

Article

Efficient Removal of Ammonia Nitrogen by an Electrochemical Process for Spent Caustic Wastewater Treatment

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Abstract: Spent caustic wastewater produced in a soda plant has a high concentration of ammonia nitrogen ($\text{NH}_4^+\text{-N}$). As excessive $\text{NH}_4^+\text{-N}$ discharging into water bodies would cause eutrophication as well as destruction to the ecology balance, developing an efficient technology for $\text{NH}_4^+\text{-N}$ removal from the spent caustic wastewater is imperative in the current society. In this study, an electrochemical process with graphene electrodes was designed for the $\text{NH}_4^+\text{-N}$ removal in the spent caustic wastewater. The removal efficiency of the $\text{NH}_4^+\text{-N}$ during the electrochemical process could reach 98.7% at 4 A in a short treatment time (within 120 s) with an acceptable energy consumption (6.1 kWh/m³-order). NO_3^- and NO_2^- were not detected during the electrochemical process. An insignificant amount of NH_2Cl , NHCl_2 , and NCl_3 produced in the treatment suggested that little of the $\text{NH}_4^+\text{-N}$ reacted with chlorine, that is, chlorination played a negligible role in the $\text{NH}_4^+\text{-N}$ removal. By electron equilibrium and nitrogen conversion analysis, we think that $\text{NH}_4^+\text{-N}$ was primarily converted to $\text{NH}_2(\text{ads})$ on the surface of a graphene electrode by one-electron transfer during the direct oxidation of the electrochemical process. Due to the high calcium ion (Ca^{2+}) in the spent caustic wastewater, the electrode scale significantly increased to 1.4 g after treatment of 240 s at 4 A. By X-ray diffraction (XRD) analysis, the composition of the electrode scale is portlandite $\text{Ca}(\text{OH})_2$. Although the electrode scale was obvious during the electrochemical treatment, it could be alleviated by alternating the electrode polarity. As a result, the life and efficiency of the graphene electrode for $\text{NH}_4^+\text{-N}$ removal could remain stable for a long time. These results suggest that the electrochemical process with a graphene electrode may provide a competitive technology for $\text{NH}_4^+\text{-N}$ removal in spent caustic wastewater treatment.

Keywords: ammonia nitrogen; electrochemistry; spent caustic; graphene electrode; electrode scale



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1. Introduction

Soda, as an important chemistry ingredient for industry (such as the glass manufacturing industry or the construction industry), has an increasing demand with rapid economic development. During soda production, a large amount of spent caustic wastewater with high alkalinity, salinity, and nitrogen would be produced. Although the nitrogen element is a necessary nutrient for plants and algae, excessive nitrogen discharging into water bodies would cause algae mass growth and eutrophication [1]. Therefore, it is critical to remove the nutrient of the nitrogen element (especially for ammonia nitrogen) from the spent caustic wastewater before it is discharged into the environment.

Up to now, the common methods for ammonia nitrogen ($\text{NH}_4^+\text{-N}$) removal in wastewater include biological nitrification [2], adsorption [3], break-point chlorination [4], and so on. Biological nitrification has been widely used for many years; however, it is only suitable for the wastewater treatment with a relatively low ammonia concentration due to the limit of the appropriate C/N ratio for microorganism growth [5]. Adsorption is a convenient method for ammonia removal. However, the adsorption efficiency of the $\text{NH}_4^+\text{-N}$ removal is affected by the pH of the water, and the used material needs to be further disposed [6]. Break-point chlorination is also a well-known classic method for

NH_4^+ -N removal. Unfortunately, the process is highly pH dependent and requires highly skilled operators [7]. In addition, due to the generation of radicals with strong oxidation, advanced oxidation processes (AOPs) have shown high efficiencies for organic contaminants and NH_4^+ -N removal [8–12]. However, potentially negative impacts of AOPs have been reported, such as the accumulation of the total dissolved solids and the limitation of the transportation and storage of liquid oxidants [12–14]. Above all, more suitable methods for NH_4^+ -N removal in the spent caustic wastewater need to be developed.

Due to its versatility and amenability to automation, the electrochemical process is a promising technology for ammonia removal in wastewater. During the electrochemical process, NH_4^+ -N can be removed via anodic oxidation, including direct electron transfer to the anode surface and mediate oxidation with oxidants generated by an anode, such as hydroxyl radicals and chlorine [15,16]. Consequently, the electrode material is crucial during the electrochemical process [17]. The previous literature reported that the boron-doped diamond (BDD), dimensionally stable anode (DSA), magnesium, Pt-Ir, etc., were efficient for NH_4^+ -N removal [16,18]. Nevertheless, the high cost of these electrodes has largely limited their application in actual wastewater treatment. Moreover, it was found that a DSA electrode would become deactivated due to surface poisoning by nitrogen adsorption [19]. Another study showed that due to the competing of carbonate oxidation, ammonia oxidation would be inhibited on the DSA electrode at a high pH [20]. Thereby, a suitable electrode for ammonia removal in wastewater should be economical, efficient, and durable.

A graphene electrode exhibits a high electronic conductivity, great mechanical strength, and low cost [21,22]. Thus, a graphene electrode could be an alternative for ammonia removal during the electrochemical process. Electrolysis with a graphene electrode used for ammonia nitrogen removal in real wastewater was rare as far as we know. Especially, the electrochemical process with a graphene electrode for ammonia nitrogen removal in spent caustic wastewater that has a high concentration of calcium ions has not been found.

The objective of this study is to evaluate whether the electrochemical process with a graphene electrode is feasible for ammonia removal in spent caustic wastewater. Ammonia nitrogen removal efficiency, energy consumption, and nitrogen transformation were investigated. Moreover, the electrode scale rate and scale composition were also analyzed. At last, a solution to alleviating the electrode scale to extend the electrode life was provided.

2. Results and Discussion

2.1. Ammonia Nitrogen Removal

Main parameters of the spent caustic wastewater are shown in Table 1. Figure 1 shows the NH_4^+ -N removal during the electrochemical treatment of the spent caustic wastewater with varying currents. In general, with increasing currents from 2 to 4 A, NH_4^+ -N concentrations in the effluent decreased continuously. The concentrations of NH_4^+ -N decreased from the initial 70.0 mg/L to 42.3, 22.7, and 0.9 mg/L after a 120 s treatment with 2, 3, and 4 A, respectively (Figure 1a). The effluent at 4 A could meet the direct emission standard of pollutants for the inorganic chemical industry of China (10 mg/L) [23]. By linearly fitting $-\ln(C/C_0)$ vs. time, the pseudo-first-order rate constants (k) of NH_4^+ -N removal can be obtained [24]. Because of the enhancement of the electron transfer rate and/or the indirect oxidation agents at a high current density, the rate of contaminant degradation increases with increasing currents [25]. For example, with currents ranging from 2 to 4 A, the k values increased from 0.0038 to 0.0126 s^{-1} , as shown in Figure 1b. Under the tested conditions, the electrochemical system could process 720 L water per day (1 L water at a treatment time of 120 s) and effectively remove the NH_4^+ -N. Moreover, the ammonia oxidation rate per m^2 of electrode per day is $1.38 \times 10^4 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ at 4 A in this study, which is more than 100 times higher than the previous literature [26,27]. Nevertheless, the electricity demand at 4 A (58 $\text{Wh} \cdot \text{gN}^{-1}$), in this study, was only slightly higher than the previous literature (42 $\text{Wh} \cdot \text{gN}^{-1}$) [26]. The results indicate the electrochemical process

may be a high-efficient and practical method for $\text{NH}_4^+\text{-N}$ removal in the spent caustic wastewater.

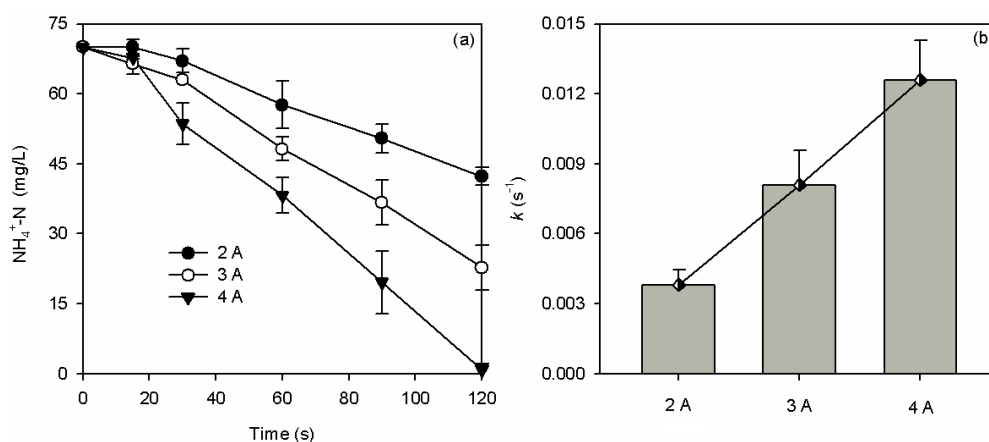
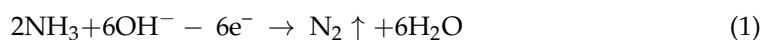


Figure 1. (a) $\text{NH}_4^+\text{-N}$ concentration evolution and (b) k of $\text{NH}_4^+\text{-N}$ removal during the electrochemistry treatment of the spent caustic wastewater with varying currents.

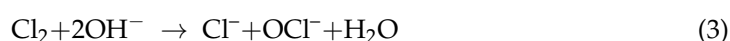
2.2. Electrochemical Oxidation for $\text{NH}_4^+\text{-N}$

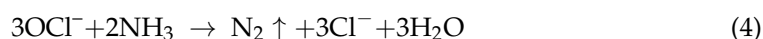
In the spent caustic wastewater (pH = 11.4), soluble NH_3 is the dominant species of ammonia nitrogen. The soluble NH_3 could be air-stripped by gas bubbles produced during the electrochemical process [28]. The previous reference reported that ~9–11% of the ammonia disappeared in an ammonia solution at pH 12 and 80 mA/cm² with a 90 min treatment only by air bubbling, similar to the gas evolution generated during the electrolysis [28]. In our study, the ammonia was treated by the electrochemical process at similar conditions, only for 2 min. Therefore, the ammonia nitrogen removal by the bubbles generated during the electrochemical process was far below 9%, that is, the removal could be neglected.

During the electrochemical process, contaminants could be removed via direct electron transfer to the anode surface (i.e., direct electrolysis) and/or via mediate oxidation with electrochemically generated oxidants, such as hydroxyl radicals and chlorine (i.e., indirect electrolysis) [15,16]. As shown in Equation (1), ammonia can be transformed to N_2 by electron transfer to the anode surface under an alkaline condition at pH > 9 [26,29]. In this study, the pH of the spent caustic wastewater was 11.4, and thus the ammonia nitrogen may be removed by direct electrolysis during the electrochemical process.



On the other hand, ammonia can be removed by indirect electrolysis due to the Cl^- transformation to chlorine during the electrochemical treatment, as shown in Equations (2)–(4) [30,31]. As shown in Figure 2, the concentration of the free chlorine residual could achieve 69 mg/L during the electrochemical treatment of the spent caustic wastewater at 4 A and 120 s. The current efficiency (CE) of the electro-generated chlorine was calculated according to Equation (5) [32] and displayed in Figure 2. The concentration of the chlorine generated by electrolysis was difficult to measure due to the contaminant existing in the spent caustic wastewater. Therefore, the free chlorine residual was an alternative to the chlorine generated by electrolysis for the CE calculation. The CE of the electro-generated chlorine gradually increased with an increasing treatment time (Figure 2). The increasing CE suggested that less free chlorine reacted with the ammonia as the ammonia concentration decreased with the increased treatment time [33].





$$\text{CE} (\%) = \frac{nF C_{\text{chlorine-E}} V}{\int_0^t I dt} \times 100 \quad (5)$$

where $C_{\text{chlorine-E}}$ is the concentration of chlorine generated by electrolysis (mol/L), n is the number of electrons transferred from Cl^- to Cl_2 , F is the Faraday constant (96485 C/mol), I is the current (A), t is the treatment time (s), and V is the solution volume (L).

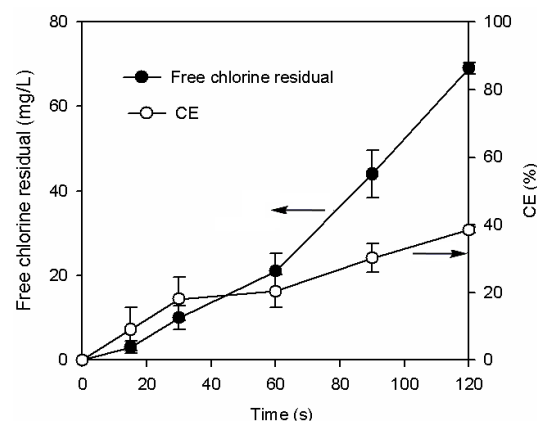
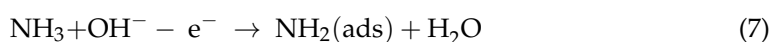


Figure 2. Free chlorine residual evolution and CE during the electrochemistry treatment of the spent caustic wastewater at 4 A.

In order to analyze the concentrations of the NH_2Cl , NHCl_2 , and NCl_3 produced in the electrochemical process, the concentration of the total chlorine was determined. For example, the concentration of the total chlorine was 74 mg/L at 120 s treatment of the spent caustic wastewater with 4 A, while the concentration of the free chlorine was 69 mg/L. As a result, the total concentration of the NH_2Cl , NHCl_2 , and NCl_3 produced in the treatment was only 5 mg/L. The finding suggests that the $\text{NH}_4^+\text{-N}$ was barely degraded by the chlorination during the electrochemical treatment.

Based on the applied current and treatment time, the total number of electrons from the electrode could be calculated, as shown in Equation (6). Thereby, the total number of electrons transferred to the surface of the graphene anode is 480 C (4.97 mmol) at 4 A and 120 s treatment. Then, according to the electron equilibrium, 3 mol electrons would be transferred when 1 mol $\text{NH}_4^+\text{-N}$ is oxidized to N_2 . As a result, at the reaction conditions (4 A and 120 s treatment), only 23.2 mg of the $\text{NH}_4^+\text{-N}$ would be oxidized as a consequence of the reactions on the anode (including direct and indirect electrolysis). Nevertheless, at the conditions (4 A and 120 s treatment), the electrochemical process removed ~69 mg of the $\text{NH}_4^+\text{-N}$ (Figure 1a), which was nearly 3 times higher than that of the three-electron transformation (23.2 mg). Therefore, one-electron transformation played a significant role for the $\text{NH}_4^+\text{-N}$ degradation in this electrochemical process, such as Equation (7) [16,34]. Because the electrons increased linearly with increasing currents, the k values for the $\text{NH}_4^+\text{-N}$ degradation would have an obviously linear correlation with varying currents, as shown in Figure 1b.

$$\text{Number of electrons (C)} = \int_0^t I dt \quad (6)$$



2.3. Nitrogen Conversion

The total nitrogen (TN) includes $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$, and organic nitrogen [35]. To analyze the nitrogen conversion during the electrochemical treatment, the TN, NO_3^- , and NO_2^- were also determined. As shown in Figure 3a, the TN concentration decreased from 122 to 71.3, 52.7, and 27.9 mg/L with 2, 3, and 4 A treatment, respectively (Figure 3a). It demonstrated that the TN removal rates increased with increasing currents.

However, both NO_3^- and NO_2^- were not detected during the electrochemical treatment. These results indicated that the $\text{NH}_4^+\text{-N}$ in the spent caustic wastewater was not oxidized to NO_3^- and NO_2^- , both of which were also contributed to eutrophication and could cause secondary pollution [36,37].

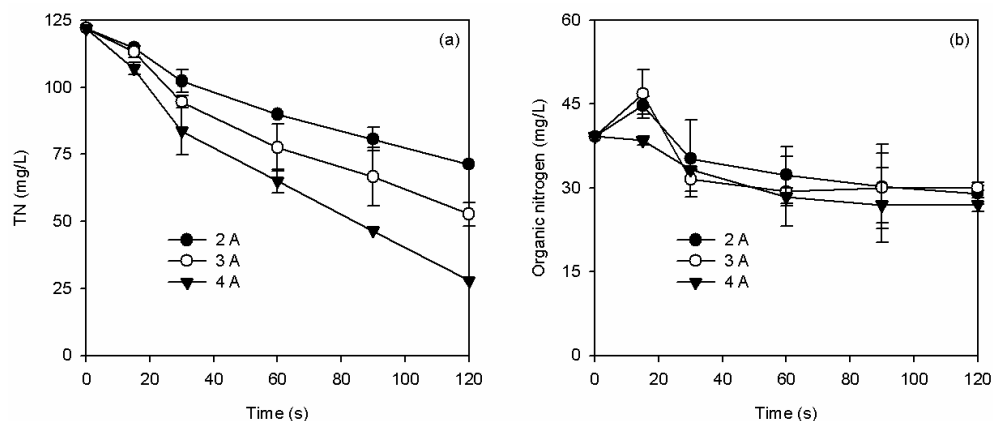


Figure 3. (a) Total nitrogen and (b) organic nitrogen evolution during the electrochemistry treatment of the spent caustic wastewater with varying currents.

In addition, the concentration of organic nitrogen can be calculated according to the analysis for $\text{NH}_4^+\text{-N}$, TN, NO_3^- , and NO_2^- [35]. Figure 3b shows that the organic nitrogen ranged from 39.2 to ~27–30 mg/L during the electrochemical process with varying currents (2–4 A), featuring only ~23–31% removal efficiencies. With the applied currents increasing from 2 to 4 A, the removal efficiencies of the organic nitrogen had little enhancement (Figure 3b). The results suggested that the organic nitrogen in the spent caustic wastewater was refractory by the direct electrolysis of the graphene electrode and chlorination. The possible reason was attributed to the low second-order rate constant for the reaction of chlorine with amines ($\sim 10^0\text{--}10^1 \text{ M}^{-1}\cdot\text{s}^{-1}$) [38] and the short treatment time (120 s).

2.4. EEO

Energy consumption is a key index for evaluating the practicability of a technology. The electrical energy demand to abate the concentration of pollutants by 1 order of magnitude in 1 m^3 of water (i.e., electrical energy per order (EEO), $\text{kWh}/\text{m}^3\text{-order}$) by the electrochemical processes is calculated using Equation (8) [39].

$$\text{EEO} = \frac{UIt}{3600V \lg \frac{C_0}{C}} = \frac{2.3UI}{3600Vk} \quad (8)$$

where U is the cell voltage (V), shown in Table 2; I is the applied current (A), shown in Table 2; t is the treatment time (s); C_0 and C are the $\text{NH}_4^+\text{-N}$ concentration at times $t = 0$ and t , respectively (mg/L); V is the solution volume (L); and k is the pseudo-first-order rate constant for pollutant removal (s^{-1}), shown in Figure 1b.

The EEO values of the $\text{NH}_4^+\text{-N}$ removal during the electrochemistry treatment of the spent caustic wastewater with varying currents were calculated according to Equation (8) and shown in Figure 4. In general, the EEO of the $\text{NH}_4^+\text{-N}$ removal decreased from 7.7 to 6.1 $\text{kWh}/\text{m}^3\text{-order}$ with increasing currents from 2 to 4 A. The result was attributed to the rapid increase in the $\text{NH}_4^+\text{-N}$ removal rate with increasing currents. For example, the k of the $\text{NH}_4^+\text{-N}$ removal was enhanced ~3.3 times while the applied current only increased 2 times (i.e., from 2 to 4 A, see Figure 1b). Above all, the $\text{NH}_4^+\text{-N}$ removal during the electrochemistry treatment of the spent caustic wastewater at 4 A is a cost-efficient choice.

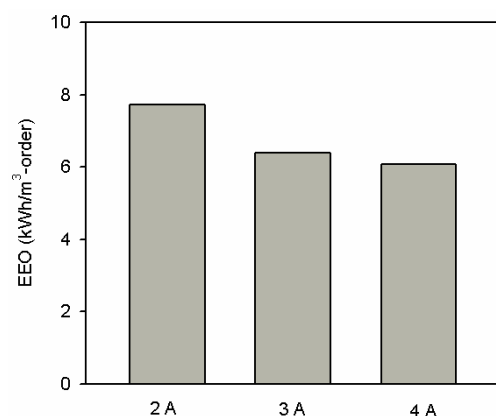


Figure 4. The EEO of NH₄⁺-N removal during the electrochemistry treatment of the spent caustic wastewater with varying currents.

2.5. Electrode Scale

As the electrode scale has a negative influence on electrode life and efficiency [40], the mass of the electrode scale needs to be considered due to the high calcium ion (Ca²⁺), as shown in Table 1. The amount of the electrode scale was determined by the mass difference values of all the electrodes before and after treatment of 240 s. Figure 5a shows that the electrode scale increased with increasing applied currents. When the applied currents increased from 2 to 4 A, the electrode scale increased from 0.55 to 1.40 g. The phenomenon was caused by the rapid mass transfer at a high current density. At a high current density, more Ca²⁺ would be transferred onto the surface of the graphene cathodes and more H₂O would decompose into the OH[−]. Thus, the solubility product of the Ca(OH)₂ would be reached quickly, and then precipitation would occur. By X-ray diffraction (XRD) analysis, and in comparison with the card of the powder diffraction file (PDF) (PDF#44-1481) [41], the composition of the electrode scale is portlandite Ca(OH)₂ (Figure 5b).

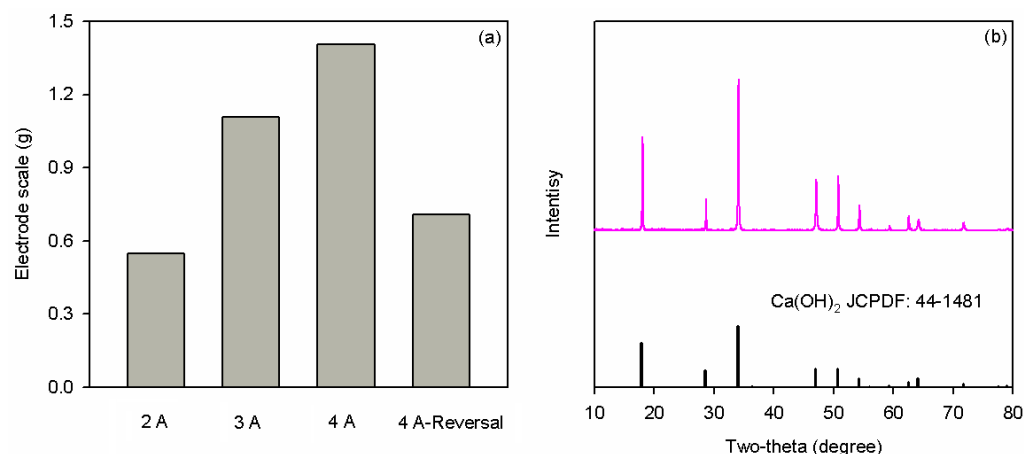


Figure 5. (a) The amount and (b) XRD analysis of electrode scale during the electrochemistry treatment of the spent caustic wastewater.

Table 1. Main water parameters of the spent caustic wastewater.

Parameter	Value
pH	11.4
NH ₄ ⁺ -N (mg/L)	70.0
TN (mg/L)	122
NO ₃ ⁻ -N (mg/L)	11.2
NO ₂ ⁻ -N (mg/L)	1.58
Ca ²⁺ (mg/L)	53,100
Na ⁺ (mg/L)	18,900
Cl ⁻ (mg/L)	111,000

Although obvious the electrode scale was observed during the electrochemical treatment, it could be alleviated by reversing the electrode polarity [42,43]. After reversing the anode and cathode, the flaky scale peeled off the electrode surface. Thereby, the electrode scale decreased from 1.40 g (4 A) with 240 s treatment to 0.71 g (4 A-reversal) after reversing the electrode polarity with 120 s treatment (Figure 5a). The scaling produced before the electrode reversal treatment could be almost completely peeled off after the electrode reversal treatment. The phenomenon was attributed to the oxygen (O₂) generation via the electron transfer of OH⁻ to the anode surface. The generated O₂ bubbles would lead to the scale being peeled off the electrode surface [44]. As a result, the electrochemical process could keep the long electrode life and be pretty efficient by continually reversing the electrode polarity. In our study, the same graphene electrodes were used in all the experiments. The electrodes were stable for at least ~20 L of the spent caustic wastewater by continually reversing the electrode polarity.

3. Materials and Methods

3.1. Chemicals and Reagents

Nessler's reagent was purchased from Tianjin Xintaiyi Co., Ltd. (Tianjin, China). Phosphoric acid, N-(1-naphthalene)-ethylenediamine, and P-aminobenzene sulfonamide were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). P-aminobenzene sulfonamide was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in this study were of analytical grade. Stock solutions were prepared with Milli-Q ultrapure water.

3.2. Water Sample

Spent caustic wastewater was sampled from a soda ash industrial park in Hebei, China, then used within one week for the electrochemical experiments. Main parameters of the spent caustic wastewater are shown in Table 1.

3.3. Electrochemical Experiments

The spent caustic wastewater (1 L) was added in a cylindrical glass reactor, then treated by the electrochemical process for 120 s (see Figure 6 for the experimental setup). For electrochemical experiments, ten electrodes were installed vertically and parallelly into the wastewater, with a gap of 3 mm between the two adjacent electrodes. The two outermost electrodes connect the positive and negative electrodes of a direct current (DC) power supply. The electrodes were graphene plates (6 × 6 cm). The electrochemical experiments were conducted under galvanostatic conditions with varying currents of 2–4 A (corresponding to current densities of 55.6–111 mA/cm² according to Equation (9)). Electrochemical conditions during the spent caustic wastewater treatment were listed in Table 2.

$$j = \frac{I}{S} \quad (9)$$

where j is the applied current density (mA/cm²), I is the applied current (mA), and S is the area of the electrode (cm²).

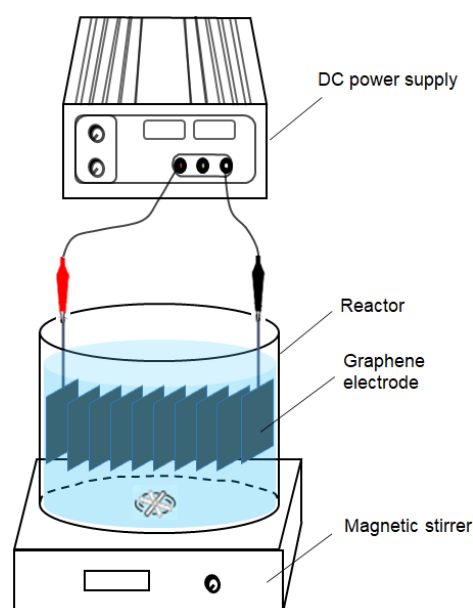


Figure 6. The experimental setup of the electrochemical process.

Table 2. Electrochemical conditions during the spent caustic wastewater treatment.

Current (A)	J (mA/cm ²)	Voltage (V)
2	55.6	23
3	83.3	27
4	111	30

3.4. Analytical Methods

Free chlorine and total chlorine were analyzed using the N,N-diethyl-p-phenylenediamine method with a Hach chlorine detector (Pocket Colorimeter, Hach, Loveland, CO, USA) [45]. $\text{NH}_4^+\text{-N}$ was determined using Nessler's reagent spectrophotometry (HJ 535-2009) [46]. Total nitrogen (TN) was measured using alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636-2012) [46]. NO_3^- was analyzed by an ion chromatograph (ICS-1100, Thermo Dionex, Waltham, MA, USA) [47]. NO_2^- was determined using N-(1-naphthalene)-ethylenediamine spectrophotometry [48].

4. Conclusions

This study introduces an electrochemical process as an efficient technology for $\text{NH}_4^+\text{-N}$ removal in spent caustic wastewater treatment. $\text{NH}_4^+\text{-N}$ in the spent caustic wastewater could be effectively removed in a short treatment time with an acceptable energy consumption. By electron equilibrium and nitrogen conversion analysis, $\text{NH}_4^+\text{-N}$ was primarily converted to $\text{NH}_2(\text{ads})$ on the graphene electrode by one-electron transfer during the electrochemical process. The little amount of the NH_2Cl , NHCl_2 , and NCl_3 produced in the treatment suggested that chlorination played a negligible role in the $\text{NH}_3\text{-N}$ removal. Although obvious the electrode scale was observed during the electrochemical treatment, it could be alleviated by reversing the electrode polarity. These results suggest that the electrochemical process may provide a competitive technology for $\text{NH}_4^+\text{-N}$ removal in spent caustic wastewater treatment.

Author Contributions: Conceptualization, methodology, validation, formal analysis, visualization, and writing—original draft preparation, and funding acquisition, S.Z.; investigation, data curation, writing—review and editing, supervision, project administration, and funding acquisition, Y.Z.;

conceptualization, methodology, and visualization, R.G. and J.C. All authors have read and agreed to the published version of the manuscript.

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