Electrochemical Removal of Ammonium Nitrogen and COD of Domestic Wastewater using Platinum Coated Titanium as an Anode Electrode

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Abstract: Biological treatment systems face many challenges in winter to reduce the level of nitrogen due to low temperatures. The present work aimed to study an electrochemical treatment to investigate the effect of applying an electric voltage to wastewater to reduce the ammonium nitrogen and COD (chemical oxygen demand) in domestic wastewater. This was done by using an electrochemical process in which a platinum-coated titanium material was used as an anode and stainless steel was used as a cathode (25 cm² electrode area/500 mL). Our results indicated that the removal of ammonium nitrogen (NH₄⁺–N) and the lowering of COD was directly proportional to the amount of electric voltage applied between the electrodes. Our seven hour experiment showed that 97.6% of NH₄⁺–N was removed at an electric voltage of 5 V, whereas only 68% was removed with 3 V, 20% with 1.2 V, and 10% with 0.6 V. Similarly, at 5 V, the removal of COD was around 97.5%. Over the seven hours of the experiment, the pH of wastewater increased from pH 7.12 to pH 8.15 when 5 V was applied to the wastewater. Therefore, electric voltage is effective in the oxidation of ammonium nitrogen and the reduction in COD in wastewater.

Keywords: electrochemical; wastewater; COD; ammonium nitrogen; voltage; anode

1. Introduction

Electrochemical wastewater treatment is a process wherein an electric field is applied between electrodes (anode and cathode) to remove various pollutants present in wastewater. Monica et al. [1] first reported that, by means of the electrochemical process, ammonium and organic pollutants could be effectively removed from domestic wastewater mixed with seawater. Since then, the electrochemical process has been successfully used for the removal of ammonium and organics from wastewater. Using an electrochemical process to reliably treat wastewater also has economic benefits [2] due to its high-operating efficiency, usefulness under a wide range of ambient operating conditions, small equipment size requirements, minimal sludge generation, and rapid start-up [3–5]. It has been applied successfully to remove COD (chemical oxygen demand) and color from wastewater generated by the
sugar industry [6], swine operations [7], the textile industry [8], local municipalities [9], and by citric acid producers [10].

The efficiency of the electrochemical removal of ammonium nitrogen and COD are affected by several factors such as Cl\(^{-}\) concentration, pH, current density [11,12], electric voltage applied [7,13], and type of electrode material used, particularly the anode material [3,14–16]. Among all of these factors, the type of anode material used and electric voltage applied are the most important factors determining the operating cost and removal efficiency of an electrochemical treatment process. For example, high current density exhibits a strong effect on pollutant removal and shortens treatment time [8,17,18]. However, higher current densities consume more electric power, which directly increases the operating cost of a wastewater treatment system. One critical challenge to the wider use of electrochemical treatments is a need to reduce the energy consumption and cost. Additionally, improving the long-term stability and electrocatalytic performance, and lowering the cost of the electrode material are the challenges for this process.

Electrochemical oxidation of ammonium and organics requires either direct or indirect anodic oxidation methods. In the direct electro-oxidation process, physically adsorbed hydroxyl radicals are used to oxidize organic compounds at the anode surface [19,20]. Marinerc et al. [21] investigated the direct electro-oxidation of ammonium on a platinum-plated anode and a titanium-plated anode and found that the direct electro-oxidation of ammonium proceeded well on a platinum anode. In addition, titanium electrodes covered with very thin layers of electrodeposited noble metals [22], ruthenium [23], and boron-doped diamond (BBD) [15] are also used to directly oxidize ammonium nitrogen and organics present in wastewater. In contrast, with indirect electro-oxidation, anodically-generated oxidizing agents (such as peroxide, Fenton’s reagent, sodium chloride, chlorine, hypochlorite, or peroxodisulfate) are added to wastewater to react with organic and inorganic pollutants [24,25]. Moreover, the evolution of chlorine gas (Cl\(_2\)) is essential for the indirect electro-oxidation process to proceed. As oxide electrodes (such as titanium coated with IrO\(_2\)) are very active during Cl\(_2\) evolution, this agent is commonly used in the process of oxidizing organic matter [26–28].

Generally, in wastewater treatment plants, ammonium is removed by applying physiological and biological treatment methods, which include several techniques such as air stripping, ion exchange, biological nitrogen removal (BNR) systems, and breakpoint chlorination. Most water treatment plants in South Korea apply biological nitrogen removal (BNR) systems to treat total nitrogen and COD. This type of system is economical to operate when compared to other types of wastewater treatment processes, but it also has many limitations. For one, it is very complicated and difficult to stabilize and optimize, and the operation of the system is inhibited when wastewater temperature falls below 10 °C.

In winter, a BNR system faces many challenges due to low water temperatures. For one, bacteria do not reproduce as rapidly during colder months and so do not oxidize BOD (biochemical oxygen demand) very effectively in winter. Bacteria generally favor temperatures between 68 °F and 95 °F (20 °C and 35 °C). In fact, for every 10 °F decrease in temperature, bacteria lose roughly 1 log of growth potential. Moreover, the optimal temperature range for nitrification and denitrification is generally considered to be 27 °C to 32 °C, but in most cities in South Korea, ambient air temperatures fall below 10 °C in winter [29], which is why wastewater treatment tends to be more problematic in winter (i.e., bacteria are less active). Under low temperatures, there is a need for a supplementary wastewater treatment process (in addition to the BNR process) to reduce the level of total nitrogen. Nitrogen reduction could be achieved electrochemically during winter.

Electrode material, especially anodes, can play a very important role in the electrolytic degradation of ammonium and COD present in wastewater. In this study, a platinum coated anode material was used to examine the efficiency of the electrochemical removal of ammonium and COD in domestic wastewater. The electrochemical oxidation of ammonium and COD of wastewater using a titanium coated electrode has not been previously reported. Moreover, the generation of chloride species like monochloramine and dichloramine and its effect in the electrochemical removal of ammonium and COD of domestic wastewater has not been previously explored. Therefore, in this study, we aimed
to determine the electrolytic ammonium and COD degradation efficiency using a platinum coated electrode. Moreover, the effect of electric voltages in the oxidation of ammonium and the pattern of chloramine generation during the electrochemical removal of ammonium nitrogen and COD from domestic wastewater were studied.

2. Materials and Methods

2.1. Electrode Preparation

Mesh-type platinum coated titanium (Pt/Ti) and flat-plate stainless steel were used as an electrode material. A squared shaped, mesh-type platinum coated titanium electrode with the dimensions of $50 \times 50 \times 1$ mm was used as the anode material, while a flat-plate, stainless steel (grade 304) of the same size was used as the cathode material. The anode material (purchased from Hyundai Plating, Korea) had a platinum coating ($1 \mu$m) and was manufactured by punching, pulling, annealing, acid-washing, and the coating process. In order to attach the electric wires to both of the electrodes, a 2-mm hole was drilled at the top of both electrodes using a drill machine. A copper wire of diameter 0.5 mm was soldered onto each hole using Emerson and Cuming conductive epoxy, followed by an application of a thin layer of non-conducting epoxy to avoid any contact of wastewater where the copper wires and electrodes were connected. The separation between the electrodes was maintained at 5 mm by securing 5 mm thick plastic beads to the four corners of the electrodes.

2.2. Influent Source and Its Characteristics

Samples of domestic wastewater were collected from the influent of a domestic wastewater treatment plant located in Gangwon-do, Chuncheon-si, South Korea. After primary treatment, wastewater samples were collected in 20 L plastic containers and stored at 4 °C for later analyses and electrochemical treatments. Characteristics of the wastewater are shown in Table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.12</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>0.65 mS/cm</td>
</tr>
<tr>
<td>Ammonium nitrogen</td>
<td>25.4 mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>&lt;20 µg/L</td>
</tr>
<tr>
<td>Nitrite</td>
<td>&lt;20 µg/L</td>
</tr>
<tr>
<td>COD</td>
<td>283 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>43.1 mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>27 NTU</td>
</tr>
</tbody>
</table>

2.3. Experimental Setup

The experiment was conducted using lab-scale electrochemical cells. Each electrochemical cell was made from 500 mL Pyrex glass beakers and placed on a magnetic stirrer set at 450–500 rpm. Each 500 mL Pyrex glass beaker was equipped with two parallel plate electrodes (anode and cathode), as described previously. In each experiment, the electrochemical test cell was filled with 500 mL of domestic wastewater and the electrodes were connected to a DC-regulated power supply (UTP3704S UNI-T), with voltages of 0 V, 0.6 V, 1.2 V, 3 V, and 5 V. The experiment, in duplicate, was conducted at room temperature of ~22 °C. For the analytical analyses, the samples were withdrawn on an hourly basis and filtered before further analysis was performed. The experiment was conducted for seven hours.

2.4. Analytical Methods

In order to view the progress of the treatment over time, the samples were collected on an hourly basis for seven hours, centrifuged, filtered, and preserved at 4 °C until further analysis. The evaluation
of the treatments included the analyses of chemical oxygen demand (COD), ammonium nitrogen (NH$_4^+$–N), nitrite and nitrate nitrogen, chlorides, turbidity, pH, and electrical conductivity (EC). The NH$_4^+$–N concentration was determined by using an ammonium electrode (Thermo Electron Corporation, USA). The closed reflux titrimetric method [26] was performed to determine COD. Chlorides, nitrites, and nitrates were measured with by ion chromatography (Dionex, ICS900, USA). Turbidity was analyzed using a turbidity meter (Orion AQ4500, USA); pH and EC were measured using a pH meter and a conductivity meter, respectively.

2.5. Calculations

The resistance of the solution (R) was calculated using Ohm’s law as in Equation (1).

\[ V = IR \] (1)

where \( V \) is the voltage (volt) applied between the electrodes and \( I \) is the current (A) flowing through the solution. Current density (mA/cm$^2$) was calculated using Equation (2).

\[ J = \frac{\sigma V}{d} \] (2)

where \( J \) is the current density (mA/cm$^2$); \( \sigma \) is the conductivity of the solution (S/m); and \( d \) is the distance between the electrode (m). Energy consumption (kWh kg$^{-1}$ COD) was calculated using Equation (3).

\[
\text{Energy consumption} = \frac{[tVA/S_v]/[1 \times 10^3]/[\Delta \text{COD}/(1 \times 10^6)]}{t \Delta \text{COD}}
\] (3)

where \( t = \) experimental time in hours; \( V \) is the applied voltage in volt; \( A \) is the current flowing through solution in ampere; \( S_v \) is the sample volume (L); and \( \Delta \text{COD} \) is the difference in COD (mg/L).

3. Results and Discussion

3.1. Ammonium Nitrogen

The removal of NH$_4^+$–N at various electric voltages is illustrated in Figure 1. In this study, 0 V (the control), 0.6 V, 1.2 V, 3 V, and 5 V electric voltages were applied to analyze the effect of these various voltage densities on the removal of NH$_4^+$–N in domestic wastewater. The initial levels of pH and EC in domestic wastewater were 7.8 and 0.7 mS/cm, respectively. Our experimental results showed that at the control (0 V) and at low (0.6 V) voltage, the concentration of NH$_4^+$–N did not decline over time, but instead remained constant throughout the seven hour experiment. Similarly, the removal of NH$_4^+$–N at 1.2 V was rather low in that it only declined from 25 mg/L to 23.1 mg/L (7.6% removal efficiency) during the experiment. Hence, NH$_4^+$–N was not effectively removed under low voltage (0.6 V and 1.2 V) conditions. In contrast, NH$_4^+$–N was effectively reduced at voltages of 3 V and 5 V. At 3 V, the NH$_4^+$–N concentration decreased from 25 mg/L to 8 mg/L (68% removal efficiency) within seven hours. However, by applying 5 V, the concentration of NH$_4^+$–N decreased rapidly from 25 mg/L to 5 mg/L after 4 h of electrolysis, and then the concentration continued to decline steadily until it reached 0.6 mg/L (97.6% removal efficiency) after seven hours of treatment. In summary, the efficiency at which NH$_4^+$–N was removed increased with increasing voltage over 5 V.
An increase in voltage increased the flow of current in the solution, and according to Faraday’s law of electrolysis, the higher current led to a greater reduction of chloride ions, thereby enhancing the electrochemical process and reduction in ammonium concentration. In fact, Mollah et al. [30] claimed that current density was the most important parameter for controlling the reaction rate during electrolysis. Additionally, Cho et al. [8] previously reported that the removal efficiencies of NH$_4^+$–N from swine wastewater were proportional to the electric voltages applied. At the 0.2% NaCl level, the removal efficiencies of NH$_4^+$–N were 15%, 46%, and 99% for the 3 V, 5 V, and 7 V applications, respectively. In the present study, the removal of NH$_4^+$–N might be due to the conversion of NH$_4^+$–N into N$_2$ gas. Many researchers have claimed that the mechanism of electrochemical nitrogen removal from wastewater is complex, being influenced by many factors such as the amount of electrolytes, type of electrode material, current density, ionic species, etc. However, during the electrochemical process, ammonium is known to be oxidized via various reactions pathways, ending with various nitrogen compounds such as nitrogen, nitrate, and NOx, etc. [31,32].

The hypochlorite ion (OCl$^-$) and hypochlorous acid (HOCl) are the most important ions responsible for the indirect oxidation of ammonium nitrogen to nitrogen gas [33]. When electricity is
applied to wastewater, oxygen gas evolves from the breakup of water molecules and chlorine gas is generated in chloride ion solutions (chloride ions occur naturally in wastewater), as shown in reactions (Equations (4) and (5)) [24].

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^\circ = -0.83 \text{ V} \quad (4) \]

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad E^\circ = -1.36 \text{ V} \quad (5) \]

The generated molecular chlorine is hydrolyzed to form hypochlorous acid (HOCl), as shown in Equation (3), which is subsequently changed to hypochlorite ion (OCl\(^-\)), depending on the pH of the solution [25,27].

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (6) \]

The hypochlorous acid and hypochlorite ion thus formed can indirectly oxidize the ammonium into nitrogen gas due to their high oxidative potentials [25], as shown in the reactions in Equations (6) and (7).

\[ 2\text{NH}_4^+ + 3\text{HOCl} \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^- \quad (7) \]

\[ 2\text{NH}_4^+ + 2\text{OCl}^- \rightarrow \text{N}_2 + 2\text{HCl} + 2\text{H}_2\text{O} + 2\text{H}^+ \quad (8) \]

Initially, the experimental wastewater contained 43 mg/L of chloride. The higher removal of ammonium nitrogen in the 5 V electric system can be explained by the indirect oxidation of ammonium to nitrogen with the help of HOCl and OCl\(^-\), as shown in the reactions in Equations (7) and (8). Moreover, the reason for the indirect electro-oxidation of ammonium to nitrogen gas is due to the initial pH of the wastewater. The initial pH of the domestic wastewater we tested was 7.2 and as treatment time increased, the pH of the wastewater also increased, but did not exceed pH 8.15. Therefore, during the treatment process, the pH of the domestic wastewater remained between pH 7.2 and pH 8.15, which is a very beneficial pH for the oxidation of ammonium to nitrogen gas via HOCl. In strong alkaline conditions, HOCl is a strong oxidation agent to ammonium.

3.2. Nitrate Nitrogen

Nitrate and nitrite ions can also be generated during the decomposition of ammonium at an anode, and so in every hourly test, we analyzed the concentration of nitrite and nitrate in the samples. Over the experimental time period, no nitrites were found, but a small amount of nitrate was detected in the samples (Figure 1b). Nitrate was generated up to 2.8 mg/L and 2.0 mg/L when 3 V and 5 V were applied to wastewater, respectively. However, only a negligible amount of nitrate (~0.4 mg/L) was detected at the lower voltages of 0.6 V and 1.2 V. In the 5 V system, the nitrate ions increased slowly over time, reached a peak (2.4 mg/L) in five hours, and then decreased gradually; a similar trend was observed in the 3 V system. This means that ammonium in the wastewater was mainly converted into nitrogen gas, but was also partially converted into nitrate. The generated nitrate could then be reduced to nitrogen, nitrogen oxides, and even ammonium [28,34]. Therefore, in order to investigate the removal of total inorganic nitrogen (NH\(_4^+\)–N + NO\(_2^−\)–N + NO\(_3^−\)–N), the concentration of inorganic nitrogen was plotted over time (Figure 1c). Although the production of nitrate nitrogen was observed in 3 V and 5 V systems, the percent of total inorganic nitrogen removed decreased with time.

To clarify the indirect oxidation effect of chlorine/hypochlorite in the electrochemical oxidation of ammonium, we also examined the concentration of free chlorine, mono-chloramine, and dichloramine (Figure 2). We clearly showed that when applying voltage to the wastewater, the concentration of free chlorine gradually increased to 0.46 mg/L (at 5 V) and to 0.42 mg/L (at 3 V) within two hours. As the treatment time increased, the amount of free chlorine in both the 5 V and 3 V applications remained almost constant during the initial five hours of treatment. The concentration of mono-chloramine and dichloramine released gradually increased from the beginning of the treatment period onward. In the
5 V application, ammonium nitrogen became almost zero after seven hours of treatment; in contrast, free chlorine started to sharply increase, while mono-chloramine and dichloramine started to decrease (Figures 3 and 4). Hence, this result revealed that free chlorine reacted with water to form HOCl, and that as the formation of mono-chloramine and dichloramine proceeded, ammonium was oxidized to nitrogen gas via breakpoint chlorination. A similar trend was also observed under the 3 V application. Therefore, the effective removal of ammonium nitrogen (98% removal) was obtained following 5 V of electric force as a higher voltage produces more chlorine gas, which in turn enhances the formation rate of HOCl. Under the low voltage scenario (1.2 V), less ammonium nitrogen was removed for 7 h (i.e., only 1.9 mg/L was removed, decreasing from 25 mg/L to 23.1 mg/L). This low removal rate may be due to the very low electric potential required to split water into oxygen gas and hydrogen gas. Chlorine gas can be formed by applying a potential difference between the cell electrodes. In theory, the thermodynamic decomposition voltage of water is 1.23 V at 298 °K and 1 atm pressure; however, to minimize overpotential reactions and losses of resistance (Ohmic voltage drop), higher voltages should be applied [35]. Otherwise, ammonium removal at low voltages is low.

Figure 2. Generation of chlorinated species (A) free chlorine, (B) mono-chloramine, and (C) di-chloramine along with the treatment time.
3.3. COD Removal

In order to investigate the effect of an electric voltage on the removal of COD in domestic wastewater, the electrochemical process was carried out using various voltages from 0 V to 5 V, as before (Figure 3). Our results revealed that in the control (0 V), the concentration of COD did not decrease and remained constant throughout the experiment. Similarly, at low voltage (0.6 V), COD removal was very low (11.6% COD removed), but about 30.9% of COD was removed at a low electric voltage of 1.2 V. Notably, the effective removal of COD was observed at 3 V and 5 V. Using the 5 V system, 97.5% of COD was removed after seven hours, whereas only 80.5% of COD was removed with the 3 V system. Initially, the COD of the domestic wastewater was 283 mg/L. As the electrochemical process proceeded, COD began to decline over time in the 1.2 V, 3 V, and 5 V systems, and by seven hours of electrochemical treatment, the COD had decreased to 191 mg/L, 55 mg/L, and 7 mg/L, respectively. Previously, Diaz et al. [36] reported that the higher the current density, the faster the COD could be removed. For example, in treating aquaculture saline water at a current density of 50 Am\(^{-2}\) and an initial COD concentration of 54.8 mg/L, they achieved a residual COD concentration of approximately 5.48 mg/L (90% removal) in 70 min. Similar results were reported by Vijayaraghavan et al. [37] for the treatment of brackish shrimp aquaculture wastewater with an initial COD of 1730 mg/L. As they increased the current density from 37.2 m\(\text{Acm}^{-2}\) to 74.5 m\(\text{Acm}^{-2}\), the COD removal efficiency increased from 31.7% to 53.46% within 15 min of applying electrolysis. In our study, the COD removal rate was quite low when compared to other researchers (Diaz et al. [36] and Vijayaraghavan et al. [37]). This can be explained by a low Cl\(^-\) concentration (43 mg/L) when compared to 17,000 mg/L and 1840 mg/L, respectively.

The electrochemical removal of organics is either described as direct anodic electro-oxidation or indirect anodic electro-oxidation. In direct electrochemical conversion, organics can be oxidized directly at the anode surfaces through physically adsorbed hydroxyl radicals, which produce carbon dioxide as a final product [20]. In indirect anodic electro-oxidation, anodically generated chlorine and hypochlorite are used as the oxidizing agents for the decomposition of organics in the presence of chloride ions [38]. As the influent of our experimental domestic wastewater contained 43 mg/L of initial chloride ions and because the Pt/Ti anode used in our experiment was an ‘active’ electrode [39,40], we believe that the decomposition and the oxidation of organics (R) and removal of COD were due to indirect anodic oxidations and active chlorine-mediated reactions. An increase in voltage leads to an increase in current density and an increased current density increases charge loading, which in turn increases the pollutant removal efficiency [41]. Hence, the removal efficiency of COD increases with an increase in electric voltage, which explains why the maximum COD removal efficiency was observed at 5 V treatment.

![Figure 3. COD removal with time during the electrochemical treatment of domestic wastewater.](image-url)
3.4. Chloride (Cl\(^-\)) Concentration

Chloride plays a very important role in the indirect electrochemical oxidation of ammonium to nitrogen gas. Figure 4a indicates the concentration of chloride in the solution in our experimental series of electric voltages: 0.6 V, 1.2 V, 3 V, and 5 V. Initially, the chloride concentration in our wastewater before treatment was 43 mg/L. Our results indicated that the concentration of chloride remained constant throughout our experiment when the lower voltages of 0.6 V and 1.2 V were applied, whereas the amount of chloride concentration decreased at the applied voltages of 3 V and 5 V. Throughout the 7 h experiment, the chloride concentration decreased from 43 mg/L to 38 mg/L under the 3 V system and decreased to 35 mg/L under the 5 V system. The chloride ions in the solution were oxidized to chlorine at the anode and hydrolyzed to form hypochlorous acid (HOCl) (Equation (2)), which was subsequently changed to hypochlorite ions (OCl\(^-\)) and hypochlorous acid, depending on the pH of the wastewater [42]. Hypochlorous acid (HOCl) reacts with NH\(_3\) or NH\(_4^+\) through breakpoint chlorination to regenerate Cl\(^-\), as shown in Equation (4). Thereafter, the Cl\(^-\) concentration was expected to remain unchanged after the reaction, serving only as a catalyst. However, our experimental results showed that the total amount of Cl\(^-\) ions in the 3 V and 5 V systems was less than the starting concentration. The reason for the decline in Cl\(^-\) ions could have been due to the escaping chlorine gas (Cl\(_2\)) from solution [16] or the electrochemical formation of chlorates and perchlorates [43].

![Figure 4](image)

**Figure 4.** Effects of electric voltages on chloride ion concentration with time (A) and mass balance of Cl with different treatment voltages (B).

3.5. pH

It has been established that the influence of pH is important in influencing the performance of electrochemical processes [41]. Although pH was not adjusted to any particular value in this experiment, changes in pH were examined over the course of the experiment (variations in pH relative to the applied voltages are shown in Figure 5). Our results illustrate that the pH of wastewater increased in systems with electric voltages of 3 V and 5 V, whereas under no or low electric voltage
conditions (i.e., 0 V, 0.6 V, and 3 V), the pH remained unchanged throughout the treatment period. At the beginning of the experiment, the wastewater was pH 7.12. As the electric voltage was applied over the seven hours of the experiment, the pH of the wastewater gradually started to increase and reached pH 8.15 (under the 5 V system) and pH 7.95 (under the 3 V system). Therefore, in the course of our electrochemical treatments, an increase in pH was observed only in the 5 V and 3 V applications. In fact, Szpyrkowicz et al. [44] previously reported that changes in pH were influenced by cathodic and anodic processes and by the sequence of the reactions of chlorine in wastewater. Hence, the increase in pH in our experimental wastewater throughout the treatment period might have been due to a reduction of water to hydrogen at the cathode. Additionally, the reaction of chlorine with organic compounds may also have resulted in an increase in the pH of the wastewater.

![Figure 5. Variation of the pH of domestic wastewater along with the experimental time at different electric voltages.](image)

3.6. Current Density and Energy Consumption

The rate of electrochemical reaction is measured as current density, current per area. The current densities for the 0.6 V, 1.2 V, 3 V, and 5 V systems were calculated as 7.2 mA/cm², 15.6 mA/cm², 39 mA/cm², and 65 mA/cm², respectively. The energy consumption (kWh/kg COD) was calculated for the 5 V system using Equation (2) where the COD decreased from 283 mg/L to 19.5 mg/L (Figure 3) within four hours of experimental time. The energy consumption was estimated in the order of 121.4 kWh/kg COD. Wang et al. [45] reported that the energy consumption was about 600 kWh/kg COD during treatment of paper mill wastewater. Moreover, about 180 kWh/kg COD energy was consumed in treating secondary influent using electrochemical treatment [46]. However, Fockedey et al. [47] reported that the energy consumption was only 5 kWh/kg COD (lower than the present study) when they treated simulated water containing phenol. The low results may be attributed to the large COD (about 2000 mg/L) concentration and distinct electrode characteristics. It is a matter of fact that the electrochemical treatment of wastewater is an energy intensive process. However, it has advantages over other approaches such as operation at ambient temperature and pressure as well as robust performance and capability to adjust to variations in the influent composition and flow rate. It is particularly well suited for decentralized water treatment because the mechanism through which electrochemical processes are controlled, the electrode potential and cell current, are easier to control remotely than conventional and biological processes.

4. Conclusions

In this research, the effects of an electric voltage on the electrochemical removal of ammonium nitrogen and COD of domestic wastewater were studied in batch electrolytic reactors.

The results of this study revealed that the electrochemical treatment of domestic wastewater offers an effective means for removing ammonium nitrogen and COD from domestic wastewater and provides an alternative to the traditional biological nitrification-denitrification processes used...
during the winter when temperatures are normally low. Electric voltage plays a crucial role in the oxidation of ammonium nitrogen and removal of the COD of wastewater. Ammonium nitrogen and COD removal efficiencies increased with increased electric voltage. Considering the overall removal efficiency of pollutants at the different voltages tested, an electric voltage of 5 V was an effective voltage for the tested electrochemical process. Under a 5 V system, the removal efficiencies of ammonium nitrogen and COD were 97.6%, and 97.5%, respectively. As domestic wastewater is chloride-rich, the oxidation of chloride ions to free chlorine took place, which was responsible for the indirect oxidation of ammonium nitrogen. Simultaneously, mono-chloramine and dichloramine were formed during the treatment, but after reaching peak values, they began to decline in concentration. Regulation levels of wastewater effluent can be achieved during winter by removing some effluent ammonium electrochemically.


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