

Nutrient Recovery from Anaerobic Membrane Bioreactor Permeate Using ion Exchange

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**NUTRIENT RECOVERY FROM ANAEROBIC MEMBRANE BIOREACTOR
PERMEATE USING ION EXCHANGE**

By

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ABSTRACT

Nutrient recovery from anaerobic membrane bioreactor permeate using ion exchange

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Marquette University, 2015

Phosphorus is a common element in wastewater streams and traditional treatment processes are often designed to remove it to achieve low effluent limits. Such processes often do not consider the potential value of the nutrient. Currently, production of phosphate fertilizers has dramatically risen causing concern for the depletion of phosphate rock reserves, bringing about exploration into alternative sources of phosphorus for agricultural use. Combining the needs of phosphorus removal from wastewaters and securing alternate sources of the nutrient provide an opportunity for recovery. This project evaluated a nutrient recovery process through ion exchange with beneficial recovery as precipitated struvite using novel anion exchange media loaded with hydrated ferric oxide (HFO) and copper (Cu^{2+}) known in literature as Dow-HFO-Cu. Previous work has not defined the exchange capacity of the media through multiple exchange cycles nor has it been tested in permeates from anaerobic membrane bioreactors (AnMBR). Batch tests were done to determine the exchange capacity of the Dow-HFO-Cu media using different regeneration solutions. Regeneration using less alkaline solutions (pH=11) provided the highest overall exchange capacity of phosphate (PO_4^{3-}) through 5 ion exchange cycles, with a regeneration solution of 2% NaCl + 0.5% NaOH providing the highest overall recovery. Column tests treating permeates from a lab-scale AnMBR were performed over 5 ion exchange cycles, resulting in exchange capacities of the Dow-HFO-Cu media ranging from 1.6 to 2.8 mg $\text{PO}_4\text{-P/g}$ media. From the removed portion, recovery of $\text{PO}_4\text{-P}$ achieved 94% and 79% of the mass of $\text{PO}_4\text{-P}$ was recovered during regeneration for column tests using permeate from an anaerobic membrane bioreactor treating synthetic wastewater and real primary effluent, respectively. Ammonium (NH_4^+) ion exchange using the natural zeolite clinoptilolite in batch tests demonstrated that more dilute sodium chloride regenerant concentrations could achieve similar performance to higher concentration solutions. Column tests of NH_4^+ removal showed decreased performance compared to batch tests as influent wastewater characteristics such as organic matter likely reduced exchange capacity. Precipitation tests using the regeneration eluate from anion and cation columns produced low molar ratios of $\text{Mg:NH}_4\text{:PO}_4$ with the best resulting ratio of 0.8:0.1:0.9, suggesting that the recovered product may not be struvite.

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1. Introduction

Phosphorus is a common element that is often looked at from two vantages: necessary or nuisance. Phosphorus is an essential nutrient vital to the growth of plants, animals, and humans alike. The use of phosphorus in agriculture has lead to increases in production and excavation of finite phosphate rock reserves at rates never before seen (Cordell, Drangert, & White, 2009; Neset & Cordell, 2012). This has brought about research into potential alternate sources of the nutrient for agricultural applications. In wastewater treatment, phosphorus is often looked at as a pollutant that can cause major environmental effects when released into surface waters, and so its must be removed to meet very low effluent regulations in wastewater treatment plants (WWTP) (Smil, 2000). This study aims to close the gap between removal and recovery of phosphorus by providing a nutrient recovery system that can achieve low effluent phosphorus concentrations in treated wastewater effluent while providing a valuable recovered nutrient product that can be used as an alternate fertilizer.

1.1 Objectives

The objectives of this study were to:

1. Evaluate the extended performance of Dow-Hydrated Ferric Oxide (HFO)-Copper (Cu) anion and clinoptilolite cation exchange media in batch tests
2. Evaluate the extended performance of Dow-HFO-Cu anion and clinoptilolite cation exchange media in column tests

3. Evaluate recovered nutrient product as precipitated struvite from column regeneration

2. Literature Review

2.1 Global Phosphorus Supply

For Earth to sustain an estimated global population of 9 billion people by 2050, the planet's ability to meet demands of agricultural food supply will play a crucial role, in turn causing food production rates and resource usage likely never seen before (Cordell et al., 2011). Perhaps one of the most important resources outside of fresh water needed to ensure high rates of future food production is phosphorus. It is well known that phosphorus is essential to all life including animals, bacteria, and plants. It is a fundamental component of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and adenosine triphosphate (ATP) which transports molecular energy through cells for metabolism in animals including humans, and is similarly a key substrate in energy metabolism, photosynthesis, and biosynthesis of nucleic acids in plants (Cordell & White, 2011; Raghothama, 1999). Phosphorus has also been found to be a limiting nutrient to plant growth in some cases and thus can limit the crop yields based on the nutrient's availability. Because of phosphorus' necessity for plant growth, nutrient-rich fertilizers containing phosphorus as phosphate (PO_4^{3-}), play an important role in agricultural crop production. These fertilizers are often land applied to agricultural fields to replace and replenish phosphorus, potassium and nitrogen from the previous harvest.

2.1.1 Phosphorus Use in Agriculture

Fertilizer use in agriculture has increased exponentially over the last century in part due to increased food demand caused by swelling global population, with an overall increase in phosphorus demand expected to continue into the future (Cordell & White, 2011). Advances in agricultural technology have also driven demand for fertilizer as the ability to cultivate more land and produce higher crop yields has led to mass industrialization of macronutrients including nitrogen, potassium, and phosphorus, which are used in commercial fertilizers. The increased use of soil fertilization became feasible through the development of the Haber-Bosch process in the early twentieth century, which allowed for the production of large volumes of nitrogenous fertilizers through the reaction of nitrogen and hydrogen gases to produce ammonia. However, unlike nitrogen, phosphorus does not take on a gaseous phase in the environment, except in minute quantities as toxic phosphine gas (PH_3) produced by a few microorganisms (Smil, 2000). This constrains the phosphorus cycle to the lithosphere and hydrosphere, between living and dead biota as well as land, soil, and aquatic sediments (Cordell & White, 2011). Animal manure and other excreta have been used as a source for phosphorus since the early stages of agricultural civilization and are still considered to be beneficial in today's agricultural production. However, their usefulness is often restricted to adjacent areas because of their bulkiness, uneven distribution, and cost of application and transportation outside of the local region where the manure was produced (Smil, 2000). In order to continually meet crop production demands, a phosphorus source was needed that could be transported across great distances and applied readily. This led to the use of natural phosphate rock sediments as a source of fertilizer production.

2.1.2 Depletion of Phosphate Rock Reserves

Mineral phosphate rock was found to be a formidable alternative nutrient source, causing a substantial increase in mining, processing, and agricultural use since the 1950s, which continues to increase today (Cordell, Drangert, & White, 2009; Smil, 2000). Phosphate rock is defined as sedimentary or igneous rock that contains around 5-13% phosphorus. Those which are technically and economically available are considered reserves, accounting for approximately 20% of the total phosphate rock found in the Earth's crust (Cordell & White, 2011). While initially considered to be an abundant source, it has become increasingly apparent over the years that available phosphate rock reserves will eventually become depleted, similar to fossil fuels such as oil and coal, which are also heavily relied upon in modern society. This is not to say that the planet will completely run out of phosphorus; the law of conservation of mass states that elemental phosphorus can neither be created nor destroyed (Cordell & White, 2011), but rather that continued use of phosphate rock reserves will cause a dispersion of the nutrient in different, unavailable forms which cannot be applied for agricultural use. Similarly, as phosphate rock is continually removed from the Earth's crust, the relative purity of the product decreases and it may include unwanted impurities such as heavy metals, requiring further energy inputs to remove contaminants (Schröder, Smit, Cordell, & Rosemarin, 2011).

Phosphorus mineral reserves are considered finite because of the 10s to 100s of millions of years that it would take for phosphorus to recycle naturally back into the igneous rock through which it is being extracted. Thus, the mining and removal of the natural phosphate reserves are orders of magnitude faster than natural renewal.

Population growth only compounds the depletion rate of these reserves as demand for food production increases the need for phosphate fertilizers. While countries that have seen constant land application of fertilizers such as the United States and parts of Western Europe have shown a stabilizing demand for phosphate fertilizer production, the overall global demand is expected to increase in the future (Cordell et al., 2009). Developing nations with emerging economies are oftentimes found in phosphorus-depleted regions, putting them at a disadvantage with their need for soil enrichment and lack of purchasing power in the international market (Cordell et al., 2011; Neset & Cordell, 2012).

2.1.3 Estimation of Reserve Depletion

Estimations of future availability of phosphate rock reserves have been a subject of debate in recent years with depletion estimates ranging anywhere from 30 to 300 years (Cordell & White, 2011). Most of the uncertainty with the depletion estimates comes from two separate variables: supply and demand. The demand-related variables include population increase, eating habits such as meat versus vegetable consumption, and agricultural efficiency, where the supply-related variables are subject to large obscurity of phosphate reserve quality, technical materials needed for extraction, and total amount of phosphorus available (Neset & Cordell, 2012). Current sources of phosphate reserves are distributed across only a few countries around the world. The United States is estimated to have 1.1 billion tons of reserves, which is dwarfed by the 50 billion tons estimated for the Morocco/Western Sahara region (USGS, 2014). Only a few other countries; China, Algeria, Syria, South Africa, and Jordan are considered to hold part of the majority of the remaining reserves (Neset & Cordell, 2012).

Depletion estimates of remaining reserves are often simplified by dividing the total reserves by an average annual consumption rate, deriving the estimated lifetime of reserves, although the assumption of an average or increased annual consumption rate often causes major discrepancies between estimates (Cordell & White, 2011; Neset & Cordell, 2012). While there has been a decrease and stabilization in demand for fertilizer in North America and parts of Europe due to over-fertilization in the past, the overall use of phosphate fertilizer is considered to have increased. This increase in consumption has been expected to stem from developing countries where the fitness of soil is often undernourished, and must be supplemented with nutrients in order to meet food production demands (Cordell et al., 2009), ultimately continuing the depletion of phosphate rock reserves.

Another method of phosphorus source estimation is the peak phosphorus theory. Initially derived by Hubbert (1949) to assess oil reserve production, Cordell & White (2011) define the peak phosphorus theory as “a critical period where a ‘peak’ in the production of the commodity will occur long before 100% of the reserve is theoretically depleted”, essentially meaning that the demand for mined phosphate rock will be greater than the annual supply will allow. Peak phosphorus estimates are inherently different from depletion estimates. Depletion estimates are used to determine when nearly 100% of available reserves are exhausted, while peak phosphorus estimates occur much sooner than those of depletion estimates, allowing time for actions towards limiting and/or finding alternate sources of usable phosphorus. From their analysis, Cordell & White (2011) arrived at a peak phosphorus date of 2033 using published global phosphate reserve estimates from 2008-2009. However, there are admitted limitations to their

appraisals, mainly constrained by the reserve estimates, mentioning that the “peak” is not necessarily a single date but rather a plateau of years before a significant decline in reserves. Overall the estimations of available phosphate rock reserves are limited to variation of estimates used in assessment and methods used to derive such numbers.

2.1.4 Environmental Impacts of Agricultural Phosphorus Use

While the mining of phosphate rock reserves is predominantly controlled by the need for agricultural fertilizer, much of the mined extracts do not make it into the plants, animals, and other food products consumed by humans (Rittmann, Mayer, Westerhoff, & Edwards, 2011). In a study from Cordell et al. (2009) identifying the flows of phosphorus through the food system from the mine to the plate, only a fifth of the phosphorus removed from reserves reaches the food consumed by the global population. Another study which analyzed the life cycle of phosphorus use efficiency of food production and consumption system in the United States determined that only 15% of the phosphorus extracted from nature to be used for food production is eventually ingested by humans, with the rest being lost to the environment (Suh & Yee, 2011). Many losses are due to refining, distribution, and application of the fertilizer.

After fertilizer product is applied to crops and arable soils, Cordell et al. (2009) estimated 46% of the phosphorus is lost to runoff from agricultural fields and soil erosion due to seasonal changes and storm events. Concentrations of phosphorus in the stormwater runoff are often low, but are part of a large volume entering into natural surface waters which are often sensitive to these low concentrations (Cordell et al., 2009; Rittmann et al., 2011). Nearly half of the original mined phosphorus being lost to the

environment demonstrates the inefficiencies of the current agricultural and commercial fertilizer production and application system, which can have severe direct and indirect environmental impacts associated with it.

One of the direct environmental impacts from these phosphorus use inefficiencies is eutrophication of natural surface waters. Eutrophication is caused by the accelerated growth of algae due to increased levels of phosphorus in surface waters, which can lead to color, odor, turbidity, loss of dissolved oxygen, fish kills, and can even have impacts on human health (Rittmann et al., 2011; Smil, 2000). Eutrophication has been found to occur at phosphorus concentrations of 0.1 mg/L or lower where factors such as light availability and increased temperatures accelerate growth (Smil, 2000). As recently as August 2014, residents in Toledo, OH were unable to use local drinking water due to massive algae blooms containing toxic microcystin caused by large amounts of agricultural runoff into Lake Erie (Goldenberg, 2014).

Agricultural runoff of phosphorus into surface waters is considered difficult to control due to the wide range of factors involved in its movement from land applied fertilizer to lakes, rivers, and streams. Therefore it is considered to be a non-point source for eutrophication. There is however various point sources of eutrophication that are more easily controlled to reduce its effects. One of the most controllable point sources is discharge from wastewater treatment. The introduction of the Clean Water Act in 1972 brought about regulations to reduce the concentration of both PO_4^{3-} and NH_4^+ in wastewater effluents, where multiple technologies that can achieve stringent effluent limits have been successfully implemented (Morse, Brett, Guy, & Lester, 1998a). However, most conventional methods of nutrient removal cannot recover a reusable

product when considering agricultural applications (Rittmann et al., 2011), and thus increased research into the recovery of nutrients from wastewater must be explored.

2.2 Nutrient Removal from Domestic Wastewaters

In order to reduce point source pollution of nitrogen and phosphorus into the environment, discharge flows of various wastewaters into the environment are often regulated to maintain low effluent limits on nitrogen and phosphorus. Thus, treatment operations tend to view these essential macronutrients as pollutants rather than recoverable products. As such, a constant, accessible flow of nutrients derived from human excreta and other industrial wastes can be found in domestic wastewater streams, providing a potential for recovery. However, recovery of both phosphorus and nitrogen from domestic wastewaters is often secondary to its removal.

2.2.1 *Biological Nutrient Removal*

Removal of phosphate from domestic wastewaters can be achieved by enhancing the storage capacity of phosphorus as polyphosphate in bacteria found in conventional activated sludge treatment facilities (de-Bashan & Bashan, 2004). Enhanced biological phosphorus removal (EBPR) uses a specific group of microorganisms known as phosphorus accumulating organisms (PAOs) to uptake the influent phosphate. When placed under anaerobic conditions, commonly the first zone of an activated sludge tank, PAOs release polyphosphates and uptake volatile fatty acids (VFAs) stored as poly- β -hydroxy-alkonates (PHA) (Morse et al., 1998a). During this anaerobic period,

components like acetate are sometimes added to the system as additional carbon sources to maintain a high level of phosphate removal in the system, resulting in additional chemical costs to the process (de-Bashan & Bashan, 2004). After the bacteria are introduced back into aerobic conditions, the PAOs utilize the energy stored from the PHAs to uptake phosphorus into the cell at greater amounts than originally released by the organisms, known as enhanced or “luxury” uptake, which removes the nutrient from the waste stream (de-Bashan & Bashan, 2004; Morse et al., 1998a). The activated sludge produced from the system, which contains organics (biochemical oxygen demand, BOD), large microbial populations, as well as organic phosphorus is often either discarded because of the high organic load or land-applied as a soil amendment. If the phosphorus removed during EBPR were to be recovered, then additional treatment to convert the organic phosphorus to more readily available inorganic phosphorus would need to be considered (Rittmann et al., 2011). Several studies have been conducted to assess the recovery of both ammonium and phosphorus as struvite from anaerobic digester side streams treating primary sludge from the EBPR process, as described in section 2.3.1 (Battistoni, 2000; Münch & Barr, 2001).

Biological removal of nitrogen from wastewaters is most commonly carried out using the nitrification/denitrification process. In biological nitrification, aerobic autotrophic bacteria such as *Nitrosomonas* oxidize ammonium (NH_4^+) to nitrite (NO_2^-), where the NO_2^- is then oxidized to nitrate (NO_3^-) using autotrophic bacteria such as *Nitrobacter* (Metcalf & Eddy, 2003). After nitrification, the NO_3^- is reduced further to nitrogen gas (N_2), known as denitrification, a wide range of bacteria have been shown to complete the degradation process (Metcalf & Eddy, 2003). Using these methods for

nitrogen removal, most of the nutrient is lost to the atmosphere as N_2 , leaving little potential for recovery. Additionally, as both EBPR and nitrification/denitrification processes require aeration to remove the targeted nutrient with little potential for recovery, a large input of energy is needed, prompting research into more efficient energy consumption and nutrient removal with the intent for recovery.

2.2.2 Physical/Chemical Nutrient Removal

Ammonium removal from wastewater can be carried out using physical/chemical methods such as air stripping and vacuum distillation, which transfers NH_4^+ to gaseous N_2 . By adjusting the pH of water to >10 , NH_4^+ is passed into the gas phase by passing it countercurrent to air in a packed bed tower, known as air stripping, or by spraying the liquid as droplets into a vacuumed tank, called vacuum distillation (El-Bourawi et al., 2007). However, the costs associated with pumping air and the conversion of the NH_4^+ to N_2 gas makes these processes undesirable when striving for nutrient recovery.

Physical and chemical removal of ammonium has also been known to occur freely through the precipitation of struvite, a combination of magnesium, ammonium and phosphate (de-Bashan & Bashan, 2004). Because of its spontaneity of precipitation in wastewater treatment systems and the ability to impact the hydraulics, struvite was often looked at as a nuisance by-product of treatment processes (Le Corre, Valsami-Jones, Hobbs, & Parsons, 2005). However, struvite has reuse value as fertilizer, leading to the implementation of struvite recovery technologies in wastewater treatment as discussed in section 2.3.1.

There are multiple methods for the removal of PO_4^{3-} from wastewater streams, with the most common conventional treatments including precipitation with metal salts including calcium salt additions. These methods incorporate the PO_4^{3-} into total suspended solids (TSS) so that they may settle out and be more easily removed, and have been used as an effective PO_4^{3-} removal process since the 1950s (Morse et al., 1998; Metcalf & Eddy, 2003). Precipitation using metal salts are a popular choice when treating wastewaters with low effluent concentration regulations because of the relatively low cost, wide availability, and high adsorption capacity (Rittmann et al., 2011). Addition of either aluminum (Al^{3+}) or iron (Fe^{3+}) salts to wastewater will react with PO_4^{3-} to form a solid precipitate based on a 1:1 molar ratio. However, competing reactions within a complex wastewater matrix do not always allow for the theoretical reaction to take place, in turn requiring equilibrium batch or jar testing to optimize dose (Metcalf & Eddy, 2003). Precipitation through addition of metal salts has operational advantages, as it can be applied at several stages during wastewater treatment, referred to as pre-precipitation, coprecipitation, and postprecipitation, but is often added after secondary treatment (postprecipitation) where organic phosphorus and polyphosphorus are transformed into more easily precipitated orthophosphate (Metcalf & Eddy, 2003). One of the most notable drawbacks of metal salt precipitation is the resultant solid sludge (estimated to contain 90% of the influent phosphorus), which has a high impact on operational costs of solids handling, energy use, and disposal (Cornel & Schaum, 2009; Rittmann et al., 2011). Also, PO_4^{3-} forms a strong bond with the Al^{3+} and Fe^{3+} metal ions, is causing it to be unavailable for agricultural applications and Al^{3+} is toxic to many plants; thus the solid sludge is often landfilled or incinerated (Morse et al., 1998a; Rittmann et al., 2011).

Another form of PO_4^{3-} precipitation uses calcium in the form of lime ($\text{Ca}(\text{OH})_2$), which when added to water, reacts with the bicarbonate alkalinity to precipitate calcium carbonate (CaCO_3). As the CaCO_3 concentration increases pH to about 10, excess calcium ions will react with PO_4^{3-} to precipitate hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (Metcalf & Eddy, 2003). Calcium phosphates are considered to be the raw material of phosphorus fertilizer, as early use of agricultural fertilization applied calcium phosphates from crushed bones. However, as calcium is not an essential macronutrient in aiding plant growth, alternative precipitate fertilizer sources should be assessed (Ashley, Cordell, & Mavinic, 2011; Morse et al., 1998a; Verstraete, Van de Caveye, & Diamantis, 2009).

As seen with majority of the nutrient removal technologies described above, very few allow for potential recovery and reuse of the removed nutrients. The primary goal of these systems is to meet effluent standards set by local and federal laws, with secondary options for post-treatment and recovery of the removed nutrients. However, struvite precipitation has the ability to remove both NH_4^+ and PO_4^{3-} from wastewater streams upon the addition of magnesium (Mg^{2+}). The resultant solid has also been increasingly studied as a land-applied fertilizer, allowing for beneficial recovery of nutrients from wastewater streams.

2.3 Nutrient Recovery Scheme

2.3.1 Nutrient Recovery as Struvite in Conventional Wastewater Treatment

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), also known as magnesium ammonium phosphate hexahydrate (MAP), can spontaneously precipitate in wastewaters at pHs above 7.5

where high concentrations of phosphorus and ammonium as well as low concentrations of suspended solids are present (de-Bashan & Bashan, 2004). While initially viewed as a nuisance product affecting the efficiency of treatment processes, struvite precipitation has recently been studied as a method of both phosphorus and ammonium recovery, due to potential as a marketable fertilizer product (Le Corre et al., 2005). This interest in recovery has led to several struvite recovery processes that have been implemented in various wastewater streams.

The first struvite recovery process reviewed in this study comes from the Shimane Prefecture Lake Shinji East Clean Centre in Japan, where a struvite recycling plant was adopted to reduce the phosphorus load of return sludge liquors and produce a recoverable, phosphorus-rich fertilizer (Ueno & Fujii, 2001). The wastewater treatment process in this particular plant is a conventional activated sludge process, where settled solids from the primary treatment are sent to an anaerobic digester. Using the dewatered filtrate from the anaerobic digester as the nutrient source, the influent is fed through an upflow fluidized bed reactor containing pre-loaded granular struvite pellets that act as seed material for newly formed precipitates. Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) is added into the reactor to achieve a Mg:P ratio of 1:1, and the pH is adjusted to 8.2-8.8 with sodium hydroxide. A retention time of ten days allows for growth of the struvite crystals, after which they are removed and sent for further processing (Ueno & Fujii, 2001). It is estimated that the three-reactor plant can produce 500-550 kg of struvite per day, which is sold to fertilizer companies to be used mostly on paddy rice (Ueno & Fujii, 2001).

Another commercially available struvite recovery process from Ostara, also uses filtrate from dewatered anaerobic digester sludge from the EBPR process as its nutrient

source. This process focuses on treating the dewatered sludge filtrate as it often has a high phosphorus content from the release of stored phosphate back into the soluble form originally removed from the microorganisms involved in EBPR (Ostara, 2015). An increased phosphorus content being returned to the start of the anaerobic zone in EBPR can have negative effects on phosphorus removal, therefore removal of it in the side stream allows an opportunity for a struvite recovery process. While the operational specifics for the Ostara® Pearl® 2000 system are unavailable, it is considered to be a similar process as described by Ueno & Fujii (2001), where Mg^{2+} addition and pH adjustment are used to produce the final struvite product. The Ostara® system can recover 555 lbs of PO_4 -P and 250 lbs of NH_4 -N, while producing 4400 lbs of fertilizer per day, and has been implemented in multiple wastewater treatment plants including Nine Springs WWTP in Madison, WI (Ostara, 2015).

One other struvite precipitation process uses a different method to remove PO_4^{3-} and NH_4^+ from wastewater streams. The REM NUT process developed in the 1980s is accomplished using two separate unit operations: ion exchange for removal of the nutrients to be concentrated into the ion exchangers' regeneration eluate, and chemical precipitation of the nutrients in the form of struvite after addition of Mg^{2+} and pH adjustment (Liberti, Petruzzelli, & De Florio, 2001). The ion exchange process utilizes two ion exchange units, one for NH_4^+ removal and another for PO_4^{3-} removal, to selectively remove the nutrients as a tertiary treatment process in small to medium size WWTPs where EBPR might not be easy to operate. After the ion exchange columns reach capacity, they are regenerated with a brine solution to concentrate the captured ions into solution. The resultant eluate from both columns are then combined with the addition

of Mg^{2+} and pH adjustment to yield struvite (Liberti et al., 2001). Results from pilot scale tests using the REM NUT process achieved a struvite content of greater than 93% by weight, but has not however reached full scale operation due to high N:P molar ratios between regeneration solutions calling for addition of chemicals to reach the necessary 1:1:1 Mg:N:P ratio for effective struvite precipitation.

2.3.2 Nutrient Recovery from Reduced Energy Wastewater Treatment

The struvite recovery processes for conventional wastewater treatment as described above are considered very advantageous by taking a resource often looked at as waste and converting it into reusable material. However, there has been a shift in the way that environmental engineers approach how municipal wastewater should be treated. The use of domestic and municipal wastewater as an energy source has been well defined, especially through the anaerobic conversion of influent organics into methane (CH_4), which is considered a useful biogas (McCarty, Bae, & Kim, 2011). The main problem is that the design of many of the treatment processes is established to meet effluent limits, and not optimization of the efficiency of treatment. The effects of overall use of energy consumption on climate change are also a growing concern, causing a reevaluation of domestic wastewaters as a potential energy source, prompting studies of new wastewater treatment technologies with lower net energy use.

It has been hypothesized by McCarty et al. (2011) that complete anaerobic treatment of domestic wastewater has the potential to achieve net energy production while meeting effluent standards put forth by the government. Continuous research on making this goal attainable has brought about one such technology that has been shown

to effectively treat wastewaters while achieving low energy input and a high CH₄ production potential: anaerobic membrane bioreactors (AnMBR). These systems are designed to treat raw wastewater or primary effluent by passing the wastewater through a membrane filter resulting in a short hydraulic residence time (HRT), while simultaneously retaining biological solids necessary for biodegradation of organics allowing for a high solids retention time (SRT) (Yoo, Kim, McCarty, & Bae, 2012). Studies have shown that the use of AnMBRs which use membranes with very small nominal pore sizes (around 0.002 μm) has the potential to reduce five-day biochemical oxygen demand (BOD₅) and total suspended solids (TSS) to less than 8 and 1 mg/L respectively (Giménez et al., 2011; Kim et al., 2011). However, as there is no mechanism for nutrient removal and the dissolved fraction may pass through the membrane, there is often very little removal of NH₄⁺ and PO₄³⁻, as well as other nutrients such as potassium. Thus, the reduction of COD and TSS concentrations with the addition of elevated nutrient levels produced in AnMBR permeates provide a promising stream for a nutrient removal and recovery system. By designing a wastewater treatment process that could provide net energy production through the conversion of organic matter to CH₄, as well as recover valuable agricultural nutrients from the influent stream, a sustainable process can be realized. The present study focuses on the mechanisms of removal for both PO₄³⁻ and NH₄⁺ through ion exchange technology, applied in AnMBR permeate for removal and ultimate recovery of the nutrients as struvite.

2.3.2 Phosphate Ion Exchange Review

In order for struvite precipitation to occur, phosphate levels must reach a concentration of about 100-200 mg/L in the presence of ammonium (Rittmann et al., 2011). With most AnMBR permeates found to have $\text{PO}_4\text{-P}$ concentrations of 3-5 mg/L (Giménez et al., 2011), it is important to choose a treatment technology that can provide a high PO_4^{3-} concentration stream at a low volume to achieve an efficient process. One such method that allows for removal of PO_4^{3-} anions and recovery as a concentrated nutrient stream is ion exchange. Ion exchange (IX) is a physical/chemical process through which ions attached to a functional group exchange for ions in a solution, based on equivalent amounts of charge (Crittenden et al., 2012). Therefore if one PO_4^{3-} ion in solution were to be removed through ion exchange using chloride (Cl^-), three Cl^- ions would be released from the media into solution. As more PO_4^{3-} ions are removed from solution, the exchange media reaches capacity where there are no more available sites for ion exchange. The biggest advantage of ion exchange is that the process is reversible. Once all exchange sites are taken up by the target ions originally in solution, a highly concentrated brine solution is often used to remove the target ions from the exchange media and replenish exchange sites. This process is known as regeneration. Regeneration is an important step in the ion exchange process as it can affect the future exchange capacity if the exchange sites are not all replenished, but is considered beneficial as it can provide a highly concentrated nutrient stream necessary for the precipitation of struvite.

Phosphate removal through fixed-bed ion exchange and adsorption processes has been well studied, where media such as granular activated alumina, hydrated ferric oxide (HFO) nanoparticles, and other inorganic adsorbents have shown efficient removal of

phosphates from wastewaters (Chubar et al., 2005; Genz, Kornmüller, & Jekel, 2004; Seida & Nakano, 2002). However, these inorganic metal oxides lack the mechanical strength necessary for prolonged use and do not achieve efficient regeneration, and as such are only considered for single use applications (Blaney, Cinar, & Sengupta, 2007; Genz et al., 2004). Synthetic polymeric exchange media has been developed in order to achieve durability, effectively providing the mechanical strength needed for an efficient ion exchange process. These synthetic media are comprised of a polymeric backbone, which contains covalently bonded functional groups with fixed ionic charges (Crittenden et al., 2013). The use of synthetic ion exchange media also allows for selective removal of anions or cations based on the functional groups involved. While the synthetic exchange media is a durable product, there have been several noted problems with its performance limiting its applications in treatment systems most notably poor selectivity toward phosphates over competing anions (Petruzzelli et al., 2004). However, there has been recent research and development using metal ligand structures on exchange media in order to obtain better selective removal of phosphates from wastewaters.

With the goal of phosphorus removal, recovery, and reuse, it is important to choose an ion exchange material that achieves efficient phosphate removal as well as high selectivity of phosphate over competing anions that are present in wastewaters such as sulfate (SO_4^{3-}), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). Other anions such as nitrate (NO_3^-), nitrite (NO_2^-), and bromide (Br^-) may also be inhibitory towards phosphate absorption, although previous studies have found that PO_4^{3-} has a higher affinity towards strong base anion exchange media (Blaney et al., 2007; Zhao & Sengupta, 1998). At near neutral pH, most phosphates are found in the monovalent (H_2PO_4^-) or divalent (HPO_4^{2-})

phosphate form, which have a greater ability to form inner sphere complexes with transition metals like copper (Cu^{2+}) of HFO over other anions such as SO_4^{2-} and NO_3^- (Blaney et al., 2007; Sengupta, 2013). This means that Cu^{2+} and HFO ligands exhibit greater selectivity towards phosphorus (Zhao & Sengupta, 1998).

The use of polymeric ligand exchangers (PLEs) has been researched in multiple studies (Sengupta & Pandit, 2011; Sengupta, 2013; Zhao & Sengupta, 1998), with some commercially available, such as LayneRT™, a polymeric base media impregnated with HFO nanoparticles. Continued research into PLEs has produced several other novel anion exchange media such as Dow-HFO-Cu developed by Sengupta & Pandit (2011), which adds a copper salt to the HFO-impregnated chelating media. The basic idea is that if two ligand exchangers (HFO and Cu^{2+}) could be loaded onto a polymeric backbone, increased sorption capacity of PO_4^{3-} could be achieved, as little or no compromise on the individual exchange capacity of the metal ligands is expected (Sengupta & Pandit, 2011; Sengupta, 2013). According to Sengupta & Pandit (2011), the Dow-HFO-Cu media can achieve an ion exchange capacity of 1 meq/mL of media. This translates into about 15 mg $\text{PO}_4\text{-P/g}$ of media. The use of Dow-HFO-Cu for phosphorus removal and recovery is a promising technology, but before it can be incorporated into treatment trains additional information regarding exchange capacity and recovery of PO_4^{3-} from the media over extended use of the product need to be established. In the Sengupta (2013) study, the Dow-HFO-Cu media was tested in fixed-bed columns to determine the media's phosphate selectivity over competing anions. For some strong base exchange media SO_4^{2-} has been shown to have a higher affinity than PO_4^{3-} , although Sengupta (2013) showed that the tested Dow-HFO-Cu media had a higher capacity for PO_4^{3-} , where breakthrough of the media was

observed at nearly 2000 bed volumes (BV) at a flow rate of 2.2 mL/min, however exchange capacities are not reported. It was also determined that no significant bleeding of Fe^{2+} or Cu^{2+} from the media occurred during the removal process. The column test results from Sengupta (2013) used a synthetic wastewater matrix containing 1.9 mg/L $\text{PO}_4\text{-P}$, 124 mg/L SO_4^{2-} , and 8.3 mg/L Cl^- , which are not expected concentrations in an AnMBR permeate. There is interest in the removal of PO_4^{3-} from AnMBR permeates using Dow-HFO-Cu media because of the low concentrations of SO_4^{2-} expected in the permeate which may allow for increased exchange capacity of PO_4^{3-} .

When considering ion exchange use in a real wastewater matrix it is important to consider effects of BOD_5 and TSS, which may cause hydraulic head loss in the system. However, AnMBR permeate contains very low concentrations of these common wastewater constituents, making it a good nutrient removal and recovery matrix. As such, to better understand how the competition between anions effect phosphate removal in a more realistic setting, it is important to test IX materials in a real wastewater matrix, specifically in an AnMBR permeate. Other design considerations include providing an exchange media that is able to achieve a stable exchange capacity over extended removal cycles, which would significantly help to attain a sustainable nutrient recovery process. The study by Sengupta (2013) demonstrated that the Dow-HFO-Cu anion exchange media could achieve a high phosphate exchange capacity, but it was not evaluated over multiple IX cycles. In order to better understand the performance of the Dow-HFO-Cu media in wastewater treatment setting, it is important to know the how multiple IX cycles affect the exchange capacity.

With focus on the recovery of PO_4 from wastewaters, regeneration of the exhausted anion media is an important step to achieve an efficient process. Previous research used a brine solution containing 2.5% NaCl + 2% NaOH for recovering PO_4^{3-} from Dow-HFO-Cu media and found that more than 90% of the removed fraction of PO_4^{3-} was recovered within 15 BV (Sengupta, 2013). Using a regeneration solution with such a high pH (~13) could cause attrition, wherein the copper ions are stripped off the media. This would negatively affect future removal capacity, and the media's potential for phosphorus recovery. An objective of the present research is to determine if different combinations of NaCl and NaOH concentrations can improve recovery. Identifying regeneration solutions that can achieve continual, effective recovery of PO_4 while using fewer chemicals has potential for both operational and economic benefits.

2.3.3 Ammonium Ion Exchange Review

Similar to PO_4^{3-} removal, the ion exchange process can be used to remove and recover NH_4^+ cations from wastewaters. Upon addition into most waters, organic and ammonia nitrogen is considered to hydrolyze to NH_4^+ , making it the target ion of removal in the ion exchange process (Sengupta, 2013). The removal of NH_4^+ from wastewaters using natural zeolites has been shown to be a successful means of producing low effluent concentrations, and is also cost effective because of its availability (Gupta & Sadegh, 2015). Natural zeolites are porous aluminum silicate minerals known to have high cation exchange capacities (Gupta & Sadegh, 2015; Hedstrom, 2001). There are many different types of zeolites available with clinoptilolite commonly suggested for wastewater treatment applications based on its affinity for ammonium and potassium (K^+) cations.

This affinity is caused when silica (Si^{4+}) is substituted by aluminum (Al^{3+}), effectively raising the negative charge of the mineral. The negative charge is then balanced by cations such as sodium (Na^+), which is then exchangeable with NH_4^+ and K^+ in solution (Hedstrom, 2001). While studies have shown that K^+ can be adsorbed to clinoptilolite to at least the same extent as NH_4^+ , the use of chemical pretreatment on the exchange media using a sodium salt has been found to increase the overall selectivity towards NH_4^+ (Gupta & Sadegh, 2015; Hedstrom, 2001). Research conducted by Sengupta (2013), tested clinoptilolite exchange media in a fixed-bed column to study its removal performance treating septic tank effluent, and found for a single removal cycle when treating an influent concentration of 30 mg/L $\text{NH}_4\text{-N}$ a maximum exchange capacity of about 11 mg N/g of media was achieved.

Regeneration of the clinoptilolite exchange media is often carried out using a high pH and high salt solution to replace adsorbed NH_4^+ with Na^+ ions. Previous work has shown that NaCl concentrations can vary over a wide range to achieve a highly concentrated NH_4^+ regeneration solution (Guo, Zeng, & Jin, 2013); however for economic purposes, relatively low concentrations of NaCl are preferable. The present study aims to evaluate the variability of the exchange capacity of clinoptilolite through multiple ion exchange cycles using different concentrations of NaCl for regeneration of the media.

2.3.4 Struvite Precipitation Review

As discussed previously, struvite is an agricultural fertilizer because of its low solubility and nitrogen and phosphorus components (El Diwani, El Rafie, El Ibiari, & El-

Aila, 2007). By combining the highly concentrated PO_4^{3-} and NH_4^+ regeneration streams along with the addition of Mg^{2+} and pH adjustment, recovery of the nutrients in the form of struvite is possible. Usually formed as white orthorhombic crystals, struvite is believed to precipitate at equivalent molar amounts of Mg^{2+} , NH_4^+ , and PO_4^{3-} , with a common target molar ratio of 1:1:1, although studies interested in increased PO_4^{3-} removal have suggested higher Mg:PO₄ ratios ranging from 1:1-1.5:1 (Beal, Burns, & Stalder, 1999; Bhuiyan, Mavinic, & Koch, 2008; Nelson, Mikkelsen, & Hesterberg, 2003). Struvite is predominantly controlled by pH, degree of supersaturation, and the presence of other ions in solution such as calcium (Doyle & Parsons, 2002). Generally, struvite solubility decreases with an increasing pH with reported precipitation occurring across a pH range of 7-11, however most successful recoveries of PO_4^{3-} and NH_4^+ are reported within a pH range of 8-9 (de-Bashan & Bashan, 2004; Doyle & Parsons, 2002; Münch & Barr, 2001). In a pilot-scale reactor study precipitating struvite from anaerobic digester effluent, it was found that 94% of the influent PO_4^{3-} was recovered as struvite at a pH of 8.5 (Münch & Barr, 2001).

Supersaturation is a measure of the increased concentration of an ion in solution in excess of equilibrium concentrations. As ion exchange media is regenerated, the captured effluent contains a high concentration of the desired PO_4^{3-} or NH_4^+ ions. The level of supersaturation present in the regeneration solution can affect the pH at which struvite formation occurs (Battistoni, 2000; de-Bashan & Bashan, 2004). Research conducted by Battistoni (2000) found that lower concentrations of PO_4^{3-} (25-50 mg/L) in anaerobic sludge liquors resulted in a higher pH (8.5-8.75) for struvite precipitation. Other ions present during struvite precipitation can also have an affect on quality and

growth rate of crystals due to blocking of active growth sites (Le Corre et al., 2005). While regeneration of the exchange media is designed to recover captured target ions, other less valuable ions that may have attached to exchange sites during the removal process could become concentrated in the regeneration effluent. Of particular interest are calcium (Ca^{2+}) ions, as they are found at relatively high levels in wastewaters and can bond with PO_4^{3-} or CO_3^{2-} anions to form hydroxylapatite or calcium carbonate respectively, and affect the final struvite quality (Le Corre et al., 2005). In a study focused on the impact of Ca^{2+} ions in struvite precipitation, it was found that increased Ca^{2+} concentrations reduced the crystal size and inhibited the struvite growth, leading to the formation of an amorphous substance rather than crystalline struvite (Le Corre et al., 2005). Research has also suggested that the addition of citrate to the struvite precipitation reaction can lead to the inhibition of hydroxylapatite formation (de-Bashan & Bashan, 2004).

The goals of this study is to assess the recovery of PO_4^{3-} and NH_4^+ as struvite from the regeneration solutions of the selected ion exchange media treating permeate from a lab-scale AnMBR. While various reports have shown recovery of these nutrient as struvite treating effluents from aerobically treated municipal wastewater using an ion exchange process (Petruzzelli et al., 2004), there is no knowledge of struvite precipitation efficiency from AnMBR permeate. A schematic system developed for the removal, recovery, and precipitation as struvite of PO_4^{3-} and NH_4^+ from an AnMBR permeate is depicted in Figure 1.

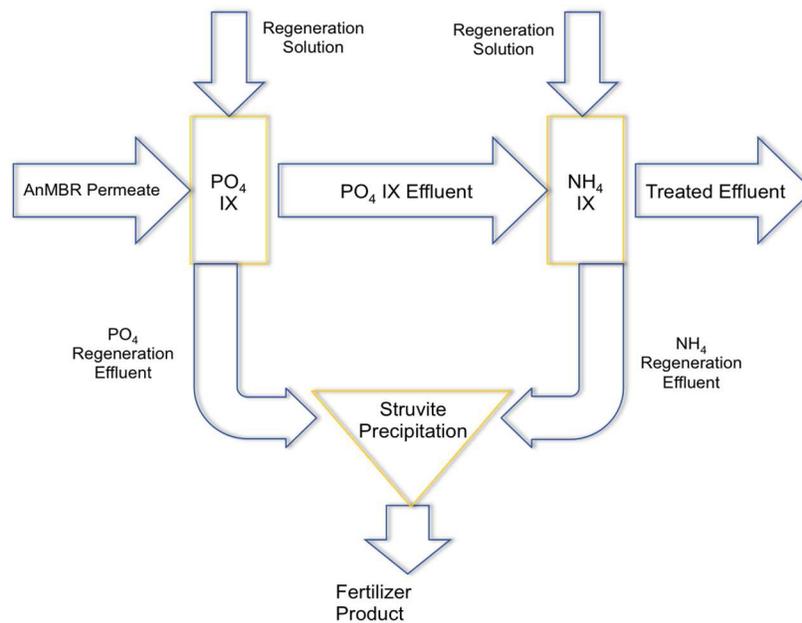


Figure 1: Ion Exchange Process

2.4 Research Objectives

This study addressed current gaps in the knowledge of ion exchange and precipitation processes targeting nutrient recovery from municipal wastewater, as described in the previous sections. The specific research objectives, tasks performed to complete these objectives, and associated hypotheses are listed following.

2.4.1 Evaluate Extended Performance of Dow-HFO-Cu Anion and Clinoptilolite Cation Exchange Media in Batch Tests

1. Determine Selective Removal Characteristics of Dow-HFO-Cu Ion Exchange Media

Hypothesis: As the Dow-HFO-Cu exchange media is loaded with both copper and HFO metal ligands, it is expected that PO_4^{3-} in the form of both HPO_4^{2-} and H_2PO_4^- will outcompete other anions such as SO_4^{2-} for available sorption sites in batch tests treating AnMBR permeate.

2. Assess Impact of Multiple Ion Exchange Cycles on Dow-HFO-Cu Anion Media Exchange Capacity

Hypothesis: It is expected that the exchange capacity will decrease after the initial removal and regeneration step due to incomplete regeneration of the exchange media. However, it is hypothesized that the exchange capacity of the media can provide consistent recovery through multiple exchange cycles in batch tests.

3. Determine Potential for Improved Recovery of $\text{PO}_4\text{-P}$ Using Varied Concentrations of Regeneration Solutions

Hypothesis: Batch test regenerations of the Dow-HFO-Cu media using reduced concentrations of NaOH than reported in literature will cause less attrition to the metal ligands, allowing for greater overall recovery of $\text{PO}_4\text{-P}$. It is also hypothesized that lower concentrations of NaCl regeneration solutions can achieve comparable performance to higher concentrations

4. Assess the Clinoptilolite Exchange Capacity Over Multiple Ion Exchange Cycles Using Different Concentrations of NaCl in Regeneration

Hypothesis: It is hypothesized that the exchange capacity will decrease initially due to incomplete regeneration, although substantial change through multiple ion exchange cycles are not expected to occur.

2.4.2 Evaluate Extended Performance of Dow-HFO-Cu Anion and Clinoptilolite Cation Exchange Media in Column Tests

1. Assess Dow-HFO-Cu Exchange Capacity Over Multiple Ion Exchange Cycles

Hypothesis: The exchange capacities recorded in column tests are expected to decrease over multiple exchange cycles due to loss of metal ligands structures and incomplete regeneration. Recorded exchange capacities in column tests are anticipated to be less than those found in batch tests although consistency in removal over multiple exchange cycles is still expected.

2. Evaluate Concentration of Recovered PO₄P Regeneration Solutions

Hypothesis: Recovery of PO₄-P from exchange media is expected to occur much faster than the removal process due to the high concentration regeneration solution used, however significant concentrations of metals such as Fe²⁺ and Cu²⁺ are expected in the regeneration eluate as a result of release from the exchange media.

3. Assess the Clinoptilolite Exchange Capacity over Multiple Ion Exchange Cycles

Hypothesis: More variability in exchange capacity compared to batch testing is expected as a result of a more complex wastewater matrix as well as differences in contact time between the influent wastewater and solid exchange media.

2.4.3 Evaluate Production and Composition of Precipitate Recovered from Combined Anion and Cation Regenerant Streams

1. Determine Molar Ratios of Mg^{2+} , NH_4^+ , and PO_4^{3-} in Recovered Precipitate

Hypothesis: It is expected that combining the two concentrated regenerant solutions from the anion and cation columns with of Mg^{2+} addition in a $Mg^{2+}:PO_4^{3-}$ ratio ranging from 1:1 to 1.3:1 and pH adjustment ranging from 8 to 9 struvite will precipitate. Complete recovery of the PO_4^{3-} may not occur due to other potential ions in the regeneration solutions such as Ca^{3+} . NH_4^+ is not expected to achieve complete recovery as struvite due to PO_4^{3-} being the limiting nutrient in the precipitation process.

3. Materials and Methods

3.1 Selection and Preparation of Ion Exchange Media

3.1.1 Anion Exchange Media

The anion exchange media used in this study, Dow-HFO-Cu, is not commercially available, and as such was prepared in the lab, in accordance with the method described by Sengupta (2013). Dowex® M4195 (Dow Chemical Company, Midland, MI) was used as a base material for the development of the metal-loaded media. A mass of 30 g of virgin Dowex® M4195 was added to a 1.5% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution at a pH of approximately 2 to assure that no $\text{Fe}(\text{OH})_3$ precipitated out of solution, and was stirred for 1 hour. The pH was then increased stepwise over 3 hours using NaOH tablets to form HFO nanoparticles. The mixing speed was reduced and media was kept in solution for 24 hours to optimize the contact time between the media and freshly formed nanoparticles. After the 24-hour mixing period, the media was removed from solution and rinsed 3 to 4 times with deionized water to remove excess precipitate, and then dried at 35°C for 24 hours. Copper was then loaded onto the media by placing the dried HFO loaded media into a 1% $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ solution at a pH of approximately 5 with gentle mixing for 24 hours. After the 24-hour mixing period, the media was removed from solution and rinsed 3 to 4 times with deionized water, followed by drying of the media at 35°C for 24 hours. Once dry, the Dow-HFO-Cu media was stored in a moisture-free glass vial.

3.1.2 Cation Exchange Media

Clinoptilolite (St. Cloud Zeolite, Tucson, AZ), a hydrous sodium aluminosilicate zeolite, was preconditioned by repeatedly rinsing the material to remove fine particles. The 30 g of clinoptilolite was then added to a 1% NaCl solution and mixed for 2 days to saturate the media surface with sodium ions, rinsed, and then dried for 24 hours at 103°C (Hedstrom, 2001; Sengupta, 2013).

3.2 Analytical Methods

All PO₄-P concentrations were analyzed using PhosVer® 3 Phosphate Reagent powder pillows (Hach Company, Loveland, CO) and spectrophotometric methods adapted from the ascorbic acid standard method 4500-P E, with a detection range of 0.006 to 0.8 mg/L PO₄-P (APHA et al., 1998). NH₄-N concentrations were analyzed using the phenate method, standard method 4500-NH₃ F, with a detection range of 0.1-1 mg/L NH₄-N. Absorbance was measured using Thermo Scientific (Waltham, MA) Genysys 20 spectrophotometer. Spectrophotometric methods were chosen for their relatively quick results and ability to test multiple samples within a sufficient time period.

Measured PO₄³⁻, SO₄²⁻, and Cl⁻ permeate concentrations from the anaerobically treated synthetic primary effluent municipal wastewater were determined using a Dionex ICS-1100 ion chromatography system (Thermo Fisher Scientific, Waltham, MA). Alkalinity was determined using Standard Method 2320 B (APHA et al., 1998). Metals concentrations of Mg²⁺, Ca²⁺, Al³⁺, Fe²⁺, and Cu²⁺ were determined by digesting 10 mL of solution using Standard Method nitric acid digestion 3030 E (APHA et al. 1998),

which was then analyzed through 7700 Series ICP-MS (Agilent Technologies, Santa Clara, CA).

3.2 Batch Tests

Batch testing was carried out in 60 mL serum vials filled with 50 mL of the tested solution along with an exchange media dose of 10 g/L. The vials were continuously mixed using a Roto Torque™ rotational motor (Cole-Parmer Instrument Company). The batch testing setup is shown in Figure 2.

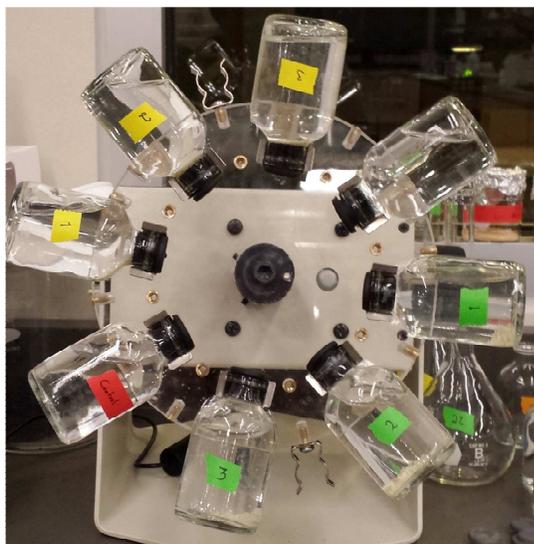


Figure 2: Batch Test Apparatus

Preliminary equilibrium tests were conducted to determine the appropriate mixing time for batch tests. A PO_4 -only solution with a concentration of 3 mg/L $\text{PO}_4\text{-P}$ was chosen based on nutrient levels expected in typical AnMBR permeate. Contents of individual vials were analyzed after 0, 10, 20, 30, 45, and 60 minutes. A removal curve

was created using the resulting data, where equilibrium was considered achieved when the difference between subsequent timepoint samples was less than 5%. This was the minimum time to equilibrium, which was used for all subsequent batch tests.

3.2.1 Dow-HFO-Cu Phosphate Selectivity

After initial PO₄-only equilibrium testing, permeate from a lab-scale AnMBR treating synthetic wastewater was used to assess the effects of competing anions on the performance of the Dow-HFO-Cu exchange media. The major ions of concern were sulfate (SO₄²⁻), chloride (Cl⁻), and bicarbonate (HCO₃⁻) as they share similar valences as those of the H₂PO₄⁻ and HPO₄²⁻ phosphate species that predominate in wastewaters at near neutral pH (Sengupta & Pandit, 2011).

3.2.2 Exchange Capacity

Exchange capacity batch testing of PO₄-P and NH₄-N removal using Dow-HFO-Cu and clinoptilolite exchange media was conducted using a 30 mg/L PO₄-P-only and 78 mg/L NH₄-N solution respectively to determine the maximum exchange capacity of each media. The high concentrations of PO₄-P and NH₄-N exceeded the theoretical exchange capacity of the media so that the maximum sorption potential of the media could be identified. Triplicate vials were run along with no media and deionized water controls to evaluate adsorption and leaching from the glass. Vial contents were mixed for 48 hours after which supernatant was analyzed for PO₄-P and NH₄-N concentration. The exchange

capacity was then calculated by dividing the mass of ion absorbed to the media by the mass of the media.

3.2.3 Regeneration

At the end of the removal test, regeneration was conducted to desorb and recover the PO_4^{3-} and $\text{NH}_4\text{-N}$ anions. The regeneration solutions tested for recovery of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ are reported in Tables 1 and 2. Regeneration solutions selected were lower chemical concentrations of those suggested in literature and were evaluated to determine if they had comparable performance to the standards from literature. Effluent solution from the removal cycle was decanted while the media was retained within the vials. The vials were then rinsed with DI water to remove any remaining effluent, and 50 mL of regeneration solution was added. The vials were then sealed and mixed on a rotational motor for 4 hours, as regeneration reaches equilibrium at a considerably faster rate than that of the removal cycle (Hedstrom, 2001; Sengupta, 2013). At the end of the test, the solution was decanted and the $\text{PO}_4\text{-P}$ or $\text{NH}_4\text{-N}$ concentration was measured. Media was then rinsed with deionized water to remove excess regeneration solution and then underwent another removal cycle. This process was carried out through 5 sequential removal and regeneration steps (ion exchange cycles), to evaluate the impacts on the exchange capacity of the media over multiple ion exchange cycles.

Table 1: Selected Dow-HFO-Cu Regeneration Solutions

PO₄-P Regeneration Solution	pH
2.5% NaCl + 2% NaOH (Sengupta, 2013)	13
1.5% NaCl + 1% NaOH	12
1% NaCl + 0.5% NaOH	11
2% NaCl + 0.5% NaOH	11
1% NaCl + 2% NaOH	13

Table 2: Selected Clinoptilolite Regeneration Solutions

NH₄-N Regeneration Solution	pH
2% NaCl + 0.5% NaOH	11
4% NaCl + 0.5% NaOH	11
6% NaCl + 0.5% NaOH	11

3.3 Column Tests

3.3.1 Removal Testing

Column testing of the exchange media was an important objective as it is the expected nutrient removal process in a full-scale ion exchange operation. Column tests differ from batch tests due to different solution-solid contact time as well as the kinetics involved with a continuous flow system. Two separate column tests were conducted, using permeate from a lab-scale AnMBR with a nominal pore size of 0.002 μm treating either a synthetic wastewater, or primary effluent from South Shore Water Reclamation Facility (Oak Creek, WI) with the goal of comparing the resulting exchange capacities through 5 ion exchange cycles.

The fixed-bed column tests were carried out by placing a 15 mL volume of exchange media in an AdjustaChrom® #11 (Ace Glass Inc., Vineland, NJ) glass column 300 mm long, with a 10 mm diameter. The media volume was weighed prior to testing in order to calculate exchange capacity. A design flow rate of 2 L/d was used to achieve a rate of 5.5 bed volumes (BV)/h and an empty bed contact time (EBCT) of 10.8 minutes. EBCT is defined as the measure of time it takes for a water to be treated is in contact with the media bed. Influent AnMBR permeate was filtered using a 1.5 µm filter to remove any large particles or biological growth in permeate piping, and placed in a 2 L container where it was continuously stirred using a stir plate and pumped through the anion column using a Masterflex® C/L® peristaltic pump (Cole-Parmer, USA). A water head of at least 3 cm was maintained to prevent media disruption from influent drops and potential short-circuiting through the column. Effluent from the anion column was collected in a continuously stirred 2L container to be used as influent for the cation column. A two-way diverter solenoid valve and CF-1 fraction collector (Spectrum Chromatography, Houston, TX) was used to collect effluent samples from the anion column every two hours. When the effluent column was 85% of the influent concentration, the column was rinsed with 5 to 10 bed volumes of deionized water to remove any remaining influent and prepare the column for regeneration. The IX column system is pictured in Figure 3.

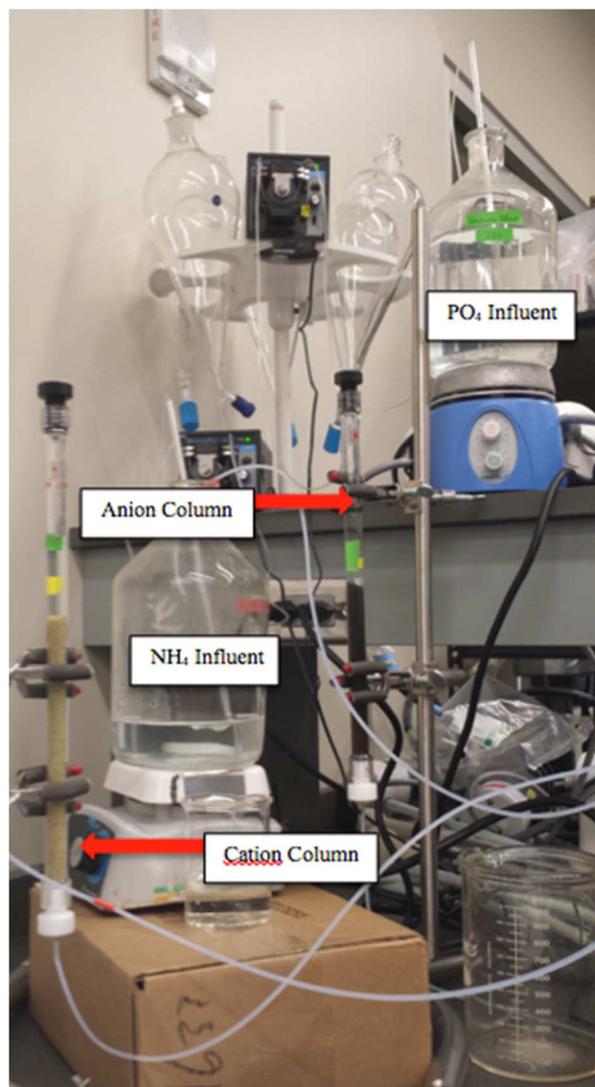


Figure 3: Column Testing Setup

Calculation of the PO₄-P removed from the system was determined by fitting multiple regression curves to sections of the effluent PO₄-P curve using Microsoft Excel and integrating to obtain the area underneath (mg PO₄-P). This value was then divided by the mass of the Dow-HFO-Cu recorded prior to the column runs to achieve an exchange capacity for the removal run (mg PO₄-P/g media). This same method was used to determine the exchange capacities for the cation column.

3.3.2 Column Regeneration

In order to recover the $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ absorbed onto the media in the column tests, regeneration using the best performing regeneration solution from batch tests was conducted. Regeneration solution was pumped through the column at a flow rate of 2 L/d. Effluent regeneration samples were collected every 30 minutes for $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ analysis. The effluent regenerant from the columns was collected for struvite precipitation tests. The regeneration was run until an effluent $\text{PO}_4\text{-P}$ or $\text{NH}_4\text{-N}$ concentration of below 10 mg/L was recorded, beyond which point it would require a much larger volume of regeneration solution to desorb a smaller fraction of the ions from the exchange media surface. After regeneration was complete 5 to 10 bed volumes of deionized water were pumped through the column to remove any remaining regenerant solution and prepare the media for the next removal cycle. The total mass of desorbed $\text{PO}_4\text{-P}$ or $\text{NH}_4\text{-N}$ during regeneration was calculated by fitting multiple trendlines to the concentration curve using Microsoft Excel and integrating to determine the area underneath.

3.4 Struvite Precipitation Tests

Struvite precipitation tests were carried out using the combined regeneration solutions from the anion and cation exchange columns. Recovery of PO_4^{3-} , NH_4^+ , and Mg^+ in precipitated solids was determined through a mass balance of the initial and final

concentrations of the regeneration solutions and supernatant, respectively. The concentration of each regeneration solution was recorded in order to determine the necessary volume required to meet the target molar ratio of Mg^{2+} , NH_4^+ , and PO_4^{3-} . Using the regeneration solutions recovered from the first ion exchange cycle of the columns, preliminary screening were conducted to determine the best performing pH and $Mg^{2+}:PO_4^{3-}$ ratio. Separate screening tests were performed for the AnMBR treating a synthetic wastewater and primary effluent from South Shore Water Reclamation Facility (SSWRF) in Oak Creek, WI. Equivalent molar amounts of each regenerant solution were added to a 125 mL Erlenmeyer flask. Then Mg^{2+} solution was added to test a range of $Mg^{2+}:PO_4^{3-}$ ratios from 1:1-1.3:1. Next, pH was adjusted to 8, 8.7, or 9 using 0.1 M HCl. The sample was allowed to settle for 30 minutes and was then filtered through a 0.45 μm glass fiber filter. The filtered sample was analyzed for PO_4 -P, NH_4 -N, and Mg^{2+} . Using the data from the screening, percent removals of PO_4 -P, NH_4 -N, and Mg^{2+} were calculated to determine the optimal pH and $Mg^{2+}:PO_4^{3-}$ ratio to be used for the remaining struvite precipitation tests.

3.5 Statistical Analysis

Results from exchange capacity batch testing underwent statistical analysis using GraphPad Prism® statistics software to determine if there was potential for exchange capacity stabilization. Using one-way ANOVA, differences between exchange capacities were detected between the capacities at each cycle for each of the regeneration solutions tested. A Tukey's multiple comparison test was conducted to determine which differences were statistically significant

4. Results and Discussion

4.1 Evaluation of Extended Performance of Dow-HFO-Cu Anion and Zeolite Cation Exchange Media in Batch Tests

Equilibrium batch testing using PO_4^{3-} solution at a concentration of 3 mg/L as $\text{PO}_4\text{-P}$, (as expected from AnMBR permeate) was performed to determine the length of reaction time for future batch tests. As depicted in Figure 4, over 90% removal of PO_4 was observed after 30 minutes, with PO_4^{3-} concentrations recorded below detection limit (0.01 mg/L $\text{PO}_4\text{-P}$) through 60 minutes.

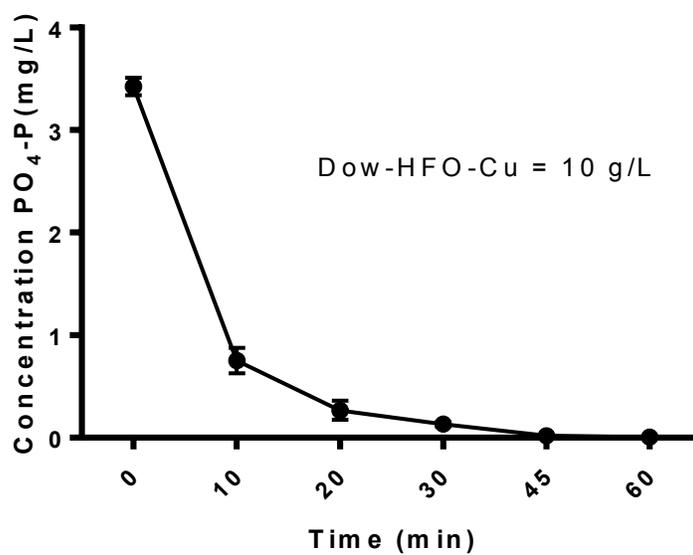


Figure 4: Equilibrium tests showing removal of $\text{PO}_4\text{-P}$ over time. All time points are triplicate averages with error bars representing one standard deviation. Some error bars are small and not visible.

4.1.1 Selective Removal Characteristics of Dow-HFO-Cu Exchange Media

With the ultimate goal of recovering and reusing captured PO_4^{3-} , it is important to consider competition from other anions that could reduce the ability to effectively capture PO_4^{3-} . Results from batch tests using permeate from a lab-scale AnMBR treating synthetic wastewater are shown in Figure 5 and 6, which illustrates that over 90% of $\text{PO}_4\text{-P}$ is removed after 45 minutes with near complete removal after 60 minutes in the presence of other competing anions. Effluent SO_4^{2-} concentrations initially decreased to less than 10 mg/L, but remained relatively constant for the remainder of the test period. This initial decrease in SO_4^{2-} concentration is considered to be due to weak Coulombic interactions as described by Blaney et al. (2007), where the anions are less selectively bound to the exchange media. The phosphate species were able to outcompete other anions such as SO_4^{2-} because their ability to form inner-sphere complexes with the immobilized Cu^{2+} on the Dow-HFO-Cu exchange media (Blaney et al., 2007; Sengupta, 2013). This is also due to higher stability constants that are associated with the Cu^{2+} and HFO metal ligands and PO_4^{3-} , where the SO_4^{2-} stability constants are much lower (Stumm, 1970).

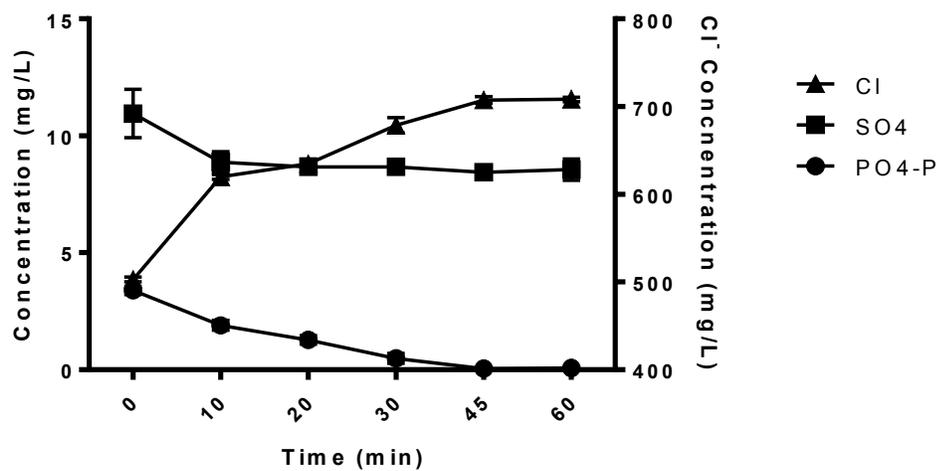


Figure 6: Effluent concentrations from AnMBR permeate treating synthetic wastewater. All time points are triplicate averages with error bars representing one standard deviation

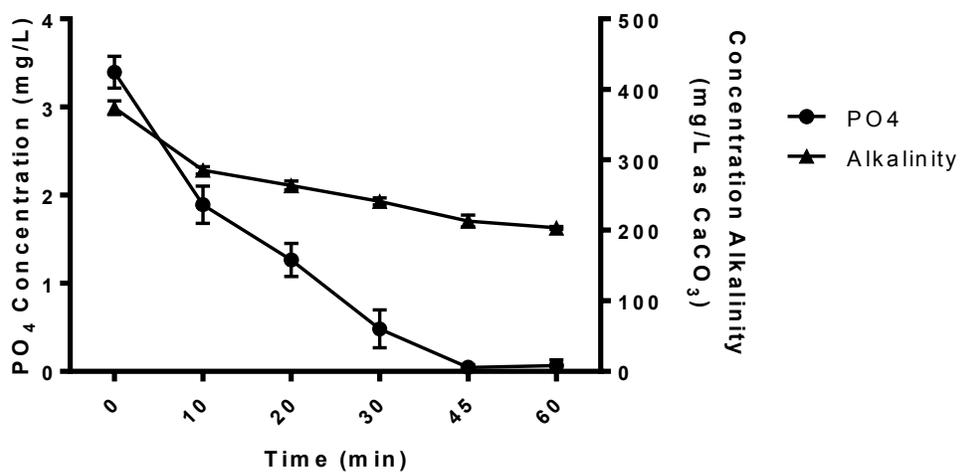


Figure 5: Effluent concentrations of PO₄-P and alkalinity from AnMBR permeate treating synthetic wastewater. All time points are triplicate averages with error bars representing one standard deviation

Chloride (Cl^-) concentration increased from 500 mg/L to 700 mg/L over the duration of the test period. The 200 mg/L Cl^- concentration increase translates into a 5.7 meq/L increase. When considering the total meq/L concentration of the combined removal of PO_4^{3-} , SO_4^{2-} , and alkalinity observed over the tested period, a concentration of 2.9 meq/L is recorded, which equates to nearly half of the Cl^- increase observed. It may be possible that initial leaching of Cl^- from the media could cause the large increase seen in batch testing. Overall, from batch tests determining the competition between PO_4^{3-} and SO_4^{2-} using an AnMBR wastewater matrix, it appears that Dow-HFO-Cu exchange media can selectively remove PO_4^{3-} , similar to results seen for Dow-HFO-Cu treating a synthetic wastewater (Sengupta, 2013).

4.1.2 Impact of Multiple Ion Exchange Cycles on Anion Exchange Capacity

Batch testing of the Dow-HFO-Cu exchange media was performed to determine the impact of multiple ion exchange cycles on the media's maximum exchange capacity. Results from the extended batch tests are found in Figure 7, and vary between the different regeneration solutions used. Initial exchange capacities recorded were between 9 and 10 mg $\text{PO}_4\text{-P/g}$ media, a similar value to the 15 mg $\text{PO}_4\text{-P/g}$ media estimated from (Sengupta & Pandit, 2011). Decreases in exchange capacity were observed as the number of ion exchange cycles increased for each tested regeneration solution. The regeneration solution of 2.5% NaCl + 2% NaOH suggested by Sengupta (2013) exhibited the largest decrease in exchange capacity, about 43%, between the first and second exchange cycles. The significant reduction of exchange capacity is believed to be from the alkaline conditions of the regeneration solution caused by the high concentration of NaOH. While

alkaline solutions are used in regeneration to break the stronger bonds between the absorbed phosphates and the metal ligands to which they are attached, a high pH (~13) can strip the exchange media of the copper metal loaded onto the polymer base, in turn eliminating exchange sites for subsequent removal cycles.

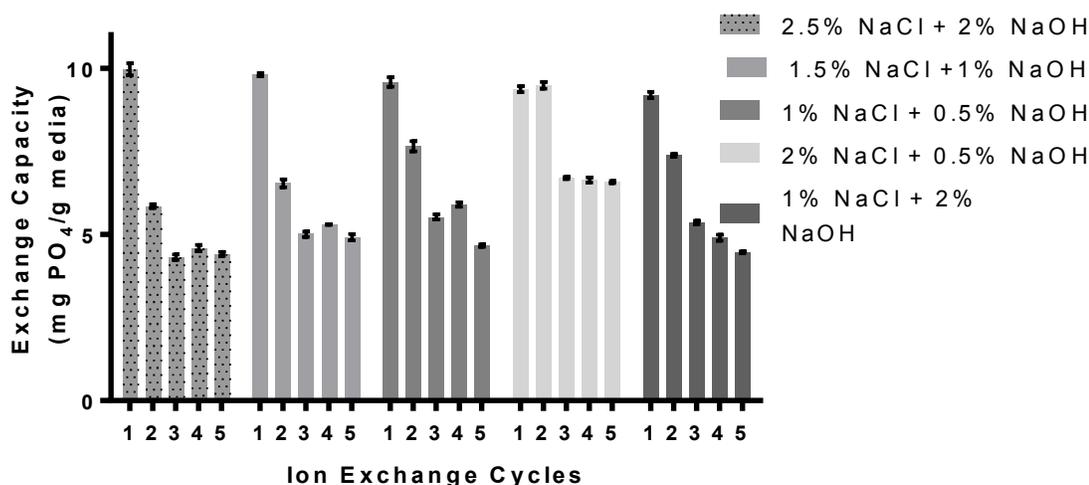


Figure 7: Exchange capacity of Dow-HFO-Cu under different regeneration conditions. All bars are triplicate averages with error bars depicting ± 1 standard deviation

Maintaining a high level of removal over multiple exchange cycles is desirable for full-scale use. Of the 5 regeneration solution tested, only two demonstrated stabilized exchange capacity through 5 ion exchange cycles: 2.5% NaCl + 2% NaOH and 2% NaCl + 0.5% NaOH. Beyond three cycles, both solutions demonstrated consistent performance (defined as no statistical difference in exchange capacities between sequential ion exchange cycles using Tukey's multiple comparison test). A complete summary of the statistical analysis can be found in Appendix A. For these two stabilized performance scenarios, the lower pH regeneration solution (2% NaCl + 0.5% NaOH) achieved a

higher stabilized exchange capacity compared to the 2.5% NaCl + 2% NaOH solution suggested by Sengupta (2013). In fact, out of all the tested regeneration solutions, the 2% NaCl + 0.5% NaOH solution was able to achieve the highest exchange capacity over 5 ion exchange cycles, with a final exchange capacity of 6.5 mg PO₄/g media. It is likely that higher pH (13) causes increased deterioration to the exchange media, specifically stripping of metal ligand structures, thereby decreasing exchange capacity.

4.1.3 Recovery of PO₄³⁻ Under Varied Concentrations of Regeneration Solutions

As described in section 4.1.2, two regeneration solutions provided a stabilized exchange capacity after 3 ion exchange cycles, with 2% NaCl + 0.5% NaOH providing the highest removal capacity: 6.5 mg PO₄/g media after 5 ion exchange cycles. In addition to efficient *removal*, efficient *recovery* is imperative. Thus, regeneration of the exhausted anion media is an important step to achieve an efficient nutrient recovery process. Identifying regeneration solutions that can achieve continual, effective recovery of PO₄³⁻ has potential for both operational and economic benefits.

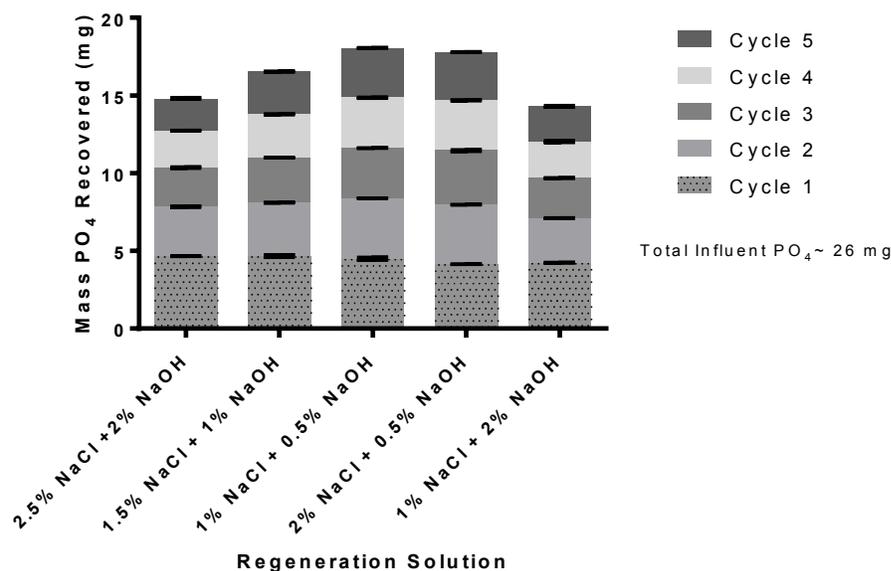


Figure 8: Recovered mass of PO_4 -P through 5 ion exchange cycles. All cycles are triplicate averages with error bars depicting ± 1 standard deviation

Figure 8 illustrates the cumulative mass of PO_4 recovered over 5 ion exchange cycles during batch testing. Regeneration solutions of 1% NaCl + 0.5% NaOH and 2% NaCl + 0.5% NaOH achieved the highest recovery, 18 and 17 mg PO_4 -P respectively. These solutions outperformed the high pH (13) 2.5% NaCl + 2% NaOH solution suggested by Sengupta (2013). As discussed in section 2.3.2 due to the increase in pH of the regeneration solutions stripping the media of the copper ligands leaving less exchange sites for phosphate ions to be removed from wastewater and ultimately lower recovery potential. Other solutions containing high concentrations of NaOH produced similar results in terms of lower PO_4 -P recovery.

In order to determine the optimal regeneration solution from those tested in this study the combination of removal and recovery performance must be considered. the 2%

NaCl + 0.5% NaOH regeneration solution demonstrated consistent performance after three ion exchange cycles and maintained the highest exchange capacity over the tested cycles while recovering the largest amount of removed PO_4^{3-} , making it the optimum regeneration solution tested. The 2.5% NaCl + 2% NaOH regeneration solution used to regenerate the Dow-HFO-Cu exchange media in previous studies also provided stabilized exchange capacity after the third ion exchange cycle. However, it offered the lowest overall exchange capacity as well as the second lowest recovery over 5 regeneration cycles and is therefore not considered ideal for long-term use. Because of the smaller exchange capacity that resulted from the use of this regeneration solution, the overall recovered mass of PO_4 during regeneration was less than other regeneration solutions. However this does not mean inefficient regeneration as greater than 80% recovery of $\text{PO}_4\text{-P}$ was recorded during each regeneration cycle for each regeneration solution tested.

4.1.4 Variability of Exchange Capacity Over Multiple Ion Exchange Cycles of Clinoptilolite Exchange Media Under Different Concentrations of NaCl in Regeneration.

To determine the effects of different saline concentrations in regeneration solutions on clinoptilolite's maximum exchange capacity through multiple exchange cycles batch testing was performed. The exchange capacities of the clinoptilolite exchange media under each regeneration solution remained within the range of 7 to 8 mg $\text{NH}_4^+\text{-N/g}$ media over the 5 ion exchange cycles tested, as shown in Figure 9. Using a one-way ANOVA test, significant differences in the exchange capacities for were demonstrated (Appendix A). A Tukey's multiple comparison test between the 5 ion exchange cycles tested for each regeneration solution showed that of the three

regeneration solutions tested, the solution of 2% NaCl + 0.5% NaOH provided the most consistent level of performance.

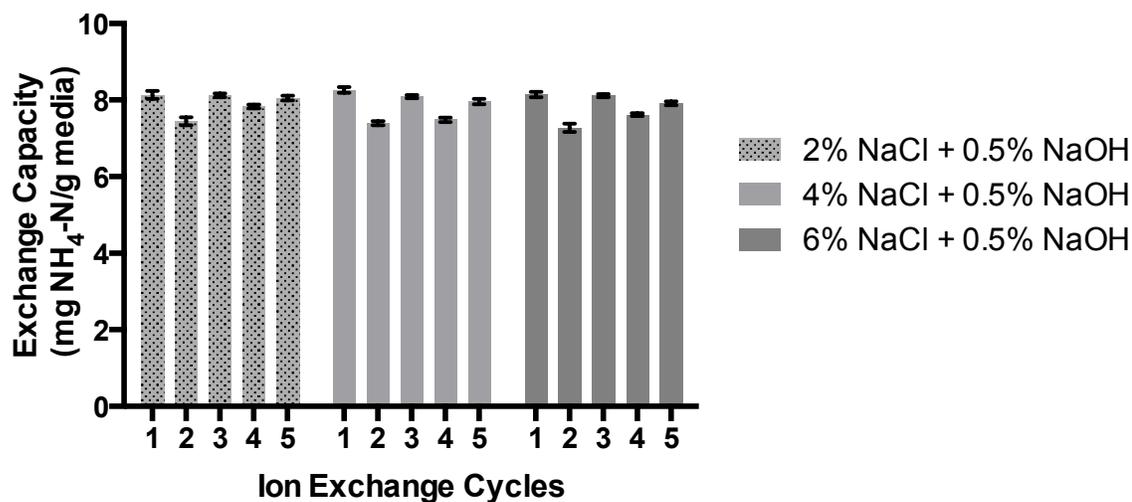


Figure 9: Exchange capacity of clinoptilolite through 5 ion exchange cycles. All values are triplicate averages with error bars depicting ± 1 standard deviation

In addition to removing nearly the same mass of NH₄-N, all of the regeneration solutions recovered approximately equal amounts of NH₄-N (greater than 14 mg NH₄-N out of a total influent of 23 mg NH₄-N), as shown in Figure 10. Thus, a more dilute saline regeneration solution can perform as well as more concentrated solutions. It should also be noted that the 2% NaCl + 0.5% NaOH regeneration solution was found to be the best performing regenerant in anion exchange media batch testing, leading to an opportunity to use the same regeneration solution for both NH₄ and PO₄ regeneration.

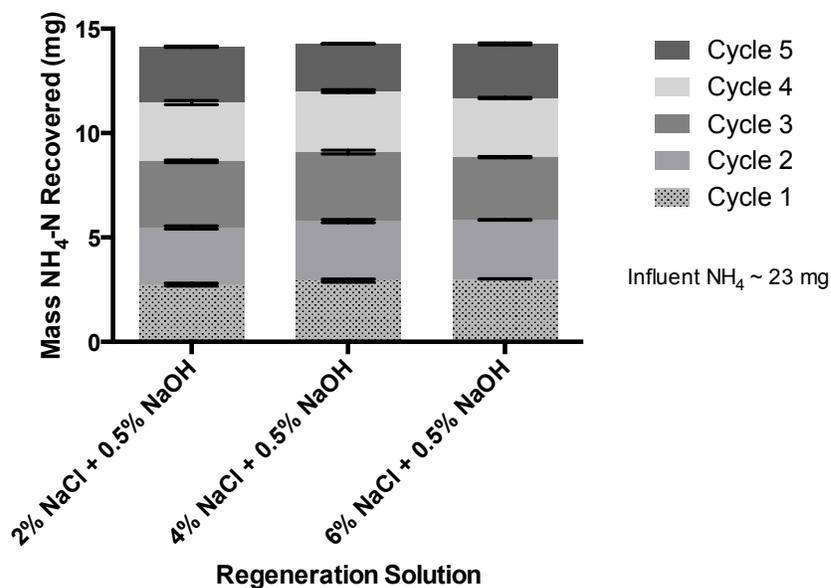


Figure 10: Recovered mass of $\text{NH}_4\text{-N}$ through 5 ion exchange cycles. All values are triplicate averages with error bars depicting ± 1 standard deviation

4.2 Evaluation of the Extended Performance of Dow-HFO-Cu Anion and Clinoptilolite Cation Exchange Media in Column Tests

4.2.1 AnMBR Permeate Characteristics

Two separate column tests were conducted to treat different lab-scale AnMBR permeates for the ion exchange process. The first column tests used permeate from a lab-scale AnMBR treating a synthetic wastewater modeled after effluent from a primary settling process. The second column tests used permeate of a lab-scale AnMBR treating real primary effluent collected SSWRF. A summary of pertinent concentrations recorded in both permeates are described in Tables 3 and 4. Target ions of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ remain within a reasonable range between the two permeates, however the SO_4^{2-}

concentration recorded for the permeate of the primary effluent is considerably higher than what was observed in the synthetic permeate. This higher concentration could increase the competition for exchange sites on the Dow-HFO-Cu media effectively decreasing the exchange capacity recorded. During column tests of the primary effluent permeate, plugging and fouling of the top of the ion exchange bed were observed, decreasing the overall flow rate through the system. Though it may not be significant in the treatment process of the AnMBR, the slight increase in biochemical oxygen demand (BOD₅) seen between permeates of the synthetic wastewater and primary effluent is believed to be the cause of fouling and decreased flow of the second column runs due to the small scale of the tests.

Table 3: Synthetic Wastewater AnMBR Permeate Characteristics

Constituent:	PO ₄ -P	NH ₄ -N	SO ₄ ²⁻	Cl ⁻	BOD ₅
n	14	14	3	3	73
Average (mg/L)	4.6	38	16	462	2.5
Standard Deviation (mg/L)	0.2	2.7	2.5	72	1.3

Table 4: Primary Effluent from SSWRF AnMBR Permeate Characteristics

Constituent:	PO ₄ -P	NH ₄ -N	SO ₄ ²⁻	Cl ⁻	BOD ₅
n	15	15	3	3	11
Average (mg/L)	4.9	34	56	536	6.0
Standard Deviation (mg/L)	0.7	5.9	10	25	3.3

4.2.2 Assessment of Multiple Ion Exchange Cycles on Dow-HFO-Cu Exchange Capacity

Removal of PO₄-P through an anion exchange column was the first step of the nutrient removal and recovery process. Using the measured concentrations from the effluent samples collected every two hours, a breakthrough curve for the first removal cycle was produced as shown in Figure 11. An effluent concentration of less than 0.075 mg/L of PO₄-P was recorded for the first 1.5 L of tested influent, or 210 BV. Results from Sengupta (2013) showed the Dow-HFO-Cu media could treat nearly 600 BV with a similar influent concentration of PO₄-P (~4 mg/L) with an EBCT of 3 minutes. However, the design EBCT used in the present study was much longer at 10.8 minutes.

The area underneath the curve was integrated to determine the mass of exchanged PO₄-P, which allowed for calculation of the exchange capacities. A summary of all removal curves for both anion column tests can be found in Appendix A. For both anion column tests conducted (using AnMBR permeate with synthetic and actual wastewater), a comparable total influent mass and removed mass of PO₄-P was observed. For the synthetic wastewater permeate, a relatively constant influent mass between 31 and 35 mg PO₄-P was treated during each exchange cycle, with nearly 94% of the influent mass being removed in cycle 1. Also, as observed in batch testing of the Dow-HFO-Cu media, the largest decrease in performance was between cycles 1 and 2. Influent mass of PO₄-P was much more variable when treating the primary effluent permeate, as it ranged from 27 to 37 mg PO₄-P per exchange cycle. Only 74% of the influent mass of PO₄-P was removed during the first exchange cycle, which is a 20% decrease in removal performance compared to the synthetic wastewater permeate.

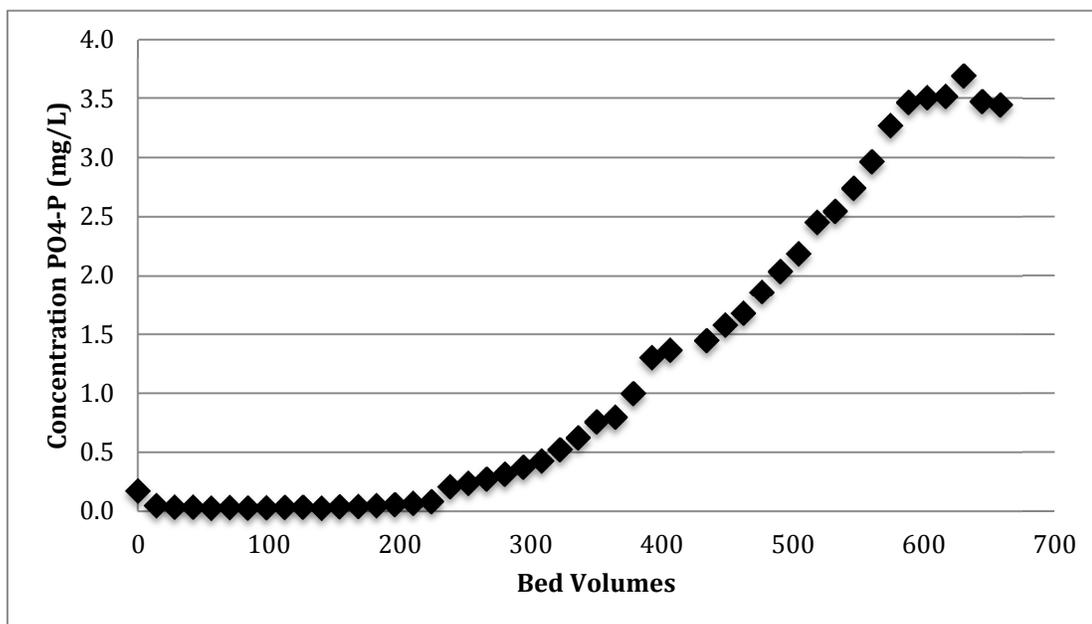


Figure 11: Breakthrough curve of Dow-HFO-Cu exchange media from the first removal cycle using synthetic wastewater AnMBR permeate. All data points are single measurement.

Using the removal data, exchange capacities were calculated for each ion exchange cycle, as shown in Figure 12. The exchange capacities recorded ranged from 1.6 to 2.8 mg PO₄-P/g media, which is substantially less than the maximum exchange capacities calculated in batch testing (9 to 10 mg PO₄-P/g media). However, this was expected as the Dow-HFO-Cu exchange media is treating a more complex water matrix in a continuous flow column system ultimately affecting the performance of the exchange media. The decrease in exchange capacities between the first and second ion exchange cycles for the synthetic wastewater and primary effluent permeate were found to be 22% and 24% respectively. Comparing exchange capacity between the two permeates, neither considerably outperformed the other, suggesting that consistent results could be obtained treating variable quality AnMBR permeate using Dow-HFO-Cu exchange media.

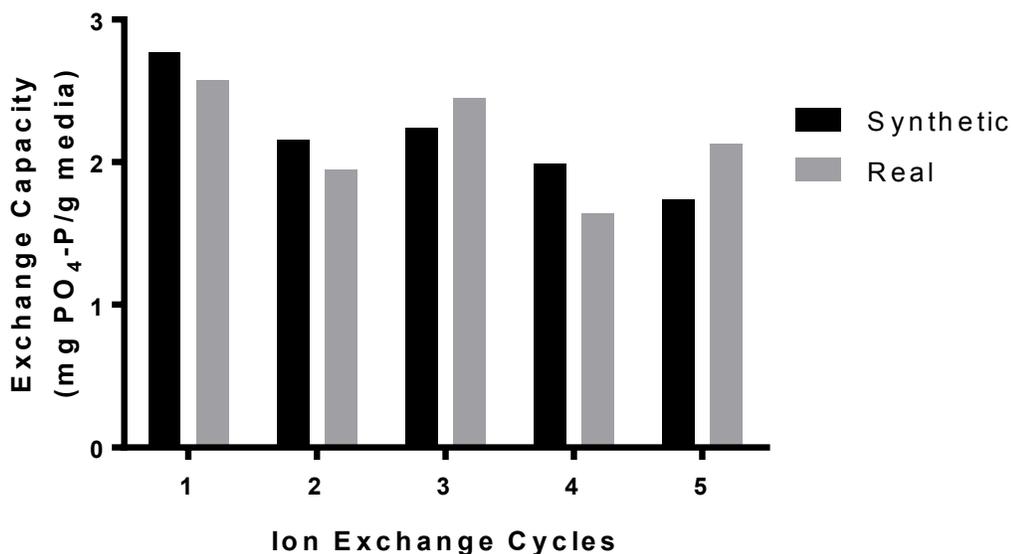


Figure 12: Exchange capacity of Dow-HFO-Cu media treating different AnMBR permeates

4.2.3 Evaluate Concentration and Content of Recovered PO₄ Regeneration Solutions

Regeneration of exchange media is perhaps the most important step in the nutrient recovery process. The regeneration solutions used to recover PO₄-P and replenish sorption sites can have significant impacts on ensuing ion exchange cycles, ultimately affecting the efficiency of the entire nutrient removal and recovery process. From batch testing, a regeneration solution of 2% NaCl + 0.5% NaOH was found to cause the least attrition to the media, while desorbing the most PO₄³⁻ ions from the exhausted media. Thus this regeneration solution was used for column testing to further assess its recovery performance in a continuous flow system. A comparison of the total mass of PO₄-P recovered from the synthetic wastewater and primary effluent permeates is depicted in

Figure 13 and 14, respectively. Regeneration of the Dow-HFO-Cu exchange media treating the synthetic permeate recovered 69% of the total influent mass over 5 IX cycles of $\text{PO}_4\text{-P}$, while only 54% was recovered from the primary effluent permeate. However, considering the percent recovery of $\text{PO}_4\text{-P}$ from the total amount removed over the 5 ion exchange cycles, much better performance was achieved with 94% and 79% recovery of $\text{PO}_4\text{-P}$ for synthetic and real wastewater permeate, respectively. During the first 5 BV of each regeneration, a concentration ranging from 150 to 200 mg/L $\text{PO}_4\text{-P}$ was recorded as the ions were being concentrated into the regenerant eluate. This is demonstrated in Figure 15 for the first regeneration cycle of the Dow-HFO-Cu media using synthetic AnMBR permeate. This is important for precipitation considerations as high concentration and low volume nutrient streams are desired.

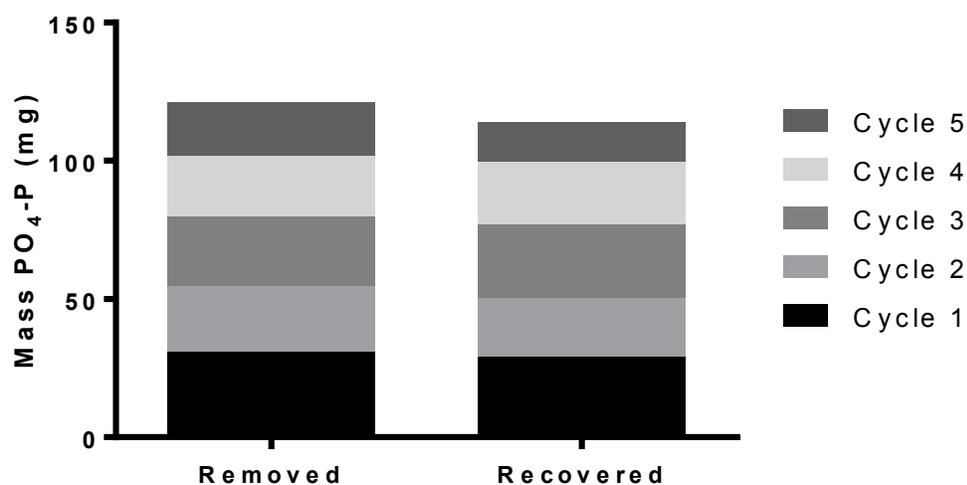


Figure 13: Removal and recovery of $\text{PO}_4\text{-P}$ through 5 IX column cycles from AnMBR treating synthetic wastewater

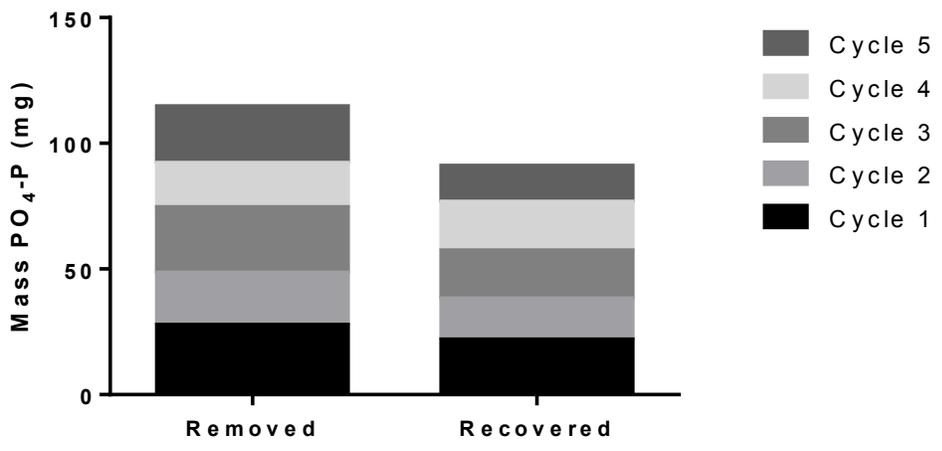


Figure 12: Removal and recovery of NH₄-N through 5 IX column cycles from AnMBR treating primary effluent from SSWRF

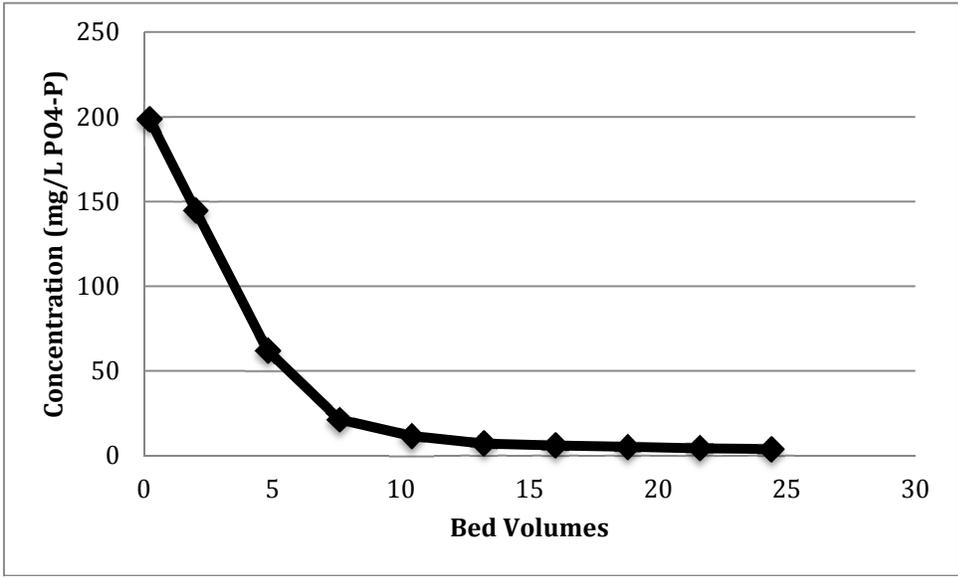


Figure 13: Regeneration curve from first ion exchange cycle of Dow-HFO-Cu media using permeate from AnMBR treating synthetic wastewater. All data points are single measurements.

The effluent regeneration solution was analyzed for metals content using ICP-MS. Metals of interest included Cu^{2+} , Al^{3+} , Fe^{3+} , and Ca^{2+} . As copper and iron are both the ligands responsible for $\text{PO}_4\text{-P}$ adsorption onto the Dow-HFO-Cu media, loss of these ions into solution would negatively impact ensuing ion exchange cycles, and could also decrease struvite fertilizer value. While iron was found at relatively low concentrations in the regeneration solution effluent, significant copper leaching occurred, as found in Table 5. For both column tests treating synthetic wastewater and primary effluent permeate, the largest loss of Cu^{2+} was recorded in the initial regeneration cycle, leaching concentrations of 8.5 and 3.5 mg/L, respectively. Unfortunately, Cu^{2+} concentrations ranging from 0.8 to 3 mg/L were also recorded in each subsequent effluent regeneration solution, effectively removing exchange sites and decreasing the exchange capacity of the media during each regeneration cycle. Methods to minimize the loss of the Cu^{2+} ion should be considered in future work using Dow-HFO-Cu exchange media, such as placing an unsaturated or “virgin” layer of exchange media at the bottom of the exchange bed to capture any bleeding Cu^{2+} ions as described in previous literature (Zhao & Sengupta, 1998).

Both Al^{3+} and Ca^{2+} ions were also found in the regeneration effluent, and their presence can be inhibitory towards struvite precipitation. From metals analysis, Al^{3+} was found to be at very high concentrations in some regeneration effluent, which when combined with PO_4 could produce AlPO_4 precipitate. The PO_4^{3-} bound in this precipitate is largely considered to be unavailable for biological growth, which decreases value of the final precipitated product as a fertilizer (Morse, Brett, Guy, & Lester, 1998b; Rittmann et al., 2011). Concentrations of Ca^{2+} were often higher than Al^{3+} , which promotes potential formation of calcium phosphates. While calcium phosphates have

been used as potential nutrient sources for plant growth, the goal of this study is to remove and recover both PO_4^{3-} and NH_4^+ (accomplished in the form of struvite), and the presence of Ca^{2+} can decrease efficiency. It should also be noted that during regeneration of both anion and cation columns, precipitation occurred in the collection bottles for nearly all eluates. A summary of metals found in the regeneration eluate for both column tests is found in Table 5.

Table 5: Metals concentrations in regeneration eluate

Ion:	Al^{3+} (mg/L)		Ca^{2+} (mg/L)		Cu^{2+} (mg/L)		Fe^{2+} (mg/L)	
Regeneration Cycle	S ^a	PE ^b	S	PE	S	PE	S	PE
1	10	17	167	16	8.5	3.5	2.0	1.0
2	4.5	7.4	55	8.9	3.0	1.5	0.86	0.26
3	4.9	5.8	18	7.4	2.4	2.5	0.36	0.25
4	3.7	2.2	10	5.5	2.9	1.4	0.37	0.20
5	13	0.65	9.7	8.8	0.78	1.2	0.19	0.20
^a S = Synthetic ^b PE = Primary effluent from SSWRF								

4.2.4 Variability of Exchange Capacity over Multiple Ion Exchange Cycles of Clinoptilolite Exchange Media

Separate fixed-bed clinoptilolite column tests were carried out using the AnMBR permeate of a synthetic wastewater and primary effluent from SSWRF to assess the exchange capacity over 5 ion exchange cycles, as shown in Figure 16. Column tests treating the synthetic AnMBR permeate achieved exchange capacities ranging from 11 to 19 mg $\text{NH}_4\text{-N/g}$ media, while a lower range of 6 to 14 mg $\text{NH}_4\text{-N/g}$ media was found

when treating AnMBR permeate from primary effluent. This reduced performance is likely caused by increased BOD_5 concentrations, as described previously. Increased competing cation concentrations not measured in the primary effluent may have also played a role in the decreased exchange capacity.

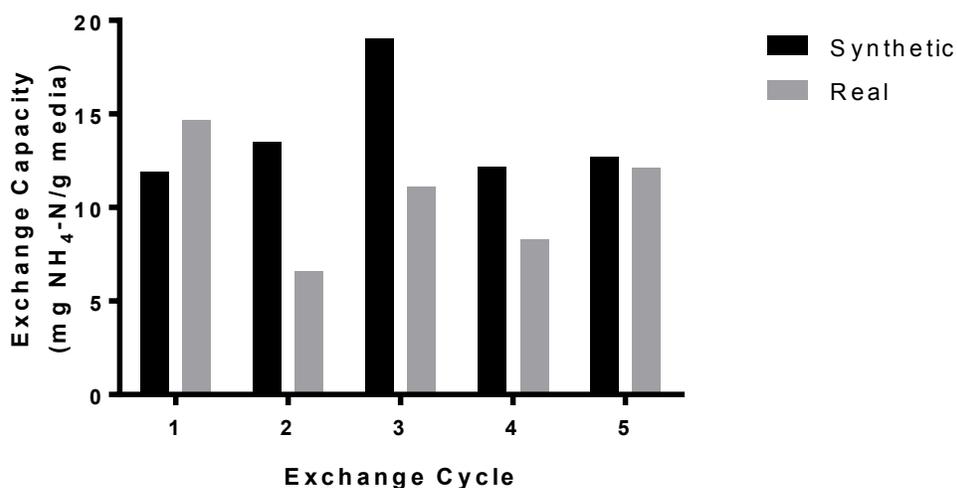


Figure 14: Exchange capacities of clinoptilolite treating different AnMBR permeates

As the column tests did not demonstrate any strong trend in exchange capacity over multiple ion exchange cycles, it is expected that the variation stems from the regeneration step performed after each removal cycle. Regeneration using 2% NaCl + 0.5% NaOH recovered less than 50% of the mass removed in nearly every ion exchange cycle tested. A comparison between column tests of the mass NH₄-N recovered for each ion exchange cycle is found in Figure 17 and 16, respectively. Multiple variables in both the removal and recovery process can affect clinoptilolite exchange capacity, and

regeneration using 2% NaCl + 0.5% NaOH solution should be studied in the future to determine if more consistent recovery of $\text{NH}_4\text{-N}$ can be achieved.

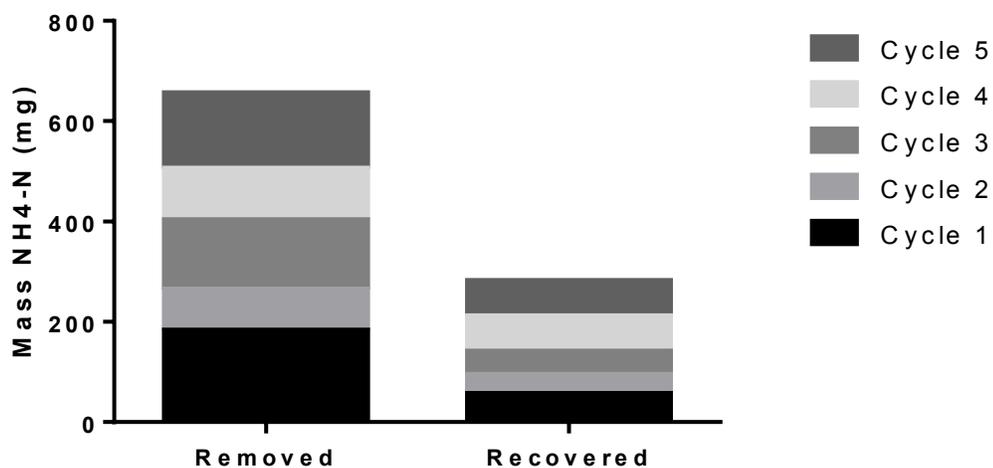


Figure 15: Removal and Recovery of $\text{NH}_4\text{-N}$ through 5 IX column cycles from AnMBR treating synthetic wastewater

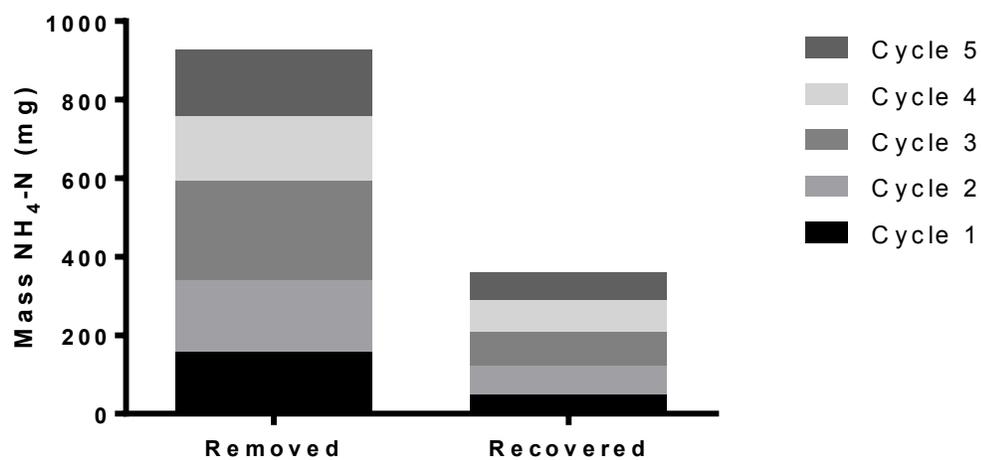


Figure 18: Removal and recovery of $\text{NH}_4\text{-N}$ through 5 IX column cycles from AnMBR treating primary effluent from SSWRF

4.3 Recovery of Nutrients as Struvite

4.3.1 Molar Ratios of Recovered Product

Through the combination of the cation and anion regeneration streams and addition of Mg^{2+} , precipitation tests were performed to determine the potential for recovery of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ as a solid struvite product. Screening tests using regeneration solutions from the first ion exchange cycle were used to determine the optimal pH within a range of 8 to 9 and $\text{Mg}:\text{PO}_4$ ratio ranging from 1:1 to 1.3:1 based on work from previous reports (Beal et al., 1999; de-Bashan & Bashan, 2004). These tests identified a pH of 8 and a ratio of 1.3:1 as optimal for synthetic wastewater column tests, while the optimal pH and $\text{Mg}:\text{PO}_4$ ratio for the regeneration solutions from primary effluent column tests were determined to be 8 and 1.1:1, respectively.

Table 6: Calculated molar ratios of solid precipitate from supernatant mass balance

Ion Exchange Cycle	Synthetic			Primary Effluent		
	Mg^{2+}	NH_4^+	PO_4^{3-}	Mg^{2+}	NH_4^+	PO_4^{3-}
1	1.1	0.1	0.4	0.8	0.1	0.9
2	1.0	0.4	0.2	0.2	0.5	0.4
3	0.9	0.5	0.3	0.5	0.4	0.2
4	0.9	0.2	0.2	0.1	0.6	0.2
5	1.2	0.2	1.0	0.4	0.9	0.1

A mass balance performed using supernatant from batch precipitation tests were carried out to determine the molar ratios in the precipitates, as shown in Table 6. While the majority of the calculated molar ratios were low, two of the tests were able to efficiently recover PO_4^{3-} and Mg^{2+} in the precipitated product with molar ratios close to or greater than 1. However, the NH_4^+ ratios calculated from the successful tests were much lower than theoretical values, suggesting that the precipitated material may not be pure struvite. Similar results were observed by Williams (2013) as percent removal of $\text{NH}_4\text{-N}$ between 16 and 21% were recorded for 4 separate media regenerants used in precipitation tests. This low recovery of NH_4^+ could be due to the high pH of the regeneration solution where increased pH can convert NH_4^+ ions to NH_3 (Hao, Wang, van Loosdrecht, & Hu, 2013).

The total influent PO_4^{3-} and NH_4^+ recovered in the precipitated solids are reported in Tables A5 through A8 in Appendix A. In most every case the total recovery of PO_4^{3-} and NH_4^+ in the solid precipitate fraction was less than 50% as majority of the nutrients remained in the regenerant brine solution. Total influent PO_4^{3-} recovery in precipitate ranged from 12 to 52% while total influent NH_4^+ recovery in the precipitate was much lower ranging from 1 to 29%. It is considered that potential inhibitory ions such as Ca^{2+} in regeneration solutions formed compounds with the PO_4^{3-} ions thus producing a solid precipitate that is not considered pure struvite. The low recoveries of NH_4^+ are an indicator that there are obvious inefficiencies with the struvite precipitation process, thus further work must be done to assess improvements in precipitation methods.

4.4 Nutrient Recovery Process in AnMBR Treatment Process

Using data from column tests of the first ion exchange cycle an overall process flow diagram (Figure 16) was created to exemplify how a nutrient recovery process may be implemented within a wastewater treatment operation using AnMBR technology. As discussed earlier, the use of anaerobic technology has the potential to provide reduced net energy compared to conventional treatment processes. The addition of a nutrient recovery treatment process can help to achieve a more complete sustainable operation by using wastewater as a resource for energy and nutrients. The average total influent of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ from the synthetic wastewater was 5 and 17 mg/L, respectively. Through the AnMBR process $\text{PO}_4\text{-P}$ concentrations remained within the same range, while $\text{NH}_4\text{-N}$ concentrations nearly doubled to 31 mg/L. During the first ion exchange cycle using AnMBR permeate treating synthetic wastewater both Dow-HFO-Cu and Clinoptilolite exchange media were able to reach low effluent concentrations below 0.075 mg/L $\text{PO}_4\text{-P}$ and 1 mg/L $\text{NH}_4\text{-N}$, respectively before breakthrough at 210 and 68 BV, respectively. The percent removed from the influent AnMBR permeate in anion and cation exchange columns was 94% and 98%, respectively for the first removal cycle.

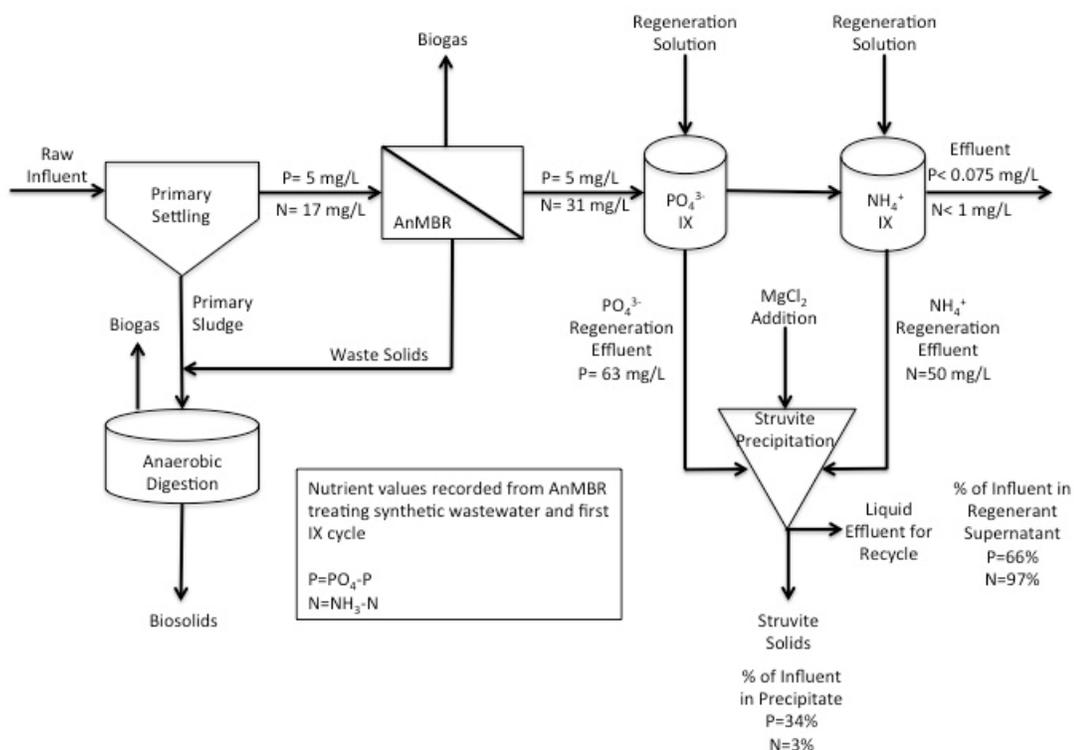


Figure19: Nutrient recovery process diagram using results from AnMBR treating synthetic wastewater and ion exchange columns

After regeneration of the media precipitation tests were conducted and found that 34% $\text{PO}_4\text{-P}$ was recovered in the precipitated solids from the total influent and only 3% of $\text{NH}_4\text{-N}$, suggesting that the precipitate may not be struvite. A data summary of the PO_4^{3-} and NH_4^+ flows through the treatment process treating synthetic wastewater and primary effluent from SSWRF can be found in Appendix A. While there are inefficiencies with the current process, particularly precipitation of struvite, ion exchange is able to achieve low effluent concentrations of both PO_4^{3-} and NH_4^+ , and recover the removed portion in concentrated regeneration streams.

5. Conclusions

Dow-HFO-Cu ion exchange media provided selective removal of PO_4^{3-} in comparison to competing anions. In batch tests, it provided a consistent exchange capacity of 6.5 mg $\text{PO}_4\text{-P/g}$ media beyond three ion exchange cycles using a regeneration solution of 2% NaCl + 0.5% NaOH. This lower pH solution provided improved performance compared to high pHs, likely due to stripping of Cu^{2+} ligand structures at higher pH (~13). This regeneration solution also provided the most consistent $\text{NH}_4\text{-N}$ recovery using clinoptilolite exchange media. Use of the same regeneration solution for both anion and cation exchange media offers operational benefits. In column tests, Dow-HFO-Cu provided an exchange capacity ranging from 1.6 to 2.8 mg $\text{PO}_4\text{-P/g}$ media through 5 ion exchange cycles.

The exchange capacities recorded in column tests are lower than those recorded in batch leaving room for improvements on the maximum exchange capacity of the Dow-HFO-Cu media in columns. However, the consistency of recorded exchange capacity in column tests between two different permeates from an AnMBR suggest that similar performance could be observed treating variable AnMBR permeates. The Dow-HFO-Cu media provided an effluent $\text{PO}_4\text{-P}$ concentration of less than 0.075 mg/L for 210 and 156 BV before breakthrough in the initial removal column runs using AnMBR permeate treating synthetic wastewater and primary effluent from SSWRF, respectively. Regeneration of Dow-HFO-Cu exchange media from column tests treating synthetic and real wastewater permeate achieved 94% and 79% recovery of $\text{PO}_4\text{-P}$ from the removed mass, respectively. However, leaching of Cu^{2+} , Al^{3+} , and Ca^{2+} during regeneration was observed and is considered undesirable for subsequent precipitation tests. Column tests to

remove NH_4^+ using clinoptilolite produced a wide range of exchange capacities.

Improved regeneration conditions may allow for more complete desorption of captured NH_4^+ and thus a better exchange capacity, as less than 50% of the removed fraction of $\text{NH}_4\text{-N}$ was recovered in nearly all regeneration steps. Precipitation tests using column regeneration eluate determined that out of 10 tests conducted, only 2 produced a $\text{Mg}:\text{PO}_4$ ratio close to the theoretical value of 1. While precipitation was observed, low molar values of NH_4^+ recorded suggest that the product may not be pure struvite. As such, further research into the use of ion exchange column regenerants should be conducted to produce an efficient precipitation process.

As an alternate, more sustainable nutrient source, ion exchange for the removal and recovery of PO_4^{3-} and NH_4^+ from AnMBR permeate is a promising technology. However, improvements at lab-scale must be considered in order to achieve a process that is both economical and operational at larger scales.

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Appendix A

Table A 1: 1-way ANOVA test summary for PO₄-P batch tests

	2.5% NaCl + 2% NaOH	1.5% NaCl + 1% NaOH	1% NaCl + 0.5% NaOH	2% NaCl + 0.5% NaOH	1% NaCl + 2% NaOH
F	1539	1935	1785	1439	2423
P value	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Are differences among means statistically significant? (P < 0.05)	Yes	Yes	Yes	Yes	Yes
R square	0.9984	0.9987	0.9986	0.9983	0.999

Table A 2: q-values from Tukey's multiple comparison test between 5 IX cycles for PO₄-P batch tests. q-values less than 5 are not considered statistically different and are highlighted

2.5% NaCl + 2% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	67.39	92.46	88.16	90.96
Cycle 2		25.07	20.77	23.57
Cycle 3			4.299	1.5
Cycle 4				2.799

1.5% NaCl + 1% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	69.73	102.5	96.37	104.6
Cycle 2		32.78	26.63	34.83
Cycle 3			6.146	2.046
Cycle 4				8.192

1% NaCl + 0.5% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	31.23	109.1	59.55	79.55
Cycle 2		77.89	28.32	48.33
Cycle 3			49.57	29.56
Cycle 4				20.01

2% NaCl + 0.5% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	2.731	66.63	67.31	69.61
Cycle 2		69.36	70.04	72.34
Cycle 3			0.6808	2.982
Cycle 4				2.302

1% NaCl + 2% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	45.05	95.17	106.5	117.4
Cycle 2		50.12	61.47	72.32
Cycle 3			11.35	22.2
Cycle 4				10.85

Table A 3: 1-way ANOVA test summary for NH₄-N batch tests

	2% NaCl + 0.5% NaOH	4% NaCl + 0.5% NaOH	6% NaCl + 0.5% NaOH
F	42.43	109.4	95.31
P value	< 0.0001	< 0.0001	< 0.0001
Are differences among means statistically significant? (P < 0.05)	Yes	Yes	Yes
R square	0.9444	0.9777	0.9744

Table A 4: q-values from Tukey's multiple comparison test between 5 IX cycles for NH₄-N batch tests. q-values less than 5 are not considered statistically different and are highlighted

2% NaCl + 0.5% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	15.49	0.3495	6.698	1.806
Cycle 2		15.14	8.795	13.69
Cycle 3			6.348	1.456
Cycle 4				4.892

4% NaCl + 0.5% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	23.75	4.722	21.39	8.084
Cycle 2		19.03	2.361	15.67
Cycle 3			16.67	3.362
Cycle 4				13.31

6% NaCl + 0.5% NaOH	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Cycle 1	23.15	0.8293	14.03	6.15
Cycle 2		22.32	9.122	17
Cycle 3			13.2	5.321
Cycle 4				7.878

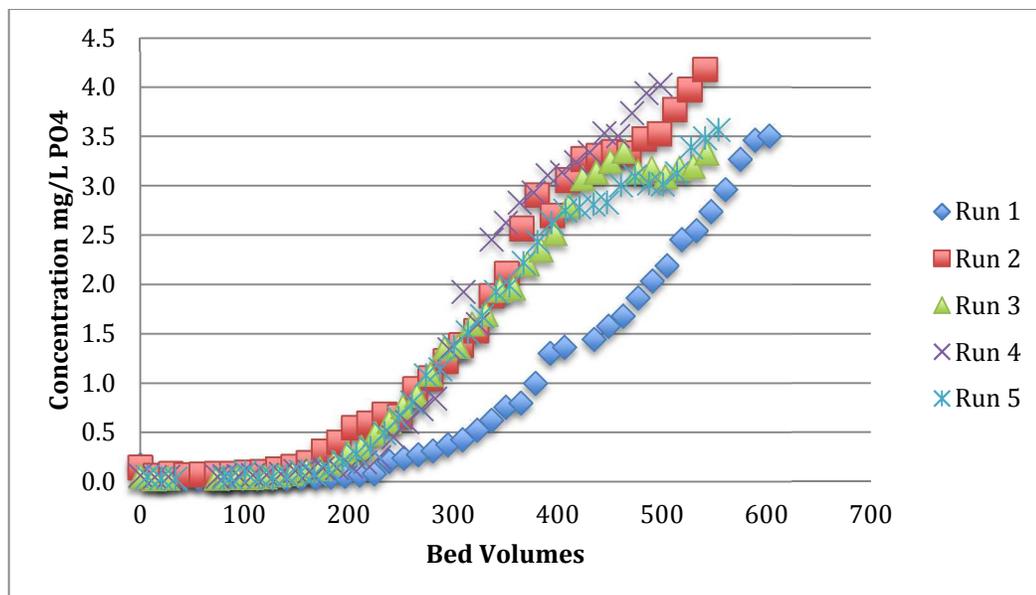


Figure A 1: Breakthrough Curves of Dow-HFO-Cu media treating AnMBR permeate of synthetic wastewater. All data points are single measurements.

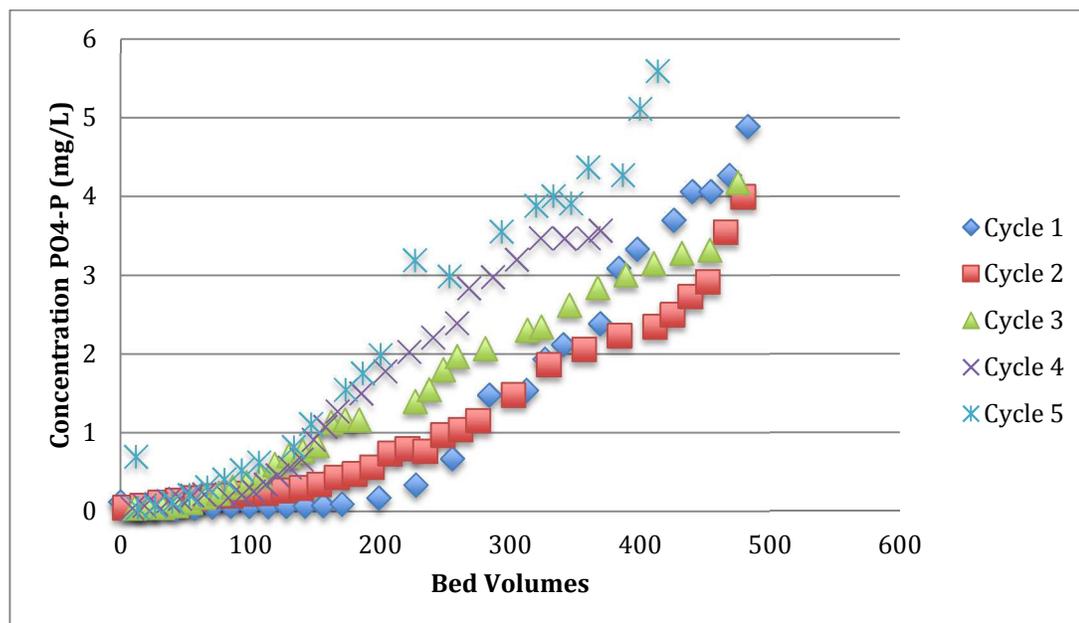


Figure A 2: Breakthrough Curves of Dow-HFO-Cu media treating AnMBR permeate of primary effluent from SSWRF. All data points are single measurements.

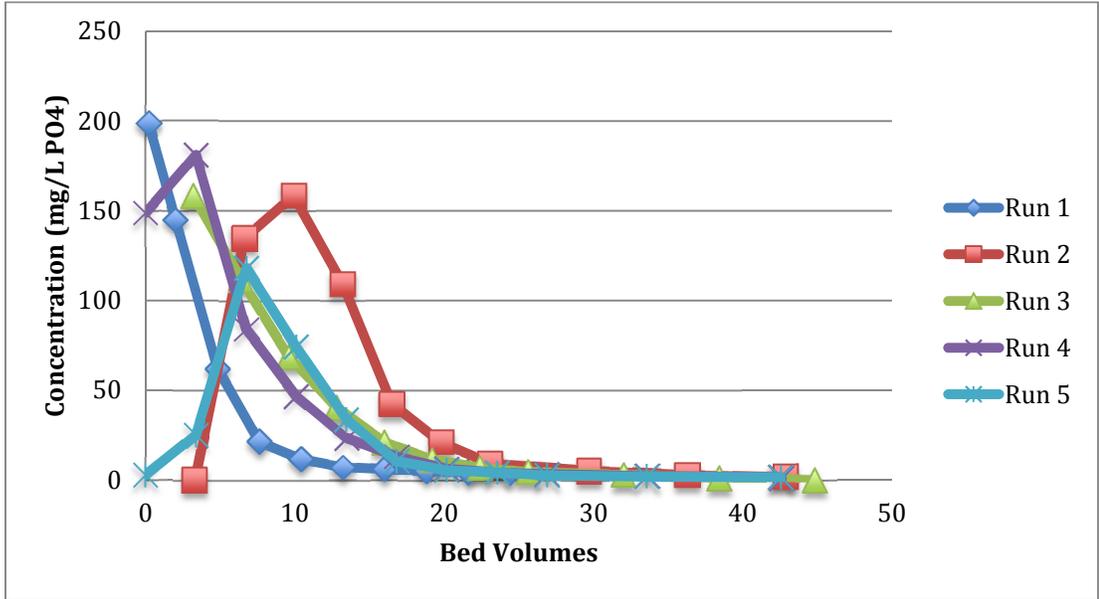


Figure A 3: Regeneration curves of Dow-HFO-Cu media from column tests treating synthetic wastewater. All data points are single measurements.

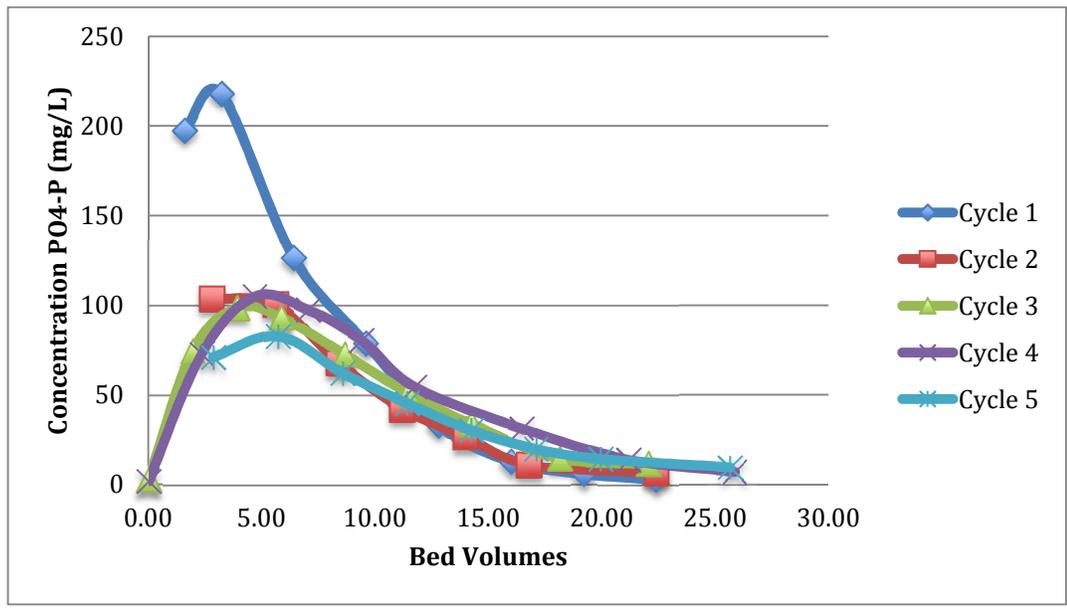


Figure A 4: Regeneration curves of Dow-HFO-Cu media from column tests treating primary effluent from SSWRF. All data points are single measurements.

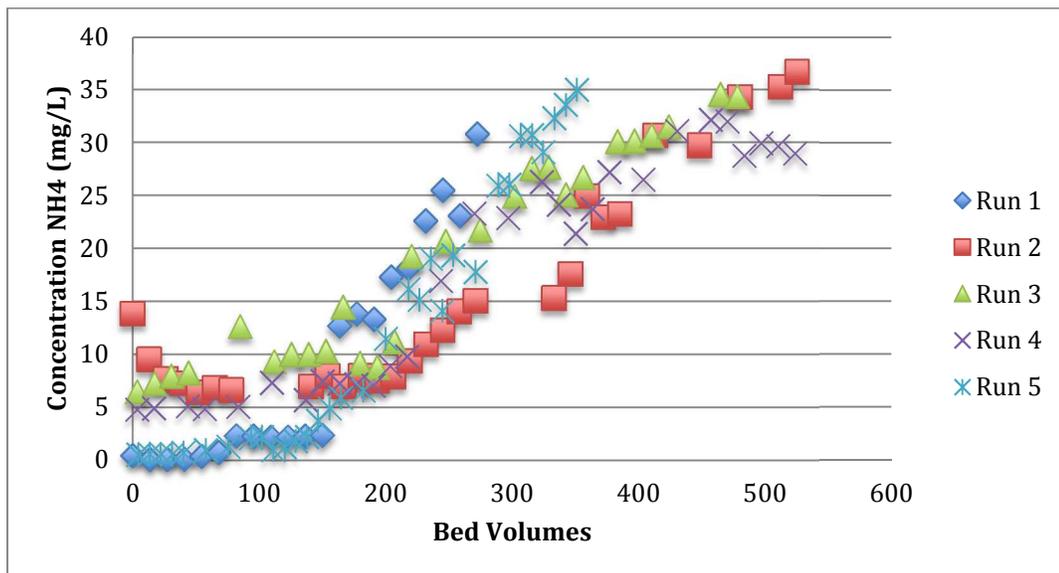


Figure A 5: Breakthrough curves of clinoptilolite media treating AnMBR permeate from synthetic wastewater. All data points are single measurements.

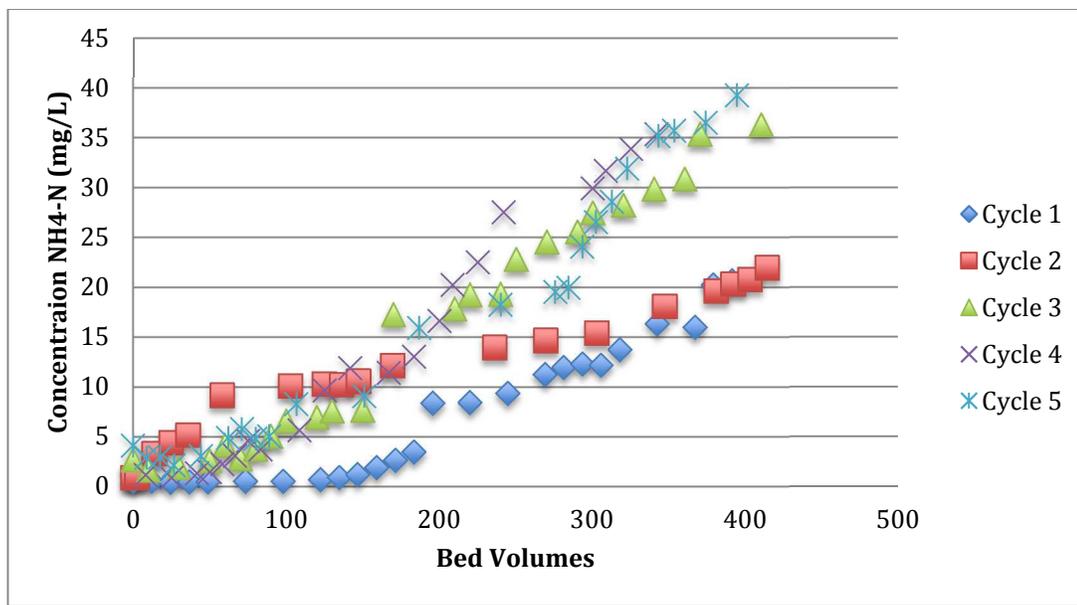


Figure A 6: Breakthrough curves for clinoptilolite media treating AnMBR permeate from primary effluent from SSWRF. All data points are single measurements.

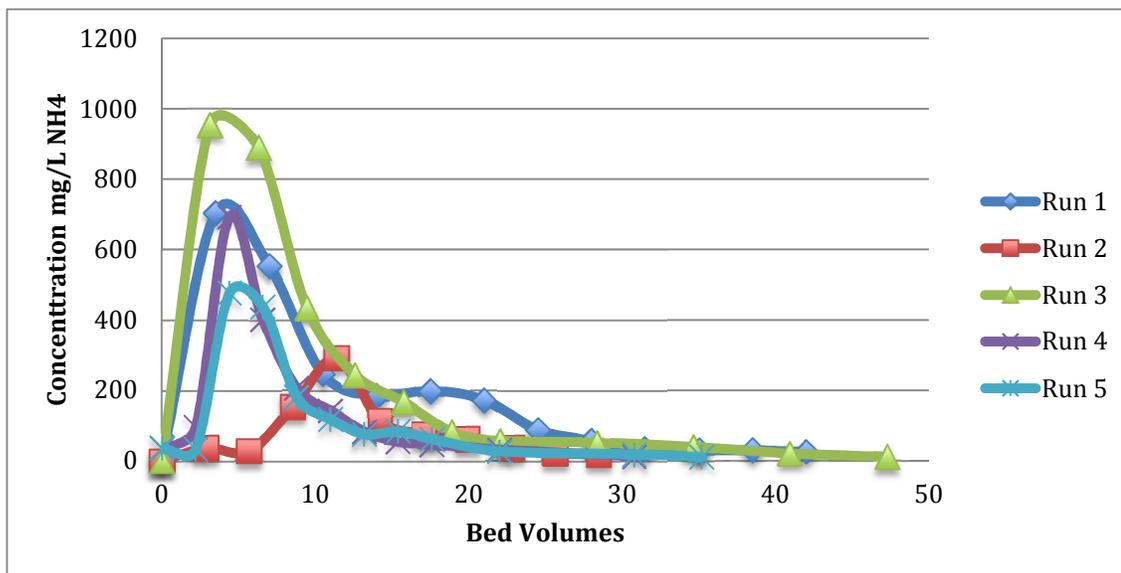


Figure A 7: Regeneration curves of clinoptilolite media from column tests treating synthetic wastewater. All data points are single measurements.

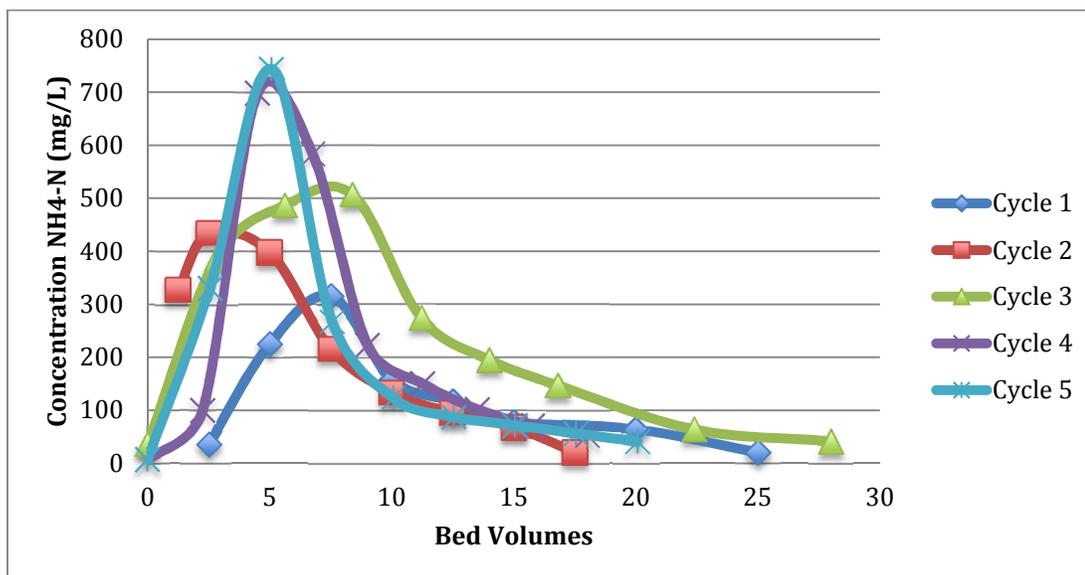


Figure A 8: Regeneration curves of clinoptilolite media from column tests treating primary wastewater. All data points are single measurements.

Table A 5: Data summary of Dow-HFO-Cu column and precipitation tests for 5 IX cycles treating synthetic wastewater

Constituent:	1	2	3	4	5
Raw Influent PO4-P (mg/L)	5	5	5	5	5
AnMBR Permeate PO4-P (mg/L)	4.3	4.8	4.4	4.4	4.5
Lowest Recorded IX effluent PO4-P (mg/L)	0.029	0.062	0.034	0.048	0.033
% PO4-P Removed	94	70	72	69	62
% Influent PO4-P Recovered in Precipitate	34	14	22	13	45
% PO4-P in Supernatant Regenerant Liquid	66	86	78	87	55

Table A 6: Data summary of Dow-HFO-Cu column and precipitation tests for 5 IX cycles treating primary effluent from SSWRF

Constituent:	1	2	3	4	5
Raw Influent PO4-P (mg/L)	5	5	5	5	5
AnMBR Permeate PO4-P (mg/L)	5.2	4.2	4.4	4.6	5.5
Lowest Recorded IX effluent PO4-P (mg/L)	0.032	0.043	0.045	0.042	0.044
% PO4-P Removed	74	71	66	64	62
% PO4-P Recovered in Precipitate	52	20	12	17	24
% PO4-P in Supernatant Regenerant Liquid	48	80	88	83	76

Table A 7: Data summary for clinoptilolite column and precipitation tests for 5 IX cycles treating synthetic wastewater

Constituent:	1	2	3	4	5
Raw Influent NH4-N (mg/L)	17	17	17	17	17
AnMBR Permeate NH4-N (mg/L)	31.2	39.1	36.8	35.8	35.2
Lowest Recorded IX effluent NH4-N (mg/L)	0.09	7.2	6.4	4.7	0.5
% NH4-N Removed	98	87	95	55	86
% NH4-N Recovered in Precipitate	3	14	15	4	7
% NH4-N in Supernatant Regenerant Liquid	97	86	85	96	93

Table A 8: Data summary for clinoptilolite column and precipitation tests for 5 IX cycles treating primary effluent from SSWRF

Constituent:	1	2	3	4	5
Raw Influent NH4-N (mg/L)	11	21	21	21	21
AnMBR Permeate NH4-N (mg/L)	36.4	25.7	36.2	34.8	34.3
Lowest Recorded IX effluent NH4-N (mg/L)	0.45	0.88	1.6	0.91	2.1
% NH4-N Removed	77	51	60	59	71
% NH4-N Recovered in Precipitate	1	11	8	23	29
% NH4-N in Supernatant Regenerant Liquid	99	89	92	77	71