

Revisiting Electrochemical Breakpoint Chlorination of Ammonium-Rich Wastewater: Reactive Chlorine Speciation on IrTaOx/TiO₂

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Significance and Relevance

Electrochemical breakpoint chlorination (EC-BC) offers a promising method for ammonia-nitrogen (N) removal, though the roles of reactive chlorine species (RCS) are not fully understood. This study explored RCS speciation on an IrTaOx/TiO₂ anode, which demonstrated superior RCS generation influenced by pH, current density, and chloride concentration. Our findings demonstrated that dichlorine radical anion (Cl_2^{--}), previously underexplored, plays a critical role in degrading ammonia-N in wastewater into nitrogen gas (N₂). Acidic pH favored Cl₂-- and chlorine evolution, while alkaline conditions enhanced NH₃ speciation, improving removal rates. We also tested the EC-BC for treatment of ammonia-rich alkaline industrial wastewater, focusing on the cathodic scale formation and operation control strategy.

Preferred and 2nd choice for the topic: Water treatment Preferred presentation: Oral preferred

Introduction and Motivations

Traditional biological wastewater treatment plants are ineffective for high-strength N and recalcitrant wastewater, such as that from industries, due to a low carbon-to-nitrogen ratios and extended retention time (on the order of several days) requirement. In this context, the EC-BC offers a promising alternative as it can handle high N loads within a few hours by controlling the production of RCS, including chlorine radicals ¹. However, the role of RCS species on the efficiency of EC-BC along with the effects of operating parameters remains being insufficiently explored^{1,2}. This study tackles this research bottleneck, while proves the practical applicability of the EC-BC to deal with industrial wastewater with variable pHs.

Materials and Methods

The EC-BC experiments were conducted using a three-electrode system consisting of an IrTaO_x/TiO₂ anode, a SUS304 cathode, and an Ag/AgCl (3M NaCl) reference electrode, with a current density of 200 A m⁻² unless otherwise specified. The reactions were carried out in a solution containing 100 mM NaCl and 50 mM (NH₄)₂SO₄, with the pH adjusted using NaOH and H₂PO₄. Radical steady-state concentrations ([radical]_{ss}) and scavenging tests in the EC-BC system were conducted using benzoic acid (BA, 50 μ M), para-chlorobenzoic acid (p-CBA, 50 μ M), and 1,4-dimethoxybenzene (DMOB, 500 μ M) as probe compounds for \cdot OH, Cl \cdot , and ClO \cdot , as well as carbamazepine (CBZ, 500 μ M) to scavenge \cdot OH, Cl \cdot , ClO \cdot , and Cl₂⁻⁻.

Results and Discussion

Fig. 1a demonstrates that CIER on $IrTaO_x/TiO_2$ anode achieves efficient EC-BC, resulting in complete conversion of ammonia to N₂ gas. However, Fig. 1b reveals that the ammonia-N degradation rate as a function of pH (pink line) has contrasting trends against a chemical breakpoint chlorination (C-BC, blue line). Notably, despite the limitation under acidic conditions, with predominant free chlorine as HOCl and ammonia-N as NH_4^+ leading to a low intrinsic bimolecular rate constant,³ the EC-BC system exhibited the highest ammonia-N degradation rate under the acidic pH. This suggests the presence of critical factors governing the EC-BC system that are absent in the C-BC system. Chlorine radical species are critical for ammonia degradation in electrochemical advanced oxidation processes (E-AOPs) during CIER. These radicals are distinctly generated in the EC-BC system but are absent in conventional C-BC system. We systematically investigated not only OH·, Cl·, ClO· but also Cl₂⁻⁻, which have been largely



overlooked in the context of ammonia degradation within E-AOPs due to their relatively low bimolecular rate constant with ammonia $(3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})$. Our results demonstrate that Cl_2^{--} plays a crucial role in the EC-BC system, with its concentration being several orders of magnitude higher than that of other radical species across all pH levels (Fig. 1c). The concentration of Cl_2^{--} is particularly elevated under acidic conditions, as confirmed by scavenging tests (Fig 1d), which indicates that Cl_2^{--} is predominantly involved in ammonia degradation. This enhanced generation in acidic environments can be attributed to an elevated equilibrium potential of the competing OER^4 . The increased efficiency of CIER promotes higher CI- production, shifting the equilibrium between CI- and Cl_2^{--} (as described in Eq. 1), thus establishing a regime where Cl_2^{--} dominates. Additionally, Fig. 2 shows that the concentration of Cl_2^{--} increases with higher initial chloride concentrations and current density, further supporting this mechanistic insight.



Figure 1. (a) Ammonia-N conversion to N_2 during EC-BC through ClER on an IrTaO_x/TiO₂ in pH 7, (b) Comparison of ammonia degradation rate between C-BC and EC-BC depending on pH, (c) [radical]_{ss} depending on pH in EC-BC system and (d) Radical scavenging test in EC-BC system at pH 4.



Figure 2. Influence of current density on $[radical]_{ss}$ of (a) Cl_2^{--} , (b) ClO_2 , and (c) Cl_2 and (d) impact of initial chloride concentration on the $[radical]_{ss}$ during EC-BC in pH 4.

The EC-BC system via ClER on $IrTaOx/TiO_2$ electrocatalyst offers a promising alternative for the denitrification of acidic wastewater, which poses challenges for conventional C-BC methods, owing to the efficient generation of Cl_2^{-} . In addition, the highest efficiency of EC-BC was obtained in an alkaline pH, which could be utilized to handle an ammonia-N rich, alkaline industrial wastewater.

References

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