

Catalytic Performance of Electro-Oxidative Natural Manganese Sand for Ammonium Nitrogen Removal

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The environmental risks associated with ammonium nitrogen ($\text{NH}_4^+\text{-N}$) pollution have led to a growing focus on prevention. Electrochemical advanced oxidation is an effective and eco-friendly method that only requires electricity and electrolytes to remove $\text{NH}_4^+\text{-N}$ from wastewater. This study assesses the effectiveness of electro-oxidative natural manganese sand (NMS) in removing ammonium nitrogen under different conditions. Due to NMS's high redox potential, it significantly enhanced the electrochemical oxidation process, increasing $\text{NH}_4^+\text{-N}$ removal and generating reactive chlorine species (ClO^-/HClO) when NaCl was added. The experiment was also conducted without a catalyst, quartz sand, and natural manganese sand, but NMS removed 86.4% of $\text{NH}_4^+\text{-N}$, outperforming the other treatments. The removal efficiency was tested at five different pH levels (3, 5, 7, 9, and 11), with NMS showing the highest efficiency of 95.2% at pH 9. At a current density of 15.5 mA/cm^2 , the removal rate reached 94.9%, and with a NaCl concentration of 9 g/L , the removal efficiency peaked at 96.2%, driven by increased production of reactive chlorine species (ClO^-). These results demonstrate the electro-oxidative NMS system as a highly efficient, scalable, and eco-friendly solution for ammonium nitrogen removal in wastewater treatment.

Keywords: Electrochemical Oxidation; Manganese Sand Catalyst; Ammonium Nitrogen Removal; Wastewater Treatment; Sustainability



Introduction:

Ammonium nitrogen ($\text{NH}_4^+\text{-N}$) is highly toxic and poses a significant threat to global water quality. It originates from various sources, including the excessive use of nitrogen fertilizers like urea, discharges from human and animal waste, agro-industrial wastewater, landfill leachate, and untreated domestic wastewater [1]. Water contamination from ammonium nitrogen has severe effects on the ecosystem [2]. High concentrations of ammonia and ammonium in water can cause unpleasant odors and tastes. Excessive intake of ammonium nitrogen can disrupt the body's acid-base balance, making the blood too alkaline and leading to serious health issues. These health concerns highlight the dangers of elevated ammonia levels in water. As a result, the WHO and EU have set a maximum permissible limit of 2 mg/L for ammonia nitrogen concentrations in water [3].

Conventional methods for removing ammonium nitrogen include air stripping [4], ion exchange and adsorption, capacitive deionization, membrane technology [5], the activated sludge process [6], and biological methods using ammonia-oxidizing bacteria (AOB) [7]. While these techniques are effective, they are not always cost-efficient and may contribute to environmental contamination. This has created a growing demand for abundant and cost-effective oxidants or catalysts [8].

Advanced oxidation processes (AOPs) have emerged as promising alternatives because they can generate powerful oxidative species to break down stubborn contaminants with minimal secondary pollution [9]. Radical-based oxidation, such as catalytic systems, is also used to treat industrial low-volatile pollutants [10]. Among these methods, the electrochemical oxidation process stands out due to its strong capability to remove ammonium nitrogen. This method offers benefits such as precise control, mild reaction conditions, and reduced environmental impact, allowing for ammonium nitrogen removal through both direct and indirect approaches [11].

Manganese is one of the most abundant elements in nature and is commonly found as manganese oxides (MnOx). Its natural abundance, high surface area, and strong redox ability make it a promising material for wastewater treatment [12]. The effectiveness of manganese in wastewater treatment can be enhanced by using chloride ions, as active chlorine is involved in the oxidation process [13]. In this study, manganese sand was electrochemically activated for ammonium nitrogen ($\text{NH}_4^+\text{-N}$) removal. Various factors were investigated, including solution pH, NaCl concentration, and current density. The goal of this study is to fill the research gap and assess the potential of electrochemically activated manganese sand in developing more effective and sustainable methods for removing $\text{NH}_4^+\text{-N}$ from wastewater, as well as integrating NMS with electrochemical processes for industrial scalability.

Objectives of the Study:

The primary objective of this study is to evaluate the catalytic performance of electro-oxidative natural manganese sand (NMS) for ammonium nitrogen ($\text{NH}_4^+\text{-N}$) removal in wastewater treatment. The specific objectives include:

- To investigate the efficiency of natural manganese sand (NMS) as a catalyst in electro-oxidation processes for $\text{NH}_4^+\text{-N}$ removal.
- To optimize key process parameters, including pH, NaCl concentration, and current density, to achieve maximum $\text{NH}_4^+\text{-N}$ removal efficiency.
- To compare the electro-oxidation performance of NMS with quartz sand and electro-oxidation alone, determining the catalytic contribution of manganese sand.
- To explore the reaction mechanisms involved in $\text{NH}_4^+\text{-N}$ removal, identifying key oxidation pathways and intermediate species.

- To assess the feasibility of NMS for practical wastewater treatment applications, including potential scalability, reusability, and cost-effectiveness.

Novelty Statement:

This study introduces natural manganese sand (NMS) as a novel catalyst for electro-oxidative ammonium nitrogen removal, offering an efficient and sustainable approach to wastewater treatment. Unlike conventional $\text{NH}_4^+\text{-N}$ removal techniques such as ion exchange, biological nitrification, and membrane filtration, which often suffer from high operational costs and secondary pollution, this research demonstrates that NMS significantly enhances electro-oxidation efficiency without requiring complex modifications.

Material and Methods:

The experiment was carried out in a batch electrolytic cell using a 250 mL beaker fitted with electrodes. A 100 mg/L ammonium nitrogen solution was prepared in distilled water, with 3 g/L of sodium chloride added. To enhance the electrochemical oxidation process, 7.1 mg/L of sodium sulfate was included as a supportive electrolyte to increase ionic strength.

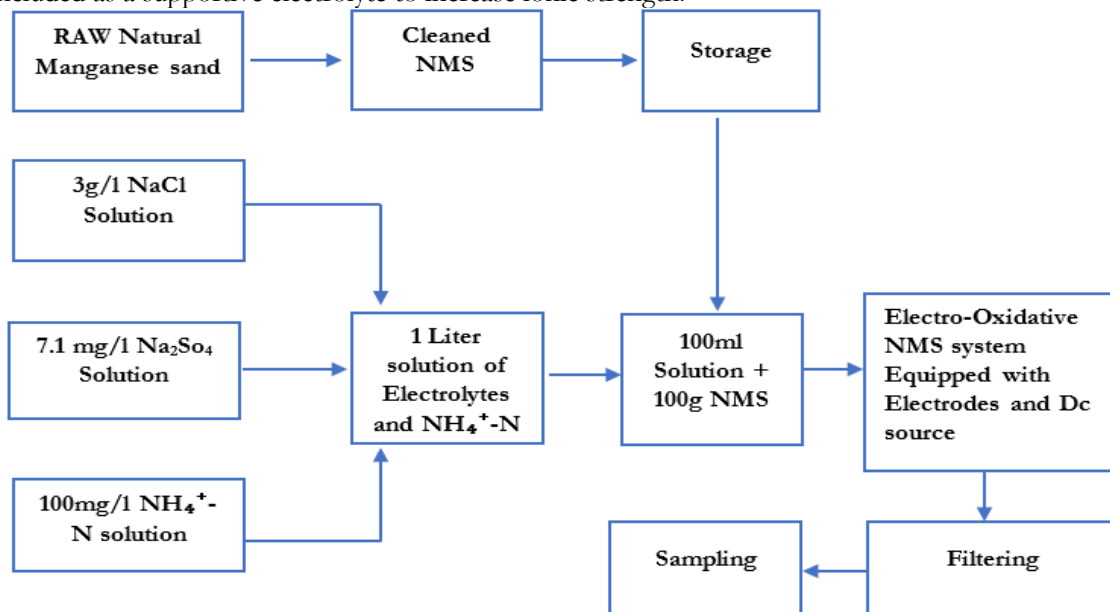


Figure 1. Flow Diagram of Methodology

A catalyst dose of 100 g of manganese sand was added to facilitate the oxidation of ammonium nitrogen. The electrochemical oxidation process was conducted for 120 minutes, with current densities ranging from 5.5 to 15.5 mA/cm². To evaluate the impact of various parameters on ammonium nitrogen removal efficiency, samples were collected at 20-minute intervals throughout the experiment. The pH of the system was maintained between 3 and 11 by adjusting with dilute HCl. After each sampling, the collected solutions were filtered to remove any solid manganese particles before analysis. Ammonium concentrations in the filtered samples were measured using a spectrophotometer coupled with an ion-selective electrode.

Additionally, the effect of varying sodium chloride (NaCl) concentrations was examined, with NaCl concentrations ranging from 1 to 9 g/L. This approach allowed for the evaluation of key factors influencing the efficiency of ammonium nitrogen removal.

Determination of Ammonia Nitrogen:

Ammonium nitrogen was determined using Nessler's spectrophotometry method [14], as shown in Figure 1. A standard curve was created using a known concentration of ammonium nitrogen, in the form of free ammonia or ammonium ions, which reacts with Nessler's reagent to form a brown complex. The absorbance of this complex was directly proportional to the ammonium nitrogen concentration. For analysis, the samples were diluted

with 50 mL of deionized water, followed by the addition of 1.0 mL of potassium sodium tartrate solution and 1.0 mL of Nessler's reagent. After the reaction, the absorbance of the samples was measured using the standard curve to determine the ammonium concentration.

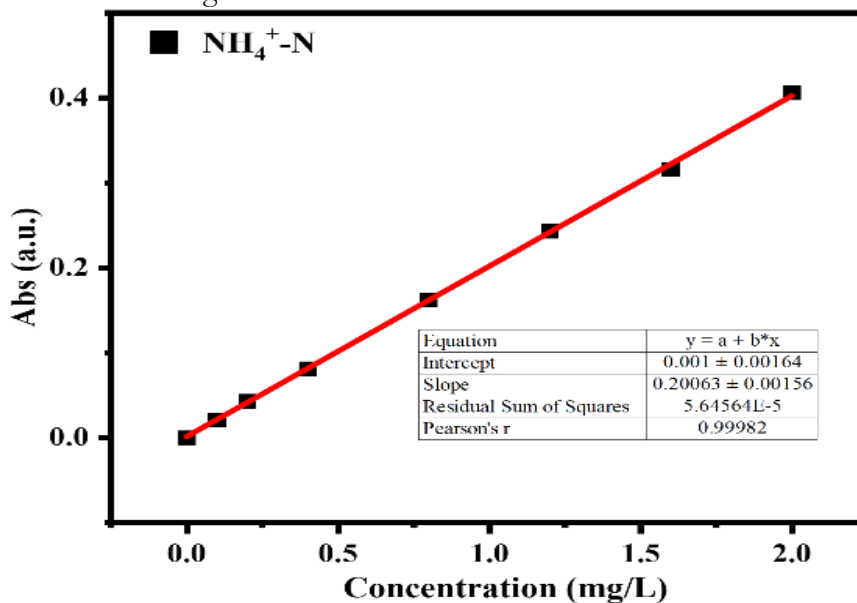


Figure 2. Standard Curve of Ammonium Nitrogen

Result and Discussion:

The catalytic performance of the electro-oxidative natural manganese sand (NMS) system for ammonium nitrogen oxidation was thoroughly investigated by comparing three systems: electro-oxidation alone, electro-oxidation with quartz sand, and advanced electro-oxidation with manganese sand. The results showed that electro-oxidation alone achieved a removal efficiency of 42.7%, and electro-oxidation with quartz sand reached 37.6%. However, with the inclusion of manganese sand, the removal efficiency significantly improved to 86.4% after 120 minutes of electrolysis, demonstrating the superior performance of the electro-oxidative manganese sand system in treating inorganic pollutants.

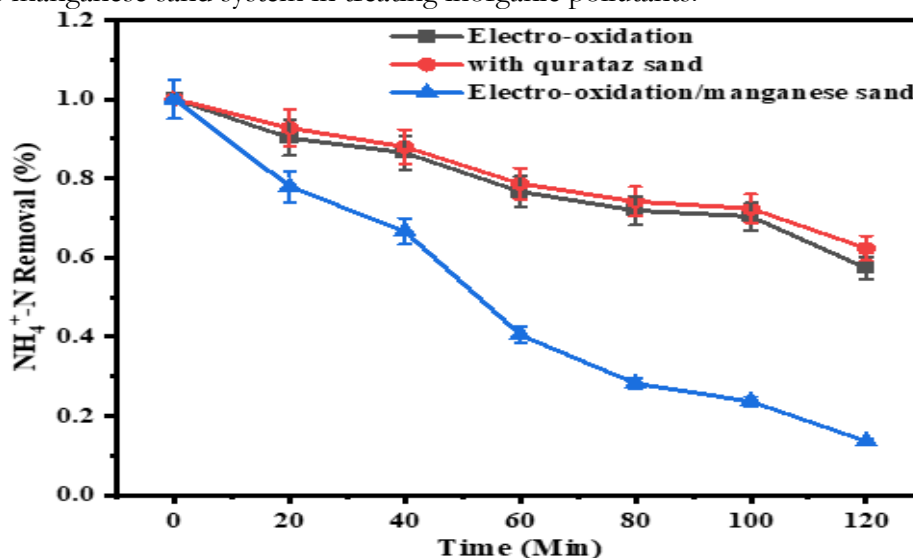


Figure 3. Performance of electro-oxidation manganese sand on removal of Ammonium

Influence of Operating Conditions on Electro-Oxidative NMS Performance: Effect of Ph on Removal Rate:

The influence of pH on ammonium nitrogen removal was evaluated, and the system showed adaptability to a wide pH range. At higher pH values, the system facilitated the

formation of easily removable ammonia (NH_3), while pH levels below 8 made ammonium nitrogen removal more challenging. The system achieved ammonium nitrogen removal efficiencies ranging from 90.45% to 94.4% across a pH range of 3 to 11 after 120 minutes. This enhanced removal efficiency was attributed to the system's ability to effectively oxidize ammonium nitrogen even at lower pH levels, ensuring the stability of the electrochemical manganese sand system.

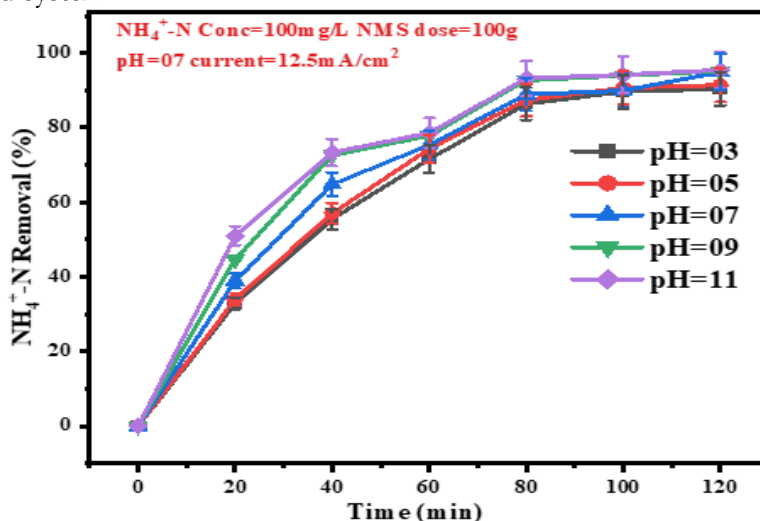


Figure 4. pH vs. $\text{NH}_4^+\text{-N}$ Removal Efficiency (%)

Effect of Current Density:

The effect of current density on ammonium nitrogen removal was also examined. As the current density increased from 5.5 to 15.5 mA/cm^2 , the removal efficiency increased accordingly. After 60 minutes, removal rates ranged from 55% to 77.3%, while after 120 minutes, the removal efficiency reached up to 94.9% at the highest current density of 15.5 mA/cm^2 . The enhancement in performance was attributed to the increased production of hypochlorite (ClO^-), which facilitated the oxidation of ammonium nitrogen.

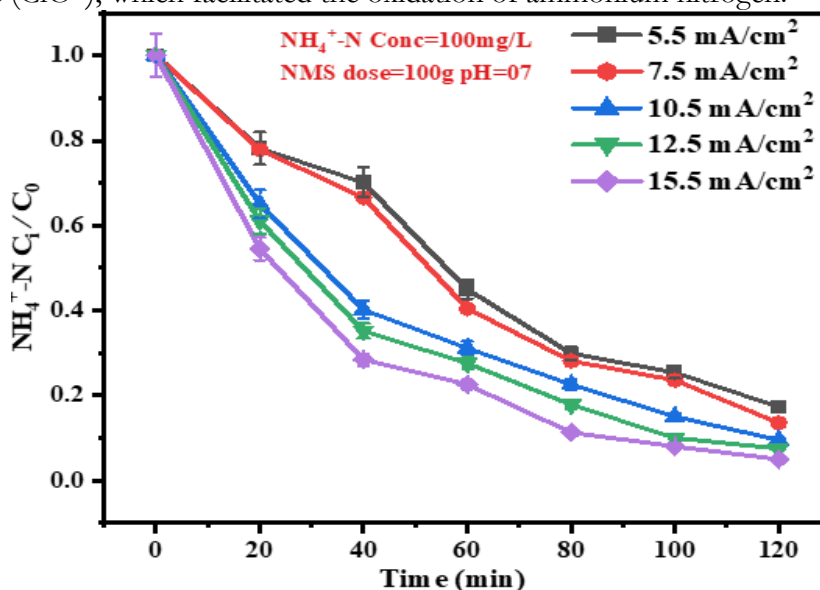


Figure 5. Current density vs. $\text{NH}_4^+\text{-N}$ Removal Efficiency (%)

Effect of NaCl Concentration:

The role of NaCl concentration in ammonium nitrogen removal was evaluated by increasing NaCl concentration from 1 to 9 g/L. Removal efficiency progressively improved, with the highest efficiency of 96.2% achieved after 120 minutes. NaCl played a crucial role in

generating hypochlorous acid (HClO) and hypochlorite (ClO^-) at the anode, which enhanced the oxidation of ammonium nitrogen. This demonstrated the potential of the NMS system as an effective technology for ammonium nitrogen removal, offering high removal rates, adaptability to varying pH conditions, and minimal secondary pollution.

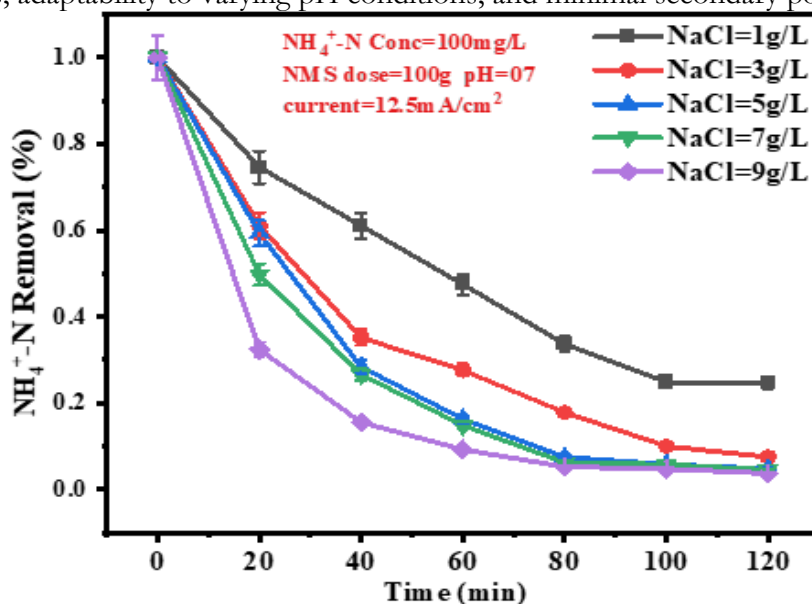
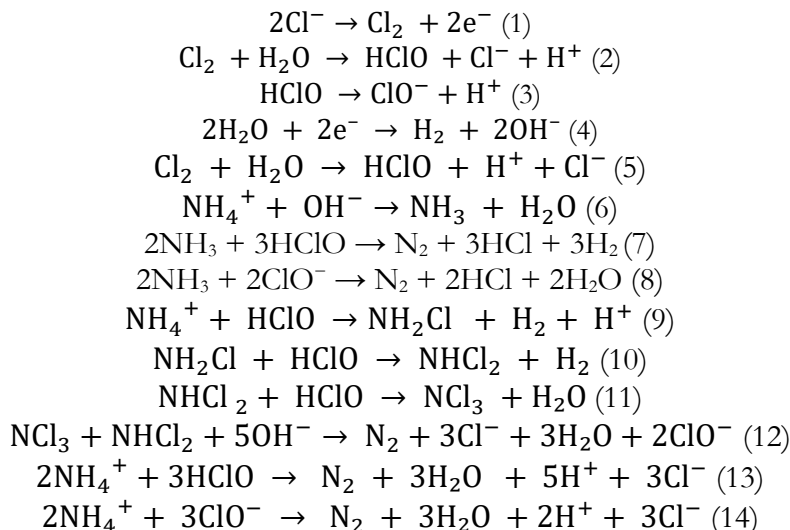


Figure 6. NaCl amount vs. NH_4^+ -N Removal Efficiency (%)

Proposed Mechanism:

The most probable reaction mechanism for eliminating ammonium nitrogen from wastewater is given below.



This mechanism is proposed to eliminate ammonium nitrogen from wastewater. Electrochemically generated chlorine reacts with water to produce hypochlorous acid (HClO) and hypochlorite (ClO^-) [15]. Ammonium ions (NH_4^+) convert to ammonia (NH_3) in the presence of hydroxyl ions [16]. Intermediate chloramines, such as monochloramine, dichloramine, and trichloramine, are then formed when ammonia combines with HClO and ClO^- . These chloramines further decompose into byproducts like nitrogen gas, hydrogen ions, and chloride ions [9].

Manganese sand acts as a catalyst, providing active sites [17] for ammonia (NH_3), ammonium ions (NH_4^+), hypochlorite (ClO^-), and hypochlorous acid (HClO). It also

facilitates electron transfer between ammonia/chloramines, hypochlorous acid, and hypochlorite.

Discussion:

The results of this study demonstrate the significant enhancement in ammonium nitrogen removal achieved through the use of electro-oxidative manganese sand (NMS) systems. In comparison to electro-oxidation alone and electro-oxidation with quartz sand, the inclusion of manganese sand greatly improved the removal efficiency, achieving a remarkable 86.4% after 120 minutes of electrolysis (Figure 3). This indicates that manganese sand plays a crucial role in facilitating the oxidation process, likely by acting as a catalyst that enhances electron transfer and supports the formation of key reactive species such as hypochlorous acid (HClO) and hypochlorite (ClO^-), which are involved in ammonium nitrogen oxidation [15][17].

The impact of operating conditions on the performance of the electro-oxidative NMS system was thoroughly investigated. A key finding was that the system exhibited high adaptability to varying pH levels, with effective ammonium nitrogen removal across a broad pH range (3 to 11), reaching removal efficiencies of over 90% in most conditions (Figure 4). The formation of ammonia (NH_3) at higher pH levels and ammonium ions (NH_4^+) at lower pH was consistent with previous findings [18], indicating that both acidic and alkaline environments are favorable for the oxidation of ammonium nitrogen. The higher removal efficiencies observed at pH values around 8 and above suggest that ClO^- ions, which are more abundant under alkaline conditions, accelerate the oxidation process, further supporting the role of manganese sand in promoting these reactions.

The effect of current density on ammonium nitrogen removal was also explored, revealing a positive correlation between increased current density and enhanced removal efficiency (Figure 5). Higher current densities generate a greater driving force for electrochemical reactions, leading to higher production of ClO^- , which facilitates the oxidation of ammonium ions. These findings align with previous studies that have shown an increased rate of pollutant removal with higher current densities in electrochemical oxidation systems [19].

Additionally, the study examined the role of NaCl concentration in the electro-oxidative NMS system. Increasing NaCl concentration from 1 to 9 g/L led to a progressive increase in ammonium nitrogen removal efficiency, reaching 96.2% at 9 g/L (Figure 6). This can be attributed to the increased production of hypochlorous acid and hypochlorite at the anode, which are key oxidizing agents that promote the oxidation of ammonium ions [20]. The synergy between NaCl concentration and manganese sand highlights the importance of optimizing these parameters to enhance the performance of electrochemical treatment systems for wastewater treatment.

Overall, the electro-oxidative NMS system demonstrates promising potential for efficient ammonium nitrogen removal from wastewater. The system's high removal efficiency, adaptability to varying pH conditions, and the synergistic effect of NaCl and manganese sand suggest that it could be an effective technology for treating ammonium nitrogen contamination in industrial effluents. Future studies should further explore the long-term stability and scalability of this system, as well as its potential application in larger-scale wastewater treatment facilities.

Conclusion:

The removal efficiency of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) was improved by adjusting various parameters such as pH, current density, and NaCl concentration. Manganese sand serves as an effective catalyst due to its high redox potential and large surface area, significantly enhancing $\text{NH}_4^+\text{-N}$ removal. Varying NaCl concentrations (1–9 g/L) notably improved the

removal efficiency, reaching 96.2%, due to the formation of reactive chlorine species (ClO^- and HClO). Increasing the current density (from 5.5 to 15.5 mA/cm^2) further enhanced performance, achieving 94.9% removal at the highest current density by generating more active chlorine species (ClO^-). The system is adaptable to a wide pH range (3–11), with the highest removal efficiency (95.2%) observed at pH 9. At this pH, NH_3 and ClO^- are more prevalent, speeding up the oxidation process and shifting the equilibrium toward NH_3 formation. However, in strongly acidic conditions, activated ions from manganese sand may leach, reducing removal efficiency and possibly deactivating the catalyst due to the reaction of byproducts [21]. This electro-oxidative NMS method is characterized by its controllability, scalability, and high removal efficiency, making it ideal for treating toxic waste in metropolitan and industrial settings. Its adaptability to various operational conditions ensures its effectiveness across multiple applications.

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