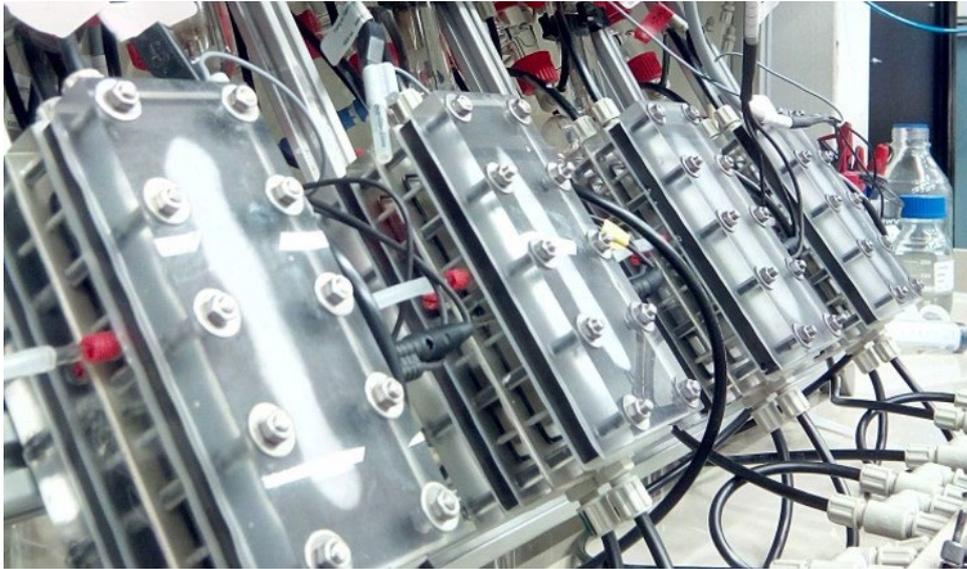


Conversion of ammonia nitrogen to electricity

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Dr. Xiaofang Yan; Prof.dr.ir Annemiek ter Heijne
Environmental Technology
Wageningen University and Research

Background and motivation

Nitrogen (N) pollution poses a significant challenge to human society, particularly in aquatic environments. Large amounts of reactive N from human activities accumulate in water bodies, exceeding their natural capacity to remove it and leading to pollution. This N pollution causes algal blooms and damages aquatic ecosystems. Additionally, N compounds such as nitrous oxide (N₂O) contribute to greenhouse gas emissions and exacerbate climate change. Therefore, effective N removal from wastewater is crucial for protecting both water quality and mitigating greenhouse gas emissions.

Wastewater with low carbon-to-nitrogen (C/N) ratios, often measured as chemical oxygen demand (COD) to total nitrogen (TN), is particularly difficult to manage using traditional biological processes due to a lack of bioavailable carbon for denitrification.

Microbial Electrolysis Cells for nitrogen removal

To provide an alternative for treatment of wastewater with low carbon-to-nitrogen ratios, Microbial Electrolysis Cells (MECs) were explored as a viable solution. In this approach, a polarized bioanode (+0.55V vs Ag/AgCl) facilitates the conversion of NH₄⁺, the predominant N form in raw wastewater, to harmless N₂ without requiring added organic matter. The electrode functions as an electron acceptor, replacing O₂ and minimizing the energy-intensive aeration step. This research has addressed critical challenges associated with NH₄⁺ oxidation rates, product selectivity, and environmental impact, particularly N₂O emissions in MEC-based NH₄⁺ removal, with a focus on bioanodes.

Enhancing removal rates through microaerobic conditions

In the first part of this project, we focused on enhancing NH₄⁺ oxidation rates at the bioanodes. In traditional nitrification processes, O₂ is the critical electron donor for NH₄⁺ oxidation. By allowing passive diffusion of O₂ from air into the liquid (dissolved oxygen, DO: 0.02–0.2 mg-O₂/L), NH₄⁺ oxidation rates at bioanodes increased by 90% compared to anoxic conditions. The rate-limiting step of bioanodic NH₄⁺ oxidation is the oxidation of NH₄⁺ to hydroxylamine (NH₂OH), a crucial intermediate, which is accelerated by O₂. While O₂ enhances the oxidation rate, it also leads to byproduct formation, including NO₃⁻ (~15% of converted NH₄⁺) and N₂O (~1% of converted NH₄⁺). In the absence of O₂, only N₂ was produced, indicating different conversion pathways with and without O₂.

Nitrogen removal at different O₂/NH₄⁺ ratios

Here, we focused on optimizing O₂ supply to balance selectivity towards N₂ and oxidation rates. A new management indicator, the O₂ to NH₄⁺-N (O₂/NH₄⁺-N) ratio, is proposed to better control O₂ supply when O₂ requirements are low and precise management is necessary. An O₂/NH₄⁺-N ratio of 0.5 yields optimal system performance, achieving a balance between N₂ selectivity (51.4% ± 4.5%) and oxidation rates (344.6 ± 14.7 mg-N/L-d), with a coulombic efficiency of 30.7% ± 2.0%. O₂ was demonstrated to be a more favorable electron acceptor compared to the electrode; Increased O₂ input resulted in higher NO₃⁻ production, whereas lower O₂ input enhanced selectivity towards N₂.

Community analysis revealed that nitrifiers and denitrifiers were the primary microorganisms responsible for N conversion at the anodes, with O_2 enriching the presence of nitrite-oxidizing bacteria, while denitrifiers may reduce oxidized N species using endogenous organics or H_2 crossover from the cathode.

Effect of anoxic conditions on N_2O emissions

Despite the advantages of O_2 in enhancing NH_4^+ oxidation rates, its presence also results in NO_3^- accumulation and N_2O emissions. Therefore, we focused on anoxic conditions and N_2O production during NH_4^+ oxidation at bioanodes. Surprisingly, in contrast to the earlier results, N_2O production became significant (~40% of the oxidized NH_4^+-N), with NH_2OH oxidation identified as the dominant pathway for N_2O formation, likely attributed to the evolution of the microbial community following the earlier experiments. Nitric oxide (NO) likely plays an intermediate role in N_2O production. While NO_2^- reduction to N_2O and N_2 was observed, this pathway was minor. Nitrifiers have been identified as primary contributors to N_2O production. Although significant N_2O was produced, N_2O reduction to N_2 was also noticed, indicating a potential sink for N_2O mitigation that is influenced by anode potential and indirectly affects H_2 production at the cathode.

The role of H_2 in preventing N_2O emissions

Based on the previous findings, we hypothesize that H_2 could aid in reducing N_2O emissions from the bioanodes. We verified the capability of anodic biomass to reduce N_2O to N_2 by increasing H_2 availability. The addition of H_2 completely eliminated the emission of N_2O without significantly impacting NH_4^+ removal efficiency, with denitrifiers primarily responsible for N_2O reduction with H_2 . This dual approach of combining NH_4^+ oxidation with denitrification presents a promising pathway for more sustainable N removal without N_2O emissions.

Application of MECs for nitrogen removal and impact of this TKI project

Here, we discuss environmental applications of MEC-based NH_4^+ removal technology. Overall, NH_4^+ is oxidized at the bioanodes to produce NO, marking a pivotal point where denitrification can take over, leading to N_2 and N_2O production. N_2O may accumulate if there are insufficient electron donors to complete denitrification. Increasing H_2 availability can facilitate the complete reduction of N_2O to N_2 and may serve as a control strategy for N_2O emissions. When O_2 is present, it functions as the primary electron acceptor, resulting in higher removal rates and increased NO_3^- production. The advantages of MEC technology for NH_4^+ removal include minimal O_2 and organic matter requirements compared to conventional nitrification and denitrification, shortened pathways from NH_4^+ to N_2 , and improved potential for N_2O control. This technology is particularly beneficial for streams with low NH_4^+ concentrations and limited carbon sources.

Overall, this work has provided crucial insights into understanding NH_4^+ oxidation processes at the bioanodes, which will aid in advancing reactor design and operation to achieve zero N_2O emissions with MEC technology.

Publications

Xiaofang Yan, Dandan Liu, Johannes BM Klok, Sanne M de Smit, Cees JN Buisman, Annemiek Ter Heijne. 2023. [Enhancement of ammonium oxidation at microoxic bioanodes](#), Environmental Science & Technology, 57 (31), 11561-11571.

Xiaofang Yan, Dandan Liu, Sanne M de Smit, Vera Komin, Cees JN Buisman, Annemiek Ter Heijne. 2024. [Oxygen-to-ammonium-nitrogen ratio as an indicator for oxygen supply management in microoxic bioanodic ammonium oxidation](#), Water Research, 261, 121993.

Xiaofang Yan, Zhenqiu Yang, Sanne M. de Smit, Dandan Liu, Cees J.N. Buisman, Annemiek ter Heijne. Understanding Nitrous Oxide Production in Anoxic Ammonium Oxidation at a Bioanode. In preparation.

Xiaofang Yan, Sanne M. de Smit, Dandan Liu, Cees J.N. Buisman, Annemiek ter Heijne. Integrating Hydrogenotrophic Denitrification in Anoxic Bioanodic Ammonium Removal to Mitigate Nitrous Oxide Emissions. In preparation.

Presentations and awards

Xiaofang Yan won the best presentation award for her presentation “Enhancement of ammonium oxidation at microoxic bioanodes” at EU-ISMET, September 2023 in Wageningen.

Xiaofang Yan won the 2023 Innovation Award for Best Technological Ddvancement, through ISMET (International Society of Microbial Electrochemistry and Technology).