Synergetic Wastewater Treatment: Implementing Annamox Enhanced Wastewater in Closed Loop Pressure Retarded Osmosis for Sustainable Energy Generation

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Abstract

Synergetic Wastewater Treatment: Implementing Annamox Enhanced Wastewater in Closed Loop Pressure Retarded Osmosis for Sustainable Energy Generation

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Exploring the symbiotic potential of wastewater treatment and sustainable energy generation, this research integrates an Anammox (Anaerobic Ammonium Oxidation) reactor with Pressure Retarded Osmosis (PRO). The investigation considers three diverse feed solutions: Deionized (DI) water, synthetic water, and a composite of synthetic water with real mine wastewater from gold mines. The study assesses the nitrogen removal efficiency in the Anammox reactor, accounting for the distinctive compositions of each feed solution. Concurrently, the power output, and overall performance of the PRO system are analyzed using the Anammox reactor effluent as the feed solution.

DI water provides a baseline for comparison, synthetic water replicates-controlled conditions, and the inclusion of mine wastewater introduces real-world complexities. The present study critically examines the chemical interactions occurring within an integrated system, focusing on the observable impact of trace elements present in gold mine wastewater on both biological and osmotic processes.

The research provides valuable insights into the interaction between biological nitrogen removal and osmotic power generation across varied wastewater matrices. Results highlight the versatility of the proposed methodology, underscoring its practical significance for sustainable energy production in mining environments.

Initially for experiments on lab-scale PRO setup, solutions of NaCl, KCl, $(NH_4)_2CO_3$ and $MgCl_2$ were used as the draw solutions. Results from this exploration offer valuable considerations for wastewater treatment and energy production in gold mining operations, highlighting the potential for sustainable practices in resource-intensive industries. After examining different draw solutions, synthetic water and composite of synthetic water with real mine tailing water were tested with 3M $(NH_4)_2CO_3$ as the draw solution which produced the average power density of 11.0 ± 0.5 W/m^2 and fouling was observed within the timespan. Results demonstrated promising power generation capabilities, with significant reductions in ion concentrations in the permeate, indicating the effectiveness of the PRO process. Recommendations for future research include comprehensive techno-economic analyses, exploration of advanced membrane technologies, and integration of other bioremediation techniques to enhance pollutant removal and system performance. Overall, the integration of Annamox-PRO represents a promising approach towards enhancing sustainability, energy efficiency, and environmental stewardship in industrial settings, particularly in challenging environments like mining operations.

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CLPRO	Closed-loop pressure retarded osmosis
CP	Concentration Polarization
CTA	Cellulose triacetate
EGE	Enhanced geothermal energy
ERD	Energy recovery device
FO	Forward osmosis
GHG	Greenhouse gas
HMIS	Hazardous material identification system
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
IEA	International energy agency
LCST	Least critical solution temperature
LGH	Low grade heat
MED	Multi-effect distillation
OLPRO	Open – loop pressure retarded osmosis
PRO	Pressure retarded osmosis

RED	Reverse electrodialysis
EDLC	Electrical Double Layer Capacitor
VPD	Vapor pressure difference
RO	Reverse osmosis
SEC	Specific energy consumption
SG	Salinity gradient
TDS	Total dissolved solids
TOC	Total organic carbon
NaCl	Sodium chloride
KCl	Potassium chloride
$MgCl_2$	Magnesium chloride
$((NH_4)_2 CO_3)$	Ammonium carbonate
MPa	Mega Pascal
LMH	Liters/m^2- h
Ω	Osmotic pressure
ρ	Density
μ	Kinematic viscosity
T	temperature

M	Molarity
DI	De-ionized water
W	Watt
Psi	pounds per square inch

Chapter 1: Introduction

1.0 Background

In these modern times, the call for sustainable energy solutions is louder than ever all over the world. In 2024, renewable energy technologies are booming with innovation, scalability, and a focus on protecting the environment. There is an urgent need to shift away from fossil fuels and combat climate change which has led to the rapid growth and widespread use of renewable energy sources. Together, these sources create a stronger and more varied energy mix for the future.

In today's world, where we focus a lot on taking care of the environment, finding new ways to treat the wastewater and producing sustainable energy has become really important. This is especially true for industries such as gold mining, where a lot of natural resources are used and which creates a big impact on the environment. The traditional ways of treating the wastewater consumes a lot of energy and have become outdated. In order to tackle such problems, it is highly important to develop new and better ways.

The first step is the Anaerobic Ammonium Oxidation (Anammox) process—a revolutionary advancement in wastewater treatment (Mohommadhosseinpour et al., 2016). At its core, Anammox offers a sustainable alternative to conventional methods, relying on the biological process of microorganisms to remove nitrogen compounds, particularly ammonium, nitrate and nitrite. In the broader context, the Anammox bioreactor, a crucial component of this process, emerges as an efficient and adaptable tool, showcasing its prowess not only in synthetic wastewater but, also in the real-world complexities too.

Alongside the advancements in Anammox treatment, the emergence of Pressure Retarded Osmosis (PRO) presents a promising pathway for sustainable energy production (Etemad Zadeh, 2022). PRO utilizes osmotic pressure disparities, contributing an eco-friendly approach towards wastewater treatment. This thesis aims to explore merging biological and osmotic processes to bolster sustainability. It will examine the intricacies and obstacles involved in this fusion, shedding light on technical nuances to unravel complexities. The thesis seeks to lay the groundwork for a pioneering method in wastewater treatment and energy production, poised to revolutionize current practices.

Throughout its successive chapters, this thesis will delve into the dynamics between biological nitrogen removal and osmotic power generation. It will provide in-depth insights into the adaptability of the proposed approach, with the overarching goal of not only advancing theoretical comprehension but also elucidating practical implications for sustainable energy generation, particularly within resource-intensive industries.

1.1 Salinity Gradient Energy (SGE)

Osmotic power, also known as salinity gradient energy (SGE), has garnered significant attention in recent years (Brauns, 2008; Labrecque, 2009; Achilli and Childress, 2010; Ramon et al., 2011; Berrouche and Pillay, 2012; Burheim et al., 2012). The global potential for harnessing power from the mixing of sea and river water exceeds 2 terawatts (TW) (Burheim et al., 2012). Several parameters, including percent recovery, average river flow rates, source salinities, and temperature, play crucial roles in influencing the generation of salinity gradient energy (Ramon et al., 2011).

Salinity gradient energy is a result of the difference in the chemical potential, linked to the osmotic pressure disparity between two solutions with varying salt concentrations. The concentration of salt and osmotic pressure exhibits a proportional relationship. In essence, a solution with high salt concentration has a correspondingly high osmotic pressure, harbouring a significant amount of energy (Brauns, 2008). The salinity gradient, responsible for the chemical potential difference, can be identified in estuaries—partially enclosed coastal areas where freshwater from streams or rivers meets saltwater from an ocean, gulf, or Salt Lake (Labrecque, 2009).

Various technologies, including Pressure Retarded Osmosis (PRO), Reversed Electrodialysis (RED), Electrical Double Layer Capacitor (EDLC), and power production by Vapor Pressure Difference (VPD), are currently in development for the generation of electric power based on salinity gradient energy (Kim et al., 2013).

1.2 Integration of Annamox reactor with Pressure Retarded Osmosis

In our efforts towards sustainability, managing wastewater and producing clean energy have become increasingly important. Industries are seeking new ways to address environmental challenges while also meeting their energy needs. This study focuses on a promising approach: integrating an Annamox reactor with Pressure Retarded Osmosis (PRO). By bringing these technologies together, study aims to treat wastewater effectively while also harnessing renewable energy in the process. This innovative combination offers a dual benefit, contributing to both environmental protection and sustainable energy production.

The wastewater treatment sector, especially in heavy - resource industries such as iron ore or coal or gold mining, is confronting significant challenges, primarily due to their substantial environmental footprint. Nitrogen compounds found in wastewater exacerbate issues like eutrophication, posing serious risks to aquatic ecosystems. Meanwhile, the urgency for sustainable energy solutions has reached towards unprecedented levels, prompting the exploration of innovative technologies capable of tackling both wastewater treatment and energy generation challenges simultaneously.

The Annamox process is well-known for its ability to efficiently remove nitrogen anaerobically, making it a crucial component of this research. By utilizing microorganisms to convert ammonium and nitrite into nitrogen gas, the Annamox reactor provides a promising method for sustainable wastewater treatment. However, this study goes beyond conventional approaches by integrating the Annamox reactor with PRO technology. PRO harnesses osmotic pressure variations to produce energy, presenting a novel solution that addresses both wastewater treatment and energy generation challenges simultaneously.

Pressure retarded osmosis (PRO) has emerged as a sustainable method for generating clean energy from salinity gradients. When integrated with the Annamox reactor, it establishes a symbiotic relationship where biological nitrogen removal and osmotic power generation work together synergistically. This fusion not only mitigates the environmental impact of wastewater but also offers substantial potential to enhance sustainable energy portfolios.

Integrating the annamox reactor with the PRO system represents a novel approach. However, it is crucial to know the technical complexities concerning reactor design, optimization, and scalability. This research endeavors to unravel the intricacies of this integrated system, bridging between the wastewater treatment and sustainable energy generation. The findings from this study hold the potential to advance practices in resource-intensive sectors, enabling synergistic wastewater treatment and energy production. Ultimately, this contributes to a more sustainable and resilient future.

1.3 Objectives of the study

The main objectives of the research are as follows:

1. Assess the feasibility of combining the Annamox reactor with Pressure Retarded Osmosis (PRO) for sustainable energy generation in wastewater treatment.

2. Evaluate key parameters to improve energy generation efficiency within the integrated system.

3. Explore and quantify the potential of osmotic power generation in the Annamox-PRO system.

4. Propose practical recommendations for implementing the integrated system, emphasizing its potential for promoting sustainability in wastewater treatment and energy generation.

1.4 Organization of the dissertation

The organization of the dissertation is as follows:

Chapter 1: A brief introduction which describes the motivation of the study, a general overview of the overall process and objectives of the study;

Chapter 2: A short description on the reviewed literature of Annamox and PRO process, state of the art technology for PRO, research gap, a summary of draw solution used for PRO;

Chapter 3: Materials and methodology;

Chapter 4: Results and discussion;

Chapter 5: Conclusions and recommendations for future directions.

Chapter 2: Literature review

2.1 Background

Utilizing renewable energies stands as a widely recognized approach to mitigate the global emission of greenhouse gases (Manzini et al., 2001). At the core of this abundant and well-established technology lies a key factor: its inherent freedom (Bilgen and Kaygusuz, 2004). Renewable energy is generated from natural resources, including but not limited to sunlight, wind, biomass, tides, water, and geothermal heat (Shi, 2010).

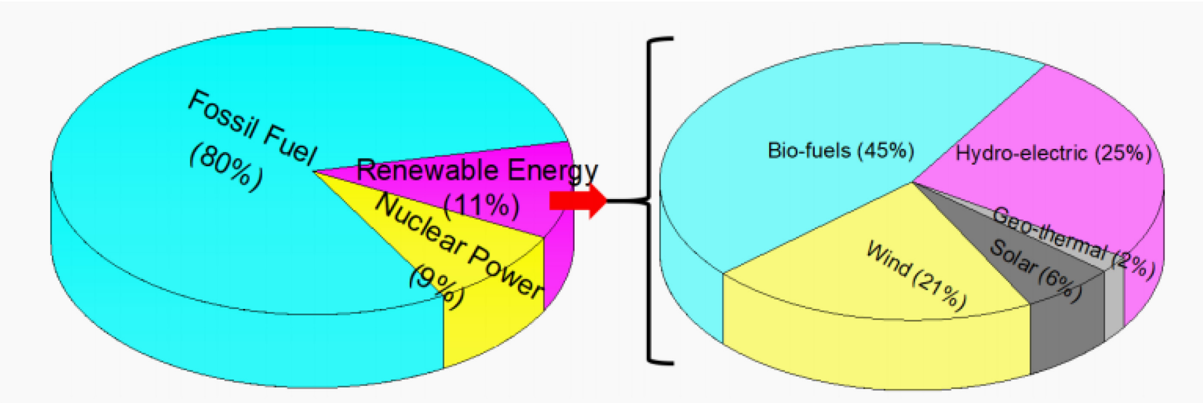


Figure 1. Consumption of energy based on their resources (Zadeh et al., 2022)

Renewable energies offer viable solutions to address the gradual decline of traditional fossil fuels and the associated environmental impacts. They have the capacity to tackle issues related to energy sustainability, economic development, and environmental safety (Kim et al., 2012). Each category of renewable energy systems is well-suited for specific applications, leveraging unique advantages such as reduced external energy dependence, minimized transmission and transformation losses, and the avoidance of gaseous or liquid pollutants. The primary drawback lies in their susceptibility to weather and climatic conditions, which introduces uncertainty in their availability (Erdinc and Uzunoglu, 2012).

As previously mentioned, solar, wind, hydro, biomass, geothermal, and marine energy are among the most advanced renewable energy sources. Marine energy generation involves various sources like tides, ocean currents, and salinity gradients, with salinity gradient demonstrating notably high energy density (Berrouche and Pillay, 2012). Osmotic power, also known as salinity gradient energy, is derived from differences in salt concentration between fresh and saltwater (Achilli and Childress, 2010).

Osmotic power and hydropower share similarities in that both generate electricity using hydro turbines. However, their distinctions lie in the type of water and energy conversion methods employed. In hydropower plants, energy is harnessed from river water and a dam, whereas in osmotic power plants, energy is generated using river water and seawater separated by a semi-permeable membrane (Kim and Elimelech, 2013).

2.2 Sustainable solutions for wastewater from mining industry

The mining industry plays a crucial role in the global economy by extracting valuable minerals, metals, and other resources used in various sectors such as manufacturing, construction, and energy production. However, mining operations often pose significant environmental challenges, particularly concerning water management.

Some key water issues in the mining industry include:

1. **Water Pollution**: Mining activities can generate various pollutants that contaminate water sources, such as heavy metals, acidic drainage, and chemicals used in the extraction process.

2. **Water Scarcity**: Mining operations require significant amounts of water for various purposes, including processing ore, dust suppression, and transportation. In regions already facing water scarcity, this can exacerbate existing challenges.

3. **Groundwater Contamination**: Improper handling and storage of mining waste, such as tailings and slurry, can lead to groundwater contamination, affecting local ecosystems and communities.

4. **Sedimentation**: Mining activities can disturb soil and rock layers, leading to increased sedimentation in water bodies, which can impact aquatic habitats and water quality.

5. **Acid Mine Drainage (AMD)**: When sulphide minerals are exposed to air and water during mining activities, they can oxidize and produce acidic runoff, known as acid mine drainage. AMD can severely degrade water quality and harm aquatic life.

To address these water issues, various technologies and approaches are being developed and implemented in the mining industry. Two promising technologies are Annamox and PRO (Pressure Retarded Osmosis), which offer potential benefits:

1. Anammox (Anaerobic Ammonium Oxidation)

1. **Nitrogen Removal:** Anammox is highly efficient in removing nitrogen compounds, particularly ammonia, from wastewater streams generated during mining operations, thereby reducing nitrogen pollution in water bodies.

2. **Reduced Chemical Usage:** Unlike conventional nitrogen removal methods that often require additional chemical inputs, Anammox operates without the need for external carbon sources, reducing chemical usage and associated costs.

3. **Energy Efficiency:** Anammox processes operate under anaerobic conditions, requiring less energy compared to aerobic treatment methods, contributing to overall energy efficiency within mining operations.

4. **Biological Stability:** Anammox processes are characterized by biological stability and resilience to fluctuations in wastewater composition, providing reliable and consistent treatment performance in mining environments.
5. **Minimization of Sludge Generation:** Anammox processes produce minimal excess sludge, reducing the need for sludge disposal and associated environmental impacts, such as land degradation and greenhouse gas emissions.

2. Pressure Retarded Osmosis (PRO)

1. **Desalination:** PRO technology can effectively desalinate brackish water or seawater, providing a sustainable source of freshwater for mining operations without overburdening local freshwater resources.
2. **Water Reuse:** PRO facilitates the reuse of water by treating contaminated or wastewater streams, reducing the need for freshwater intake and minimizing the discharge of pollutants into the environment.
3. **Resource Efficiency:** By recovering clean water from wastewater streams, PRO contributes to resource efficiency within mining operations, reducing water consumption and associated costs.
4. **Energy Generation:** In addition to water treatment, PRO systems can generate energy through osmotic pressure differentials, providing an additional benefit in terms of sustainability and cost-effectiveness.
5. **Environmental Protection:** By reducing freshwater intake and minimizing wastewater discharge, PRO helps mitigate the environmental impact of mining activities, preserving local ecosystems and water quality.

By leveraging the advantages of PRO and Anammox technologies, mining companies can improve water management practices, minimize environmental impacts, and enhance the sustainability of their operations.

2.3 Pressure Retarded Osmosis (PRO) – An Emerging Technology

In the current era of renewable energy exploration, where pushing the boundaries of innovation is crucial for addressing global energy challenges, Pressure Retarded Osmosis (PRO) stands out as a promising and cutting-edge technology. Built upon the fundamental principles of osmosis, PRO has emerged as a clever solution for harnessing the untapped energy stored within the osmotic gradients between solutions of varying salinity. This innovative approach presents a new pathway toward sustainable and environmentally friendly energy production which showcases its potential to make significant contributions to the quest for clean energy alternatives.

Figure 2. Energy generation by mixing two different salinity gradient solutions

The core tenet of PRO revolves around the exploitation of osmotic pressure differentials between a high-concentration saline solution, often termed the "draw solution," and a low-concentration solution, referred to as the "feed solution." separated by a semi-permeable membrane, these solutions create a natural osmotic flow, wherein water molecules migrate from the low-concentration side to the high-concentration side (Adhikary, 2019). This migration of water induces a pressure differential, which is called osmotic pressure, which can be used to propel a turbine, thereby generating electricity.

Pressure Retarded Osmosis (PRO) is appealing due to its unique ability to exploit osmosis to transform it into a sustainable energy resource. This technology offers versatile applications beyond traditional energy generation methods, presenting an eco-friendly alternative that circumvents the environmental concerns typically associated with combustion-based approaches.

PRO distinguishes itself from traditional energy production methods by offering the potential for environmental friendliness and scalability. Unlike the processes reliant on fossil fuel combustion or extensive infrastructure, PRO operates without such requirements. This aligns well with the global imperative to reduce carbon footprints and transition towards sustainable energy systems.

As countries and industries face the dual challenge of meeting growing energy needs while minimizing environmental harm, exploring PRO technology becomes paramount. Its ability to harvest energy from natural osmotic differences offers a promising avenue for a cleaner, more sustainable energy future.

2.4 Biological Nitrogen Removal Processes

Biological nitrogen removal processes are essential components of wastewater treatment systems designed to reduce and eliminate nitrogen compounds from wastewater. These processes rely on the activities of specific microorganisms to transform nitrogen-containing compounds into nitrogen gas or other environmentally benign forms. The primary biological nitrogen removal processes include nitrification, denitrification, and annamox wastewater treatment.

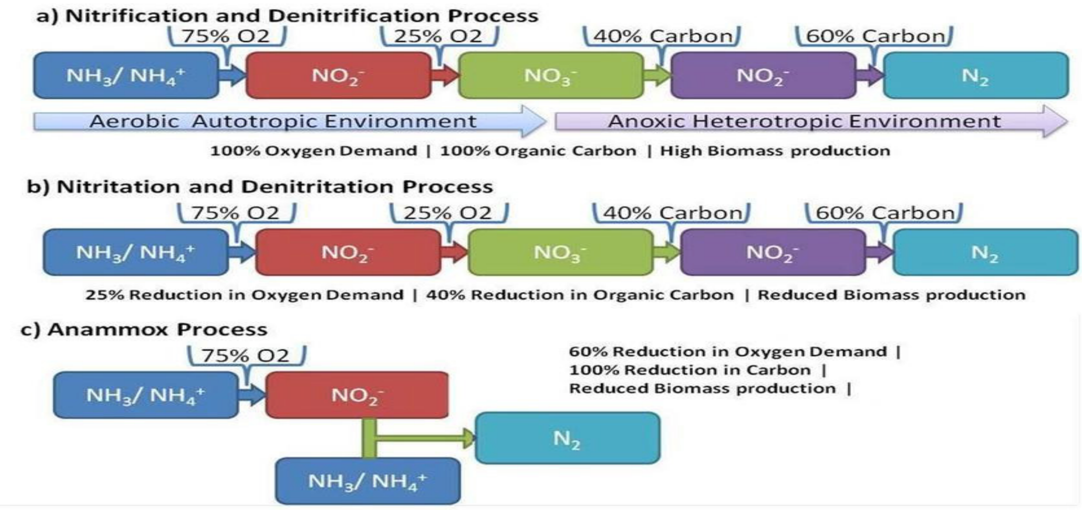


Figure 3. Three Major biological Nitrogen Removal Processes (Mohammadhosseinpour et al. 2016)

2.5 Anaerobic Ammonium Oxidation (Anammox) process

The presence of nitrogen compounds in wastewater poses a significant environmental concern due to their contribution to eutrophication and nitrite enrichment. Eutrophication, can be defined as an excess of algae and aquatic plants, leads to reduced dissolved oxygen levels and the emergence of taste and odor issues (National Academy of Sciences, 1969). To address these challenges, diverse nitrogen removal methods, spanning physical, chemical, and biological processes, have been implemented.

Among the biological techniques for ammonia removal, the anammox process is noteworthy, standing alongside nitrification and denitrification. These processes are vital for eliminating ammonia from wastewater with high nitrogen concentrations and low organic carbon content. Specific approaches such as Sequencing Batch Reactor (SBR), SHARON, CANON, and OLAND facilitate these biological processes (Strous et al., 1998; Dongen et al., 2001; Hendrik & Strous, 2002; Li et al., 2008).

Tailored for concurrent removal of organic and inorganic compounds, including nitrogen and phosphorus, the Bio-CAST reactor exhibits distinctive characteristics. The coexistence of suspended and immobilized biomass, coupled with diverse zones providing various environmental conditions, creates an optimal environment for the growth and activity of anammox bacteria. This facilitates nitrogen removal through combined nitrification and anammox processes, diverging from conventional nitrification and denitrification linked with this technology (Yerushalmi et al., 2011; Alimahmoodi et al., 2012).

The potential of Bio-CAST technology to leverage the capabilities of anammox bacteria is explored, offering a promising avenue for sustainable and efficient nitrogen removal in wastewater treatment. The intricate design of the Bio-CAST system, featuring varied environmental zones, positions it as a viable platform for promoting synergistic nitrification and anammox processes, contributing to the evolution of sustainable wastewater treatment practices.

2.5.1 History of Annamox

Hamme and Thompson (1941) proposed that bacteria in the oceans could be linked to the dissolved nitrogen sink, a phenomenon now identified as anaerobic ammonia oxidation (Randall & Thompson, 1941). Subsequently, Richards (1965) demonstrated the unexpected elimination of ammonium under anoxic conditions (Richard, 1965). Broda (1977) identified the absence of two types of lithotrophs through Gibbs free energy calculations, laying the groundwork for the hypothesis of the first possible anammox source (Broda, 1977). The anammox process was first discovered in a denitrifying pilot plant for wastewater treatment from the Gist-Brocades yeast factory in 1990 (Mulder et al., 1995).

In 1998, Strous identified nitrite as a crucial electron acceptor in the anammox process (Strous et al., 1998), and in 1999, Strous et al. (1999) purified anammox bacterial cells from laboratory enrichment culture. These purified cells demonstrated the ability to convert ammonia and nitrite to nitrogen gas in the absence of oxygen. Following this discovery, *Brocadia* *anammoxidans* was chosen as the name for the identified anammox bacteria, and the status of "candidatus" was given due to not meeting classical microbiological purity standards. Till date, five anammox species have been identified with 16S rRNA gene sequence identities ranging between 87% and 99% of total annamox bacteria kingdom (Jetten et al., 2009).

Four "Candidatus" anammox species have been identified in activated sludge:

- *Kuenenia* (Schmid et al., 2000; Strous et al., 1999)

- *Brocadia* (Kartal et al., 2008; Kuenen & Jetten, 2001; Strous et al., 1999)

- *Anammoxoglobus* (Kartal et al., 2007) and "Jettenia" (Quan et al., 2008)

- *Candidatus Scalindua* (Kuypers et al., 2003; Schmid et al., 2003; Van de Vossenberg et al., 2008)

The fifth anammox species is frequently found in natural habitats, particularly in the sea floor and marine sediments with minimal oxygen. Research indicates that in the Black Sea, these species contribute to 30–50% of nitrogen consumption on the planet (Dalsgaard et al., 2005; Van Niftrik et al., 2004; Penton et al., 2006; Schmid et al., 2007; Woebken et al., 2008).

2.5.2 Characterization of Annamox bacteria

Coccoid anammox bacteria typically exhibit a diameter of less than 1 µm, with a duplication time ranging from 10 to 30 days. These bacteria function as anaerobic chemolithoautotrophs, specializing in converting ammonium to nitrogen gas while utilizing nitrite as the electron acceptor (Van Niftrik et al., 2004). In the nitrogen removal process, ammonia undergoes partial oxidation to nitrite under aerobic conditions. In the anammox process, nitrite is initially reduced to hydroxylamine, which is then coupled with ammonium to generate hydrazine. Subsequently, hydrazine undergoes oxidation to atmospheric nitrogen (Van de Graaf et al., 1997). Both hydrazine and hydroxylamine serve as catabolic intermediates in the anammox process. Due to the inherent difficulty in the isolation process, there is no pure culture for anammox bacteria. However, enriched cultures of anammox bacteria can be obtained from wastewater facilities (Dalsgaard et al., 2005).

2.5.3 Multi-zone Wastewater Treatment System- Bio-Cast Reactor

The Bio-CAST technology comprises two interconnected bioreactors, as outlined by Yerushalmi et al. (2011). Each bioreactor is characterized by distinct zones, offering a variety of environmental conditions. In the first bioreactor, aerobic, microaerophilic, and anoxic zones, along with a clarification zone, are present. The volumes of the laboratory-scale reactor zones are 17 L, 61 L, 22 L, and 85 L for the aerobic, microaerophilic, anoxic, and clarification zones, respectively. The diameters of these zones are 16.7 cm, 35.7 cm, and 49.5 cm, respectively. The heights of the aerobic and microaerophilic zones are 91 cm and 100 cm, respectively. The second bioreactor encompasses an anaerobic zone at the bottom, a solid-liquid separation zone in the middle, and a filtration unit at the top. The filter medium is chosen based on effluent characteristics and process scale. The second bioreactor has a diameter of 12 cm and a total volume of 12 L, with a height of 1.13 m.

The design of the aerobic zone adheres to air lift reactor principles, facilitating upward flow in the aerobic zone (riser) and downward flow in the microaerophilic zone (downcomer) continuously. Three custom-built air diffusers at the bottom of the aerobic zone and above the anoxic zone introduce air, supporting aerobic biological processes, liquid mixing, and circulation between adjacent zones. The aerobic zone accommodates both suspended and attached-growth microorganisms. A cylindrical stainless-steel structure, wrapped in non-woven geotextile, serves as microbial support in the aerobic zone, fostering microbial biomass attachment and biofilm formation. Due to the low growth rate of anammox bacteria, support media, such as geotextile strips inside the microaerophilic zone, are employed to encourage biomass attachment and biofilm formation. A real-time control system, developed by

Behzadian et al. (2010), continuously monitors operating parameters, including temperature, aeration rate, and dissolved oxygen concentrations in both the aerobic and microaerophilic zones. The integrated multi-zone wastewater treatment system is schematically depicted in Figure 4.

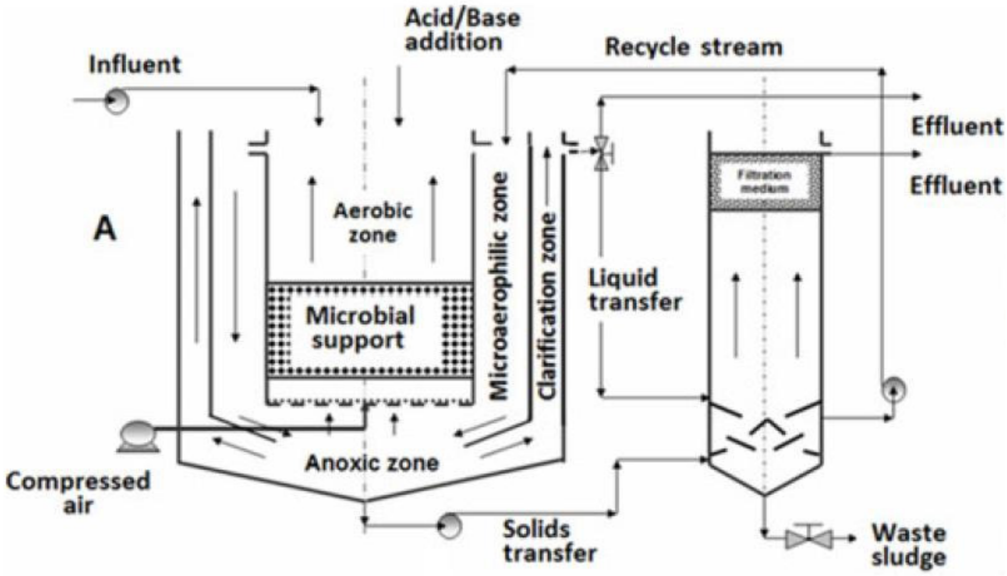


Figure 4. Schematic Diagram of Bio-Cast Reactor (Mohammadhosseinpour et al. 2016)

2.5.4 Key factors for controlling Annamox processes in the Bio-Cast Reactor

The Bio-CAST technology, designed for simultaneous removal of organic and inorganic compounds, offers a unique approach to nitrogen removal through the combined partial nitrification (PN) and Anammox processes. This innovative system retains microorganisms in both suspended growth and immobilized forms, creating a favorable environment for the growth and activity of ammonia-oxidizing bacteria (AOB) and Anammox bacteria.

Controlling the Anammox process in the Bio-CAST technology involves managing key operating parameters to support the growth of AOB and Anammox bacteria while suppressing the activity of nitrite-oxidizing bacteria (NOB). These parameters include dissolved oxygen

(DO), pH, temperature, and nitrite accumulation, which need to be carefully regulated to create an optimal environment for the Anammox process (Mohammadhosseinpour et al. 2016).

The establishment of favorable operating conditions is essential for the maximum growth of Anammox bacteria and the minimum activity of NOB. For instance, the Bio-CAST technology applies low levels of DO in the aerobic and microaerophilic zones, ranging from 0.9-1.2 mg/l and 0.1-0.4 mg/l, respectively, to achieve high total nitrogen (TN) removal efficiency and ammonium removal (Mohammadhosseinpour et al. 2016). This careful control of environmental conditions and operating parameters contributes to the success of the Anammox process within the Bio-CAST technology.

Moreover, the unique characteristics of the Bio-CAST technology, such as the presence of both suspended and immobilized biomass, as well as the multiplicity of zones with various environmental conditions, create an ideal environment for the growth and activity of Anammox bacteria. This innovative approach to nitrogen removal has demonstrated significant efficiencies, with TN removal and ammonium removal reaching 81.2% and 85.5% respectively, showcasing the effectiveness of the Bio-CAST technology in wastewater treatment (Mohammadhosseinpour et al. 2016).

In this biological process, which is named as annamox process, where nitrite and ammonium ions are converted to diatomic nitrogen and water.

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

In conclusion, the Bio-CAST technology's ability to create favorable environmental conditions and carefully manage operating parameters is essential for the successful control of the Anammox process. This innovative approach represents a significant advancement in wastewater treatment technology, offering a sustainable and efficient method for nitrogen removal in synthetic wastewater without the need for organic carbon addition (Mohammadhosseinpour 2016); Yerushalmi et al. 2011).

2.6 Pressure Retarded Osmosis

In Pressure Retarded Osmosis (PRO), water acts as an inquisitive explorer, moving across a semi-permeable membrane from a low-salinity to high-salinity. This movement is guided by osmotic gradients, which pull water towards regions of greater solute concentration. As the water progresses, it experiences a fascinating change, migrating towards the side under pressure with elevated salinity and increased osmotic pressure. This process resembles the movement of molecules which is supported by the natural forces present in water.

At the core of this setup lies within the equilibrium of osmotic pressure differentials across the membrane, which surpasses the applied pressure (ΔP) on the draw side. As water permeates through the membrane, the draw solution gradually dilutes, while the feed solution experiences an increase in the concentration. This intricate interplay continues until reaching a state of equilibrium.

The integration of a turbine into this system allows the extraction of power through the controlled depressurization of the permeate. Notably, the PRO process has with two distinct configurations which has different operational conditions: open-loop (OLPRO) and closed-loop (CLPRO) (Pattle, 1954).

In open-loop PRO (OLPRO), the process involves a one-way flow of water through the system. Water moves from the feed solution to the draw solution, generating power through osmotic pressure. Once this occurs, the water is typically discarded, making it a continuous, unidirectional process.

On the other hand, closed-loop PRO (CLPRO) operates with a recirculating flow system. Water passes from the feed solution to the draw solution, where energy is extracted. However, rather than being disposed of, the water is recirculated back to the feed side, creating a closed loop. This configuration allows for more efficient water usage and is often preferred for sustainability reasons.

Although Pressure Retarded Osmosis (PRO) shows promise for future applications, it's important to address some inherent issues. One major challenge is reverse salt flux (RSF), where salts move from the draw side back to the feed side. This leads to concentration polarization (CP), which includes both internal and external concentration polarization. To improve PRO systems, we need to carefully consider and understand these complexities to make them more efficient and sustainable.

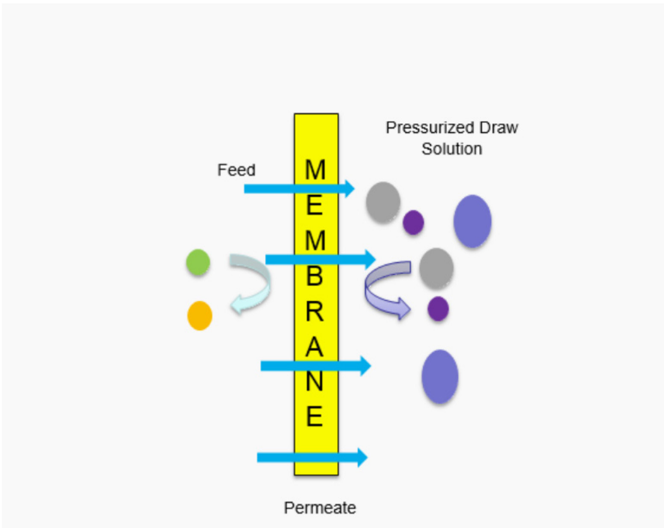


Figure 5. Working mechanism of PRO process (Adhikary 2019).

2.6.1 Classification of PRO

In the field of hydraulic pressure-based salinity gradient power systems, there are two main configurations: Closed-Loop Pressure Retarded Osmosis (CLPRO) and Open-Loop Pressure Retarded Osmosis (OLPRO). Despite sharing basic principles, these setups differ significantly in how they operate, where their draw solutions come from, their potential for power generation, economic factors, and environmental effects (Loeb ,1998; Pattle, 1954).

In the OLPRO paradigm, draw solutions predominantly derive from natural saline sources, such as seawater and hypersaline lakes. In contrast, the feed solution spans a spectrum from freshwater to wastewater, including seawater with lower concentration. OLPRO installations thrive in locations where both feed and draw solutions are abundant and proximate, ensuring optimal operational efficiency.

On the flip side, CLPRO sets itself apart through a continuous regeneration process. Employing methods like heat or alternative approaches, CLPRO ensures the perpetual renewal of both feed and draw solutions. While this regeneration demands energy for re-concentrating the draw solution and extracting water, the flexibility it offers in selecting the draw solution stands out. This unique advantage allows system designers to tailor configurations based on the available energy sources at a specific location, enhancing the adaptability of CLPRO.

Despite its advantages, OLPRO faces some serious challenges. The need for pre-treating both feed and draw solutions, coupled with the energy consumption associated with transporting streams from natural or industrial sources to the PRO plant, significantly impacts overall costs. Moreover, the susceptibility to membrane fouling is heightened in open-loop systems, resulting in escalated membrane expenses. Geographical limitations further characterize OLPRO, restricting plant locations to areas near inlet streams, thereby limiting its applicability range.

In contrast, CLPRO operates with high flexibility and a reduced footprint, with the exception of osmotic heat engines requiring proximity to low-grade heat (LGH) sources for recovering the diluted draw solution. Notably, CLPRO distinguishes itself as an environmentally friendly option, with no discharge—a advantage over OLPRO, where outlet streams are discharged, especially when natural sources are employed.

In the comprehensive evaluation of these configurations, CLPRO emerges as a more versatile and practical option, showcasing superior applicability in the intricate realm of Pressure Retarded Osmosis (PRO). Its flexibility reduced environmental impact, and efficient operational characteristics position CLPRO as a promising choice for advancing the practical application of salinity gradient power systems, marking a paradigm shift in sustainable energy solutions.

2.7 Draw Solutions

The draw solute plays a pivotal role played in the Pressure Retarded Osmosis (PRO) process. Functioning as the catalyst for creating osmotic gradients across semipermeable membranes, the draw solute acts as the driving force behind power generation. While the ideal scenario envisions semipermeable membranes solely permitting the passage of water, real-world complexities arise from the chemistry and physical structure of the draw solute, leading to reverse flux across membranes and potential fouling.

The transportation of the draw solute in the support layer introduces the risk of concentration polarization, a phenomenon that poses a threat to overall process performance. Additionally, challenges in the regeneration of draw solutes from diluted draw solutions and the production of clean water add complexity, especially when inappropriate draw solutes and recycling processes are employed, demanding energy-intensive solutions.

Draw solute selection is a critical prelude to advancing the PRO process, with several key considerations that underscore its pivotal nature. (Hickenbottom et al., 2016)

1. Robust Osmotic Pressure

- A chosen draw solute must generate a substantial driving force across the semipermeable membrane interface.

- Maintaining a robust driving force requires a draw solute with a higher osmotic pressure, ensuring effective osmotic gradients for optimal power generation.

2. Minimal Reversal Salt Flux

- The draw solute should exhibit minimal reversal salt flux to mitigate concentration polarization risks.

- The transportation of solute into the membrane support layer has the potential to induce concentration polarization, diminishing the effective driving force. Therefore, minimizing salt flux is imperative for sustained efficiency.

3. Ease of Regeneration

- Draw solutions in closed-loop PRO systems must be selected with an emphasis on ease of regeneration.

- In closed-loop systems, continuous regeneration is a necessity, often coupled with downstream separation processes. Choosing draw solutes that can be easily regenerated is crucial to minimize energy consumption and overall operating costs.

The judicious consideration of these factors underscores the intricate nature of draw solute selection, highlighting its potential to significantly reduce costs and enhance the overall efficiency of the PRO system. As researchers and engineers delve into the complexities of draw solution chemistry and behavior, advancements in draw solute technologies are poised to play a transformative role in the future of PRO-based sustainable energy solutions.

2.7.1 Factors Influencing Draw Solute Selection

In the complex arrangement of Pressure Retarded Osmosis (PRO), the draw solution plays a crucial role, significantly impacting key factors that shape how well the process works and the amount of power density it produces. The methodology proposed by Achilli et al. (2010)

presents a systematic framework for selecting inorganic draw solutions, encompassing desktop screening, laboratory analysis, and modelling assessments.

Achilli's stipulated criteria outline the essential characteristics that define an ideal draw solute:

1. Solubility and Stability

- The draw solute must exhibit solubility in water and stability under ambient temperature and pressure conditions.

2. Non-Toxicity and Safety

- Non-toxicity is a prerequisite, with adherence to Hazardous Materials Identification System (HMIS) codes ensuring minimal danger. Safety considerations are paramount, with codes above 2 denoting minimal danger and 4 representing severe or lethal hazard.

3. Osmotic Pressure Generation

- An optimal draw solute should generate an osmotic pressure exceeding 1 MPa (145 psi) at saturation concentration, forming the basis for an effective driving force in PRO.

4. Cost Efficiency

- The draw solute's specific cost, i.e., the cost to produce one liter of draw solution capable of generating 2.6 MPa (406 psi) of osmotic pressure, should be less than 10 USD/L.

While non-toxicity is not mandatory for Closed-Loop Pressure Retarded Osmosis (CLPRO), where the draw solution is not intended for human or animal consumption, cost considerations are integral. In CLPRO, where solute recoverability is feasible, the impact of cost on overall energy expenses is deemed minimal.

2.7.2 Classification of Draw Solutes as Explored in Existing Literature

Draw solutes, an integral part for the success of the Pressure Retarded Osmosis (PRO) process, undergoes certain classifications based on their physio-chemical attributes. Extensive research endeavors which direct towards optimizing draw solutions, particularly in the context of Closed-Loop Pressure Retarded Osmosis (CLPRO). This overview examines primary draw solutions referred in the literature, providing a structured analysis based on their osmotic pressure, power density, recovery method, and a detailed exploration of their pros and cons in the context of Pressure Retarded Osmosis (PRO).

2.7.2.1 Inorganic Draw Solutes: Unveiling the Potential and Challenges

In the dynamic world of inorganic draw solutes in Pressure Retarded Osmosis (PRO), monovalent salts like sodium chloride (NaCl) have captured significant attention. NaCl stands out for its ability to generate high osmotic pressure and strong water flow. Its advantages include low viscosity at high concentrations, fast diffusion, and easy separation through heat processes, making it widely appealing. Its cost-effectiveness and abundant availability further enhance its appeal. However, a major downside is its small ion size, which increases Reverse Salt Flux (RSF), reducing flux and overall PRO performance. Additionally, this reverse flux can lead to organic fouling on the feed side of the membrane, posing challenges to system maintenance.

In the research study by Straub et al. (2016), the effectiveness of 3 M NaCl as a draw solute was showcased, achieving a remarkable power density of 59.7 W/m² and an impressive water flux of 44.5 LMH using an HTI TFC membrane under 48.3 bars of hydraulic pressure. This study suggests the potential for even higher power densities with the utilization of more robust commercial membranes, projecting the prospect of reaching 75 bars under 100 bars of applied pressure.

Anastasio et al. (2015) more focused on the influence of draw solution temperature on power density, revealing that increased temperature positively impacts water flux, resulting in higher power density. However, as elevated temperatures concurrently lead to increased salt flux, causing a decline in water flux and promoting Internal Concentration Polarization (ICP).

Hickenbottom et al. (2016) took significant steps with regards to NaCl as the draw solute, by evaluating various Forward Osmosis (FO) membrane performances in PRO. Their study underscored the significant impact of membrane choice and spacer design on power density, ultimately recommending $CaCl_2$ as the most suitable draw solute, considering various parameters such as specific cost, RSF, power density, membrane distillation, water flux, thermal efficiency, net power generation, and electricity generation cost.

Shaulsky et al. (2015) took an innovative approach, by investigating the use of an organic solvent, methanol, as an alternative draw solute for LiCl. Despite exhibiting lower water flux than LiCl-water, LiCl-methanol showcased higher efficiency in terms of reverse diffusion, demonstrating its potential as a potent draw solution for PRO. However, challenges were identified in current membranes withstanding the required applied pressure of 114 bars.

Hickenbottom et al. (2017) further expanded the scope by assessing various inorganic and organic ionic salts for closed-loop Osmotic Heat Engines (OHE). Among the tested draw solutes, H-COONa emerged with the highest water flux and power density, with $CaCl_2$ being recommended as the best draw solute, considering specific cost, RSF, power density, MD water flux, thermal efficiency, net power generation, and electricity generation cost.

Gong et al. (2017) evaluated the complexities of ion transport dynamics during PRO, comparing three inorganic salts: NaCl, $MgCl_2$, and $MgSO_4$. Their investigation shed light on the impact of ion size on solute permeability, emphasizing the crucial trade-offs involved in selecting the optimal draw solution.

Moon et al. (2020) contributed to the discourse by exploring a novel membrane type in OHE, specifically PBO-TFC-F5, modified through direct fluorination. This membrane significantly increased transmembrane water flux compared to un-fluorinated PBO-TFC. This was attributed to reduced ICP resulting from super hydrophilicity and a crumpled selective layer. The study showcased the potential feasibility and practical implementation of PRO at an industrial scale, achieving high power density in closed-loop systems, surpassing the performance of HTI-TFC membranes under the same experimental conditions.

In essence, the exploration of inorganic draw solutes unfolds a spectrum of possibilities and challenges, emphasizing the need for a judicious selection process considering various parameters to optimize the performance of PRO systems.

2.7.2.3 Organic Draw Solutes: Harnessing Advantages Amid Challenges

For draw solutes in Pressure Retarded Osmosis (PRO) processes, organic compounds emerge as a distinct category, presenting advantages over their inorganic counterparts, primarily attributed to their larger hydrated ion sizes. These characteristic yields improved membrane selectivity, leading to lower Reverse Salt Flux (RSF) and mitigated water flux decline during operation. The tailoring ability of organic draw solutes stands out as a unique feature, allowing for engineered properties to enhance their performance in PRO applications. However, the inherent challenges associated with their larger size, including lower diffusion coefficients and increased viscosity at higher concentrations, necessitate addressing these obstacles to ensure optimal PRO system efficiency.

a. Simple Organic Ionic Salts

In a study by Islam et al. (2018), organic ionic were evaluated in CLPRO, demonstrating superior performance compared to commonly used inorganic salts such as NaCl and NH_4HCO_3. The research highlighted that, at concentrations generating equal osmotic pressure

(42 bars), organic salts exhibited enhanced water flux and power density in comparison to their inorganic counterparts. This superiority was attributed to lower RSF, stemming from the larger sizes of their hydrated ions. The study emphasized the critical need for robust membranes to fully leverage the potential of these organic draw solutes, particularly at their solubility limits, where osmotic pressures ranged from 70-1300 bars.

A unique category within organic draw solutes is Switchable Polarity Solvents (SPS). These solvents undergo a reversible transition from water-soluble to water-insoluble states with the addition of CO_2. This distinctive property positions SPS's as promising draw solutes in PRO, offering potential advantages in separation processes utilizing low-grade heat sources and N_2 gas.

b. Hydro-Acid Complexes

Introducing a novel approach, hydro-acid complexes composed of metal(s) and ligand(s) parts offer versatility in draw solute design. In a demonstration by Han et al. (1995), the $Na_5[Fe(C_6H_4O_7)_2]$ (Na-Fe-CA) hydro-acid complex exhibited superior performance in closed-loop PRO. The hydrophilic groups with multi-charged anions contributed to a higher osmotic pressure, surpassing NaCl at the same concentration. Successful regeneration of the diluted draw solution through ethanol precipitation showcased its potential for sustainable osmotic energy production. However, challenges arose at concentrations exceeding 1 M, emphasizing the importance of considering viscosity and energy consumption in pumping.

In conclusion, while organic draw solutes bring forth notable advantages, including lower RSF and potential tailoring of properties, careful consideration is required due to challenges related to diffusion coefficients, viscosity, and performance at high concentrations. The potential for innovative solutions and sustainable energy production is evident, provided these challenges are taken into consideration.

2.7.2.4 Functionalized Nanoparticles: Unlocking Potential Amidst Challenges

In some recent research, functionalized nanoparticles, particularly magnetic nanoparticles (MNPs), have gained prominence in the prospect of draw solutes for PRO. This heightened interest is attributed to the exceptional characteristics of MNPs, characterized by a remarkable surface-area-to-volume ratio and inherent magnetic properties. The structural composition of MNPs, featuring a magnetic core enveloped by a polymer shell, allows for strategic surface modifications, enhancing their performance in osmotic applications.

A key advantage of MNPs lies in the traceability of the magnetic separation methods, facilitated by an external magnetic field acting on the magnetic core within the nanoparticles. However, a persistent challenge arises in the form of particle agglomeration during the magnetic recovery phase, posing economic viability concerns for prolonged operational endeavors. In response to this challenge, Ling and Chung (2011) conducted a comprehensive investigation into the application of ultrasonication to mitigate nanoparticle agglomeration. While successful in reducing agglomeration, the study revealed a discernible decline in the magnetic properties of the nanoparticles over time. This decline-imposed limitations on the overall recovery potential through magnetic separation methods, especially over successive operational cycles. The study underscores the need for a nuanced understanding of the interplay between ultrasonication, magnetic recovery, and sustained magnetic properties of functionalized nanoparticles, contributing valuable insights to the evolving landscape of draw solutes in pressure-retarded osmosis applications.

In essence, the exploration of functionalized nanoparticles introduces both potential advancements and challenges, emphasizing the imperative of a holistic understanding to harness their capabilities effectively in PRO systems.

2.8 Application of PRO

Pattle's exploration of harnessing energy from varying water salinities in 1954 marked the inception of this concept. Subsequently, in 1970, Loeb (1981) introduced the term Pressure Retarded Osmosis (PRO) and developed the first experimental apparatus. A pivotal advancement occurred in 2000 when Loeb enhanced the PRO process by integrating a pressure exchanger, effectively reducing energy consumption. The initial large-scale PRO facility was established in Norway by Statkraft in 2009, utilizing freshwater as the feed solution and seawater as the draw solution. However, with a power density of 3 W/m^2, deemed insufficient for practical electricity production, the plant eventually closed. Economic feasibility has been elusive for PRO due to its struggle to attain the recommended power density of 5 W/m^2, primarily attributed to the limited osmotic power potential between seawater and river water.

An innovative approach emerged when He et al. (2015) integrated the PRO process with reverse osmosis (RO). The RO-PRO prototype in Fukuoka, Japan, employed RO brine as the draw solution for PRO, utilizing 420 m^3/day of wastewater effluent as the feed solution. Employing hollow fiber membranes, this hybrid system achieved a notable power density of 13 W/m^2 at a hydraulic pressure of 30 bars. The "Global MVP" project in Korea further explored the feasibility of the RO-MD-PRO hybrid process to simultaneously reduce water concentration and energy demand.

Membrane Distillation (MD) also played a role in this innovative landscape, as it is a thermally driven, membrane-based phase change process transporting water vapor from a hot feed side across a hydrophobic membrane to a colder permeate side. The integration of a pressure exchanger (PX) between an RO and PRO system was experimentally demonstrated by Achilli et al. (2010) and Prante et al. (2014) evaluated PRO in conjunction with an RO in an RO-PRO desalination system, assessing its specific energy consumption and unveiling a power density of 10 W/m^2 with a specific consumption of 1.0 kWh.

Nevertheless, challenges persist in establishing PRO as an economically viable process and implementing practical PRO hybrid systems. One proposed solution involves elevating draw solution concentrations to enhance the osmotic differential pressure between the feed and draw solutions, ultimately increasing power densities—an integral factor in the economic viability of PRO plants. To fully tap into the high-power density potential of concentrated draw solutions, the PRO system, including membranes, must withstand hydraulic pressures approximately half the osmotic pressure of the concentrated draw solution.

2.9 Limitations of PRO

Research into Pressure Retarded Osmosis (PRO) processes has predominantly concentrated on mitigating the inherent challenges associated with this innovative technology. A thorough review of existing literature reveals several key challenges, as identified by various authors:

Concentration Polarization: Concentration polarization, both external and internal, poses a significant obstacle in PRO processes. External concentration polarization (ECP) occurs on the membrane's surfaces, while internal concentration polarization (ICP) takes place within the membrane support layer. Strategies to combat ECP typically involve enhancing crossflow velocities across the membrane channel. Meanwhile, addressing ICP requires structural or chemical modifications to the support layer to facilitate the preferential transport of water and salts.

Salt Flux Reverse: Reverse salt flux, involving the movement of salts from the draw solution into the feed solution through the semi-permeable membrane, compromises membrane efficiency and increases overall process costs. Countermeasures include optimizing the design of the membrane's active layer to achieve high selectivity. Managing the salt permeability of the active layer is crucial to counteracting reverse salt flux encountered in the support layer.

Fouling: Fouling, characterized by the accumulation of undesired substances on membrane surfaces, obstructs membrane pores, leading to reduced water flux and increased energy consumption in PRO. Variables influencing fouling encompass solution chemistry, pre-treatment levels, operating conditions, and inherent membrane properties.

Draw Solution Recycling and Separation: The selection of a suitable draw solution is pivotal for the effective operation of PRO. However, challenges arise in the recovery, regeneration, and recycling processes of the draw solution (DS), potentially amplifying operational costs. Exploring alternatives such as utilizing concentrated brine from reverse osmosis (RO) as a draw solution can mitigate energy costs in desalination.

Addressing these challenges necessitates a comprehensive approach that integrates advancements in membrane technology, structural modifications, and operational strategies. While these issues have been extensively discussed in existing literature, opportunities for further research lie in innovative solutions and interdisciplinary collaborations to enhance the economic viability and practical application of PRO technology in harnessing osmotic energy.

2.10 Membrane Development in Pressure Retarded Osmosis (PRO)

Membrane development in Pressure Retarded Osmosis (PRO) is crucial for process efficiency. These membranes must meet key criteria: strong mechanical stability to endure varying conditions, minimized support layer thickness to combat Internal Concentration Polarization (ICP), and consideration of salt permeability to enhance effectiveness. Mitigating fouling through membrane design is essential to maintain long-term efficiency.

Two primary types of PRO membranes have been extensively studied: flat-sheet membranes like Cellulose Acetate (CA) and Thin-Film Composite (TFC), and hollow fiber membranes. CA membranes, pioneered by Loeb and Sourirajan, offer advantages like hydrophilicity and robust mechanical strength, with innovations like highly porous support layers enhancing performance. TFC membranes, comprising two materials, address sensitivities and have seen advancements like nano-fiber support layers to reduce ICP impact.

Hollow fiber membranes, with modifications such as polyamide incorporation, exhibit impressive power densities. Surface enhancements result in membranes with high asymmetry, porosity, and narrow pore size distribution, enhancing PRO effectiveness. Continued research and innovation in membrane development are vital for overcoming challenges and realizing osmotic energy's full potential.

2.11 Challenges associated in PRO

1. Membrane Fouling Membrane fouling is a persistent challenge in Pressure Retarded Osmosis (PRO), occurring when particles, organic matter, or minerals accumulate on the membrane surface. This accumulation impedes water flux, diminishing the overall efficiency of the process. To address fouling, researchers are actively developing anti-fouling membranes with improved resistance to particle adhesion. Additionally, refining pre-treatment processes and implementing effective cleaning strategies are crucial to mitigate fouling effects and sustain optimal PRO performance over time (Mckenna et al., 2016).

2. Membrane Degradation The degradation of membranes in PRO systems is a complex issue resulting from exposure to high pressures, temperature variations, and harsh chemicals within the feedwater. Extensive research is focused on enhancing membrane durability and resilience against degradation factors. Innovations in membrane materials, coatings, and fabrication techniques aim to extend membrane lifespan, ensuring sustained and stable performance in PRO applications (Matsuyama et al., 2020).

3. Selectivity and Membrane Permeability Achieving membranes with high water permeability while maintaining selectivity for water molecules over solutes is a fundamental challenge in PRO. Researchers are exploring advanced membrane materials and fabrication methods to optimize these properties. Striking the right balance between permeability and selectivity is crucial for improving overall efficiency and ensuring that PRO systems effectively separate water from contaminants (Matsuyama et al., 2020).

4. Scaling Issues Scaling, the precipitation of minerals on the membrane surface, poses a significant challenge to PRO systems. The development of innovative strategies for scaling prevention and effective cleaning methods is paramount. Research focuses on understanding the mechanisms of scaling formation and implementing measures to prevent or mitigate scaling effects, ensuring sustained membrane efficiency and prolonging operational periods.

5. Energy Consumption The energy-intensive nature of PRO, particularly in high-pressure pumping of feedwater and brine, requires innovative solutions to enhance energy efficiency. Researchers are exploring energy recovery devices and system design improvements to minimize overall energy consumption. Striking a balance between energy input and output is crucial for making PRO more economically viable and environmentally sustainable in the long run.

6. High Capital Costs The initial capital investment required for setting up PRO systems, encompassing the purchase of high-quality membranes and installation of infrastructure, presents a notable barrier. Efforts are underway to reduce capital costs through technological advancements, economies of scale, and innovative financing models. Lowering entry barriers will facilitate broader adoption of PRO technologies in diverse geographical and economic contexts (Prante et al., 2014).

7. Feedwater Quality Variability PRO performance is influenced by variations in feedwater salinity and composition. Adapting the process to handle fluctuations in feedwater quality necessitates the development of advanced control systems and real-time monitoring capabilities. By optimizing PRO systems to operate efficiently under varying conditions, researchers aim to enhance the process's adaptability and reliability.

8. Environmental Impact The concentrated brine produced during PRO processes raises concerns regarding its environmental impact. Research is focused on developing environmentally friendly disposal methods for brine and minimizing its potential ecological consequences. Addressing the environmental implications of brine discharge is crucial for ensuring the overall sustainability and acceptance of PRO as a water treatment and energy generation technology.

9. Lack of Standardization The absence of standardized testing methods and performance metrics in PRO hampers effective comparison and evaluation of different systems. Industry stakeholders are working towards establishing comprehensive standards and protocols to ensure consistency and reliability across various PRO technologies. Standardization efforts aim to streamline assessments, promote best practices, and facilitate the widespread acceptance of PRO in diverse applications.

2.12 Modelling and Simulation of Pressure Retarded Osmosis (PRO) Systems

Pressure Retarded Osmosis (PRO) stands at an intersection of water treatment and energy generation, holding significant promise for sustainable solutions. To comprehend and optimize the intricate dynamics of PRO systems, researchers have extensively focused on mathematical modelling and simulation studies. This discussion explores the evolution of mathematical models, highlighting their role in predicting and enhancing the performance of PRO systems. Moreover, it examines the advancements in modelling techniques, emphasizing their relevance to real-world applications.

Foundational Mathematical Models: In the early stages of PRO research, foundational mathematical models emerged to describe the osmotic pressure-driven phenomenon. These models typically incorporated principles of mass transfer, fluid dynamics, and thermodynamics. One such notable model is the solution-diffusion model, which considers the permeation of water and solutes through semi-permeable membranes. As PRO gained prominence, more sophisticated models evolved, including those integrating electrokinetic and fluid flow dynamics.

Optimization through Modelling: The primary goal of mathematical modelling in PRO is not merely to describe the system's behavior but to optimize its performance. Researchers employ optimization algorithms within the framework of these models to identify key parameters influencing efficiency. This optimization process aids in determining the ideal conditions for maximum water flux, energy extraction, and overall system productivity. The synergy between modelling and optimization serves as a powerful tool for PRO design and operation.

Advancements in Modelling Techniques: Recent years have witnessed substantial advancements in modelling techniques, propelled by innovations in computational power and simulation tools. Computational Fluid Dynamics (CFD) has gained prominence, allowing researchers to simulate the intricate fluid flow within PRO channels. Multiphysics modeling, which combines multiple physical phenomena such as heat transfer and membrane transport, offers a more holistic representation of PRO systems. Machine learning approaches, leveraging vast datasets, further enhance predictive capabilities.

Relevance to Real-World Applications: The practical application of PRO systems requires models that not only capture theoretical intricacies but also align with real-world scenarios. modelling techniques have evolved to consider the impact of variables such as membrane fouling, temperature fluctuations, and varying salinity in feedwater. As a result, these models offer valuable insights for designing PRO systems capable of adapting to dynamic environmental conditions.

Challenges and Future Directions: While modelling and simulation have significantly contributed to understanding and optimizing PRO systems, challenges persist. Accurate representation of fouling and scaling phenomena remains a complex task. Additionally, integrating environmental factors and economic considerations into comprehensive models presents ongoing challenges. Future directions in this field involve refining models to address these complexities and expanding their application to large-scale industrial PRO implementations.

In conclusion, the modelling and simulation of PRO systems have evolved as indispensable tools in the quest for efficient and sustainable water treatment and energy generation. From foundational models to advanced techniques, researchers continuously push the boundaries to bridge the gap between theoretical insights and real-world applications. As technology progresses, the synergy between mathematical modelling and PRO systems will play a pivotal role in unlocking the full potential of this innovative and interdisciplinary approach.

2.13 Utilizing Wastewater as Feed Solution in Pressure Retarded Osmosis (PRO)

The integration of treated wastewater into Pressure Retarded Osmosis (PRO) systems has been a focal point of research, offering a unique avenue for sustainable energy production. One noteworthy exploration conducted by Matsuyama et al. (2020) ventured into using sewage-treated water alongside seawater as the draw solution. Their tests, conducted at varied applied pressures, demonstrated a power density of 3.1 W/m^2 at 15 bars. Setting a target net output power of 2.8 W/m^2, the study suggested scalability for systems using 300,000 to 1,000,000 m^3 of seawater daily, with estimated power generation costs ranging from 0.25 to 0.20 $/kWh.

In a parallel effort, Sakai et al. (2020) investigated the substitution of seawater with SWRO brine as the draw solution, aiming to capitalize on increased osmotic pressure for heightened water flux and power density. The experiments, employing a 10-inch module and an applied pressure of 25 bars, yielded a maximum power density of 13.5 W/m^2. The net output power in PRO surpassed expectations due to optimized permeation ratios and concentrated brine flow rates. Calculated generation costs, based on a power density of 10 W/m^2 and 30,000 m^3/d of concentrated brine, stood at 0.25 $/kWh. Forecasts indicated that achieving a power density of 12 W/m^2 with a modified membrane, could potentially reduce the electricity generation cost to 0.088 $/kWh for 1,000,000 m^3/d of concentrated brine from SWRO.

Furthermore, investigations like that of Wan and Chung (2015) explored PRO systems employing seawater brine (SWBr) and wastewater retentate (WWRe) as draw and feed solutions. Their experiments at 20 bars applied pressure showcased a power density of 27 W/m^2 with baseline solutions of 1 M NaCl and DI water. Subsequent substitutions involving SWBr and 0.81 M NaCl demonstrated power densities of 21.3 W/m^2 and 21.1 W/m^2. Challenges emerged when replacing DI water with WWRe, resulting in a drastic decrease in water flux due to membrane fouling. Implementing ultrafiltration (UF) and nanofiltration (NF) as pretreatment steps successfully mitigated fouling effects, achieving a power density of 9.31 W/m^2. Further modifications involving SWBr and actual RO brine demonstrated the adaptability of PRO systems, with power densities reaching 8.9 W/m^2.

These diverse studies underscore the versatility and potential benefits of incorporating treated wastewater into PRO processes for energy generation. By addressing specific challenges, optimizing system parameters, and exploring different draw and feed solutions, researchers aim to establish wastewater-fed PRO as a viable and sustainable source of energy, contributing to the broader landscape of renewable energy technologies. Through these efforts, the research community envisions a future where wastewater becomes a valuable resource in the quest for cleaner and more sustainable energy solutions.

2.14 Evaluating Annamox enhanced wastewater in Pressure Retarded Osmosis

The mining industry, particularly gold mining, confronts a dual challenge of managing wastewater with high salinity and various pollutants while simultaneously striving for sustainable energy practices. This review delves into the potential synergy between the Annamox process and Closed Loop Pressure Retarded Osmosis (CLPRO) as an innovative approach to efficiently treat mining wastewater and generate electricity. The complex composition of mine tailing water necessitates advanced treatment methods, and the Annamox process, known for its ability to remove nitrogen compounds from high-nutrient wastewater, emerges as a promising solution. By leveraging this anaerobic ammonium oxidation technique, the mining industry can significantly reduce its environmental impact.

Some wastewater generated from the mining has high amounts of cyanide present in them. This cyanide is commonly used in the mining industry for gold and silver extraction from ore through processes such as heap leaching and gold cyanidation. During these processes, cyanide solutions were used to dissolve precious metals from the ore, forming a cyanide-containing wastewater known as "cyanide leachate". This cyanide leachate contains nitrogen. Cyanide compounds, including hydrogen cyanide (HCN) and cyanide ions (CN^-) have nitrogen present in them. In the Annamox process, the bacteria responsible for this conversion, called Anammox bacteria, oxidize ammonium with nitrite as the electron acceptor, producing nitrogen gas as a byproduct. This process eliminates the need for external carbon sources, making it highly efficient and environmentally friendly.

After the Annamox process effectively removes nitrogen from the wastewater, the treated water can then be utilized for power generation through technologies like Pressure Retarded Osmosis (PRO). In PRO, osmotic gradients created between a concentrated solution and freshwater are harnessed to generate hydraulic pressure, which is then used to drive a turbine and produce electricity.

CLPRO, a cutting-edge osmotically driven process, offers an avenue for sustainable energy generation. This method utilizes the salinity gradient between a high salinity draw solution and a low salinity feed solution to produce power. The integration of Annamox-treated mine tailing water into CLPRO creates a closed-loop system, where the exciting wastewater not only undergoes efficient treatment but also contributes to electricity generation. The nitrogen-rich permeate from the Annamox process becomes a valuable resource for CLPRO, providing a dual-purpose solution to wastewater treatment and clean energy production.

However, the implementation of this synergetic system comes with challenges. Membrane fouling, scalability, and the selection of suitable draw solutes are key issues that require careful consideration. Overcoming these challenges presents opportunities for developing efficient, sustainable, and economically viable wastewater treatment and energy generation processes. The closed-loop system, once optimized, has the potential to transform wastewater from a liability into a valuable resource for the mining industry.

In considering the environmental and economic implications, the synergetic approach between Annamox and CLPRO offers a holistic solution. It not only addresses environmental concerns related to mining wastewater but also provides economic benefits. By converting wastewater into a resource for electricity generation, goldmines can potentially reduce their environmental footprint and operational costs. The treated wastewater, enriched with nitrogen compounds, holds promise for non-potable purposes, thereby reducing the demand on freshwater resources.

To illustrate the practical application of this synergetic approach, a case study within a goldmine is considered. The wastewater, post Annamox treatment, serves as the feed for CLPRO, generating electricity for on-site use. The integration of these processes demonstrates a circular economy approach, where resources are efficiently utilized and environmental impacts are minimized.

In conclusion, the synergy between Annamox-enhanced wastewater treatment and CLPRO represents a promising avenue for sustainable energy generation within the mining industry. This innovative approach has the potential to redefine the relationship between wastewater management and energy production, contributing to the overall sustainability of mining operations. Further research, development, and pilot-scale studies are imperative to validate the feasibility and optimize the performance of this integrated solution in real-world applications.

Chapter 3: Materials & Methodology

3.1 Experimental Setup

The laboratory-scale system for implementing Annamox-enhanced wastewater treatment in closed-loop pressure-retarded osmosis (PRO) is designed to systematically investigate the integrated process. The physical setup has various components, reactors, and specialized equipment tailored to replicate and assess the proposed treatment approach. The laboratory-scale PRO setup and its components are shown in Figure 6.

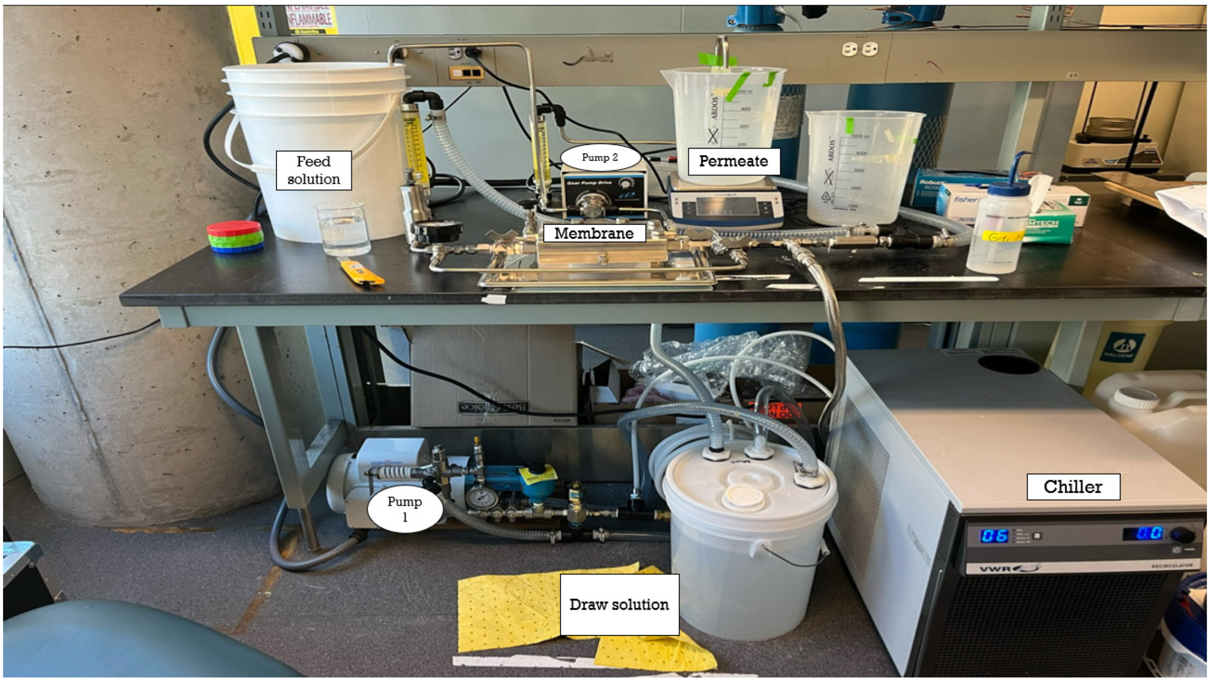


Figure 6. Lab-scale PRO setup

3.2 Materials

The mining wastewater analyzed was obtained from Agnico Eagle Mines Limited, situated in Rouyn-Noranda, QC, CA. The samples were taken post cyanide removal process within the wastewater treatment system. The membrane that was used for these experiments was a flat sheet Cellulose Tri-Acetate (CTA) membrane which was provided by Sterlitech Inc. (Auburn, Washington, USA). The membranes are composed of cellulose and show low fouling effects.

The CTA membranes are able to process the precipitating salts and polymerized organics with minimal impact on the operating process. The membrane specifications are illustrated in Table 1. For preparation of synthetic feed solution and draw solution chemicals such as NaCl, KCl, $MgCl_2$, ($(NH_4)_2 CO_3$) from Fisher Scientific Co. (Toronto, ON, CA) had been purchased. DI water (Millipore, Billerica, MA) was utilized for the preparation of different draw solutions. Different inorganic chemicals were mixed with DI water to produce draw solutions. A calibrated pH meter was used to measure various characteristics of water.

Table 1. Membrane Specifications

Manufacturer	Sterlitech Inc.
Membrane Material	Cellulose Tri-Acetate
Operating Conditions	Maximum operating temperature: 50°C pH range: 3-7 Maximum chlorine: 2 ppm Minimum transmembrane pressure: 34.47 kPa Maximum inlet pressure: 517.11 kPa Recommended pre-filtration: 100 µm or lower (if particulates are present).
Packaging and Storage	Storage: (3-25 °C) Membrane must be kept moist at all the times
Shelf Life	Up to 3 years

Source: https://www.sterlitech.com/ftsh2o-flat-sheet-membrane-cta-fo-cf042-5-pk.html

3.2 Feed solution preparation

The feed solution in a Pressure Retarded Osmosis (PRO) experiment refers to a solution with a lower concentration of solutes compared to the draw solution. It was placed in contact with the draw solution across a semi-permeable membrane. The feed solution acted as the source of water molecules that naturally diffuse through the membrane into the draw solution due to the osmotic pressure gradient. This movement of water generates a positive water flux, which can be utilized for various purposes such as power generation or water purification.

Here, the synthetic wastewater was used in two different kinds of Annamox Bio-Cast reactors. The annamox enhanced synthetic water was then used as the feed solution in the PRO system. The first one was prepared with various chemicals and trace metals. The constituents used are described in Tables 2 and 3. After preparing the synthetic feed solution of 100 liters, the water was passed through the Annamox reactor to remove nitrites and nitrate compounds in the form of nitrogen gas. This process was particularly designed for the removal of nitrogen compounds, specifically ammonium (NH_4^+) and nitrite (NO_2^-), from wastewater. The Anammox bacteria thrive in the controlled conditions provided by the reactor, utilizing the ammonium and nitrite present in the wastewater as their energy source and oxidizing agent, respectively. As a result, they multiply and actively perform the Anammox reaction. The treated effluent, now depleted of significant nitrogen compounds, can be further processed or discharged into the environment with reduced environmental impact. The annamox reaction shows that the present ammonium and nitrite compounds are converted to nitrogen and water.

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

The permeate from this Annamox reactor was used as the feed solution in the PRO setup to produce energy from the gathered wastewater.

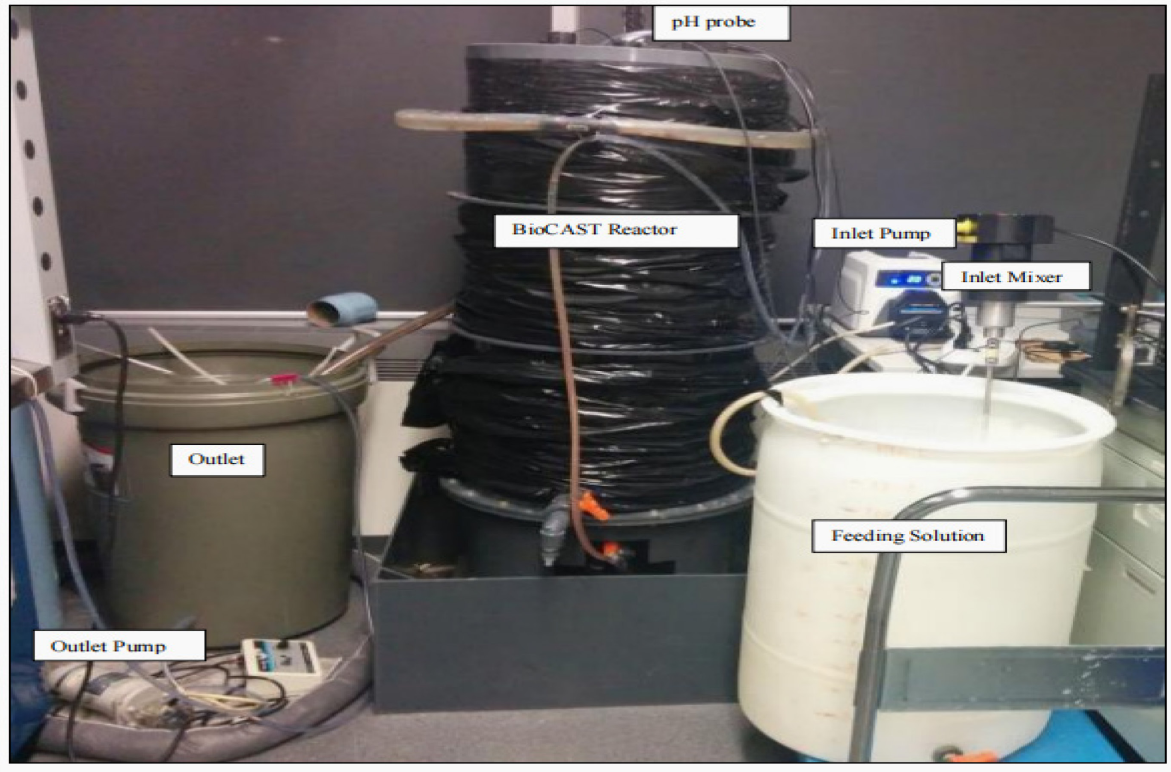


Figure 7. Bio-Cast Annamox Reactor with synthetic water (Source: Mohammadhosseinpour et al. 2016)

Table 2.Constituents of Synthetic Wastewater

Synthetic Waste Water	
Chemical	g/100L
EDTA	0.625
$FeSO_4$	0.625
KH_2PO_4	5.66
$MgSO_4$	20
$CaCl_2$	30
$NaHCO_3$	120
NH_4Cl	96
Trace elements	100 ml

Table 3. Constituents of trace elements

Trace Elements	
Chemical	g/L
EDTA	15
$ZnSO_4.7H_2O$	0.43
$CoCl_2.6H_2O$	0.24
$MnCl_2.4H_2O$	0.99
$CuSO_4.5H_2O$	0.25
$NaMoO_4.2H_2O$	0.22
$NiCl_2.6H_2O$	0.19
$NaSeO_4.10H_2O$	0.21
H_3BO_4	0.014

In the second type of Bio-Cast reactor the synthetic water prepared was mixed with the real mine water of higher salinity in lower proportions. In order to maintain the stability of the Bio-cast rector and provide favorable surroundings to grow the annamox bacteria in the reactor, the real mine wastewater provided by Agnico Eagle Mines Limited, situated in Rouyn-Noranda, QC, CA was used in the proportions of 1L, 2L, 4L with 19L, 18L and 16L of synthetic water respectively.

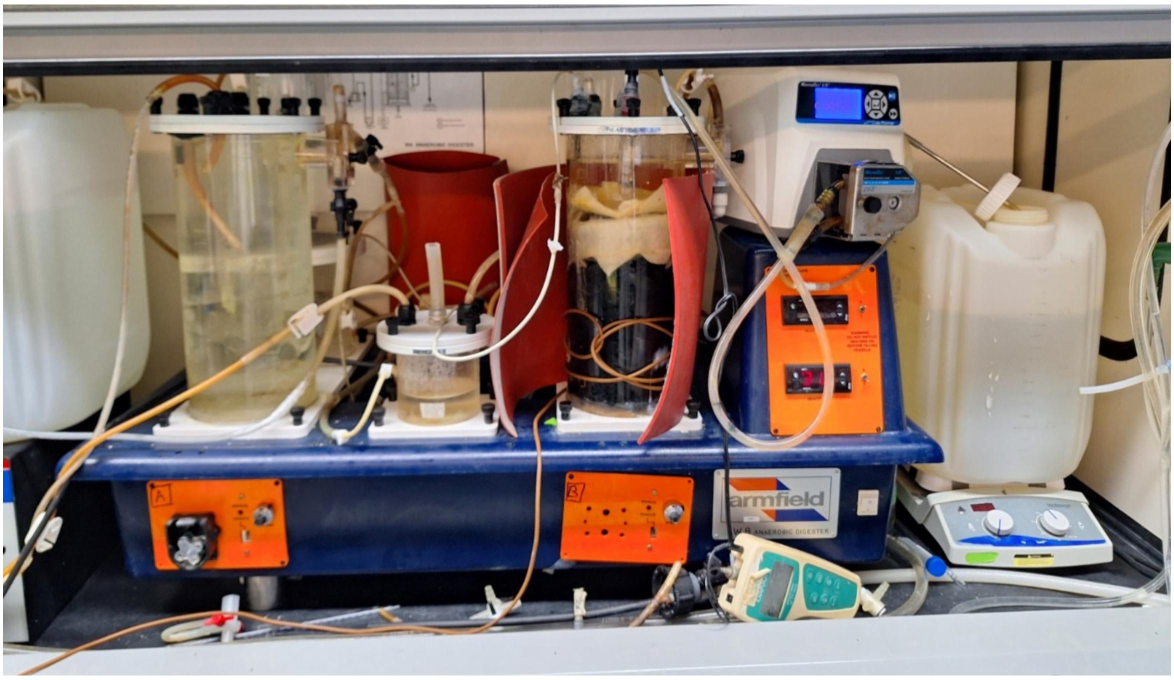


Figure 8. Mini Annamox Bio-Cast reactor

Mini Annamox Bio-Cast reactor was used as shown in Figure 8 where one liter of mine tailing was mixed with 19L of synthetic water as feed solution. After achieving the sustainable bacterial growth, the proportion of mine tailing water was increased respectively to make the solution higher in salinity. The permeate from this system was utilized as the feed to run through the laboratory setup of PRO for energy generation.

3.3 Draw Solution Preparation

The draw solution in a Pressure Retarded Osmosis (PRO) experiment refers to a highly concentrated solution placed in contact with a feed solution of lower concentration across a semi-permeable membrane. It plays a crucial role in generating osmotic pressure and driving the flow of water from the feed solution to the draw solution, which can be utilized for power generation or water purification purposes.

The research aimed to identify an optimal draw solution for Pressure Retarded Osmosis (PRO) processes, particularly focusing on its efficacy under varying salinity conditions. Initial experiments utilized synthetic water as the feed solution, examining different chemicals such as NaCl, KCl, $MgCl_2$, and ($(NH_4)_2CO_3$) at different concentrations. Among these, ammonium carbonate emerged as the most promising draw solution due to its consistent performance across a range of salinity levels. The findings underscore the significance of draw solution selection in PRO processes and suggest that ammonium carbonate shows remarkable potential for both low and high salinity scenarios, particularly when dealing with synthetic water mixed with mine tailing water.

3.4 IC and ICP MS Analysis

Ion chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) 930 compact IC flex (Metroohm, Mississauga, ON) were utilized to detect ions and heavy metals in the water, respectively. For performing both tests, 10 ml of samples are needed. In the ICP-MS procedure, samples were passed through pneumatic nebulization, where they are exposed to high-temperature plasma composed of argon gas. The plasma's energy is transferred to the sample stream, which causes the target elements to dissolve and ionize. Subsequently, by the use of mass spectrometer (either quadrupole or magnetic) the resulting ions are separated from the plasma based on their mass-to-charge ratio. An electron multiplier detector than detects the separated ions, and the data is processed by the computer. The samples from the untreated synthetic wastewater, treated synthetic wastewater, synthetic wastewater with different draw solutes and treated synthetic wastewater with real mine tailings and PRO processed wastewater were collected for analysis.

On the other hand, ion chromatography (IC) is a form of liquid chromatography which was used to measure the concentration of the ions present in the samples on the basis of their interaction with resin (stationary phase) and the eluent (mobile phase). The equipment used was 930 compact IC flex (Metroohm, Mississauga, ON). There are two columns, an anion column (Metrosep A Supp 5: 4.0 × 150 mm) and a cation column (Metrosep C 6: 4.0 × 150 mm) (Metroohm, Mississauga, ON), which can be used each at a time, used to attract the anions and cations present. Based on their affinity for the specific resin, the ions present in the chromatographer column moves on a definite speed, then they will be separated on the basis of their size and ion charge. Moving forward, the eluent passes through the column and the ions which are having weak attraction to the column's eluate faster. Meanwhile a conductivity meter will detect the exit of ions from the column and plots a graph of conductivity vs. time. At several points, each ion produces a peak in the graph, which shows its concentration in the sample. Here, oxalic acid and sodium carbonate of 98% concentrations diluted by 100 times, were used as eluents for cations and anions respectively. The samples from the untreated synthetic wastewater, treated synthetic wastewater, synthetic wastewater with different draw solutes and treated synthetic wastewater with real mine tailings and PRO processed wastewater were taken each after 6-hour run on the PRO setup and were filtered using the syringe and then diluted by the factor of 20, which means that every 0.5 ml of sample was mixed with 9.5 ml of DI water. Dilution for this test is necessary due to their measurement limits where the calibration range for cation column is 1-15 ppm and for anion column is 1-20 ppm. At the end of data collection, each value is multiplied by the dilution factor of 20 in order to obtain the actual concentrations.

3.5 Draw solution evaluation for PRO experiments

A bench scale PRO setup was used to perform experiments for choosing an appropriate draw solution for energy generation. For all tests performed, the membrane used was cellulose triacetate (CTA) membrane, which was soaked in DI water for more than an hour prior to the experiment, and after that it was placed in the cross-flow cell with the effective membrane area of 33 cm^2. The lab scale setup was done as per Figure 9. For performing the test, 15 L of synthetic wastewater i.e., the permeate from the annamox bio-reactor was used as feed solution, which was connected with a variable feed gear pump (from Cole-Parmer Instrument Company, Vernon Hills, Illinois, USA). For the side of draw solution, 15L of the draw solutions were prepared for 1M concentration of sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride ($MgCl_2$), and ammonium carbonate ($(NH_4)_2CO_3$) with the help of magnetic stirrer a night before performing the experiment. While running the experiment both feed solution and draw solution were placed at the respective places and the high-pressure pump was used at the pressure of 1241.04 kPa. A pressure gauge was placed near the cell to observe the applied pressure on the membrane. An after pressure gauge a flow meter was also inserted to maintain the flow rate of feed solution as 1.2 L/ (m^2.h) or (LMH) and on the draw side it was maintained at 0.8 L/ (m^2.h) or (LMH). A chiller (VWR International, Montreal, Quebec) was used to keep the constant temperature of the system at 20 °C. The permeate discharged from the other side of the cell is collected in a container which was placed on the balance (VWR International, Montreal, Quebec). This balance was connected to the laptop via USB port and under a specific application the data was stored every 1 minute for the duration of 6 hours. At the end of each test, the salinity of the draw solution was measured to know the dilution. It was compared with the salinity of the draw solution before the test was performed. After the experiment various types of characteristic tests were performed on the feed and permeate to know the characteristics of the effluent. Following the analysis of the experimental results and multiple characteristic tests, a most suitable draw solute for further experimentation was determined. Subsequently, experiments involving synthetic water mixed with real mine wastewater were performed using this selected draw solute only.

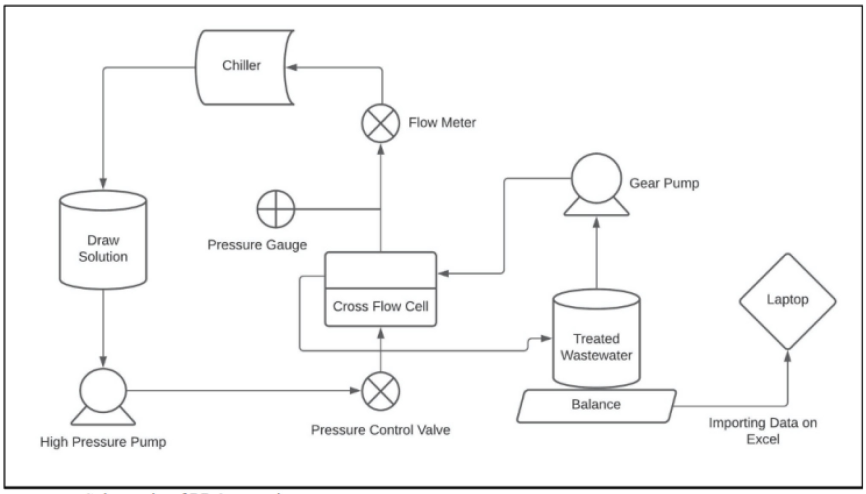


Figure 9. Schematic diagram for evaluation of draw solute

3.6 PRO Experiment

The lab scale set-up for PRO is shown in Fig.10. Firstly, the membrane was soaked in DI water for more than an hour to achieve the best performance. Then the membrane was rinsed throughout with DI water before placing it in the cross-flow cell which has an effective area of 33 cm^2. The active layer of the membrane is facing the draw side while the support layer is faced by the permeate side. Spacers were provided by Porifera which were placed below the membrane in such a way that the membrane avoids the direct contact with the streams and a meshed metal sheet was placed above the membrane to keep the membrane steady when the pressure is applied on it, in order to avoid membrane rupture. A variable feed gear pump (from Cole-Parmer Instrument Company, Vernon hills, Illinois, USA) was used for the circulation of feed solution in a closed loop cycle at the rate of 1.2 LMH. While, on the other hand, the draw solution, was circulated and pressurized by a high – pressure pump at the constant pressure of 180 psi, and the flow was maintained at 0.8 LMH. A chiller (from VWR International, Montreal, Quebec) was used to maintain the temperature at 20 °C of draw solution, to prevent the high – pressure pump heating up and also to neglect the temperature effect on the experiment. At the beginning of the experiment, 15 L of annamox enhanced synthetic water mixed with real mine tailing water was taken as feed solution, while, ammonium carbonate was used as the draw solution. The pressure of the system was increased gradually to 180 psi using the valve placed on the pump. After the initial fluctuation settles down and the system gets stable, then the trans-membrane water flux was measured over the time period of 6 hours. The permeate discharged on the other side of the cell was collected in a container which was placed on the balance (VWR International, Montreal, Quebec). This balance was connected to the laptop via USB port and under a specific application the data was stored for every 1 minute for the duration of 6 hours. Data collection was started once the system gets stabilized and the pressure increases to the desirable amount. The total experiment was performed for 6 hours. The chiller could not maintain the temperature at the set amount after 6 hours of performance. Using the equation, the permeate flux of the various permeate was calculated:

$$J_w = \frac{\Delta m}{\rho \, Am \, \Delta t} \quad \text{.......... (1)}$$

Where J_w is the water flux, Δm is the amount of permeate collected in the given interval of time, ρ is the density, and A_m is the effective area of the membrane, and t is the duration of time when data is collected which is 1 min. The salinity of the draw solution was measured before and after performing the experiment to know the dilution. After the experiment various types of characteristic tests were performed on the feed and permeate in order to know the characteristics. By multiplying the water flux with the applied pressure, the amount of power generated per unit of membrane area (W/m^2) was calculated by the equation:

$$W = J_w \times \Delta P \quad \text{.......... (2)}$$

Where W is the power generated (W/m^2), J_w is the permeate flux and ΔP is the pressure applied per unit area.

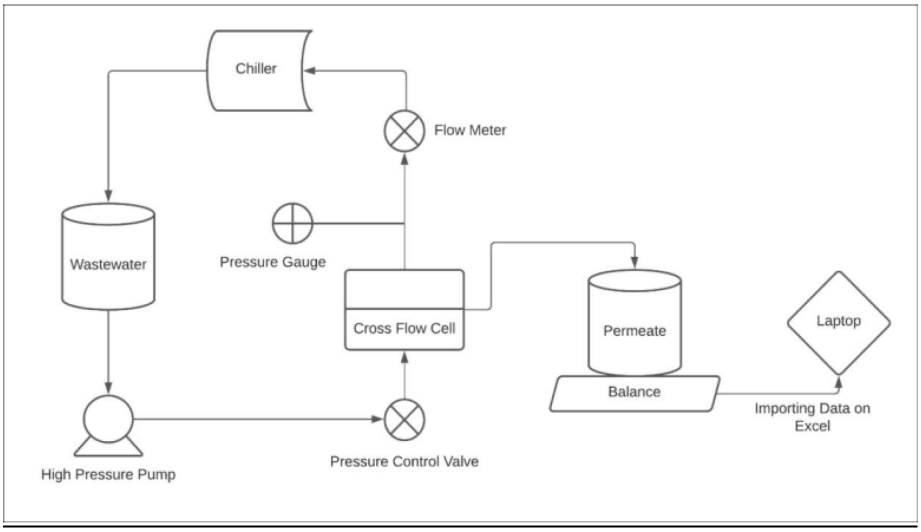


Figure 10. Schematic diagram for PRO experiment

Chapter 4: Results and Discussion

4.1 Characteristic Analysis of Feed Solution

The annamox treated synthetic water was used as the feed solution in the PRO experiment for energy generation. Two types of synthetic water were used in performing PRO experiments. The synthetic water prepared in lab from the various chemicals and trace elements, which is of low salinity as compared to the real mine tailing effluent, which was passed through the annamox reactor to remove ammonia, nitrate and nitrite. As the salinity of the real mine tailing water is high which can lead to many instabilities in the annamox bioreactor, synthetic wastewater was used in the annamox reactor. This synthetic wastewater was used to carry out initial experiments on the lab scale PRO system. Evaluation of the draw solution and determining the suitable draw solution for carrying out further PRO experiments was carried out. For further experiments on the PRO system to generate power density, the synthetic water blended with real mine tailing wastewater at different concentrations, was passed through the annamox bio-cast reactor and used as the feed solution.

Firstly, the working of annamox bioreactor was evaluated, as the wastewater from the mining industry is rich with nitrogen compounds. In order to remove ammonia in form of nitrite and nitrate it is passed through annamox bioreactor. The IC analysis of the feed and effluent from the annamox bioreactor are displayed in Table 4. The concentrations of heavy metals and ions have changed after passing it through the annamox bioreactor, with notable decrease in NO_2^-, NH_4^+ present in the synthetic water after the process of annamox treatment, which is used as feed solution in PRO. Here, the concentrations of calcium and magnesium are high which can lead to reaction with sulphate ions and can cause scaling. The concentration of sodium is high due to addition of sodium carbonate ($NaHCO_3$) in the synthetic wastewater. The presence of ammonium chloride can also be observed in the concentration of the solution.

Table 4.Concentration of the ions in the synthetic feed solution and effluent from the Annamox Bio-reactor by IC analysis.

Ion	**Cl^-**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**PO_4^{3-}**	**Na^+**	**NH_4^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Feed (mg/L)	647.8	365.6	49.14	127.4	32.2	820.6	206.2	343.2	172.2	551.6
Effluent (mg/L)	636.14	18.88	123.42	125.86	31.9	821.3	98.9	332.7	170.9	558.6

The characteristic tests of the solution are mentioned in Table 5 where the pH seems to be slightly alkaline in nature while the conductivity indicates the presence of different ions in the solution. The TDS values represents the total concentration of dissolved solids in the water, including salts, minerals, and organic matter. The resistivity of the solution shows low conductivity which indicates that the water is suitable for specific experiments. The TOC concentrations are much higher which can lead to reduction in permeate flux and water recovery due to presence of decayed organic matter such as annamox bacteria in the wastewater and other decayed natural organic matter.

Table 5. Characteristics of synthetic effluent from Annamox.

pH	7.97
Conductivity (mS/cm)	3.205
TDS (mg/l)	0.000001226
Resistivity (Ω.cm)	392.2
TOC (mg/L)	30.9

4.2 Evaluation of draw solution for PRO

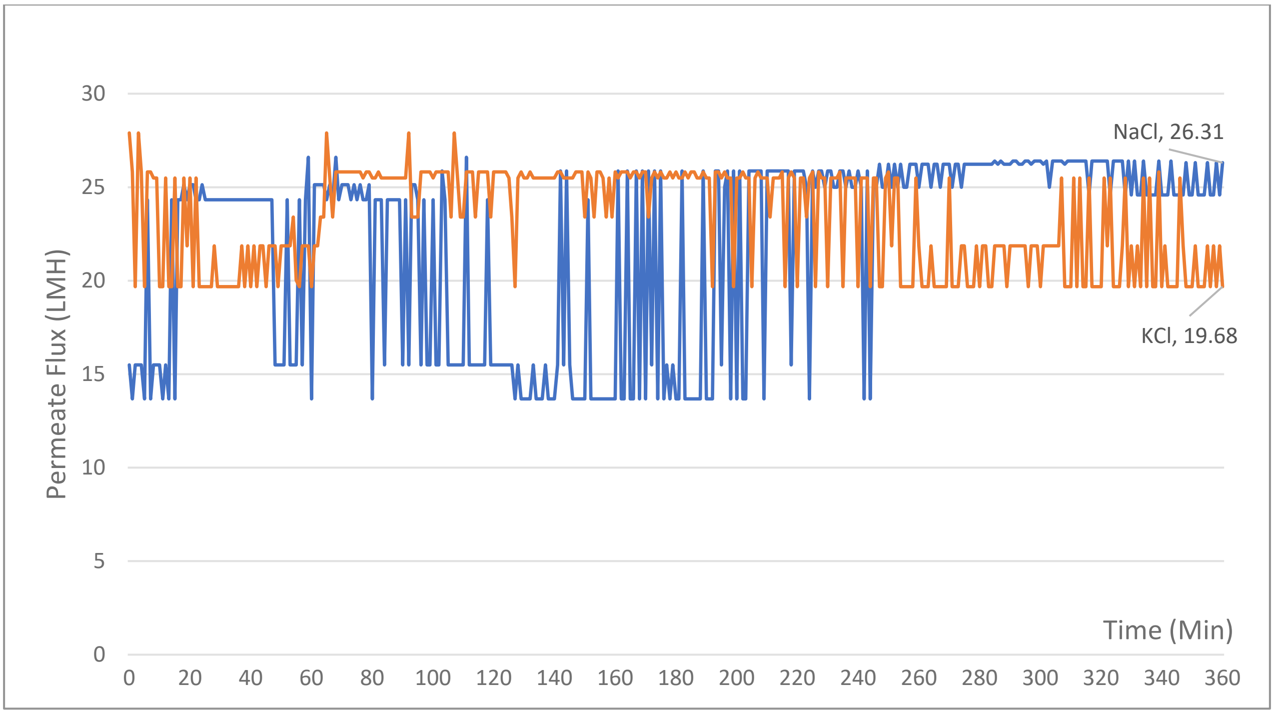
The selection of the draw solutes for efficient energy generation through PRO must consider the low salinity of synthetic wastewater but also its effectiveness across various salinity levels. Factors such as osmotic pressure, scaling potential, membrane compatibility, and cost are crucial in this evaluation. Performance testing across salinity ranges is necessary to ensure the chosen draw solute's efficacy in diverse conditions. One M concentrations of sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride ($MgCl_2$), and ammonium carbonate ($(NH_4)_2CO_3$) were tested while maintaining the pressure of 1241.06-1378.95 kPa. After testing each draw solution with feed solution as synthetic water for 6 hours, each draw solution was experimented three times with the synthetic wastewater as feed solution and the average results for power density, permeate flux and characteristic test of each draw solutions were discussed in Tables 6 and 7 respectively.

Table 6. Evaluation of various draw solutions for efficient energy generation through PRO.

Draw solution (1M concentration)	**Permeate flux generated (LMH)**	**Power density (W/m^2)**
NaCl	26.6	10.21
KCl	27.9	10.69
$MgCl_2$	25.8	9.89
$(NH_4)_2CO_3$	33.9	13.02

Table 7. Characteristics of draw solutions.

Characteristic tests	NaCl	KCl	$MgCl_2$	$((NH_4)_2CO_3)$
pH	7.0	6.53	6.57	7.97
Conductivity (mS/cm)	51.63	19.52	15.4	2.296
TDS (mg/l)	1.663×10^{-5}	6.207×10^{-5}	4.847×10^{-5}	8.887×10^{-5}
Resistivity (Ω.cm)	26.47	71.47	93.320	498.6
TOC (mg/L)	20.39	16.54	15.52	18.6



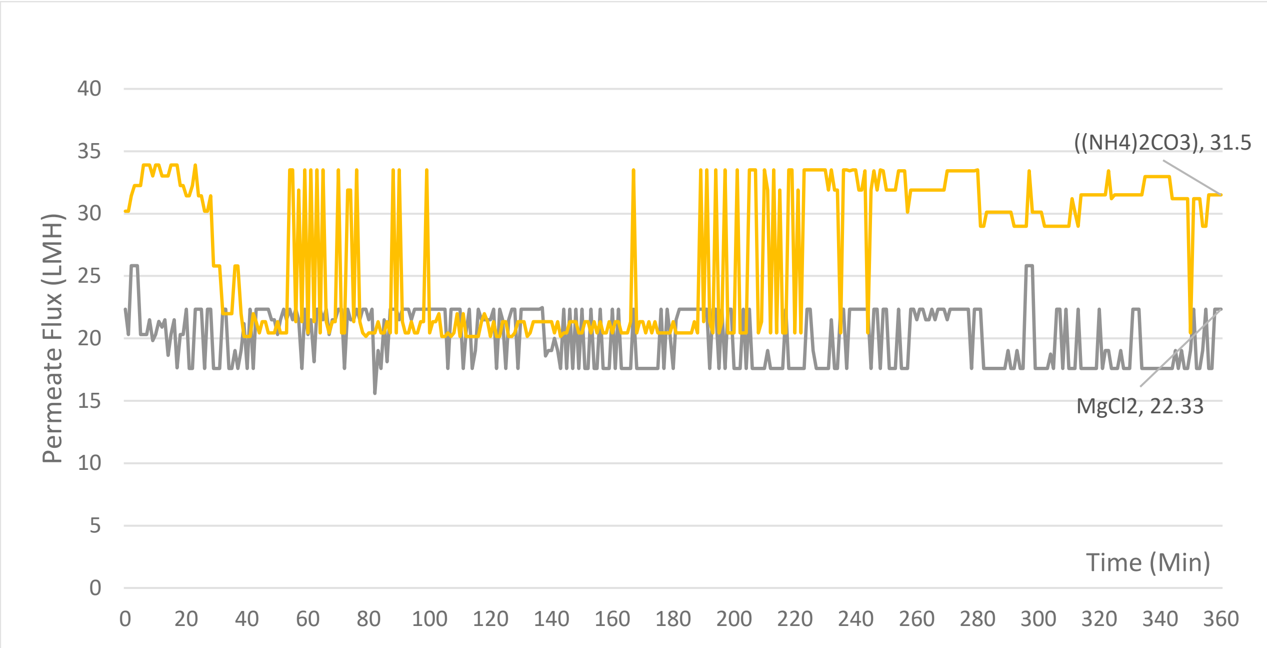


Figure 11. Permeate Flux (LMH) vs Time (Min) for various draw solutions

Based on the following factors, ammonium carbonate ($(NH_4)_2CO_3$) was observed to be performing better than other draw solutions. Here are the reasons to choose ammonium carbonate ($(NH_4)_2CO_3$) as a suitable draw solution with the feed solution as annamox treated synthetic wastewater mixed with real – mine tailing water.

1. Compatibility with Annamox Treated Synthetic Wastewater: Ammonium carbonate is composed of ammonium ions (NH_4^+) and carbonate ions (CO_3^{2-}). Since the feed solution is annamox treated synthetic wastewater, which likely contains ammonium ($NH4^+$) as a key component, using ammonium carbonate as the draw solution ensures compatibility and effective osmotic potential.

2. High Osmotic Pressure: Ammonium carbonate has a relatively high osmotic pressure compared to NaCl, KCl, and $MgCl_2$. This property is essential for driving water across the membrane in the PRO process. Higher osmotic pressure can lead to greater water flux, enhancing the efficiency of the process.

As shown in Figure 11, it is observed that, increasing the osmotic pressure gradient between the feed and draw solution will generally lead to increase in permeate flux. This is because a higher osmotic pressure gradient provides a greater driving force for water to move through the membrane.

The osmotic pressure of a solution depends on the concentration of solute particles within it. Ammonium carbonate $(NH_4)_2CO_3$ has a higher osmotic pressure compared to NaCl, KCl, and $MgCl_2$ because it dissociates into more particles in solution, thus increasing the concentration of solute particles and subsequently raising the osmotic pressure.

When ammonium carbonate dissolves in water, it dissociates into three ions: two ammonium ions ($NH4^+$) and one carbonate ion (CO_3^{2-}). This means that each molecule of ammonium carbonate generates three solute particles in solution, contributing to a higher overall solute concentration and thus higher osmotic pressure. While sodium chloride dissociates into two ions when dissolved in water: one sodium ion (Na^+) and one chloride ion (Cl^-). Therefore, each molecule of sodium chloride generates two solute particles in solution. Similar to sodium chloride, potassium chloride also dissociates into two ions in solution: one potassium ion (K^+) and one chloride ion (Cl^-). Magnesium chloride dissociates into three ions in solution: one magnesium ion (Mg^{2+}) and two chloride ions (Cl^-).

Comparing the number of solute particles generated by each compound, we can see that ammonium carbonate generates more solute particles per molecule compared to sodium chloride and potassium chloride, but the same number of solute particles per molecule as magnesium chloride. Therefore, when all other factors are constant, a solution of ammonium carbonate will have a higher osmotic pressure compared to solutions of sodium chloride and potassium chloride, but potentially similar osmotic pressure compared to magnesium chloride, depending on the concentration of the solutions.

3. Ion Selectivity: Ammonium carbonate provides specific ion selectivity due to the presence of ammonium and carbonate ions. This selectivity can minimize undesired ion leakage and improve the purity of the permeate, which is beneficial for applications where water quality is critical, such as wastewater treatment plant.

When considering the use of draw solutions in Pressure Retarded Osmosis (PRO) processes, opting for environmentally friendly options such as ammonium carbonate aligns with sustainable practices and helps to minimize the environmental footprint of the process. By using biodegradable draw solutions like ammonium carbonate, the potential for environmental contamination and long-term impacts on ecosystems is reduced. This supports the overall goal of achieving sustainable and environmentally responsible water treatment and energy generation processes.

4. Chemical Stability: Ammonium carbonate is chemically stable under typical operating conditions, ensuring consistent performance and reliability over time. This stability is crucial for the long-term operation of PRO systems.

In conclusion, selecting ammonium carbonate as the draw solution for further PRO experiments offers compatibility with annamox enhanced synthetic wastewater, high osmotic pressure, ion selectivity, cost-effectiveness, and chemical stability, making it the most suitable choice.

4.3 Pressure Retarded Osmosis Experiments

The sole purpose of performing PRO is to generate electricity, synthetic water mixed with real mine tailing water was used as the feed solution. The real mine tailing water was mixed in proportions of 1L, 2L and 4L with 19L, 18L, and 16L of synthetic feed water and was passed through the annamox bioreactor and the permeate was used for the PRO experiment. On the draw solution side, as the salinity of feed solution is lower to produce efficient energy, the draw solution with a concentration of 3M was prepared by mixing 9 moles (864g) of ammonium carbonate with DI water and each test was performed for 6 hours of time. Fouling was observed after 4 hours of continuous testing, when the permeate flux reduced significantly during that time. The average achieved permeate flux was 28.97 ± 1.36 LMH as shown in Figure 11. The salinity of the draw solution was measured before and after performing the experiment which decreased from 28.09 ppt to 17.3 ppt which showed that the draw solution was diluted and needed to be recovered after 6 hours of the continuous experiment.

Figure 12 shows the results of the permeate flux with respect to time, where synthetic water was mixed with 1 L, 2 L, and 4 L of real mine water and draw solution as 3M ammonium carbonate named as trial 1, trial 2 and trial 3, respectively. The average generated power density was 11.0 ± 0.5 W/m^2. According to a previous study (Gerstandt et al., 2008), for any profitable

PRO plant, the power density should be between the range of 4-6 W/m^2. Therefore, the power density achieved using the synthetic wastewater mixed with real mine water, which was investigated in the study, showed a promising result.

Another test was performed using DI water as the feed solution and ammonium carbonate as the draw solution, which generated the power of 20.09 W/m^2 and permeate flux of 52.2 LMH which showed the effect of fouling is mentioned in Figure 12. Whereas based on previous studies (Wan and Chun, 2019), the effective testing between DI water as feed solution and 3M ammonium carbonate as draw solution to evaluate the fouling effect in the membrane support layer and as the feed was not saline and the draw solution was highly saline, it shows the water flux and power densities are higher which clearly shows the detrimental effect of fouling (Figure 12). On the draw side the hydrodynamic shear force induced by crossflow prevents solute deposition on the active layer of the membrane, while on the support layer, there is no shear force and thus the solute deposition causes a decline in permeate flux. Kim et al. (2015) investigated the fouling propensity of organic and inorganic matter in the membrane support layer and concluded that the inorganic scaling has a superior effect on flux reduction compared to the organic scaling. The initiative of combining the annamox process and PRO process to achieve wastewater reuse and power generation shows good potential.

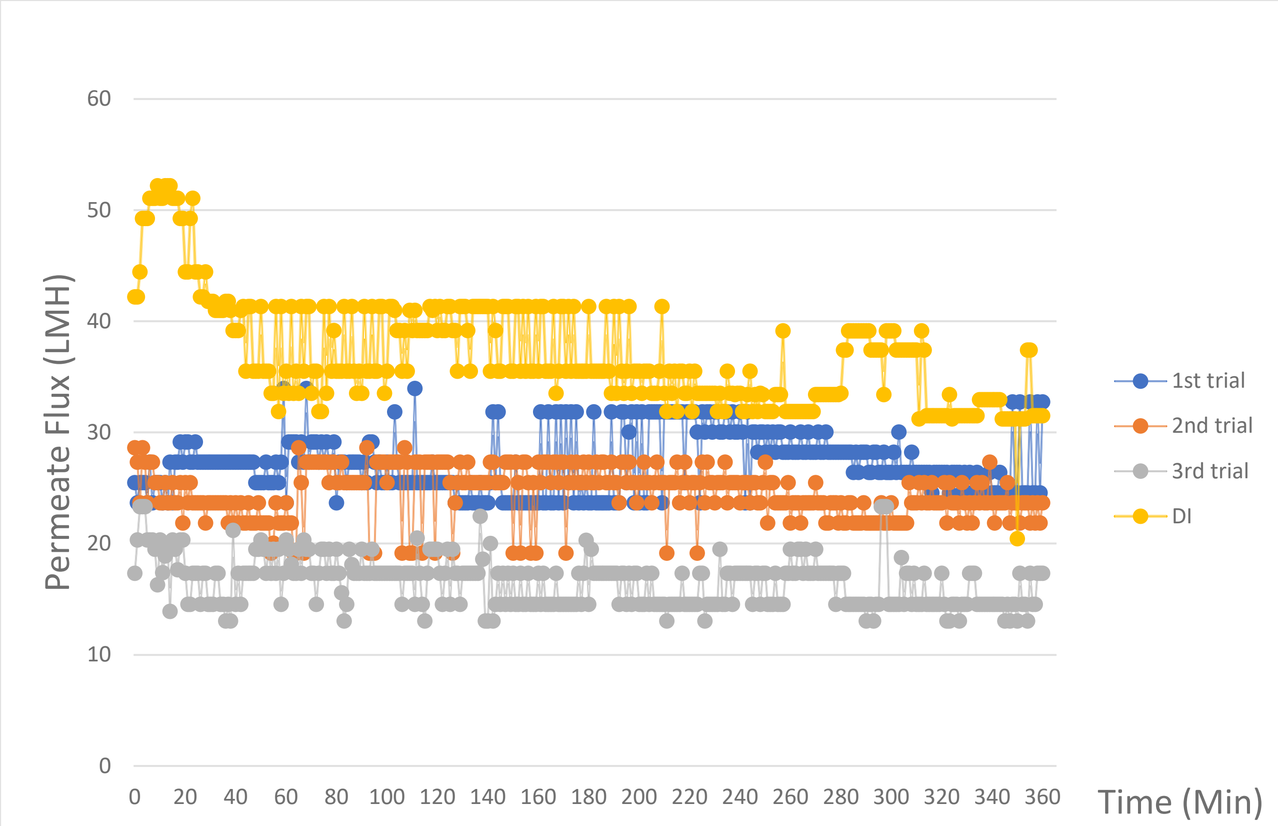


Figure 12.Permeate flux (LMH) vs Time (min) for various PRO experiments were

Trial 1: 1L real mine water + 19L synthetic water

Trial 2: 2L real mine water + 18L synthetic water

Trial 3: 4L real mine water + 16L synthetic water and

DI water was used as feed solution against 3M ammonium carbonate as Draw solution.

Table 8. Concentration of the ions in feed and permeate solutions of the final trial.

Ion	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
Feed (mg/L)	636.14	18.88	123.42	190.86	17.60	352	103.60	34.88	38.32	223.31
Permeate (mg/L)	277.38	0.328	37.24	180.06	6.96	311.92	3.16	1.23	6.42	112.82
Total Removal Efficiency (%)	56	98	70	6	61	12	97	96	83	50

After performing the PRO experiment for the final trial, the samples of feed solution and permeate solution were collected and filtered through the syringe, the samples were diluted 20 times. As shown in Table 8, this IC analysis provides insights into the effectiveness of the PRO process in removing various ions. It indicates significant reductions in concentrations for some ions (e.g., nitrite, ammonium) and more moderate reductions for others (e.g., chloride, nitrate). Additionally, it highlights the various removal efficiencies and concentrations of different ions in the feed and permeate solutions.

Table 9. The concentration of heavy metals in the permeate solution of trial 3.

Element	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Cd	Sb	Pb
Concentration (µg/L)	2.09	0.11	14.18	249.7	68.21	49.10	467.01	135.7	0.57	67.02	0.13	0.21	0.7

While Table 9 shows the presence of heavy metals in the permeate collected after 6 hours of experimenting for trial 3. For ICP-MS analysis the samples were diluted for 10 times. The concentrations of heavy metals provided through ICP-MS analysis in the permeate indicate the levels of these contaminants that have passed through the membrane. The presence of heavy metals in the permeate suggests that the membrane used in the PRO process may not be completely impermeable to these contaminants, or that some heavy metals may be able to bypass the membrane due to their physicochemical properties.

Table 10. Characteristic tests of the permeate shows the results of various characteristics present in permeate of trial 3 (final trial).

pH	7.1
Conductivity (mS/cm)	32.05
TDS (mg/l)	1.032×10^{-5}
Resistivity (Ω.cm)	126.2
TOC (mg/L)	17.9

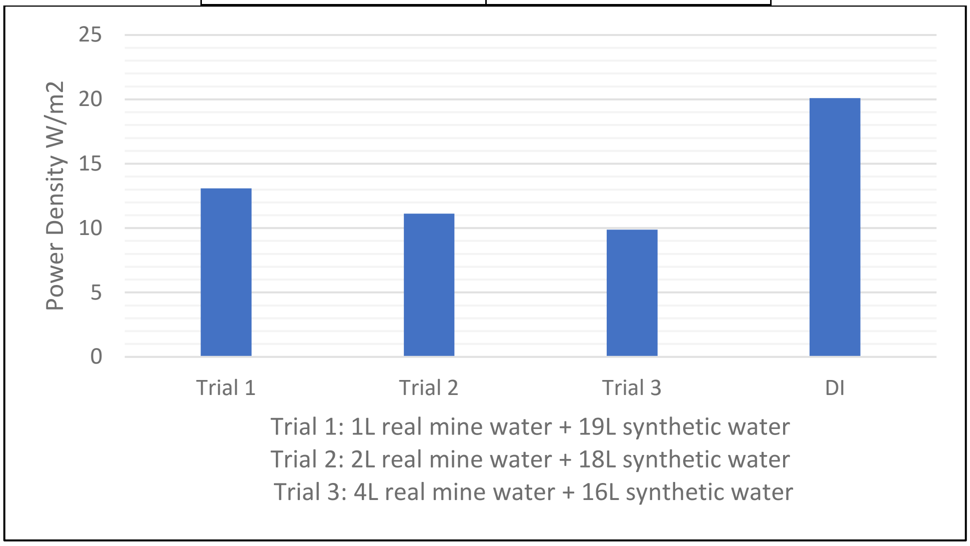


Figure 13. Achieved power density (W/m^2) for various trials.

Table 10 provides various characteristics of the permeate from the Pressure Retarded Osmosis (PRO) experiment. The permeate from the Pressure Retarded Osmosis (PRO) experiment exhibits several key characteristics indicating its quality and composition. With a pH of 7.1, the water is considered neutral, making it suitable for various applications. However, its conductivity of 32.05 mS/cm indicates a notable presence of dissolved ions, likely stemming from the osmotic process through PRO. This is further supported by the TDS concentration of 1.032×10^{-5} mg/L, which reflects the total dissolved solids in the water. The resistivity of 126.2 Ω.cm suggests a moderate resistance to the flow of electricity, corroborating the conductivity measurement. Additionally, the permeate contains a TOC concentration of 17.9 mg/L, indicating the presence of organic carbon compounds. Figure 13 shows the achieved power densities in W/m^2 of the various trials performed. In conclusion, the integration of an Anammox reactor into the wastewater treatment process of mining operations followed by the utilization of the treated wastewater as a feed solution in Pressure Retarded Osmosis (PRO) presents a promising approach for sustainable energy generation.

The Anammox process efficiently removes nitrogen compounds from mining wastewater. Subsequently, the treated wastewater enriched with nitrogen compounds becomes an ideal feed solution for PRO, leveraging osmotic pressure differentials to drive water transport across semi-permeable membranes and generate energy. This integrated approach not only addresses environmental concerns associated with mining wastewater but also offers a renewable energy source through PRO, contributing to the overall sustainability of mining operations.

4.4 Performance Evaluation of Draw Solutions and Experimental Trials in PRO Systems

The analysis of the two sets of experimental data presented in Tables 11 and 12 provides valuable insights into the performance of draw solutions and experimental trials in Pressure Retarded Osmosis (PRO) systems. Upon examination of the coefficient of variation (CV) values, it is evident that the variability observed within each draw solution and experimental trial falls within the lower to moderate range. The CV values provided in the data suggests that there is low to moderate variability within each condition, and all CV values are less than 20%. For draw solutions, a difference can be seen in the mean values which shows a significant difference in the results of the experiment. Each draw solution, including NaCl, KCl, $MgCl_2$, and $(NH_4)_2CO_3$, underwent three separate trials, each lasting for 6 hours or 360 minutes. Data was collected at an interval of 1 minute, resulting in a total of 1080 data points for each draw solution. For Trial 1 and Trial 2, the number of data points evaluated ranged from 360 to 362 as they were performed once. While Trial 3 was performed three times, and had a consistent evaluation of 1080 data points.

Table 11. Performance analysis of draw solutions in PRO

	NaCl	KCl	$MgCl_2$	$((NH_4)_2CO_3)$
Mean (LMH)	21.9	23.2	20.2	31.9
Variance	17.89	7.01	5.27	31.9
Standard deviation	4.23	2.6	2.29	5.6
CV (%)	19.3	11.36	11.40	17.6

Table 12. Performance of experimental trials in PRO

	Trial 1	Trial 2	Trial 3	DI
Mean (LMH)	27.18	24.49	16.48	37.02
Variance	7.36	5.12	4.75	24.21
Standard deviation	2.71	2.26	2.18	4.92
CV (%)	9.98	9.24	13.24	13.28

In Table 11, which compares the mean flux, variance, and CV for different draw solutions (NaCl, KCl, $MgCl_2$, and $(NH_4)_2CO_3$)), the CV values range from 11.36% to 19.3%. Similarly, Table 12, represents the statistical data for experimental trials (Trial 1, Trial 2, Trial 3, and Draw Solution (DI)), demonstrates CV values ranging from 9.244% to 13.289% which are values less than 20, so the observed variability is consistent, and it can be accepted.

The variability in the draw solutions is notably different. For instance, $(NH_4)_2CO_3$ has the highest variability (±5.6 from the mean), followed by NaCl, KCl, and $MgCl_2$, in descending order. This indicates that $(NH_4)_2CO_3$ solution has the widest spread of data points around its mean compared to the other solutions. While the variability among trials also varies. Trial 1 has the highest mean and standard deviation, indicating the widest spread of data points, followed by Trial 2 and then Trial 3. Therefore, there is a significant difference in variability among different draw solutions where $(NH_4)_2CO_3$ exhibits the highest variability, followed by NaCl, KCl, and $MgCl_2$. Variability among trials is also significant where Trial 1 shows the highest variability, followed by Trial 2 and Trial 3. Thus, the results indicate that there is lower to moderate variability within each condition.

Chapter 5: Conclusions and Recommendations

Over the past decade, significant research has been done on the potential of salinity gradient (SG) as a viable energy source, with particular focus on its utilization through Pressure Retarded Osmosis (PRO). In this study, the integration of Annamox enhanced wastewater treatment with Closed Loop Pressure Retarded Osmosis (PRO) represents a promising solution for addressing environmental and energy challenges in industrial settings, especially in sectors like gold mining. This system combines biological nitrogen removal with osmotic power generation, offering a multifaceted approach to sustainable energy generation and wastewater treatment.

The research essentially creates a bridge between two technologies were on one end there is biological nitrogen removal while with that electricity generation also goes hand in hand. The synthetic wastewater was produced in laboratory's biological reactor to replicate the real mine wastewater, the water used in mining which shows presence of significant amount of cyanide in it which shows that the amount of nitrogen present in it is high. While passing it through the annamox bioreactor it eliminates the nitrites, nitrates and ammonium present in it makes the wastewater reusable. The pH seems to be slightly alkaline in nature while the conductivity indicates the presence of different ions in the solution. The TDS values represents the total concentration of dissolved solids in the water, including salts, minerals, and organic matter. The resistivity of the solution shows low conductivity which indicates that the water is suitable for specific experiments.

The annamox (anaerobic ammonium oxidation) bioreactor is a sustainable wastewater treatment technology that selectively removes nitrogen compounds from wastewater, particularly ammonia (NH_4^+). Operating under anaerobic conditions, it facilitates the conversion of ammonium and nitrite into nitrogen gas, reducing the need for external carbon sources and minimizing energy consumption compared to conventional methods. A significant decrease in ammonium and nitrogen compounds can be observed after passing the synthetic wastewater from the bioreactor. The effluent from the annamox BIOCAST reactor was used as the feed solution in lab-scale setup of Pressure Retarded Osmosis (PRO). The second step was to select an appropriate draw solution for PRO experiments. The selection of the draw solutes for efficient energy generation through PRO must consider the low salinity of synthetic wastewater but also its effectiveness across various salinity levels. One M concentrations of sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride ($MgCl_2$), and ammonium carbonate ($(NH_4)_2CO_3$) were tested. Based on the experiments performed the achieved permeate flux for ammonium carbonate was 33.9 LMH and considering other factors such as better compatibility, high osmotic pressure, ion selectivity and chemical stability was selected as a favorable choice to continue further experiments.

For performing PRO experiments, the synthetic water was mixed with 1 L, 2 L and 4 L of real mine water which was used as feed solution and 3M ammonium carbonate was used as draw solution to carry out the experiments. For the final results, which showed the achieved permeate flux of 28.97 LMH and average power density of 11.0 ± 0.5 W/m^2. The salinity of the draw solution was measured before and after performing the experiment which decreased from 28.09 ppt to 17.3 ppt which showed that the draw solution was diluted and needed to be recovered after 6 hours of the continuous experiment. Therefore, the power density achieved using the synthetic wastewater mixed with real mine water, which was investigated in the study, showed a promising result. Another test was performed using DI water as the feed solution and ammonium carbonate as the draw solution, which generated the power of 20.09 W/m^2 and permeate flux of 52.2 LMH. IC analysis provides insights into the effectiveness of the PRO process in removing various ions. It indicates significant reductions in concentrations for some ions (e.g., nitrite, ammonium) and more moderate reductions for others (e.g., chloride, nitrate). The concentrations of heavy metals provided through ICP-MS analysis in the permeate indicate the levels of these contaminants that have passed through the membrane. The presence of heavy metals in the permeate suggests that the membrane used in the PRO process may not be completely impermeable to these contaminants, or that some heavy metals may be able to bypass the membrane due to their physicochemical properties.

The PRO experiments demonstrated promising results in power generation, with power densities achieved within a range considered profitable according to previous studies (Gerstandt et al., 2008). The use of synthetic wastewater mixed with real mine water showed potential for efficient energy generation, although fouling effects were observed, particularly when using deionized (DI) water as the feed solution.

IC analysis revealed significant reductions in concentrations of various ions in the permeate, indicating the effectiveness of the PRO process in reducing the concentrations. However, ICP-MS analysis showed the presence of heavy metals in the permeate, suggesting potential limitations in membrane impermeability or bypass mechanisms for certain contaminants where arsenic, copper, mercury, cadmium, and zinc shows major reductions which are frequently encountered in real mining effluents.

In conclusion, the study underscores the potential of PRO for energy generation using synthetic wastewater, particularly when combined with real mine tailing water. The choice of draw solution, such as ammonium carbonate, plays a crucial role in maximizing energy generation efficiency and ensuring compatibility with feed solutions.

For future recommendations, the integration of Annamox enhanced wastewater treatment with Closed Loop Pressure Retarded Osmosis (PRO), the addition of ultrafiltration and nanofiltration techniques following the Closed Loop Pressure Retarded Osmosis (CLPRO) process represents a pivotal step in enhancing the efficacy of wastewater treatment systems. By implementing these advanced filtration methods, heavy metals and ions present in the wastewater are effectively removed, ensuring the purity of the treated water. This post-treatment filtration not only meets stringent quality standards but also aligns with regulatory requirements governing wastewater discharge. The utilization of ultrafiltration and nanofiltration technologies underscores a commitment to achieving high-quality effluent and sustainable water management practices. In industrial and environmental contexts, this integrated approach offers a robust solution for addressing complex wastewater challenges, contributing to improved environmental stewardship and resource conservation. Moreover, it is imperative to conduct a comprehensive techno-economic analyses to assess the sustainability and feasibility of the system. These analyses should evaluate not only the environmental impact and energy efficiency but also the cost-effectiveness and potential economic benefits compared to conventional methods. Additionally, exploring the use of different membrane materials and designs can enhance system performance and efficiency. By utilizing advanced membrane technologies, such as high-selectivity membranes or membranes with improved fouling resistance, the overall effectiveness of the integrated system can be optimized. Furthermore, integrating other bioremediation techniques alongside the Annamox treatment, such as bioaugmentation or phytoremediation, can enhance pollutant removal and overall system performance. Additionally, implementing multi-stage remediation approaches, where wastewater undergoes sequential treatment processes, can further improve treatment efficiency and resource recovery. By incorporating these strategies into the integrated Annamox-PRO system, sustainability, energy efficiency, and environmental stewardship in various industrial settings, including challenging environments like mining operations can be enhanced.

In summary, the integration of Annamox enhanced wastewater treatment with Closed Loop Pressure Retarded Osmosis holds promise for enhancing sustainability, energy efficiency, and environmental stewardship in industrial settings, particularly those facing complex wastewater challenges like mining operations. It significantly shows an effort towards sustainably and economically treating nitrogen in wastewater from gold mines in Quebec.

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