Removal of Organic and Ammonium Nitrogen Pollutants in Swine Wastewater Using Electrochemical Advanced Oxidation

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In this study, tests were performed to examine the effects of with/without chloride addition, electrolyte (NaCl vs. Na2SO4), anode material (boron-doped diamond (BDD) vs. PbO2), current density (0.10–0.50 A/cm2), and anode area (2–6 cm2) on the electrochemical abatements of organic pollutants (in terms of total organic carbon (TOC) or chemical oxygen demand (COD)) and ammonia nitrogen in swine wastewater. The results showed that the TOC degradation was greater in the absence of chloride, but an opposite trend was observed for NH3-N electrochemical abatement. A similar phenomenon was also observed when replacing chloride with sulfate. In the presence of chloride, the NH3-N removal efficiencies were similar on BDD and PbO2, although the former anode was better for TOC degradation than the latter. The removal of both COD and NH3-N increased with increasing current density or anode area on BDD. During the electrolysis of the wastewater, nitrite was not detected in the presence of chloride except in the absence of chloride, in the presence of Na2SO4, or on PbO2 at 0.25 A/cm2 and on BDD at 0.50 A/cm2 in the presence of chloride. In the presence of chloride, the concentration of nitrate increased and then decreased with increases in electrolysis time for almost all the tested conditions. At 25°C and 0.25 A/cm2, the pseudo-first-order rate constants for COD and NH3-N removal were 7.05×10⁻⁴ and 6.40×10⁻⁴ 1/s, respectively, while the general current efficiency and specific energy consumption were 15% and 9 kWh/kg-COD, respectively on BDD (4 cm²).

Keywords: swine wastewater; organic pollutants; ammonia nitrogen; electrochemical degradation; boron-doped diamond (BDD) electrode

1. INTRODUCTION

Livestock wastewater is of great concern due to its adverse impacts on the environment and health. In the United States, expansion and intensification of large-scale animal feeding operations has caused concern about environmental contamination and its potential public health impacts [1].
Likewise, in some Europe and Asian countries, where the livestock density per unit area is especially high, are experiencing serious environmental problems [2]. Increasing demand for pork has led to increasing discharge of piggery wastewater in China [3]. Swine wastewater is one of the major sources of water pollution in Taiwan, where ~5.5 million pigs were raised in 2017, ranking Taiwan as second globally in pig feeding density before the outbreak of foot-and-mouth disease on the island in 1997.

Organic and nitrogen-containing compounds are two types of key pollutants emerging from livestock operations and animal manure [4], which can also degrade environmental quality, particularly surface and ground water if not managed appropriately [5]. During the last few decades, different processes have been studied and used for the removal of the organic matter and nutrients in swine wastewater. In general, biological aerobic treatment followed by nitrogen removal through nitrification–denitrification has been used to treat the nitrogen surplus in these wastes [6,7]. Recently, a method using vertical subsurface flow constructed from wetlands planted with Napier grass [8] or integrated laboratory systems comprising three stages – an activated sludge reactor, a biofilter, and a subsurface vertical flow wetland [9] was proposed for the treatment of swine wastewater; however, these methods are still under study. In Taiwan, a three-step waste treatment system that includes solid-liquid separation, anaerobic treatment, and aerobic treatment, has been accepted for swine wastewater treatment since 1987 [10]. Nevertheless, more efficient approaches for swine wastewater treatment are greatly needed.

To address the removal of organic and nitrogen-containing compounds in wastewater, much attention has been paid to electrochemical advanced oxidation processes (EAOPs) because pollutants can be degraded by both direct and mediated electrochemical oxidation on an anode surface or in a bulk solution, in association with the electrochemical generation of a highly reactive hydroxyl radical ($\cdot$OH) or other oxidants depending on the electrolytes added in the treatment [11–13]. Non-active anode materials with good $\cdot$OH generation capability such as RuO$_2$, PbO$_2$, and BDD have been employed for treating organic pollutants [11–13]. Moreover, a process, based on ion-exchange and electrochemical regeneration derived from a study for ammonia removal [14], was tested for anaerobic-lagoon swine waste treatment [15]. However, this process is more complicated than the electrochemical oxidation alone for swine wastewater treatment which has presently received little attention. Therefore, in this study, we examined the removals of organic and ammonium nitrogen pollutants in swine wastewater using electrochemical advanced oxidation under different operating parameters: addition of chloride, electrolyte type, anode material, current density, and anode area.

2. MATERIALS AND METHODS

2.1. Collection and chemical analysis of swine wastewater

The samples of swine wastewater after solid/liquid separation treatment were collected twice at different times from the same pig farm in Kaohsiung City, Taiwan. The samples were kept refrigerated before the experiments. The total organic carbon (TOC) was analyzed using a Shimadzu TOC-L analyzer. Prior to the TOC analysis, each wastewater sample was filtered using a 0.45 μm filter and
then the filtrate was collected for TOC analysis, so the TOC was converted to dissolved organic carbon (DOC). The analyses of chemical oxygen demand (COD) (National Institute of Environment Analysis (NIEA) W517.52B), dissolved oxygen (DO) (NIEA W455.52C), conductivity (EC) (NIEA W203.51B), ammonium nitrogen (NH$_3$-N) (NIEA W448.51B), nitrite nitrogen (NO$_2^-$-N) (NIEA W418.53C), nitrate nitrogen (NO$_3^-$-N) (NIEA W419.51B), and pH (NIEA W424.52A) all followed the regulatory methods established by the Environmental Protection Administration, R.O.C. (Taiwan).

A Gerhardt VAP-200 Kjeldahl nitrogen distillation system was adopted to achieve the required digestion for ammonia measurements. The photometric determination of NH$_3$-N at 640 nm (Hitachi U-2900) was based on the reaction of ammonia with phenol and hypochlorite catalyzed by nitroprusside to form intensively blue indophenol in an alkaline medium (Berthelot reaction). For the determination of nitrite, the NO$_2^-$-N in each sample was diazotized with sulfanilamide followed by coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED), and the concentration of nitrite was then spectrophotometrically measured at 543 nm. Nitrate was determined by using its absorbance at 220 nm through deduction of the double absorbance at 275 nm for each sample.

The chemical oxygen demand (COD) was analyzed with a COD analyzer (COD Reactor CR25, Rocker) coupled with a colorimeter (Hach-DR890). A Lutron DO-5510 instrument was used to measure dissolved oxygen (DO). The pH and EC were measured using a TS-100 pH meter and an SC-170 conductivity meter (Suntex, Taiwan), respectively. A redox potential titrator (Metrohm 702 SM Titrino) was used to quantitatively determine the chloride concentration. All chemicals used in the experiments were reagent grade.

2.2. Electrolytic removals of organic and NH$_3$-N pollutants

An undivided and thermostatted (25°C) electrochemical cell was used to test the swine wastewater with/without the addition of either 0.05 M NaCl or Na$_2$SO$_4$. The removal of aqueous organic and NH$_3$-N pollutants was performed under various operational parameters (electrolyte addition, anode material, current density, and immersed anode area/sample volume). For the electrolytic operation in the undivided cell, the anode was a boron-doped diamond (BDD/Nb (Neocoat, Germany)) or a lab-prepared PbO$_2$ electrode, whereas the cathode was a Ti plate. The procedure for the PbO$_2$ electrode fabrication was provided in our previous study [16]. All the electrolytic experiments were performed using a DC power supply (Twintex TP2H-20S, Taiwan). The cell voltage and current were monitored with time based on the DC power supply readings.

The degradation or removal efficiency of TOC, COD, or NH$_3$-N is expressed as the following equation:

\[
\text{Degradation or removal efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{1}
\]

where $C_t$ is the residual concentration of TOC, COD, or NH$_3$-N at a given electrolysis time and $C_0$ is the initial concentration of TOC, COD, or NH$_3$-N.

In anodic oxidation, current efficiency for COD removal can be calculated using general current efficiency (GCE) [12,17]:

\[
\text{GCE} = \frac{[(\text{COD}_0 - \text{COD}_t)/MIt] \times nFV_S}{[(\text{COD}_0 - \text{COD}_t)/8It] \times FV_S} \tag{2}
\]
where \( n \) is the number of electrons required for water oxidation \( (n = 4, 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-) \); \( F \) is the Faraday constant \((96487 \text{C/mol})\); \( V \) is the electrolyte volume \((\text{L})\). \( \text{COD}_0 \) and \( \text{COD}_t \) are the COD values measured at time \( t = 0 \) and \( t \) \((\text{in g O}_2/\text{L})\), respectively; \( M \) is the molecular weight of oxygen \((32 \text{g/mol})\); \( I \) is the applied current \((\text{A})\); and \( t \) is the time over which the treatment occurs \((\text{s})\). With values of \( n \) adjusted, an analogous approach can be used for ammonia or organic contaminants.

The specific energy consumption \( (E_{SP}) \) \((\text{kWh/kg-COD})\) is calculated using the following relation \([12,17]\):

\[
E_{SP} = \frac{UIt}{(C_t - C_0)V_S},
\]

where \( U \) is the average cell voltage, and the other terms are as mentioned above.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characteristics of swine wastewater

The concentrations of COD in swine wastewater samples (WS I and II) were 1933 and 1166 mg/L, respectively, while those of TOC were 1933 and 1166 mg/L, respectively (Table 1). In WS I, the concentration of \( \text{NH}_3\text{-N} \) was 61 mg/L, whereas \( \text{NO}_2^-\text{-N} \) and \( \text{NO}_3^-\text{-N} \) were not detected. The concentrations of \( \text{NH}_3\text{-N}, \text{NO}_2^-\text{-N}, \) and \( \text{NO}_3^-\text{-N} \) in WS II were 73, 33, and 2.9 mg/L, respectively. The values of \( \text{Cl}^- \), EC, and \( \text{pH} \) were roughly similar in WS I and II.

**Table 1.** Parameters \((\text{TOC, COD, NH}_3\text{-N, NO}_2^-\text{-N, NO}_3^-\text{-N, Cl}^-, \text{EC} \ (\mu\text{s/cm}), \) and \( \text{pH} \)\) of the tested swine wastewater samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>COD</th>
<th>TOC</th>
<th>NH(_3)-N</th>
<th>NO(_2)-N</th>
<th>NO(_3)-N</th>
<th>Cl(^-)</th>
<th>EC*</th>
<th>pH</th>
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</thead>
<tbody>
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<td>WS I</td>
<td>1933</td>
<td>348</td>
<td>61</td>
<td>ND</td>
<td>ND</td>
<td>186</td>
<td>1837</td>
<td>6.72</td>
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<tr>
<td>WS II</td>
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<td>390</td>
<td>73</td>
<td>33</td>
<td>2.9</td>
<td>106</td>
<td>1982</td>
<td>7.66</td>
</tr>
</tbody>
</table>

WS: wastewater sample. ND: not detected \((< 0.01 \text{mg/L})\). $: [\text{Cl}^-] = 2186 \text{ and } 1885 \text{ mg/L for WS I and II, respectively, after addition of } 0.05 \text{ M NaCl.}$. $: \text{EC} = 7220 \text{ after addition of } 0.05 \text{ M NaCl for WS I; EC} = 7330 \text{ and } 10210 \mu\text{s/cm after addition of } 0.05 \text{ M NaCl and Na}_2\text{SO}_4, \text{ respectively, for WS II.}$

#### 3.2. Effect of addition of NaCl on TOC and NH\(_3\)-N electrochemical removals

Figure 1 shows the effect of the addition of NaCl on TOC and \( \text{NH}_3\text{-N} \) electrochemical abatement on a BDD anode at 0.25 A/cm\(^2\) and 25°C. It was observed that the TOC degradation was greater for the swine wastewater (WS I) without NaCl than for the one with NaCl; furthermore, the TOC degradation efficiency was 100% for the former, while it was 85% for the latter after 240 min of electrolysis (Figure 1a). A similar observation was reported for the electrochemical oxidation of acid black 210 dye on BDD \([18]\). Nevertheless, the addition of 0.05 M NaCl into the swine wastewater...
increased its conductivity from 1837 to 7220 μs/cm, leading to the observation that the removal efficiency of NH₃-N was significantly better in the salted swine wastewater sample (100% at 60 min) than in the unsalted sample (76% at 240 min) (Figure 1b). The 100% NH₃-N removal was better than that (>90% NH₄⁺ removal) from anaerobic-lagoon swine waste effluents using an electrochemically-regenerated ion exchange process (Ti/RuO₂ anode) which is different from our approach (electrochemical advanced oxidation alone) [15]. The 100% of NH₃-N or TOC removal efficiency of this study was also greater than that (99% NH₄⁺-N and 64% TOC removals) of a swine wastewater electrolysis process using a Ti/IrO₂ anode operated at 6 h of hydraulic retention time and addition of 0.05% NaCl [19]. Hence, the addition of 0.05 M NaCl into swine wastewater improved its NH₃-N removal, but it was not favorable for TOC mineralization. The removal of NH₃-N on BDD in water or wastewater can be achieved by indirect (mediated) or direct electrochemical reactions [13,20,21].

![Graphs showing the effect of NaCl addition on TOC, NH₃-N, NO₂⁻-N, and NO₃⁻-N removal](figure1.png)

**Figure 1.** Effect of addition of NaCl on TOC (a) and NH₃-N (b) electrochemical removal along with nitrite (c) and nitrate (d) concentration variations with time (on BDD at 0.25 A/cm² and 25°C).
In addition to solution conductivity, the oxidation of chloride to form active chlorine is also useful for NH$_3$-N removal during wastewater electrolysis. It was reported that electro-generated active chlorine (e.g., Cl$_2$, HOCl, and OCl$^-$) sharply increased and reached a steady-state due to formation of chlorate during electrolysis of 0.1 M sodium chloride solution on BDD involving the following reactions (Eqs. 4–8) [20]:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \\
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \\
\text{HOCl} \rightarrow \text{OCl}^- + \text{H}^+ \\
2\text{HOCl} + \text{OCl}^- \rightarrow \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^- \\
6\text{HOCl} + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 12\text{H}^+ + 4\text{Cl}^- + 1.5\text{O}_2 + 6e^- \\
\]

Chlorate formation may be accomplished chemically (Eq. 7) or electrochemically (Eq. 8). NH$_3$ or NH$_4^+$ can be oxidized by HOCl via Eqs. 9–11 [14] or to form chloramines via Eq. 13–15 [20,22]:

\[
3\text{HOCl} + 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3\text{H}^+ + 3\text{Cl}^- \\
3\text{HOCl} + 2\text{NH}_4^+ \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^- \\
4\text{HOCl} + \text{NH}_4^+ \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 6\text{H}^+ + 4\text{Cl}^- \\
4\text{OCl}^- + \text{NH}_3 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+ + 4\text{Cl}^- \\
\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \\
\text{NH}_2\text{Cl} + \text{HOCl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \\
\text{NHCl}_2 + \text{HOCl} \rightarrow \text{NCl}_3 + \text{H}_2\text{O} \\
\]

However, the formation of chloramines is insignificant at pH values higher than 8 [21]. These mediated (indirect) electrochemical ammonia oxidation reactions are also applicable for the electrolysis of real water or wastewater on BDD [14,21,23].

On the other hand, it was reported that the direct (non-mediated) electrochemical oxidation of ammonia on the BDD electrode occurs mainly at high pH (> 8) via free ammonia (NH$_3$) oxidation (Eq. 16), while the oxidation of ammonia at pH < 8 can be enhanced or mediated by active free chlorine [20].

\[
2\text{NH}_3 \rightarrow \text{N}_2 + 6\text{H}^+ + 6e^- \\
\]

Note that the NH$_4^+$ ↔ NH$_3$ and HOCl ↔ OCl$^-$ pK$_a$ values are approximately 9.24 and 7.50, respectively. The solution pH values ranged from 7.23–9.02 which covered those favored for both direct and indirect electrochemical oxidation of ammonia and showed insignificantly dominant speciation for ammonia or hypochlorite.

Moreover, solution pH also influences the efficiency of hydroxyl radical (•OH) electrochemically generated on BDD and the •OH may degrade/mineralize the organic pollutants (R) in solution through Eqs. 17 and 18, respectively [24]:

\[
\text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD(•OH)} + \text{H}^+ + e^- \\
\text{BDD(•OH)} + \text{R} \rightarrow \text{M} + m\text{CO}_2 + n\text{H}_2\text{O} + \text{H}^+ + e^- \\
\]

where the actual values of $m$ and $n$ depend on the elemental composition of $R$ to be oxidized. Interestingly, the electrochemical generation of hydroxyl radicals are not favored in solution at pH > 9 [25]. Hydroxyl radicals may also react with Cl$^-$ to form OCl$^-$, which can further react with •OH to produce ClO$_2^\cdot$, ClO$_3^\cdot$, and ClO$_4^-$ stepwise [26,27]. NH$_4^+$ and NH$_3$ may be oxidized by •OH, but the rates of these reaction are slow [28,29]. Therefore, it is complicated for the reactions occurring on
BDD and in solution. Briefly, the competition between TOC degradation and NH$_3$-N removal was present during the electrolysis of the swine wastewater tested in this study, and better NH$_3$-N removal was obtained at the expense of partial TOC degradation.

Figure 1c clearly shows that during the electrolysis of wastewater, nitrite was not detectable (< 0.01 mg/L) in the presence of chloride, but the nitrite concentration increased over time after 30 min although the presence of chloride significantly improved the removal of ammonia (Figure 1b). This phenomenon is associated with the oxidation of either NH$_3$ or NH$_4^+$ to form N$_2$ (Eqs. 9 and 10) or NO$_3^−$ (Eq. 11) by HOCl electrochemically generated from chloride oxidation. Even though nitrite was probably electrochemically generated on BDD, it could be oxidized to nitrate according to the following Eq. [22]:

\[
\text{NO}_2^− + \text{OCl}^− \rightarrow \text{NO}_3^− + \text{Cl}^−. \tag{19}
\]

Hence, nitrate did not accumulate in the solution, so its concentration was too low to be detected. In the absence of chloride, the nitrite with low concentrations (< 3 mg/L as NO$_2^−$-N) was possibly generated from the electrochemical oxidation of ammonia on the anode (Eq. 20) or the electrochemical reduction of nitrate on the cathode (Eq. 21 [30]):

\[
\begin{align*}
\text{NH}_4^+ + 2\text{H}_2\text{O} & \rightarrow \text{NO}_2^− + 8\text{H}^+ + 6\text{e}^- \tag{20} \\
\text{NO}_3^− + \text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{NO}_2^− + 2\text{OH}^- \tag{21}
\end{align*}
\]

Along with the removal of ammonia, the concentration of nitrate increased over time for the electrolysis of wastewater with the addition of NaCl; however, the nitrate concentration reached a maximum and then decreased over time until the end of operation (Figure 1d). This finding along with non-detectable nitrite supports that the nitrate produced from the electrochemical oxidation of ammonia was electrochemically reduced on the cathode to possibly form either NO$_2^−$ (Eq. 21), which was instantaneously further electrochemically reduced to other products (e.g., NO [31]), or N$_2$, which was electrochemically generated by the following reaction [32]:

\[
2\text{NO}_3^− + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2. \tag{22}
\]

Without the addition of NaCl into the wastewater, the nitrate concentration initially increased, then fluctuated and rose again during electrolysis, regardless of the accumulation of nitrite, revealing the co-presence of reactions 11 and 21 and supporting the occurrence of reaction 19. Accordingly, the incorporation of NaCl into the wastewater was used to carry out the subsequent tests in this study.

### 3.3. Effect of electrolyte on TOC and NH$_3$-N electrochemical removal

For comparison, sodium sulfate (versus sodium chloride) was also tested as an electrolyte added into swine wastewater (WS II) for TOC and NH$_3$-N removal on BDD in the electrochemical degradation experiments. The TOC degradation was better for the wastewater with the addition of 0.05 M Na$_2$SO$_4$ than for the one with the addition of 0.05 M NaCl. In addition, the difference in TOC degradation increased over time, resulting in 240-min TOC degradation efficiencies of 80% and 58% for the former and latter, respectively (Figure 2a). Again, this phenomenon was partially attributed to the higher conductivity in the former (10210 µs/cm) as compared to the latter solution (7220 µs/cm). In addition, the persulfate (S$_2$O$_8^{2−}$) electrochemically produced in the aqueous media containing sulfate...
[12,13, 33−35] was more powerful than the active chlorine electrochemically generated in the media containing chloride in terms of organic pollutant oxidation or degradation, although the scavenging of •OH by sulfate occurred at a higher rate than it did by chloride [11,20]. Similarly, the conversion of ammonia to nitrogen was reported to be better in the ammonium chloride solution than in the ammonium sulfate solution [36].

![Figure 2](image)

**Figure 2.** Effect of electrolytes on TOC (a) and NH$_3$-N (b) electrochemical removal along with nitrite (c) and nitrate (d) concentration variations over time (on BDD at 0.25 A/cm$^2$ and 25°C).

However, the removal efficiency of NH$_3$-N was significantly better in the swine wastewater with NaCl added (100% at 60 min) than in the wastewater with Na$_2$SO$_4$ added (63% at 240 min) (Figure 2b). Through electrochemical generation, the active chlorine was thus superior to persulfate for NH$_3$-N removal. During the electrolysis of wastewater in the presence of chloride, the concentration of nitrite was below the detection limit (< 0.01 mg/L) (Figure 2c), which was related to its instantaneous oxidation by electrochemically generated HOCl or nitrate reduction pathways, but that of nitrate increased and then decreased over time after 120 min (Figure 2d). A discussion of this phenomenon is mentioned in Section 3.2. Differently, the concentrations of nitrite and nitrate increased with
increasing time when replacing NaCl with Na$_2$SO$_4$ as the added electrolyte. The nitrite should be generated mainly from the electrochemical reduction of nitrate on cathode as discussed in section 3.2, indicating that persulfate was not useful for nitrite scavenging, similar to that obtained without adding any electrolyte in the wastewater.

3.4. Effect of anode material on TOC and NH$_3$-N electrochemical removal

Figure 3 presents a comparison between BDD and PbO$_2$ for the electrochemical removals of TOC and NH$_3$-N in swine wastewater (WS II). For the 240-min electrolysis, the complete mineralization of TOC occurred on BDD whereas the degradation efficiency of TOC was only 78% on PbO$_2$ (Figure 3a). Several studies also reported better organic pollutant degradation performance in real water on BDD than on PbO$_2$ because the oxygen evolution potential was higher for the former (2.2−2.6 V vs. SHE) than for the latter (1.8−2.0 V vs. SHE) [11]. Thus, the electrochemical generation of $\cdot$OH was more favored on BDD than on PbO$_2$ [11,35,37].

Figure 3. Effect of anode material on TOC (a) and NH$_3$-N (b) electrochemical removals along with nitrite (c) and nitrate (d) concentration variations over time (at 0.25 A/cm$^2$ and 25°C).
Nevertheless, both the anodes exhibited similar degradation efficiencies of NH$_3$-N (Figure 3b), which were associated with their similar capacities for electrochemical generation of active chlorine. The nitrite concentration was below the detection limit when using BDD as the anode while a small amount of nitrite accumulated in the solution when using PbO$_2$ (Figure 3c); additionally, more nitrate was produced on BDD than on PbO$_2$ (Figure 3d). A study reported that the removal efficiencies of NH$_4^+$ in sanitary landfill leachates were similar on these two anodes, and the partial oxidation of ammonium to nitrogen gas occurred on Ti/Pt/PbO$_2$, whereas ammonium tended to be oxidized to nitrate on BDD [25].

3.5. Effect of current density on COD and NH$_3$-N electrochemical removal

Figure 4a shows that the COD abatement increased with increases in current density. 100% COD removal was accomplished at 0.25 and 0.50 A/cm$^2$ for 180 and 60 min of electrolysis, respectively, whereas the COD removal was 94% at 0.10 A/cm$^2$ for 180-min of electrolysis. The increase in organic pollutant degradation with increases in current density was also presented in the literature [11,18,35,38]. This result was attributed to the greater generation of •OH with an increase in current density, although the rates of parasitic reactions (e.g., oxygen evolution) were also promoted [11].
Figure 4. Effect of current density (0.10–0.50 A/cm²) on COD (a) and NH₃-N (b) electrochemical removal along with nitrite (c) and nitrate (d) concentration variations over time (on BDD with the addition of 0.05 M NaCl at 25°C) (inset: Ln(Ct/C₀) against time, C = COD or NH₃-N).

A similar tendency of COD abatement for NH₃-N removal was also observed (Figure 4b), which was also attributable to greater generation of active chlorine species with increases in current density. The apparent COD degradation rate constants (k) (4.57×10⁻⁴–1.35×10⁻³ 1/s) (Table 2) were calculated using the pseudo-first-order reaction kinetics (Figure 4a inset) which is usually adopted for organic pollutant degradation in electrochemical processes [35,39,40]. The corresponding k values for NH₃-N removal ranged from 1.91×10⁻⁴–1.37×10⁻³ 1/s (Figure 4b inset), which was greater than those obtained by data fitting and solving a set of kinetic equations at [Cl⁻] = 14.1 mol/m³ (2.6×10⁻⁵ and 2.1×10⁻⁵ 1/s for converting NH₃ into N₂ and NO₃⁻, respectively) [22].

Table 2. Pseudo-first-order rate constants (k, 1/s) for COD degradation and NH₃-N removal on BDD, general current efficiency (GCE, %), and specific energy consumption (E_SP) (kWh/kg-COD) for the tested swine wastewater with the addition of 0.05 M NaCl at different current densities (anode area = 4 cm²) or anode areas (current density = 0.25 A/cm²).

<table>
<thead>
<tr>
<th>Current density (A/cm²)</th>
<th>Anode area (cm²)</th>
<th>k_C (10⁻⁴ 1/s)</th>
<th>k_N (10⁻³ 1/s)</th>
<th>GCE (%)</th>
<th>E_SP (kWh/kg-COD)</th>
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<td>172</td>
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</table>

Subscripts C and N denote COD and NH₃-N, respectively.

Increasing the current density from 0.25 to 0.50 A/cm² caused the accumulation of nitrite (Figure 4c). Moreover, the increase and then decrease in the nitrate concentration with electrolysis over time was faster with increases in current density (Figure 4d), suggesting that the rate of nitrite formation was faster than that of nitrite removal at the higher current density. For the electrochemical removal of COD, the general current efficiency (GCE) and specific energy consumption (E_SP) were 9%–32% and 4–11 kWh/kg-COD, respectively (Table 2). The calculation of E_SP was based on the final COD concentration of 600 mg/L which is the effluent limit of treated swine wastewater regulated by the Taiwan Environmental Protection Administration (EPA). It should be noted that it is not appropriate to use the data from Figure 4b to calculate the GCE and E_SP of NH₃-N, since electrochemically-generated active chlorine significantly contributed to the NH₃-N removal.

3.6. Effect of anode area on COD and NH₃-N electrochemical removals

Different anode areas (2–6 cm²) were tested for the COD and NH₃-N electrochemical removals at the same current density (0.25 A/cm²) and solution volume (200 mL). The electrochemical removal efficiencies of both COD and NH₃-N increased with the increase in the anode area (Figures 5a and b, respectively). This result was associated with the increase in the hydroxyl radical and generation of
active chlorine because the total current and active site for the reaction increased when the anode area was increased at the same current density. A similar result was also reported for the electrochemical oxidation of acesulfame [35] or Ce(III) [41]. Despite the difference in the anode area, nitrite was not detected during electrolysis (Figure 5c), and the increase and subsequent decrease in the nitrate concentration with electrolysis over time was also observed when increasing the anode area (Figure 5d), which was similar to the result obtained with increases in the current density. For the tested BDD anode with different areas, the COD and NH$_3$-N removal k values ranged from $2.95 \times 10^{-4}$–$8.25 \times 10^{-3}$ and $6.90 \times 10^{-4}$–$2.61 \times 10^{-3}$ 1/s, respectively, while the GCE and E$_{sp}$ for the COD electrochemical removal were 7%–21% and 124–233 kWh/kg-COD, respectively (Table 2).

Figure 5. Effect of anode area (2–6 cm$^2$) on COD (a) and NH$_3$-N (b) electrochemical removal along with nitrite (c) and nitrate (d) concentration variations over time (on BDD with the addition of 0.05 M NaCl at 0.25 A/cm$^2$ and 25°C) (inset: Ln(C$_0$/C) against time, C = COD or NH$_3$-N).

4. CONCLUSION
The electrochemical treatment of swine wastewater showed that the TOC degradation was greater in the absence of chloride. On the contrary, higher NH$_3$-N electrochemical abatement was observed in the presence of chloride. Replacing NaCl with Na$_2$SO$_4$ also result in better TOC degradation along with worse NH$_3$-N removal. However, the NH$_3$-N removal efficiencies were similar on BDD and PbO$_2$ although the former anode exhibited better TOC degradation than the latter. Abatement of both COD and NH$_3$-N increased with increases in the current density or anode area on BDD.

During the electrolysis of wastewater, the concentration of nitrite was below the detection limit in the presence of chloride under several tested conditions, while very little nitrite accumulation was observed in the absence of chloride, in the presence of Na$_2$SO$_4$, or in the presence of chloride on PbO$_2$ at 0.25 A/cm$^2$ and on BDD at 0.50 A/cm$^2$. In the presence of chloride, the concentration of nitrate increased and then decreased over time under almost all the tested conditions, except that on PbO$_2$ or in the presence of Na$_2$SO$_4$ on BDD. The COD and NH$_3$-N removal pseudo-first-order rate constants ranged from 4.57×10$^{-4}$–1.35×10$^{-3}$ and 1.91×10$^{-4}$–1.37×10$^{-3}$ 1/s, respectively; the GCE and E$_{SP}$ were 9%–32% and 4–11 kWh/kg-COD, respectively, on BDD at 25°C and 0.10–0.50 A/cm$^2$.

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