Development of a Reusable Nutrient Recovery System to Sustainably Integrate Small-Scale Sanitation and Agriculture

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Development of a Reusable Nutrient Recovery System to Sustainably Integrate
Small-Scale Sanitation and Agriculture

by

Jorge Luis Calabria

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Environmental Engineering
Department of Civil and Environmental Engineering
College of Engineering
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Date of Approval:
June 21, 2019

Keywords: anaerobic membrane bioreactor, hydroponics,
nitrogen management, ion exchange, zeolite

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DEDICATION

To Maria, for seeing in me what others do not.

“Tus ojos me alumbran la vida, me alumbran el corazón”
ACKNOWLEDGMENTS

This work would not have been possible without the generous financial support granted to me by the Alfred P. Sloan Foundation, the Florida Education Fund’s McKnight Dissertation Fellowship, the Allen H. Seckinger Memorial Fund, The Bill and Melinda Gates Foundation, and the National Science Foundation’s Bridge-to-Doctorate Fellowship and PIRE (Partnerships for International Research and Education) Grant. I am eternally grateful for the comradery of my colleagues: Melanie Pickett for her crucial support, Robert Bair and Manny Delgado for the adventures over the years and across the globe, Cynthia Castro for her advice and support, Erkan Uman, Kamal Taha, Gary Shyu, Talon Bullard, and Jerry Jumbo for their friendship and assistance; current and former lab mates that contributed to my journey: Onur Ozcan, George Dick, Ivy Drexler, Judian Duran, and Varun Malaviya. A special thanks to John Sutton for his assistance IC analyses, as well as Laura Rodriguez, Veronica Aponte, Emma Lopez, Christy Prouty, Michelle Henderson, Maya Carrasquillo, Wainella Isaacs, Lorena Sanchez, Colleen Naughton, Matt Verbyla, and Pablo Cornejo for their comradery during this journey. I wish to thank the entire USF CEE staff, especially Barbara Johnson, Stefanie Lovelace and Camille Mourant, the ever-patient, Catherine Burton; and the Environmental Engineering Faculty at USF who have all contributed to my development as a globally-competent and conscious researcher. Immense gratitude is owed to Dr. Jim Mihelcic, Dr. Jose Zayas-Castro and the incredibly supportive Bernard Batson for the countless opportunities and limitless support I have received because of them. I gratefully acknowledge the diverse wisdom, guidance, and support provided by the members of my committee: Dr. Norma Alcantar, Dr. Piet Lens, Dr. Bob Rubin, and Dr. Maya Trotz. Lastly, I wish to thank my adviser, Dr. Daniel Yeh, whose unlimited optimism and ideas have facilitated my growth through a wealth of unforgettable opportunities and experiences for which I am forever grateful, 谢谢！
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ABSTRACT

Emerging technologies in sanitation and food production foster the potential to advance progress towards key sustainable development goals of ensuring adequate sanitation and food security to all. Non-Sewered Sanitation Systems (NSSSs), as detailed by the recent International Organization for Standardization’s (ISO) 30500 standard, are being developed to overcome challenges of lacking sanitation infrastructure and resource scarcity by providing autonomous, off-grid wastewater treatment (WWT) service in a much smaller footprints than large centralized treatment facilities. A promising NSSS platform is the anaerobic membrane bioreactor (AnMBR) that can achieve high (WWT) throughput in a small footprint using ultrafiltration (UF) membrane filtration to actively separate solids. AnMBR effluents (membrane permeate), contain high concentrations of nitrogen and phosphorus (N and P) requiring 70% and 80% removal prior to effluent discharge or reuse in non-potable applications (as stipulated by ISO 30500). Ion exchange processes with natural clinoptilolite zeolite perform well at removing total ammonia nitrogen (TAN) from AnMBR permeate because of the low solids, low turbidity, near neutral pH, and high TAN concentrations that are commonly observed characteristics of this waste stream. The regeneration of exhausted clinoptilolite presents challenges of high chemical and energy requirements that can limit the feasibility for implementing these potentially-low cost TAN removal processes.

This research proposes a reusable nutrient recovery system (RNRS), based on natural clinoptilolite zeolite, which releases captured nutrients into adaptive, low-footprint agricultural systems (e.g., vertical hydroponics) to demonstrate reuse of recovered nutrient materials via plant growth. The RNRS was developed to enable recovery and reuse of TAN from AnMBR permeates for fertigation applications that can enhance local socio-economic conditions or food security by providing agricultural
fertilizer inputs. The RNRS column prototype reached 10% TAN breakthrough after approximately 30 bed volumes (BV) of synthetic AnMBR permeate solution was passed. Elution of TAN from exhausted RNRS columns revealed that a low, yet constant effluent TAN concentration can be achieved with tap water elution, however roughly 80% of clinoptilolite-bound TAN remained after 120 BV of tap water had been passed. Batches of the desorption solution that resulted from tap water elution were used to cultivate lettuce in vertical hydroponic systems. A short hydroponic growth study demonstrated that RNRS implementation mitigates the effects of inhibitory materials like Na⁺, Cl⁻, and dissolved organic compounds that can be deleterious to crop development. A second RNRS bioregeneration study considered recirculation of a fixed volume of tap water eluent solution to facilitate accumulation of nutrient materials released by the RNRS. Recirculation of the RNRS eluent solution was more effective at enhancing the RNRS column TAN release rate and duration. Performance data collected from RNRS testing was used to conduct a sustainability analysis to quantify potential environmental and economic impacts associated with the implementation of the proposed RNRS compared to other possible TAN treatment scenarios deemed suitable for an AnMBR-NSSS application. The proposed RNRS minimized environmental impacts by facilitating reuse of zeolite materials and minimizing chemical regeneration inputs as well as recovering nitrogen fertilizer. While nitrogen removal capacities are well defined, methods for phosphorus recovery and reuse were not fully developed in this work and is an important topic for future research that can enhance the feasibility of the RNRS to integrate WWT resource recovery and agricultural reuse,
CHAPTER 1: INTRODUCTION

1.1 Motivation

The United Nations estimates the world population will reach 9.7 billion, with 2 out of every 3 people dwelling in cities by the year 2050 (United Nations, 2017). Sixty percent of the world population currently lacks access to safely managed sanitation facilities, which results in increased risks to human and environmental health as conventional sanitation infrastructures struggle to adapt to increasing population and population densities, more stringent treatment parameters, and variability of socioeconomic conditions (Reymond et al., 2016). In addition to concerns regarding sanitation, a recent report by the World Resources Institute concluded that the agricultural sector must meet a 56% increase in the amount of calories produced in 2010 by the year 2050 while using the same amount of agricultural land used in 2010 to meet anticipated caloric demands of the future population and avoid triggering an ecological collapse in the process (Searchinger et al., 2018). In a response to these and many other global concerns, the United Nations issued the 2030 Agenda for Sustainable Development outlining 17 strategic sustainable development goals (SDGs) as a global call-for-action to end poverty, improve human health, spur economic growth and protecting the environment (Transforming our world: The 2030 agenda for sustainable development, 2015). Advancements in sanitation technologies that enhance sustainability by facilitating the recovery of nutrient, energy, and water resources have significant potential for amplifying progress towards achieving the UN’s SDGs and realizing circular economies (Trimmer et al., 2017).

Recent advancements in wastewater treatment technologies have fostered the development of non-sewered sanitation systems (NSSS) to better serve populations across the globe that lack adequate sanitation. NSSSs have been shown to provide safe sanitation while making possible the recovery of valuable resources (e.g., nutrients, energy, and water) from human waste (Bair et al., 2015; Deng, 2014; Ozgun et al., 2013; Reymond et al., 2016). The International Organization for Standardization (ISO) has
recently developed a technological standard: ISO 30500 to establish regulatory standards and performance benchmarks for NSSSs to advance economic, social, and environmental performance. The ISO 30550 standard mandates that NSSS designs should minimize resource consumption and increase opportunities for resource recovery (ISO, 2018). Leveraging the resource recovery capabilities of NSSSs to facilitate integration with resource reuse practices, e.g., agriculture, can have significant, positive impacts in low-developed areas, ultimately amplifying progress towards many of the sustainable development goals (Trimmer et al., 2017).

Anaerobic membrane bioreactors (AnMBR) are a promising NSSS technology platform that can achieve high throughput in small-system footprints, made possible using membrane ultrafiltration that effectively excludes pathogens and wastewater solids from permeating the membrane barrier. The resulting AnMBR permeate is rich in dissolved nitrogen (N) and phosphorus (P) and potassium (K) materials that can recover for use as fertilizer in local agricultural operations. Removal of N and P from AnMBR permeate for agricultural reuse presents a mutually beneficial nutrient management practice; the AnMBR nutrient removal load is lessened while a valuable resource is generated to support local communities. Additionally, current methods of removing nitrogen from wastewater raise logistical and technical challenges when considering application in NSSSs serving developing areas. According, to ISO 30500, deployment and operation of a NSSS to handle and treat human waste in the developing world must meet reliability and resilience criteria to safeguard human and environmental health. Thus, systems and methods for facilitating recovery, access, and reuse of NSSS-derived, recovered nutrient materials should adhere to similar criteria. Current AnMBR nutrient recovery practices do not present immediately safe or accessible opportunities for nutrient reuse in agriculture which can present a technological barrier to realizing these opportunities in challenging contexts. This research serves to develop a system for streamlining the recovery and reuse of nutrient materials recovered from human wastes treated by an AnMBR-NSSS operating in compliance with ISO 30500.
1.2 Scope

The scope of this dissertation focuses on addressing current technical, logistical, and sustainability gaps and challenges associated with providing sustainable nitrogen recovery from decentralized wastewater treatment system (1 – 1000 people) effluents to facilitate reuse in appropriate, low-footprint, hydroponic cultivation systems.

1.3 Theoretical and Practical Relevance

This work contributes to the scientific body of knowledge through its development and assessment of a novel, material-efficient method for regenerating natural clinoptilolite zeolite (CZ) exhausted with ammonium (NH$_4^+$) from AnMBR system effluents to facilitate reuse of CZ, nutrient removal, recovery, and reuse. Essentially, exhausted CZ is regenerated biologically via recirculation in a vertical hydroponic system, providing simultaneous fertigation of hydroponic crops. This Hydroponic-Bioregeneration (HBR) requires less chemical and energy inputs to facilitate CZ-regeneration while supporting plant growth. Existing chemical regeneration methods facilitate reuse of natural CZ and regenerant solution materials by using highly concentrated brine (10 mg/l NaCl) at high pH (pH: 10-12) to remove NH$_4^+$ from both CZ and the regenerant solution via Na$^+$ exchange and volatilization of NH$_4^+$ to NH$_3$ gas. A pathway to nutrient recovery exists through use of a sulfuric acid scrubber that yields highly concentrated ammonium sulfate that can be sold or used as a valuable nutrient fertilizer (Boyer, 2014; Deng, 2014; Trotochaud et al., 2019). However, this pathway requires high energy and chemical input for regeneration and yields chemical hazards from the handling of acidic and caustic materials (Trotochaud et al., 2019). Hybrid methods that use background solution ions to facilitate ion exchange (IX) with CZ-bound NH$_4^+$ followed by biological conversion of NH$_4^+$ to NO$_3^-$ (i.e., nitrification) demonstrate direct reuse of TAN removed from wastewater for fertilizer reuse. The use of plant macronutrient cations (i.e., K$^+$, Ca$^{2+}$, Mg$^{2+}$) instead of Na$^+$ to facilitate the release of NH$_4^+$ from CZ while avoiding the negative effects of sodium on plants and soils (Boyer, 2014; Calabria et al., 2019; Markou et al., 2014; Smith & Smith, 2017; Richards et al., 1954). Regeneration with Mg$^{2+}$, Ca$^{2+}$, and K$^+$ reduces the overall ammonium
exchange capacity of the CZ in subsequent TAN removal cycles, prompting the need for virgin CZ material to replace spent materials (Boyer, 2014; Huang et al., 2014; mazloomi & jalali, 2016).

Other methods that demonstrated reuse of TAN recovered with CZ in agricultural applications did not recover CZ for reuse, but rather directly used the nutrient loaded CZ material as a nutrient delivery material for use in soil or soil-less (i.e., hydroponics) cultivation systems (Bernardi et al., 2015; Guaya et al., 2018; Poulet et al., 2016). While these pathways demonstrated beneficial resource recovery that supported agricultural practices, they were not able to feasibly demonstrate reuse of CZ materials, implying the need for input of virgin CZ to maintain constant TAN removal functionality.

A novel, reusable nutrient recovery system (RNRS) is developed to address spatial and temporal challenges that affect nutrient recovery practices at small-scales. The approach taken during RNRS development utilizes passive processes to facilitate reuse of clinoptilolite for TAN removal from a wastewater stream while enabling access to recovered TAN for fertigation application in appropriate agricultural systems. The proposed RNRS demonstrates practical relevance by providing efficient TAN removal performance with relatively low material costs. Safe access to recovered TAN is enabled for use as a nitrogen fertilizer source with little to moderate training required to facilitate this function, fostering the potential for enhancing local, socio-economic conditions (Trimmer et al., 2017). The ability to selectively recover, store, transport, and release recovered nutrient materials into a low-footprint hydroponic system overcomes spatial and temporal challenges to nutrient recovery as the RNRS enables safe access and transport of nutrients recovered in a solid medium. The selectivity for ammonium over sodium that can be observed in natural clinoptilolite zeolites bears implications for mitigating the recovery of sodium in addition to ammonium during ion exchange with CZ.

1.4 Objective

The objective of this dissertation is to enable safe and sustainable recovery of AnMBR permeate nitrogen content for fertigation reuse in low-footprint hydroponic systems. The secondary objective of this dissertation is to quantify the economic and environmental impacts of the TAN recovery system developed by this research and other appropriate TAN removal processes to assess their sustainability.
1.5 Description of Research Design

This design phase, preliminary material testing, prototype development, prototype testing, and Life Cycle Analyses of the reusable nutrient recovery system developed by this work were performed at the University of South Florida, College of Engineering’s Membrane Biotechnology Laboratory in Tampa, FL beginning June 2015 thru December 2018 under the tutelage of Dr. Daniel H. Yeh. A proof-of-concept study demonstrating TAN removal from synthetic AnMBR permeate and reuse for hydroponic fertigation of *Lactuca sativa* (buttercrunch lettuce) in vertical hydroponic columns was performed at IHE-Delft Institute for Water Education in collaboration in Delft, The Netherlands, in collaboration with Dr. Piet N. L. Lens.

1.6 Dissertation Outline

This dissertation begins by providing a detailed background of the problems that motivate this research and surveys promising solution pathways (Chapter 2). Challenges associated with the solutions surveyed are highlighted to motivate the proposal of a new method that integrates various systems to address challenges of access to recovered nutrient materials, thus establishing the subject of this research. The following chapter (Chapter 3) describes the general analytical methods and apparatuses used to conduct the research described in the following chapters. Chapter 4 describes the concept development methods used to develop the reusable nutrient recovery system (RNRS) concept that is investigated and assessed in the following chapters. Preliminary capacity testing of the RNRS prototype designed and developed in Chapter 4 is conducted in Chapter 5. Three major functions of the RNRS are investigated: (1) Total ammonia nitrogen (TAN) removal from pertinent, simulated “waste” streams, (2) accessible methods for releasing TAN to yield solutions with fertigation potential, and (3) enabling feasibility for TAN reuse in adaptive hydroponic systems. Performance data is used to perform a sustainability analysis to quantify economic and environmental impacts associated with the integration of the proposed RNRS with decentralized sanitation systems (Chapter 6). The final chapter (Chapter 7) summarizes the findings of the research work and highlights pertinent areas requiring further development to inspire and guide future research efforts.
CHAPTER 2: BACKGROUND

2.1 Introduction

Since the turn of the 20th century, advancements in wastewater treatment were reactionary developments to address the mounting burdens and threats that wastewater constituents posed to human societies and the environment (Tchobanoglous et al., 2014). Various methods have been developed to facilitate efficient nutrient removal from wastewater to avoid eutrophication when discharged into receiving water bodies; nitrogen (N) and phosphorus (P) being the main perpetrators. However, an industry-wide paradigm shift promotes wastewater as an abundant, renewable resource with the potential to alleviate many societal ills, -not create them- especially in resource-limited areas (Wichelns et al., 2015). Most materials found in wastewater are valuable to society, e.g., water, nutrients for fertilizer (nitrogen, phosphorus, potassium, magnesium, sulfur), and carbon-based material that can supplement feedstock, amend soils, fuel incineration or whose carbon-content can be degraded anaerobically to yield methane-rich biogas (Guest et al., 2009).

Currently, wastewater treatment (WWT) and resource recovery (RR) processes require controlled operation by trained personnel to maintain and operate crucial machinery and oversee treatment processes. As a result, WWT is usually performed at a large, centralized facility serving many users in a region (Tchobanoglous et al., 2014). This leads to WWT and RR occurring at the location of the wastewater’s highest entropy (i.e., the end of the sewer line entering a WWT facility), which is inefficient and increasingly difficult to accomplish in dense, urban landscapes of developing and developed nations (Katukiza et al., 2012; Tchobanoglous et al., 2014). Modern trends of increasing urban populations, declining supply of fresh water, and increasingly stringent treatment standards all highlight the need for well-planned, integrated networks of satellite, decentralized, and centralized facilities that are properly
equipped to recover resources, enable reuse at pertinent locations and lessen the overall burden of treatment at larger centralized facilities (Figure 2.1). Treatment networks such as these facilitate circular economies by enabling localized recovery and reuse of valuable resources which, as a result lessen contaminant loads at end-of-the-line treatment facilities. Decreased burden of treatment at centralized facilities accommodates more specialized treatment that can address the issues of emerging contaminants and micro-pollutants (Capodaglio, 2017; Diaz-Elsayed et al., 2019; Gikas & Tchobanoglous, 2009; Harder et al., 2019).

Furthermore, nutrient and energy recovery for local reuse can support local communities by enabling community-based agriculture that produces food for local consumption or commerce (Orsini et al., 2013). Low-footprint farming methods like hydroponics require nutrient fertilizer inputs to operate,
but these inputs could be generated from resource recovery practices. Implementation of decentralized WWT facilities capable of resource recovery could simultaneously provide safe sanitation and enhance food security, significantly impacting the quality of life for people residing in resource-limited urban and rural settings (Trimmer et al., 2017).

A promising decentralized wastewater treatment technology platform known as the anaerobic membrane bioreactor (AnMBR) is introduced as a potential vehicle for realizing decentralized wastewater treatment and enabling nutrient resource recovery that bridges a gap between sanitation and food production in challenging contexts (e.g., low-income urban communities, rural and urban areas of developing countries). Nutrients that are present in AnMBR treatment effluent represent a potential renewable source of fertilizer available at low-cost that can support local agriculture. This chapter identifies the opportunities and challenges associated with decentralized WWT and local agriculture practices, including attempts to integrate these practices, and why such an integration is necessary to enhancing sustainability.

2.2 The Role of Urban Agriculture

The global population continues to climb towards 10 billion people by the year 2050 where the United Nations predicts 70% of people will dwell in cities (United Nations, 2015). A recent report by the World Resources Institute (2018) estimates that the future population will require a 50% increase in total food production. Furthermore, this increased agricultural output must be accomplished without increasing land used for agriculture to prevent further ecological damage (Searchinger et al., 2018). Meeting future food demand presents a global, technological challenge as agriculture currently occupies approximately 40% of the terrestrial landscape and drives deforestation and the conversion of natural habitats to crop and pasture lands (referred to as agricultural land shifting). If the current agricultural productivity and agricultural land shifting rates are maintained, a land area twice the size of India would be required to meet future caloric demands, which would emit copious amounts of sequestered carbon making global average temperature rise inevitable (Searchinger et al., 2018). Therefore, technological advances are required to enhance agricultural productivity on lands where agriculture already exists and on lands with
the lowest carbon and environmental opportunity costs such as urban and peri-urban areas (Fisher, 2014; Orsini et al., 2013; Searchinger et al., 2018; Specht et al., 2014; Thomaier et al., 2014; Trompette, 2014). Urban agriculture can play a crucial role in meeting future caloric needs without expanding agricultural land and potentially enhance urban environmental, social, and economic conditions while doing so.

Urban agriculture (UA) is defined as production in the home or plots located in urban or peri-urban areas. UA practices have proven to be effective at increasing agricultural productivity in urban areas where it was previously non-existent, providing food security, urban greening, and economic opportunities, ultimately serving to enhance urban landscapes (Poulsen et al., 2015; Tixier & De Bon, 2006). UA emerged out of necessity to combat food insecurity among urban poor in developing countries where an estimated 60-85% of income is spent to acquire food. Food insecurity arises from the lack of access to highly nutritious foods, i.e., fruits and vegetables, resulting from limited supply or limited funds to purchase high quality foods. The lack of arable land has spurred intensification of horticultural techniques to cultivate nutrition-providing crops (i.e., fruits and vegetables) in small footprints to meet dietary needs (Tixier & De Bon, 2006). The cultivation of crops in small spaces, e.g., in-and-on buildings, is made possible by utilizing unused rooftops for soil-based farming in above-ground planters and by low-footprint farming methods like hydroponics that enable vertical farming (Schnitzler, 2013; Specht et al., 2014).

2.2.1 Intensified Horticulture

Ease of access to high quality materials, fertilizer, water, stable electric grids and structurally sound facilities enable UA practices in the developed world, however access to these inputs can vary in low-development countries (LDCs) ultimately reducing feasibility of UA implementation (FAO et al., 2013; Orsini et al., 2013; Verbyla et al., 2013). Nonetheless, UA has taken form in simplified, low-footprint horticulture systems that have proven successful in improving local food-security and socio-economic conditions (Orsini et al., 2013). Space-efficient horticultural practices like hydroponics and organoponics can increase yields in smaller footprints and do not always require fertile, vacant plots of land. The capacity to execute these farming methods on rooftops and on building facades makes possible
the concept of zero-acreage farming (ZFarming) (Specht et al., 2014; Thomaier et al., 2014). ZFarming techniques, when implemented well, can provide 20% or more of a city’s caloric needs (Cities Farming for the Future: Urban Agriculture for Green and Productive Cities, 2014; Tixier & De Bon, 2006). ZFarming is made possible because components necessary to grow plants, i.e., root or plant support structure or media, nutrients, water, and light, directly to the crop, are provided directly to crops, allowing for ZFarming system designs that use significantly less space. Conventional, in-soil cultivation practices use soil located on-site to provide support to growing crops and roots, and to store nutrients and moisture from rain or irrigation; water and nutrient fertilizers are added when soil conditions are not adequate.

Organoponics usually consists of organically derived nutrients and soil matter from composting processes that are contained within above-ground containers. The organoponic media serves as plant support and a nutrition source for growing plants and water is added through manual or automated irrigation. Organoponics facilitates the cultivation of organic produce using locally derived and composted organic waste, e.g., food scraps and agricultural waste (Orsini et al., 2013). However, the grow-bed structures used in organoponics provide a controlled barrier to poor, local agricultural conditions like low soil fertility, high salinity, and low moisture, and can be more space-efficient than conventional in-soil farming (Figure 2.2). Additionally, implementing organoponic methods in dense, urban contexts can be challenging where space and access to fertile soil is limited.

Simplified hydroponic systems deliver dissolved nutrient materials to plant roots via a liquid medium (Figure 2.2). Plants in hydroponic systems supported by an inert media which suspends plants above the liquid nutrient solution ensuring adequate exposure to air and root contact with the liquid nutrient solution (Resh, 2013). The inert nature of the plant support structures allows reuse of these materials, minimizing costs for input materials (Figure 2.2). Hydroponic systems exhibit efficient water use as water loss through soil evaporation is not existent; lettuce grown in a simplified hydroponics system in Brazil used 2.0-2.5 l m⁻² of water compared to 10-12 l m⁻² that would be required for soil-grown lettuce (Orsini et al., 2013). Additionally, soil-less systems can achieve almost double the crop density as in-soil cultivation. A well-maintained hydroponics system occupying 18 m² was enough to meet the needs
of a small household in northern Brazil (Orsini et al., 2013). Grewal and Grewal (2018) calculated that optimized hydroponic systems used in small-scale urban agriculture operations occupying 80% of every vacant urban lot, 7.2% of every residential lot (400 ft²), and 62% of every industrial and commercial rooftop, could provide 100% self-reliance for fruit and vegetable consumption in Cleveland, Ohio (Grewal & Grewal, 2012).

Figure 2.2 Intensification of horticultural practices via organoponics and/or hydroponics. Organoponics use the soil matrix to maintain moisture, nutrients, and beneficial microorganisms while supporting root and crop development. Crops in hydroponic systems are supported by inert media with root structures exposed to a passing liquid nutrient solution.

Cultivation in simplified hydroponic systems forgoes advanced environmental monitoring and control equipment, increasing the risk for reduced yield but allowing for crop cultivation where soil-cultivation is not feasible. However, soil is an effective storage media for moisture and nutrients, as well as beneficial microorganisms that help control pests and deliver nutrients to plants. Therefore the lack of soil in hydroponic systems means that constant monitoring of the liquid nutrient solution status (i.e., level, salinity, pH, temperature), and ambient environmental conditions (i.e., pests, lighting, temperature, ventilation) is imperative as plants are more vulnerable to inconsistent conditions in hydroponic mediums (Resh, 2013). Additional input of electricity for pumping is necessary to continuously recirculate hydroponic fertigation solution, ensuring uniform mixing and aeration (Orsini et al., 2013; Resh, 2013).
Investment for water storage and conveyance infrastructure is required to capture rainwater to ensure adequate water supply and quality. Regardless of these costs, simplified hydroponic systems have exhibited sustainability in several developing world contexts achieving return on initial investments in less than one year (Orsini et al., 2013).

Thus, the feasibility of intensifying agriculture practices for smaller footprints in urban contexts depends on the availability and access to crucial, consumable components of nutrients, water, and electricity. Urban areas can often have some level of access to water and electricity, however the necessary inputs of land and nutrient fertilizers are often not available. Orsini et al. (2013) states that the success of hydroponic systems rely on the nutrient solutions supplied to the plants, their availability, affordability and supply reliability as users would require daily, or weekly access (Orsini et al., 2013). Simplified hydroponic systems have demonstrated adequate agricultural productivity in limited space so long as necessary agricultural inputs are provided. Nutrient fertilizers for hydroponic system are comprised of mineral salts that are dissolved in water and mixed prior to fertigation in hydroponic cultivation systems. Geographic and economic factors can limit access to synthetic fertilizers, highlighting the need for local production or recovery of nutrient fertilizer materials necessary for soil-less systems. The realization of circular economies considers wastewater as a potential resource for nutrients, water, and energy to support urban agriculture (Davidson et al., 2015; Diaz-Elsayed et al., 2019; Verbyla et al., 2013).

2.2.2 Opportunities in Wastewater

The practice of utilizing wastewater to fertilize and irrigate soil-grown crops has existed for hundreds, if not thousands of years by remote, rural populations across the world (FAO, 2011; Harder et al., 2019; WHO, 2006). It is estimated that at least 10% of the world’s population consumes foods produced by irrigation with wastewater, thus the World Health Organization (WHO) established wastewater reuse guidelines to ensure safe reuse practices (WHO, 2006). Using wastewater for irrigation is so alluring that farmers in Pakistan pay fees for access to wastewater since it allows them to triple crop harvests each year, resulting in increased earnings of $300 USD each year compared to farmers using
fresh water for irrigation (WHO, 2006). If properly managed, wastewater can be an effective and reliable source of water, plant macronutrients (i.e., nitrogen, phosphorus, potassium, calcium, and magnesium) and biodegradable organic matter that can reconstruct depleted soils (Harder et al., 2019). Past studies have observed improved crop yields and fruit quality with the use of treated wastewater for irrigation of soil-grown crops (Oyama et al., 2005; Prazeres et al., 2017). Two obvious benefits arise from using wastewater in hydroponic systems: (1) plants are provided nutrients necessary to produce valuable fruits and vegetables and (2) nutrient and organic matter contaminants are removed from the wastewater via biological processes (Prazeres et al., 2017). Despite the advantages of sustainable resource management associated with wastewater reuse for irrigation, many inherent risks to human and environmental health raise concerns. Guidelines established by WHO advise the combination of wastewater treatment processes and irrigation techniques like localized drip irrigation (resembling the localized irrigation that takes place in hydroponics) to achieve pathogen reduction necessary to protect public health (WHO, 2006).

Recovery of nutrient resources like nitrogen, phosphorus, and potassium as well as water from WWT systems has been predicted to have significantly higher positive impacts than energy recovery. Areas where food security is a major concern stand to benefit from stable access to nutrient fertilizers (Orsini et al., 2013; Trimmer et al., 2017). Trimmer and Guest (2018) estimated that at least six of the world’s least developed countries could double or offset all projected nutrient and energy use in the year 2030 if sanitation systems capable of resource recovery from wastewater are installed to achieve universal sanitation coverage (Trimmer et al., 2017). Most of the countries that would benefit most from the nutrient resource recovery are in sub-Saharan and West Africa, as well as many countries in Asia (Figure 2.3). This research focuses specifically on nutrient recovery from wastewater to enable reuse in appropriate horticultural systems in challenging locations. Potential barriers to WW resource recovery practices include: lack of supporting infrastructures, policy, reliable utility grids for water and energy, poor socioeconomic conditions, population density, resource scarcity, climactic conditions, and cultural
perception; resource recovery practices must consider these factors to succeed in both rural and urban areas of developing nations (Katukiza et al., 2012; Mihelcic et al., 2017; Verbyla et al., 2013).

Figure 2.3 Potential impacts of integrated sanitation and resource recovery. Impacts relate to the projected use of fertilizer nutrients per hectare of cropland and per capita electricity use in 2030. Maps on the left depict potential impacts per country resulting from the installation of new wastewater treatment systems capable of resource recovery, normalized to projected consumption in the year 2030. Reprinted with permission from (Trimmer, J.T., Cusick, R.D., & Guest, J.S. (2017). Amplifying Progress toward Multiple Development Goals through Resource Recovery from Sanitation. Environmental Science & Technology. doi:10.1021/acs.est.7b02147. © 2018 American Chemical Society.)
Other important factors to consider for reusing wastewater in agriculture include: wastewater quality, volume of treated wastewater to be used, physicochemical properties of receiving soils, nutritional needs of crops, accessibility of existing water sources, and risks of animal and human contamination (Prazeres et al., 2017). Low-footprint farming practices like organoponics and hydroponics require high quality water for irrigation to ensure favorable crop yield and quality, therefore wastewater use in these systems would require some level of treatment. However, irrigation water is used more efficiently in low-footprint farming, minimizing the overall water demand (Orsini et al., 2013; Resh, 2013).

In addition to nutrients and water, wastewater can contain pathogens, heavy metals, salinity and other materials that can affect crop production or jeopardize human and environmental health, warranting the need for standards that ensure adequate wastewater treatment and reuse practices. The World Health Organization’s (WHO) guidelines for wastewater reuse in agriculture establishes pertinent treatment targets agricultural reuse applications (WHO, 2006). The United States Environmental Protection Agency (USEPA) also developed guidelines for reuse of treated wastewater (USEPA, 2012). Generally, treatment guidelines and management practices are employed to yield tolerable, additional disease burdens of $\leq 10^{-6}$ DALY (disability-adjusted life years) per person per year (WHO, 2006). Exposure to harmful materials in treated wastewater can be mitigated by a combination of appropriate wastewater treatment processes that remove pathogens and irrigation practices that avoid the transmission of pathogens to edible portions of crops.

Low-footprint farming methods like hydroponics and organoponics prioritize resource efficiency, thus the most appropriate irrigation methods are those that deliver water directly to the root zone, thus minimizing evaporative losses. This type of localized irrigation can be performed by drip irrigation or hydroponic configurations like the nutrient film technique (NFT) where the fertigation solution is constantly recirculated past plant roots and exposure to the atmosphere and other portions of the plant are limited, yielding a 2 and 4 log-removal value for low- and high-growing plants, respectively (Resh, 2013; WHO, 2006). Selection of crops with edible portions that grow low to the irrigation zone like lettuce
benefit from processes that remove pathogenic bacteria, viruses, and helminths from wastewater reused for irrigation. Ultimately, implementation of accessible technological solutions coupled with best management practices, or BMPs, can realize the safe reuse of materials from wastewater to support agricultural practices (USEPA, 2012).

The advantage of utilizing wastewater as a resource is that wherever people exist, so does wastewater. Thus, if a technology that enables access to the resources within wastewater proves beneficial, then so does a technology that enables the use of those recovered resources. The emergence of advanced, decentralized wastewater treatment technologies that couple sanitation with resource recovery presents synergies with decentralized urban agriculture practices that can significantly advance progress towards the UN’s sustainable development goals (Trimmer et al., 2017). Enabling access to crucial resources of fertilizer, energy, and water, amplifies progress towards achieving several SDGs by stimulating growth from within communities, liberating time spent procuring resources for other activities like skill development, education, or wage-labor (Transforming our world: The 2030 agenda for sustainable development, 2015).

2.3 Decentralized Wastewater Treatment and Resource Recovery

A growing trend in the field of wastewater treatment is the decentralization of wastewater treatment facilities which shifts dependence away from large, centralized treatment facilities to multiple smaller, semi-independent facilities, forming a treatment network that serves an entire region or a component of a larger region with a population ranging from 1-1000 people (Figure 2.1) (Diaz-Elsayed et al. 2019). Each approach has their own advantages, disadvantages, and ideal contexts. In resource-limited contexts, decentralized facilities can be more advantageous as they can require less infrastructure, maintenance, and cost to construct and operate (Gikas & Tchobanoglous, 2009). Simplistic operation and maintenance in addition to affordability have become crucial design criteria given the global rate of urbanization, specifically in least developed countries (LDCs), where sanitation infrastructure is often neglected (Trimmer et al., 2017). Decentralized sanitation systems are more adaptive due to their smaller system size which allows rapid deployment to areas where sanitation infrastructure is lacking. WWT
executed at the point of wastewater generation, e.g. public toilets, can provide much needed sanitation without the need for expensive sewer infrastructure, making decentralization an attractive option for urban areas in developing countries. Additionally, the inherent flexibility of small-scale and decentralized WWT can improve sustainability by facilitating resource recovery. Emerging, autonomous WWT systems, referred to as non-sewered sanitation systems (NSSS) are a potential solution to the sanitation crises plaguing the urban poor of least-developed countries (LDCs). Enhanced treatment capacity afforded by advanced NSSSs can increase the overall safety and feasibility of multi-barrier approaches to wastewater reuse for agriculture, especially in rapidly growing urban contexts (USEPA, 2012).

2.3.1 Non-Sewered Sanitation Systems (NSSS)

The United Nations has outlined an agenda to address social, economic, and environmental issues afflicting the world’s poorest populations; the agenda identifies a list of 17 Sustainable Development Goals (SDGs) to guide the efforts of the agenda (Transforming our world: The 2030 agenda for sustainable development, 2015). SDG 6 endeavors to ensure access to safe drinking water and sanitation for all; it’s estimated that 2.3 billion people continue to lack access to basic sanitation systems. Consequences associated with the lack of inadequate sanitation result in an estimated 1.8 billion people across the world drinking faecally contaminated water and the annual deaths of 361,000 children due to diarrheal diseases (WHO & UNICEF, 2017). Emerging, autonomous sanitation technologies, also known as non-sewered sanitation systems (NSSS), can address sanitation needs in a variety of contexts while promoting social, economic, and environmental sustainability by minimizing system input requirements and recovering valuable output materials.

The International Organization for Standardization (ISO) developed ISO standard 30500 to establish NSSS design criteria and performance benchmarks necessary to ensure relevant, safe, and sustainable NSSS technologies (ISO, 2018). A NSSS is comprised of at least, two main system components: (1) at least one front-end sanitation user-interface, and (2) a backend treatment process that transforms NSSS inputs into safe outputs (Figure 2.3). The front-end component contains the contextually
relevant sanitation infrastructure which safely evacuates waste materials to the backend component. The backend component is tasked with the transformation of waste materials into safe outputs (Figure 2.3).

Figure 2.4 Conceptual diagram of a complete non-sewered sanitation system (NSSS).

The ISO 30500 standard mandates NSSS designs that ensure system safety and reliability but only encourages sustainable NSSS designs. Sustainable NSSS designs are considered to significantly lower material and energy inputs required to provide safe and efficient sanitation service. The ability to generate usable outputs, i.e., resource recovery, from wastewater enhances the sustainability of a NSSS, however is not mandated by ISO 30500. ISO 30500 does mandate that recovered materials exhibit a high level of safety for reuse. Conventional wastewater treatment process utilize biological processes to transform wastewater pollutants to more benign by-products via naturally-occurring processes like aerobic cell respiration or anaerobic digestion. These processes reduce chemical usage, but aerobic processes can require high energy inputs to maintain adequate dissolved oxygen (DO) concentrations for respiration to occur; anaerobic processes do not require aeration, thus further reduce required inputs
(Tchobanoglous et al., 2014). Biological wastewater treatment pathways achieve adequate treatment performance and reliability under ideal operating conditions but can become unreliable at smaller scales as influent flow rate and composition can fluctuate.

2.3.2 Anaerobic Membrane Bioreactors (AnMBRs)

Anaerobic processes have gained recognition as a WWT solution for their relatively low energy use as aeration is not required to maintain the driving biological processes, and furthermore, the biogas produced by the anaerobic digestion (AD) process is a valuable energy resource that can be used for heating and/or generating electricity. Anaerobic membrane bioreactor (AnMBRs) technology upgrades AD processes with the addition of membrane ultrafiltration or nanofiltration (Figure 2.4), decoupling the system’s solids retention time (SRT) and hydraulic retention time (HRT) of the anaerobic reactor, and ultimately enhancing the solids degradation process by providing a physical barrier to undegraded materials while significantly reducing system footprint (Galib et al., 2016; Harb & Hong, 2017; Jain, 2018; Pretel et al., 2016; Rashidi et al., 2015). Nutrients (e.g., nitrogen, phosphorus, and potassium) bound up in complex, organic solids are liberated during AD and dissolved into the bulk liquid solution which permeates the membrane filtration module, yielding an AnMBR system effluent, or “permeate”, with high nutrient concentration, low chemical oxygen demand (COD), and low total suspended solids (TSS) (Bair et al., 2015; Batstone et al., 2015; Calabria, 2014; Jain, 2018; Rashidi et al., 2015). Removal of nitrogen and phosphorus from AnMBR effluent, or AnMBR permeate, is imperative as discharging these nutrients into water bodies results in eutrophication and environmental/ecological degradation (Tchobanoglous et al., 2014). However, nutrient-rich AnMBR permeate can be a valuable, renewable source of nitrogen and phosphorus fertilizer that can support local agriculture (Calabria, 2014; Smith & Smith, 2017).
Bair et al. (2015) assessed the feasibility of applying an AnMBR for onsite sanitation and resource recovery in urban slums by combining with a public toilet serving a small community (100 events*d⁻¹*toilet⁻¹) in the south-India state of Kerala (Bair et al., 2015). The researchers’ model reported that approximately 90% of the influent total nitrogen mass can be recovered in the AnMBR system effluent for use as fertilizer (Figure 2.6). The degradation of complex organic compounds in the AnMBR system yields a methane-rich biogas that can be combusted to generate heat and electricity. Bair et al. (2015) reported that the decentralized AnMBR system they modelled could theoretically produce enough energy from biogas to operate the treatment process, however it was noted that the AnMBR treatment process required additional treatment to remove the excess nitrogen and phosphorus present in the membrane permeate (Bair et al., 2015). Opportunities for energy recovery by AnMBR-WWT are promising, however Trimmer, Cusick, and Guest (2017) concluded that nutrient recovery practices imply significantly higher positive impacts in least-developed countries (LDCs) than energy recovery, observing that newly installed sanitation systems with resource recovery-embedded design could double or offset all projected nutrient and energy use in some areas by the year 2030 (Trimmer et al., 2017). Thus, incorporating nutrient resource recovery into the design of promising sanitation platforms such as the AnMBR is a design imperative.
2.3.3 Small-Scale Nutrient Removal and Recovery for AnMBR-NSSS

Any treatment process considered for a small-scale sanitation system like the AnMBR-NSSS platform should follow low-footprint design principles to maintain adaptability and applicability in challenging contexts where space is a limited-resource. Nutrient removal and recovery processes at the small-scale represent a technological gap in the emerging NSSS space as NSSS design criteria mandate small system footprints as well as reduced inputs requirements presents fundamental design and operational challenges to long-established industry practices. (Smith et al., 2012; Trotochaud et al., 2019).

2.3.3.1 Biological Nitrogen Removal

Biological nitrogen removal (BNR) uses the innate metabolic processes of microorganisms to remove nitrogen from the wastewater and is the preferred treatment pathway adopted by many large, centralized treatment facilities (Ergas & Aponte-Morales, 2014; Tchobanoglous et al., 2014). The allure of BNR is attributed to the relatively low cost in terms of chemical usage and energy consumption, however these advantages may be offset in decentralized applications. Large reactor volumes and quality control executed by trained personnel is required to ensure proper performance of BNR processes which may not always be feasible in decentralized applications with space limitations, especially in LDCs.
(Batstone et al., 2015; Capodaglio, 2017). Additionally, the nature of small-scale systems implies fluctuations in treatment system flow, potential for shock loads, and other uncontrollable system stresses that can be deleterious to the microbiomes responsible for biological treatment (Ergas and Aponte, 2014; Capodaglio, 2017; Trotochaud et al., 2019). Biological processes for phosphorus removal have not been considered for small-scale treatment scenarios as the removal mechanism relies on the over-assimilation of phosphorus into biological cells which must then be removed from the treatment system, implying the need for even greater reactor footprints and process control for sludge handling and disposal; as a result, small-scale phosphorus removal processes are usually performed via adsorption or chemical precipitation processes, discussed further below (Bunce et al., 2018; Loganathan et al., 2014).

Despite these concerns, some BNR processes have been recognized for their ability to reduce reactor volume and energy requirements. Anaerobic ammonia oxidation (ANAMMOX) could compliment an AnMBR WWT process as most of the nitrogen in AnMBR permeate is in the ammonia/ammonium form (Lin et al., 2016; Prieto et al., 2013; Tchobanoglous et al., 2014). Anammox uses slow growing chemolithotrophs, Brocadia anammoxidans, to oxidize ammonia while using nitrate as the electron acceptor, yielding N\textsubscript{2} gas (Ergas & Aponte-Morales, 2014). The anammox process uses approximately 63% less aeration than traditional nitrification processes as only half of the total Kjeldahl nitrogen (TKN) is oxidized to yield a nitrite:ammonia ratio of 1:1. Additionally, anammox sludge production rates are relatively slow, minimizing sludge handling requirements, but slow growth rates can be disadvantageous if the microorganisms are compromised by the introduction of inhibitory materials and contaminants. As a result, anammox processes require careful process control by maintaining ideal wastewater quality composition and aeration; this process control requirement in addition to the energy required for aeration, though less than nitrification, can be present challenges in decentralized contexts (Trotochaud et al., 2019).

Another BNR process, nitrate shunt, performs partial aeration and selection pressure to select for ammonia-oxidizing bacteria (AOB) over nitrite-oxidizing bacteria (NOB), which allows for the reduction of nitrite to N\textsubscript{2} gas. Like anammox, nitrate shunt requires less aeration to remove N from the wastewater
stream, however a carbon source is required to serve as the electron donor which could imply additional input requirements (Ergas & Aponte-Morales, 2014). Autotrophic denitrification pathways have received attention for their ability to remove nitrate using inorganic electron donors like H₂ or elemental sulfur while yielding less sludge production due to the low growth rate of autotrophic microorganisms. Thus, autotrophic denitrification reduces the need for organic carbon addition by using H₂ produced on-site or sulfur-containing oil-processing byproducts combined with solid-phase alkalinity sources in packed-bed reactors (Ergas and Aponte-Morales, 2014).

Anammox, nitrate shunt, and autotrophic denitrification are potential pathways for removing N from AnMBR permeate to meet ISO 30500 standards for TN removal, however they are ineffective at recovering nitrogen for reuse. As mentioned earlier, nutrient recovery can significantly impact progress towards several SDGs and facilitating circular economies, thus is considered a design imperative for NSSSs deployed in developing regions (Mihelcic et al., 2017; Trimmer and Guest, 2017).

Nutrient recovery at the small scale was successfully demonstrated in Durban, South Africa through the installation of urine-diverting toilets that provided sanitation in underserved, rural and peri-urban communities. Feces collected from the toilets was treated by dehydration while captured urine was collect and transported to a small, decentralized treatment facility for nutrient recovery. Nutrient recovery from captured urine was performed by first stabilizing captured urine via an efficient nitrification process using a moving bed biofilm reactor (MBBR); stabilized, nitrified urine was then distilled for volume reduction, yielding a highly concentrated nutrient fertilizer solution (Fumasoli et al., 2015; Udert et al., 2016). However, nitrogen recovery via nitrification, followed by distillation required approximately 9.5 W g N⁻¹ d⁻¹. In addition to the energy requirements, supervision of the biological processes was required to control the accumulation of process-inhibiting nitrite during nitrification (Fumasoli et al., 2015).

Assimilation of N and P by phototrophic organisms like algae and plants can be more energy-efficient for recovering nutrients via harvested biomass while also exhibiting the capacity to degrade organic pollutants; harvested algae can be used as a soil-fertilizer or animal feed (Batstone et al., 2015; Harder et al., 2019). Similarly, constructed wetlands containing higher order plants have demonstrated
direct reuse of wastewater nitrogen and phosphorus to support crop growth in (Gao et al., 2017; Kusumitha et al., 2019; Prazeres et al., 2017). Phototrophic processes exhibit the capacity for passive operation, however large cultivation area is required to facilitate large-scale nutrient uptake and photosynthetic growth, presenting challenges for integration into NSSSs, especially in urban areas. Opportunities for optimizing biological nutrient removal pathways exist but there remains a large knowledge gap regarding the viability of biological nutrient removal processes in NSSS contexts (Harder et al., 2019; Trotochaud et al., 2019)

2.3.3.2 Physical and Chemical Nutrient Removal Processes

Nutrient recovery facilitated by physical and/or chemical processes can be more feasible at smaller scales than biological pathways due to more attractive economies of scale (Capodaglio, 2017; Trotochaud et al., 2019). Furthermore, efficient removal of COD and TSS via AnMBR can facilitate more efficient nutrient removal and recovery via physical/chemical processes as most reaction inhibiting materials have been removed (Jain, 2018; Trotochaud et al., 2019). Common physical/chemical processes used for removing and/or recovering nutrients from AnMBR effluents include electrochemical oxidation, chemical precipitation, ion-exchange, adsorption, and air stripping.

2.3.3.2.1 Precipitation

Removal and recovery of phosphorus from AnMBR permeate via precipitation recovers solid forms of phosphorus minerals like magnesium ammonium phosphate (MAP or struvite), potassium struvite, calcium phosphate, iron phosphate after inducing precipitation and settling of large particles (Bunce et al., 2018). Precipitation is induced by the addition of caustic materials to raise the solution pH. Precipitated materials are then separated from the liquid stream by filtration or settling. Recovered precipitate can be marketed as a slow-release nutrient fertilizer, although the presence of heavy metals and pathogenic materials is a possibility (Harder et al., 2019). Regardless, P-containing precipitated material is a valuable nutrient fertilizer that recovers both nitrogen and phosphorus. However, continuously inducing precipitation requires the regular consumption of caustic chemicals which can also
imply the need for handling and storage of chemicals which is a challenge in NSSS contexts (Bunce et al., 2018; Trotochaud et al., 2019).

2.3.3.2.2 Air Stripping

Air stripping is an effective physical pathway for removing and recovering ammonia nitrogen from ammonia-rich wastewaters (Deng et al., 2014; Harder et al., 2019). Air stripping of ammonia is made possible through manipulation of aqueous conditions, i.e., pH and temperature, to favor conversion of ammonium (NH$_4^+$) to free ammonia (NH$_3$). Free ammonia volatilizes out of solution at high pH and temperature, implying the consumption of chemicals to raise and lower pH before and after ammonia-stripping. Additional chemical usage is needed to recover stripped ammonia in an acidic solution. Chemical usage for stripping can be decreased by using an electrochemical cell (Christiaens et al., 2019; Trotochaud et al., 2019). Though ammonia stripping is effective and can recover valuable, concentrated nutrient solutions, the infrastructure required (e.g., air stripping tower, blower motor, heater, and chemical storage) to facilitate nutrient recovery via air stripping presents challenges for NSSS integration (Deng et al., 2014; Trotochaud et al., 2019).

2.3.3.2.3 Electrochemical Processes

Electrochemical processes are being investigated for their ability to generate oxidants and selective separation of ionic materials when coupled with ion-specific membranes (Bian et al., 2019; Christiaens et al., 2019; Trotochaud et al., 2019). Some electrochemical configurations can significantly minimize chemical input requirements by using electricity to fuel chemical reactions for wastewater treatment, which may be desirable in areas where resources are scarce, but electricity can be generated on-site using solar photovoltaic cells. Electrochemical oxidation via the generation of chlorine can remove ammonia-nitrogen from wastewater through the breakpoint chlorination process (White, 2010). However, removing ammoniacal ammonia from treated wastewater can be inefficient if dissolved organic compounds that contribute additional chlorine demand are present. The energy needed to achieve breakpoint chlorination is increased significantly when ammonia nitrogen is present, which also contributes to increased wear on expensive electrochemical cell materials (White, 2010).
2.3.3.2.4 Adsorption and Ion-Exchange

Adsorption, or sorption, and ion exchange (IX) processes have been used widely for removal of nutrients and organic contaminants and are excellent candidates for use in developing contexts as operation of adsorption/IX processes are relatively simple. Different carbon and mineral-based sorbents like activated carbon and zeolites can be used to recover different dissolved nutrient compounds from AnMBR permeate and simultaneously provide additional treatment capacity by removing dissolved organic compounds, pathogens, and turbidity, further improving permeate quality (Guaya et al., 2018; Harder et al., 2019; Jain, 2018; Smith & Smith, 2017). Nutrient materials can be recovered as solids attached to spent sorbents removed from treatment processes or the sorbent materials can be used to transport nutrient materials from one liquid medium to another via the process of regeneration (Deng et al., 2014; Harder et al., 2019). Concerns over the cost of replacing or regenerating spent adsorbent/IX materials to maintain continuous nutrient removal are the main barriers to the use of adsorption processes. Although some applicable adsorbent/IX materials are relatively inexpensive and widely available, constant consumption and disposal of adsorbent material is not a sustainable practice and may not be feasible in remote locations or developing areas (Mihelcic et al., 2017). Regeneration of spent material can be more sustainable as dependence on additional input materials are minimized, yielding more autonomous NSSS operation (Boyer, 2014; Deng et al., 2014).

Carbonaceous adsorbents like charcoal, biochar, and granular-activated carbon (GAC) can recover heavy metals, negatively-charged materials, urea-bound nitrogen in addition to other dissolved organics present in permeate (Harder et al., 2019; Lehmann & Joseph, 2015; Mohan et al., 2014). Application of carbon-based sorbents spent with recovered organic and nutrient materials can be used to increase the fertility and water storage capacity of nutrient-depleted soils adding value to an otherwise wasted by-product (Ahmad et al., 2014). The replacement costs associated with the constant use of carbon-based sorbents can be avoided by producing bio-char from discarded plant and animal mass. Biochar production can be simple, as production practices can be traced back to indigenous peoples of the Amazon before the arrival of European settlers (Lehmann et al., 2011). However, biochar production
involves the pyrolysis of organic materials at high temperature, implying requirements of space, energy, and appropriate safety precautions to be in place for biochar production to be feasible.

Ion-exchange (IX) closely resembles adsorption in operation, however IX processes can be completely reversible, allowing reuse of IX materials for multiple treatment cycles. Natural, mineral-based adsorbents like aluminosilicates, i.e., zeolites, can exhibit impressive cation exchange capacities and selectivity for \( \text{NH}_4^+ \) and \( \text{K}^+ \) (Boyer, 2014; Hedstrom, 2001). Zeolite materials and their various applications are discussed in detail in the following section. The advantages of sorption and/or IX processes are that they contribute little complexity to treatment and resource recovery operation, and depending on the designed service life, can operate in relatively small footprints, exhibiting high potential for integrating well with NSSSs. (Lin et al., 2016; Trotochaud et al., 2019).

2.3.4 Recovery Challenges

The sustainability of technological interventions in the developing world depends on more than simply technological performance, but also on context-sensitive approaches to design and implementation of technologies (Mihelcic et al., 2017). Using low-cost and accessible materials increases the sustainability of a technical solution; a major research question driving this research is: can low-cost materials be used to create effective systems that enable safe, wastewater resource recovery for reuse in agriculture? Naturally occurring aluminosilicate minerals known as zeolites, have proven effective in both being able to remove ammonia-nitrogen from wastewater and in their use as a soil additive capable of slow-fertilizer release, which is beneficial for nutrient depleted soils, however a pathway for integration of continuous nutrient recovery and reuse, has yet to be demonstrated. Additionally, horticultural nutrient demands can vary depending on crop type and growth stage while nutrient availability from waste water can vary daily and seasonally.

Additionally, the scale of the sanitation system service can affect the efficacy of resource recovery practices (Diaz-Elsayed et al., 2019). Generally, economies-of-scale favor resource recovery at medium-to-large scale facilities, however passive recovery pathways can improve feasibility at smaller scales. A specific class of zeolites, clinoptilolites, have been investigated extensively for their capacity to
remove TAN from wastewater effluents like AnMBR permeates via simple, ion exchange pathways. Furthermore, clinoptilolite-IX (CZ-IX) processes have demonstrated consistency with the low system and energy footprints of the AnMBR platform, highlighting the potential to overcome challenges pertaining to small-scale systems (Deng et al., 2014; Gupta et al., 2015).

2.4 Natural Zeolites

The term zeolite refers to a class of micro-porous, crystalline, aluminosilicates with a negatively charged framework that results when aluminum ($\text{Al}^{3+}$) replaces a silica ($\text{Si}^{4+}$) atom in the silicate framework; the net-negative charge is neutralized by extra-framework cations. Clinoptilolite, the most abundant type of zeolite, is defined as a zeolite having the framework topology of heulandite and having a Si:Al molar ratio greater than or equal to four (Boyer, 2014; Wang & Peng, 2010). Extra-framework cations of clinoptilolite, typically sodium, potassium, and calcium, can exchange freely with other cations present in a passing fluid under certain conditions (Figure 2.6), resulting in ion-exchange (IX) (Payra & Dutta, 2003). Furthermore, the topology of clinoptilolite particles contains a high degree of microporosity, lending to its use as a molecular sieve.

![Figure 2.7](image.png)

Figure 2.7 The crystalline, aluminosilicate cage structure of clinoptilolite allows exchange of extra-framework cations.

Clinoptilolite zeolite (CZ) deposits are located around the world, however the mineral composition of clinoptilolites can vary depending upon the environmental conditions when the CZ was
formed (Payra & Dutta, 2003). CZs are usually identified by the extra-framework cation with highest concentration (e.g., Ca$^{2+}$, Na$^+$, K$^+$) in the CZ and by the country of origin (Boyer, 2014; Hedstrom, 2001). Industrial applications for zeolites like CZ are mainly adsorption, catalysis, and ion exchange processes. The availability, cost, and contaminant removal properties of zeolite make them an attractive material for use in wastewater treatment and agricultural applications, even when bulk quantities are required (Boyer, 2014; Payra & Dutta, 2003).

### 2.4.1 Zeolite Applications in Wastewater Treatment

The ion exchange capacity, morphology, and molecular sieve properties of zeolites make them an excellent material for removing cations, namely ammonium (NH$_4^+$) from wastewater. Clinoptilolite is commonly used for ammonium removal as it is available in many deposits world-wide, relatively inexpensive, and exhibits a well-documented affinity for NH$_4^+$ ions relative to other ions present in wastewater. The selectivity of clinoptilolite is a result of clinoptilolite morphology and the effect of hydration on the size of the ionic radii of ions (Figure 2.7) (Railsback, 2006); ionic radii are reported in units of angstroms (Å); 1 Å = 100 pm = 10$^{-9}$ mm. Clinoptilolite’s relatively high selectivity for ammonium ions (NH$_4^+$) makes it an excellent material for the removal of ammonium from wastewaters high in total ammonia nitrogen (TAN) such as piggery wastewater, landfill leachate, or anaerobic digester centrate (Amini et al., 2017; Apontes-Morales, 2015; Boyer, 2014). TAN in wastewater requires removal prior to discharging into the environment avoid eutrophication of receiving water bodies whereas other cations found in wastewater (i.e., Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$) do not pose the same environmental threats thus do not require removal despite potentially high concentrations. Most of the literature surrounding clinoptilolite reports the following cation selectivity sequence: Cs$^+$ > Rb$^+$ > K$^+$ > NH$_4^+$ > Ba$^{2+}$ > Sr$^{2+}$ > Na$^+$ > Ca$^{2+}$ > Mg$^{2+}$ (Boyer, 2014; Hedstrom, 2001; Payra & Dutta, 2003). Examination of Figure 2.6 and the effect of hydration on ionic radii reveals that the reported selectivity of clinoptilolite correlates to the radii of ions once hydrated (Crittenden, 2012; Railsback, 2006).

Selective and passive NH$_4^+$ removal via IX with clinoptilolite is an attractive option for decentralized WWT and non-sewered sanitation systems (NSSS) that are constrained by system footprint.
and energy requirements (Trotochaud et al., 2019). However, other cations in wastewater, namely K⁺, Na⁺, Ca²⁺, and Mg²⁺, compete with NH₄⁺ for clinoptilolite exchange, reducing the overall TAN removal capacity. The presence of Na⁺ and K⁺ are of prime concern as the selectivity of clinoptilolite for these ions is very similar, especially K⁺ which has a similar ionic radius when hydrated, meaning that even low concentrations will compete with NH₄⁺ for IX onto clinoptilolite (Boyer, 2014).

![Figure 2.8 Effect of hydration on ionic radii of ions. Reproduced with permission from Railsback, B. 2006. Variation in hydrated radius of ions. Railsback's Some Fundamentals of Mineralogy and Geochemistry. [Illustration] Retrieved from http://railsback.org/Fundamentals/815HydratedCationRadii04LS.pdf]

2.4.2 Regeneration Methods

Favorable TAN removal performance from wastewater with clinoptilolite is well documented (average of 91% ±7% NH₄⁺-N removal for 218 ±95 bed volumes treated (Boyer, 2014)), however regeneration of exhausted clinoptilolite presents barriers for implementation in challenging contexts as
concentrated brines and/or actively powered processes are required to remove captured TAN content. Regeneration of clinoptilolite exhausted with NH$_4^+$ is performed by reversing the IX process using a regenerant liquid consisting of a counter-ion, usually Na$^+$, or to a lesser extent: K$^+$, Ca$^{2+}$, or Mg$^{2+}$ (Hedstrom, 2001). The high counter-ion concentration of the bulk solution creates a concentration gradient to drive the regeneration process until equilibrium is reached (Boyer, 2014; Crittenden, 2012). Spent regenerant solution is then either discharged to the sewer for downstream treatment at a centralized facility or treated on-site via chemical or biological pathways. Chemical processes can remove TAN by oxidation, or volatilization. Oxidation of TAN can be performed through breakpoint chlorination by either adding NaOCl or electrochemical oxidation with chloride ions in solution (Li et al., 2010). Volatilization requires a basic solution to raise the pH of the regenerant solution to convert spent regenerant solution TAN from NH$_4^+$ to NH$_3$ form which can be volatilized out of solution to the atmosphere or captured in a sulfuric acid scrubber (Deng et al., 2014).

Biological treatment of spent regenerant uses salt-tolerant ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) to nitrify the spent regenerant TAN content, allowing reuse of the regenerant solution (Hedstrom, 2001). Nitrification of TAN to nitrate allows reuse of the resulting sodium nitrate brine for future regeneration cycles. Alkalinity addition is required to replace alkalinity consumed during nitrification. The biological and chemical regeneration methods mentioned allow reuse of the regenerant solution for future regeneration cycles, but these processes introduce additional requirements of salt and alkaline chemical additives, energy to drive TAN oxidation, volatilization, or aeration for nitrification, adding dependency on consumed, material and energy inputs (Boyer, 2014). The constant requirement of consumable chemical materials or energy for aeration can reduce feasibility for implementing clino-IX and TAN recovery processes in challenging contexts like LDCs (Mihelcic et al., 2017).

Deng et al. (2014) demonstrated both clinoptilolite reuse and regenerant solution reuse with high clinoptilolite regeneration efficiency (85%) and a 10x reduction in chemical costs by optimizing salt concentration and pH of the regenerant brine (10g/L NaCl; pH=12) (Deng, 2014; Deng et al., 2014).
Deng (2014) also performed TAN recovery by capturing volatilized ammonia in a sulfuric acid scrubber after air stripping at high pH and temperature. The resulting highly concentrated ammonium sulfate was considered a recovered fertilizer product, however higher air temperatures (25-50 °C) and flow rates were needed to recover 90% of the TAN removed from clinoptilolite (Deng, 2014; Deng et al., 2014).

Recovering air stripped TAN avoids non-compliance for the NH₃ emission standards set forth by ISO 30500 and creates a valuable fertilizer product, however the infrastructure, chemical, and energy inputs necessary to maintain the system proposed by Deng (2014) may prove unfeasible for integration with a NSSS, especially in LDC contexts.

Another option for dealing with exhausted clinoptilolite is to regularly replace the exhausted clinoptilolite with virgin material to maintain constant and efficient TAN removal. Constant replacement of clinoptilolite implies a constant cost, however the exhausted clinoptilolite loaded with NH₄⁺ can be used or sold as a slow-release fertilizer product for adding to soils for farming or gardening, potentially offsetting acquisition cost. The logistics and costs associated with frequent transport of bulk quantities zeolite will vary based on geographic location and size of the clino-IX system, presenting their own challenges for continuous treatment alongside NSSS in challenging contexts. Thus far, the state of the art for regenerating exhausted zeolite involves high chemical and energy inputs, reducing the feasibility for use in resource limited areas. Furthermore, while regeneration can be avoided by replacing spent clinoptilolite with virgin material, this implies a constant-consumption scenario which can lead to increased environmental impacts.

2.4.3 Zeolite Applications in Agriculture

The physical properties of zeolites present opportunities for their beneficial use in a variety of plant and soil supporting processes. Granular and powdered zeolite can be used as soil amendments to enhance the soil’s total nutrient holding capacity and to prevent nutrient wash-out during rain events (Guaya et al., 2018). The high porosity of clinoptilolite and its hygroscopic properties bind water enhancing moisture retention within the soil matrix. Application for NH₄⁺-exhausted clinoptilolite as a soil amendment for nutrient-depleted soils can build soil nitrogen stores (Amini et al., 2017; Huang et al.,
This is an attractive option where land is widely available and in-soil agriculture is desired; proper equipment is required for transport and dispersal of bulk zeolite to be added to soil. In an urban context land application may not be as feasible but could potentially buttress small-scale urban agriculture practices that utilize above ground beds (Thomaier et al., 2014).

Zeolites have also been used in soil-less, hydroponic systems. Researchers at NASA developed a system for using granular zeolite in soilless growing systems, giving rise to a new form of hydroponics known as “Zeoponics” which uses zeolite as both plant support and nutrient delivery material (Eckart, 1996). Zeoponics utilizes granular zeolite preloaded with ammonium to slowly release NH$_4^+$ according to crop uptake. Synthetic apatite mineral is mixed with the granular zeolite media to provide calcium, potassium and phosphorus. The slow-release action of these materials is activated with water during irrigation, allowing ions in solid form to dissolve into the root zone for plant uptake over time. One NASA study found that the zeoponic nutrient stores lasted for three generations of wheat crops being grown in the zeoponic substrate. However, as the zeolite ammonium content (Z-NH$_4^+$) decreases, the driving force for releasing NH$_4^+$ also decreased, resulting in decreased yields in future crop generations (Eckart, 1996; Steinberg et al., 2000). A method for recharging zeoponic media with pertinent nutrients is required for continued nutrient delivery.

NH$_4^+$ release from zeoponic substrate increases NH$_4^+$ in the bulk soil solution, lowering the driving force to release bound NH$_4^+$. If the zeoponic substrate is not kept abiotic, then nitrifying bacteria can accumulate and nitrify bulk solution NH$_4^+$ to NO$_3^-$, thus maintaining a NH$_4^+$ deficit in the bulk solution. McGilloway et al. (2003) observed that nitrification rates could exceed nitrogen assimilation rates of radishes being grown in the zeoponic substrate, avoiding inhibitory effects of NH$_4^+$-N nutrition (McGilloway et al., 2003). The researchers also observed a significant drop in pH and limited buffering capacity of the zeoponic substrate. Acidic conditions can lead to decreased nitrification and destabilization of the zeolite structure, leading to attrition of zeolite granules and reducing the zeoponic substrate mass overtime as smaller particles may be flushed and lost from the system (McGilloway et al., 2003).
2.4.4 Opportunities for Integrating Wastewater Treatment and Agriculture

Researchers have sought to utilize the TAN recovery capacity of clinoptilolite for transferring nutrients into various horticultural applications to release CZ-bound nutrients as fertilizers. Smith and Smith (2016) used CZ to recover 95% of the total nitrogen from an upflow, anaerobic sludge blanket reactor (UASB). Once CZ was exhausted with TAN (72% breakthrough), spent clinoptilolite was transferred to a flood-drain hydroponic grow-bed to serve as a plant-support media for *Solanum lycopersicum* (a.k.a. cherry tomato). The spent CZ demonstrated nitrogen release, achieving adequate growth when additional plant macronutrients are added to the recirculating hydroponic solution; crops grown in exhausted zeolite without supplemental nutrition did not demonstrate adequate growth (Smith & Smith, 2016). The work conducted by Smith and Smith (2016) demonstrates the transport of nitrogen recovered from anaerobic treatment system effluent to a desirable nitrogen sink, i.e., crops grown in a low-footprint hydroponic system. However, the researchers failed to report a proposed method for reusing or handling the zeolite after the hydroponic cultivation phase. It is likely the CZ materials will require disposal or be land applied and replaced to maintain TAN removal from the anaerobic system effluent. Recovery of used zeolite after crop cultivation would facilitate reuse for additional TAN recovery, achieving a more “closed-loop” overall process.

Smith and Smith (2016) demonstrated how zeolite can be used to remove nitrogen for improving WWT system effluent quality and transporting the nitrogen via zeolite to a horticultural system. Essentially, zeolite served as a carrier to transport nitrogen recovered from waste to horticultural reuse locations. Other similar work demonstrated capture, transport, and release of wastewater-derived nitrogen via zeolite for the cultivation of cyanobacteria in photobioreactors (Markou et al., 2014). Zeolite demonstrated selective capture of nitrogen from the wastewater while excluding uptake of suspended solids and contaminant materials that would inhibit algal growth. Selective nitrogen capture, transport, and release capacities of zeolite fosters implications for enabling plant growth where ever human waste is collected and/or treated.
Separation of zeolite from plant roots in zeoponic systems could facilitate simple transport between nutrient discharge at crop fertigation locations and nutrient uptake at wastewater treatment locations. Cyclical, selective nutrient uptake from wastewater for discharge as fertilizer could enable more sustainable food production and waste treatment in the most remote locations where humans dwell, ranging anywhere from remote, single family homes in rural areas of developing countries to state-of-the-art, interstellar life-support habitats on the Moon or Mars (Eckart, 1996; Wheeler, 2017). The nature of extra-terrestrial contexts implies limited supplies of life-supporting resources (i.e., food, water, and oxygen), therefore preservation of food supplies through continuous recovery of nutrients for food production could support long-duration space missions.

Additionally, the nutrient removal capacity of zeolite via passive IX could support wastewater treatment processes by dampening nitrogen concentration spikes if necessary, to protect downstream treatment processes concerned with water recovery (Beler-Baykal et al., 1996; Wheeler, 2017). The nitrogen-dampening performance of CZ (Figure 2.7) is beneficial for equalizing nutrient loading rates, protecting sensitive biological treatment processes downstream. Nutrient dampening and passive nitrogen recovery via IX is also conducive to sewer mining of nitrogen from municipal wastewater and stormwater conveyance systems which would simultaneously mitigate non-point source nutrient discharges while recovering ammoniacal nitrogen; additional safety precautions are warranted as zeolite could also uptake heavy metals (Harder et al., 2019). Also, the dampening effect can overcome the inconsistencies between wastewater nutrient flux and agricultural nutrient demand. CZ-IX can attenuate wastewater nutrient loads and then the release into a horticultural system can be controlled per plant requirements. The release rate of CZ-bound TAN is influenced by the regenerant solution’s characteristics; therefore, manipulation of the salt concentration and chemical composition determines the rate at which NH$_4^+$ is released (Boyer, 2014; Crittenden, 2012; Nakhli et al., 2017). CZ has demonstrated accommodation of nitrogen shock loads, nitrogen storage, and nitrogen release into horticultural various systems, however, reuse of CZ after nitrogen release has not been demonstrated.

### 2.4.5 Challenges for Sustainable Nutrient Recovery in NSSS Contexts

Zeolites have proven to be highly versatile materials in both wastewater treatment and agricultural applications. The abundance of natural clinoptilolite deposits world-wide and their low-cost explains the widespread application of CZ for TAN removal processes. Although CZ is considered abundant and CZ deposits are found on every inhabited continent, regeneration of CZ to allow continuous reuse is more feasible in LDCs where dependable access to materials is not always guaranteed. Development of low-cost regeneration methods that enable continuous, efficient use of CZ for TAN recovery are required to improve the feasibility of implementation into NSSSs.

Smith and Smith (2016) demonstrated how zeolite can be loaded with nitrogen from wastewater for later use as a nitrogen-releasing, hydroponic support media, resembling zeoponics. Zeoponics was developed by NASA as a potential method for growing food in remote locations where fertile soil is non-existent. However, methods for loading TAN onto zeoponics substrates have not been developed.
Zeoponic systems can expose zeoponic substrates to damage from the encroachment of plant roots (Poulet et al., 2016; Steinberg et al., 2000). As with zeoponic systems, contacting plant roots directly with zeolitic mediums can lead to the damage and loss of zeolitic material post-harvest as root systems become heavily entrenched in growth media over time, ultimately fouling the zeolite medium (Resh, 2013). Maintaining the structural integrity of zeolite granules is important for preserving CZ as well as pumping equipment that can become damaged by the accumulation of fine particles.

Table 2.2 provides an overview of promising, sustainable methods for regenerating exhausted-clinoptilolite and, if applicable, the respective pathways for nutrient recovery. Each method presents limitations for use in NSSS contexts due to their associated requirements of material and energy inputs. Regeneration can be challenging within the operational confinements of a NSSS, however CZ regeneration can be performed off-site following a hub-spoke model, thus increasing its feasibility as the complexity of regeneration can be centralized (Trotochaud et al., 2019). Other methods presented observed that reuse of spent zeolites led to attrition or disintegration if subjected to high shear stresses, highlighting the preference for low-flow rate operation (Wachinski, 2016).

One major disadvantage of natural clinoptilolite is the inability to recover phosphorus effectively without chemical intervention or pretreatment implying additional treatment processes and infrastructure will be needed to recover phosphorus (P) present in AnMBR-NSSS effluents prior to discharge (Lin et al., 2014; Trotochaud et al., 2019; Wang & Peng, 2010). ISO 30500 mandates 80% removal of influent P during NSSS treatment to prevent environmental degradation after discharge. Recovery of P can significantly decrease the environmental impacts associated with eutrophication while recovering valuable phosphorus that can be used as fertilizer (Lin et al., 2014; Lin et al., 2016). Magnesium and calcium salts have been added to zeolite IX processes to simultaneously recover N and P by forming phosphate precipitates in addition to ammonium-exchanged zeolite (Lancellotti et al., 2014; Lin et al., 2014; Xu et al., 2015).
Table 2.1 Summary of zeolite regeneration pathways for TAN recovery and their potential limitations for use in NSSSs per ISO 30500.

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<tr>
<td>Air stripping + acid scrubbing to capture TAN</td>
<td>High pH sodium solution 10-20 mg/L NaCl + NaOH @ pH = 12</td>
<td>NaCl, NaOH, energy for blower and heating</td>
<td>Concentrated NH₄SO₄, reusable NaCl + NaOH regenerant solution</td>
<td>Space, energy, and noise for air stripping tower. Chemical requirement</td>
<td>(Deng, 2014)</td>
</tr>
<tr>
<td>Algal mass assimilation</td>
<td>Zarrouk medium¹</td>
<td>Energy for aeration, Zarrouk medium chemicals</td>
<td>Algal biomass</td>
<td>Operation and maintenance of algal photobioreactor. Energy use for aeration. Handling of spent zeolite after algal cultivation</td>
<td>(Markou et al., 2014)</td>
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<tr>
<td>Direct nutrient uptake: Hydroponic crop growth</td>
<td>Supporting macronutrient solution (P, K, Ca, Mg, S) for hydroponics recirculation</td>
<td>Virgin clinoptilolite to replace spent zeolite, additional plant macronutrients</td>
<td>Macrophyte biomass</td>
<td>Handling of zeolite after exhaustion phase.</td>
<td>(Smith &amp; Smith, 2016)</td>
</tr>
<tr>
<td>NH₄⁺-CZ + Precipitation of struvite</td>
<td>No regeneration: Exhausted zeolite and precipitated solids are replaced</td>
<td>Magnesium salt (MgO or MgCl₂) added during TAN removal or in clinoptilolite pretreatment solution</td>
<td>Struvite + NH₄⁺-clino</td>
<td>Continuous replacement of exhausted clinoptilolite</td>
<td>(Huang et al., 2014)</td>
</tr>
<tr>
<td>Electrochemical oxidation of TAN (no recovery) TAN oxidized to N₂</td>
<td>Concentrated NaCl</td>
<td>Electrode metals, electricity for electrolysis, Highly concentrated NaCl brine</td>
<td>Regenerated clinoptilolite (Efficiency: 97%)</td>
<td>Replacement of costly noble metals, electricity and NaCl requirement.</td>
<td>(Li et al., 2010)</td>
</tr>
<tr>
<td>Nitrate recovery via nitrification of CZ-TAN</td>
<td>Concentrated NaCl + salt-tolerant nitrifying sludge</td>
<td>Energy for aeration, anion exchange resin</td>
<td>Nitrate solution</td>
<td>Sludge handling, Aeration energy demand, anion exchange resins</td>
<td>(Hedstrom, 2001)</td>
</tr>
</tbody>
</table>

¹Zarrouk medium consisted of 16.8 g/L NaHCO₃, 2.5 g/L NaNO₃, 16.8 g/L NaHCO₃, 2.5 g/L NaNO₃, 0.5 g/L KH₂PO₄, 1.0 g/L K₂SO₄, 1.0 g/L NaCl, 0.04 g/L CaCl₂, 0.08 g/L Na₂EDTA, 0.2 g/L MgSO₄•7H₂O, 0.01 g/L FeSO₄.

A factor not widely reported in literature, yet warranting consideration is the transport and handling of spent and virgin clinoptilolite materials. It is important to consider that the low cost of clinoptilolite can result in the continuous consumption of virgin zeolite material, implying transport and handling of raw zeolite materials from extraction to processing to the consumer, as well as the handling and disposal of used zeolite. While continuous, consumptive use of zeolite may be less expensive, the increased transport and handling could potentially bear significant environmental costs as well as logistical challenges in developing contexts. Although it is worth noting that nitrogen-loaded clinoptilolite can be valued, marketed, and sold as a slow-release nitrogen fertilizer for land applications (Lancellotti et al., 2014). However, logistics and material costs associated with the continuous consumption of CZ in addition to the environmental impacts of continuous extraction or raw materials and their transport can negatively impact the overall sustainability of the nutrient recovery operation (Lin et al., 2016). Transport
and handling of spent and virgin clinoptilolite materials requires consideration as these processes can be relatively inexpensive while contributing significant environmental impacts and logistical challenges (Trotochaud et al., 2019). This is an important consideration to highlight as the low cost of clinoptilolite often warrants forgoing regeneration. Additionally, nitrogen-loaded clinoptilolite can be marketed and sold as a slow-release nitrogen fertilizer for soil-based agriculture (Lancellotti et al., 2014). Efficient integration of advanced, decentralized sanitation via the NSSS platform with low-footprint urban agriculture fosters implications for advancing towards meeting many SDGs (FAO et al., 2013; Specht et al., 2014; Trimmer et al., 2017). Efficient yet feasible TAN recovery is essential to supporting nutrient recovery efforts in many contexts (Harb & Hong, 2017).

2.5 Research Questions

In summary, the existing field of research surrounding zeolite and more specifically, clinoptilolite is extensive and highlights its successful use for facilitating TAN removal from even highly concentrated wastewaters. However, implementation, operation, and maintenance of clino-IX systems for TAN removal consist of highly active means in terms of energy and chemical requirements for regeneration and recovery of captured TAN, ultimately creating a barrier to widespread use in NSSS and LDC contexts. To address the limitations outlined in Table 2.2, the following research questions are asked, forming the basis for this research:

1. How is the nutrient recovery capacity of CZ affected by AnMBR permeate?
2. Can regeneration processes of ammonium-exhausted clinoptilolite be optimized to enable resource recovery for hydroponic fertigation?
3. How does the recovery of nitrogen from clinoptilolite regeneration for reuse as fertilizer impact sustainability?
CHAPTER 3: MATERIALS AND METHODS

3.1 Introduction

A variety of analytical methods were used to carry out the research experiments described in the following chapters. Water quality analyses relied heavily upon the use of colorimetric methods, probes, and ion chromatography. Additionally, methods for estimating the growth performance and quality of vegetable crops is described below. This chapter serves to provide in-depth descriptions of each analytical method used, including required equipment, materials, and calibration curves when applicable. The development of a synthetic anaerobic membrane bioreactor permeate solution (SynPerm) for test purposes is also described in this chapter.

3.2 Water Quality Analyses

3.2.1 Ammonia-Nitrogen, Salicylate Method

Ammonia-nitrogen was analyzed via three methods: the salicylate method, the phenate method, and with an ammonium ion selective electrode (ISE). The salicylate method, described here, was conducted with the Hach High Range Test’N’Tube™ Method 10031 (Hach, Loveland, CO, USA). Analysis vials were prefilled with 5 mL of deionized water and 1 mL of sample was then added to the vial. An analysis blank was prepared using deionized water in place of the sample. Two reagent packets, the Ammonia Salicylate Reagent Powder Pillow (sodium salicylate and sodium nitroferricyanide) and the Ammonia Cyanurate Reagent Powder Pillow (sodium dichloroisocyanurate, lithium hydroxide, sodium citrate and sodium tartrate) were then added to the sample vials in that order. Monochloramine was formed when the ammonia present in the samples reacted with the chlorine in the reagents. When the salicylate was added, 5-aminosalicylate was formed, which was then oxidized by the addition of a sodium nitroprusside catalyst. The resulting blue-colored compound mixed with excess reagent to yield a green-colored solution with intensity proportional to the amount of ammonia present in the sample. The
chemical reactions were given at least 20 minutes to react. At the end of the reaction period, the 
absorbance (as relative absorbance units, RAU) of each sample vial was measured in a spectrophotometer 
(Hach DR/4000, Loveland, CO, USA) with innate analysis calibration curve and internally compared the 
sample absorbance to that of the blank at 655 nm. The RAU was converted to mg NH$_3$-N/L by the 
internal calibration curve.

3.2.2 Ammonia-Nitrogen, Phenate Method

Total ammoniacal nitrogen (TAN) was also measured using the Phenate Method (4500-NH$_3$ F.) 
presented in “Standard Methods for the Examination of Water and Wastewater, 2018”, to preserve 
materials as reagents for this method can be made with chemicals found in the analytical laboratory’s 
chemical inventory. Ammonia-nitrogen is measured by spectrophotometric absorbance at 640 nm of an 
intensely blue compound, indophenol, that develops after the ammonia in solution reacts with 
hypochlorite and phenol catalyzed by sodium nitroprusside. Calcium and magnesium complexes are 
formed with citrate, eliminating potential interferences produced by these ions at high pH. Trivalent forms 
of nitrogen do not cause interferences either. Turbidity, if present in the sample to be analyzed, was 
removed by filtration with 0.45 μm glass fiber filter (Whatman GF 934-A). This method is applicable 
to measured samples with TAN ranging from 0.0 to 0.6 mg/L NH$_3$-N; deionized water was used 
for sample dilution when necessary.

Five reagents were required for the Phenate Method: Reagent A (phenol solution) was prepared in 
a fume hood and required the addition of 1.11 mL of phenol to a 10 mL volumetric flask brought to 
volume with ethyl alcohol; reagent A was prepared weekly. Reagent B (0.5% sodium nitroprusside) was 
prepared by dissolving 0.5 g of sodium nitroprusside in 100 mL of deionized water and transferring the 
solution to an amber bottle; reagent B was prepared monthly. Reagent C (alkaline citrate) was prepared 
by dissolving 200 g of trisodium citrate and 10 g of sodium hydroxide in deionized water which was 
brought to 1L volume with deionized water; reagent C was replaced when necessary. Reagent D (5% 
sodium hypochlorite) consisted of commercially available, off-the-shelf (COTS) concentrated bleach;
replaced every 2 months. Reagent E (oxidizing solution) consisted of combining Reagent C with Reagent D at a 4:1 (C:D), ratio. Ammonia-nitrogen standards of the following concentrations were made to develop the appropriate calibration curve: 0.0, 0.05, 0.1, 0.3, and 0.6 mg/L NH₃-N (Figure 3.1).

The procedure was used to measure a total sample volume of 5 mL (including dilution volume) in an appropriately sized spectrophotometric vessel (glass test-tube or cuvette with 1 cm path length) and required the addition of 0.2 mL reagent A, 0.2 mL of reagent B, and 0.5 mL of reagent E, in this order, with thorough mixing after each addition. The analytical blank was prepared with 5 mL of deionized water. After adding the reagents, the samples were tightly covered and stored in subdued light at room temperature for at least 1 hour to allow for color development. The absorbance of samples at 640 nm was taken within 24 hours to avoid any deterioration of color.

![Figure 3.1 Phenate method calibration curve for the analysis of NH₃-N in standard solutions. RAU = relative absorbance units.](image)

3.2.3 Probeware

3.2.3.1 pH

The pH of all samples was measured using a digital pH meter (Corning pH/ion analyzer 350) in combination with glass pH electrodes (Oakton Instruments, Vernon Hills, IL, USA). Prior to pH measurement of the samples, the probes’ calibrations were checked using pre-mixed calibration solutions
of pH 4.0, 7.0, and 10.0 (Fisher Scientific, Pittsburg, PA). The probes were recalibrated if they read above +/- 0.05 pH units from the calibration solution’s expected value. Probes were rinsed with deionized water and pat-dried with clean laboratory wipes after the measurement of each sample.

3.2.3.2 Conductivity

Electrical conductivity (EC) of liquid solutions was measured using an alternating current conductivity probe in conjunction with a LabQuest2 portable digital interface or LabView software that was installed on to a laboratory computer (Vernier Instruments, Beaverton, OR, USA). The EC probe was set to a range of 0 – 20,000 μS cm⁻¹. The calibration solution used for the conductivity probe was a 500 mg/L sodium chloride solution prepared in the laboratory; recalibration with this standard solution was performed as needed. The conductivity probe was rinsed with deionized water and dried with a clean laboratory tissue between sample measurements. Time was allotted for EC measurement stabilization for at least three minutes prior to recording.

3.2.3.3 Ion Selective Electrodes

Additional measurements for nitrate-nitrogen (NO₃⁻-N) and ammonium-nitrogen (NH₄⁺-N) were conducted using Neulog (NeuLog, Rochester, NY) NUL-241 nitrate and a NUL-240 ammonium ion selective electrodes (ISE) in combination with a USB-200 USB module NUL-240 connected to a laboratory workstation computer with an installation of the NeuLog™ Application Ver. 3.70 (Scientific Educational Systems, Rishon-Lezion, Israel). Use of the ammonium ISE and nitrate ISE required calibration with 10 mg/L NH₄⁺-N and 10 mg/L NO₃⁻-N standard solutions, respectively, and with each solution containing the respective ISE probe’s ionic strength adjustment (ISA) solution at a volume ratio of 1:50; ISA to sample volume.

3.2.4 Ion Chromatography

The concentrations of various ions within a relatively clean water sample i.e., a sample low in total solids (TS), can be measured simultaneously through ion chromatography (IC). The anions sulfate (SO₄²⁻), phosphate (PO₄³⁻), nitrite (NO₂⁻), nitrate (NO₃⁻) and chloride (Cl⁻) were measured using a Metrohm
881 Compact IC Pro (Herisau, Switzerland) equipped for anion analysis. Ammonium (NH$_4^+$), Calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), sodium (Na$^+$) and potassium (K$^+$) were measured using a Metrohm 881 Compact IC Pro (Herisau, Switzerland) equipped for cation analysis. All samples that were collected for analyses of total ammoniacal nitrogen (TAN) were kept at frozen at -20°C in climate-controlled storage for no longer than 33 days to avoid changes in concentration during storage. Sample preparation for IC analysis was executed by filtering samples with a 0.45 μm glass fiber filter (Whatman GF 934-A). Filtered samples were then transferred to a plastic IC analysis vial and diluted to a final volume of 10 mL with deionized water.

3.2.5 Atomic Absorption Spectroscopy

Atomic absorption spectrophotometry (AAS) was used to determine the concentration of cations in solution, specifically calcium (Ca$^{2+}$) and sodium (Na$^+$). AAS is spectro-analytical procedure for determining the quantity of chemical elements in a fluid using the absorption of optical radiation (light) by free metallic ions in a gaseous state. AAS was performed using a Perkin Elmer AAnalyst 100 Flame Atomic Absorption Spectrometer (Perkin Elmer, Inc., Shelton, CT) equipped with compressed air and acetylene gas for burner combustion. Prior to sample analysis, calibration solutions of pertinent ions were prepared using high quality deionized water and clean glassware. Standard dilutions were prepared as follows: 0.1, 0.2, 0.5, and 1 mg/l for low range linear correlation and 1, 2, 5, 10, 20, 30, 40, and 50 mg/L higher range linear correlation. The range of linear correlation is dependent on the ion being measured. After standard preparation, analysis of standard solutions was conducted to generate absorbance data for the generation of a calibration curve (Figure 3.2). The procedure for analyzing sample begins with first powering up the AAS instrument and running all system checks. Deionized water was used to thoroughly flush aspiration plumbing before and after each sample aspiration, this step helps to prolong the functionality of the AAS instrument as well as mitigate measurement error and interference. The AAS instrument was set to report the average of ten continuous readings (1 reading/second) and this absorbance value was the value recorded for the sample analyzed. Samples were analyzed in order from
lowest concentration to highest concentration to avoid any possible interference from highly concentrated solutions. The AAS instrument shutdown procedure was initiated after sample analysis was concluded. Shutdown procedure was performed by thorough aspiration of deionized water, then by shutting off the flame, closing gas cylinder valves, and then venting the gas lines to release pressure.

![Calibration curve](image)

**Figure 3.2 Calibration curve used for the determination of Ca\(^{2+}\) concentration via AAS**

3.3 Crop Quality Analyses

3.3.1 Fresh and Dry Weight

Crop mass accumulation was measured at the end of the experiments’ predetermined crop growth cycles. Crop were first harvested by cutting the cutting the base of the crop where the plant stem meets the grow media surface of which the crop was grown in. Sheets of aluminum foil were weighed on an analytical balance and the masses of each aluminum foil sheet were recorded. The harvested crop was then transferred to a sheet of aluminum foil and the fresh weight was measured by subtracting the weight of the aluminum foil from the combined weight of the aluminum foil and the harvested crop. The measurement of dry weight was measured after recording the fresh weight of the respective crop. The harvested crop and aluminum foil were placed in an oven and dried at 70 °C for at least 12 hours, and then brought to room temperature by placing inside of desiccator to cool. After cooling, the dried crop
samples were measured on an analytical balance and the dry weight was calculated by subtracting the weight of the aluminum foil from the total weight of the aluminum foil and dried crop sample.

### 3.3.2 Macrophyte Pigment Development

Pigment development in phototrophic organisms can indicate photosynthetic performance and health of the organism [Wintermans, 1965]. Chlorophyll-a and chlorophyll-b, the pigments responsible for photosynthesis in algal cells and the green leaf cells of larger order plants (macrophytes), as well as their decomposition products (phaeopigments) were measured according to the method developed by Wintermans and De Mots (1965) [Wintermans & De Motts, 1965].

Sample collection and the procedure for chlorophyll analysis were all performed under dim-light conditions to prevent the decomposition of the samples’ chlorophyll content by light. Five mL of 96% ethanol in a capped measuring cylinder was set aside for each sample. Approximately 100 to 300 mg fresh weight of plant material per sample was ground using a mortar and 2 mL of the allocated 5 mL of ethanol. Grinding of plant material was carried out until all visible solids disappeared, yielding a green suspension. The suspension was then quantitatively transferred to a screw-capped centrifuge tube. The remaining 3 mL of ethanol was used to rinse off the pestle and mortar and convey the rinsed residues to the same centrifuge tube. Ethanol was added to bring the centrifuge tube to a final volume of 5 mL and then tightly capped to avoid further evaporation of ethanol. Suspension samples were then stabilized for at least 12 hours in dark storage at room temperature to promote maximum extraction. After the 12-hour extraction period elapsed, the samples were centrifuged for at least 10 minutes at 3000 rpm yielding a clear supernatant. Samples were stored in the darkest environments possible while awaiting spectrophotometric measurement.

#### 3.3.2.1 Chlorophyll

Prepared samples were first analyzed for chlorophyll content. The spectrophotometer was zeroed with ethanol at all wavelengths. Three mL of the prepared supernatant was carefully transferred into a cuvette and absorbance was measured at 750, 666, and 655 nm. Next, 0.5 mL of 0.06 M HCl was added
to the cuvette and absorbance was measured again at 750, 666, and 655 nm. The following calculations were used to derive the pigment content of the samples:

Chlorophyll-a \[= 13.70 \times (A_{665} - A_{750}) - 5.76 \times (A_{649} - A_{750}) \]

Chlorophyll-b \[= 25.80 \times (A_{649} - A_{750}) - 7.60 \times (A_{665} - A_{750}) \]

Total phaeopigments-a \[= 24.50 \times (A_{666} - A_{750a}) - 9.32 \times (A_{665} - A_{750a}) \]

Total phaeopigments-b \[= 36.97 \times (A_{665} - A_{750a}) - 18.48 \times (A_{666} - A_{750a}) \]

where $A_{750a}$ = absorbance at 750 nm after acidification with HCl. Chlorophyll-a is calculated and expressed as mg/g of leaf by the following equation:

\[
\text{Chl-a} = \frac{13.70 \times (A_{665} - A_{750}) - 5.76 \times (A_{649} - A_{750}) \times V_e \times D \times C}{(AFDW \text{ of Sample}) \times 1000}
\]

where,

- $V_e$ = extraction volume
- $D$ = sample dilution
- $C$ = extra dilution factor (after acidification, adding 0.5 mL to 3 mL sample in cuvette = 3.5/3; before acidification: $C = 1$

AFDW = ash-free dry weight converted from the fresh weight of the sample (FWs): AFDWs = FWs*(AFDW/FW)

### 3.3.2.2 Phaeopigments

Equation (X) was used to determine chlorophyll-a and b content as well as total phaeopigments-a and b. Original sample phaeopigments are determined by subtracting the measured chlorophyll-a content from the total phaeopigment-a content (Wintermans & De Motts, 1965).

\[
\text{Phaeopigments-a in sample} = (\text{total phaeopigments-a}) - (\text{chlorophyll-a})
\]

### 3.4 Synthetic AnMBR Permeate Solution

A synthetic anaerobic membrane bioreactor solution was formulated to mimic the ionic conditions typically found in AnMBR permeates reported in literature. The synthetic AnMBR permeate solution (SynPerm) was produced by adding 0.445 g NH$_4$Cl/L, 0.092 g K$_2$HPO$_4$/L, 0.074 g Na$_2$SO$_4$/L,
and 0.254 g NaCl/L were added to a reservoir containing the desired solution volume of tap water and a magnetic stir bar. The solution was mixed with a magnetic stir plate until all chemical salts were dissolved and electrical conductivity measurements had stabilized for three minutes indicating that no more salts have dissolved. All chemicals were reagent grade quality and suitable for laboratory analytical purposes. The SynPerm formulation was designed to yield a solution with the approximate ion concentrations depicted below (Table 3.1).

Table 3.1 Ionic species and concentrations in the synthetic AnMBR permeate (SynPerm) solution

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>150</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>50</td>
</tr>
<tr>
<td>K⁺</td>
<td>40</td>
</tr>
<tr>
<td>Na⁺</td>
<td>100</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>50</td>
</tr>
</tbody>
</table>
4.1 Introduction

This research strives to design, develop, and investigate the performance of a new solution for an old problem in challenging contexts. A methodical approach to design is essential to properly define the problem of which the design is to address, and to anticipate and understand all applicable contextual constraints, ensuring an appropriate and sustainable design. This chapter describes the approaches taken to define the problem, design a system concept, evaluate applicable pathways, and finally the development of a working prototype.

In the previous chapter, a general background of the problem to be addressed by this research was presented as well as potential solutions that embody the current “state of the art”. The challenges and limitations surrounding current systems using clinoptilolite zeolite (CZ) for total ammonia nitrogen (TAN) recovery via ion exchange (IX) were associated with the regeneration of spent CZ. Regeneration processes become necessary in resource-limited contexts, but more sustainable CZ-IX processes are required to support the operation of non-sewered sanitation systems (NSSS) in challenging contexts (Trotochaud et al., 2019). Minimizing costs and required inputs of chemicals and energy are intrinsic to the success and sustainability of any technology but become even more imperative when considering operation in resource-limited locales.

The objective of this chapter is to develop a reusable nutrient recovery system (RNRS) concept that addresses the sustainability challenges that arise from consideration of application in NSSS contexts. The design process used to develop a solution to the challenges defined adheres to the methods described in “Design approach, philosophy, and normal approach design model” by Johnson and Gibson (2014), in their book, *Sustainability in Engineering Design*. The sustainable engineering design process resulted in
the development of an integrated, low-cost TAN recovery and reuse concept: the reusable nutrient recovery system (RNRS). The RNRS represents a potential solution to the challenges of regenerating clinoptilolite by coupling regeneration with a nutrient utilization process, i.e., fertigation in hydroponic systems. Benchmarks and standards for NSSS performance established in ISO 30500 were used to inform the design and development of the RNRS concept and prototype (ISO, 2018). The system description of the RNRS prototype investigated in subsequent chapters are also described herein.

4.2 Concept Design Development Methods

The methods used for concept development and design of an appropriate technology adhere to the principles of the “product realization process” and approaches to the design of appropriate technology presented in relevant texts like Field Guide to Appropriate Technology by Hazeltine and Bull (2003) (Hazeltine & Bull, 2003). The overarching methodology is conveyed in Figure 4.1 which graphically depicts the stages of the design process. The first stage in the engineering design process is defining the problem followed by a survey process to identify limitations or constraints presented by the context of the application (Hazeltine & Bull, 2003). Background information was synthesized in the previous and the challenges concerning CZ-TAN recovery in NSSS contexts were highlighted. These challenges form the bases for the problem definition and the ensuing concept design.

The International Standardization Organization (ISO) developed the ISO 30500 standard establishing design and performance benchmarks for NSSS. Thus ISO 30500, along with conditions encountered in relevant field contexts were used to establish constraints and limitations for the concept design process. Ideation was used to explore possible designs, methodologies, and materials applicable to addressing the defined problem. Design approaches generated during ideation were then evaluated based on their appropriateness for NSSS contexts and sustainability criteria. After the design approach and form factor were selected, a prototype was developed for testing under relevant operational conditions to generate initial performance data for further refinement of the RNRS prototype.
4.2.1 Problem Definition

The problem definition was developed by identifying key functions of the TAN recovery system and the challenges associated with performing those functions in NSSS contexts. AnMBR permeate is considered the TAN source and the intended destination (i.e., atmosphere, biomass, recovered solid or liquid concentrate) of recovered TAN is referred to as the TAN sink for the purposes of concept development. Ideal sinks are edible food crops that can be grown in hydroponic systems. The primary function (F1) of the TAN recovery system is to recover TAN from the TAN source. The secondary function (F2) of RNRS to facilitate the transfer of TAN to the TAN sink via regeneration. The third function (F3) is to facilitate the reuse of the TAN recovery system materials. These functions are necessary for addressing the challenges associated with regeneration and reuse of spent CZ that were highlighted in Chapter 2. Figure 4.2 depicts F1, F2, and F3 in a functional flow diagram. The different pathways available to perform F3 harbor challenges for integration into NSSS due to chemical, energy, and reactor infrastructure requirements. A material and energy conservative method for performing F2 without compromising F1 is required. The three functions that are crucial to addressing the problem definition are defined in Table 4.2
Table 4.1 Function identification of clinoptilolite-IX process for use in NSSS

<table>
<thead>
<tr>
<th>Process Function</th>
<th>Function ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recover TAN from TAN source (AnMBR permeate)</td>
<td>F1</td>
</tr>
<tr>
<td>Facilitate transfer of TAN to TAN sink(s) (plants)</td>
<td>F2</td>
</tr>
<tr>
<td>Minimize material and energy inputs for F1 and F2</td>
<td>F3</td>
</tr>
</tbody>
</table>

4.2.2 Identification of Contexts and Criteria

The International Organization for Standardization (ISO) recently developed a regulatory standard: ISO 30500:2018(E) (referred to as ISO 30500) to support the development of stand-alone sanitation systems designed to address the United Nation’s (UN) Sustainable Development Goals (SDGs) of ensuring access to water and sanitation where conventional sewered sanitation infrastructure is nonexistent nor feasible. ISO 30500 establishes design standards and performance thresholds for non-sewered sanitation systems (NSSS) to provide safe sanitation while minimizing resource consumption (e.g., energy, water) and converting human excreta to safe outputs (ISO, 2018). Additionally, ISO 30500 serves to promote the design and operation of sustainable sanitation systems. Therefore, the performance specifications established by ISO 30500 were used to identify constraints for this concept development process. The specific NSSS platform considered for this design process is the AnMBR platform which has demonstrated treatment capacity in this application (Bair et al., 2015; Batstone et al., 2015; Pretel et al., 2016; Rashidi et al., 2015; Sharma & Kazmi, 2016; Xie et al., 2016).
4.2.2.1 Sustainability Considerations

Additional consideration is given to sustainable design criterion that lessen environmental impacts of the design by minimizing material and energy consumption as well as waste generation resulting from the production and operation of the design. Facilitating recovery and reuse of TAN materials is also considered an important sustainability criterion and a main objective of this overall research. TAN recovery from wastewater will reduce social and environmental impacts associated with fertilizer access and production, respectively, and enhances socio-economic opportunities by generating valuable nutrient resources that can support local enterprise (Gallego-Schmid & Tarpani, 2019; Molinos-Senante et al., 2014; Rahman et al., 2016). Relevant design criteria considered for guidance in the engineering design process are discussed below.

4.2.3 Ideation

Ideation was performed by surveying the academic literature surrounding the use of clinoptilolite and other natural IX materials for nutrient recovery to identify capacities and behaviors under different environmental conditions (i.e., temperature, TAN concentration, contact time, wastewater composition, and regeneration pathways). Findings from the survey of the existing literature were discussed in the previous chapter. Observations and applications demonstrated in literature informed development of a concept-map that explored plausible pathways for performing the necessary functions established by the problem definition. Relationships between system functions and potential system embodiments are represented in the concept map. Effort was made to avoid developing “incremental improvement-solutions that yield limited degrees of freedom in terms of addressing the conditions that perpetuate the problems defined in the problem statement (Figure 4.3). For example, developing zeolite pretreatment methods to enhance nitrogen and phosphorus removal capacities is an example of an incremental improvement. Maximizing nutrient removal is worthwhile, but only incrementally improves of a previously existing function, i.e., cation exchange capacity (CEC). Increased nutrient uptake would result in increased nutrient release during regeneration, affecting the embodied energy of processes downstream. A more holistic approach to address the problem statement aims to synthesize key functions of waste
treatment and agricultural production practices by leveraging existing synergies, e.g., nutrient removal from wastewater and nutrient uptake into plant biomass via hydroponic fertigation (Calabria, 2014; Calabria et al., 2019).

Figure 4.3 Examples of creative approaches to designing solutions. Approaches generated during ideation are evaluated with potential benefits associated with their resulting designs. Adapted from Graedel, T.E., & Allenby, B.R. (2010). *Industrial Ecology and Sustainable Engineering*: Prentice Hall.

### 4.2.4 Evaluation of Alternatives

Evaluation of the idealized system concepts was performed by using an evaluation matrix that is comprised of pertinent system design criteria assigned an importance factor. Examples of design criteria commonly applied to product systems (Table 4.1) guided the development of design criteria for the evaluation matrix. The sum of the importance factor across all criteria was equal to one, with levels of significance assigned to criteria coinciding with the levels of importance conveyed in ISO 30500 for NSSS. Criteria of utmost importance (e.g., safety, contaminant removal performance, durability) were assigned a higher level of importance than other desired criteria not considered to be as crucial for
adequate function of the system (i.e., use of local materials, and ease of operation). Systems assumed to achieve the best performance for a respective criterion received the highest score for that criterion, the next best performing technology received the next best ranking and so on. The summation of the criterion ranking multiplied by the associated importance factor resulted in an evaluation score which was interpreted as the best plausible system concept for further exploration.

Table 4.2 Common design attributes for comparing various design options during evaluation.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assembly (A)</td>
<td>Design consideration for assembleability, including the ease of assembly, chance of faulty assembly, use of common parts, etc.</td>
</tr>
<tr>
<td>Compliance (C)</td>
<td>Design consideration for meeting pertinent regulatory compliance in manufacturing, operation, maintenance, performance, etc.</td>
</tr>
<tr>
<td>Disassembly (D)</td>
<td>Design consideration of end-of-life processes for decommissioning, disassembly, refurbishment, recycling or disposal</td>
</tr>
<tr>
<td>Environmental Impact (EI)</td>
<td>Design consideration for minimizing ecological footprints associated with assembly, use, and end-of-life processes</td>
</tr>
<tr>
<td>Material Logistics and Component Applicability (MC)</td>
<td>Design consideration for supply chain feasibility and efficiency</td>
</tr>
<tr>
<td>Reliability (R)</td>
<td>Design consideration for maintaining functionality under variable operation conditions</td>
</tr>
<tr>
<td>Serviceability (S):</td>
<td>Designed consideration for facilitation of installation, maintenance, repair and in-field modification</td>
</tr>
<tr>
<td>Safety and Liability Prevention (SL)</td>
<td>Design consideration to facilitate adherence to safety standards and avoid misuse</td>
</tr>
</tbody>
</table>

4.2.5 Prototype Development

An initial prototype of the RNRS was developed to identify morphological and operational limitations associated with the form factor. Prototype testing used to assess the performance of the prototype resembled bench scale, IX batch and column studies, and are described in greater detail in the next chapter. The RNRS prototype design and operation was investigated until an adequate form factor was established and mode of operation was identified. Commercially-available, off-the-shelf (COTS) items were surveyed to yield a RNRS prototype that could readily interface with common plumbing hardware. Household water filters consisting of a plastic housing and a refillable canister insert were selected.
4.2.5.1 Nitrogen Mass Balance Estimation

Nitrogen loading rates were calculated using an average total per capita nitrogen excretion rate (urine and feces) of 4.46 kg per capita per year (4.37-4.55 kg N p⁻¹ y⁻¹) (Anand & Apul, 2014). A moderate cation exchange capacity (CEC) for RNRS-CZ of 10 mg NH₄⁺-N g⁻¹ CZ was assumed; reported CEC of CZ range from 3.3 to 25.9 mg NH₄⁺-N g⁻¹ CZ (Boyer, 2014). A conservative nitrification rate of 0.1 g N m⁻² d⁻¹ was chosen to predict nitrification in the ZGT system based on reported nitrification rates for aquaculture trickling filters (0.1 to 0.9 g N m⁻² d⁻¹) (Ebeling et al., 2006).

4.3 Reusable Nutrient Recovery System Concept

4.3.1 Problem Definition

The following problem statement was defined based on the observations made during review of pertinent literature: “The feasibility of TAN recovery from AnMBR-NSSS permeate via CZ-IX is reduced by the energy and material inputs required to facilitate regeneration or replacement of exhausted CZ.” Access to nutrients recovered from wastewater via CZ-IX is hindered by input requirements for chemicals and energy to facilitate the availability of TAN for use as fertilizer. Furthermore, current CZ regeneration process involve the use of materials (i.e., concentrated brines) that can negatively affect crop yields. Clinoptilolite presents an affordable pathway to removing TAN from AnMBR wastewater but conventional regeneration hinders sustainability for use in NSSS. Efficient TAN removal via CZ-IX requires low-input method for regeneration that enables safe and easy access to recovered TAN for fertilizer reuse. To put it simply, passive, low-cost processes to facilitate TAN transport from source to sink are needed.

4.3.2 TAN Recovery System Design Criteria and Constraints

Decentralized, AnMBR-NSSS platforms treating wastewater generated by a small community (approx. 100 people) must be able to remove 70% of incoming nitrogen and 80% of incoming phosphorus. The AnMBR platform considered for this RNRS concept resembles the off-grid AnMBR system proposed by Bair et al. (2015) (Bair et al., 2015). TAN recovery performed by the RNRS should resemble operation of the AnMBR: low maintenance, low energy, low footprint, and low chemical use.
Material and energy requirements to facilitate TAN recovery should resemble the inputs required for AnMBR operation. Per ISO 30500m, system maintenance should be minimal or should be able to be performed by someone who has received 1 hour of training to ensure adequate operation of the RNRS. ISO 30500 outlines more system design and performance specifications for non-sewered sanitation systems (NSSS). An extensive list of relevant ISO 30500 design criteria and constraints used to inform the design process of the RNRS are listed in the Table B1 of appendix.

4.3.2.1 Safety Constraints

The World Health Organization’s guidelines for the reuse of wastewater in agriculture establishes log removal values (LRV) required to mitigate the spread of infectious disease caused by the consumption of crops irrigated with wastewater (WHO, 2006). Irrigation techniques and the type of crops grown determines the required level of treatment. The RNRS is designed for localized irrigation delivered directly to the root zone of crops with edible portions grown above-ground, for example: a bacterial pathogen LRV of 4 and 6 is required for low- and high-growing crops, respectively. Additionally, ISO 30500 establishes pathogen removal requirements for NSSS liquid effluents. Pertinent treatment requirements for wastewater-derived fertigation solutions are listed in Table 4.3.

Table 4.3 Pertinent safety targets for the use of treated wastewater in appropriate, low-footprint horticultural systems. Localized drip irrigation and hydroponic techniques were considered

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Log-reduction values (LRVs) and maximum allowable concentrations required for human health protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pathogen class)</td>
<td>WHO (2006)</td>
</tr>
<tr>
<td></td>
<td>ISO 30500 (2018)</td>
</tr>
<tr>
<td>Bacterial pathogens</td>
<td>LRV: 4 (low growing crops)</td>
</tr>
<tr>
<td></td>
<td>LRV: 2 (high growing crops)</td>
</tr>
<tr>
<td>Human enteric viruses</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>LRV ≥ 6</td>
</tr>
<tr>
<td>Human enteric helminths</td>
<td>≤1 helminth egg per liter (low growing crops)</td>
</tr>
<tr>
<td></td>
<td>LRV ≥ 4</td>
</tr>
<tr>
<td>Human enteric protozoa</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>LRV ≥ 6</td>
</tr>
</tbody>
</table>

4.3.2.2 Sustainability Considerations

4.3.2.2.1 User Considerations

The primary objective of this research is to enable nutrient recovery to support local horticulture practices in adaptive low-footprint systems, e.g., simplified hydroponics. Safety and performance are of utmost priority. The operation of the RNRS can be performed by various users, mandating resilient yet
simple designs to prevent misuse. In addition to the regulatory constraints set forth by ISO 30500, cultural constraints are also considered a potential limitation, especially in least developed countries (LDCs) where local culture and customs can vary significantly from developed areas. Orsini et al. (2013) observed that women comprise most small-scale urban gardeners, thus an appropriate design for agricultural use should also facilitate interaction and handling by women workers as they account for more than 60% of farm workers and gardeners across the world (Orsini et al., 2013).

4.3.2.2 Material Flow Systems: Open and Closed Loop

Closed-loop cycles imply reuse or recycling of a portion of the materials in a product for complete or partial use as raw material for the next generation of products (Johnson & Gibson, 2014). Closed loop cycles reduce overall use of materials, extending the life of finite material reserves (e.g., zeolites, mineral fertilizers), reduce waste materials sent to landfills, reduce embedded energy as less energy is needed to refurbish or refabricate products, and less energy is needed for the transport of new and raw materials (Johnson & Gibson, 2014). Reuse of exhausted clinoptilolite via low-cost regeneration (F3) exemplifies closed-loop material flow, as does the recovery and reuse of TAN for fertilizers (F1+F2). While clinoptilolite and ammonia-nitrogen fertilizers have relatively low economic cost, their continuous consumption increases extraction of raw materials and energy use, implying increased environmental impacts (Guest et al., 2009; Trimmer et al., 2017).

4.3.2.3 End of Life Considerations

Sustainable engineering design includes consideration and planning for the fate of materials used. An “End-of-life decision chart” (Figure B1 in Appendix) is a tool used to ensure proper action is taken when a system component has reached a point of significant wear (Johnson & Gibson, 2014). When a system component reaches concerning state of wear (i.e., 25%, 50%, 75%, 100%) the end-of-life decision chart instructs the proper course of action (i.e., disposal, repair, observe, clean) for a component of concern and when a replacement component is required. The RNRS components shall adhere to the design life requirements established by ISO 30500: 10 years. CZ materials may require replacement if
structural damage of CZ granules due to hydraulic conditions occurs. Land application of replaced CZ is preferred and can be marketed as slow-release fertilizer and soil amendment (Hermassi et al., 2019).

4.3.3 Concept Development

4.3.3.1 Evaluation of Alternative Approaches

A conceptual, mind-map was developed to visualize potentially low-cost TAN recovery pathways that could feasibly integrate with an AnMBR-NSSS (Figure 4.4). The capacity to regenerate spent CZ and the respective input requirements for the most plausible pathways were indicated where applicable; these attributes are the main drivers for development of the RNRS. Biological pathways for CZ regeneration were favored, minimizing chemical regeneration requirements. Technological alternatives considered for low-cost, CZ regeneration are described in Table 4.4.

Minimizing chemical use and facilitating simple operation resulted in more favorable evaluation. Chemical process, i.e., precipitation and air stripping, rely on operation by skilled personnel, decreasing their applicability to some contexts where NSSSSs could be deployed, i.e., remote, rural areas in least developed countries (Trotochaud et al., 2019). A3, consisting of a portable cartridge that recovers TAN
via CZ-IX and facilitates safe transport of exhausted CZ, within a reasonable distance, to an appropriate horticultural system (TAN sink) for simultaneous TAN release (regeneration) and fertigation, yielding the most favorable evaluation (Table 4.5). A fourth alternative (A4) considered a vertical hydroponic wetland system containing CZ for TAN recovery and release to crops grown directly in the CZ, resembling a zeoponic system (Guaya et al., 2018). In A4, the TAN sink is co-located with the TAN source, which could limit application of this approach in locations where conditions at the TAN source are not conducive to plant growth.

Table 4.4 Pros and cons of alternative pathways for facilitating low-cost regeneration.

<table>
<thead>
<tr>
<th>Alternatives</th>
<th>Description</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1: Chem. Regen. + Air Stripping</td>
<td>Exhausted CZ is regenerated with NaCl + NaOH. TAN is recovered from regenerant via air stripping (AS) + sulfuric acid scrubbing yielding concentrated (NH₄)₂SO₄</td>
<td>Continuous CZ-regeneration; High quality fertilizer recovery</td>
<td>NaCl, NaOH and energy inputs; air stripping infrastructure + process control</td>
</tr>
<tr>
<td>A2: Fluidized CZ + struvite</td>
<td>Simultaneous CZ-IX and regeneration in same vessel. TAN removal coupled with struvite precipitation (P-recovery) through addition of MgO. Mg²⁺ IX with CZ-NH₄⁺</td>
<td>Enhanced nutrient recovery in a solid form (N and P)</td>
<td>High chemical and energy inputs and process control required, process</td>
</tr>
<tr>
<td>A3: Portable CZ-IX cartridge + hydroponics</td>
<td>Portable CZ-IX cartridge is regenerated by discharge into a hydroponics system</td>
<td>Efficient TAN removal + regeneration coupled with reuse</td>
<td>Special housing and hydroponic system required, energy and alkalinity inputs</td>
</tr>
<tr>
<td>A4: Horizontal flow in CZ+GAC beds + Hydroponics</td>
<td>AnMBR permeate flows through hydroponic troughs filled with CZ and GAC. Nitrification of TAN regenerates CZ, nitrates removed by plants or denitrification</td>
<td>Low energy input, low chemical input, low cost</td>
<td>Maintenance to reduce clogging, increased exposure to NSSS effluent, unknown TAN removal performance</td>
</tr>
</tbody>
</table>

Table 4.5 Evaluation matrix for the evaluation of TAN removal system alternatives

<table>
<thead>
<tr>
<th>Alternatives</th>
<th>Low Cost</th>
<th>RR</th>
<th>Ease of Operation / Process Control</th>
<th>Size</th>
<th>Low input use</th>
<th>Use of local materials</th>
<th>TAN Removal Capacity</th>
<th>Safety</th>
<th>Durable</th>
<th>Low env. impact</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1: Chem. Regen + Air Stripping</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3.19</td>
</tr>
<tr>
<td>A2: Fluidized CZ + struvite</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>5</td>
<td>3.81</td>
</tr>
<tr>
<td>A3: Portable CZ-IX cartridge + hydroponics</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>4.16</td>
</tr>
<tr>
<td>A4: Horizontal flow in CZ+GAC beds + Hydroponics</td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>3.86</td>
</tr>
</tbody>
</table>

4.3.3.2 RNRS Concept: General Process

Integration with a decentralized, AnMBR system operating off-grid with power generated on-site via solar photovoltaic (PV) panels favors the use of as many passive treatment processes as possible to
preserve overall system energy demand. Passive TAN removal can be achieved through simplified, flow-through adsorption and/or ion-exchange processes using low-cost clinoptilolite materials. Furthermore, regeneration procedures can be simplified through integration with TAN reuse processes, i.e., plant cultivation, accomplishing CZ regeneration and TAN reuse simultaneously.

A3 conveys the greatest potential for facilitating F2 and F3, while preserving F1 performance and allows decoupling of TAN recovery and reuse locations. An expanded system boundary is considered to include extraction and reuse of recovered TAN, recognizing that the TAN source (i.e., wastewater) is not always co-located with the TAN sinks, i.e., horticultural application (Trimmer et al., 2017; Trimmer & Guest, 2018). A process flow diagram for the RNRS (Figure 4.5) depicts the operation of the proposed RNRS based on the design concept “A3”. CZ regeneration (F2), supports sustainable TAN recovery by minimizing regeneration costs and waste material, while generating value from recovered nutrient material. TAN recovery (F1) represents the “charge”, or “loading” phase; TAN is recovered by the RNRS until exhaustion. The regeneration of the exhausted CZ is represented as the “discharge” or “release” phase, where recovered TAN is discharged at the TAN sink (F2).

![Figure 4.5 Process flow diagram of post-membrane TAN removal via the RNRS platform](image-url)
The RNRS operation concept facilitates delivery of TAN recovered from the AnMBR permeate source, to the desired sink: plants. The design of the RNRS overcomes the dependency on-location of the TAN sink and source (Figure 4.6), through the ability to transfer CZ-bound TAN in solid form to TAN sink location, regardless of its proximity (Figure 4.7). Co-location dependence was a drawback of on-site hydroponic cultivation, limiting applicability, especially in densely populated urban contexts (Orsini et al., 2013; Qadir et al., 2010; Trimmer et al., 2017). Figure 4.7 depicts decoupling of the charging location made possible using a portable form factor facilitates transport from the TAN source site to the TAN sink site. Portability of recovered nutrients in a safe, accessible form factor foster implications for enabling local reuse of recovered nutrient materials. Figure 4.8 depicts what a potential reuse scenario at the single residential building scale could look like if local reuse of recovered resources (i.e., nutrients and water) were implemented.

Figure 4.6 RNRS process flow diagram for adjacently-located nutrient source and sink.

Figure 4.7 RNRS process flow diagram where nutrient sink location is agnostic to location of nutrient source.
Figure 4.8 suggests a decentralized WWT technology, like an AnMBR-NSSS, treating wastewater generated by the inhabitants of a multi-family residential building and demonstrating reuse of nutrients recovered from the AnMBR-NSSS via onsite, low-footprint horticultural systems. An AnMBR-NSSS can generate permeate for direct fertigation reuse if local conditions deem it feasible (Figure 4.8, left). Although, some urban contexts may require for onsite sanitation infrastructure to be consolidated into the building’s footprint (Figure 4.8, right). The proposed RNRS allows recovery of TAN from wastewater generated by the building’s inhabitants, storing it use in fertigation applications. The stored potential to release nutrients for fertigation resembles the stored potential of conventional batteries that release electrons.

![Figure 4.8 Examples of building-level sanitation via a NSSS. Onsite fertigation practices at various locations are supported by the RNRS integrated with a NSSS providing on-site sanitation and resource recovery. Recovered nutrients can be reused directly in horticultural systems within proximity (left) to the NSSS or RNRSs can be used to overcome spatial challenges that discourage direct connection (right).](image-url)
4.3.3.3 RNRS Concept: Discharge Phase

Removing the dependency of co-location to facilitate both access and use of recovered nutrients fosters implications for expanding potential socioeconomic impacts in developing areas (Trimmer et al., 2017). The RNRS enables access to recovered nutrients by its ease of operation and design that readily interfaces with a variety of nutrient sink applications including small scale, soil-based farming, urban agriculture, organoponics, landscape irrigation, simplified hydroponics and low-footprint horticultural methods like green walls or vertical farms for application in densely populated urban areas. Figure 4.10 depicts the release of captured TAN from the RNRS into TAN sinks of varying scale and purpose. TAN release via fertigation should theoretically perform regeneration of TAN-exhausted clinoptilolite via desorption and IX; the extent of regeneration is dependent on desorption solution (i.e. irrigation water) composition (Guo et al., 2013). Saline water sources enhance regeneration rates but may negatively impact fertigation. Background Ca$^{2+}$, Mg$^{2+}$, and K$^+$ ions could enhance CZ regeneration and support fertigation as these ions are considered important plant macronutrients (Resh, 2013). Figure 4.9 depicts idealized elution curves for exhausted IX materials used in water treatment practices compared to the idealized elution curve for RNRS regeneration via fertigation.

![Figure 4.9 Ideal exhaustion cycle and elution curve profiles of RNRS during sorption and desorption phases. Water treatment (WT) applications favor rapid release of sorbate at high concentrations; redirecting eluent use for fertigation takes advantage of less ideal elution curves for supporting long plant growth cycles.](image-url)

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RNRS discharge is performed by connecting the charged RNRS to the irrigation line of an appropriate horticultural system, (TAN sink) (Figure 4.10). Hydroponic systems are an ideal sink for RNRS discharge as they are designed to achieved optimal plant growth and minimal water loss by facilitating the recirculation of liquid nutrient solutions (Resh, 2013). Additionally, inherent requirements for aeration of plant roots and fertigation solution drives in-situ nitrification, converting TAN to nitrate, resulting in a deficit of bulk solution TAN, further driving the release of TAN from CZ (Gupta et al., 2015; McGilloway et al., 2003; Smith & Smith, 2016). The combination of biological regeneration (i.e., nitrification) of CZ with a nitrogen sink (i.e., plants) that spontaneously removes nitrified TAN, can facilitate sustainable CZ regeneration and access to nitrogen fertilizer, effectively minimizing chemical and energy inputs to support local sanitation and farming practices (Eugene et al., 2017; Hedstrom, 2001). When the RNRS is no longer discharging, it can be exchanged with another exhausted RNRS cartridge to maintain continuous nutrient discharge. Complete regeneration and optimum TAN recovery can be ensured by treating the RNRS-CZ material with concentrated Na\(^+\)-brine prior to charge phase operation.

Figure 4.10 Examples of RNRS release into nutrient sinks. Potential RNRS fertigation applications include in-line fertigation of local landscaping (a), recirculating fertigation solution in a soil-less (i.e., hydroponics) plant cultivation system (b), or nutrient amendment to a larger scale, micro-irrigation system for in-soil cultivation (c).
### 4.3.3.3.1 Hydroponic System Configuration

Ideal hydroponic configurations that facilitate simultaneous regeneration and fertigation of the RNRS-CZ must conserve space, materials and energy while providing enough aeration and surface area for attached growth microorganisms to promote nitrification activity. Vertical hydroponic systems are capable of 4 to 5 times higher crop densities per farm footprint than traditional land-based agriculture (Hochmuth & Toro, 2014). Vertical hydroponic configurations involve conveying fertigation solution to a set high elevation point, fertigation solution then flows by gravity past plant roots supported by a vertical growth structure. The ZipGrow™ tower product (ZipGrow Inc., Cornwall, Ontario) was chosen as an ideal hydroponic configuration for its ability to facilitate nitrification via passive aeration within the root zone. The ZipGrow™ tower (ZGT) uses fibrous, non-woven polyethylene to support plant roots (Figure 4.11) and provide biological surface area (BSA) for nitrifying bacteria. The plant support media of the ZGT achieves a high void ratio (91%), maximizing hydraulic conductivity and has a specific surface area of 960 m²/m³ (Storey, 2013). Recirculation of RNRS desorption solution through a ZGT should be able to support crop growth and RNRS regeneration with relatively small space, energy and material footprints.

![Figure 4.11 Diagram of the ZipGrow™ tower system.](image-url)
4.3.3.4 RNRS Service Distribution Concept

Another advantage of the portable and reusable form factor of the RNRS concept is the possibility for overcoming geospatial transport challenges using unmanned aerial vehicles (UAVs), a.k.a. drones, for delivery of RNRS payloads across challenging terrain (Figure 4.12). UAVs have proven effective for supporting humanitarian efforts to deliver aid by overcoming last-mile distribution problems that arise from infrastructure collapse after natural disasters (Rabta et al., 2018). Combining UAV delivery with a hub and spoke model for RNRS charging and discharging supports realization of the proposed RNRS concept. Scheduled delivery of charged RNRS components can create a constant supply of fertilizer nutrients at designated sink locations. Furthermore, the wastewater treatment facility avoids the burden of nutrient removal treatment costs by out-sourcing the nutrient removal process to users.

Figure 4.12 Transport of captured nutrient to sinks in challenging locations can be supported by unmanned aerial vehicles (UAVs). RNRS delivery and pickup can be automated and controlled at the location of the nutrient source.

UAVs have proven effective for supporting humanitarian efforts to deliver aid by overcoming last-mile distribution problems that arise from infrastructure collapse after natural disasters (Rabta et al., 2018). Combining UAV delivery with a hub and spoke model for RNRS charging and discharging further facilitates realization of the proposed RNRS concept. Scheduled delivery of charged RNRS components
can create a constant supply of fertilizer nutrients at a designated sink location. The wastewater treatment facility avoids the burden of nutrient removal treatment costs by crowd sourcing the nutrient removal process.

4.3.4 RNRS Prototype Development

This section describes the development of the RNRS morphology. The following chapter investigates the technical capacity and performance of the proposed RNRS under simulated field conditions. The development of the RNRS prototype was guided by the contextual constraints and limitations identified in the second phase of the design process. The specifications for the design of NSSS established in ISO 30500 regarding water tightness, accessibility, cleanability, durability of materials, operating conditions, and aesthetics were given close attention. Prototype development was expedited by the reapplication of existing products for the purposes of the RNRS concept.

4.3.4.1 Prototype Refinement

Preliminary prototypes resembled a common IX column system, consisting of a cylindrical structure equipped with a fine mesh barrier to contain CZ within the column. Improvements to the initial RNRS prototype were made to expedite the processes of connecting and disconnecting the RNRS column from service, enhance water tightness and overall component integrity, and to minimize the loss of IX and adsorbent media during maintenance procedures. The preliminary RNRS column contained plumbing connections on the top and bottom surface of the column that eventually led to leaks when disconnecting from service; ISO 30500 specifically mandates designs that avoids spills. Additionally, this first prototype (Figure 4.13, left image) did not facilitate ease-of-handling during operation, requiring fabrication of a support structure to maintain the column in place during operation.

Design of appropriate RNRS column support structures represent an important ergonomic criterion to facilitate a pleasant experience when handling the RNRS that also promotes cleanliness. These concerns led to the utilization of common household water filtration units (Figure 4.14) and cartridge filters, providing a preliminary foundation for the design of the RNRS prototype as these
products have been designed and fabricated for durability and minimal, yet simple maintenance by non-technical personnel, i.e., homeowners.

Figure 4.13 Stages of RNRS prototype development. Preliminary CZ-column (left), Filtration housing upgrade with inner-influent down-spout for upward flow through CZ bed (middle), and refillable filter cartridge upgrade with opaque housing to reduce algal growth (right).

Figure 4.14 Size and material variations of water filter housings.

The second prototype added an influent downspout that introduced fluid at the bottom of the column, yielding upward flow through the IX bed (Figure 4.16, left). Upward flow through the CZ bed was elected to minimize channeling that could occur in downward flow operation if a flow distributor is not used. Further investigation of household water filtration products and accessories led to the discovery
and implementation of refillable filtration media cartridges (Figure 4.15, right) made of polystyrene that can be filled with media and inserted into the filtration housing. Use of the refillable cartridge vastly improved RNRS ergonomics as these cartridges can be exchanged quickly and media can be removed and thoroughly cleaned if necessary, with minimal losses.

Figure 4.15 Flow profile of RNRS prototypes without cartridge (left) and with cartridge (right)

The initial RNRS prototypes utilized 2.5” x 9.75” (6.35 cm x 24.765 cm) filter housings (Size 1 of Figure 4.15). The filter housing was slightly modified to accommodate a drainage valve at the bottom of the housing (center image of Figure 4.13; left image of Figure 4.15). An advantage of the in-line filter and cartridge design is the ability to manipulate flow direction upward or down-ward through the media depending on how the unit is connected, allowing reversal of the service flow direction during regeneration without additional modifications to the RNRS design (Crittenden, 2012). Use of the filter housing for prototyping was advantageous as it is a widely accepted form factor with established ergonomic design. Various housing sizes are commercially available and can be considered used to expand the capacity of RNRS service cycles (Figure 4.14).

4.3.4.2 RNRS Maintenance and End of Life Considerations

A major objective of this research is to develop the RNRS in a way to facilitate its use and handling by users with a low level of training. The role of User is assumed by persons whom will reuse TAN recovered by the RNRS as fertilizer in an appropriate horticultural system. Professional service
personnel that are charged with maintenance of NSSSs may also interact with the RNRS to perform TAN recovery and replacing exhausted RNRSs with fresh ones to maintain TAN recovery performance.

Components that experience continuous stress and exposed to poor quality water may require frequent replacement. For example, gaskets and O-rings used to maintain water tightness during operation of the RNRS frequently experienced high amounts of wear and were subjected to treated wastewater conditions within the filter housing requiring a supply of replacement parts and regular cleaning. The gasket at the top of the refillable cartridge may require regular replacement as signs of deterioration were observed (Figure 4.16). Regular rinsing of the RNRS components should be performed, if possible, at the end of each regeneration cycle to remove biofilm that may clog portions of the RNRS (Figure 4.16, left). Filter housings that have maintained structural integrity throughout their design life can be reused for additional RNRS operation. Structurally compromised RNRS materials should be recycled or repurposed to avoid being landfilled. Minor, replaceable parts like O-rings and gaskets may require disposal. The majority of the RNRS system consists of durable, recyclable plastic that is capable of long operational life if proper care is taken to minimize damage caused by ultraviolet light. Major recurring RNRS operational tasks are listed in Table 4.6, per ISO 30500’s requirements for NSSS manufactures; Table 4.7 provides a description of difficulty level ratings for operational tasks (ISO, 2018).

Figure 4.16 Biofilm growth (left) and gasket deterioration (right) on the RNRS cartridge.
Table 4.6 Recommended major configuration, adjustment, and maintenance activities of the RNRS.

<table>
<thead>
<tr>
<th>Who is to perform the activity (user/professional service personnel)</th>
<th>Type of activity</th>
<th>Complexity of task (per Table X)</th>
<th>Frequency</th>
<th>Expected duration per activity (person hours)</th>
<th>Required parts, components or consumables</th>
</tr>
</thead>
<tbody>
<tr>
<td>professional service personnel</td>
<td>RNRS Installation and removal before and after charge phase</td>
<td>Low</td>
<td>2-3 times/week</td>
<td>≤ 1</td>
<td>Filter housing wrench</td>
</tr>
<tr>
<td>user/professional service personnel</td>
<td>RNRS transport to and from nutrient discharge/reuse location</td>
<td>Low</td>
<td>once weekly</td>
<td>≤ 1</td>
<td>leak-proof, secondary containment</td>
</tr>
<tr>
<td>User</td>
<td>RNRS cleaning/rinsing</td>
<td>Low</td>
<td>Twice weekly</td>
<td>≤ 1</td>
<td>Wash water, gloves</td>
</tr>
<tr>
<td>User</td>
<td>Nutrient discharge into plant growth system</td>
<td>Low</td>
<td>once weekly</td>
<td>≤ 2</td>
<td>irrigation water, reservoir, plumbing connections, bicarbonate salt</td>
</tr>
<tr>
<td>user/professional service personnel</td>
<td>RNRS Na-pretreatment/regeneration</td>
<td>Medium</td>
<td>once weekly</td>
<td>≤ 4</td>
<td>10-20% sodium chloride solution, sodium hydroxide, PPE</td>
</tr>
<tr>
<td>professional service personnel</td>
<td>Repair and replacement of RNRS parts</td>
<td>Low</td>
<td>Once a month</td>
<td>≤ 1</td>
<td>Replacement parts</td>
</tr>
</tbody>
</table>

Table 4.7 Complexity of configuration, adjustment, and maintenance activities. Adapted from ISO 30500 (2018).

<table>
<thead>
<tr>
<th>Complexity</th>
<th>Technical competence</th>
</tr>
</thead>
<tbody>
<tr>
<td>very low</td>
<td>No skills (background education, experience) and no training required</td>
</tr>
<tr>
<td>Low</td>
<td>Basic skills and less than 1 h training required</td>
</tr>
<tr>
<td>Medium</td>
<td>Requires certain skills that can be acquired by training lasting no more than 1 day</td>
</tr>
<tr>
<td>High</td>
<td>Requires high technical skills (e.g. technical education in the field related to the activity), more than 1 day of training, and at least 6 months of work experience</td>
</tr>
<tr>
<td>Very high</td>
<td>Requires very high and specialized technical skills (e.g. advanced technical education in the field related to the activity), extensive training, and at least 1 year of work experience</td>
</tr>
</tbody>
</table>

4.3.4.3 RNRS Process: Anticipated Nitrogen Mass Flow

The dimensions of the 10” (25.4 cm) filter cartridge can accommodate approximately 512 g of clinoptilolite. Assuming a maximum cation exchange capacity of 10 mg NH₄⁺-N g⁻¹ NZ estimates that 5120 mg NH₄⁺-N can be recovered from AnMBR permeate before exhaustion of the 10” RNRS cartridge. Average daily nitrogen mass loading per person (feces and urine) equates to approximately 12.22 g N capita⁻¹ d⁻¹, of which 70% is assumed recovered as NH₄⁺-N, yielding 8.55 g NH₄⁺-N recovered daily. A preliminary nitrogen mass balance conveys that two 10” RNRSs would be required per person per day as the RNRS-CZ will theoretically reach exhaustion after approximately 14 hours. The actual cation exchange capacity (CEC) of the RNRS-CZ and the time to exhaustion is dependent on the wastewater composition and flowrate (Crittenden, 2012; Hedstrom, 2001). Theoretical nitrification rates for trickling filters combined with the biological surface area of the ZGT system should accommodate a nitrification...
rate of 14.78 g N d$^{-1}$ ZGT$^{-1}$ under ideal conditions (Ebeling et al., 2006; Storey, 2013). Nitrification is often reported as the rate-limiting step during biological regeneration of exhausted clinoptilolite, however it may be possible to support enhanced nitrification through pH buffering and by leveraging passive aeration of the ZGT system (Storey, 2013) (McGilloway et al., 2003).

4.4 Conclusions

The final design concept and form factor of the TAN removal system was dictated by consideration of the primary functions identified by the problem statement. Realization of the final system design and operation schema came from the integration of two established product designs: The use cycle schemes of rechargeable batteries, and the established form factor of household, in-line water filtration units with exchangeable cartridges. Ideation exercises resulted in reconsidering the system boundary for CZ-IX regeneration (F2), exploring the possibility to simultaneously regenerate CZ, while enabling access to released TAN for fertigation reuse (F3).

Other alternatives for low-cost TAN removal for NSSSs considered on-site reuse of TAN via assimilation into crop masses but also create risks of exposure to partially treated wastewater and fugitive odor emissions. Additionally, the footprint and solar radiation required for these systems may present issues in certain contexts where NSSSs can be applied (Figure 4.9, right) e.g., the basement of a residential building. Furthermore, ISO 30500 prioritizes safety, simple operation, and low input material and energy requirements to maintain operation. ISO 30500 also notes that NSSSs should be representative of sustainable sanitation technologies with verification provided through the execution of a Life Cycle Analysis (LCA). The proposed RNRS concept fosters potential for overcoming spatial and sustainability challenges related to the dependency of co-location for using nutrients recovered from wastewater treated by an NSSS. Optimization of TAN recovery efficiency is necessary to increase the total nitrogen removal capacity and to reduce the total number of units needed and frequency of regeneration processes needed. The RNRS desorption phase must be assessed to determine the additional material and/or energy input required, if necessary, to facilitate targeted release of recovered TAN.
CHAPTER 5: RNRS PROTOTYPE CAPACITY TESTING AND EXPERIMENTATION

5.1 Introduction

Extensive studies surrounding the total ammonia nitrogen (TAN) recovery performance of clinoptilolites exist but experimental conditions, materials, and results vary widely (Boyer, 2014). The objective of this overall body of work is to develop a reusable nutrient recovery system (RNRS) that uses low-cost clinoptilolite materials to enable safe, efficient access to nitrogen recovered from AnMBR permeate for reuse in fertigation applications. This chapter describes the experimental procedures used to assess the proposed RNRS’s performance under relevant conditions, conveys the results of the experimental procedures, and provides discussion of the observations. Performance data generated by this chapter are used to inform a sustainability analysis performed in the following chapter.

5.1.1 TAN Recovery and Release Capacity of RNRS Prototype

Clinoptilolite zeolite is used to facilitate TAN removal from AnMBR permeate via ion exchange (IX) with other ions in the zeolite. The maximum ammonium exchange capacity (AEC) of clinoptilolite has been well documented, however the varying characteristics of AnMBR permeate can affect the AEC of clinoptilolite material, thus warrants investigation under relevant conditions (Boyer, 2014). Additionally, past research has shown that AEC of clinoptilolite can be enhanced by pretreatment with solutions containing either a mixture cations or highly concentrated brines of a single cation, i.e., Na⁺, Ca⁺, K⁺, or Mg²⁺, yielding a homo-ionic form of clinoptilolite (Apontes-Morales, 2015). However, concentrated NaCl solutions that are commonly used for regenerating exhausted zeolite is deleterious to

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1 Portions of this chapter were published in: Calabria, J. L., Lens, P. N. L., & Yeh, D. H. (2019). Zeolite ion exchange to facilitate anaerobic membrane bioreactor wastewater nitrogen recovery and reuse for lettuce fertigation in vertical hydroponic systems. Environmental Engineering Science. Final publication is available from Mary Ann Liebert, Inc., publishers http://dx.doi.org/[10.1089/ees.2018.0439].s
plant growth and should be avoided to enable reuse of the recovered TAN solutions for fertigation. Land application of solutions containing recovered nitrogen is a potential nutrient reuse practice, thus regeneration solutions devoid of sodium can mitigate negative impacts caused by an increased soil sodium adsorption ratio (SAR) (Rengasamy & Marchuk, 2011).

5.1.2 Feasibility for Agricultural Reuse via Adaptive Hydroponics

Potassium, calcium, and magnesium salts are considered candidates for supporting regeneration of exhausted RNRS zeolite for hydroponic fertigation reuse as these ions are important plant macronutrients that support plant growth (Resh, 2013). Tap water containing high calcium and magnesium content is utilized as a readily available regenerant solution achieving a sustained release of TAN from the exhausted RNRS column. The desorption solution generated from elution of RNRS-bound TAN with tap water was used as a fertigation solution to support the growth of *Lactuca sativa* (buttercrunch lettuce) in vertical hydroponic systems. Methods to improve hydroponic performance through simultaneous nitrogen and phosphorus recovery were also investigated.

5.2 Materials and Methods

5.2.1 Natural Clinoptilolite Zeolite

Clinoptilolite zeolite comprises the main ion-exchange medium used for this research due to its availability world-wide and its selectivity for ammonium. Analysis of the capacity of clinoptilolite for removing ammonium from liquid streams with characteristics resembling that of a NSSS-AnMBR platform was conducting clinoptilolite from two sources from the United States of America: ChemSorb® clinoptilolite filter media comprised of Bear River Zeolite (BRZ™) clinoptilolite (Bear River Zeolite Co., Inc., Thompson Falls, MT) mined in Preston, ID (Table 5.1) and KMI Zeolite® (Pahrump, NV) clinoptilolite (Table 5.2), mined from the Amargosa Valley in Nevada, U.S.A., characterized as at least 96.9% pure, Na-clinoptilolite (Al$_{1.2}$Ca$_{1.58}$H$_{30}$O$_{46.9}$Si$_{16.8}$), 2.30% montmorillonite (KSi$_4$Al$_2$Mg$_{12}$O$_{30}$), 0.7% phlogopite (Al$_{1.22}$Fe$_{0.799}$H$_1$), and 0.2% Stibnite-Ca (Al$_{2.10}$Ca$_{0.8}$H$_{0.2}$). All the natural zeolite clinoptilolite (NZ) used for analysis was sieved to yield a mean particle diameter in the range of 0.5 – 1.0 mm. After sieving the zeolite granules, to achieve a uniform granule size sample, the zeolite granules were rinsed
with distilled water to remove excess dust and dried in an oven at 100 °C for at least 24 hours. Sieved, rinsed, and dried NZ was then stored in a desiccator prior to use.

Table 5.1 Chemical composition as mass percentages of natural clinoptilolite zeolites (CZ) tested.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MnO</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ChemSorb® CZ</td>
<td>67.4</td>
<td>10.60</td>
<td>1.70</td>
<td>2.23</td>
<td>0.45</td>
<td>0.59</td>
<td>4.19</td>
<td>&lt;0.01</td>
<td>0.27</td>
</tr>
<tr>
<td>KMI Zeolite ® CZ</td>
<td>66.7</td>
<td>11.48</td>
<td>0.9</td>
<td>1.33</td>
<td>0.27</td>
<td>3.96</td>
<td>3.42</td>
<td>0.025</td>
<td>0.13</td>
</tr>
</tbody>
</table>

5.2.1.1 Zeolite Pretreatment

Clinoptilolite zeolite was converted to various homo-ionic forms by contacting zeolite granules in an excess of highly concentrated brine solutions. Natural clinoptilolite zeolite (CZ) that was previously rinsed and dried, was converted to sodium form (Na-CZ), calcium form (Ca-CZ), and potassium form (K-CZ) by contacting with 2 M solutions of NaCl, CaCl₂, and KCl, respectively, for 24 hours. After concentrated brine contact, pre-treated zeolite was rinsed with distilled water, and then dried at 100 °C for at least 24 hours prior to storage in a desiccator. Another portion of Ca-CZ underwent additional pretreatment via calcination at 500 °C for 1 hour in a furnace.

5.2.1.2 Batch Adsorption Isotherms

The adsorption isotherm is used to describe the amount of solute (i.e., NH₄⁺-N) adsorbed onto the solid (zeolite) and the equilibrium concentration of the solute in solution at a given temperature (Crittenden, 2012). Adsorption isotherms were performed using Na-CZ and Ca-CZ in NH₄Cl solution (1000 mg/l NH₄⁺-N) to obtain a maximum cation exchange capacity (CEC). Diluted urine and synthetic permeate (SynPerm) were also used as solute containing substrates to observe the effect of these mediums on the theoretical maximum CEC of pretreated CZ. Batch CEC experiments were performed by placing varying mass quantities (0, 0.5, 1, 2.5, 5, 7.5, and 10 g) of pretreated CZ in contact with a fixed volume (100 mL) of 1000 mg NH₄⁺-N l⁻¹ solution in a 250 mL, Erlenmeyer flask. The flasks were sealed to maintain constant volume. Constant temperature was maintained at 25 °C and constant agitation of the flask contents was performed by a shaker plate set to 200 rpm to ensure complete mixing over a 48-hour period when equilibrium was assumed. Initial and final liquid samples’ TAN content were analyzed using
the colorimetric methods described in Chapter 3 (sodium salicylate method). Equilibrium adsorption data were evaluated via linear analysis using the Langmuir (Eq. 1) and Freundlich (Eq. 2) isotherm models (Crittenden, 2012):

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad \text{[Eq. 5.1]}
\]

\[
q_e = K_F C_e^{1/n} \quad \text{[Eq. 5.2]}
\]

where \( q_e \) represents the zeolite phase NH\(_4^+\)-N concentration (mg NH\(_4^+\)-N g\(^{-1}\) CZ); \( C_e \) represents the liquid phase NH\(_4^+\)-N concentration at equilibrium (mg NH\(_4^+\)-N L\(^{-1}\)); \( q_{\text{max}} \) is the theoretical maximum adsorption capacity for forming a single layer (mg NH\(_4^+\)-N g\(^{-1}\) CZ); \( K_L \) is the Langmuir adsorption equilibrium constant (L/mg); \( K_F \) is the Freundlich adsorption capacity parameter (mg/g)(L/mg)\(^{1/n}\); and \( 1/n \) is the Freundlich adsorption intensity parameter (unitless) (Crittenden, 2012). The Langmuir isotherm constants were obtained through linear regression of the plot of \( 1/q_e \) vs. \( 1/C_e \) which yields a straight line with intercept: \( 1/q_{\text{max}} \) and slope: \( 1/K_L q_{\text{max}} \). Freundlich isotherm parameters were obtained through linear regression of the plot of \( \log(q_e) \) vs. \( \log(C_e) \) which yields a straight line with intercept: \( \log(K_F) \) and slope: \( \frac{1}{n} \).

### 5.2.1.3 Batch Desorption and Regeneration

Batch desorption of CZ exhausted with NH\(_4^+\)-N was performed by first saturating 20 g of CZ in 2 liters of 1000 mg NH\(_4^+\)-N L\(^{-1}\) solution for 24 hours. The NH\(_4^+\)-CZ was then rinsed with distilled water and dried at 70 °C for 3 hours, and then placed in a desiccator to cool. Regenerant solutions of CaCl\(_2\) and KCl were prepared with the following molarities: 0.001, 0.01, 0.1, and 1.0 M. The following sodium-based regeneration solutions were prepared: 10 g NaCl L\(^{-1}\), 20 g NaCl L\(^{-1}\), 10 g NaCl L\(^{-1}\) + NaOH (pH:12), 20 g NaCl L\(^{-1}\) + NaOH (pH:12), 10 g NaCl L\(^{-1}\) + 1.5:1 NaOCl:N, 20 g NaCl L\(^{-1}\) + 1.5:1 NaOCl:N, 10 g NaCl L\(^{-1}\) + 2:1 NaOCl:N, and 20 g NaCl L\(^{-1}\) + 2:1 NaOCl:N. Batch desorption and regeneration commenced when 25 mg of NH\(_4^+\)-CZ was placed in contact with 50 mL the regenerant with constant mixing, lasting 24 hours. At the end of the regeneration period, a liquid sample was taken to measure the liquid phase TAN concentration. The remaining solution was decanted, and 25 mL of 0.1 M HCl solution was added to elute
all remove all NH$_4^+$ N from the CZ. A liquid sample was collected to quantify the amount of TAN remaining on the CZ after the regeneration period.

5.2.2 RNRS Column Operation

5.2.2.1 TAN Removal: Charge Phase

The RNRS column prototype was used to facilitate total ammonia nitrogen (TAN) removal from a synthetic AnMBR permeate /ionic cocktail solution, (SP). Ten to 20 liters of SP solution was prepared at regularly to serve as feed solution during RNRS column operation. The bench-scale RNRS column contained 500 g of rinsed, and dried CZ and a bed volume (BV) of approximately 495 cm$^3$. The column exhaustion cycle was operated in upflow mode with a typical feed flow rate of 12 BV h$^{-1}$ (100 ml min$^{-1}$). Real time measurement of total dissolved solids was measured via electrical conductivity probes (Vernier Software and Technology, Beaverton, OR) placed in the influent solution, at the column outflow, and in the collection reservoir (Figure 5.1). Effluent ammonium concentration was measured with an ammonium ISE (NeuLog, Rochester, NY).and effluent pH was measured using a Vernier pH probe (Vernier Software and Technology, Beaverton, OR). The exhaustion cycle was terminated when 30% of the influent TAN concentration was observed in the effluent, i.e., 30% breakthrough.

![Figure 5.1 Schematic of the experimental RNRS column setup](image_url)
5.2.2.2 TAN Release: Discharge Phase

Release of TAN recovered by the RNRS column was facilitated by operation resembling that of the exhaustion cycle operation, differing only in the feed solution used. The RNRS discharge phase utilized tap water collected from laboratory faucets as the eluent solution for releasing CZ-bound TAN. The discharge phase with tap water operated until $dEC_{out}/dt = 0$, (typically around 40 BV).

5.2.2.3 RNRS Zeolite Regeneration

Regeneration exhausted RNRS columns was performed using 20 g/l NaCl solution. A 2 M CaCl$_2$ solution was used for RNRS regeneration. Approximately 4 BV of NaCl regenerant solution was conveyed through the RNRS column at a flow rate of approximately 2.5 BV h$^{-1}$. The RNRS column was flushed with 2 BV of DI H$_2$O after the regeneration process. The volume of CaCl$_2$ regenerant required to regenerate the RNRS column was unknown, thus a regeneration cycle column study was performed to assess the performance of CaCl$_2$ regenerant. EC was monitored at the RNRS inlet and outlet. Grab samples were taken periodically for TAN analysis via the sodium salicylate colorimetric method.

5.2.3 Hydroponic-BioRegeneration (HBR) Process

The hybrid, hydroponic-biological-regeneration process (HBR) proposes the regeneration of RNRS-CZ with cations that can support plant growth (i.e., K$^+$, Ca$^{2+}$, and Mg$^{2+}$) to achieve simultaneous hydroponic fertigation and biological regeneration via IX and nitrification. Tap water collected from laboratory faucets at the University of South Florida and IHE-Delft constituted the solute medium used for the HBR processes that were examined. Two modes of HBR were examined: (1) batch desorption mode and (2) recirculation mode.

5.2.3.1 RNRS Batch Desorption for Hydroponic Fertigation

Tap water collected from the laboratory at IHE-Delft in the months of April through May of 2017 was used to generate a 50 L batch of RNRS desorption solution (DS). First, a RNRS column was exhausted to 30% BT of TAN via exhaustion cycle operation with synthetic permeate (SP). After 30% BT was achieved, the RNRS column feed was switched to tap water to induce the release of TAN recovered from SP. TAN discharge operation endured until a 50 L batch of DS was produced. The batch of
desorption solution was divided into two 10 L volumes of DS and two 10 L volumes of DS amended with acetic acid to yield 0.02% acetic acid solution with a pH: 4.5. SP diluted with tap water to yield a final TAN concentration equal to that of DS served as the control. A 10 L solution of tap water (TW) served as the experimental blank solution. The prepared fertigation solutions were used as a hydroponic nutrient solution to support the development of *Lactuca sativa* in vertical hydroponic towers (Figure 5.2).

![Diagram of fertigation study](image)

**Figure 5.2 Experimental design of HBR: batch mode fertigation study.** Batch mode fertigation used diluted synthetic permeate (SP), tap water (TW), RNRS desorption solution (DS), and RNRS desorption solution amended with acetic acid (DSa).

### 5.2.3.1.1 Hydroponic Crop Cultivation

Three to four seeds of *Lactuca sativa* (buttercrunch lettuce) were placed in a rockwool substrate hydrated with tap water. Prior to planting, the rock wool cubes were stabilized in a diluted citric acid solution (pH: 5.5). Germination occurred in a covered, seedling growth tray under ambient lighting conditions. After a germination period of 14 days, one *L. sativa* seedling was transplanted into each ZG tower segment (2 seedlings per 10 L fertigation solution), marking the start of the 14-day hydroponic cultivation cycle. Fertigation solution grab samples were collected daily from the solution feed ports at
the top of each tower and analyzed for pH, TAN, NO$_3^-$—N via colorimetric method and ion chromatography, respectively. Lettuce crops were harvested at the end of the crop cultivation cycle for analysis of the following parameters: fresh weight, dry weight, and chlorophyll pigment content of new and old leaves.

5.2.3.1.2 Lighting Conditions

Two lighting conditions were tested: low photon flux (10-15 mol m$^{-2}$ s$^{-1}$) and high photon flux (150-200 mol m$^{-2}$ s$^{-1}$) to assess the effects of lighting on the HBR process. Low photon flux (10-15 mol m$^{-2}$ s$^{-1}$) lighting was supplied by 38 cm segments of 4:1, red and blue LED light strips adhered to a parabolic light concentrator of the same (Figure 5.3, left). High photon flux lighting (150-200 mol m$^{-2}$ s$^{-1}$) was supplied by an OSRAM HQI-T 400 W/D PRO metal halide lamp (OSRAM GmbH, Munich, Germany) pictured in Figure 5.3 (right). Photon flux was measured with a LI-COR Biosciences Li-250A photometer (LI-COR, Inc., Lincoln, NE).

Figure 5.3 Light assemblies for HBR in (batch) hydroponic growth studies. Low photon flux (left) and high photon flux (right).
5.2.3.2 HBR Recirculation Mode

Hydroponic-Biological Regeneration (HBR) of an RNRS column in recirculation mode was performed using an initial 10 L volume of tap water that was continuously recirculated through an exhausted RNRS column. An RNRS pretreated with 4 BV of 20 g NaCl l\(^{-1}\) was first exhausted with TAN from synthetic AnMBR permeate during exhaustion cycle operation. The exhausted RNRS column was then connected inline of the HBR recirculation setup consisting of a 10 L fertigation solution reservoir and two 15” (38.1 cm) ZG towers. The effluent of the RNRS column was directed to the top of the ZG towers, trickled down into through the ZG towers into the HBR solution reservoir located below the ZG towers. A peristaltic pump was used to continuously recirculate HBR solution from the bottom of the HBR reservoir, into the RNRS column and then into the top of ZG towers (Figure 5.4). HBR recirculation was conducted indoors at a constant ambient temperature of 25 °C, over a 33-day period. Tap water was periodically added to the HBR solution reservoirs to replace water volume loss due to evaporation. Grab samples were collected from the ZG tower feed port at 2 to 3-day intervals. The pH, EC and concentrations of the following ions were analyzed: Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), NH\(_4^+\), Cl\(^-\), NO\(_2^-\), NO\(_3^-\), SO\(_4^{2-}\), and PO\(_4^{3-}\). Synthetic permeate solution was recirculated at a similar and higher flow rate two additional hydroponic recirculation systems containing only ZG towers.

Figure 5.4 RNRS HBR process setup in recirculation mode.
5.2.3.3 Mass Balance Analysis: HBR Process

The HBR process in recirculation mode was developed to facilitate regeneration of the exhausted RNRS via biological nitrification. A mass balance analysis of the RNRS-HBR process was performed by identifying the RNRS-HBR system boundary (Figure 5.5). The system boundary was used to identify nitrogen flows in and out of the RNRS-HBR system (Crittenden, 2012).

The time period chosen for the mass balance analysis was the 33-day HBR recirculation period. The RNRS-HBR system was modelled as a completely mixed batch reactor (CMBR) as there is no net flow in or out of the system, i.e., \( Q_{\text{in}} = Q_{\text{out}} = 0 \). Additionally, concentration was assumed to be uniform throughout the control volume, i.e., as RNRS-bound TAN is released, a uniform liquid TAN concentration is assumed throughout the HBR process control volume. The HBR process control volume of 10 liters was assumed constant throughout the experiment, i.e., \( \frac{dV}{dt} = 0 \). A formula used to generalize the mass balance analysis of the HBR system is:

\[
\text{Input} + \text{generation} - \text{loss} - \text{output} = \text{accumulation}
\]
The general mass balance equation can be simplified further to reveal that the TAN “generation” rate (TAN release) can be determined by the sum of the observed TAN (accumulation) and nitrate (loss) concentrations over time. TAN concentration data were correlated with reaction kinetics.

**5.2.4 Phosphate Recovery**

Investigation of potential phosphate recovery was performed in a batch and column experiment. MgO was added at a molar ratio of 1.2:1 Mg:P to an Erlenmeyer flask containing Ca\(^{2+}\)-CZ in diluted urine with an initial total phosphorous (TP) concentration of 165.3 mg PO\(_4^{3-}\) P l\(^{-1}\) and mixed for 24 hours at 200 rpm. Aqueous solution samples were decanted and collected for TAN and TP analysis. The remaining CZ-containing solids were placed on a pre-weighed, pre-rinsed, 0.45 μm glass micro-fiber filter with vacuum applied. The filter and captured solids were dried at 100 °C for 24 hours, then cooled in a desiccator, and then weighed to quantify additional precipitate mass formed.

A second investigation of phosphorus recovery involved pretreatment of RNRS-CZ with 2 M MgCl\(_2\). Four BV of 2 M MgCl\(_2\) were passed through an RNRS column at 2.5 BV h\(^{-1}\) yielding a Mg\(^{2+}\)-pretreated RNRS (Mg\(^{2+}\)-RNRS). An exhaustion cycle was then conducted using the Mg\(^{2+}\)-RNRS to remove TAN from 20 liters of synthetic AnMBR permeate (SP) conveyed through the Mg\(^{2+}\)-RNRS at a flow rate of 12 BV h\(^{-1}\). The Mg\(^{2+}\)-RNRS exhaustion cycle was stopped after 20 liters of SP solution had been passed through the column. Grab samples were taken at t = 1, 5, 10, 20, 45, 60, 120, 180, and 200 minutes after the exhaustion cycle began. The exhausted Mg\(^{2+}\)-RNRS was then connected inline to the HBR process described in section 5.2.3.2 of this work. HBR of a Mg\(^{2+}\)-RNRS and a Na\(^+\)-RNRS was performed simultaneously under the same HBR conditions described in section 5.2.3.2.

Samples of clinoptilolite zeolite (CZ) were taken from the RNRS system to observe the effects of Mg\(^{2+}\)-pretreatment: raw CZ, Na\(^+\)-pretreated CZ, Mg\(^{2+}\)-CZ, and another Mg\(^{2+}\)-CZ sample collected from an RNRS cartridge after servicing 2 BV of synthetic permeate during an exhaustion cycle. RNRS-CZ was rinsed with deionized water and then dried in an oven at 100°C for 1 hour. Dried RNRS-CZ samples were then analyzed using a scanning electron microscope (SEM) equipped with an x-ray spectrometer for elemental analysis via energy dispersive spectroscopy (Hitachi, Ltd., Tokyo).
5.3 Results and Discussion

5.3.1 TAN Removal

5.3.1.1 Natural Clinoptilolite Pretreatment

The maximum cation exchange capacity of the ChemSorb® clinoptilolite for ammonium was derived from using the Langmuir and Freundlich isotherms models for modelling the equilibrium adsorption behavior of a sorbent-sorbate system. Although ion exchange (IX) is the mechanism responsible for NH₄⁺-N removal, past literature has shown that Langmuir and Freundlich adsorption isotherm models can be applied to describe the CEC of CZ under ideal conditions. Langmuir and Freundlich parameters for CZ pretreated with Ca²⁺, K⁺, and Na⁺ are summarized Table 5.2. Both Langmuir and Freundlich models correlated well to the linearized experimental data of Na⁺-CZ ($R^2 \geq 0.90$). The Langmuir expression is most commonly used to describe CZ adsorption equilibria as it assumes that sorbent surface exchange sites can only be occupied by one sorbate molecule (monolayer adsorption) which is consistent with IX processes (Boyer, 2014; Crittenden, 2012). The Langmuir expression also provides a convenient method for calculating the experimental maximum adsorption capacity of the sorbent under the isotherm testing conditions. Higher $Q_{\text{max}}$ was obtained by Na⁺-CZ compared to Ca²⁺-CZ. The highest $Q_{\text{max}}$ observed was 36.10 mg NH₄⁺-N/g CZ (2.58 meq/g CZ) by Na⁺-CZ, averaging a $Q_{\text{max}}$ value of 34.37 mg/g (1.91 meq/g) agreeing with the CEC specification provided by the zeolite manufacturer’s technical data sheet: 1.9 to 2.2 meq/g CZ and the data reported in literature (Wang & Peng, 2010).

<table>
<thead>
<tr>
<th>NZ Type</th>
<th>Langmuir Model Data</th>
<th>Freundlich Model Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{max}}$ (mg TAN/g NZ)</td>
<td>$K_L$ (l/mg)</td>
</tr>
<tr>
<td>Ca²⁺-CZ</td>
<td>20.88</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca²⁺-CZ (Urine)</td>
<td>26.46</td>
<td>0.0019</td>
</tr>
<tr>
<td>Na⁺-CZ</td>
<td>32.05</td>
<td>0.0043</td>
</tr>
<tr>
<td>Na⁺-CZ</td>
<td>34.97</td>
<td>0.0013</td>
</tr>
<tr>
<td>Na⁺-CZ</td>
<td>36.10</td>
<td>0.0024</td>
</tr>
</tbody>
</table>
Linearization of adsorption equilibrium data obtained by Na\textsuperscript{+}-CZ is depicted in Figure 5.6. Plotting the inverses of the experimental equilibrium concentrations in solid phase \((q_e)\) and liquid phase \((C_e)\) yields a straight line with intercept: \(\frac{1}{Q_{\text{max}}}\) and slope: \(\frac{1}{K_LQ_{\text{max}}}\) (Figure 5.6, left).

Plotting \(\log q_e\) v. \(\log C_e\) yielded a straight line with an intercept: \(\log K_F\) and slope: \(1/n\) (Figure 5.6, right). Eq. 1 and Eq. 2 used the Langmuir and Freundlich expression constants to generate Langmuir and Freundlich adsorption plots for comparison to the experimental data (Figure 5.7). The Langmuir model describes the adsorption behavior relatively well according to linear correlation data.

Figure 5.6 Langmuir (left) and Freundlich (right) isotherm models fitted to NH\textsubscript{4}\textsuperscript{+}-N adsorption equilibrium data obtained by Na\textsuperscript{+}-clinoptilolite in NH\textsubscript{4}Cl \((C_{0,\text{TAN}} = 1085 \text{ mg l}^{-1} \text{TAN})\).

The Freundlich model seemed to better describe the adsorption behavior of Ca\textsuperscript{2+}-CZ in a diluted urine matrix. The Freundlich model is better suited to describe the adsorption behavior of heterogeneous adsorbents such as activated carbon that exhibit heterogeneous adsorption, i.e., the adsorbent’s micropores can accommodate more than one adsorbate molecule. This is not to suggest that Ca\textsuperscript{2+}CZ can exchange more than one NH\textsubscript{4}\textsuperscript{+} molecule per IX site, violating a fundamental principle of the process where one ion is exchange for another while maintaining electroneutrality (conservation of charge).
Figure 5.7 Comparison of equilibrium adsorption models and experimental data. Freundlich and Langmuir isotherm models were compared to equilibrium adsorption data for natural clinoptilolite zeolite (NZ) in different homoionic forms and TAN substrates: (a) Ca\(^{2+}\)-NZ in NH\(_4\)Cl solution, (b) Ca\(^{2+}\)-NZ in diluted urine, and (c) Na\(^{+}\)-NZ in NH\(_4\)Cl solution.

Figure 5.8 conveys a discrepancy in the preservation of electroneutrality during Ca\(^{2+}\)-CZ IX as more meq of NH\(_4^+\) were removed from solution than Ca\(^{2+}\) was released into solution. A possible explanation for these observations is the fact that the hydrated ionic radius of Ca\(^{2+}\) is larger than NH\(_4^+\) which can limit the intraparticle diffusion capacity of Ca\(^{2+}\). The smaller hydrated ionic radius of NH\(_4^+\) allows greater intraparticle diffusion, thus NH\(_4^+\) migrate deeper into the microporous structures of the CZ granule (Koon & Kaufmann, 1975).

The limiting effect of intraparticle diffusion can be mitigated by using smaller diameter CZ granules (Boyer, 2014; Gupta et al., 2015; Koon & Kaufmann, 1975; Railsback, 2006; Wang & Peng, 2010). The size of the hydrated ion radius depends on the electrostatic attraction of water molecules to
that ion which is a function of the ion’s charge density, thus higher-charge ions will have a greater hydrated radius (Koon & Kaufmann, 1975; Railsback, 2006).

Figure 5.8 NH$_4^+$-N removal capacity of Ca$^{2+}$-CZ at different doses.

The equilibrium adsorption data, i.e., $Q_{\text{max}}$, conveys more Ca$^{2+}$-CZ would be required to remove the same quantity of TAN compared to Na$^+$-CZ. The preferred performance of Na$^+$-CZ over Ca$^{2+}$-CZ is well documented in the literature, however using Ca$^{2+}$ for simultaneous CZ regeneration and hydroponic fertigation is more favorable than Na$^+$ regeneration as Ca$^{2+}$ is a plant macronutrient and high Na$^+$ concentration in fertigation mediums is deleterious to crop development and negatively impacts the stability of soils if applied to land (Al-Maskri et al., 2010; EPA, 2012; Müller & Cornel, 2016). This warranted analysis of Ca$^{2+}$-CZ TAN removal performance under pertinent conditions for use in the proposed RNRS.

Interestingly, the Langmuir adsorption equilibrium model yielded a higher $Q_{\text{max}}$ for Ca$^{2+}$-CZ in diluted urine solution than in NH$_4$Cl solution. The observed increase in $Q_{\text{max}}$ could be attributed to the increased ionic activity resulting from the mixture of ions contained within the diluted urine substrate (Huang et al., 2014). The effect of the diluted urine substrate on Ca$^{2+}$-CZ TAN removal is depicted in Figure 5.9.
A Ca\textsuperscript{2+}-CZ dose of 100 g l\textsuperscript{-1} achieved 100% TAN removal from a liquid solution containing only NH\textsubscript{4}Cl with initial TAN concentration: C\textsubscript{0} = 1027.5 mg NH\textsubscript{4}\textsuperscript{+}-N. At this same dosage, TAN removal decreased by 20% in the diluted urine substrate. The complete composition of the urine substrate was unknown but TAN removal performance decrease due to solution composition was apparent, although TAN removal performance seemed unaffected at doses of 10 g l\textsuperscript{-1} Ca\textsuperscript{2+}-CZ or lower. At lower CZ doses, the bulk solution concentration gradient relative the solid phase concentration yields a relatively high driving force that promotes intraparticle diffusion of NH\textsubscript{4}\textsuperscript{+} ions and IX with CZ-bound Ca\textsuperscript{2+} ions (Boyer, 2014; Crittenden, 2012). Linearized experimental data of Ca\textsuperscript{2+}-CZ adsorption equilibria in diluted urine is displayed in Figure 5.10 with the pertinent Langmuir expression parameters for reference.

\begin{equation}
  y = 0.0378x + 19.645 \\
  R^2 = 0.9194
\end{equation}

\[ Q_{\text{max}} = 26.46 \text{ mg/g} \]
\[ K_L = 0.002 \text{ L/mg} \]
5.3.1.2 RNRS Column Operation

The RNRS column maintained consistent TAN removal performance from influent synthetic permeate (SP) after several regeneration cycles. Influent SP with an initial TAN concentration of 150 ± 5 mg/L NH$_4^+$-N, was conveyed through the RNRS column at 100 ml/min yielding a service flow rate (SFR) of 12 BV/h and TAN loading rate of 0.9 g TAN hr$^{-1}$. The breakthrough curve of an RNRS column previously regenerated with 20 g/L NaCl is depicted in Figure 5.12. The RNRS prototype column serviced approximately 30 BV when C$_{out}/C_{in}$ reached 0.3, i.e., 30% breakthrough. Alternatively, TAN breakthrough was reached in less than 5 BV following 2 M CaCl$_2$ regeneration (Figure 5.12).

![Figure 5.11 RNRS column TAN breakthrough profile after NaCl regeneration](image1)

![Figure 5.12 RNRS column TAN breakthrough profile after CaCl$_2$ regeneration.](image2)
5.3.2 TAN Release

5.3.2.1 Tap Water Desorption

The use of tap water as an eluent solution to release TAN removed from synthetic permeate via IX with the RNRS column yielded a desorption effluent with TAN concentration of 10 mg l⁻¹ \(\text{NH}_4^+\)-N, that was sustained throughout the desorption run period of 120 BV (Figure 5.14). An initial spike of TAN in the RNRS column effluent was observed at the beginning of each desorption cycle. We attribute this to legacy \(\text{NH}_4^+\) ions that remained weakly attached to the CZ granule surfaces after the exhaustion cycle was stopped and the RNRS-CZ column was drained. Complete dehydration of RNRS-CZ never occurred, thus it is possible for extra-particle TAN to remain in the hydrated films surrounding CZ granules. The initial release of weakly bonded total dissolved solids (TDS) material is observed in Figure 5.13.

![Graph showing electrical conductivity (EC) of deionized water (DI) and tap water (TW) used for rinsing the RNRS column prior to chemical regeneration.](image)

Figure 5.13 Electrical conductivity (EC) of deionized water (DI) and tap water (TW) used for rinsing the RNRS column prior to chemical regeneration.

Rinsing the exhausted RNRS column with deionized water (DI H₂O) caused a spike in electrical conductivity (EC) of RNRS desorption effluent. RNRS effluent EC sharply dropped within the first five BV of DI rinse but was still two orders of magnitude greater than the influent DI EC, indicating that TDS
was still being released but the rate of change of the effluent EC with respect to time \( \left( \frac{\Delta EC}{\Delta t} \right) \) had neared zero after 12 BV of DI had passed. DI pH increased from neutral to near 9.7 at RNRS column exit, indicating IX was performed according to the following reaction (Townsend & Coker, 2001):

\[
\begin{bmatrix}
Na^+ \\
K^+ \\
Ca^{2+} \\
Mg^+ \\
NH_4^+
\end{bmatrix}_{\text{Zeolite}} + H_2O \leftrightarrow H_3O_{\text{Zeolite}}^- + OH_{\text{solution}}^- + \begin{bmatrix}
Na^+ \\
K^+ \\
Ca^{2+} \\
Mg^+ \\
NH_4^+
\end{bmatrix}_{\text{solution}} \quad \text{[Eq. 5.3]}
\]

Contrarily, RNRS desorption effluent pH decreased after the influent elution solution was switched from DI to tap water (TW). RNRS desorption with TW demonstrated that \( \frac{\Delta EC}{\Delta t} \) neared 0 within 15 BV (Figure 5.14). However, EC increases from approximately 700 \( \mu \)S/cm to 1000 \( \mu \)S/cm through the RNRS column. The increase in effluent EC can be sustained for at least 20 BV. A gradual decrease in RNRS effluent TAN and EC was observed over the course of 120 BV of TW desorption; releasing approximately 20% of the RNRS-recovered TAN content (Figure 5.15).

![Figure 5.14 Electrical conductivity (EC) during RNRS desorption with tap water (TW).](image)

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5.3.2.2 Enhancing RNRS TAN Release and Regeneration

Tap water amended with CaCl₂ to 0.2 M was used to increase the concentration and rate at which TAN is released during RNRS desorption. Regenerant flow rate (Q) was varied and the effect on the rate of TAN release is observed in Figure 5.16.

---

**Figure 5.15** TAN desorption profile of RNRS column utilizing tap water as regenerant.

**Figure 5.16** Effect of CaCl₂ regenerant flow rate on the TAN release rate of the RNRS column.
The RNRS TAN release rate was increased with CaCl$_2$ solution and with increasing Q. Lower Q yielded a higher effluent TAN concentration. TW introduced after initial desorption was performed with 0.2 M CaCl$_2$ was less effective at releasing RNRS TAN. Effluent TAN was sustained near 100 mg l$^{-1}$ NH$_4^+$-N using 0.2 M CaCl$_2$ as an eluent solution Q $\approx$100 mL/min.

Batch desorption experiments observed greater TAN release from exhausted natural clinoptilolite zeolite (NZ) when K$^+$ was used as the major counter-ion in the regenerant solution instead of Ca$^{2+}$ (Figure 5.11). Regenerant solution with 1 M K$^+$ content released nearly 17 mg TAN g$^{-1}$ NZ, which is half of the maximum adsorption capacity analytically derived through Langmuir adsorption expression and more than 3x the observed RNRS-CZ TAN uptake (5 mg TAN g$^{-1}$ CZ). NZ modified via calcination (MZ) exhibited a significantly lower capacity for releasing TAN, especially when Ca$^{2+}$ eluent was used.

Modification of natural zeolite through calcination has been shown to improve the CEC of NZ by removing impurities within the zeolite’s crystalline matrix, and by increasing the average por structure diameter and overall volume of pores (Huang et al., 2014; Liang & Ni, 2009; Wang & Peng, 2010). However, subsequent TAN release processes seem to be hindered by NZ modification.

![Figure 5.17 Desorption capacity of natural (NZ) and modified (MZ) clinoptilolite zeolite in Ca$^{2+}$ and K$^+$ regenerant solutions of various molar concentrations.](image-url)
Complete regeneration of exhausted NZ was observed in batch experiments using Na\textsuperscript+-based regenerant solutions. Na\textsuperscript+ regenerant comprised of 20 g NaCl l\textsuperscript{-1} with NaOH added to increase solution pH to 12 was able to fully regenerate NH\textsubscript{4}\textsuperscript+-saturated CZ. Additionally, 87% of TAN released from CZ via IX was removed from solution via volatilization. Lowering regenerant strength to 10 g NaCl l\textsuperscript{-1} was still able to release 99% of CZ-TAN content but less of the TAN released was removed from solution overall (73%). The addition NaOCl (bleach) at a molar ratio of 2:1 NaOCl:TAN removed an average of $44.7 \pm 1.7\%$ of TAN released from CZ (Figure 5.18).

![Figure 5.18 Regeneration of NH\textsubscript{4}\textsuperscript+-exhausted CZ with Na\textsuperscript+-based regenerant solutions.](image)

5.3.3 RNRS Integration with Adaptive Hydroponic Systems

5.3.3.1 Hydroponic-BioRegeneration (HBR): Batch Mode

RNRS desorption solution facilitated faster nitrification of TAN in the hydroponic fertigation solution. The presence of acetate resulting from the addition of acetic acid delayed nitrate formation, but TAN was still completely removed after 9 days as was in the SP fertigation solution. The diluted synthetic permeate (SP) also displayed fast nitrification comparable to that of DS and all TAN from the SP fertigation solution after 9 days.
Analysis of the hydroponic solutions revealed decreasing ammonia and increasing nitrate concentrations in DS, SP, and DSa solutions. DS showed a higher maximum nitrification rate, generating 3.6 g NO$_3^-$ m$^{-3}$ d$^{-1}$, while SP and DSa achieved 3.0 g NO$_3^-$ m$^{-3}$ d$^{-1}$ and 0.14 g NO$_3^-$ m$^{-3}$ d$^{-1}$, respectively, over the same period. Most of the TAN released into the desorption solution (DS) was removed after 6 days of recirculation through the hydroponics system and nitrate production peaked after seven days when TAN was completely removed from DS and lettuce crop nitrogen assimilation was ongoing. Acetic acid amended-DS (DSa) did not exhibit significant nitrate removal as seen in the DS and SP crop series but did remove TAN from solution after 9 days. SP reached a higher overall maximum nitrate concentration as the initial nitrogen content was slightly higher (Figure 5.19). While all hydroponic solutions showed complete removal of NH$_3$-N by day 9, a higher initial NH$_3$-N removal rate was observed in the DS system. The hydroponic solutions exhibited varying effects on solution pH (Figure 5.20). An initial increase of solution pH was observed in all solutions except with tap water. A trend of decreasing pH was observed at from day 5 to day 7 which correlates with the observed peak of nitrate production in DS and SP systems, indicative of biological nitrification (Ergas & Aponte-Morales, 2014). No significant change of pH was observed in hydroponic systems containing tap water. DSa solution pH rose rapidly from 4.7 to 7.7 by day five.

![Figure 5.19 Fate of TAN in fertigation solutions during the hydroponic growth period.](image-url)
5.3.3.1 Batch HBR: Hydroponic Crop Development

Desorption solution (DS) crops accumulated 11% and 19% more fresh and dry mass, respectively, as well as a higher chlorophyll (Chl-a and Chl-b) content in new leaf growth compared to the SP crops. SP crops maintained higher chlorophyll content in older leaves (Figure 5.21).

![Figure 5.20 Fertigation solution pH during the hydroponic growth period.](image)

5.3.3.1.1 Batch HBR: Hydroponic Crop Development

Desorption solution (DS) crops accumulated 11% and 19% more fresh and dry mass, respectively, as well as a higher chlorophyll (Chl-a and Chl-b) content in new leaf growth compared to the SP crops. SP crops maintained higher chlorophyll content in older leaves (Figure 5.21).

![Figure 5.21 Mass and pigment development of hydroponic lettuce crops. Lettuce crops were grown in synthetic permeate (SP), desorption solution (DS), DS amended with acetic acid (DSa), and tap water (TW) for 13 days.](image)
DS crops exhibited a higher chlorophyll (a and b) content in newer leaves as well as a higher Chl a/b ratio in newer leaves. Phaeopigments resulting from the decomposition of chlorophyll by acidification with HCl were only observed in SP crop tissues, indicating some form of toxicity of deficiency was taking place. Lettuce crops grown in DSa solution accumulated less mass than crops grown in the tap water (blank) solution, resulting in insufficient mass development for chlorophyll analysis. Inspection of the hydroponic system at the end of the growth cycle revealed fungal growth in the root zone, indicating the occurrence of root rot and resulting in low mass development observed by DSa crops (Figure 5.22).

Figure 5.22 Fungal growth in ZipGrow™ tower with DSa solution.
5.3.3.1.2 Effect of Lighting During HBR

The integrated HBR process facilitated nearly complete removal of TAN after 5 days of fertigation solution recirculation. DS in dim lighting facilitated the fastest initial nitrification rate, yielding a TAN removal rate of 56.82 mg NH₃-N m⁻¹d⁻¹. Lighting conditions did not significantly affect ammonia removal rates as all hydroponic systems reached complete ammonia nitrogen reduction by day eight (Figures 5.23a and 5.23b). The observed production of nitrate (Figures 5.23c and 5.23d) correlated with TAN removal and solution pH data, indicative of nitrification. Hydroponic systems in low light conditions displayed nitrate accumulation with little nitrate removal. The low light conditions retarded plant growth and nitrate uptake. Hydroponic systems in well-lit conditions experienced more nitrate reduction as nitrate was assimilated into plant tissue. The addition of acetic acid delayed the production of nitrate in both light and dark environments. DSa in dim light conditions had the lowest observed nitrate production of all systems tested. Slight decreases in pH were observed on day 7 in both lighting conditions systems (Figures 5.23a and 5.23b) correlating to the observed peak of nitrate production by day 7.

Lettuce crops grown in hydroponic systems nourished by RNRS desorption solution (DS) and synthetic AnMBR permeate (SP) developed the most crop mass, with DS solution supporting slightly higher crop mass development than SP solution crops (Figure 5.24). Crops grown in dark DS and SP systems developed more vegetative mass than crops in DSa and blank, tap water systems. Single factor analysis of variance (ANOVA) conveys significant difference (P<0.05) in mass accumulation of crops grown in DS and SP solutions under low light conditions (P=0.015). However, single factor ANOVA revealed non-significant difference in crop mass accumulation of DS and SP crops in high-light conditions (P=0.81).

As expected, light conditions significantly affected crop mass development. Nitrification occurred faster in DS solution under dimly lit conditions. Generally, nitrification rates were not significantly impacted by lighting conditions. The presence of fungal growth in the root zone of DSa crops under high-light conditions resulted in less mass accumulation than DSa crops grown in dimly lit conditions. The
fungal growth resulted was caused by the presence of acetate resulting from the addition of acetic acid added for pH adjustment. The increased dissolved organic carbon content created conditions favoring the proliferation of heterotrophic bacteria, and then fungi, affecting the development of lettuce crop roots.

Figure 5.23 Effect of light conditions on biofiltration performance in vertical hydroponic systems with various fertigation solutions. Fertigation solutions consisted (SP), desorption solution (DS), desorption solution with acetic acid (DSa), and tap water (TW). Light (a) and dark (b) effects on ammonia removal, light (c) and dark (d) effects on nitrate production, and light (e) and dark (f) effects on solution pH.
5.3.3.2 HBR Process Performance: Recirculation Mode

Recirculation of RNRS DS effluent was more effective for removing TAN from the exhausted RNRS column and required significantly less tap water volume. Continuous recirculation of tap water-based HBR solutions through the vertical, hydroponic ZG towers resulted in continuous TAN removal from the bulk solution via nitrification, which in turn facilitated continuous TAN release from the RNRS column. HBR recirculation yielded a net accumulation of TDS throughout the HBR process period (Figure 5.24). The lack of a nitrate sink (i.e., plants, algae, or denitrification) resulted in the accumulation of total nitrogen (TN), up to 700 mg N l$^{-1}$ (Figure 5.27).

Recirculated HBR solution contained higher concentrations of Na$^+$, Ca$^{2+}$, and K$^+$ than what was observed in tap water (Figures 5.26a, 5.26b, and 5.27c) indicating the release of these ions during HBR of the RNRS. Higher TN accumulation and TAN release rates were observed by the RNRS column pretreated with MgCl$_2$ (Mg$^{2+}$-RNRS or NB2), however twice the amount of sodium was released by this column (Figure 5.26), indicating that a larger amount of clinoptilolite-IX sites were occupied by Na$^+$ during the RNRS exhaustion cycle, thus TAN breakthrough is reached faster than with Na$^+$-pretreated RNRS (NB1).
K⁺ was also released at a higher concentration by NB2 than NB1, although not as high as Na⁺ since the SP solution K⁺ concentration is nearly a quarter of the SP-Na⁺ concentration (Figure 5.25) thus the driving force for K⁺ IX onto RNRS-CZ would be lower. Both Na⁺ and K⁺ are commonly present in wastewaters and AnMBR permeate at concentrations high enough to significantly impact the TAN removal performance of CZ-IX processes (Boyer, 2014; Gupta et al., 2015; Wang & Peng, 2010). IX responsible for the release of TAN was facilitated by the presence of Ca²⁺ in the tap water make up solution (C₀ =150 mg Ca²⁺ l⁻¹) added to the recirculation solution reservoir to replace volume losses due to evaporation and leaks (Figure 5.27).

“Hard” tap water used during HBR recirculation supported the RNRS-HBR process because of the presence background divalent cations (Figure 5.26, left) that can support the release of TAN during RNRS-HBR (Figure 5.27). Removal of Na⁺, Ca²⁺, K⁺, and Mg²⁺ that was initially released during RNRS-HBR was observed until day 10, when a re-release of the ions was observed (Figures 5.27). The background ions that were present in solution during the HBR process are also present in many commercial hydroponic fertigation solutions, indicating a potential synergy between the HBR process that was demonstrated and hydroponic fertigation (Resh, 2013). For example, background sulfate was also present in the tap water used during the HBR process (Figure 5.26), however it is unlikely that sulfate ions contribute directly to the release of ammonium from the RNRS-clinoptilolite.

The increase in nitrification activity caused an initial decrease in the recirculation solution pH. The continuous addition of tap water to maintain constant reservoir volume and exposure to the atmosphere facilitated the continuous introduction of alkalinity and hardness into the system, resulting in stabilization of recirculation solution pH and accumulation of Ca²⁺. Continuous nitrification activity
Figure 5.25 TDS composition of the Na⁺-pretreated (left) and Mg²⁺-pretreated (right) RNRS column eluent solution recirculated continuously during HBR for 33 days.
Figure 5.26 TDS composition of tap water (left) and full-strength SP in HBR recirculation (right) for 32 days.
Figure 5.27 Na\(^+\), NH\(_4\)\(^+\), K\(^+\), and Ca\(^{2+}\) released during HBR of RNRS columns pretreated with 20 g/L NaCl (NB1) and 2 M MgCl\(_2\) (NB2).

Figure 5.28 Recirculation solution pH during HBR of Na\(^+\)-pretreated RNRS column (NB1) and Mg\(^{2+}\)-pretreated RNRS column (NB2)

5.3.3.2.1 HBR Recirculation: Nitrogen Mass Balance

The speciation of nitrogen observed during the recirculation study conveys that nitrification is the rate limiting reaction during the HBR process. TAN accumulation and nitrate production data from two RNRS-HBR processes (Figure 5.29) were used to calculate the RNRS TAN release rate during the HBR process. Mass balance analysis yielded second order TAN release rates and first order rate of nitrification.
throughout the 33-day HBR period. A second order rate expression of TAN accumulation was derived
through non-linear regression of TAN concentration in the systems. Observation of excess TAN
concentrations conveys nitrification as being the rate limiting step during the HBR process.

Figure 5.29 Total nitrogen accumulation during RNRS-HBR of two exhausted RNRS columns. NB1 with
Na+-pretreatment (left) and NB2 with Mg2+-pretreatment (right)

Each 15” (38.1cm) ZipGrow™ tower reached an apparent maximum nitrification rate of
approximately 52 mg N d⁻¹ per 15” ZGT (26.9 g N m⁻³ d⁻¹) and 44.7 mg N d⁻¹ per 15” ZGT (22.9 g N m⁻³
d⁻¹) in NB2 and NB1, respectively. Assuming a specific surface area (SSA) of 960 m²/m³ is provided by
the ZipGrow™ tower for biological nitrification (OEM specification), yielding nitrification rates of 0.03
and 0.02 g N m⁻² d⁻¹ for NB2 and NB1, respectively. For comparison, TAN removal rates for trickling
filters used in commercial aquaculture are reported in the range of 0.1 to 0.9 g m⁻² d⁻¹, however these
systems use filter material with SSA in the range of 100 to 300 m²/m³ implying a larger volume is
required to provide enough SSA (Ebeling et al., 2006).

5.3.4 Phosphate Recovery

The addition of MgO at a molar ratio of 1.2:1 Mg:P to batch adsorption vessels containing Ca²⁺-
CZ and diluted urine resulted in an average of 20% removal of TP. Initial solution TP concentration: C₀ =
165 mg PO₄³⁻P l⁻¹ and TAN: C₀ = 802 mg TAN l⁻¹. The addition of MgO reduced the TAN removal
performance of Ca²⁺-CZ by an average of 20% at CZ doses of 25, 50, 75, and 100 g CZ l⁻¹. Alternatively,
increasing zeolite dose above 5 g CZ l⁻¹ did not exhibit any apparent benefit to TP removal (Figure 5.30).
The mechanism attributed to TP removal was the precipitation of phosphate solids, i.e., struvite and calcium phosphates which has been documented in literature (Huang et al., 2014). Pretreatment of the RNRS column with 2 M MgCl₂ yielded a similar result of enhanced phosphate removal during the exhaustion cycle made apparent by the increased release of PO₄³⁻ during the HBR process (Figure 5.31).

Figure 5.30 TAN and TP removal of Ca²⁺-CZ in diluted urine with and without MgO addition.

Figure 5.31 Mg²⁺ and PO₄³⁻ concentrations RNRS column pretreated with Na⁺ (NB1) and Mg²⁺ (NB2).

Pretreatment of the RNRS with MgCl₂ resulted in a higher mass percentage of Mg²⁺ in the Mg²⁺-RNRS’s clinoptilolite observed during EDS analysis. During the RNRS exhaustion cycle, Mg²⁺ was
released in exchange for NH$_4^+$, Na$^+$, K$^+$, and Ca$^{2+}$. An increase in the surface concentration percentage of phosphorus was detected on the exhausted Mg$^{2+}$-pretreated zeolite samples detected during EDS analysis (Table 5.3). The surface of clinoptilolite samples taken from the Mg$^{2+}$-pretreated RNRS after 2 BV of synthetic permeate contained 8% higher phosphorus. However, surface magnesium concentration decreased while surface calcium increased, indicating a higher probability of the formation of calcium phosphate precipitates over magnesium ammonium phosphate (struvite) precipitates (Table 5.3). This observation corroborates work performed by Amini (2014) that reported a decrease in aqueous calcium concentrations of anaerobic digestion effluents after induced precipitation of phosphate (Amini, 2014), which can be expected given the high background concentration of Ca$^{2+}$ present in the tap water used in synthetic permeate solution (Figure 5.25 and Figure 5.26). An increase in surface phosphorus concentration was detected (Table 5.3 and Figure 5.32).

<table>
<thead>
<tr>
<th>Sample</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw CZ</td>
<td>42.79</td>
<td>0.18</td>
<td>0.63</td>
<td>6.73</td>
<td>37.06</td>
<td>4.06</td>
<td>5.18</td>
<td>-</td>
</tr>
<tr>
<td>Na$^+$-CZ</td>
<td>28.44</td>
<td>2.21</td>
<td>0.88</td>
<td>14.24</td>
<td>38.75</td>
<td>5.26</td>
<td>1.09</td>
<td>0.046</td>
</tr>
<tr>
<td>Mg$^{2+}$-CZ</td>
<td>41.87</td>
<td>1.47</td>
<td>1.31</td>
<td>7.38</td>
<td>40.70</td>
<td>4.14</td>
<td>2.54</td>
<td>0.59</td>
</tr>
<tr>
<td>Mg$^{2+}$-CZ after 2 BV SynPerm</td>
<td>41.70</td>
<td>0.000</td>
<td>0.71</td>
<td>7.37</td>
<td>39.78</td>
<td>4.53</td>
<td>3.33</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Figure 5.32 EDS imaging of phosphorus on Mg$^{2+}$-pretreated CZ before (left) and after (right) contact with synthetic AnMBR permeate.
5.4 Conclusions

5.4.1 RNRS TAN Recovery Performance

Pretreatment of RNRS clinoptilolite should consider the conditions of the service exhaustion cycle and waste stream characteristics. The SP solution used for RNRS column testing contained high sodium content, which hindered TAN removal. High concentrations of counter-ions in the waste streams intended for RNRS TAN recovery via CZ-IX result in breakthrough occurrence prior to reaching measured maximum uptake capacities, especially if a Ca\(^{2+}\)-form zeolite is used (Boyer, 2014).

Na\(^{+}\)-pretreated RNRS columns exhibited the most favorable TAN removal performance, exhibiting the capacity to service 20 BV of SP prior to reaching 10% breakthrough at service flow rate (SFR) of approximately 10 BV/h. The normalized operating AEC equated to approximately 5 mg NH\(_4^+\)-N g\(^{-1}\) NZ, nearly a sixth of the maximum adsorption capacity that was derived analytically under ideal conditions. Other studies have observed longer duration exhaustion cycles and higher operating AEC by lowering the SFR (increasing the column HRT). Adequate treatment of clinoptilolite prior to exhaustion cycle operation (pretreatment) or after TAN discharge into a hydroponic system via the HBR process (complete regeneration) should consider the use of sodium-based regenerant solutions as they have exhibited CZ regeneration efficiencies upwards of 97%.

5.4.2 RNRS TAN Release Performance

Tap water and calcium added to tap water can be used as eluent solutions to release RNRS bound TAN, yielding a TAN-containing solution that can support plant growth via fertigation. RNRS desorption solution presents advantages over the use of synthetic AnMBR permeate (SP) by mitigating the presence of materials commonly found in wastewater that would be deleterious to plant development if supplied in fertigation solution; sodium, chloride, and dissolved organic carbon such as acetate can negatively impact plant development, especially in hydroponic systems where plant roots are more vulnerable (Resh, 2013). TAN recovery from synthetic AnMBR permeate via RNRS intervention favored IX with ammonium over sodium, allowing the majority of AnMBR permeate-sodium to pass through during the nutrient charging
phase. Consequently, the effect of sodium is lowered in RNRS fertigation solution, proving favorable over direct use of AnMBR permeate as a hydroponic solution.

An additional advantageous phenomenon of passive phosphorus recovery and release was observed during RNRS operation. An increase in surficial calcium and phosphorus was detected on RNRS-zeolite granules after a nutrient charging phase. A noted increase in phosphate was then observed during the HBR process that correlated with increasing phosphorus and magnesium. It is concluded that dissolution of precipitated phosphorus occurred as a result of the decrease in pH due to nitrification activity.

5.4.3 Feasibility of Hydroponic Integration

The large requirement of tap water for RNRS desorption is avoided by the HBR process that recirculates tap water through the exhausted RNRS and vertical hydroponic columns simultaneously. This process facilitated passive RNRS regeneration by the combination of IX with tap water cations, i.e., $\text{Ca}^{2+}$, and nitrification resulting from continuous recirculation through vertical hydroponic columns. The vertical hydroponic columns provided passive aeration through plant support media eliminating the need for additional aeration and mixing equipment while serving a dual purpose as a biofilter for attached microbial growth and a hydroponic plant support structure (Storey, 2013). Nitrification rates during the RNRS-HBR process are initially outpaced by the RNRS-TAN release rate but begin to dominate after the initial high release of RNRS-TAN as the driving force of TAN-release is minimized. HBR recirculation released up to 7 g of TAN over the course of 33 days, equating to approximately 36% regeneration of the RNRS-CZ. Additional counter-ions should be added to HBR recirculation solution to enhance TAN-release rates. A potential method for introducing counter-ion to promote TAN release is to use carbonates of potassium, calcium, or magnesium which would provide dual benefits of increased counter-ion concentration and buffering of pH drops resulting from increased nitrification activity. Alkalinity can be sourced locally and added to local, hydroponic systems to support the HBR process, for example alkalinity can be derived from potash produced or oyster shells (Miller, 1980; Xiong & Ye, 2006).
CHAPTER 6: SUSTAINABILITY ANALYSIS

6.1 Introduction

Technological advancement plays an important role in increasing quality of life while decreasing waste. Common metrics used to gauge the performance of a technology include efficiency: a ratio of resource outputs to resource inputs, and economic costs. However, it is important to consider that technological solutions do not operate inside of a vacuum and are part of a larger system where economic impacts are not the only parameter of interest when considering the sustainability of the larger system. Sustainability requires not only favorable economic performance, but beneficial social and more importantly, environmental impacts as well; sometimes referred to as the triple-bottom line.

Environmental engineers tasked with the development of sustainable technical and/or practical solutions must assess the sustainability of these solutions to aid in the decision-making process regarding the implementation of solutions (Mihelcic et al., 2017).

Life Cycle Analyses (LCA) are used to quantify the environmental impacts of products, processes, and/or services in different contexts, providing a widely accepted metric for environmental performance. The International Organization for Standardization created standards (ISO 14040 and ISO 14044) that outline the best practices for conducting LCAs (ISO 2006a, ISO 2006b). This chapter uses the LCA framework defined by ISO 14040 to assess the environmental impacts associated with the life cycles of various nitrogen removal systems that are appropriate for complimenting a decentralized sanitation process based off the anaerobic membrane bioreactor (AnMBR) platform. Engineering design, operational parameters, and system assumptions were derived from literature and experimental findings in previous chapters of this work. A life cycle-cost analysis (LCCA) is performed to assess economic
impacts associated with material acquisition, system operation, and waste disposal for the treatment scenarios assessed.

### 6.1.1 System Background

The system considered for this assessment is a decentralized, non-sewered sanitation system (NSSS) designed to treat waste generated by a small community (approximately 100 people per day for 10 years) in compliance with ISO 30500 for wastewater treatment and water recycling performance. The AnMBR technology platform is considered for this assessment based on proven performance for COD and TSS removal and the requirement for TAN removal from AnMBR permeate to meet ISO 30500 standard (Bair et al., 2015; Harb & Hong, 2017; Jain, 2018). Relevant operational parameters for the AnMBR system considered in this study are listed in Table 6.1. ISO 30500

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design Users per day</td>
<td>100</td>
<td>users/day</td>
</tr>
<tr>
<td>Membrane operation duration</td>
<td>16</td>
<td>hours/day</td>
</tr>
<tr>
<td>Q\textsubscript{permeate}</td>
<td>75</td>
<td>L/h</td>
</tr>
<tr>
<td>MAX daily Q\textsubscript{permeate}</td>
<td>1200</td>
<td>L/day</td>
</tr>
<tr>
<td>AnMBR Permeate (TAN)</td>
<td>120</td>
<td>mg/L NH\textsubscript{3}-N</td>
</tr>
<tr>
<td>AnMBR Permeate TN</td>
<td>150</td>
<td>mg/L N</td>
</tr>
<tr>
<td>AnMBR Permeate TP</td>
<td>30</td>
<td>mg/L PO\textsub{4}^{3-}-P</td>
</tr>
</tbody>
</table>

This assessment also considers the material and energy inputs for an electrochlorination process downstream of the TAN removal system as the presence of TAN can significantly affect the function and duration of the chlorination process (White, 2010). The electrochlorination system that is considered is an electrolytic diaphragm cell that via electrolysis of Cl\textsuperscript{-} in an aqueous solution can generate chlorine gas on-site providing disinfection and a chlorine residual for recycled water used for flushing sanitation infrastructure. ISO 30500 mandates a 70% removal of the influent wastewater’s total nitrogen (TN) content to remain in compliance, thus several nitrogen removal systems that can feasibly integrate with the AnMBR platform are considered for environmental impact and economic assessment. ISO 30500 also mandates the use of the metric system of measurement, therefore all system specifications and parameters are reported as such. Other ISO 30500 performance parameters that are relevant to choosing possible
technologies include: 80% TP removal, noise requirements (ISO 30500:2018), air emissions, expected design lifetime, aspirational and ergonomic design, and minimal chemical and biological additives.

Figure 6.1 Graphical representation of a decentralized, wastewater recycling facility serving a small community. This model depicts NSSS scenario where the community (1), dwells near a front-end sanitation interface (2) where wastewater is collected for treatment by an AnMBR NSSS (3). Recovered water (4) is recycled to the front-end sanitation component for re-use in flushing of sanitary components. Recovered nutrients and water (5) are reused for fertigation of nearby crops.

6.2 Materials and Methods

6.2.1 Life Cycle Analysis

The steps for conducting a Life Cycle Assessment were performed pursuant to ISO 14040. The first of the four phases of the LCA (Figure 6.2) identifies the intended purpose of the assessment. The second phase of the LCA is the life cycle inventory (LCI), which involves the gathering of input/output data about the system(s) being studied as they pertain to the goals defined in the first phase. The third phase of the LCA is the life cycle impact assessment (LCIA) which calculates the environmental significance of the input/output data of the LCI of the systems being studied. The final phase of the LCA is the interpretation phase in which the results from the LCIA and the LCI are summarized and discussed.
to draw conclusions and recommendations to support decision-making aligning with the goal and scope defined earlier in the LCA.

Figure 6.2 The four phases of the LCA and their influence upon each of the other phases.

6.2.1.1 Goal and Scope

The goals of this LCA are to quantify the potential impacts to human and environmental health resulting from the fabrication and operation of several TAN removal treatment scenarios designed to facilitate compliance with ISO 30500 for an AnMBR-NSSS treating wastewater generated by a community sanitation facility. The system boundary for LCA purposes encompasses “cradle to use”, which includes raw material extraction, processing, production, transport of consumable and waste materials, operation, and the reuse of recovered materials throughout the lifetime of the system analyzed.

Figure 6.3 provides a graphical representation of the processes and products considered within the boundary of this assessment. The provision of nitrogen fertilizer for plant cultivation within the community is considered in the scope of this analysis to assess potential benefits of recovering nitrogen fertilizer for reuse benefitting the local community serviced by the NSSS. Compliance with ISO 30500 mandates that NSSS effluents demonstrate a minimum of 80% removal of total phosphorus and are within
a pH range of 6 to 9, considerations for meeting these requirements are not considered within the scope of this assessment.

![Figure 6.3 Depiction of the system boundary used for the LCA of TAN removal systems](image)

The functional unit defines the basis upon which each of the treatment systems will be evaluated and compared. The desired function of the systems is to provide total nitrogen (TN) removal for a non-sewered sanitation platform pursuant to ISO 30500:4.5 (i.e., 70% removal of TN). Therefore, the functional unit (FU) considered for this analysis is the daily removal of 90% of the AnMBR permeate TAN for 10 years. A 90% TAN removal target was chosen because approximately 80% of the permeate TN concentration is comprised of TAN, thus 90% removal of AnMBR permeate TAN would still comply with ISO 30500 by achieving at least 72% removal of total influent nitrogen.

### 6.2.1.1 Evaluation Scenarios

Several treatment scenarios applicable for removing TAN from the AnMBR-NSS were considered for this assessment to compare their environmental impacts and economic performance. The evaluation scenarios for consideration are listed below along with the respective short-hand identifier:

1. Electrochlorination (EC)
2. Reusable Nutrient Recovery System with biological regeneration (RNRS+BR)
3. Clinoptilolite ion-exchange fixed bed with chemical regeneration (IX+CR)

4. Clinoptilolite ion-exchange without regeneration (IX+NR)

Details describing the major components of each treatment scenario and accompanying flow diagrams are included in the following sections. The system descriptions explain how each treatment system is designed to operate to meet the requirements established in ISO 30500.

6.2.1.1.1 Electrochlorination

TAN removal in this scenario is accomplished through breakpoint chlorination. AnMBR permeate is conveyed to a vessel for chlorination with Cl₂ gas generated onsite. NaCl, electricity, and tap water are considered the main inputs of the system. No additional TAN removal components are needed as the decentralized AnMBR of this study is already equipped with an electrolysis cell, however the anticipated burden of TAN present during chlorination is assumed to shorten the life expectancy of the electrolytic cell, prompting replacement during the AnMBR-NSSS life cycle. This scenario is considered the “do-nothing” scenario as no additional components for TAN removal are required. A system flow diagram of this TAN removal scenario is provided in Figure 6.4.

Figure 6.4 System flow diagram of the electrochlorination scenario.
No TAN is recovered in this scenario, so nitrogen fertilizer is considered additional input required to meet the needs of the local community to facilitate crop production. Other outputs considered for this scenario include H$_2$ gas and 50% sodium hydroxide solution produced as by-products of the electrolysis process (White, 2010).

### 6.2.1.1.2 RNRS with Hydroponic-BioRegeneration

TAN removal in this scenario is performed by IX using clinoptilolite zeolite (CZ) within RNRS columns that were introduced in earlier chapters of this dissertation. At the end of the exhaustion cycle (determined experimentally in the previous chapter), regeneration is commenced by transporting exhausted RNRS columns to nearby vertical, hydroponic cultivation systems for desorption into the recirculating hydroponic fertigation solution reservoir. Electrical energy input is required to power recirculation pumps operating 24 hours a day to facilitate adequate mixing, aeration, and nitrification in the hydroponic system(s). The TAN released into the recirculating hydroponics systems undergoes nitrification, accumulating nitrate-nitrogen in the hydroponic solution, replacing the need for nitrogen fertilizer (i.e., avoided product). Additional chemical and material inputs to support the biological regeneration process within the hydroponic system (e.g., alkalinity from calcium carbonate and/or potassium carbonate) are considered (Boyer, 2014; Ergas & Aponte-Morales, 2014). When most of the RNRS-NZ has been regenerated, a 10% NaCl solution is used to pretreat the RNRS-NZ prior to each subsequent sorption phase. A system flow diagram of the RNRS+BR treatment scenario is depicted in Figure 6.5.

![Figure 6.5 System flow diagram of the RNRS + biological regeneration scenario](image)
6.2.1.1.3 CZ-IX Fixed Bed: Chemical Regeneration

AnMBR permeate TAN removal is performed through ion exchange (IX) using CZ and chemical regeneration (CR) to facilitate reuse of CZ materials (IX+CR). A vertical tank (V=0.23 m$^3$) provides a larger bed volume (BV) than the RNRS while maintaining consistency with the low-footprint design of the AnMBR-NSSS. The increased CZ BV implies that TAN breakthrough is reached with much less frequency, requiring fewer regeneration cycles in a given year of operation. The exhaustion cycle is performed in up-flow mode at the AnMBR membrane flow rate (Q = 75 l h$^{-1}$). When breakthrough is reached in the first column, an operator will switch AnMBR permeate flow to a second fixed-bed column containing CZ to maintain continuous operation pursuant to ISO 30500. Chemical regeneration (CR) of the exhausted NZ column is performed in counter-current mode with a 10% NaCl solution (Crittenden, 2012). Spent regenerant solution is transported to an off-site facility for treatment. The impacts associated with the mass and distance of transported materials required to perform this regeneration are accounted for in this LCA; the impacts associated with off-site treatment are not accounted for in this study. TAN is not recovered for use on-site, thus the production, purchase, and transport of nitrogen fertilizer are considered additional inputs required meet the nitrogen fertilizer demands of the community. A system flow diagram of the IX+CR TAN removal scenario is provided in Figure 6.6.

![System flow diagram for the IX+CR scenario.](image-url)
6.2.1.1.4 CZ-IX Fixed-Bed: No Regeneration

This treatment scenario closely resembles the previous scenario as the exhaustion cycle of the CZ-IX process is identical. However, once exhaustion is reached in the first column, the column is removed from service and emptied. Virgin zeolite is purchased and transported to replace the exhausted CZ material. Exhausted zeolite is then transported off-site for disposal or marketed as a soil amendment product providing revenue. The context of this assessment describes a requirement by the community for nitrogenous fertilizer for use in a hydroponic system, therefore the spent zeolite would not be considered appropriate for hydroponic use in its loose form as loose NZ particles would cause damage to equipment. Additionally, storage of large quantities of spent zeolite on-site is not considered a feasible option given the low footprint of the NSSS. The spent zeolite fertilizer value was assumed to be 10% of the market value of the respective synthetic nutrient fertilizer equivalent. A system flow diagram of this TAN removal scenario is provided in Figure 6.7.

![Figure 6.7 System flow diagram of the IX+NR scenario.](image)

6.2.1.2 Life Cycle Inventory

Data used to generate LCIs of the treatment scenarios was gathered from literature, industry practitioners, and original equipment manufacturer (OEM) specifications to inform engineering design calculations. Experimental data from previous chapters were used to model the performance of the RNRS
In general, assumptions for calculation of treatment scenario inputs and outputs were made to achieve performance specifications set forth by ISO 30500, outlined in Chapter 4, (e.g., system operating life of 10 years, 70% removal of total nitrogen, etc.).

Table 6.2 Design assumptions for LCI input/output calculations

<table>
<thead>
<tr>
<th>Assumption Item</th>
<th>Assumption Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl required for electrolytic Cl\textsubscript{2} generation</td>
<td>Reaction stoichiometry derived to yield a minimum Cl\textsubscript{2}:N mass ratio of 12:1 for breakpoint chlorination of WW</td>
<td>White (2010)</td>
</tr>
<tr>
<td>Energy for electrolytic cell</td>
<td>Reaction stoichiometry, Faraday’s law: 135,000 Amps yields 9053 lbs. Cl\textsubscript{2} per day</td>
<td>White (2010)</td>
</tr>
<tr>
<td>Number of IX BV treated before 10% BT (90% TAN removal)</td>
<td>Experimentally derived; supported by values in literature</td>
<td>Boyer (2014); Hedstrom, (2001)</td>
</tr>
<tr>
<td>CZ replenishment rate</td>
<td>10% of BV after 5 regeneration cycles</td>
<td>(Deng et al., 2014; Guo et al., 2013)</td>
</tr>
<tr>
<td>TAN Removal Efficiency</td>
<td>90% TAN removal to ensure 70% TN removal assuming AnMBR permeate TAN:TN ratio of 0.8</td>
<td>(Bair et al., 2015; Prieto et al., 2013)</td>
</tr>
<tr>
<td>Avg. material transport distance</td>
<td>Assumed arbitrary distance of 20 km</td>
<td>-</td>
</tr>
<tr>
<td>Chemical regeneration solution</td>
<td>10 BV of 10% NaCl solution typical industry design value</td>
<td>Crittenden (2012)</td>
</tr>
<tr>
<td>Regenerant volume required for chemical regeneration</td>
<td>10 BV conservative value from industry practice</td>
<td>Crittenden (2012)</td>
</tr>
<tr>
<td>Recirculation Pump Power Wattage</td>
<td>Assumed 50 Watts</td>
<td>OEM specs</td>
</tr>
<tr>
<td>ZipGrow™ Tower SSA</td>
<td>147 m\textsuperscript{2} tower\textsuperscript{-1}</td>
<td>OEM specs</td>
</tr>
<tr>
<td>Nitrification rate</td>
<td>Conservative value of 0.1 g N m\textsuperscript{-2} d\textsuperscript{-1}; range for trickling filters reported in literature: 0.1-0.9 g N m\textsuperscript{-2} d\textsuperscript{-1}</td>
<td>Ebeling et al. (2006)</td>
</tr>
<tr>
<td>Alkalinity requirement</td>
<td>Derived stoichiometrically (7.14 g CaCO\textsubscript{3} g N\textsuperscript{-1})</td>
<td>Ebeling et al. (2006)</td>
</tr>
<tr>
<td>Spent zeolite nutrient content</td>
<td>1% K\textsubscript{2}O as KNO\textsubscript{3} by mass; 2% NH\textsubscript{4}\textsuperscript{+}-N by mass</td>
<td>Amini et al. (2017)</td>
</tr>
</tbody>
</table>

The scope of this assessment does not include consideration of methods for removing total phosphate, thus the AnMBR permeate total phosphate (TP) content is considered to remain constant through the treatment scenarios and is represented as an emission an unspecified water source, in consistence with methods demonstrated by Lin et al. (2016) (Lin et al., 2016). The operational
specifications of the AnMBR-NSSS further establish an operational cycle lasting 16 hours a day, implying AnMBR permeate is being generated 16 hours each day. The operation cycle affected the exhaustion cycle time as the IX process is considered stagnant while the AnMBR-NSS is not operating. The daily 8 h stagnation period is assumed to have no effect on the exhaustion cycle and the kinetics of CZ-IX are relatively fast (Boyer, 2014). The electrochlorination process used for disinfection and breakpoint chlorination in the AnMBR-NSSS consists of an electrolytic diaphragm cell is used to produce chlorine gas via electrolysis of a highly concentrated NaCl solution through the following overall reaction (White, 2010):

\[
\text{NaCl + H}_2\text{O} \xrightarrow{\text{electricity}} \text{NaOH} + \frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{H}_2
\]  

[Eq. 6.1]

### 6.2.1.3 Life Cycle Impact Assessment

The life cycle impact Assessment (LCIA) was calculated using SimaPro Version 7 software (PRé Sustainability BV, Amersfoort, The Netherlands). The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI) impact analysis method was used to quantify potential human and environmental health stressors impacts across nine categories: global warming potential (GWP), acidification, carcinogenic compounds, harmful yet non-carcinogenic compounds, respiratory effects, ozone depletion, eutrophication, ecotoxicity, and smog (Bare, 2002). A one percent cut-off is applied to focus on significant impacts associated with the operation and materials used by each of the treatment scenarios. An additional assumption made pertains to the inventory data regarding the supply chain of clinoptilolite materials. Information regarding the raw material extraction and processing practices for clinoptilolite is insufficient, thus bentonite was used as a surrogate material input for LCIA analysis as the material extraction, processing, and supply chain processes are similar (Amini, 2014). The cation exchange capacity (CEC) of the clinoptilolite used for IX under the permeate conditions specified by the AnMBR-NSSS were assumed to be 10 and 20 percent by weight for K\(^+\) and NH\(_4^+\), respectively. The assumed CEC was used to calculate recovered nutrient fertilizer mass quantities or consideration as avoided product (Lin et al., 2016).
6.2.2 Life Cycle-Cost Analysis

The expected life-time costs for each of the treatment scenarios was calculated by performing a life-time cost assessment (LCCA) according to the standard procedure established in ISO 15686-5, using the input/output data resulting from the LCI. Capital expenses (CAPEX) and operating expenses (OPEX) were derived using the information from commercial manufacturers and literature. OPEX are assumed to be recurring costs that will be incurred in the future; representing these costs as a present value requires conversion to the uniform present value (UPV). The UPV for the OPEX of each system was calculated by applying a UPV factor to the calculated annual OPEX value. The UPV factor is calculated using an assumed interest rate of 6%, and assumed system lifespan of 10 years, and equation 6.2.

\[
\text{UPV factor} = \frac{1-(1+i)^{-n}}{i} = \frac{1-(1+0.06)^{-10}}{0.06} = 7.36
\]  

[Eq. 6.2]

where “i” represents the assumed interest rate. The CAPEX is already represented as net present value (NPV). Payback periods, if applicable, were calculated by division of the total CAPEX by the total income OPEX; the UPV is not applied in this calculation. The electrochlorination treatment scenario (scenario 1) is considered the “as-is” or “do-nothing” scenario where no additional infrastructure is allocated for TAN removal. Material and energy inputs resulting from the burden of increased TAN content at the final chlorination process are calculated and compared to the calculated lifetime costs of the systems proposed. A cost per kg of TAN removed is also calculated by dividing the total lifetime cost by the theoretical total mass of TAN removed over the systems’ lifetimes.

6.2.3 Sensitivity Analyses

Sensitivity analyses were used to assess impact of uncertain variables, e.g., electricity source, distance for transport of bulk goods, and zeolite treatment capacity. The sensitivity analyses also considered the impact of carbon taxation on the LCCA for each treatment scenario. The production of CO₂ mass equivalents for functional units of goods and services is relevant to the economic Carbon taxation provides an economic incentive for implementing sustainable designs that initially appear more
expensive in terms of the NPV of CAPEX and OPEX alone, therefore a scenario that considers the reality of carbon taxes imposed based on CO₂ generation is relevant for analysis.

6.3 Results and Discussion
6.3.1 Life Cycle Inventory Results

The overall results of the LCI analysis for each of the treatment scenarios is summarized in Table 6.2. The anticipated daily TAN loading rate was calculated to be 144 g TAN/day based on an assumed average AnMBR permeate TAN concentration of 120 mg/l NH₃-N, flow rate of 75 l/h, and run time of 16 h/day. TAN treatment system infrastructure and operation parameters were designed for IX operation until 90% breakthrough was reached. The RNRS+BR treatment scenario required significant system infrastructure to be able to meet ISO 30500 requirements for continuous operation of the AnMBR-NSSS considered in this study.

<table>
<thead>
<tr>
<th>LCI Inventory Item</th>
<th>RNRS+BR</th>
<th>IX+CR</th>
<th>IX+NR</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank/Housings (no.)</td>
<td>40</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Total treatment train series</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cartridges (no.)</td>
<td>50</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Clinoptilolite requirement (kg/y)</td>
<td>44</td>
<td>198</td>
<td>2190</td>
<td>0</td>
</tr>
<tr>
<td>Energy Requirement (kWh/y)</td>
<td>4.4</td>
<td>0.1</td>
<td>2979.6</td>
<td>0</td>
</tr>
<tr>
<td>NaCl requirement (kg/y)</td>
<td>671</td>
<td>2102</td>
<td>0</td>
<td>780</td>
</tr>
<tr>
<td>Nitrogen recovered per year (kg N/y)</td>
<td>32</td>
<td>0</td>
<td>47</td>
<td>0</td>
</tr>
<tr>
<td>Potassium recovered (kg K/y)</td>
<td>3</td>
<td>0</td>
<td>131</td>
<td>0</td>
</tr>
<tr>
<td>Transport (kg*km)/y</td>
<td>16240</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>H₂ gas Emissions (kg H₂/y)</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>ZipGrow Towers (no.)</td>
<td>438</td>
<td>442</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Water Use (m³/yr.)</td>
<td>10</td>
<td>38</td>
<td>38</td>
<td>n/a</td>
</tr>
</tbody>
</table>

The amount of transport, represented as km* kg, was higher in treatment systems that required regular inputs of NaCl, nitrogen fertilizer, and transport of chemical regenerant materials back and forth. The IX+CR scenario amassed a large quantity of transport km*kg as transport of large volumes of regenerant solution to and from the site were required. The long exhaustion cycles of the IX+CR and IX+NR systems minimized the frequency of regeneration, therefore minimizing the km*kg needed to
transport spent zeolite. High water use is required in regenerated system to facilitate the release of CZ-bound TAN recovered from AnMBR permeate.

The electrochlorination treatment scenario (EC) was calculated to require an annual NaCl input of 780 kg to produce enough Cl₂ for breakpoint chlorination. The Cl₂ mass requirement for breakpoint chlorination of AnMBR of most of the TAN and any resulting chloraminated compounds was based on a Cl₂:N mass ratio of 10:1 recommended for chlorination of WW to reach breakpoint chlorination (White, 2010). The relatively high inputs for transport resulted from the mass of NaCl and fertilizer that required transport to the NSSS location (average travel distance assumed = 20 km).

<table>
<thead>
<tr>
<th>Table 6.4 LCI for electrochlorination treatment scenario</th>
<th>Input Parameter</th>
<th>Quantity</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual chlorine demand for 90% N-removal (10:1 mass Cl₂:N)</td>
<td>525.6</td>
<td>kg Cl₂/yr.</td>
<td></td>
</tr>
<tr>
<td>EC Salt Demand</td>
<td>866.5</td>
<td>kg NaCl/yr.</td>
<td></td>
</tr>
<tr>
<td>Electricity demand (current efficiency = 95.8%) (White, 2010)</td>
<td>17243.25</td>
<td>amps/yr.</td>
<td></td>
</tr>
<tr>
<td>EC yearly power consumption</td>
<td>3310.7</td>
<td>kWh/yr.</td>
<td></td>
</tr>
<tr>
<td>H₂ gas production</td>
<td>14.9</td>
<td>kg H₂/yr.</td>
<td></td>
</tr>
<tr>
<td>Replacement electrolytic diaphragm cell</td>
<td>1</td>
<td>count</td>
<td></td>
</tr>
</tbody>
</table>

6.3.2 Life Cycle Environmental Impact Analysis Results and Interpretation

The results of the impact analysis reflect the environmental impacts associated with the assembly and operation of the TAN removal systems throughout the designed, 10-year operational lifespan. Treatment scenario contributions to each of the impact categories defined by the TRACI method are depicted in Figures 6.8-6.13. The environmental impact associated with the production of power-grid electricity accounted for most of each treatment scenario’s impact. Figure 6.8 conveys the impacts of the treatment scenarios with solar photovoltaic (PV)-generated electricity to power pumps for regenerant solution recirculation and electrochlorination.

The IX+NR scenario generated the greatest impacts across all impact categories as calculated by the TRACI impact assessment method. Figure 6.8 conveys the processes of the IX+NR treatment scenario and their effect across each of the impact categories throughout the treatment scenario service lifetime. The high consumption of clinoptilolite (modeled as bentonite) required continuous TAN removal which was responsible for generating the majority of the IX+NR treatment scenario’s impact. The RNRS+BR
system generated the lowest total amount of CO$_2$ equivalents used to calculate the global warming potential (GWP). The avoided nitrogen and potassium fertilizer products significantly reduced impacts on GWP, acidification, and smog. Though electricity usage in the RNRS+BR system was low, the observations represented in Figure 6.4 imply a 50% reduction of GWP is achieved using solar PV energy to power the hydroponic recirculation pumps.

![Figure 6.8](image)

**Figure 6.8** Regeneration process energy source effect on LCIA for TAN removal scenarios across four environmental impact categories. Impact categories are reported as follows: eutrophication (a), global warming potential (GWP)(b), ecotoxicity (c), respiratory effects (d), acidification (e), and smog (f).

Figure 6.9 conveys the percent of impact contributed by specific processes in the RNRS+BR treatment scenario for each impact category. The relatively high eutrophication, carcinogenic, non-carcinogenic, and eco-toxicity impacts calculated for RNRS+BR treatment (Figure 6.9) are attributed to the assembly of the plastic components used in the RNRS+BR treatment system and the extraction and processing of natural zeolite. 90% recovery of TAN for use as a nitrogen fertilizer was calculated to offset GWP, acidification, respiratory, and smog impacts by diverting fertilizer production (Figure 6.9). Further
reduction of environmental impacts may be possible by redesigning the RNRS infrastructure to minimize the use of plastic components. Additionally, the use of lower-cost, natural, and/or local sources of alkalinity like oyster shells or potash can offset requirements for limestone which can further lower ecotoxicity impacts (Liu et al., 2010).

![Figure 6.9 RNRS+BR LCIA process impacts across nine TRACI categories](image)

The IX+CR scenario required large NaCl input for each regeneration cycle which was the largest impact contribution in each category (Figure 6.10). The inability of the chemical regeneration method to recover nutrient resources resulted in additional impacts associated with the production and delivery of synthetic fertilizers to the site. The IX+CR process potentially contributes more environmental impact outside of the system boundary considered in this study as spent regenerant solution is transported offsite for treatment. Methods for recovering TAN from spent regenerant brines are well developed and discussed in Chapter 2, but those methods are not considered feasible for using in a NSSS due to their material, energy, and process control requirements (Deng, 2014; Trotochaud et al., 2019).

The treatment process for the spent regenerant is assumed to be executed at a wastewater treatment facility, however the pertinent input data considered in this assessment was transport to the offsite treatment facility and an assumed cost of treatment per m$^3$, reflected in LCCA in the following section. IX+NR treatment consisted of two main inputs to achieve continuous removal of TAN within the AnMBR-NSS: the acquisition and transport of virgin clinoptilolite to replace exhausted materials, and
electrochlorination of the IX process effluent. The impacts with clinoptilolite extraction and processing (modelled as bentonite) compounded to yield significant impacts across all categories for this scenario (Figure 6.11).

![Figure 6.10 IX+CR treatment process impacts across nine TRACI categories](image)

EC treatment required significant input energy to facilitate the electrolytic process to generate Cl\(_2\) gas using concentrated brine made with NaCl delivered to the NSSS site. NaCl is considered widely available and affordable, suitable for use in NSSS. However, due to the lack of a TAN removal or buffer component, the EC process was overburdened, resulting in high use of both electricity and NaCl. Also, it has recently been noted that electrochlorination processes’ primary function should not be TAN removal via breakpoint chlorination in NSSS as the high concentration of TAN as well as dissolved organic compounds can yield carcinogenic compounds during the oxidation process (Trotochaud et al., 2019; White, 2010).

Furthermore, there is insufficient field data regarding the expected life-span of electrolytic diaphragm cells used for electrochlorination of wastewater under the proposed operating conditions. The
components most prone to failure in the electrolytic cell are the electrodes which are made of costly noble metals that would require replacement or chemical additives to extend their life-spans via polarization, representing materials and costs not considered in this assessment, though likely to increase both environmental and economic impacts of EC treatment (Trotochaud et al., 2019; White, 2010).

Additionally, the relatively high concentration of TAN yields a relatively high chlorine demand due to the numerous by-products that result from the interaction of chlorine with ammonia-nitrogen (White, 2010).

Figure 6.11 LCIA of IX+NR treatment per kg TAN removed.
Figure 6.12 LCIA of EC treatment per kg of TAN removal

GWP is a widely recognized metric used to quickly gauge the impacts a product or practice will have in terms of greenhouse gas production (Hauschild et al., 2018). Powering electricity-intensive processes with electricity generated from solar photovoltaic (PV) cells instead of electricity from fossil-fuel powered electric grids can substantially lower impacts of GWP. GWP associated with EC treatment was lowered 90% when PV energy was considered (Table 6.5). The use of PV energy is consistent with NSSS design and off-grid operation capacity.

Table 6.5 Impact of electric power source in mitigating GWP in terms of kg CO\(_2\) eq. generated per kg TAN removed in NSSS.

<table>
<thead>
<tr>
<th>Power Source</th>
<th>RNRS+BR</th>
<th>IX+CR</th>
<th>IX+NR</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric grid (mixed sources)</td>
<td>2.50</td>
<td>11.04</td>
<td>23.60</td>
<td>46.96</td>
</tr>
<tr>
<td>Solar PV</td>
<td>1.25</td>
<td>10.54</td>
<td>19.38</td>
<td>4.8</td>
</tr>
</tbody>
</table>

6.3.3 Life Cycle-Cost Analysis Results

The overall results of the life cycle-cost analysis are based off LCI input data for 10 years of AnMBR-NSS and TAN removal system operation. An interest rate of 6% was used to calculate the
present values of yearly operating costs for the LCCA. Table 6.3 contains CAPEX and OPEX values for the TAN treatment systems in the base operating scenario where power for pertinent system functions is provided from the electrical grid at an assumed cost of $0.20/kWh (Table 6.6).

Table 6.6 LCCA summary for TAN removal systems (electricity from grid)

<table>
<thead>
<tr>
<th>Treatment Scenario</th>
<th>Expenditure Type</th>
<th>Base Date Cost ($)</th>
<th>Present Value; NPV ($)</th>
<th>Lifetime Cost ($)</th>
<th>Payback Period (Y)</th>
<th>Cost per kg TAN Removed $</th>
<th>kg CO₂/kg TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNRS + BR</td>
<td>CAPEX</td>
<td>3667.54</td>
<td>3667.54</td>
<td>4188.09</td>
<td>42</td>
<td>8.85</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>70.73</td>
<td>520.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX + CR</td>
<td>CAPEX</td>
<td>1676.51</td>
<td>1676.51</td>
<td>4134.16</td>
<td>-</td>
<td>8.74</td>
<td>11.04</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>333.92</td>
<td>2457.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX w/o Regen</td>
<td>CAPEX</td>
<td>1587.21</td>
<td>1587.21</td>
<td>3660.61</td>
<td>31</td>
<td>7.74</td>
<td>23.60</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>281.71</td>
<td>2073.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochlorination</td>
<td>CAPEX</td>
<td>1430.00</td>
<td>1430.00</td>
<td>8377.26</td>
<td>-</td>
<td>15.94</td>
<td>46.96</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>943.91</td>
<td>6947.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Changing power supply from grid power to PV reduced EC treatment scenario OPEX by 60%.

The assumed rate for electricity derived from PV was $0.03/kWh. It was assumed that at least three additional PV panels ($1.20/watt) would be needed upon system startup contributing to the CAPEX of the RNRS+BR systems. The locations for bio regeneration of exhausted RNRS columns can be separate, following a hub and spoke model of a network where the NSSS site is the hub where TAN is accumulated in the RNRS column. Then exhausted columns are transported to various bioregenerative fertigation applications offsite creating various locations of “spokes” to the NSSS hub, however each bioregeneration location will require power for recirculating the desorption/fertigation solution.

Table 6.7 LCCA summary for TAN removal systems (solar-PV powered)

<table>
<thead>
<tr>
<th>Treatment Scenario</th>
<th>Expenditure Type</th>
<th>Base Date Cost ($)</th>
<th>Present Value; NPV ($)</th>
<th>Lifetime Cost ($)</th>
<th>Payback Period (Y)</th>
<th>Cost per kg TAN Removed $</th>
<th>kg CO₂/kg TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNRS + BR</td>
<td>CAPEX</td>
<td>4027.54</td>
<td>4027.54</td>
<td>4515.07</td>
<td>45</td>
<td>8.89</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>69.98</td>
<td>4542.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX + CR</td>
<td>CAPEX</td>
<td>1677.71</td>
<td>1677.71</td>
<td>4135.17</td>
<td>-</td>
<td>8.74</td>
<td>10.54</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>333.89</td>
<td>2457.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX+NR</td>
<td>CAPEX</td>
<td>1587.21</td>
<td>1587.21</td>
<td>3660.61</td>
<td>31</td>
<td>7.74</td>
<td>19.38</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>281.71</td>
<td>2073.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>CAPEX</td>
<td>2110.28</td>
<td>2110.28</td>
<td>4926.78</td>
<td>-</td>
<td>9.18</td>
<td>4.80</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>382.67</td>
<td>2816.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Solar PV operation slightly increased the cost of operating the RNRS+BR system, but greatly reduces the cost of EC, which is used to a degree in all scenarios. Off-grid power generation is a must-have for NSSS operating in challenging, off-grid contexts, thus is worth the extra investment.

Table 6.8 LCCA of treatment scenarios with $15/metric ton CO$_2$ carbon tax

<table>
<thead>
<tr>
<th>Treatment Scenario</th>
<th>Expenditure Type</th>
<th>Base Date Cost ($)</th>
<th>Present Value; NPV ($)</th>
<th>Lifetime Cost ($)</th>
<th>Payback Period (Y)</th>
<th>Cost per kg TAN Removed $</th>
<th>kg CO$_2$/kg TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNRS + BR</td>
<td>CAPEX</td>
<td>3667.54</td>
<td>3667.54</td>
<td>533.60</td>
<td>4201.13</td>
<td>8.88</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>72.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX + CR</td>
<td>CAPEX</td>
<td>1713.67</td>
<td>1713.67</td>
<td>503.18</td>
<td>4201.13</td>
<td>11.45</td>
<td>11.04</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>503.18</td>
<td></td>
<td>3703.42</td>
<td>5417.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX w/o Regen</td>
<td>CAPEX</td>
<td>1587.21</td>
<td>1587.21</td>
<td>302.31</td>
<td>3812.24</td>
<td>8.06</td>
<td>23.60</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>302.31</td>
<td></td>
<td>2225.03</td>
<td>3812.24</td>
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<tr>
<td>Electrochlorination</td>
<td>CAPEX</td>
<td>1430.00</td>
<td>1430.00</td>
<td>416.00</td>
<td>4491.77</td>
<td>16.22</td>
<td>46.96</td>
</tr>
<tr>
<td></td>
<td>OPEX</td>
<td>416.00</td>
<td></td>
<td>3061.77</td>
<td>4491.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.4 Conclusions

The results of the LCIA convey that the TAN removal treatment scenario that generated least environmental impact in terms of GWP was the RNRS+BR treatment scenario. This treatment scenario minimized material consumption while recovering nutrient fertilizer for simultaneous IX-regeneration and hydroponic fertigation. The use of solar photovoltaic energy as a power source further reduced impacts across all treatment scenarios except IX+NR as electrical energy input for this scenario was minimal.

Observation of the impact contributions across the TRACI categories consistently showed the production of potassium carbonate as the main contributor to impact for the RNRS+BR scenario (Figure 6.6). Therefore, it is possible to significantly decrease the environmental impact of the RNRS+BR treatment scenario by using a locally-derived source of alkalinity like potash, or the crushed shells of mollusks.

Many important logistical inputs and considerations were not included in the LCIA, such as the person-hours required for transport, operation and maintenance of the RNRS columns. The proposed RNRS+BR usage scenario involves heavy input from the end-user, albeit the required skill level is low per ISO 30500 standards regarding complexity of required tasks.
The LCCA reveals that the IX+NR process is most economical due to low costs of clinoptilolite materials and transportation, and not requiring inputs for regeneration. Additionally, the marketable value of the clinoptilolite exhausted with K$^+$ and NH$_4^+$ could reduce costs even further, potentially offsetting costs immediately. Although a market for spent CZ may exist, the logistics of replacing bulk quantities (230 kg) of spent and virgin CZ on a monthly basis may prove unfeasible in some NSSS contexts where accessibility is limited (Trotochaud et al., 2019). High capital costs of treatment system infrastructure will eventually be overcome as the housing and cartridge components are made of sturdy materials, allowing reuse even after the intended design life.
CHAPTER 7: CONCLUSIONS AND FUTURE WORK

7.1 Summary of Findings

This research work sought to develop a pathway that enables access to nutrient resources recovered from decentralized sanitation systems, and specifically for reuse in simple, low-footprint hydroponic cultivation systems. The non-sewered sanitation system (NSSS) containing a back-end anaerobic membrane bioreactor (AnMBR) treatment system has showcased potential for meeting sanitation demands in challenging contexts with relatively low material and energy input requirements opportunities for nutrient recovery (Bair et al., 2015). However, the dependency on co-location to utilize recovered nutrient materials for agriculture encountered spatial and temporal challenges resulting from discrepancies between nutrient supply and nutrient demand. The reusable nutrient recovery system (RNRS) proposed in this work demonstrated the capacity to recover, store, transport, and release nutrients into an adaptive hydroponic system. The developed RNRS represents a promising first step towards enabling wastewater nutrient recovery and reuse by facilitating the integration of sanitation and agricultural productivity in challenging contexts. The following observations support these claims.

This work proposed an expansion of the sanitation service-system boundary to include systems and locations where reuse of nutrient materials recovered from a decentralized AnMBR are performed, yielding an “out-sourced” nutrient recovery scheme that can be mutually beneficial to end-users of nutrients and sanitation objectives. Total ammonia nitrogen (TAN) in AnMBR permeate was recovered via ion exchange (IX) onto clinoptilolite housed within a portable cartridge. Recovered TAN content was then released via elution with tap water, yielding a solution suitable for fertigation of hydroponic crops. Tap water elution of clinoptilolite-bound TAN content could not fully regenerate clinoptilolite in a favorable time interval, thus a thorough chemical regeneration process using sodium-based regenerants is
recommended to optimize TAN recovery in subsequent TAN recovery cycles (Boyer, 2014). However, TAN release from clinoptilolite was enhanced when the elution solution was recirculated in a low-footprint, vertical hydroponic system, indicating the potential of small-scale agriculture operations to reduce the environmental and economic impacts associated with clinoptilolite regeneration processes. The simplistic operation of the RNRS can be optimized to ensure safe recovery of TAN from AnMBR-NSSS permeate through the addition of disinfection and/or advanced oxidation processes prior to RNRS intervention for TAN recovery.

7.2 Research Limitations and Recommendations for Future Work

Methods for enhancing the release, or regeneration, of exhausted CZ that can facilitate both favorable crop growth and a reduction of regeneration inputs (i.e., sodium salts and regenerant brine solution). Additionally, a context-sensitive approach for facilitating reuse of recovered TAN in pertinent, intensified horticultural systems presently supporting urban agriculture practices in developing countries is necessary to accurately assess the potential social impact of the RNRS proposed by this work. Future work should identify key characteristics of applicable contexts that could serve to disable or enable implementation of the RNRS.

A major limitation of this research is the low recovery of phosphorus, a key plant macronutrient and potential nutrient contaminant. Future research should strive to facilitate the simultaneous recovery of phosphorus and nitrogen to improve both fertigation value of the RNRS desorption solution and nutrient removal performance to better adhere to the treatment standards established in ISO 30500. Phosphorus recovery has been demonstrated using Mg$^{2+}$-pretreated and Ca$^{2+}$-pretreated zeolites to induce precipitation of struvite and calcium phosphates in zeolite media (Taheri Soudejani et al., 2019; Wan et al., 2017; Xu et al., 2015). Phosphorus recovery via precipitation could promote synergistic phosphorus release phenomena during hydro-bioregeneration (HBR) via dissolution of phosphate-precipitates as solution pH declines due to nitrification activity. A pertinent research endeavor in addition to the feasibility of these processes, is assessing whether the precipitation of phosphates inside the RNRS would yield deleterious hydraulic conditions that could damage RNRS hardware.
Another possible application for the proposed RNRS involves algal cultivation in low-footprint, algae photobioreactors to support the production of biofuels, animal feeds, nutraceuticals, or even oxygen. Algae photobioreactors (AlPBRs) equipped with membrane separation could be used to simultaneously regenerate a “charged” RNRS and provide nutrients for algal biomass assimilation (Markou et al., 2014). The AlPBR could support ammonia-N removal through assimilation into algal biomass and nitrification; the resulting decreased TAN concentration in the AlPBR permeate can be recycled back to the RNRS to support continued release of RNRS-bound TAN.

The capacity to support the growth of algae and higher order plants, in controlled, low-footprint systems fosters implications for supporting horticulture in unlikely locations, including outer-space (Eugene et al., 2017; Wheeler, 2017). Operation of the RNRS in space-based contexts would allow passive nutrient harvesting from crew waste, dampening of nutrient shock loads to protect waste treatment equipment, and transport of recovered nutrient materials to dedicated plant growth units, regardless of their location, i.e., on-board spacecraft or respective location on a planetary or lunar base. Further research is required to assess if the governing mass-transfer forces of film-diffusion and intraparticle diffusion are affected in low-gravity contexts. Biological pathways for treating human wastes on lunar and planetary bases could prove more feasible than physical and chemical processes, implying that decentralized treatment technology platforms like AnMBRs could be developed for such applications. Consequently, the RNRS proposed in this work could comprise a portion of a multi-step approach to perform nutrient conditioning of AnMBR system effluents to optimize treatment and reuse efforts to support food production (Figure 7.1).

The RNRS provides portable storage of nutrients recovered from AnMBR streams which can be leveraged to “dampen” shock nutrient loads. Additionally, integration of the RNRS with an adaptive, vertical hydroponic system facilitated the conversion of released TAN content to nitrate via nitrification, which is the preferred form of nitrogen nutrition for most higher-order plants (Resh, 2013). However, the RNRS platform alone may not be able to recover and release a complete spectrum of required crop nutrients, thus supplementation of essential plant macronutrients, micronutrients, and materials to enhance
water quality may be required to optimize plant growth conditions. Undesirable materials that hinder plant growth or compromise human health would also require removal to optimize food production. Further development of the RNRS platform should strive to integrate these functions to enhance food production performance, safety, and feasibility in a variety of contexts.

Figure 7.1 Multi-step approach to nutrient conditioning of AnMBR effluents to support food production.

The main advantage of the proposed RNRS is the capacity to passively recover NH₄⁺-N via in-line, flow-through operation, allowing re-use in appropriate, low-footprint horticultural systems. Demonstration of the RNRS’s passive TAN recovery followed by TAN release for crop fertigation embodies the “low hanging fruit” paradigm championed by resource recovery practices.


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Pertinent design criteria for non-sewered sanitation systems (NSSSs) that were applicable to the design of the RNRS proposed by this research were identified and listed in Table B.1 below.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Parameter description</th>
<th>ISO 30500 Item Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General requirements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatable input</td>
<td>Human feces, urine, menstrual blood, bile, flush water, anal cleansing water, toilet paper and other bodily fluids/solids.</td>
<td>4.3.1</td>
</tr>
<tr>
<td>User requirements</td>
<td>Safe for users with little to no literacy</td>
<td>4.1</td>
</tr>
<tr>
<td>Metric system</td>
<td>All system specifications shall be reported in metric units</td>
<td>4.2</td>
</tr>
<tr>
<td>Overload protection</td>
<td>Safety factor applied:</td>
<td>4.3.4</td>
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<tr>
<td>Operability following non-usage</td>
<td>Normal operation after 60 hours of non-usage</td>
<td>4.3.5</td>
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<td>Operability following short term shutdown</td>
<td>Immediate operation after a 60 h or less shutdown</td>
<td>4.3.6</td>
</tr>
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<td>Operability following short term shutdown</td>
<td>Long term shutdown procedure &lt; 10 h; immediate operability upon startup</td>
<td>4.3.7</td>
</tr>
<tr>
<td>Continuous use</td>
<td>Allows for continuous use</td>
<td>4.3.8</td>
</tr>
<tr>
<td>Safe state indication</td>
<td>Visual or audible</td>
<td>4.3.9</td>
</tr>
<tr>
<td>Aspirational and ergonomic design</td>
<td>Design for function, comfort, aesthetics and sensory appeal; evoke cleanliness</td>
<td>4.6</td>
</tr>
<tr>
<td><strong>Operating Conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient air temperature operational range</td>
<td>5 °C to 50 °C</td>
<td>4.8.1</td>
</tr>
<tr>
<td>Humidity range</td>
<td>20% to 100%</td>
<td>4.8.2</td>
</tr>
<tr>
<td>Atmospheric pressure range</td>
<td>Sea level (101 kPa) to 2 500 m altitude (76 kPa)</td>
<td>4.8.3</td>
</tr>
<tr>
<td>Hygienic design</td>
<td>Mitigate risk of infection, minimize entry of insects and vermin</td>
<td>4.9.2</td>
</tr>
<tr>
<td>Cleanability of surfaces</td>
<td>Overall cleanability min. value equal to that of No. 3 100 to 120 grit finish of stainless steel</td>
<td>4.9.4</td>
</tr>
<tr>
<td>Chemical and biological additives</td>
<td>Should minimize chemical and/or biological additive use</td>
<td>4.9.5</td>
</tr>
<tr>
<td>Durability of materials</td>
<td>Structurally stable, durable, water tight, resistance to reasonably foreseeable misuse. Shall prevent detrimental UV radiation effects</td>
<td>4.10.1</td>
</tr>
<tr>
<td>Connections and joining elements</td>
<td>Connections shall resist corrosion, incorrect connection shall be impossible by design</td>
<td>4.11</td>
</tr>
<tr>
<td>Safety of edges, angles, surfaces</td>
<td>Surfaces and parts should be free of rough or sharp edges</td>
<td>4.12.1</td>
</tr>
<tr>
<td>Structural Integrity</td>
<td>Materials should be capable of of withstanding static and dynamic stresses; strength safety factor (SSF) ≥ 2 [ISO 14622]</td>
<td>4.12.3</td>
</tr>
<tr>
<td>Prevention of contact with unsafe effluent and reuse</td>
<td>Meet guidelines for reuse type, i.e., irrigation in 7.2.9.4</td>
<td>4.12.4</td>
</tr>
<tr>
<td>External Impacts</td>
<td>Shall be stable enough to prevent tilting, falling, or uncontrolled movement</td>
<td>4.12.6</td>
</tr>
<tr>
<td>Information and warnings</td>
<td>Capacity (number of uses/day); instructions for service; min and max. operating temperatures, items to avoid, min &amp; max operating temperature, specify intended purpose of effluent output, provide effluent information, clearly indicate safety risks</td>
<td>4.13.1</td>
</tr>
</tbody>
</table>
### Table B.1 (continued)

#### Maintenance Requirements

<table>
<thead>
<tr>
<th>Description</th>
<th>Requirement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reasonable configuration</td>
<td>Shall be designed in a way that allows adjustment, maintenance, and</td>
<td>4.14.1</td>
</tr>
<tr>
<td></td>
<td>configuration by users and professional service personnel respective to</td>
<td></td>
</tr>
<tr>
<td></td>
<td>reasonable levels of technical capacity</td>
<td></td>
</tr>
<tr>
<td>Location, access, adjustment and</td>
<td>Accessible maintenance points, separate from hazards</td>
<td>4.14.2</td>
</tr>
<tr>
<td>configurations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge and Cleaning</td>
<td>No discharged of partially treated materials during cleaning</td>
<td>4.14.3</td>
</tr>
<tr>
<td>Tools and devices</td>
<td>Shall specify specialized tool requirement in user manual</td>
<td>4.14.4</td>
</tr>
<tr>
<td>User Manual</td>
<td>Shall provide a user manual with detailed instructions to users and/or service</td>
<td>4.14.5</td>
</tr>
<tr>
<td></td>
<td>personnel. Define all necessary procedures, activities and schedules.</td>
<td></td>
</tr>
<tr>
<td>Handling and Transport</td>
<td>Shall not produce unintended discharge during transport</td>
<td>4.14.6</td>
</tr>
<tr>
<td>Safety Assessment</td>
<td>Determine particular health and safety requirements that apply; determine risk</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>mitigation strategies; demonstrate safety throughout expected life cycle of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NSSS giving consideration to expected use and reasonably foreseeable misuse</td>
<td></td>
</tr>
</tbody>
</table>

#### Operational Requirements

<table>
<thead>
<tr>
<th>Description</th>
<th>Requirement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intentional starting and stopping of system operation</td>
<td>Starting and restarting of the system through voluntary action or logical sequence of controlled actions: mechanical force requirement not to exceed 25N</td>
<td>5.2.1, 5.2.2</td>
</tr>
<tr>
<td>Pressurized or vacuum equipment</td>
<td>Equipment pressurized above kPa shall be equipped with appropriate pressure</td>
<td>5.4.1</td>
</tr>
<tr>
<td></td>
<td>relief valves</td>
<td></td>
</tr>
<tr>
<td>Pipes, hoses and tanks</td>
<td>Shall be positioned and restrained to minimize deterioration from contact with</td>
<td>5.4.2</td>
</tr>
<tr>
<td></td>
<td>other elements and fitting shall be safely accessible for inspection. Tanks</td>
<td></td>
</tr>
<tr>
<td></td>
<td>shall be able to withstand stresses of prolonged containment; shall contain means of liquid level determination</td>
<td></td>
</tr>
</tbody>
</table>

#### Performance

<table>
<thead>
<tr>
<th>Description</th>
<th>Requirement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen (TN) removal</td>
<td>70% TN removal</td>
<td>7.2.9.4</td>
</tr>
<tr>
<td>Total Phosphorus (TP) removal</td>
<td>80%</td>
<td>7.2.9.4</td>
</tr>
<tr>
<td>Effluent pH</td>
<td>6 - 9</td>
<td>7.2.9.4</td>
</tr>
<tr>
<td>Odor emission requirements</td>
<td>10% max of observations reported as “unpleasant”, 2% as “unacceptable” in or</td>
<td>7.2.9.5</td>
</tr>
<tr>
<td></td>
<td>near the NSSS</td>
<td></td>
</tr>
<tr>
<td>Noise thresholds</td>
<td>&lt;60 dBA; 85 dBA (7.2.9.6)</td>
<td>7.2.9.6</td>
</tr>
<tr>
<td>Indoor air emissions requirements</td>
<td>Shall not exceed respective thresholds in given timeframes: NH₃: 25 ppmv in 1 h; NOₓ: 99 ppbv in 1h; CO₂: 1000 ppmv in 1h;</td>
<td>7.2.9.7 Table 11</td>
</tr>
<tr>
<td>Outdoor exhaust or vent air emissions (1 h average)</td>
<td>Shall not exceed: 50 ppmv (NH₃); 195 ppmv (NOₓ); 10 mg/m³ (PM₂.₅)</td>
<td>7.2.9.7 Table 12</td>
</tr>
<tr>
<td>Expected design Lifetime</td>
<td>10 Years (minimum)</td>
<td>4.5, 4.14</td>
</tr>
</tbody>
</table>

#### Sustainability

<table>
<thead>
<tr>
<th>Description</th>
<th>Requirement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nutrient Recovery</td>
<td>Shall specify type, subtype, concentrations, and amount of nutrients contained in final solid and/or effluent output and shall specify assumptions made for these calculations</td>
<td>8.2</td>
</tr>
<tr>
<td>Water consumption</td>
<td>Shall calculate water use as both per-flush and per user per day and specify assumptions used for calculation; shall indicate water quality and quantity required for operation</td>
<td>8.3.1, 8.3.2</td>
</tr>
<tr>
<td>Reuse of effluent</td>
<td>Shall indicate required dilution volume, if required.</td>
<td>8.3.3</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>Shall indicate energy required to operate NSSS (kWh/yr)</td>
<td>8.4.2</td>
</tr>
<tr>
<td>Life cycle assessment</td>
<td>A life cycle assessment should be conducted based on ISO 14040 and 14044</td>
<td>8.5</td>
</tr>
<tr>
<td>Recurring operational requirements</td>
<td>Shall convey relevant information: recommended maintenance activities and identification of parts/components expected to require periodic replacement and estimated complexity of maintenance tasks; include estimated annual energy consumption (kWh/year), estimated water consumption (liters/year), estimated annual consumption of other resource such as chemical and biological additives and specialized cleaning or maintenance tools</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Development, operation, and refinement of the RNRS prototype allowed for the identification of maintenance procedures necessary to ensure reliable operation and favorable use of the RNRS. Per ISO 30500 requirements, regular maintenance tasks and their required level of skill are summarized in Table B.2 below. The level complexity for each task is further defined in Table B.3.
**Table B.2 RNRS maintenance task schedule**

<table>
<thead>
<tr>
<th>Who is to perform the activity (user/professional service personnel)</th>
<th>Type of activity</th>
<th>Complexity of task (per Table B.3)</th>
<th>Frequency</th>
<th>Expected duration per activity (person hours)</th>
<th>Required parts, components or consumables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Professional service personnel</td>
<td>RNRS Installation and removal before and after charge phase</td>
<td>Low</td>
<td>2-3 times/week</td>
<td>≤ 1</td>
<td>Filter housing wrench</td>
</tr>
<tr>
<td>User/professional service personnel</td>
<td>RNRS transport to and from nutrient discharge/reuse location</td>
<td>Low</td>
<td>Once weekly</td>
<td>≤ 1</td>
<td>Leak-proof, secondary containment</td>
</tr>
<tr>
<td>User</td>
<td>Nutrient discharge into plant growth system</td>
<td>Low</td>
<td>Once weekly</td>
<td>≤ 2</td>
<td>Irrigation water, reservoir, plumbing connections, bicarbonate salt</td>
</tr>
<tr>
<td>User/professional service personnel</td>
<td>RNRS Na⁺-pretreatment/regeneration</td>
<td>Medium</td>
<td>Once weekly</td>
<td>≤ 4</td>
<td>10-20% sodium chloride solution, sodium hydroxide, PPE</td>
</tr>
</tbody>
</table>

**Table B.3 Definitions of maintenance task complexity**

<table>
<thead>
<tr>
<th>complexity</th>
<th>Technical competence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very low</td>
<td>No skills (background education, experience) and no training required</td>
</tr>
<tr>
<td>Low</td>
<td>Basic skills and less than 1 h training required</td>
</tr>
<tr>
<td>Medium</td>
<td>Requires certain skills that can be acquired by training lasting no more than 1 day</td>
</tr>
<tr>
<td>High</td>
<td>Requires high technical skills (e.g. technical education in the field related to the activity), more than 1 day of training, and at least 6 months of work experience</td>
</tr>
<tr>
<td>Very high</td>
<td>Requires very high and specialized technical skills (e.g. advanced technical education in the field related to the activity), extensive training, and at least 1 year of work experience</td>
</tr>
</tbody>
</table>
ABOUT THE AUTHOR

Jorge grew up in the Tampa Bay area and received his Bachelors of Science degree in civil and environmental engineering and his Master’s of Science degree in environmental engineering from the University of South Florida. Jorge’s passion for sustainable living influenced his decision to continue his studies at USF under the tutelage of Dr. Daniel Yeh, where he was able to dedicate his research efforts to develop sustainable sanitation and resource recovery technologies. As a research assistant, Jorge has contributed to the development of an off-grid, autonomous wastewater treatment system called the NEWgenerator™, which is designed to provide safe sanitation services in challenging, developing world contexts. The Bill and Melinda Gates Foundation-funded NEWgenerator™ project presented Jorge invaluable opportunities to travel and collaborate with stakeholders in Southern India and South Africa, in an effort to address urgent water and sanitation issues. Jorge’s research interests also led him to The Netherlands, home to some of the world’s most advanced water engineering and horticultural operations, where he performed part of his Ph.D. research at IHE-Delft Institute for Water Education, that facilitated networking and knowledge exchange with the international community of IHE-Delft research students. These experiences instilled an appreciation for global competency that is necessary for developing appropriate and effective solutions for society. Jorge hopes to continue to dedicate his skills towards the development of technologies, policies, and practices that enable the sustainable existence of the human race.