBU concentration, initial pH, inorganic anions and humic acid on the degradation of IBU were systematically explored. Additionally, the degradation kinetics were also investigated. Moreover, the reaction by-products of IBU and major reactive oxygen species involved in the EC/Fe3+/PDS system were determined. Finally, the reaction mechanism of the EC/Fe3+/PDS system and IBU degradation pathways were proposed.
2. Results and Discussion

2.1. Comparative Study of Different Processes

IBU removal was carried out in various processes: PDS alone, electro-oxidation (EC), EC/PDS, the Fe\(^{3+}\)/PDS process, EC/Fe\(^{3+}\) and EC/Fe\(^{3+}\)/PDS system (Figure 1). The kinetic model of the EC/Fe\(^{3+}\)/PDS system for IBU degradation was investigated by the pseudo-first-order according to Equation (6) [29].

\[
\ln \frac{C}{C_0} = -kt
\]  (6)

where \(k\) represents the rate constant for IBU removal, min\(^{-1}\); \(C_0\) refers to the initial IBU concentration and \(C_t\) refers to the IBU concentration at time \(t\), mg/L; \(t\) is the reaction time, min. As shown in Table 1, the degradation kinetics of IBU obeyed the pseudo-first-order model according to the correlation coefficient values (R\(^2\) > 0.97). As illustrated in Figure 1, PDS alone could hardly oxidize IBU, and the remaining PDS accounted for 98.0% of the initial PDS concentration. The reason was that PDS was stable and the oxidation capability of PDS was limited (E\(_0\) = 2.01) at an ambient temperature [21,30]. The IBU removal in the Fe\(^{3+}\)/PDS process was nearly the same as that in the presence of PDS alone, and the remaining percentage of PDS was 97.6%, indicating that Fe\(^{3+}\) could hardly activate PDS to generate reactive radicals. A previous study also reported the low effectiveness of the Fe\(^{3+}\)/PDS system in iohexol degradation [31]. In the EC process, about 50.91% of IBU was eliminated and the \(k\) value was 0.0120 min\(^{-1}\). The result of cyclic voltammograms for RuO\(_2\)-IrO\(_2\)/Ti was shown in Figure 2. As observed, no obvious oxidation or reduction peaks could be identified. This phenomenon indicated that the degradation of IBU was attributed to the indirect oxidation process by \(\bullet\)OH formed by water discharge at the surface of the DSA anode [25]. The introduction of Fe\(^{3+}\) into the electro-oxidation process formed the electro-Fenton (EF) reaction, and generated little amounts of \(\bullet\)OH, accelerating the IBU removal [32]. However, these hydroxyl radicals were insufficient to completely degrade IBU over a 60 min reaction. The combination of EC and PDS slightly improved the removal of IBU (60.12%) due to the SO\(_4^{2-}\) generated through the reaction of electron transfer (Equation (4)). In this case, the remaining percentage of PDS was 69.5%. Remarkably, the removal of IBU achieved 90.91% and the residual percent of PDS was 46.1% in the EC/Fe\(^{3+}\)/PDS system. This was because Fe\(^{2+}\) could be formed by the cathodic reduction of Fe\(^{3+}\), and then sulfate radicals could be continuously formed by the reaction between Fe\(^{2+}\) and PDS, thus enhancing the degradation process.

![Figure 1](image-url)  
**Figure 1.** IBU removal (a) and remaining percentage of PDS (b) under different systems; ((initial IBU concentration) = 30 mg/L, (Fe\(^{3+}\) concentration) = 1 mM, (PDS concentration) = 8 mM, current density = 15 mA/cm\(^2\), initial pH = 3).
Table 1. The kinetics for IBU degradation in the EC/Fe$^{3+}$/PDS system.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>EC/Fe$^{3+}$/PDS</th>
<th>EC</th>
<th>EC/Fe$^{3+}$</th>
<th>EC/PDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>k (min$^{-1}$)</td>
<td>0.0408</td>
<td>0.0120</td>
<td>0.0143</td>
<td>0.0150</td>
</tr>
<tr>
<td>Half-Life ($t_{1/2}$, min)</td>
<td>16.99</td>
<td>57.76</td>
<td>48.47</td>
<td>46.21</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.994</td>
<td>0.998</td>
<td>0.997</td>
<td>0.994</td>
</tr>
</tbody>
</table>

| PDS concentration (mM)       | 6               | 8           | 10          | 12     | 14     |
| k (min$^{-1}$)               | 0.0215          | 0.0408      | 0.0482      | 0.0508 | 0.0457 |
| Half-Life ($t_{1/2}$, min)   | 32.24           | 16.99       | 14.38       | 13.64  | 15.17  |
| $R^2$                        | 0.996           | 0.994       | 0.994       | 0.995  | 0.994  |

| Fe$^{3+}$ concentration (mM) | 0.5             | 1.0         | 1.5         | 2.0    | 2.5    |
| k (min$^{-1}$)               | 0.0255          | 0.0508      | 0.0598      | 0.0851 | 0.0657 |
| Half-Life ($t_{1/2}$, min)   | 27.18           | 13.64       | 11.59       | 8.15   | 10.55  |
| $R^2$                        | 0.988           | 0.995       | 0.997       | 0.983  | 0.995  |

| Current density (mA/cm$^2$)  | 5               | 10          | 15          | 20     |
| k (min$^{-1}$)               | 0.0193          | 0.0364      | 0.0851      | 0.0829 |
| Half-Life ($t_{1/2}$, min)   | 35.91           | 19.04       | 8.15        | 8.36   |
| $R^2$                        | 0.993           | 0.996       | 0.983       | 0.979  |

| IBU concentration (mg/L)     | 30              | 40          | 50          | 60     |
| k (min$^{-1}$)               | 0.0851          | 0.0507      | 0.0356      | 0.0277 |
| Half-Life ($t_{1/2}$, min)   | 8.15            | 13.67       | 19.47       | 25.02  |
| $R^2$                        | 0.983           | 0.993       | 0.986       | 0.981  |

| pH                            | 3               | 5           | 7           | 9      |
| k (min$^{-1}$)                | 0.0851          | 0.0640      | 0.0465      | 0.0345 |
| Half-Life ($t_{1/2}$, min)    | 8.15            | 10.83       | 14.91       | 20.09  |
| $R^2$                        | 0.983           | 0.987       | 0.982       | 0.987  |

Figure 2. Cyclic voltammograms of RuO$_2$-IrO$_2$/Ti in 0.5 mol/L Na$_2$SO$_4$ solutions in the presence and absence of IBU (30 mg/L) at a scan rate of 10 mV/s.

2.2. Impact Factors

2.2.1. The Effect of PDS Concentration

PDS is the main source for the generation of SO$_4$$^{•−}$$. Thus, the influence of initial PDS concentration on IBU removal efficiency was displayed in Figure 3a. The IBU removal raised gradually from 73.45% to 94.91% with the PDS concentration increasing from 6 to 12 mM, and the $k$ value increasing from 0.0215 min$^{-1}$ to 0.0508 min$^{-1}$. However, the removal of IBU declined to 93.37% as the PDS concentration further increased. Previous studies have also reported that raising the PDS concentration to a certain value could generate more reactive radicals [33,34], resulting in acceleration of the decomposition of IBU. Whereas, in accordance with the literature [35,36], excessive addition of PDS could...
reduce the degradation efficiency due to the self-quenching reactions of reactive radicals as well as their reaction with PDS (Equations (7)–(11)). Therefore, 12 mM was used as an optimum value of PDS for the downstream experiments.

\[
\begin{align*}
\text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \quad (7) \\
\cdot\text{OH} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{OH}^- + \text{S}_2\text{O}_8^{2-} \quad (8) \\
\text{SO}_4^{2-} + \text{SO}_4^{2-} & \rightarrow \text{S}_2\text{O}_8^{2-} \quad (9) \\
\cdot\text{OH} + \text{SO}_4^{2-} & \rightarrow \text{HSO}_5^- \quad (10) \\
\cdot\text{OH} + \cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad (11)
\end{align*}
\]

Figure 3. Effect of PDS concentration (a), Fe\textsuperscript{3+} concentration (b), current density (c), initial IBU concentration (d), initial pH (e), inorganic anions and HA (f) on IBU removal. ((initial IBU concentration) = 30 mg/L, (Fe\textsuperscript{3+} concentration) = 1 mM, current density = 15 mA/cm\textsuperscript{2}, initial pH = 3; (initial IBU concentration) = 30 mg/L, (PDS concentration) = 12 mM, current density = 15 mA/cm\textsuperscript{2}, initial pH = 3; (initial IBU concentration) = 30 mg/L, (Fe\textsuperscript{3+} concentration) = 2 mM, (PDS concentration) = 12 mM, current density = 15 mA/cm\textsuperscript{2}, initial pH = 3; (initial IBU concentration) = 30 mg/L, (Fe\textsuperscript{3+} concentration) = 2 mM, (PDS concentration) = 12 mM, current density = 15 mA/cm\textsuperscript{2}, initial pH = 3; (initial IBU concentration) = 30 mg/L, (Fe\textsuperscript{3+} concentration) = 2 mM, (PDS concentration) = 12 mM, current density = 15 mA/cm\textsuperscript{2}, initial pH = 3; (initial IBU concentration) = 30 mg/L, (Fe\textsuperscript{3+} concentration) = 2 mM, (PDS concentration) = 12 mM, current density = 15 mA/cm\textsuperscript{2}, initial pH = 3).
2.2.2. The Effect of the Initial Fe\(^{3+}\) Concentration

The influence of the Fe\(^{3+}\) concentration on the degradation of IBU was performed (Figure 3b). Increasing the Fe\(^{3+}\) concentration from 0.5 mM to 2 mM meant the IBU removal increased from 78.24% to 99.37%, while the \(k\) value augmented from 0.0255 min\(^{-1}\) to 0.0851 min\(^{-1}\). The upward trend of removal efficiency implied that increasing Fe\(^{3+}\) could generate more Fe\(^{2+}\) to activate PDS to degrade the IBU molecules. The continuing increase in the Fe\(^{3+}\) concentration up to 2.5 mM caused a slight decrease in IBU removal (97.83%) as well as the \(k\) value (0.0657 min\(^{-1}\)). This result could be attributed to the scavenging of reactive radicals by the redundant Fe\(^{2+}\) (Equations (12) and (13)).

\[
\text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad (12)
\]

\[
\cdot\text{OH} + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+} \quad (13)
\]

2.2.3. The Effect of Current Density

As is well known, in the electrochemical process, current density plays a vital role in organic contaminant degradation. The influence of current density (5–20 mA/cm\(^2\)) was investigated and displayed in Figure 3c. By raising the current density from 5 mA/cm\(^2\) to 15 mA/cm\(^2\), the IBU removal increased from 67.33% to 99.37%, and the \(k\) value increased progressively from 0.0193 min\(^{-1}\) to 0.0851 min\(^{-1}\). Higher current density would enhance the cathodic reduction of Fe\(^{3+}\) according to Equation (3), and then accelerate the decomposition of PDS to form active radicals [37]. Moreover, at the cathode, higher current density would strengthen the electron transfer to activate PDS, resulting in more generation of sulfate radicals. Meanwhile, higher current density promoted the generation of hydroxyl radicals at the anode. However, the removal of IBU and \(k\) value dropped to 99.30% and 0.0829 min\(^{-1}\), respectively, as the current density further increased to 20 mA/cm\(^2\). This phenomenon was attributed to the occurrence of side reactions initiated by the higher current density, such as the reaction of H\(_2\) evolution at the cathode (Equation (14)) and O\(_2\) evolution at the anode (Equation (15)) [32,38,39]. These side reactions would compete with the IBU removal, PDS activation and Fe\(^{3+}\) reduction.

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (14)
\]

\[
4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \quad (15)
\]

2.2.4. The Effect of the Initial IBU Concentration

The IBU removal and the \(k\) value gradually decreased with the increment of its concentration (Figure 3d). This result was in accordance with the finding of Shen et al. [9]. As the initial IBU concentration was elevated from 30 mg/L to 60 mg/L, the IBU removal and the \(k\) value reduced from 99.37% and 0.0851 min\(^{-1}\) to 81.07% and 0.0277 min\(^{-1}\), respectively. The reactive radicals generated were relatively stable when the PDS concentration, Fe\(^{3+}\) dosage and current density were fixed. However, higher amounts of intermediates could be formed at higher initial IBU concentration, which would compete for reactive radicals with the IBU molecules, slowing the decomposition of the IBU.

2.2.5. The Effect of the Initial pH

As displayed in Figure 3e, the influence of solution pH on IBU removal was carried out in the range of 3–9. The IBU removal dropped from 99.37% to 88.12% as the pH increased from 3 to 9, correspondingly, the \(k\) value dropped from 0.0851 min\(^{-1}\) to 0.0345 min\(^{-1}\). Clearly, an acidic pH facilitated the removal of IBU in this system, which agreed with that of recent studies via the EC/Fe/PS system [40,41]. The phenomenon was interpreted by the following aspects. In acidic conditions, the presence of H\(^+\) enhanced the formation of sulfate radicals in accordance with Equations (16) and (17) [42]. On the other hand, at higher pH levels, ferrous ions can be precipitated in the formation of ferric hydroxide, leading to the decrease in soluble Fe\(^{2+}\), thereby suppressing the activation of PDS [43].
In addition, under alkaline conditions, the $\text{SO}_4^{2-}$ could convert to $\text{•OH}$ by reacting with $\text{OH}^-$. The lifetime of $\text{•OH}$ was shorter in comparison with $\text{SO}_4^{2-}$. In addition, the standard oxidation potential of $\text{•OH}$ was 2.7 V under acidic conditions, while the standard oxidation potential of $\text{•OH}$ was only 1.8 V with neutral conditions [44], indicating that the oxidation ability of $\text{•OH}$ was stronger at a lower pH level.

$$\text{H}^+ + \text{S}_2\text{O}_5^2^- \rightarrow \text{HS}_2\text{O}_5^-$$  \hspace{1cm} (16)

$$\text{HS}_2\text{O}_5^- \rightarrow \text{H}^+ + \text{SO}_4^{2-} + \text{SO}_3^{2-}$$  \hspace{1cm} (17)

### 2.2.6. Effect of Co-Existing Components

It should be noted that the water and waste water had abundant inorganic anions ($\text{HCO}_3^-$, $\text{Cl}^-$, $\text{NO}_3^-$, $\text{H}_2\text{PO}_4^-$) and humic acids (HA) as natural organic matter (NOM). Hence, it is of great importance to investigate their effects on IBU removal in the EC/Fe$^{3+}$/PDS system. The experiments were performed with 10 mM inorganic anions and 10 mg/L HA, respectively (Figure 3f). Inorganic anions inhibited the IBU removal, and the inhibitive effect of inorganic anions on IBU removal kept the ascending order: $\text{HCO}_3^-$, $\text{HA}$, respectively (Figure 3f). Inorganic anions inhibited the IBU removal, and the inhibitive effect of inorganic anions on IBU removal kept the ascending order: $\text{HCO}_3^-$, $\text{HA}$, respectively (Figure 3f). Inorganic anions inhibited the IBU removal, and the inhibitive effect of inorganic anions on IBU removal kept the ascending order: $\text{HCO}_3^-$, $\text{HA}$, respectively (Figure 3f).

At the anode, the $\text{Cl}^-$ could be oxidized to free chlorine (e.g., $\text{HClO}$, $\text{ClO}^-$) with weaker oxidation capacity. This was a side reaction compared with the production of $\text{•OH}$ at the anode. $\text{Cl}^-$ could consume $\text{SO}_4^{2-}$ and $\text{•OH}$ to form less reactive radicals ($\text{Cl•}$ and $\text{HOCI•}$) ((Equations (18) and (19)) [45]. As previous reports demonstrate, the occurrence of complexation reactions of $\text{Cl}^-$ with $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ generated $\text{FeCl}_2^+$, $\text{FeCl}^+$, etc, reducing the concentration of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ [46], and consequently weakening the removal of IBU.

$$\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl•}$$  \hspace{1cm} (18)

$$\text{•OH} + \text{Cl}^- \rightarrow \text{HOCI•}^-$$  \hspace{1cm} (19)

There are two reasons for a slightly decreasing trend caused by $\text{NO}_3^-$. (1) $\text{NO}_3^-$ could compete with IBU for the $\text{•OH}$ and $\text{SO}_4^{2-}$, leading to the formation of some inactive radicals ($\text{Cl•}$ and $\text{HOCI•}$) ((Equations (20) and (21)) [47]; (2) The addition of $\text{NO}_3^-$ increased the ion strength of the solution, resulting in a slower decomposition of PDS.

$$\text{SO}_4^{2-} + \text{NO}_3^- \rightarrow \text{SO}_4^{2-} + \text{NO}_3^-$$  \hspace{1cm} (20)

$$\text{•OH} + \text{NO}_3^- \rightarrow \text{OH}^- + \text{NO}_3^-$$  \hspace{1cm} (21)

The inhibition of $\text{HCO}_3^-$ could be explained as follows: the reaction of $\text{•OH}$ and $\text{SO}_4^{2-}$ with $\text{HCO}_3^-$, leading to the production of less reactive radical ($\text{CO}_3^{2-}$) ((Equations (22) and (23)) [48]. (2) $\text{HCO}_3^-$ could affect the involved oxidation reactions by changing the solution pH. As discussed above, increasing the pH had a negative effect on the oxidation process.

$$\text{HCO}_3^- + \text{•OH} \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$$  \hspace{1cm} (22)

$$\text{HCO}_3^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{H}^+$$  \hspace{1cm} (23)

The negative effect of $\text{H}_2\text{PO}_4^-$ was related to the scavenging effect ((Equations (24) and (25)) [49]. In addition, the formation of $\text{H}_2\text{PO}_4^-$-Fe complexes species decreased the active iron ions, inducing inhibition of the degradation process.

$$\text{H}_2\text{PO}_4^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{PO}_4^+$$  \hspace{1cm} (24)

$$\text{H}_2\text{PO}_4^- + \text{•OH} \rightarrow \text{OH}^- + \text{H}_2\text{PO}_4^+$$  \hspace{1cm} (25)

Besides the inorganic anions, the HA had a detrimental influence on IBU removal. The removal of IBU decreased from 99.37% to 90.50% after the addition of 10 mg/L HA.
HA, rich in carboxyl and hydroxyl functional groups, usually acts as a scavenger of SO\textsuperscript{4}\textsuperscript{•−} and •OH due to the high reactivity towards •OH (k\textsubscript{•OH/HA} = 1.39 × 10\textsuperscript{8} M\textsuperscript{−1}S\textsuperscript{−1}) and SO\textsuperscript{4}\textsuperscript{•−} /HA = 7.8 × 10\textsuperscript{7} M\textsuperscript{−1}S\textsuperscript{−1}) \[50,51\]. Aside from the ability to quench radicals, it is easier to seize the dissolved Fe\textsuperscript{2+} and Fe\textsuperscript{3+} owing to the feature of a strong ligand, leading to the decrease in IBU removal \[52\].

Overall, the effects of inorganic ions and HA on the IBU degradation should be adequately considered.

2.3. Comparison with Other Technologies

The energy consumption of the EC/process was assessed by the electrical efficiency per log order (EE/O) according to Equation (26) \[53\].

\[
\text{EE/O (Wh/L)} = \frac{U \times I \times t}{V \times \log(C_0/C_t)} \quad (26)
\]

where U is the recorded average electrolysis voltage (V), V is volume (L), I is the electrolysis current (A), t is the electrolysis time (h).

Moreover, the energy efficiency was estimated by Equation (27) \[54\].

\[
\text{Energy efficiency (mg/Wh)} = \frac{m}{U \times I \times t} \quad (27)
\]

where U is the recorded average electrolysis voltage (V), I is the electrolysis current (A), t is the electrolysis time (h), m is the amount of contaminant degraded (mg).

The EE/O of the EC/Fe\textsuperscript{3+}/PDS process was 2.79 Wh/L, which was lower than the EE/O for electro-oxidation of IBU by Ti/SnO\textsubscript{2}-Sb/Ce-PbO\textsubscript{2} (4.3–30.6 Wh/L) \[2\]. Moreover, the energy efficiency was 8.15 mg/Wh in our study, which was much higher than the decomposition of IBU by ozonation (2.15 mg/Wh) or by DBD plasma (2.5 mg/Wh) \[55\]. Moreover, the degradation performance of the EC/Fe\textsuperscript{3+}/PDS system was compared with other technologies. As can be seen from Table 2, the EC/Fe\textsuperscript{3+}/PDS system performed better in IBU removal than other methods, indicating that the EC/Fe\textsuperscript{3+}/PDS system is a potential technology for IBU degradation in water.

Table 2. Comparison with other technologies for IBU degradation.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Experimental Conditions</th>
<th>IBU Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro-oxidation (Ti/SnO\textsubscript{2}-Sb/Ce-PbO\textsubscript{2})</td>
<td>V = 30 mL; IBU = 20 mg/L; current density = 10 mA/cm\textsuperscript{2}</td>
<td>90% removal in 60 min</td>
<td>[2]</td>
</tr>
<tr>
<td>BaTiO\textsubscript{3}/PDS under ultrasonic-wave</td>
<td>V = 25 mL; PS = 1.0 mM; IBU = 6.0 mg/L; BaTiO\textsubscript{3} = 2.0 g/L</td>
<td>99% removal in 60 min</td>
<td>[7]</td>
</tr>
<tr>
<td>Electro-Fenton</td>
<td>V = 200 mL; IBU = 10 mg/L; pH = 3.0; Fe\textsuperscript{2+} = 0.7 mM</td>
<td>94.8% removal in 150 min</td>
<td>[56]</td>
</tr>
<tr>
<td>UV/H\textsubscript{2}O\textsubscript{2}</td>
<td>IBU = 10 µM; H\textsubscript{2}O\textsubscript{2} = 0.5 mM; pH = 5.2</td>
<td>95% removal in 240 min</td>
<td>[57]</td>
</tr>
<tr>
<td>Photo-Fenton (HSO\textsubscript{3}-MIL-53(Fe))</td>
<td>V = 50 mL; IBU = 10 mg/L; H\textsubscript{2}O\textsubscript{2} = 20 mM; HSO\textsubscript{3}-MIL-53(Fe) = 200 mg/L; pH\textsubscript{0} = 8.0</td>
<td>100% removal in 90 min</td>
<td>[58]</td>
</tr>
<tr>
<td>Photocatalysis (phosphorus and sulfur co-doped graphitic carbon nitride (PSGCN) and AgBr particle)</td>
<td>Photocatalyst = 100 mg/100 mL; IBU = 15 mg/L</td>
<td>90% removal in 100 min</td>
<td>[59]</td>
</tr>
<tr>
<td>EC/Fe\textsuperscript{3+}/PDS</td>
<td>V = 200 mL; pH = 3; IBU = 30 mg/L; current density = 10 mA/cm\textsuperscript{2}; Fe\textsuperscript{3+} = 2.0 mM; PDS = 12 mM</td>
<td>99.37% removal in 60 min</td>
<td>this work</td>
</tr>
</tbody>
</table>

2.4. Determination of Reactive Species

Quenching experiments were conducted to determine the generation of reactive radicals. Methanol (MA) was utilized as a capturer for both SO\textsuperscript{4}\textsuperscript{•−} and •OH, as it had similar quenching rate with •OH (k\textsubscript{•OH/MA} = 9.7 × 10\textsuperscript{8} M\textsuperscript{−1}S\textsuperscript{−1}) and SO\textsuperscript{4}\textsuperscript{•−} /MA = 7.8 × 10\textsuperscript{7} M\textsuperscript{−1}S\textsuperscript{−1} \[50,51\].
1.61 × 10^7 M^{-1}S^{-1}) [60,61]. Tert-butyl alcohol (TBA) was regarded as •OH scavenger (k_{•OH/TBA} = 9.7 × 10^8 M^{-1}S^{-1}) as its rate constant with •OH was approximately 1000-fold times than that for SO_4^{•−} [62]. As displayed in Figure 4, both MA and TBA inhibited IBU removal. Specifically, the removal of IBU reached 99.37%, whereas it decreased to 29.36% and 63.92% after the addition of MA and TBA. The result indicated that both SO_4^{•−} and •OH participated in the process, and the contribution of SO_4^{•−} and •OH for IBU degradation in the EC/Fe^{3+}/PDS system was almost equal.

![Figure 4. Effect of TBA and MA on IBU degradation. ((initial IBU concentration) = 30 mg/L, (Fe^{3+} concentration) =2 mM, (PDS concentration) =12 mM, current density =15 mA/cm^2, initial pH = 3, (MA concentration) = 500 mM, (TBA concentration) = 500 mM).](image)

2.5. Proposed Mechanism of the EC/Fe^{3+}/PDS Process

According to the results and previous reports, the reaction mechanism of the EC/Fe^{3+}/PDS process was proposed (Figure 5). Fe^{2+} could be reproduced from the reduction of Fe^{3+} at the cathode, and then activated PDS to produce SO_4^{•−}. What is more, SO_4^{•−} could be generated by an electron transfer reaction. Additionally, •OH could be produced on the surface of the DSA anode, enhancing the degradation process. SO_4^{•−} could be converted to •OH by reacting with H_2O and OH−. Finally, IBU was degraded to CO_2 and H_2O by the oxidation of both SO_4^{•−} and •OH.

![Figure 5. Reaction mechanism of the EC/Fe^{3+}/PDS system.](image)

2.6. Oxidation Products and Proposed Pathway of IBU Degradation

The degradation intermediates of IBU were identified using LC-MS/MS. Consequently, a total of seven intermediates were determined (Figure 6). The chemical structure, reaction time, molecular formula and weight of IBU degradation products were summarized in Table 3, and the oxidation pathways of IBU degradation were presented in Figure 7.
Table 3. Main intermediates for the degradation of IBU in the EC/Fe\textsuperscript{3+}/PDS system.

<table>
<thead>
<tr>
<th>Product</th>
<th>Reaction Time</th>
<th>Molecular Weight</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBU</td>
<td>6.24</td>
<td>206</td>
<td><img src="" alt="IBU Chemical Structure" /></td>
</tr>
<tr>
<td>P1</td>
<td>5.26</td>
<td>222</td>
<td><img src="" alt="P1 Chemical Structure" /></td>
</tr>
<tr>
<td>P2</td>
<td>2.81</td>
<td>164</td>
<td><img src="" alt="P2 Chemical Structure" /></td>
</tr>
<tr>
<td>P3</td>
<td>3.40</td>
<td>134</td>
<td><img src="" alt="P3 Chemical Structure" /></td>
</tr>
<tr>
<td>P4</td>
<td>5.36</td>
<td>222</td>
<td><img src="" alt="P4 Chemical Structure" /></td>
</tr>
<tr>
<td>P5</td>
<td>6.54</td>
<td>178</td>
<td><img src="" alt="P5 Chemical Structure" /></td>
</tr>
<tr>
<td>P6</td>
<td>7.53</td>
<td>150</td>
<td><img src="" alt="P6 Chemical Structure" /></td>
</tr>
<tr>
<td>P7</td>
<td>8.52</td>
<td>118</td>
<td><img src="" alt="P7 Chemical Structure" /></td>
</tr>
</tbody>
</table>

Figure 6. Mass spectra of the products generated during the degradation of IBU in EC/Fe\textsuperscript{3+}/PDS system.
where C
subscript\text{water} (18 M/v/v) Acetonitrile (A) and water containing 0.1\% acetic acid were used as the mobile phase, at a flow rate of 0.3 mL/min. The UV-visible detector was set at 220 nm. A mixture of 63:37 (v/v) acetonitrile/water (containing 0.1\% acetic acid) was used as the mobile phase, at a flow rate of 1.0 mL/min. The byproducts were analyzed with a Waters Acquity UPLC-QTOF-MS/MS (Xevo G2) system, operating in a negative ion mode with an electrospray ionization source. A Waters Acquity UPLC BEH C18 column (50 mm \times 2.1 mm, 1.7 \mu m) was used to separate chromatograph. The mobile phase was composed of acetonitrile (A) and water containing 0.1\% formic acid (B), with 0.3 mL/min flow rate. Component B was maintained at 10\% during the first 1 min, then B was changed to 100\% in 1–10 min. Finally, component B returned to 10\% during the last 2 min.

The degradation efficiency is calculated by the Equation (28) [67].

\[
\text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \tag{28}
\]

where \(C_0\) refers to the initial IBU concentration and \(C_t\) refers to the IBU concentration at time \(t\), mg/L.
3.3. Experimental Procedure

The removal of IBU was performed in an undivided 250 mL glass beaker which contained 200 mL of IBU solution. The glass beaker was immersed in a water bath to keep the temperature constant at 25 °C. The reaction solution was mixed continuously with a magnetic stirrer. The schematic of EC/Fe\(^{3+}\)/PDS system was shown in Figure 8. A RuO\(_2\)-IrO\(_2\)/Ti mesh (3 cm × 5 cm) was applied as anode while Ti plate (3 cm × 5 cm) was served as cathode. 0.05 mol/L Na\(_2\)SO\(_4\) was applied as supporting electrolyte. Ferric sulfate (Fe\(_2\)(SO\(_4\))\(_3\)) was employed to provide Fe\(^{3+}\) to avoid the interference of other anions. The distance between the anode and the cathode was maintained as 1.5 cm. The solutions were unbuffered to avoid the quenching effect of buffers, and the initial pH of the IBU solution was adjusted with H\(_2\)SO\(_4\) and NaOH (0.1 mol/L) and measured with a pH meter (FE28-CN, Mettler Toledo). A digital DC power (DH1718E-5, 35 V, 5 A, Dahua Electronic Co., Beijing, China) was used to provide constant electric current for electrochemical experiments. After addition of a certain amount of PDS and Fe\(^{3+}\) solution, the DC power supply was started immediately. Periodically, reaction solution samples (2 mL) were withdrawn and directly filtered using a 0.45 µm microfiltration membrane and quenched with methanol before analysis. All the experiments were performed in triplicate.

![Figure 8. Schematic of the EC/Fe\(^{3+}\)/PDS system.](image)

The cyclic voltammetry was performed using an electrochemical workstation (Chenhua, CHI 660, China) equipped with a typical three-electrode system. The Ti (10 mm × 20 mm) was used as the working electrode. A platinum plate (10 mm × 20 mm) was employed as the counter electrode. The Ag/AgCl electrode was employed as the reference electrode. The cyclic voltammetry experiment was conducted at room temperature with the absence of 30 mg/L IBU in 0.5 mol/L Na\(_2\)SO\(_4\). The scan rate was set at 10 mV/s.

4. Conclusions

An electro-assisted Fe\(^{3+}\)/PDS process (EC/Fe\(^{3+}\)/PDS) was investigated for IBU degradation in an aqueous solution. The combination of Fe\(^{3+}\)/PDS and electro-oxidation was displayed to be effective to degrade IBU. The synergistic effect was attributed to the following aspects: (1) the electro-oxidation; (2) sulfate radicals generated from the activation of PDS by ferrous ions formed via cathodic reduction; (3) sulfate radicals generated from the electron transfer reaction. Free radicals quenching experiments revealed that both SO\(_4^{2-}\) and \(\cdot\)OH contributed to the excellent removal of IBU. Based on the above analysis, the enhanced catalytic mechanism was also elucidated. Furthermore, increasing the current density (5–15 mA/cm\(^2\)), PDS concentration (6–12 mM) or Fe\(^{3+}\) concentration (0.5–2 mM) enhanced the IBU degradation while a slight inhibitory effect was obtained with a further increase in these parameters. Compared with neutral and alkaline conditions, an acidic pH facilitated the IBU degradation. Moreover, the removal of IBU decreased with increasing the initial IBU concentration. All degradation processes of IBU in the system followed the pseudo-first order reaction kinetic models. At optimum conditions ((Fe\(^{3+}\) concentration) = 2.0 mM, (PDS concentration) = 12 mM, (initial IBU concentration)
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