TURNING TRASH INTO TREASURE:
NITRATE UPCYCLING AND WASTEWATER TREATMENT FOR AMMONIA PRODUCTION

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Abstract

Nitrogen pollution in irrigation runoff is prevalent in many agriculturally intensive countries. This pollutant takes the form of nitrogen oxyanions, mainly nitrate. This issue has various detrimental effects to the environment and human health, causing algal blooms and respiratory disorders. Considering nitrogen can also form value-added products such as ammonia which are crucial in for plant growth, finding a method which can both offput nitrate while producing ammonia is intriguing, as traditional methods are environmentally polluting. This research focuses on developing a wastewater treatment system which involves novel electrochemical methods to promote direct reduction of nitrate to ammonia, while also developing baseline data for the calculation of the pollutant and products, mainly using colorimetric and ionic detection methods. The results show that the baseline data is suitable for product and pollutant quantification, but a more long-term testing is deemed necessary to predict a solid trend. Additionally, techno-economical analysis estimates that despite the prototype system requires an overall higher energy compared to the industrialized methods. The system we developed emits less carbon footprint and develops an additional valuable product of drinking water. Showing a promising and considerable environmentally friendly ammonia production alternative in the future, given the energy consumption issue can be addressed.

Keywords: *nitrate, removal, pollution, ammonia production, electrochemical, energy consumption*

A. Introduction

The background of this research the problem of nitrogen pollution, which is a major environmental issue that affects both human health and the environment. Nitrogen is an essential nutrient for plant growth, but excessive nitrogen in the environment can lead to a range of negative impacts, such as eutrophication, acidification, and the production of greenhouse gases. Despite over 100 Tg of fixed nitrogen is used as fertilizer each year, only 17% is actually ingested as protein by humans and livestock. The remainder of the fixed nitrogen is converted to various nitrogen oxyanions and gases by soil organisms and lost to volatilization or in runoff to waterways. Once in waterways, nitrate can lead to eutrophication and hypoxia, ultimately forming aquatic “dead zones”. In total, eutrophication is estimated to cause $2.2 billion of damages annually. [1]

Additionally, methods of ammonia production prior to electrocatalysis, the Haber Bosch method have various adverse effects. The Bosch process requires high energy output, which is typically supplied by fossil fuels such as natural gas. Therefore, it emits significant amounts of greenhouse gases such as carbon dioxide and nitrous oxide.[4] The process is also extremely economically demanding and impractical for small scale applications.

Therefore, because of the adverse potentials of current methods and biological denitrification processes are overwhelmed by anthropogenic nitrogen,[1] there is a need for new methods of chemical nitrate removal that both eliminate damaging waste streams and yield value-added products, which in our project we are focusing on upcycling said pollutants to ammonia and reuse it as fertilizer.

In this research, the author focuses on developing a wastewater treatment prototype model, which includes the use of heterogeneous catalyst systems which have high NH_3 yields and Faradaic Efficiency. The prototype will mainly utilize the concept of reverse osmosis for the initial wastewater treatment, followed by electrochemical treatment with the electrocatalyst for direct electroreduction from NO_3^- to NH_3. This prototype is predicted to not only effectively produce NH_3 without emitting the polluting greenhouse gases like CO_2 which is largely emitted by the traditional Haber-Bosch process, with the addition of producing drinkable water, which may address various problems at once in regions where nitrate pollution in water is dominant and drinking water is scarce.

B. Methodology

1. Development of Ammonia Standard Curve

As this research will be focused on creating the baseline analysis data for the large-scale project of NO_3^- upcycling and wastewater treatment, the first objective of the research was the development of the NH_3 standard curve. The purpose of developing the NH_3 standard curve from the beginning is because this data will be used to determine and quantify the NH_3 in the future parts of this project. This includes detecting and quantifying the innate NH_3 in the wastewater samples, and NH_3 quantification in post electrochemical testing products.

In this project, Indophenol blue method similar to the research [9], was adopted for NH_3 quantification. There are 4 main components of the indophenol blue reaction. First, for solution A, dissolve 0.529 g of phenol in 5mL of absolute ethanol. Next, for solution B, dissolve 0.05 g of Sodium Nitroprusside in 10 mL DI water. Next, for solution C, consists of 2 main elements. First, dissolve 11%-14% NaClO with DI water to 5% NaClO solution. Then for the second part, 5 g NaOH and 100 g trisodium citrate was dissolved in 500 mL Milli-Q water. Specifically, in this method, the NaOH and trisodium citrate were mixed first, and then was dissolved together with the DI water. For the last part, to obtain solution C, in a separate flask, mix the two solutions together in a ratio of 1 parts NaClO solution and 4 parts NaOH and trisodium citrate solution. The last main component of the indophenol blue method is the NH_3 standard solution of varying concentrations. We did this by diluting a 10000 ppm NH_3 stock solution with DI water into a 1000 ppm solution, then a 100 ppm solution, then to a 10 ppm solution, and finally end up with a 1 ppm NH_3 solution. From the 1 ppm solution, we dissolved it with DI water with varying ratios to finally obtain a 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8 ppm NH_3 stock solutions to plot the NH_3 standard curve.

After preparing all the main components of the indophenol blue method, we mixed 5mL of each NH_3 stock solution, 0.2 mL of solutions A and B respectively, and 0.6 mL of solution C to obtain a final volume of 6 mL. The resulting solution was then kept in the dark for 4 hours.

Standard curve was plotted using the absorbance at 630 nm at different NH_3 concentrations. The absorbance data was acquired via UV-Vis spectroscopy, which in our experiment, we used an Implen NP80 instrument type, using the wavescan method in cuvette mode.

2. Ammonia Calculation in Sample

For the next part, samples from two identical hydroponics systems were collected for 12 days from 10th July 2023 to 21st July 2023 for detection and calculation. The hydroponics systems were $2m^2$ each, and were supported by a 25 W pump for irrigation. In addition to these 12 samples, water samples from the first day of the hydroponics development were also analyzed. In this part, the same indophenol blue method which was used in the standard curve plotting was applied. 5 mL of hydroponics sample water from each day was taken, then it was mixed with 0.2 mL of solution A, 0.2 mL of solution B, and 0.6 mL of solution C, resulting in the final volume of 6 mL. The resulting solution was kept in the dark for 4 h. Next, UV-Vis wave-scan spectroscopy was also analyzed to gather the absorbance data at 630 nm. Then, this data was used and compared against the standard curve to quantify the NH_3 in the samples.

3. Nitrate Detection and Calculation in Sample

For NO_3^- detection and quantification, colorimetric detection methods as like the ones used during ammonia detection were no longer done. Instead, the nitrate contents within the samples and wastewater will be quantified using Ion Chromatography (IC). For this detection, we used a Thermo Fisher Dionex ICS-1100 machine. For the eluent, a carbonate-based eluent was used as it is commonly used for anion detection in IC methods.[5] Specifically in our sample testing, a 1:1 mixture of 4.5 mM of sodium carbonate and 1.4 mM sodium bicarbonate was used. Each part was first dissolved in a 1 L volumetric flask, then the both solutions are mixed together inside the 3 L eluent container.

In this IC testing of samples, each scan was set to be for 20 minutes, as this duration was tested to show all the peaks of anions which are present in the sample. Additionally, before proceeding to sample testing, a stable baseline needs to be acquired. To achieve a stable baseline, the a few scan cycles using DI water needs to be done before scanning the hydroponics samples. In this research, we focus on analyzing the peaks around 5-6.5 minutes, as this was determined to be the peak for NO_3^- through our testing. To finally determine the concentrations of NO_3^- in each sample, the 5-6.5 minutes peak height was compared to the NO_3^- standard curve based on various concentrations.

4. Water Treatment System Model Building

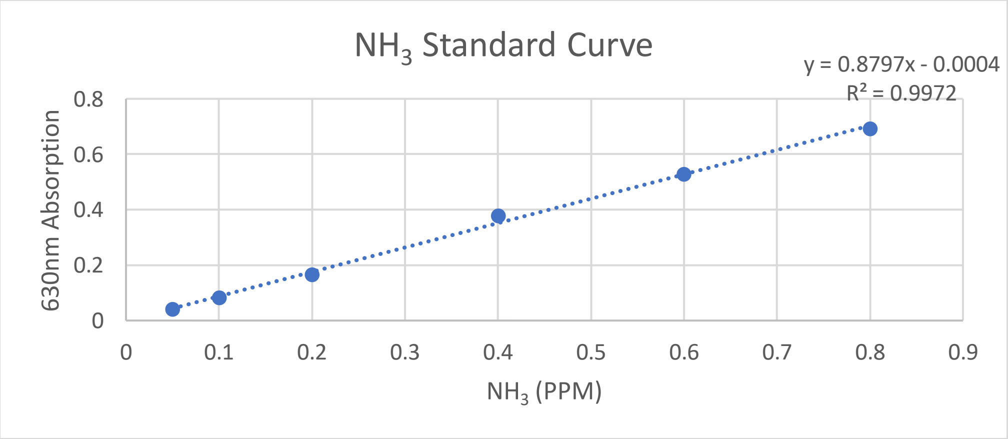
Image 1: Water Treatment Prototype

In this large-scale project, the water treatment prototype building was also a necessary part. For the prototype, it has two main components, which is the Reverse Osmosis water filtration system, and the non-precious metal catalyst model attached to it. The general Idea of this prototype is that the agriculture wastewater will first be treated and filtered by the reverse osmosis system. This will result in drinkable RO water and wastewater with more concentrations of wastes such as nitrate.

Then, the waste outlet will be connected via a pipe directly to the catalyst plate so it can be electrochemically processed by the catalyst into value-added products such as ammonia. For the water treatment prototype, this project plans to utilize a CuCoAl LDH catalyst, which has been previously developed by Ms. Wang and Dr. Tse's team. The catalyst has a NH_3 Faradaic efficiency of 99.6%, and yield of 0.22 mM h^{-1} mg_{cat}^{-1} Additionally, the utilization of an additional peristaltic pump is also being considered if future testing deems an increase of wastewater flow to the catalyst is necessary.

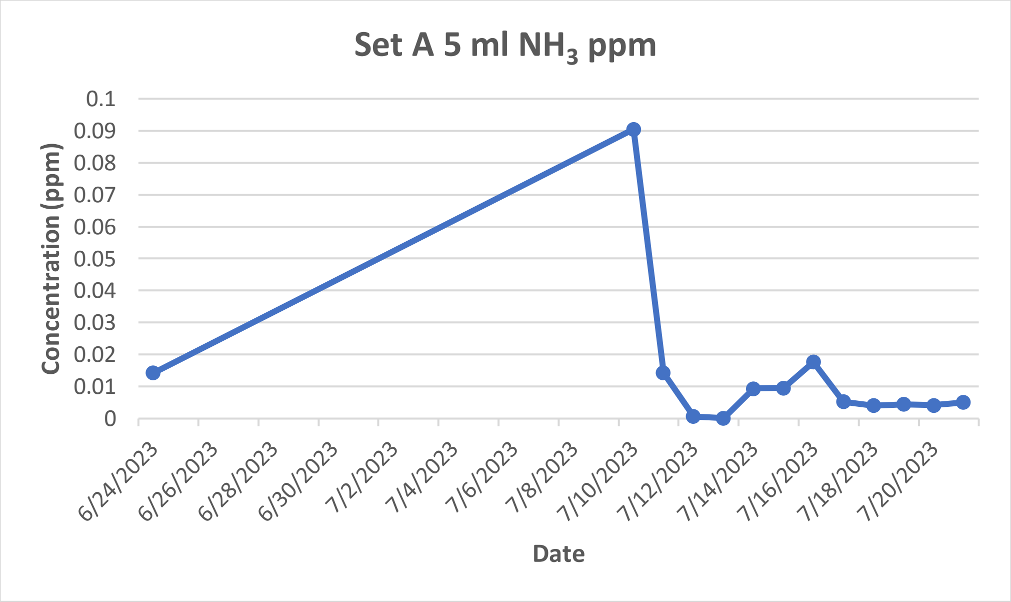
C. Results and Discussion

1. Ammonia Detection Results



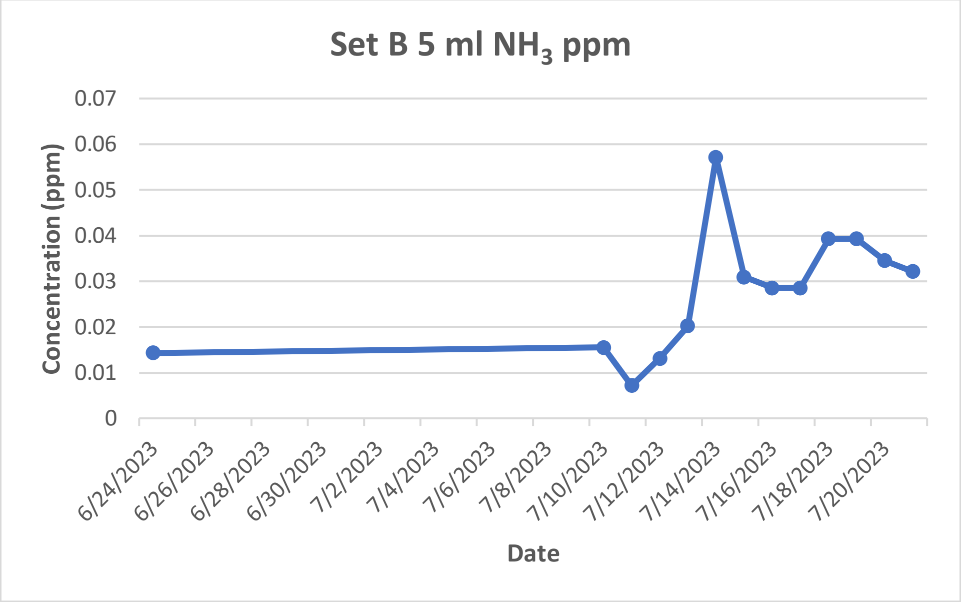
Graph 1: Ammonia Standard Curve

Based on the methodology, the NH_3 concentrations on the samples for the first day and 12 days from July 10th to July 22nd were able to be calculated. These values were obtained by comparing the 630nm adsorption peaks with the NH_3 standard curve and acquired these results:



Graph 2: Hydroponics Set A Ammonia Concentrations

For the hydroponics set A, in the beginning of the 12-day sampling period, it initially displayed a peak concentration of 0.09 ppm of NH_3. Then, it decreased drastically and showed more stable fluctuations ranging within 0.004 ppm to 0.018 ppm. The 12-day average concentration is 0.0138 ppm, with the minimum value of 0.000155 ppm and maximum value of 0.0905 ppm reached on the first day of the 12-day sampling period.

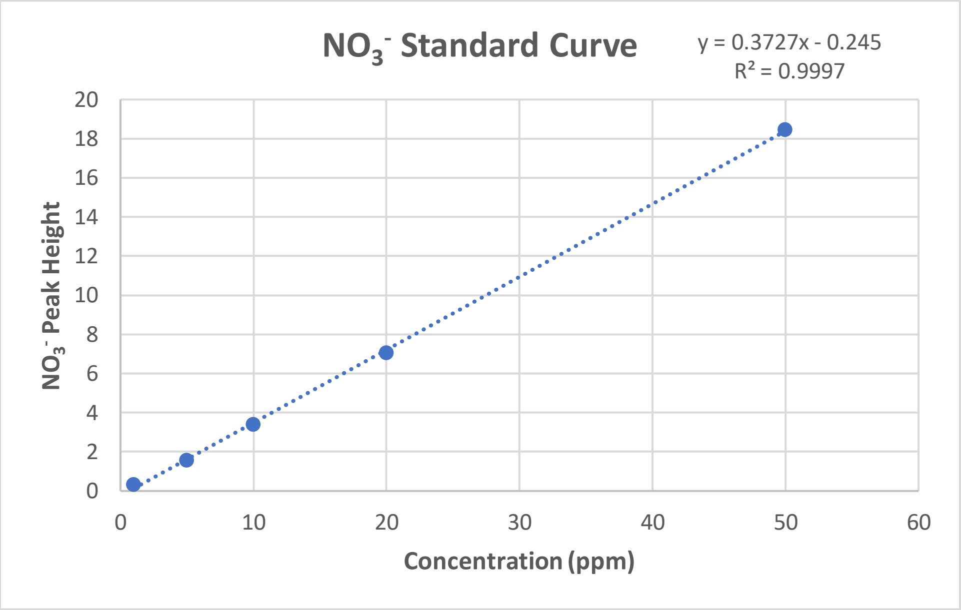


Graph 3: Hydroponics set B Ammonia Concentrations

For hydroponics set B, the NH_3 concentrations also displayed fluctuations, however there are some differences compared to set A. In set B, the first few samples, specifically from July 10th to July 15th showed a stable increase until it peaked on July 15th. After the NH_3 concentration peaked, the concentration started to decrease and showed more stable fluctuations from the July 17th to 21st, in the ranges of 0.019 ppm to 0.04 ppm. Overall, for set B, the average concentration was 0.289 ppm, the maximum concentration was 0.057 ppm, while the minimum concentration was 0.0071 ppm.

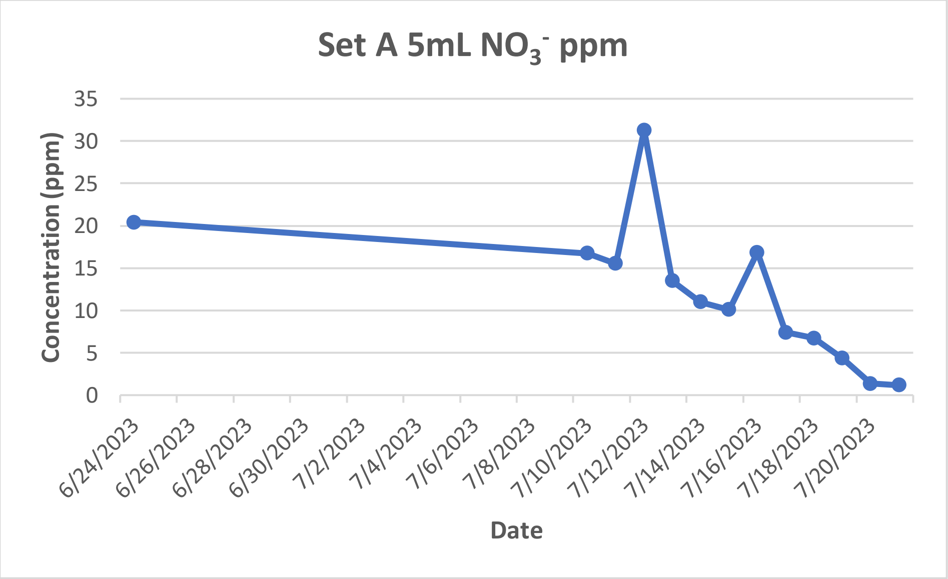
In comparison, from sets A and B, it can be seen that set B has the higher average concentration. This is because in the start of the 12-day sampling period A has already reached its peak concentration, and in the following days the NH_3 concentration in A just fluctuated at lower rates, whereas for B, in the first few days the ammonia concentration is still rising to its peak until the middle of the period. Additionally, it can be noticed that in both hydroponics sets, that the NH_3 concentrations will first increase to a certain peak from the start date and will decrease after reaching its peak, then proceed to fluctuate in lower concentration ranges. However, despite this observation, a solid conclusion of the trend of the ammonia concentrations would require more future data before being drawn.

2. Nitrate Detection Results



Graph 4: Nitrate Ion Chromatography Standard Curve

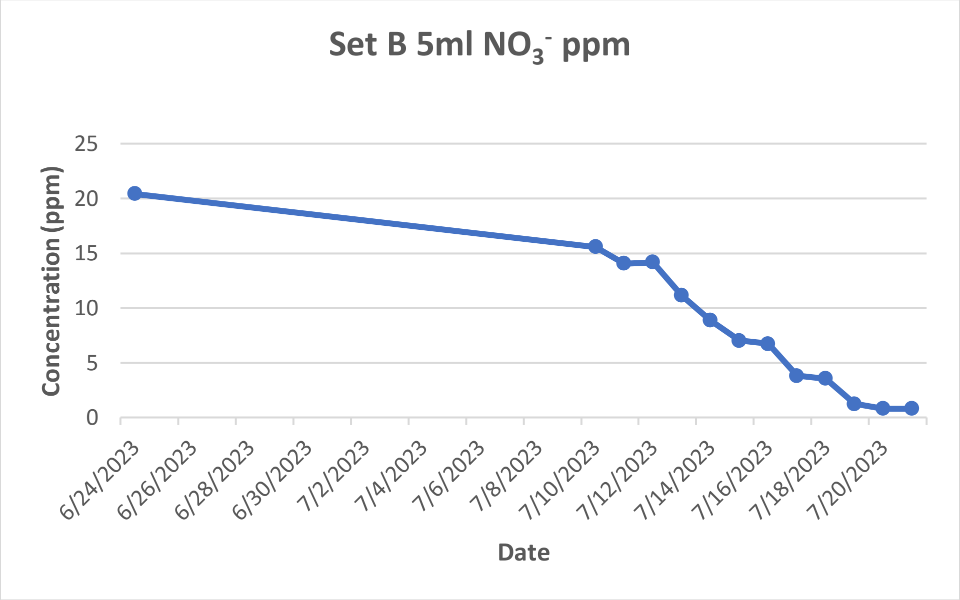
For the NO_3^- concentrations, it was calculated based on the standard curve above. The standard curve measured NO_3^- peaks for different concentrations ranging from 0.5 to 50 ppm. Then, the concentration of each sample was measured by comparing the NO_3^- peak heights of the sample to the standard curve.



Graph 5: Hydroponics set A Nitrate Concentrations

For the Hydroponics set A, it can be noticed that the NO_3^- concentrations display a general downtrend from the starting concentration of ~20 ppm.

However, in some days, the NO_3^- concentration displayed an increase and reached peak concentrations surpassing the initial concentration, specifically, the NO_3^- concentration reached its peak on July 12th which was the 3rd day of sampling from the 12-day sampling period. Since reaching its peak, the NO_3^- concentrations proceeded to decrease and in the last 2 days of sampling, the NO_3^- concentrations remained quite stable fluctuating at low concentrations in the ranges of 1.1-1.4 ppm. Overall, for set A the average NO_3^- concentration within the sampling period is 11.3 ppm NO_3^-, with the maximum concentration at 31 ppm NO_3^- reached on the 3rd day of the sampling period, and a minimum concentration of 1.16 ppm NO_3^- reached on the 12th day of the sampling period.



Graph 6: Hydroponics Set B Nitrate Concentrations

For the hydroponics set B, it can be noticed that there it displays a clearer downtrend of NO_3^- concentrations. Within the 12-day sampling period, all samples show lower concentrations compared to the first day sample of the hydroponics. Additionally, for set B, it can be seen that the NO_3^- concentrations started to fluctuate more stable from days 10 to 12. In this period, the concentrations fluctuated in the ranges of 0.8 ppm to 1.25 ppm. For set B, the 12-day average concentration was 7.3 ppm, the maximum value was 15.56 ppm, while the minimum value was 0.79 ppm NO_3^-.

In comparison of the two hydroponics sets, it could be seen that both systems show a continuous downtrend of NO_3^- concentrations as time increases. However, further testing is still required to probe the reasons for the NO_3^- concentration peaks that occur on the hydroponics set A, and a longer duration may still be needed to find out whether there are any further NO_3^- concentration changes after it stabilizes in low concentrations as shown in the end of the 12-day testing period. Additionally, with the data of NO_3^- concentration on the samples, this data can be used to project a techno-economical analysis with the prototype electrocatalysis system we developed. For these further calculations, the combined average concentration from set A and B will be used, which is a 9.3 ppm NO_3^- concentration for a 2 m^2 hydroponics plantation.

3. Techno-Economical Analysis of the Prototype and Catalyst

As we have acquired the nitrate calculations in our sample and the performance specifications of the catalyst we are using in our prototype, a projection model can now be estimated, comparing the energy consumption of this catalyst model to the traditional Haber-Bosch Process for ammonia production. In this techno-economical analysis, we will compare the energy requirements to produce ammonia from hydroponics wastewater, general wastewater using available data, and from the Haber Bosch Process.

3.1 Comparing Energy Consumption of Haber-Bosch to Electrocatalytic Reduction to Produce NH_3

In 2020, the estimated gross average of energy consumption by the Haber-Bosch Process for ammonia production is 46 GJ/ton of NH_3.[2] Thus, to produce 1 kg of NH_3, would require 46000 kJ of energy. Additionally, the Haber-Bosch does not offput the NO_3^- pollution as the electrocatalytic method does. So, if this factor were to be included, additional energy would be required for the traditional methods to perform equivalently to the electrocatalytic methods. According to the research [10], using controlled bio-cathodic denitrification (CBD), to reduce NO_3^- pollution in water would require 10.003 kJ to remove 1 kg NO_3^- -N. This is equivalent to removing 4.43 kg of NO_3^- . Thus, to remove 1 kg of nitrate from wastewater, an additional energy consumption of 2258 kJ is required. Thus, to both produce NH_3 and remove NO_3^- from wastewater, non-electrochemical methods would require a total energy consumption of 48258 kJ or ~13.41 kWh per kg of NH_3 produced and NO_3^- removed.

Whereas for the energy consumption for the electrochemical methods, based on our calculations (shown in appendix), for one electrocatalysis cycle using 20 mg of the CuCoAl LDH catalyst, with a Faradaic efficiency of 99.6% and yield of 0.22 mmol h^{-1} mg_{cat}^{-1} or 3.882 mg_{NH3} h^{-1} mg_{cat}^{-1}. The electrocatalysis to produce 1gof NH_3 from NO_3^- would require ~17.25 kJ of energy. Thus, to produce 1 kg of NH_3, the energy required from electrocatalysis would be ~17250 kJ or ~4.8 kWh.

In comparison, in terms of NH_3 production and NO_3^- removal alone, the electrochemical methods show superior performance in energy consumption compared to the Haber-Bosch, requiring approximately a third of the energy consumption by Haber-Bosch. Additionally, in terms of carbon footprint, the Haber-Bosch directly produces a substantial amount of CO_2. According to the CO_2 emissions report in 2022, a total of 36.8 GT of CO_2 wam2s produced globally.[3] Furthermore, the Haber-Bosch has been estimated to contribute to 1.44% of the global CO_2 emission.[4] Subsequently, the mean NH_3 production in 2020-2021 is 148500 kilotons.[8] From these data, the total CO_2 emitted per kg of NH_3 produced by the Haber-Bosch method can be calculated (calculations shown in appendix). For each kg of NH_3 produced, a direct emission of 3.57 kg of CO_2 is also produced via the Haber-Bosch. This shows just how large the carbon footprint is contributed by the Haber-Bosch and its adverse environmental effects.

3.2 Water Treatment System Energy Consumption for the Upscaled Hydroponics Plantation

From our sample testing, we were able to calculate that the mean NO_3^- concentration of the 2 m^2 hydroponics plant is 9.3 mg/l. If this hydroponics system were to be upscaled to a 100 m^2 plantation, then the estimate NO_3^- concentration of this sample is calculated to be 465 mg/l. As the catalyst used in our system has a Faradaic efficiency of 99.6% for NH_3 production, we calculate that to produce 1000 mg of NH_3 would require a NO_3^- content of 1004 mg in the wastewater. So, for this upscaled sample, the prototype system would need to treat ~2.16 l to produce 1 g of NH_3. Subsequently, to produce 1 kg of NH_3 would require the prototype to treat ~2160 l sample, with a byproduct of ~720 l drinking water as the system has a wastewater to drinking water produced ratio of 2:1.

The average reverse osmosis system is able to process and filter 33.3 l of water per 1 kWh of power consumption [6]. With this data, the final amount of energy consumption required to produce 1 kg of NH_3 with the upscaled wastewater sample of the hydroponics system is calculated to require 64.8 kWh.

Additionally, for this hydroponics system, the energy consumption for running the hydroponics pump should also be included for the techno-economical analysis. Based on our calculations (shown in appendix), for 1 hydroponics pump to run for 24 hours for 12 days, would require 25920 kJ or ~7.2 kWh. As the pump in our system may support up to 5 m^2 of hydroponics, in this upscaled calculation it is assumed that 20 pumps would be needed to run a 100 m^2 of hydroponics plants. Thus, the for the upscaled calculation, a 100 m^2 hydroponics system would consume 144 kWh.

Thus, the total energy required for the prototype water treatment system, the hydroponics pump, and the electrocatalysis would be 213.6 kWh.

3.3 Water Treatment Prototype Energy Consumption for Wastewater Samples in Pakistan

An extensive study focusing on Nitrate Contamination in Groundwater shows that the mean NO_3^- concentration in a wastewater sample is 240 mg/l. [7]

With this data, we are able to calculate an estimate energy consumption if the prototype water treatment system were to be used to treat this sample. Similar to the hydroponics sample calculation, to produce 1000 mg NH_3 would require 1004 mg NO_3^- in the wastewater. As this waste has a mean NO_3^- concentration of 240 mg / l, then the prototype would need to treat around 4.2 l of wastewater to produce 1 g of NH_3. Thus, to produce 1 kg of NH_3, the prototype would need to treat 4200 l of wastewater, with a byproduct of ~1400 l of drinking water, as the developed prototype system has a wastewater to drinking water produced ratio of 2:1.

Using the same calculations done for the upscaled hydroponics energy consumption, the final amount of energy consumption required to produce 1 kg of NH_3 with the wastewater sample from Pakistan based on the extensive study is calculated. To Produce 1 kg of NH_3, the energy required by the prototype system is 126.13 kWh, Thus, if the energy consumed via electrocatalysis (calculations shown in appendix) is also included, the total energy consumption of the prototype system to produce 1 kg of NH_3 from NO_3^- is 130.93 kWh.

3.4 Overall Techno-Economical Analysis Comparison

From the techno-economical analysis of each ammonia production method, it can be seen that in terms of ammonia production alone, electrocatalytic methods perform better than the traditional industrialized Haber-Bosch. However, combined with the water treatment system, the combined energy consumption of the prototype and the catalyst is larger than the overall energy consumption of the Haber-Bosch with added NO_3^- removal. The Haber Bosch only consumes a total energy of 13.41 kWh, whereas the prototype consumes 214.6 kWh and 130.93 kWh respectively when treating a hydroponics system wastewater and a general groundwater wastewater in Pakistan. This shows that in terms of energy consumption alone, the Haber-Bosch reigns supreme to the water treatment prototype and catalyst.

When comparing the 2 methods of using the prototype, it can be seen that the prototype shows better efficiency for the hydroponics system compared to the general wastewater as the NO_3^- concentration can be directly upscaled using hydroponics systems. The downside of the hydroponics comes from the energy consumption to run the hydroponics pump and irrigation. However, if future prototype models can improve this flaw, and create a more efficient, or possibly a zero-energy irrigation system for the hydroponics, then the overall energy consumption can be lowered. Additionally, in terms of environmental effects the electrochemical method prototype is superior to the Haber-Bosch, as it does not directly emit CO_2 as the Haber-Bosch does, conversely it produces a valuable byproduct which is drinking water which are needed in some regions where drinking water is scarce.

D. Conclusions

In conclusion, this research has successfully built a baseline for further testing for the water treatment prototype and NO_3^- and NH_3 detection and quantification. However, we conclude that a more extensive sampling period is necessary for future testing and research to gain more data points and predict a more dependable and long-term trend for the contaminants.

Additionally, for the water treatment prototype, this research has successfully designed a working prototype which can produce drinking water and NH_3 simultaneously without emitting CO_2 as the Haber-Bosch does. However, in terms of energy consumption, the electrochemical prototype system consumes more energy than the Haber-Bosch despite the lower carbon footprint and drinking water production. Thus, this research suggests that in the future, the prototype design, especially in terms of hydroponics irrigation system, can be further improved to reduce inefficient energy consumption to run the hydroponics alone as the main consumer of energy. Addressing this issue is essential to designing a more energy efficient ammonia producing water treatment prototype in the future.

Lastly, in terms of the electrocatalyst design alone, the proposed CuCoAl LDH electrocatalyst priorly developed by Dr. Tse’s team currently shows superior performance compared to other electrocatalyst systems due to its high NH_3 selectivity and Faradaic efficiency. Thus, future prototype models will still use this catalyst and further testing of the threshold of the catalysts stability and performance altogether with the prototype system needs to be done.

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APPENDIX

1. Calculations for energy consumption via electrocatalysis

Yield= 0.22 mmol h^{-1} mg_{cat}^{-1} → 3.8082 mg h^{-1} mg_{cat}^{-1}

* Values based on past electrolysis with 0.021 mg of catalyst

* For the Techno-economical analysis, we upscale the catalyst used in one electrocatalysis to 20 mg

Total yield via electrolysis= 76.164 mg $_{NH3}$ h^{-1}

V= -1.4 V

J= 18.6 mA/cm^2

A= 0.007068 cm^2

I= J/A = 263.158 mA

I= 0.2632 A

P = I x V

P= 0.3684 watts

t= 1000mg/ 76.164 mg $_{NH3}$ h^{-1}

t= 13.13 h

E = P x t

E= 0.3684 x 13.13 x 3600

E= ~17.25 kJ → ~ 0.0048 kWh kg $_{NH3}^{-1}$

To Produce 1 kg of NH3, from 1 kg of NO_3^- :

E= 4.8 kWh kg_{NH3}^{-1}

2. Calculations for CO_2 emission for 1 kg NH_3 production

*In 2022, a total of 36.8 GT of CO_2 was produced.[3]

*The Haber-Bosch process contributes to 1.44% of global CO_2 emissions.[4]

*Mean NH_3 production via Haber-Bosch in 2020-2021 = 148500 kilotons.[8]

CO_2 Emission from haber bosch: 52.99 x 10^7 tons

52.99 x 10^7 tons = 148.5 x 10^6 tons

3.57 tons CO_2 emitted = 1 tons NH_3 produced

CO_2 **Emission Rate = 3.57 kg $_{CO_2}$ kg $_{NH_3}^{-}$**

3. Calculations for energy consumption by hydroponics pump

P= 25 W

T= 288h

E= 25 x 288 x 3600 = 25920 kJ

E= ~7.2 kWh

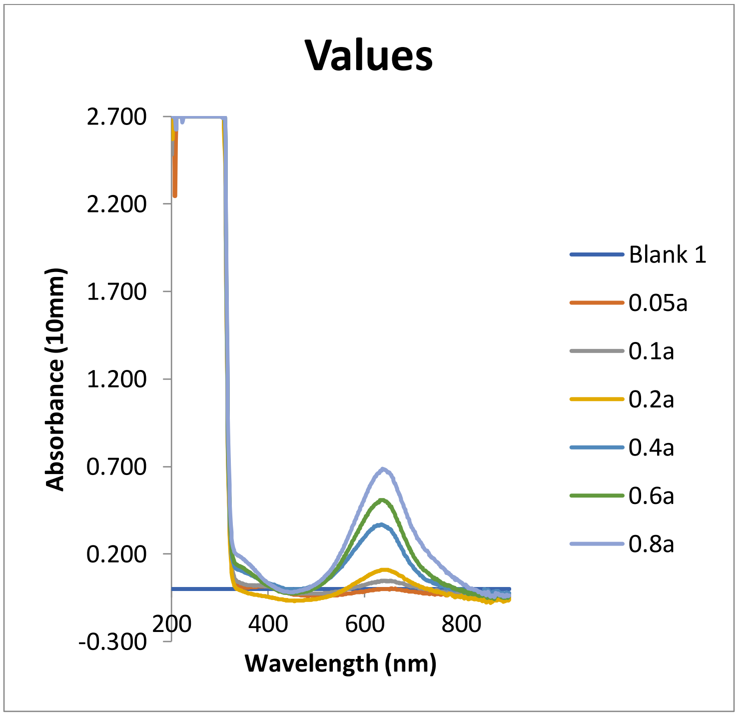
*1 hydroponics pump is assumed to suffice to run water for 5 m^2 of hydroponics

Thus, for 100 m^2 of hydroponics plants, would require:

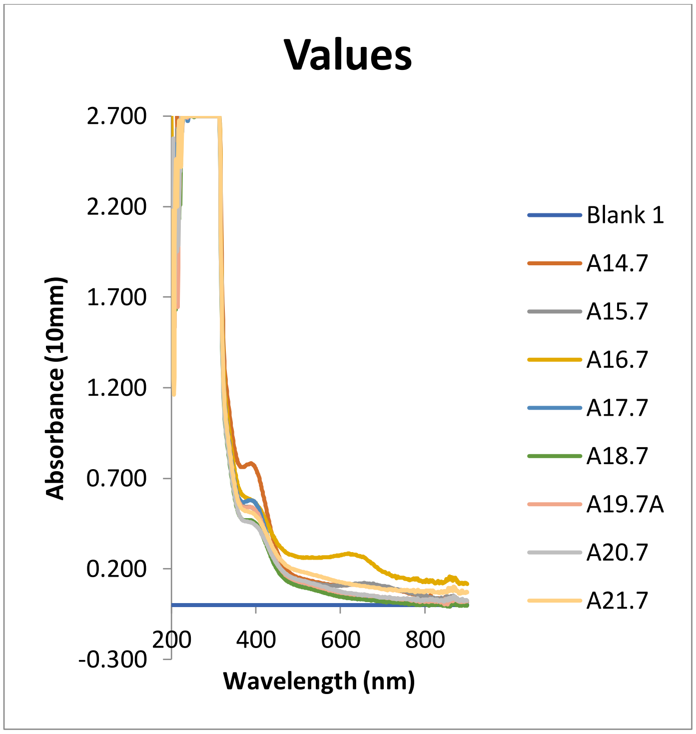
E= ~7.2 kJ x 20 pumps

E= ~144 kWh

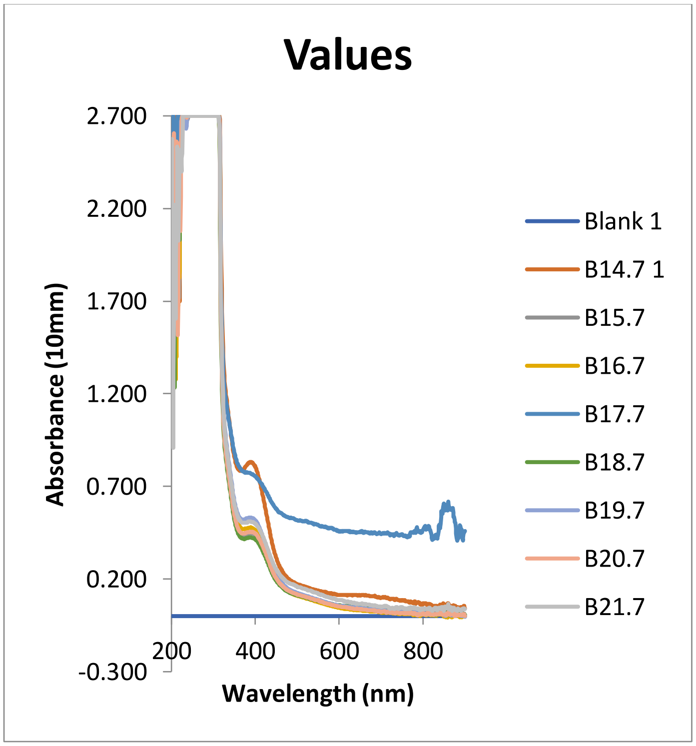
4. UV-Vis scan results for ammonia standard curve



5. UV-Vis scan results for hydroponics set A



6. UV-Vis scan results for hydroponics set B



7. **Specifications of the RO system**
    - Brand: Leviti/Longtai
    - Model: E-5A 400G
    - Wastewater to Drinking Water Ratio: 2:1
    - Output: 60L/hour