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Research Article

Techno-Economic Analysis and Life Cycle Assessment of Hydroxylamine Eco-Manufacturing via Wastewater Electrochemical Reduction

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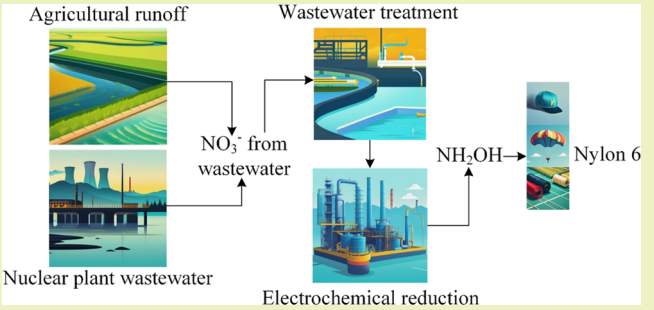
ABSTRACT: There is a growing need to develop novel technologies that reduce reactive nitrogen concentrations in wastewater streams and decrease our reliance on fossil fuel energy required to produce N-based chemicals and fertilizers. This study conducts a techno-economic analysis (TEA) and a life cycle assessment (LCA) of the electrochemical conversion of nitrate ions (NO_3^-) present in wastewater to hydroxylamine (NH_2OH), a valuable chemical intermediate. We employ experimental data and modeling assumptions to determine NH_2OH production costs and life cycle emissions for a small-scale facility (producing 1500 kg-NH_2OH/day) and a large-scale facility (producing 50,000 kg-NH_2OH/day) integrated into a wastewater treatment plant. The present NH_2OH production costs for the small- and large-scale facilities are estimated at \$6.14/kg-NH_2OH and \$5.37/kg-NH_2OH, respectively. The parameters dominating the electrochemical reactor cost are electrolyte, separations, and fixed cost, with their values as \$1.48, \$0.96, and \$0.53/kg. Future cost reduction projections indicate that the present NH_2OH production costs for the small- and large-scale facilities can be reduced to \$2.79/kg-NH_2OH and \$2.06/kg-NH_2OH (NH_2OH market price = \$1.72/kg), respectively, with improvements in the sensitivity analysis parameters. LCA results indicate that the proposed electrochemical pathway to produce NH_2OH has lower life cycle impacts than the conventional pathway.



KEYWORDS: *electrochemical reduction, hydroxylamine, techno-economic analysis, life cycle assessment, eco-manufacturing*

INTRODUCTION

Population growth has led to the rapid expansion and intensification of modern agricultural practices. Modern agriculture relies on synthetic fertilizers to provide plant nutrients, such as nitrogen (N) to increase crop productivity. Since the 1960s, global fertilizer consumption has increased from 50 to more than 200 million tons per year,[1] and synthetic fertilizer production accounts for 2% of the world's energy use.[2,3] Modern agriculture is one of the most significant contributors to anthropogenic non-CO_2 greenhouse gas (GHG) emissions due to emissions from fertilizer nitrous oxide (N_2O), ammonia (NH_3), and methane (CH_4). Agriculture contributes up to 24% of anthropogenic GHG emissions[4] through organic decomposition, denitrification, and eutrophication processes. Wastewater treatment can reduce these emissions but is expensive and produces low-value heat and electricity. Electrochemical reduction is an alternative eco-manufacturing strategy that can produce high-value chemicals like hydroxylamine (NH_2OH) from wastewater powered by renewable electricity while avoiding environmental impacts.

Plants need N to form primary biological structures, but cannot directly utilize atmospheric nitrogen (N_2). They rely on natural and artificial nitrogen cycles, as illustrated in Figure 1. The natural nitrogen cycle balance is divided into biological nitrogen fixation and high-energy nitrogen fixation. Microorganisms help plants by promoting N fixation from N_2 into ammonia (NH_3)/ammonium ion (NH_4^+) or nitrogen oxides (NO_x). In biological nitrogen fixation, the nitrogenase enzyme (produced by bacteria in leguminous plants) reduces atmospheric N_2 to NH_3/NH_4^+. High-energy N fixation can occur due to natural phenomena, which convert atmospheric N_2 eventually to form nitrate ions (NO_3^-). These oxides then arrive on the soil along with rain to fertilize the soil.[5,6]

Artificial nitrogen fixation techniques are gaining popularity in agriculture. The Haber–Bosch process is an artificial nitrogen fixation technique that has dominated the industrial production of ammonia since its discovery at the beginning of the 20th century. This process was a scientific breakthrough, as

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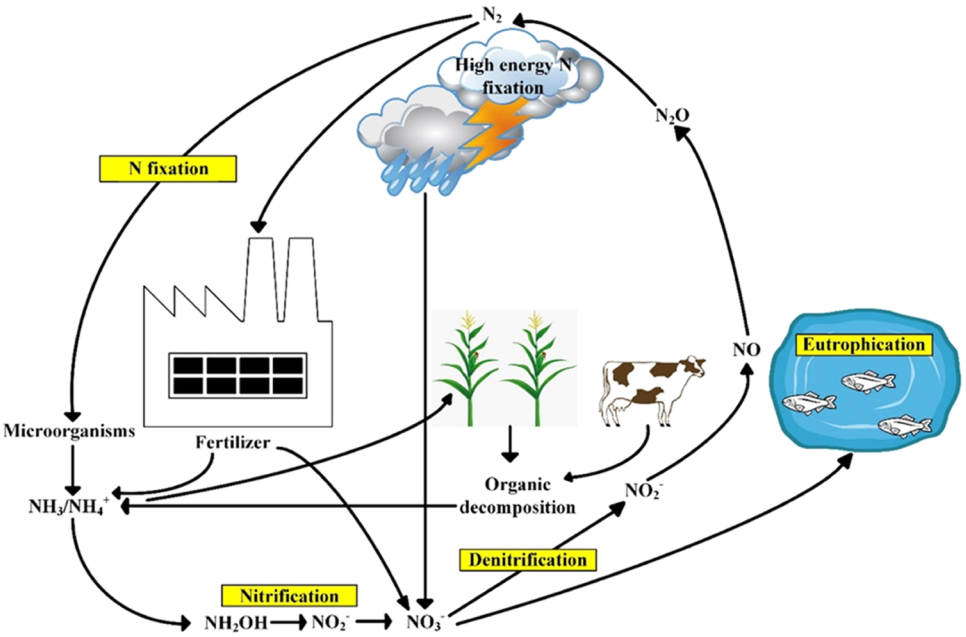

Figure 1. Simplified nitrogen cycle. Atmospheric N_2 becomes available to plants through nitrogen fixation, fertilizer synthesis, nitrification, organic decomposition, and high-energy N fixation. Denitrification and eutrophication lead to N losses (derived from Lehnert et al., 2018[7]).

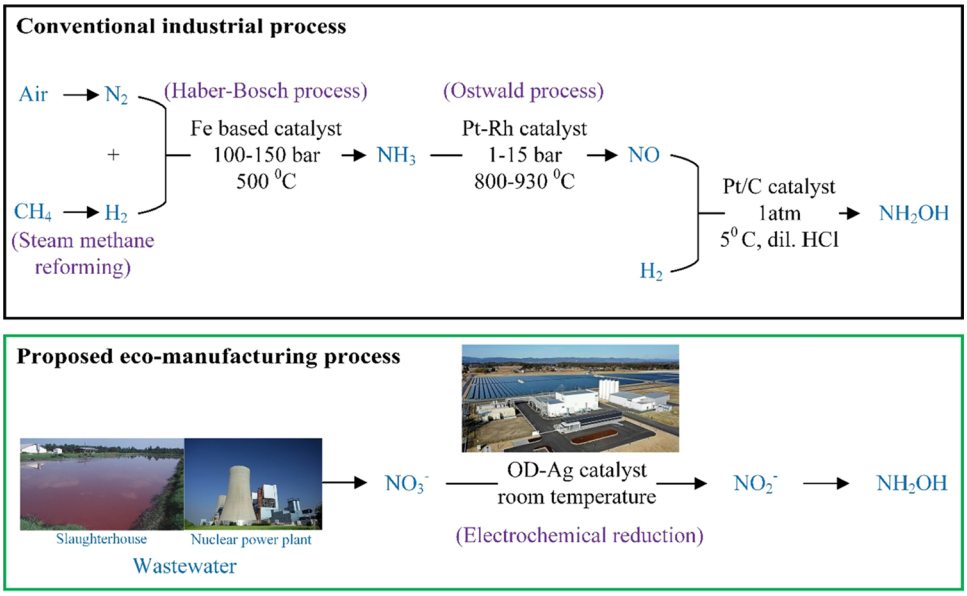

Figure 2. Conventional industrial (Haber−Bosch, Ostwald, and hydrogenation) and proposed eco-manufacturing (electrochemical reduction) process for hydroxylamine (NH_2OH) production via OD-Ag (oxide-derived Ag) catalyst.

it was the first time NH_3, a highly reactive nitrogen species, was synthesized from its two simplest substances, nitrogen and hydrogen: N_2 and H_2. However, seeking an alternative to the Haber−Bosch process is essential to reduce its adverse environmental impacts, such as high energy consumption and significant CO_2 emissions (400 t of CO_2 annually, equivalent to 1.6% of the global CO_2 emissions) mainly due to H_2 production from steam methane reforming (SMR), which dumps CO_2 stoichiometrically.[8,9]

An alternative to the Haber−Bosch process is producing N-based chemicals from reactive nitrogen, NO_3^- found in wastewater. Excess fertilizer use results in runoff (and, subsequently, groundwater) concentrated in NH_3/NH_4^+. Soil microorganisms convert nitrogen into different forms, such as nitrites (NO_2^-) and nitrates (NO_3^-) by nitrification, which can leach from the soil to groundwater. The release of nitrates is a significant challenge as it leads to groundwater and surface water contamination and eutrophication, resulting in a loss of aquatic biodiversity.[10] There are various other sources of NO_3^- pollution in wastewater, such as nuclear power plants and slaughterhouses. Low-level nuclear waste contains the highest concentration of NO_3^- among the listed sources. It contains 1.95 M $NaNO_3$ and other chemicals in lower concentrations—0.60 M $NaNO_2$ and 1.33 M NaOH.[11,12] There is a potential to use inexpensive nuclear energy to valorize wastewater from nuclear power plants and manufacture NH_2OH. Approximately 150 kg of nitrate-nitrogen (NO_3^--N) per day was discharged into waterways from a typical slaughterhouse in

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2017. This amount of waste NO_3^- could be obtained in untreated sewage from a human population of 14,000.[13] The total NO_3^- concentration in wastewater due to the 800 federally inspected slaughterhouses in the US is around 45,000 tons of NO_3^--N per year.[14] Thus, a large amount of NO_3^- is available in wastewater, providing immense potential for conversion to valuable chemicals.

Soil microorganisms can perform denitrification to convert soil NO_3^- to N_2 via nitric oxide (NO) or nitrous oxide (N_2O), as illustrated in Figure 1. The intermediate N_2O, which has a global warming potential of 298 over 100 years, usually finds its way into the atmosphere. NO can also escape into the atmosphere and contribute to ozone layer depletion. To prevent these direct harmful impacts of NO_3^- and the indirect effects of its conversion, it becomes essential to convert it into valuable chemicals. The production of chemicals from waste NO_3^- would help to reduce its harmful concentrations, improve the ecosystem, and reduce our dependence on the Haber−Bosch process. Scientists are developing novel technologies to reduce emissions associated with fertilizer use in agriculture.[15]

This paper focuses on the techno-economic analysis (TEA) and life cycle assessment (LCA) of hydroxylamine (NH_2OH) production from waste NO_3^-. NH_2OH is an essential chemical intermediate with an annual production capacity of 800,000 tons.[16] Over 95% of the produced NH_2OH is utilized to produce its isomers—caprolactam and cyclohexanone oxime ($C_6H_{11}NO$), intermediates in synthesizing nylon-6, a widely used polymer for manufacturing fibers.[16] The conventional industrial process for NH_2OH production and an alternative eco-manufacturing process are illustrated in Figure 2. The proposed alternative process involves the electrochemical reduction of waste NO_3^- found in wastewater streams from slaughterhouses, agricultural runoff, and nuclear power plants to NH_2OH.

Electrochemical processes are typically executed at ambient temperature and pressure, thus requiring mild operating conditions and a low process energy. The electricity for electroreduction can be obtained from renewable sources, such as wind and solar power, to make the process sustainable. Kani et al. (2021) utilized solar energy for the NO_3^- electroreduction (NO_3ER) to NH_3 using oxide-derived Co as the catalyst. They obtained a high NH_3 faradaic efficiency (FE_{NH3}) of 92.37 ± 6.7% and a high solar-to-fuel efficiency of 11%.[17]

Many researchers have performed NO_3ER using various cathode materials as catalysts like Fe,[18] Ir-deposited carbon fiber electrode,[19] Pd/Sn/Au electrodes,[20] Sn-modified Pt electrode,[21] and Pt[22] and obtained multiple products, including NO_2^-,[2222] NH_3,[19] and N_2.[19,20] There is an increasing interest in synthesizing HNO_3[23] and NH_3 using TiO_2 nanotubes,[24] a cobalt macrocycle complex,[25] $Cu_{50}Ni_{50}$ alloy,[26] Fe single-atom catalyst,[27] Cu-based catalysts,[28−31] and Sn[32] via waste NO_3^- instead of producing from the stable and inert molecule, N_2. A comprehensive literature review is provided in the Supporting Information (SI). Liu et al. used an oxide-derived Ag (OD-Ag) electrocatalyst for converting NO_3^- to NO_2^-. They obtained 98% selectivity and 95% faradaic efficiency of NO_2^- (FE_{NO2-}).[33] Further reduction of NO_2^- to NH_4^+ was performed, and they could achieve faradaic efficiency of NH_4^+, FE_{NH4+} as 89%. They also designed an innovative combined electrocatalytic−catalytic process for the NO_3ER and achieved 95+% reduction to N_2 while producing negligible NO_x gases. There is an increasing focus on producing NH_2OH from the electrochemical reduction of nitrogen-containing chemicals, especially NO_2^- using Cu,[30] Fe,[34] Rh,[35] Sn,[36,37] Pd,[38] and Pt[39] electrodes (details in the SI). Table 1 shows results from the literature for the faradaic efficiency of NH_2OH (FE_{NH2OH}) and selectivity from different catalysts and electrodes.

Table 1. NH_2OH Faradaic Efficiency (FE) and Selectivity[a]

FE_{NH2OH} (%)	NH_2OH selectivity (%)	electrocatalyst/electrode used	ref
93	na	FeN_5H_2	34
na	83	Pt and PtSn	36
na	25	Pt with Ge	39
60	na	Pt, Pd, and Pt+Pd with Ge	38

[a]Not available (na).

There are a few studies on the TEA of electrochemical systems. The US Department of Energy (DOE) developed the benchmark Hydrogen Analysis (H2A) that calculates the production costs of H_2 and compares different H_2-producing technologies. The models require the desired internal rate of return (IRR), lifetime, and other parameters as the input. It provides the H_2 selling cost in $/kg of H_2 produced as the output. The H2A models have been adapted by researchers synthesizing other chemicals via similar electrochemical technologies.[40] Colella et al. (2014) used the DOE H2A model to assess the economic feasibility of current and future PEM electrolysis systems.[41]

A few models in the literature perform TEA of the CO_2 electroreduction (CO_2ER) pathways to various chemicals. They include Leow et al.,[42] Bushuyev et al.,[43] Ozden et al.,[44] Verma et al.,[45] Jouny et al.,[46] Shin et al.,[47] and Na et al.[48] Gomez and Garzon used their model for NH_3 production cost calculation,[49] and James et al. used it for solid oxide fuel cells (SOFC) and proton exchange membrane systems (PEMs).[50] (details in the SI)

METHODOLOGY

Techno-Economic Analysis of the Haber−Bosch Process. The conventional industrial method to produce NH_2OH is depicted in Figure 2. It consists of the Haber−Bosch process, the Ostwald process, and the NO hydrogenation. The TEA of the Haber−Bosch process was adapted from Wang et al.,[51] and the market price of NH_2OH ($1.72/kg) is used as the cost of the conventional industrial route (see the SI for more details).[52]

Techno-Economic Analysis of the Eco-Manufacturing Process Description of the NH_2OH Production Pathway. NH_2OH from NO_3^- follows a two-step electrochemical process. First, NO_3^- is converted to NO_2^-; in the next step, NO_2^- is converted to NH_2OH, as illustrated in eqs 1 and 2.

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \quad (1)$$

$$NO_2^- + 4e^- + 4H_2O \rightarrow NH_2OH + 5OH^- \quad (2)$$

The rate-determining step in the electroreduction of NO_3^- is its reduction to NO_2^-, as illustrated in eq 1.

The proposed eco-manufacturing process to produce NH_2OH depicted in Figure 2 is illustrated in detail in Figure 3. The figure shows that the entire process is divided into four subsystems. The conversion of NO_3^--rich wastewater to

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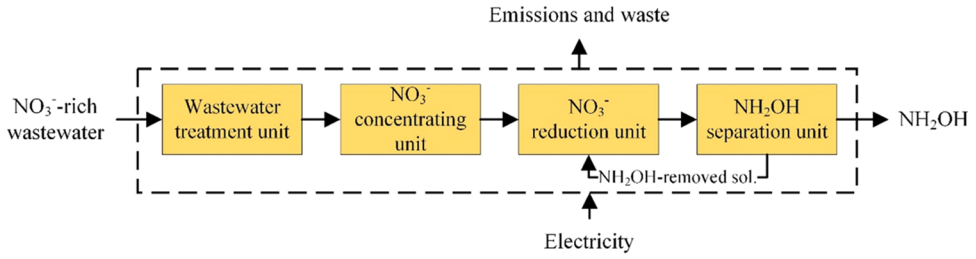

Figure 3. Process system for NO_3^- conversion to NH_2OH, along with the considered system boundary (in dotted lines)

NH_2OH occurs in four steps: wastewater treatment, NO_3^- concentration, NO_3^- reduction, and NH_2OH separation.

The following text details the TEA methodology followed to calculate the cost for these subsystems.

Wastewater Treatment Unit. We obtain the cost of small- and large-scale wastewater treatment plants from Hernandez-Sancho et al. (2011). The technology chosen for wastewater treatment is activated sludge, which removes suspended impurities from incoming wastewater. Table 2 lists the wastewater treatment costs obtained from the reference study, with their units converted to $\frac{\$}{\text{kg - NH}_2\text{OH}}$.

Table 2. Wastewater Treatment Cost for Small- and Large-Scale Facilities

	small-scale facility	large-scale facility
wastewater treatment costs in $\frac{\$}{\text{kg - NH}_2\text{OH}}$	2.09	1.48

NO_3^- Concentrating Unit. The unit process shown in Figure 3 is the NO_3^- concentrating unit. We assume a membrane-operated electrodialysis (ED) unit, as depicted in Figure S1, to concentrate the NO_3^- ions present in wastewater. ED uses electricity to separate a stream containing dissolved ions into a concentrated and dilute stream at atmospheric pressure. The concentrating step becomes necessary as the wastewater is too dilute in NO_3^- to be sent to the NO_3ER unit. Based on personal communication with Dr Shuang Gu, the ED unit increases the NO_3^- concentration from 7.14 mM to 2 M.[53]

For the small-scale facility, we obtained the ED life cycle cost as $\frac{\$\,0.13}{\text{kg - NH}_2\text{OH}}$ based on the assumptions listed in the SI, which also shows the detailed calculation. For the large-scale facility, we obtained the ED life cycle cost as $\frac{\$\,0.09}{\text{kg - NH}_2\text{OH}}$.

NO_3^- Reduction Unit. The following unit process shown in Figure 3 is the NO_3^- reduction unit. This work builds upon the results of Liu et al. and preliminary experiments by Yifu.[33] Liu et al. performed the electroreduction of NO_3^- to NO_2^- using an OD-Ag electrocatalyst. The electrochemical cell's experimental data and design parameters, taken as the input for our TEA model, are listed in Table S2.

Cost Estimate for NH_2OH. To the best of our knowledge, this is the first TEA and LCA study calculating the NH_2OH production cost using wastewater (containing NO_3^-) as a feedstock. We conduct a TEA of our electrochemical conversion system and calculate the NH_2OH production cost by adapting the general electrochemical TEA model developed by Orella et al. (2020).[54] Their MATLAB-based model can perform a preliminary TEA of an electrochemical system. The model is built with the help of previous TEA studies of electrochemical processes by Verma et al.,[55] Ainscough et al.,[56] and James et al.[57] The TEA results presented here are preliminary estimates for a conceptual *n*th plant design. An nth plant design assumes that all technical and engineering breakthroughs required for commercialization have been achieved, and the process operates as an industrially mature technology.

The NH_2OH production cost and its breakdown are plotted in Figure S2 (methodology detailed in the SI). We obtained the same production cost for both scenarios considered. Thus, we did not find any cost reduction due to economies of scale. Orella et al. also mention the same result and state that the effect of economies of scale on production cost is unclear due to a limited number of large-scale electrochemical plants.[54] The results are discussed in the Results and Discussion section.

NH_2OH Separation Unit. The unit process shown in Figure 3 is the NH_2OH separation unit. As shown in Figure S4, we assume a membrane-operated ED unit similar to that we had for the NO_3^- concentration (Figure S1).

The TEA of this unit was conducted based on the analysis by Vineyard et al. and their companion study, which we also used for the TEA of the NO_3^- concentration unit.[58,59] For the small-scale facility, we obtained the ED life cycle cost as $\frac{\$\,0.13}{\text{kg - NH}_2\text{OH}}$. For the large-scale facility, we obtained the ED life cycle cost as $\frac{\$\,0.09}{\text{kg - NH}_2\text{OH}}$.

Life Cycle Assessment (LCA). LCA is a methodological framework to estimate the environmental emissions and impacts on human health of a product or a chemical throughout its life cycle. It is also used to compare different products based on their life cycle environmental impacts and thus can effectively guide the production of more sustainable products. The life cycle of a product (referred to as "Cradle to Grave") begins with raw materials extraction, followed by manufacturing, transport, and use, and ends with waste management.

Goal and Scope Definition. The first step in beginning an LCA study is writing the goal and scope statements. The goal of this LCA study is to calculate the environmental impacts of the proposed eco-manufacturing route to produce NH_2OH in a wastewater treatment plant in Iowa. The reason for the study is to determine if the proposed alternative method of producing NH_2OH is a sustainable option compared to the most prevalent route of making almost every N-based chemical, the Haber–Bosch process. The obtained results are thus compared with the conventional method of NH_2OH production. Scope answers the question, "what is included in the study?" by defining the functional unit, product system studied, and system boundary considered. The functional unit we used for this study is "1 kg of NH_2OH produced".

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Life Cycle Inventory. The next step is to determine a life cycle inventory (LCI) consisting of the input and output data for each unit process within the product system, as obtained from the literature or simulation calculations. Inventory data for this study were obtained from balanced chemical reactions, our preliminary TEA model, and the literature, which are scaled to the functional unit: 1 kg of NH_2OH produced. We performed a "Cradle to Gate" analysis, focusing on the system from resource extraction to transport and not including the use and waste management phases of NH_2OH. We used openLCA 1.11.0 to perform an LCA of the conventional industrial route and the proposed pathway using Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) 2.1 as the impact assessment method, which evaluates these impact categories: acidification, carcinogenics, ecotoxicity, eutrophication, fossil fuel depletion, global warming, noncarcinogenics, ozone depletion, respiratory effects, and smog. The life cycle impacts for these impact categories are discussed in the Results section.

Some studies comparing the electrocatalytic pathway of manufacturing chemicals with the conventional routes (fossil fuel-based and biocatalytic) based on their environmental emissions (detailed literature review in the SI) have been referred to for this study. These studies report the emissions from various products of CO_2ER (carbon emissions)[60] or a particular product such as formic acid (carbon emissions and fossil resources consumption)[61,62] or dimethyl carbonate (global warming potential).[63]

To the best of the authors' knowledge, there are no previous literature studies on the TEA and LCA of NH_2OH production via electrochemical NO_3^- reduction. We developed a TEA model using experimental data and modeling assumptions to fill this gap to calculate the NH_2OH production cost based on the alternate proposed pathway depicted in Figure 2. Based on this model, we calculate the cost for two NH_2OH production facilities integrated with a wastewater treatment unit. This integration would help the wastewater treatment plant owners earn extra revenue by selling the produced NH_2OH. We considered two scenarios: a small-scale facility producing 1500 kg-NH_2OH/day and a large-scale facility producing 50,000 kg-NH_2OH/day. These production rates are based on the DOE H2A model.[40] We compared the NH_2OH production cost from the alternate proposed pathway (for both facilities) to the production cost via the conventional pathway (NH_2OH market price). We conduct a sensitivity analysis to identify key TEA parameters affecting production costs. Then, we estimate the projected costs of electrochemical NH_2OH based on combined TEA improvements. Finally, we perform an LCA of electrochemical NH_2OH production scenarios and compare it to the conventional method.

The conventional method to produce NH_2OH is depicted in Figure 2. It consists of steam methane reforming, the Haber–Bosch process, the Ostwald process, and the NO hydrogenation. A few studies compared the emissions from the Haber–Bosch process to other pathways.[64−66]

As shown in Figure 3, the first unit process for the alternate pathway is the wastewater treatment unit. We obtained the LCA results for this unit from a study by Jeong et al., who evaluated the environmental impacts of the centralized water system of Atlanta, Georgia.[67] The results are discussed in the wastewater treatment unit section.

LCA of the Conventional Industrial Route. Table S4 shows the life cycle impacts of producing 1 kg NH_2OH using the conventional industrial route (Figure 2) in Iowa, as obtained from openLCA. The conventional pathway for the small- and large-scale facilities is a combination of wastewater treatment and NH_2OH production. The impacts of NH_2OH production are obtained from openLCA, and those for the wastewater treatment unit are obtained from Jeong et al.[67] We then compare these life cycle impacts to those obtained for the proposed pathway in Tables S11 and S12.

LCA of the Proposed Eco-Manufacturing Route. Figure 3 shows the process system studied and the overall system boundary (in dotted lines). The individual processes inside the system boundary are called unit processes and are reviewed in detail, and their LCA results are summed up to conduct an LCA of the entire system.

Wastewater Treatment Unit. As mentioned in the LCA literature review section in the SI, we obtained the LCA results for the wastewater treatment from Jeong et al.[67] Table S5 shows the life cycle impacts per kg-NH_2OH produced.

NO_3^- Concentrating Unit. Vineyard et al. (2021) conducted an LCA of an NH_4^+ concentrating unit using TRACI 2.1, and their results are used as a reference for NO_3^- concentrating unit.[58] We follow their methodology and calculate the energy consumption for this unit (details in the SI), which is then used to evaluate the life cycle environmental impacts. The LCA results for electricity obtained from the US average grid, solar photovoltaics (PV), and Midwest electricity are shown in Table S6 (for the small-scale facility) and Table S7 (for the large-scale facility). We observe that solar PV electricity has the least environmental impact for each impact category compared to the two grid scenarios. For both production scenarios, the Midwest electricity grid has higher life cycle emissions than the US average for most impact categories.

NO_3^- Reduction Unit. The following unit process shown in Figure 3 is the NO_3^- reduction unit. Figure S5 shows its process schematic along with the considered system boundary. The process system is adapted from Dominguez-Ramos et al. (2015) and Orella et al. and described in the SI.[68,54] We performed LCA for this unit and evaluated the environmental impacts for the two production scenarios shown in Table S8. Here, we also obtained a similar trend of reduced life cycle impacts from solar PV electricity and higher impacts for the Midwest grid compared to the US average grid, as we observed in the NO_3^- concentration unit. The impacts obtained for the reduction unit were higher than the NO_3^- concentration unit for all of the scenarios due to higher electricity consumption.

NH_2OH Separation Unit. We again follow the methodology from Vineyard et al. (2021) to evaluate environmental impacts for our NH_2OH separation ED unit, and the results are presented in Tables S9 and S10.[58]

RESULTS AND DISCUSSION

Techno-Economic Analysis. We discuss the TEA results of the NO_3^- reduction unit in detail in this section. The NH_2OH production cost is obtained as \$3.79/kg. The parameters dominating the cost are electrolyte, separations, and fixed cost, with their values being \$1.48, \$0.96, and \$0.53/kg, respectively. We performed a sensitivity analysis for both reduction steps (NO_3^- and NO_2^- reduction) to assess the potential production cost reduction and discover the parameters influencing it. We considered the separation factor (the cost of separating and recycling the solvent, electrolyte, and unreacted reactants), lifetime, conversion, electricity price,

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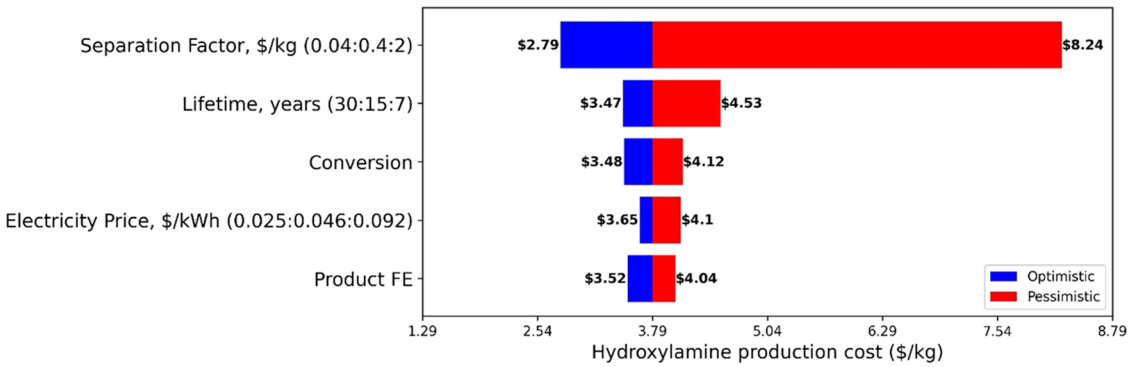

Figure 4. NH_2OH production cost sensitivity analysis to key techno-economic parameters.

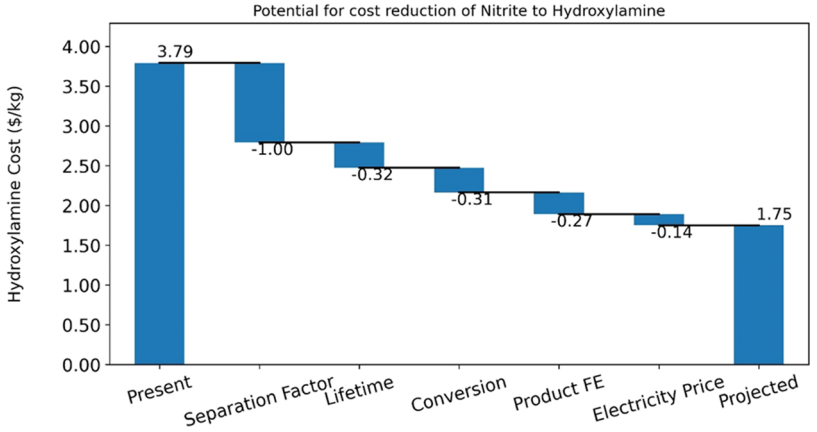

Figure 5. Potential for cost reduction of the NO_2^- to NH_2OH pathway based on improvements to the separation factor, project lifetime, electricity price, product faradaic efficiency, and catalyst loading.

product FE, and catalyst loading as the sensitivity analysis parameters. The final projected NH_2OH production cost was calculated by subtracting the present cost with the possible reductions due to improved parameters and plotted in a waterfall chart. The assumed optimistic, base-case, and pessimistic scenarios for some of the parameters for sensitivity analysis are specified in Table S3.

Figure 4 shows the sensitivity of the NH_2OH production costs to key model parameters. As shown in Figure 4, the separation factor has the most considerable impact on the production cost, resulting in its most significant reduction, followed by lifetime, conversion, and product FE. A detailed analysis is provided in the SI.

Figure 5 shows the possible reductions in the NH_2OH production cost, as estimated by the sensitivity analysis. The projected cost in the rightmost bar in both figures shows the minimum possible cost considering the cumulative cost reductions due to the parameters. It can be seen from Figure 5 that the present cost of NH_2OH production, \$3.79/kg, can be reduced by 53% to \$1.75/kg (the separation factor is responsible for half of the reduction), considering the technological advancements in the parameters. Considering the sensitivity analysis results from the first reduction step (NO_3^- reduction to NO_2^-), we obtain a projected NH_2OH production cost of \$0.5/kg. Figure S3 shows the possible reductions in the NO_2^- production cost, as estimated by the sensitivity analysis.

The total costs (\$/kg) for the electrochemical reactor of the small- and large-scale facilities are mentioned in Table 3 and compared for the present and optimistic scenario.

Table 3. TEA Comparison of the Present and Optimistic Costs of Small- and Large-Scale Eco-Manufacturing Pathways

	optimistic production cost (\$/kg-NH_2OH produced)		present production cost (\$/kg-NH_2OH produced)	
unit process name	small-scale	large-scale	small-scale	large-scale
pretreatment	2.09	1.48	2.09	1.48
NO_3^- concentration	0.1	0.07	0.13	0.09
NO_3^- reduction	0.5	0.5	3.79	3.79
NH_2OH separation	0.10	0.011	0.13	0.014
Total	2.79	2.06	6.14	5.37

TEA Comparison of the Conventional and Proposed Pathways. Table 3 shows that the present costs of both scenarios are higher than the NH_2OH market price, of \$1.72/kg.[52] However, after considering future technological improvements in parameters such as electricity price, conversion, faradaic efficiency, lifetime, separation factor, and catalyst loading, it is possible to reduce the production cost in a large-scale facility to \$2.06/kg. This projected NH_2OH cost is very close to its market price, which shows that the eco-manufacturing pathway can be economically feasible in the future, if not at present. Thus, our analysis is promising and suggests future research for improving the considered parameters. These results show that the potential for enhancing production costs is massive and a competitive market price is attainable. For the small-scale scenario, the

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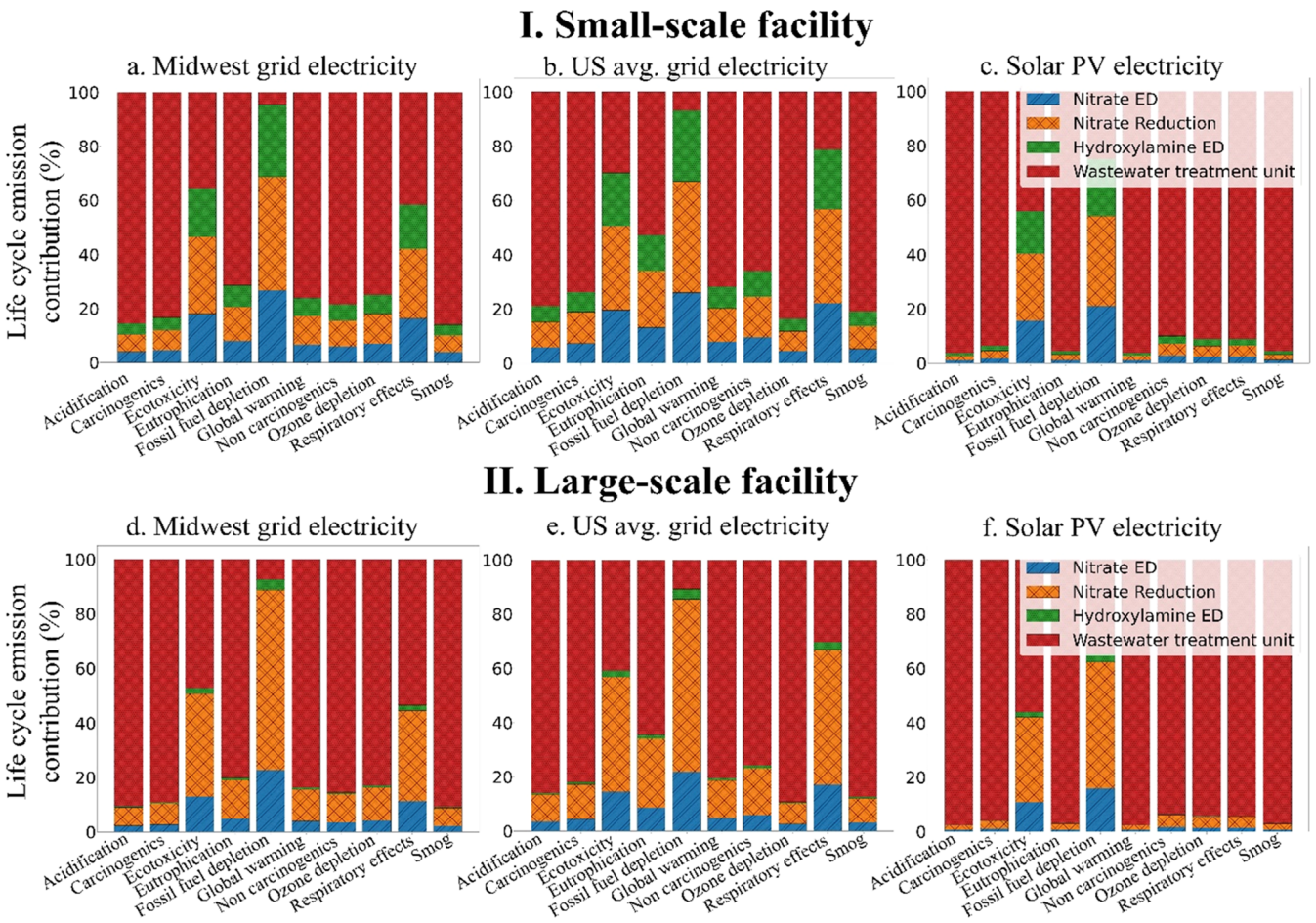

Figure 6. Life cycle emission contributions from the unit processes (using TRACI 2.1 in openLCA) for I. A small-scale facility $\left(1500\frac{\text{kg - NH}_2\text{OH}}{\text{day}}\right)$ using (a) midwest grid electricity, (b) US avg. grid electricity, (c) solar PV electricity and II. A large-scale facility $\left(50,000\frac{\text{kg - NH}_2\text{OH}}{\text{day}}\right)$ using (d) midwest grid electricity, (e) US avg. grid electricity, (f) solar PV electricity.

present cost is 6.14/kg. The wastewater treatment plant must spend an extra cost to produce NH_2OH. This additional cost (calculated as a difference between total cost and wastewater treatment plant cost) equals \$4.05/kg and \$3.89/kg for small-scale and large-scale facilities, respectively. These values are higher than the NH_2OH market price of \$1.72/kg, suggesting that integrating a wastewater treatment plant and an electrochemical NH_2OH production process is not economically feasible yet. The current total costs for the small- and large-scale scenarios could be reduced by around 60% due to future technological improvements. This cost reduction is significant and encourages future research into integrating wastewater treatment plants and simultaneous NO_3^- reduction to NH_2OH. The total cost (\$) of the entire NH_2OH production facility is shown in Table S3.

Life Cycle Assessment Results. Figure 6 shows the relative magnitudes of the life cycle impacts of small- and large-scale facilities for different electricity-source scenarios. For the small-scale facility (Figure 6a–c), we observe a consistent trend: the wastewater treatment unit has the highest life cycle impacts, followed by the NO_3^- reduction unit, NO_3^- concentration unit, and NH_2OH separation unit. The life cycle impacts are directly related to the electricity consumption—higher electricity consumption of a unit leads to its higher life cycle impacts. We calculated the electricity consumption of units (mentioned in Table 4) and observed that the electricity consumption decreases in this order: NO_3^- reduction, NO_3^- concentration unit, and NH_2OH separation unit. The LCA results of the wastewater treatment unit (for both scales) are obtained from a literature study discussed in the Methodology section. Thus, we did not calculate its electricity consumption. For the large-scale facility (Figure 6d–f), the highest life cycle impacts were obtained for the wastewater treatment unit, followed by the NO_3^- reduction unit, NO_3^- concentration unit, and NH_2OH separation unit. This trend is also due to the electricity consumption of the units in that order. A common observation for both small- and

Table 4. Calculated Electricity Consumption of Units

unit process name	electricity consumption for a small-scale facility (kWh/kg-NH_2OH)	electricity consumption for a large-scale facility (kWh/kg-NH_2OH)
NO_3^- concentrating unit	1.33	0.72
NO_3^- reduction unit	2.06	2.06
NH_2OH separation unit	1.33	0.13

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large-scale facilities is that the wastewater treatment unit dominates the life cycle impacts for most of the impact categories. Solar PV electricity has the least impact out of the three electricity scenarios considered, which suggests that the life cycle impacts of the proposed eco-manufacturing method could be reduced if we use renewable energy to power the system.

A comparison of the small- and large-scale facilities shows that the latter facility always has lower life cycle impacts (on a per kg-NH_2OH basis), as shown in Tables S11 and S12. Thus, on a per unit production basis, it is environmentally friendly to produce NH_2OH on a larger scale of 50,000 kg/day instead of 1500 kg/day due to the lower electricity consumption on a large scale.

LCA Comparison of the Conventional and Proposed Pathways. We now compare the LCA results of the proposed pathway to the conventional one. For this, we combined the results for each unit described above to evaluate the total environmental impacts of the proposed pathway. Tables S11 and S12 show these total life cycle impacts. The results shown under the column "proposed pathway" are the sum of results from Tables S5−S10. The impacts from the conventional pathway include the wastewater treatment process and the hydroxylamine production process obtained from openLCA, as mentioned in the LCA of the Conventional Industrial Route section. The comparison results are also shown in Figure S6. For both small- and large-scale facilities, the proposed pathway has lesser environmental impacts than the conventional pathway for all of the impact categories. Comparing the three electricity scenarios, we observe that Midwest electricity has the highest impact, followed by US average grid and solar PV electricity, resulting from their different electricity mix compositions in openLCA. The life cycle impacts of the electricity scenarios per kWh (in the openLCA database) show the same trend as that obtained in our results. The openLCA database gathers the emission data for different electricity technologies from the EPA website.[69] The solar PV scenario has fewer emissions than the conventional pathway for both scales, with most impacts being less than 50% of the latter. Therefore, we conclude that the proposed small- and large-scale pathways have lesser environmental impacts than the conventional pathway for all scenarios.

Conclusions and Future Work. Concerns about the environmental impacts of increasing nitrogen emissions and concentrations in wastewater streams exist. However, our analysis shows that wastewater containing NO_3^- can be converted electrochemically to NH_2OH using renewable electricity. We calculated the NH_2OH production cost based on a 1500 kg/day small-scale NH_2OH production facility and a 50,000 kg/day large-scale NH_2OH production facility. According to the authors' knowledge, this is the first TEA and LCA study calculating the cost and life cycle impacts of using wastewater (containing NO_3^-) as a feedstock for NH_2OH production. The conclusions and future work from the study are listed below:

(1) Based on the current laboratory data, an NH_2OH production cost of \$6.14/kg is estimated for the small-scale facility, and \$5.37/kg is estimated for the large-scale facility. We found that the technical performance parameters of electrochemical cells, including the separation factor, lifetime, and conversion, are the most influential factors in the final production cost from the sensitivity analysis. A parameter improvement results in a lower (large-scale) NH_2OH production cost of \$2.06/kg, close to its market price of \$1.72/kg. The preliminary TEA conducted here suggests that producing economically feasible NH_2OH from wastewater containing NO_3^- could be possible in the future.

(2) The LCA results presented here suggest that the proposed eco-manufacturing pathway produces less environmental impact than the conventional pathway for the small- and large-scale facilities, meaning that producing NH_2OH from wastewater containing NO_3^- is environmentally friendly too. Thus, there is a promising opportunity to convert waste NO_3^- into an important chemical intermediate and to reduce the dependency on the Haber−Bosch process.

(3) Future work would involve using process modeling software such as Aspen Plus to calculate mass and energy balance for the system, both of which were developed from a TEA model from the literature.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c03336.

Introduction; methodology of TEA and LCA; process schematic of electrodialysis units; production cost distribution figure; production cost reduction potential figure; life cycle impact tables for conventional industrial process; and all unit processes of the proposed pathway (PDF)

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Notes

The authors declare no competing financial interest.

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