

WASTEWATER TREATMENT BY NOVEL HYBRID BIOLOGICAL – ION EXCHANGE PROCESSES

BY

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THESIS

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ABSTRACT

This study presents two novel methods for treating important environmental contaminants from two different wastewater streams. One process utilizes the kinetic advantages and reliability of ion exchanging clinoptilolite in combination with biological treatment to remove ammonium from municipal sewage. A second process, HAMBgR (Hybrid Adsorption Membrane Biological Reactor), combines both ion exchange resin and bacteria into a single reactor to treat perchlorate contaminated waters. Combining physicochemical adsorptive treatment with biological treatment can provide synergistic benefits to the overall removal processes. Ion exchange removal solves some of the common operational reliability limitations of biological treatment, like slow response to environmental changes and leaching. Biological activity can in turn help reduce the economic and environmental challenges of ion exchange processes, like regenerant cost and brine disposal.

The second section of this study presents continuous flow column experiments, used to demonstrate the ability of clinoptilolite to remove wastewater ammonium, as well as the effectiveness of salt regeneration using highly concentrated sea salt solutions. The working capacity of clinoptilolite more than doubled over the first few loading cycles, while regeneration recovered more than 98% of ammonium. Using the regenerant brine for subsequent halotolerant algae growth allowed for its repeated use, which could lead to cost savings and production of valuable algal biomass. The algae were able to uptake all ammonium in solution, and the brine was able to be used again with no loss in regeneration efficiency. This process has significant advantages over conventional biological nitrification; shorter retention times, wider range of operational conditions, and higher quality effluent free of nitrate. Also, since the clinoptilolite is continually regenerated and the regenerant is rejuvenated by algae, overall input costs are expected to be low.

The third section of this study introduces the HAMBgR process for the elimination of perchlorate and presents batch isotherm experiments and pilot reactor tests. Results showed that a variety of ion-exchange resins can be effectively and repeatedly regenerated biologically, and maintain an acceptable working capacity. The presence of an adsorbent in the HAMBgR process improved bioreactor performance during operational fluctuations by providing a physicochemical backup to the biological process. Pilot reactor tests showed that the HAMBgR process reduced effluent perchlorate spikes by up to 97% in comparison to a conventional membrane bio-reactor (MBR) that was subject to sudden changes in influent conditions. Also, the HAMBgR process stimulated biological activity and lead to higher biomass concentrations during increased contaminant loading conditions. Conventional MBR systems can be converted into HAMBgR's at a low cost, easily justifiable by the realized benefits. The concepts employed in the HAMBgR process can be adapted to treat other target contaminants, not just perchlorate.

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1. INTRODUCTION

1.1. Motivation

1.1.1. Need for Enhanced Water Quality

Source water protection is becoming increasingly important as we develop more advanced contaminant detection techniques and a more thorough understanding of the human and environmental health impacts of water pollution. Advanced treatment of wastewater is being practiced more as we continue to stress our water sources with increased contaminant loads and rising clean water demands. In a 2004 report to Congress, the EPA estimated that 64% of assessed lakes and 44% of assessed rivers were considered impaired (U.S. Environmental Protection Agency, 2004). With municipal, industrial and agricultural wastewater playing a major role in these figures, our existing treatment practices will need to be adapted or enhanced in order to meet growing water quality concerns.

1.1.2. Limitations of Current Wastewater Treatment Practices

Conventional treatment systems were not designed to meet the quality levels that we are looking for now. Most of the common processes were developed in a time when we were limited by technology as far as pollutant detection and what those pollutants meant to our health. Therefore, if we want to maintain control of safe water sources we need to adapt our traditional wastewater treatment systems and incorporate new and innovative technologies. We know that chemical oxygen demand (COD), NH_4 , and solids must be removed from wastewater before we discharge that water back into the environment. Biological treatment of COD and NH_4 is effective and well understood, but is highly sensitive to temperature, loading rate, and aeration and can require longer reaction times than other methods of treatment, such as ion exchange, adsorption, or filtration (Wiesmann, 1994; Antoniou et al., 1990). This translates into large reactors, large footprints, and high energy costs. Also, we are becoming concerned with a more complex array of contaminants in our wastewater. Conventional systems cannot easily address most of those concerns.

In California, advanced wastewater treatment is taking place in some locations where sewage is treated and recycled back to the groundwater to recharge depleting aquifers. In these cases, conventional wastewater treatment effluent is usually polished by reverse osmosis filtration before injecting the treated water into the ground. This allows for decreased dependence on imported water and also serves as a barrier to infiltration of the aquifer by seawater (Asano and Cotruvo, 2004; Lozier and Ortega, 2010). California is by no means alone in their move to secure safe water sources. Many parts of the United States and the world have been developing technology and legislature around wastewater reclamation and water reuse (Asano, 2007). However, if the end goal is to eliminate contaminants from water we need to have either chemical or biological oxidation/reduction steps or biological assimilation of our target contaminants. Biological treatment processes have an advantage over similar chemical processes in that they are generally more cost effective, but usually have longer reaction times and are more limited in operating conditions. For complex wastewaters, chemical or biological inhibition can be a concern and may restrict the ability of the system to treat multiple contaminants at the same time. For instance, enhanced biological phosphorous removal (EBPR) in sewage requires anoxic conditions, whereas ammonia and COD oxidation require aeration. Innovative reactor designs have made EBPR possible, but consistent operation is challenging and is therefore often avoided when not required (Barnard, 1982).

1.1.3. Focus on Emerging Contaminants

The EPA regulates more than 90 contaminants in drinking water and there are now 116 other unregulated contaminants that have been placed on the third version of the candidate contaminant list (CCL 3). Of those, 104 are chemical or chemical group contaminants, which are mostly due to the manufacturing of industrial and pharmaceutical products (U.S. Environmental Protection Agency, 2008). Treatment objectives are being expanded to include contaminants that research has shown to have negative medical or environmental health implications. These emerging contaminants are being given more attention in research and within regulatory agencies (Richardson and Ternes, 2005). Though most of the focus in this field is placed on drinking water treatment, wastewater treatment facilities can play a vital role as a barrier or gateway for certain contaminants entering the water systems (Krasner et al., 2009; Glassmeyer

et al., 2005). Emerging contaminants can be generated by municipal, agricultural, and industrial waste streams. Industrial wastewater is unique amongst these three because the array of pollutants produced and concentrations vary from site to site. Development of specialized treatment technologies requires an immense understanding of removal mechanisms and the limitations of those practices.

Perchlorate, a highly reactive oxidant commonly used in solid rocket fuels and explosives, has been identified as a human health risk and is a highly debated and challenging emerging contaminant. There is currently no perchlorate guidelines set by the EPA as the available health risk data is still somewhat incomplete, though it is on the EPA's list of secondary contaminants (Kucharzyk et al., 2009). Perchlorate contamination is commonly associated with its release from the rocket fuels and explosives manufacturing facilities of the Department of Defense and military contractors. Widespread perchlorate contamination of surface water and groundwater has been discovered throughout most of the US, which can be attributed to both natural occurrence and a result of manufacturing (Srinivasan and Viraraghavan, 2009). Some states, such as California and Massachusetts, have set perchlorate action levels, which can require drinking water facilities to treat low concentration source waters (Kucharzyk et al., 2009). The two most viable treatment technologies available for treating these low levels of perchlorate include biological reduction and ion exchange separation (Srinivasan and Sorial, 2009). However, military munitions production facilities generate large amounts of highly concentrated perchlorate wastewater that may require future treatment if regulations are put into place. Development of effective and reliable treatment techniques that can be applied to both situations is important to minimizing exposure.

1.1.4. Ion Exchange Treatment

Development of ion exchange resins and characterization of naturally occurring ion exchange materials has demonstrated a wide range of possible applications of the technology in water and wastewater treatment (Gu et al., 1999; Velizarov et al., 2008; Wang and Peng, 2010). Synthetic ion exchange resins are commonly used in pharmaceuticals production, water softening, metal separation, and production of high purity water. There are many

manufacturers of ion exchange resins and resin systems. All ion exchange resins will demonstrate ion selectivity based on the type of resin and resin structure, removing either cations or anions. Some resins have been designed to target specific chemicals for removal and some are designed to perform in particular conditions. As mentioned previously, ion exchange is being used to treat perchlorate contaminated waters (Srinivasan and Sorial, 2009). The advantage of this is that many anionic exchange resins have the ability to separate out perchlorate amongst other common anions. Once the capacity of the resin is exhausted, they can be regenerated and used further. Some single use resins have higher perchlorate selectivity and are designed to operate at lower concentrations (Gu et al., 1999). The selectivity of an ion exchange media can be described by the selectivity coefficient described by equation 1 (Crittenden, 2005).

$$K_j^i = \frac{C_j^n q_i}{q_j^n C_i} \quad (1)$$

Where,
 C_j = concentration of target ion in solution, eq/L
 q_i = concentration of counterion on resin, eq/L
 C_i = concentration of counterion in solution, eq/L
 q_j = concentration of target ion on resin, eq/L
 n = valence of the exchanging ion.

1.1.5. Natural Ion Exchange

Naturally occurring ion exchange material functions much the same as synthetic resin but with a different structural makeup. Some of the most popular and widely available natural ion exchangers are zeolites, which consist of an aluminosilicate molecular structure with weak cationic bonding sites (Guisnet and Gilson, 2002). Natural zeolites have been avoided in high purity processes or where consistency is vital because of irregularities and impurities of the material. However, zeolites have been used in many applications where uniformity is less critical, such as treating of waste streams and metals separation. There are as many as fifty different types of zeolites and one in particular, clinoptilolite, has made its way into many homes. Clinoptilolite is known for having a natural affinity for ammonium (NH_4^+) ions, which makes it ideal for mixture into commercial cat litter and aquarium purification products. This property has also been investigated as an alternative to nitrification, the common ammonium

removal method in sewage treatment and industrial wastewater management. However, longevity of the process requires salt regeneration of the clinoptilolite and brine disposal, which can be costly and even more challenging due to the high concentrations of salt and ammonium (Miladinovic and Weatherley, 2008).

1.2. Objectives

As water quality requirements become more restrictive, we will need technologies that can offer reliability and performance in variable conditions. Both ion exchange and biological treatment offer tremendous benefits to water quality but are unfortunately hindered by unavoidable limitations. A marriage of these two technologies may offer us the ability to achieve our overall treatment goals and remain within economic constraints.

The objective of this research is to exhibit the potential benefits and applications of hybrid biological ion-exchange systems used to treat targeted contaminants in various wastewaters. Demonstration of this concept through laboratory and pilot scale experiments shows how it can be applied to two very different cases, which represent two important water quality concerns.

- ❖ The first scenario targets ammonium for removal from municipal wastewater by using biological treatment to enhance the performance of a clinoptilolite ion exchange system.
- ❖ The second scenario targets concentrated perchlorate for removal from industrial wastewater where biological reduction in a membrane bioreactor is improved by adding synthetic ion exchanging resins.

These two examples were chosen to demonstrate a range of possible applications of hybrid biological ion exchange systems. The processes developed in this study have not been discussed before in literature, through biological augmentations of ion exchange processes and vice-versa are not novel concepts. The works presented in this research are meant to expand on previous researchers' findings by developing creative approaches to synergistic relationships between two treatment alternatives.

2. NOVEL PROCESS FOR TREATMENT OF WASTEWATER AMMONIUM

2.1. Introduction

2.1.1. Ammonia Nitrogen Pollution

Ammonia is one of the most important and widespread fresh water pollutants in the United States. Concern over ammonia in the environment is caused largely by its acute toxicity to fish and other freshwater organisms. When ammonia enters surface waters at concentrations as low as 0.02 mg/L it can have detrimental effects on aquatic wildlife (Nimmo et al., 1989). When the concentration of ammonia in the fresh water ecosystem increases, the fish have no barrier to protect them from penetration. Since fish regularly excrete toxic ammonia from their bodies through a permeable membrane, increased dissolved ammonia levels can shift the concentration gradient and even cause the fish to uptake ammonia, which can quickly lead to convulsions and death (Randall and Tsui, 2002). Ammonia can also exert an oxygen demand as it becomes oxidized to nitrite and nitrate by bacteria, which can lower dissolved oxygen concentration, stressing or killing any organisms that cannot quickly escape into healthier water (Robarts et al., 2005). The nitrate and nitrite are more prolific in the environment and will remain in the water until they are utilized by algae or other aquatic plants. This causes eutrophication of lakes and streams, which eventually leads to decomposition of algae and further oxygen depletion (Camargo and Alonso, 2006). The Gulf of Mexico Dead Zone (Figure 2.1) is an example of the effects of anthropogenic nitrogen pollution. As a result of these effects, regulatory agencies and wastewater treatment industries have made strong efforts to limit the addition of ammonia to the environment (Sperling, 2007).

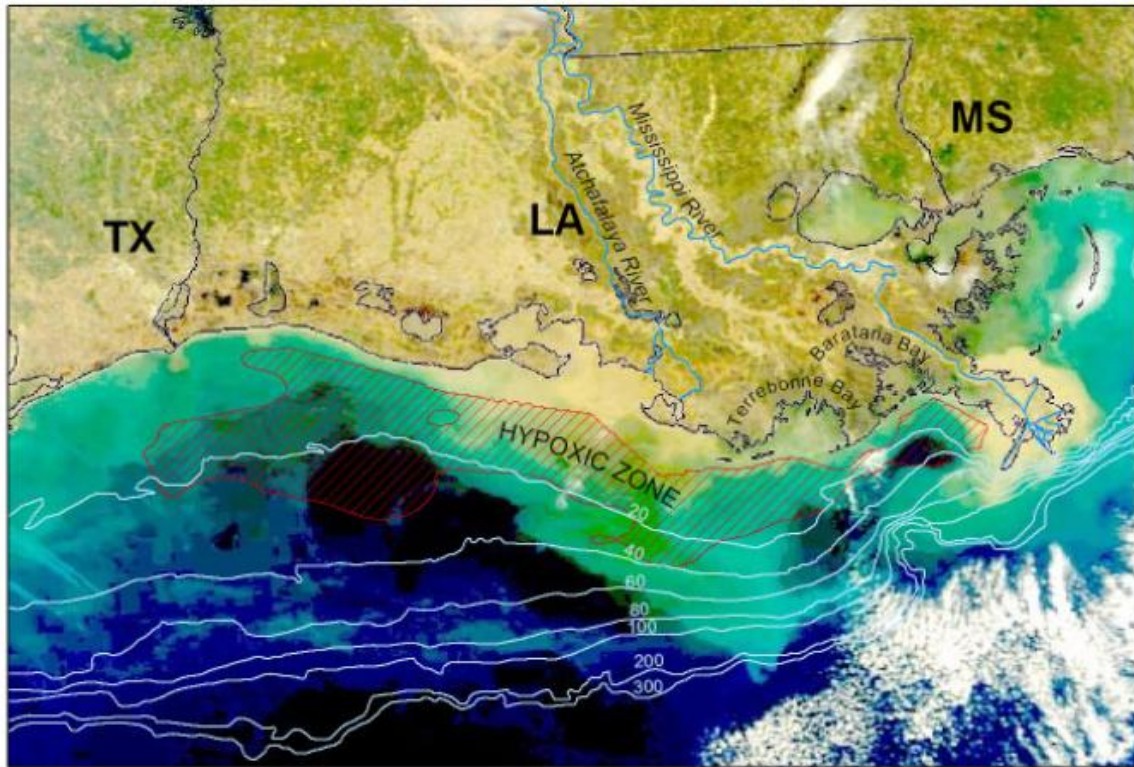


Figure 2.1. Extent of the Gulf Hypoxic Zone in 2002 (Krug, 2007).

Sources of ammonia include human and animal waste, organic matter breakdown, nitrogen-fixing bacteria as well as industrial production. Most chemically produced ammonia is sold as fertilizer, which is one of the most important agricultural inputs. The primary method for ammonia production is through the energy intensive Haber-Bosch process, where methane is oxidized to carbon dioxide and hydrogen gas. The hydrogen gas is then reacted with nitrogen gas to form gaseous ammonia, which can be maintained in liquid form (anhydrous ammonia) at low temperature or high pressure (Travis, 1993).

Runoff from fertilized agricultural land is one important non-point source of ammonia pollution into the aquatic environment, which makes it difficult to regulate and treat. Human and animal wastewaters, however, are significant point sources of ammonia, where organic nitrogen waste is broken down into inorganic ammonia and remains primarily as ionic ammonium at pH values less than 9.25 (Mueller and Helsel, 1996). The ammonium concentration in municipal sewage can range from 20 – 35 mg/L, depending on the type of

sewer and inputs (Tyagi, 2004). Animal waste streams can be significantly more concentrated, with nitrogen levels reaching 7000 mg/L (Blanchet and Schmidt, 2007). In order to protect and improve environmental water quality the EPA has established the National Pollutant Discharge Elimination System (NPDES), which establishes limits and regulations on discharging wastewater. Since this program can feasibly only be applied to point source polluters, agricultural inputs are often not required to obtain permits. Municipal and industrial wastewater producers are the main targets of the program. Ammonia is regulated on site-by-site basis and the acceptable discharge levels depend on local watersheds' sensitivity. The Urbana Champaign Sanitary District treats an average of about 8 million gallons per day (MGD) of domestic and industrial wastewater. The NPDES permit issued in 2008 regulates discharge of ammonia nitrogen to a monthly average of 1.5-1.9 mg/L with a daily maximum of 3-10.1 mg/L. The most common method for treating ammonia in wastewater is biological nitrification, where autotrophic nitrifying bacteria will use ammonia as their electron donor, instead of organic carbon, oxidizing it to nitrate (NO_3^-).

2.1.1.1. Municipal Sewage Treatment

Municipal wastewater characteristics vary widely across space and time but there are some common pollutants that can be attributed to most waters. Chemical oxygen demand (COD), suspended solids, and ammonia were the original targets for treating wastewater and still remain as the primary removal objectives. Even though advanced technology has been developed for monitoring and controlling our wastewater treatment systems, the main removal mechanisms remain unchanged over the years. Most conventional sewage treatment systems consist of primary, secondary and tertiary treatment processes. Primary treatment removes large solids from the water by gravity sedimentation. Secondary treatment involves biological oxidation of COD and ammonia followed by another settling step. Tertiary treatment provides a final polishing of the water before it is discharged. Sand filtration is common, and disinfection by chlorine or UV is also practiced by many facilities for part of the year (Tchobanoglous et al., 2003).

2.1.1.1.1. Biological Nitrification to Treat Ammonia

Biological nitrification consists of two distinct chemical reactions that are carried out by two different groups of bacteria, ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). *Nitrosomonas* sp. are commonly associated with the conversion of ammonia to nitrite (equation 2), while *Nitrobacter* sp. are associated with converting nitrite to nitrate (equation 3) (Dworkin and Falkow, 2006).



The rate of nitrification is limited by the growth of AOB (Antoniou et al., 1990). AOB are considered slow growing, relative to the heterotrophic bacteria that oxidize COD in wastewater. Nitrifying bacteria are also very sensitive to pH variations. Ruiz et al. (2003) found that if pH increases above 8.95 or falls below 6.45, complete nitrification inhibition occurs. Similar results were published by Villaverde et al. (1996), which reports that fixed film nitrification rate is reduced by about 13% per unit drop in pH from 8.5 – 5.0. The subtle differences in the reported pH values of inhibition from these two studies could easily be attributed to variations in growth and environmental conditions. In addition to pH inhibition, influent ammonia shock loads can be toxic to AOB. Nitrification also produces hydrogen ions, which will consume alkalinity (ALK). Alkalinity is an important buffer and will help maintain pH between 7 and 8. Alkalinity can be expressed as milligrams CaCO_3 equivalents per liter. For 1 mg ammonia oxidized to nitrate 8.14 mg CaCO_3 equivalents are consumed. Typical influent concentrations of alkalinity can range from 100-250 ppm CaCO_3 (Sperling, 2007). At the above NH_3 :ALK ratio, the average influent alkalinity could only support nitrification of ammonia concentrations from 12-30 ppm NH_3 . The typical range of ammonia in the influent is 20-35 ppm NH_3 (Sperling, 2007). It is common for wastewater influent to be limiting in alkalinity, and the addition of alkali is sometimes necessary.

2.1.1.1.2. Denitrification to Remove Nitrate

Though biological nitrification can effectively remove toxic ammonia from wastewater, there are unfavorable side effects of the process besides the depletion of alkalinity mentioned

above. The discharge of additional nitrate presents several water quality concerns. Nitrate contributes to eutrophication of water bodies, which eventually leads to depleted dissolved oxygen levels, as mentioned above. In cases of direct or indirect potable reuse, nitrate is a potential health hazard. Nitrates in drinking water are associated with blue baby syndrome, and the EPA has set treatment standards (Powlson et al., 2008). Some wastewater treatment plants have total nitrogen limits on discharge which may require them to remove nitrate from the wastewater. Denitrification with heterotrophic bacteria utilizes a carbon source as electron donor and nitrate, the electron acceptor, will be reduced to nitrogen gas as shown in equation 4.



To achieve successful denitrification, external carbon source addition is needed. Blue Plains AWTP in Washington D.C. uses methanol as a carbon source in denitrification. Acetate, ethanol and corn syrup are also suitable carbon source alternatives for denitrification, but each source will affect the rate of nitrate removal (Mohseni-Bandpi and Elliott, 1998; Mokhayeri et al., 2006). The use of external carbon sources for denitrification has several drawbacks. Increasing cost of inputs as fuel and feedstock prices increase as well as the addition of atmospheric carbon dioxide may become even more important in the future and may cause treatment plants to look to alternative technologies for nitrogen removal.

2.1.2. Removal of Ammonium by Natural ion Exchange Material

2.1.2.1. Clinoptilolite Redefined

Clinoptilolite is a type of natural zeolite that has gained a reputation for having a notably high affinity for the ammonium (NH_4^+) ion. It was first discussed in literature in 1923, but only in 1960 was it revealed as a unique mineral zeolite, which has been found in large quantities throughout the world. Some of its defining properties include monovalent cationic exchange sites and thermal stability up to 700 °C (Mumton, 1960). Early research on the material was more focused on its cation exchange properties for the adsorption of radionuclides and heavy metals (Frysjer, 1962; Arnold and Crouse, 1965; Nelson et al., 1964). At the same time, researchers were giving much attention to synthesis of zeolitic materials as a way of avoiding

natural impurities (Ames Jr., 1967; Kerr, 1966; Breck et al., 1956). As water quality science progressed, research began giving more attention to clinoptilolite's ammonia removal properties (Koon and Kaufman, 1975; Mercer et al., 1970). Detailed pilot plants investigations were conducted to evaluate the operational parameters and economic feasibility of using clinoptilolite to treat ammonium in sewage (Koon et al., 1972; Pacific Northwest Laboratory, 1971; U.S. Environmental Protection Agency, 1971).

2.1.2.2. Ammonium Capacity of Clinoptilolite

Ames (1967) suggested using clinoptilolite for wastewater treatment after testing its ammonium selectivity against other zeolites and a synthetic zeolite. Howery and Thomas (1964) determined that a relatively pure form of clinoptilolite has an ammonium capacity of about 2 milliequivalents per gram (meq/g). It is known, though, that there are many factors that determine the capacity of a specific material in a given system. In batch tests, the ion exchange capacity is usually higher than in continuous flow tests. Sarioglu (2005) determined a cation exchange capacity of 1.65 meq/g for Turkish clinoptilolite with an initial NH_4^+ concentration of 40 mg/L. Ashrafizadeh et al. (2008) achieved 1 meq/g with Iranian clinoptilolite and an initial concentration of 50 mg/L. Moazed (2004) displayed very different results, only about 1 mg/g (0.06 meq/g) with an influent concentration of 40 mg/L. Variability in results is likely due to differences in experimental setup and purity of the clinoptilolite sample.

2.1.2.3. Clinoptilolite in Continuous Flow

Batch tests can be used to develop isotherms which can allow us to compare ion exchangers and determine maximum capacities. However, most practical applications of ion exchange systems are continuous flow column setups. The measured capacity under this mode of operation is expected to be much lower than under batch mode, with the tradeoff of achieving lower effluent concentrations. Mercer et al. (1970) looked extensively into clinoptilolite column setups for treating secondary wastewater effluent with ammonia concentrations from 10-19 mg/L. They were able to achieve 99% removal of influent ammonium with a two column system in the lab and 97% in a pilot scale system. Breakthrough of the primary column occurred within 100 bed volumes (BV), but the effluent was polished

through a second column, which extended operation up to 300 BV. Sarioglu (2004) achieved nearly 100% removal of low concentration (5 mg/L) wastewater with a single column, but ammonium capacity was low at only 0.7 mg/g. Jorgensen et al. (1976) measured capacities from 0.94 – 2.41 mg/g by testing different clinoptilolite particle sizes in continuous flow.

2.1.2.4. Factors Determining Capacity of Clinoptilolite

Most studies agree that pH and particle size are important determinants of clinoptilolite capacity. Rahmani et al. (2004) investigated the effect of clinoptilolite particle size on ion exchange capacity. The column tests revealed that breakthrough capacity increased from 9.61 mg/g to 11.17 mg/g as particle size decreased from 0.83 mm to 0.42 mm. This indicates that smaller particle size exposes more surface exchange sites that were previously hidden. Jorgensen et al. (1976) tested 3 particle sizes and found that decreasing average particle size from 3.75 mm to 1.7 mm increased the capacity of the material from 0.94 mg/g to 2.41 mg/g. The trend across these two studies is consistent with the results discovered within each even though specific experimental conditions were different.

Ammonia is removed by clinoptilolite when it becomes protonated at pH values less than 9.24. Below pH 7 more than 99% of ammonia is acid form NH_4^+ . Figure 2.2 shows speciation of ammonia at different pH values. Sarioglu (2004) studied the effect of pH on ion exchange capacities during continuous operation. Decreasing pH from 7.5 to 4.0 increased ammonium capacity from 0.67 mg/g to 1.08 mg/g. Another study focusing on clinoptilolite treatment of fertilizer production wastewater reported a doubling in ammonium capacity as pH decreased from 9.01 to 7.24 (Beler-Baykal and Allar, 2008). Ashrafizadeh et al. (2008) suggested maintaining influent pH between 5.5 and 7.5 in order to maximize removal efficiency. Though a decrease in pH may improve adsorption capacity, at pH values too low, acid damage could negatively affect the structure of clinoptilolite (Klieve and Semmens, 1980).

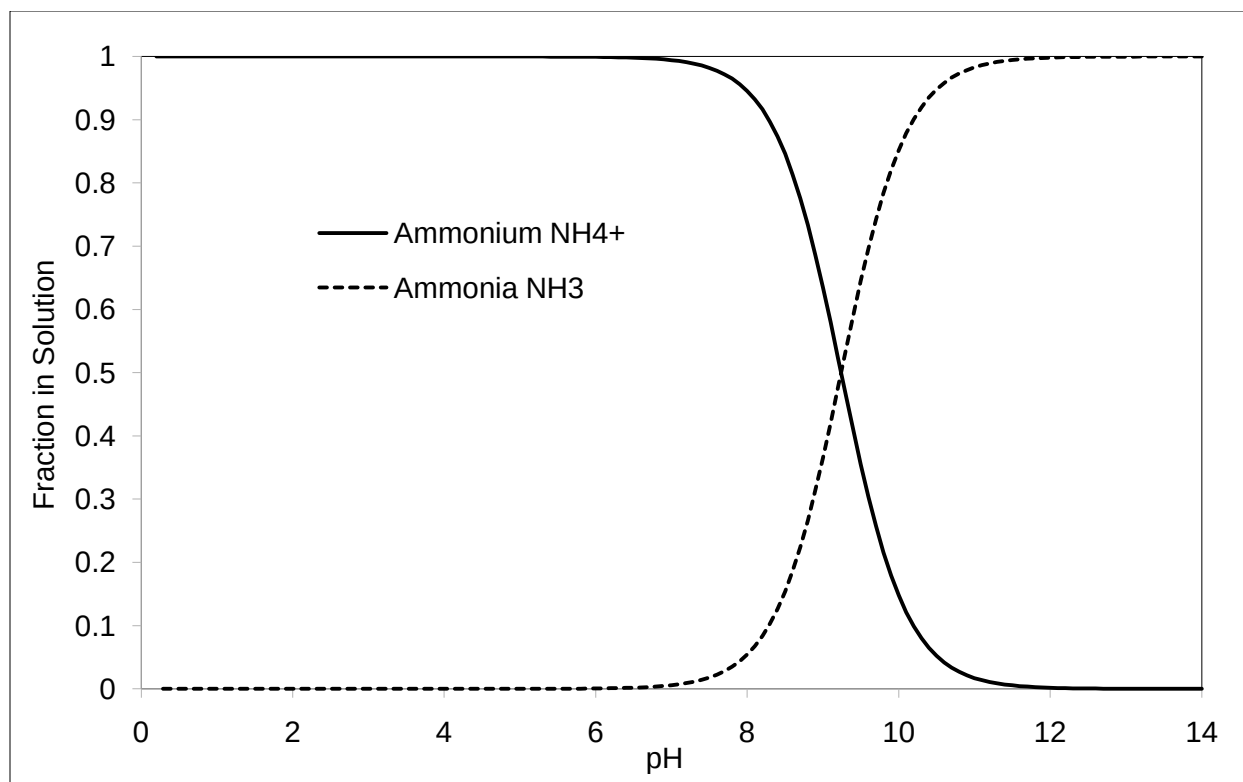


Figure 2.2. Speciation of ammonia in aqueous solution (pKa = 9.24).

Several studies have reported on the effect of preconditioning on clinoptilolite capacity. Klieve and Semmens (1980) examined different methods of pretreatment thought to be beneficial. They determined that acid and steam pretreatment did not increase capacity, but heat treatment did seem to increase the ammonium capacity amongst competing cations and NaOH treatment only increased ammonium capacity in pure NH_4Cl solutions. Others have noticed site activation in pretreated samples, where certain techniques could essentially “activate” sites that were previously not available for ion exchange. Zamzow et al. (1990) achieved higher ammonium capacity with clinoptilolite conditioned with sodium. Jorgensen et al. (1976) and Rahmani et al. (2004) reported increasing ammonium capacity throughout several loading and regeneration cycles using NaOH and NaCl regenerants respectively.

2.1.2.5. Regeneration of Clinoptilolite and Fate of Brine

The performance of clinoptilolite in treating ammoniacal solutions is well documented and can, in some ways, be expected to exceed other forms of treatment. However, possibly

more important than ion exchange capacity is whether or not the material can be regenerated and reused. There are some processes that desire single-use or 'use-and-burn' applications, but most ion exchange processes employed in the water and wastewater treatment industries require many loading regeneration cycles in order to remain economical. Clinoptilolite has been proven to perform well over several regeneration cycles (Jorgensen et al., 1976). There are several methods for regeneration, some more complex than others. Regardless of method, though, replacement cations must be present in the solution. Sodium is the most common replacement ion for several reasons. Many natural forms of clinoptilolite are initially loaded with sodium or a large percentage of sites are Na-form. Also, during operation clinoptilolite has less selectivity for sodium, making it easy to exchange for ammonium, even at low concentrations. Finally, sodium is a relatively cheap counterion and is environmentally acceptable. Regenerating with Na^+ as opposed to Ca^{+2} does not add hardness to the water and is possibly more efficient (Mercer et al., 1970). The actual cost of regeneration depends heavily on the type of salt used and method of application.

Rahmani et al. (2004) used three concentrations of NaCl solution for regeneration. Increasing salt concentration from 0.3 M to 1 M decreased the amount of regenerant needed by more than 50%. After treating more than 200 BV of ammonium wastewater with clinoptilolite, Ashrafizadeh et al. (2008) regenerated with 33 BV of 1 M NaCl solution. The regenerated material had slightly higher capacity than the virgin type. Sarioglu (2004) showed that flowrate can affect the volume of regenerant needed. Decreasing flowrate from 0.3 ml/min to 0.1 ml/min (67%) reduced the amount of solution used by about 67%.

Recirculation of the regenerant solution can help minimize the volume of solution needed for elution. In this case, the flowrate used is not critical to the volume used. Other factors become more important, such as counterion concentration and pH. Mercer et al. (1970) recycled caustic solution at pH 12 for elution on ammonium from clinoptilolite used to treat wastewater. The increased pH causes a shift in speciation of the ammonium ion, which can make it easier to replace with the sodium ion producing a highly concentrated ammonia solution. The effluent solution which contained high concentrations of ammonia was then air-

stripped to volatilize $\text{NH}_{3(\text{aq})}$ to $\text{NH}_{3(\text{g})}$. Higher air:liquid ratios produced better ammonia removal rates in the spent regenerant, up to 98% at $0.82 \text{ m}^3/\text{L}$. The rejuvenated solution could be reused several times for regeneration of the column, which increases the economic feasibility of the process. Jorgensen et al. (1976) also used NaOH regeneration with air-stripping and reported total ammonia removal from secondary effluent at least 90% with the ability to reuse regenerant. The efficiency of the air-stripping process is highly dependent on the amount of air supplied by blowers, which consume energy and have associated costs. Also, increasing atmospheric ammonia is controversial and may not be a viable solution for some places.

Electrochemical oxidation uses an anode and cathode to supply current to an electrolytic solution containing a reduced ammonia species. Li et al. (2010) used this technique to regenerate a synthetic zeolite loaded with ammonium. After loading the zeolite in batch mode, the zeolites were placed into a NaCl electrolyte solution with the electrodes. Electrochemical oxidation will convert ammonium directly to nitrogen gas, which then volatilizes, and Na^+ ions are adsorbed onto the zeolite. In Li et al. (2010), Conversion of 97% of the sorbed ammonium to nitrogen occurred, with less than 3% going to nitrate. The rate of nitrate production was dependent on the concentration of NaCl and on the current supplied to the solution. The regenerant solution was able to be reused at least five times. A similar technology available in the market, called AmmEl is a patented process developed by Enpar Technologies Inc., Ontario, Canada. The process uses electrochemical oxidation and zeolite ion exchange to treat ammonium in wastewater. They report to have total ammonia removal >93% for both low and high concentration wastes ($5 - 1000 \text{ mg NH}_3\text{-N/L}$). The company also reported operating costs at \$2.20 - \$2.40 per kg nitrogen removed. Advantages of electrochemical oxidation-regeneration include the efficient removal of N under range of temperatures, no adaptive or acclimation period, and relatively small footprint. However, production of poisonous Cl_2 gas is possible, and eventually the expensive electrodes will need to be replaced.

Biological regeneration of clinoptilolite is described by Tsuno et al. (1994). Clinoptilolite acting as a media for fixed film growth of nitrifying bacteria can offer temporary sorption of ammonium in wastewater. The study proved that clinoptilolite can simultaneously adsorb and

desorb ions while nitrifiers oxidize up to 90% of influent ammonium at a rate of 0.15 mg-N (g-zeolite-hr)⁻¹. Lahav and Green (1997) achieved slightly better results with an ammonia removal rate of 0.21 mg-N (g-zeolite-hr)⁻¹. Zheng et al. (2009) reported that high rates of zeolite regeneration up to 100% are possible when the reactor is cohabitated with nitrifying and heterotrophic bacteria. Park et al. (2002) also reported that clinoptilolite addition to activated sludge accelerated nitrification rates because of a lower C:N ratio. An advantage of attached film growth on clinoptilolite is the ability to use much lower salt concentrations during regeneration. Lahav and Green (1997) reported that 50 meq/L is a sufficient regenerant concentration and that much higher concentrations may inhibit nitrification. Also, biological regeneration eliminates issues with ammoniacal brine disposal. However, issues with nitrification still exist. The supply of oxygen is critical to the performance of the process, and even though ammonia is oxidized, nitrate persists in the effluent, which can still lead to water quality issues (Miladinovic and Weatherley, 2008).

Combining nitrification and denitrification in a sequencing batch operation with powdered synthetic zeolite can remove up to 85% of total nitrogen, as reported by Jung et al. (2004). The effectiveness of this concept is dependent on the sequence of operational stages chosen. Anoxic filling and aerated mixing allow for the best performance, with maximum adsorption occurring in the filling stage and maximum biological regeneration occurring in the mixing stage. Operated continuously for 30 hours with a 12 hour hydraulic retention time, this mode of operation experienced total nitrogen removal from 80 – 86%, with a general increase in concentration over time. The results showed possibilities of using combined nitrification/denitrification with zeolites, though the longevity and reproducibility of this process can be questioned. Also, even though high removal rates were achieved in the study, effluent total ammonium-nitrogen was over 50 mg/L, which exceeds the effluent standards set for many, if not all wastewater treatment facilities.

Though most studies on clinoptilolite regeneration have focused on the eventual elimination of nitrogen from solution through oxidation or volatilization, various processes have been developed with the goal of maintaining the nutritive value of ammonia. This approach to

wastewater treatment can dramatically affect the economic outlook of ion exchange removal processes because there is possibility of recovering the nutrients, as opposed to the purely eliminatory approach of other methods. Ashrafizadeh et al. (2008) suggested loaded clinoptilolite as a slow release fertilizer because of low elution rates when rinsed with tap water. Lind et al. (2000) also suggested using urine with a struvite-clinoptilolite combination to form a possible fertilizer alternative. Millán et al. (2008) tested ammonium-loaded clinoptilolite against urea fertilizer and determined that the clinoptilolite enhanced yield and nitrogen uptake in ryegrass.

Using loaded clinoptilolite as fertilizer is environmentally safe, does not generate complicated brines, and can offer some cost recovery if the material can be sold. However, this is a single-use process that would require constant replacement of zeolites if used for treating wastewater, which is not economically or environmentally suitable. Recovering nitrogen from wastewater, whilst continually reusing ion exchange material, has the potential to be very profitable. One process, patented by ThermoEnergy Corporation (Little Rock, AR), uses ion exchange to concentrate anaerobic digester centrate ammonia and, through a series of chemical and thermal additions, obtains ammonium sulfate crystals which are sold as fertilizer. Figure 2.3 shows average yearly market prices for ammonium sulfate fertilizer from 1960 – 2009 (Huang, 2010). Notice that the price for ammonium sulfate has jumped by more than 100% from the year 2000. From this figure it is clear to see how the potential economic benefit of nutrient recovery can lead to a shift in treatment strategies, even if those new processes are more costly.

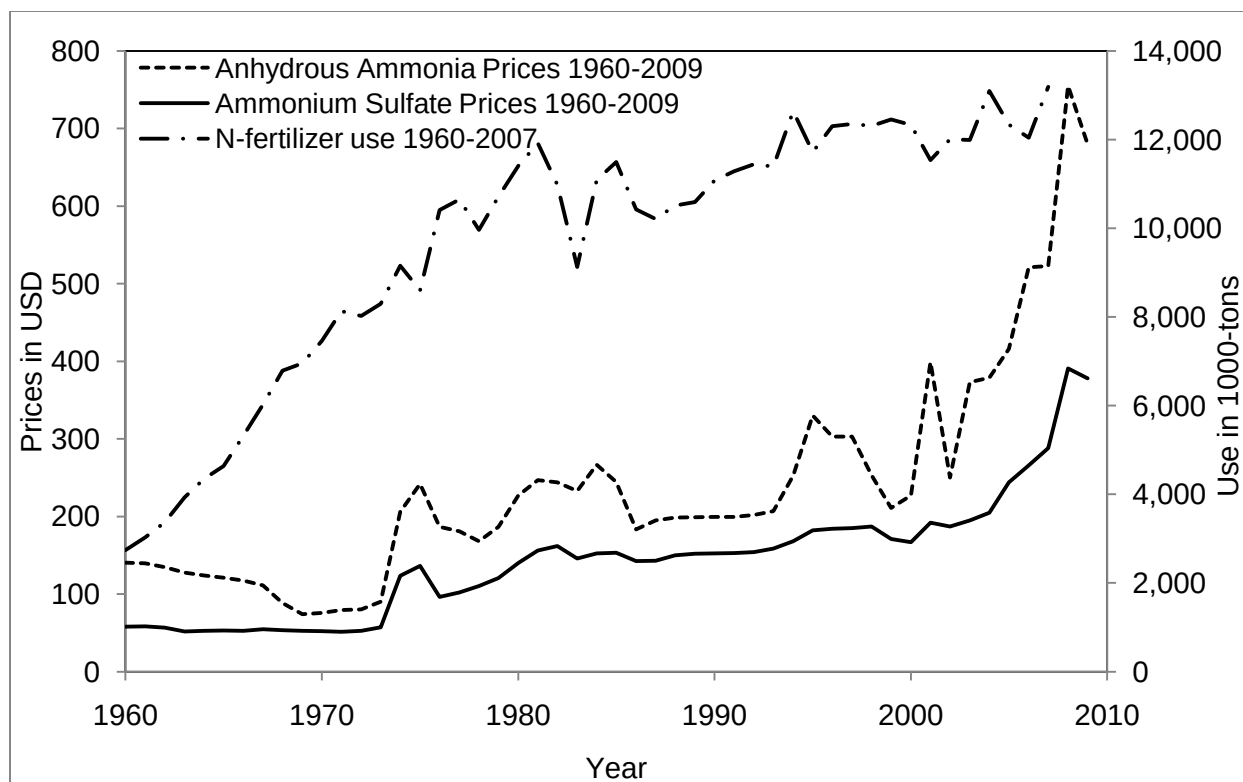


Figure 2.3. Yearly farm fertilizer prices for anhydrous ammonia and ammonium sulfate and average yearly nitrogen fertilizer use. Data adapted from Huang (2010).

2.1.3. Algae Production

As mentioned in previous sections, nutrient contamination leading to eutrophication can eventually result in low oxygen conditions for many surface waters. The Dead Zone of the Gulf of Mexico was given as an example. As the coastal waters begin to warm and nutrients are delivered by rivers, the onset of primary production and eventually large scale algal blooms provide plentiful resources for the aquatic wildlife that feed on the algae. However, once those nutrients become depleted and as the algae are completing their growth cycles, death and decomposition actually consumes dissolved oxygen to very low levels and fish and other wildlife are forced to move to healthier waters or suffocate. This phenomenon, called hypoxia, is seen throughout the world and has been documented for years. The potential for algae to provide nutrient removal from contaminated waters is not only obvious, but is often an unplanned nuisance. For this reason, many different species of algae have been investigated as an alternative to conventional forms of wastewater treatment and nutrient control.

2.1.3.1. Algae for Wastewater Treatment

Early studies of algae and wastewater were dedicated to characterizing the natural growth patterns and centered on eradicating their presence in plant effluents and eutrophied water bodies (Goldman et al., 1972; Srinath and Pillai, 1972; Middlebrooks et al., 1971; Forsberg, 1972). A common conclusion by most was that algae had the ability to uptake nutrients in the water under various conditions, but certain limitations occurred on a site-by-site basis. Algal-based wastewater treatment was also growing research topic in the 1970's. Raschke (1970) used a mixed algae and bacteria pond to treat sewage with moderate success. Of the constituents measured in the pond effluent, ammonium was one of the most completely treated with removal from 60 – 100% of the influent concentrations. Complete treatment of wastewater by algae is not likely because of the presence of organic carbon and suspended solids that must also be removed. In maintaining the benefits of using algae for nutrient removal, successful wastewater treatment was shown in systems that use higher organisms, such as brine shrimp, in conjunction with algae (Michel and Michel, 1973; Goldman et al., 1974). However, the degree and efficiency of nutrient removal in wastewater treatment systems is largely dependent on the species of algae present. Of course, in most cases a mixed culture will prevail, but may be dominated by one or few species. Goldman and Stanley (1974) characterized wastewater treatment and growth for 16 different algae species in a mixture of sewage and seawater. They found that some species, which were not present in a pilot plant, were able to survive and grow in lab conditions. Other species, such as *Dunaliella tertiolecta* performed well in pure cultures, but were quickly outcompeted when other species were introduced, showing that environmental conditions play a decisive role in determining dominant species.

Algal ponds are an alternative wastewater treatment alternative, where natural selection and nutrient inputs determine which species proliferate. Pond-based treatment can also be called controlled eutrophication, where a mix of nature and engineering is responsible for the processes that take place. Management of inputs, retention times, and algae harvesting will affect the efficiency of the treatment and can help guide selection of certain species. Shelef et al. (1973) estimated growth of algae based on solar irradiance measurements and reported

on organic removal from wastewater using algal pond treatment. Though some species of algae can grow on organic carbon, a majority or all of the COD removal in these pond systems can be attributed to heterotrophic bacteria. Lazar John and Bokil (1973), for example, operated a combined flocculating algae-bacteria pond, which showed COD, N, and P removal of 80, 65, and 75 percent, respectively. The relationship between algae and bacteria in wastewater treatment is somewhat complex and usually symbiotic. Algae can uptake nitrogen and phosphorous quickly and provide oxygen to heterotrophic bacteria, which oxidize organic carbon compounds, producing extra CO₂ that algae use as a carbon source. A study of heat and light tolerant algae by de-Bashan et al. (2008) showed that ammonium uptake and algae growth rates increased in *Chlorella sorokiniana* when cells were co-immobilized with bacterial cells.

Although biological nitrification is a more common wastewater industry process, algal-based treatment of ammonia is advantageous in several ways. A comparative study by Ebeling et al. (2006) demonstrated these benefits with measured and stoichiometric results (Figure 2.4). Per gram of nitrogen consumed, algae consume less than half the amount of alkalinity as autotrophic bacteria. Also, algae will consume at least 18.07 g CO₂ and produce 15.14 g O₂, whereas autotrophic bacteria consume 4.18 g O₂ and produce 5.85 g CO₂. This has significant environmental and economic implications, as aeration is a major cost of nitrification and the carbon footprint is highly positive. In terms of suspended solids, nitrification produces only 0.2 grams volatile suspended solids (VSS) compared to 15.85 g VSS of algae produced per gram nitrogen. In a pure water quality sense, this is a major drawback of algal-based treatment. However, given that algal biomass has many valuable uses, this turns out to be in fact quite attractive.

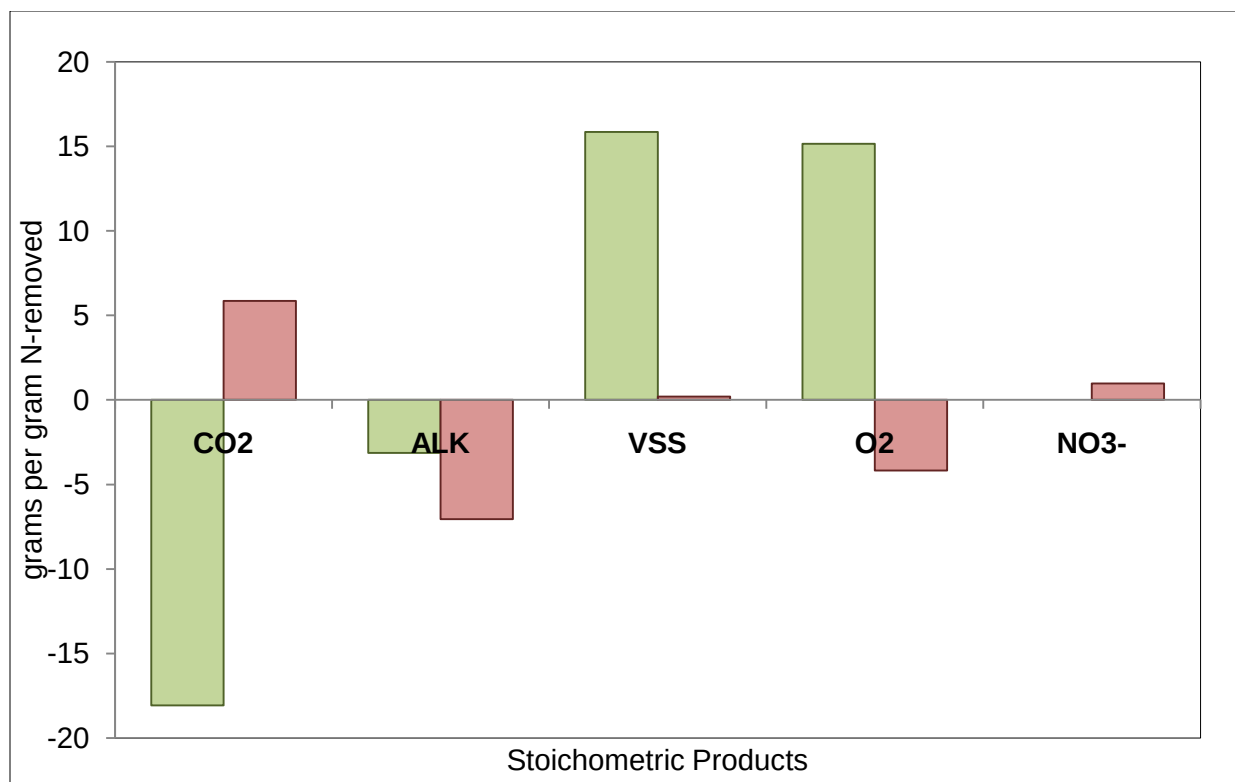


Figure 2.4. Stoichiometric products of ammonium removal in autotrophic algae (green, left) and autotrophic nitrifying bacteria (red, right). Negative values correspond to consumption and positive values correspond to production. Data adapted from Ebeling et al. (2006).

Separation of algal biomass from treated wastewater is important for several reasons. The effluent water must be low in suspended solids, death and decomposition of algae consumes oxygen and generates odor, and the biomass itself can have significant value as a protein source or possible biofuel feedstock (discussed in a later section). Przytocka-Jusiak et al. (1984) used rotating disks as an algae support media for fixed growth in a wastewater treatment scheme. Fixed film as opposed to suspended growth allows biomass harvesting to be straightforward and cost effective. Course filtration is an effective method for harvesting suspended cultures (Peoples and Cravens, 1978; Dodd, 1979). Other methods of harvesting, such as alum flocculation, filtration, and mechanical separation, have been proposed as a means of obtaining biomass for feed protein (Dodd, 1979; Shelef, 1982).

2.1.3.2. Algae and Nutrients

A majority of algae production takes place under low or moderate nitrogen concentrations, and growth at high ammonia concentrations is not well characterized for most species. Though some algae may use ammonium as the preferred nitrogen source, many species experience toxicity at high concentrations and especially in the presence of NH_3 . The concentration at which a certain alga experiences inhibition or toxicity is largely species dependent. Gonzales et al. (2008) used *Chlorella sorokiniana* in an algal-bacterial system to treat high nitrogen piggy wastewater. Concentrations of NH_4^+ above 1000 mg-N/L inhibited growth and nitrogen reduction. Also, as pH increased NH_3 -inhibition was observed at concentrations around 400 mg/L. Under favorable conditions, ammonium concentrations of 373 mg N/L were reduced by nearly 88%, though a significant fraction of the reduction was attributed to nitrification. In a pure culture of *C. sorokiniana* de-Bashan et al. (2008) measured complete ammonium removal from initial 10 mg/L with growth rate of 0.26 d^{-1} . Many species of *Chlorella* are known for their ability to adapt and proliferate in extreme or unfavorable growing conditions. Tam and Wong (1996) examined the effect of high ammonia concentrations on the growth and nitrogen utilization of microalga, *Chlorella vulgaris*. The authors showed that the algae could grow at all initial concentrations of ammonia from 0 to 1000 mg N/L with relatively similar growth rates. From concentrations 10 to 1000 mg N/L the growth rates ranged from 0.199 to 0.236 d^{-1} , but did not correlate to initial ammonia concentration. Yun et al. (1997) also used *C. vulgaris* to completely remove ammonia from initial concentrations of 60 mg/L with elevated CO_2 concentrations. These results are not typical of most algae species, as many may experience ammonia toxicity at much lower levels. For example, Källqvist and Svenson (2003) determined ammonia toxicity of the sensitive microalga *Nephroselmis pyriformis* by measuring the EC_{50} at $32.8 \text{ } \mu\text{g NH}_3\text{-N/L}$, while ammonium toxicity was $3140 \text{ } \mu\text{g NH}_3\text{-N/L}$.

In algal-based wastewater treatment systems, species selection can be an important factor as there is little control over input constituents. Natural selection, though, has essentially guided this selection process, and often the most suitable strains will present themselves when the conditions are favorable for them. In municipal wastewater, constituent levels are relatively constant and predictable, so nitrogen toxicity should not be an issue for most of the algal

species present. In some instances, it may even be that nitrogen in wastewater is a limiting nutrient for algae growth. Tam and Wong (1996) reported that chlorophyll formation in *C. vulgaris* was limited by influent nitrogen concentrations up to 50 mg/L. Jin et al. (2006) increased the exponential growth phase of *C. vulgaris* and *Scenedesmus* sp. by 3 days when they maintained NO_3^- concentrations between 15 and 20 mg N/L, which consequently increased CO_2 fixation.

2.1.3.3. Algae and Salt

Though nitrogen toxicity varies widely between species, it is generally accepted that marine species can have higher tolerance to nitrogen toxicity. Several researchers have used marine phytoplankton to remove wastewater nutrients in mixtures of seawater and wastewater. Goldman and Stanley (1974) tested growth of 16 marine algal species in mixtures of seawater and wastewater and found that many of the commonly found species were able to grow quite well with initial ammonium concentrations ranging from 1 to 7 mg N/L. Craggs et al. (1997) reported complete NH_4^+ -N and P removal in a 1:1 mixture of seawater and wastewater, but the ammonium concentrations were also very low. However, the dilution of wastewater into seawater may have affects related to changes in salt concentration.

Most marine algae species are evolved to grow in salinity conditions of normal seawater, from 2.5 – 3.5 ppm (2.5 – 3.5%). A few species have adapted to grow in concentrations much higher than average. *Dunaliella* sp. have been known to flourish under extreme environmental conditions, where few or no other organisms are found. Adaptation for survival in highly saline environments is what separates *Dunaliella* sp. from other marine algae. In fact some species of *Dunaliella* are considered halophilic and their growth is inhibited by low salt concentrations (Johnson et al., 1968). Unique responses to increased external osmotic pressure allow these algae to survive in hypersaline conditions, approaching and even exceeding maximum saturation of saltwater. In cells of *D. parva* and *D. tertiolecta* the formation of intracellular glycerol to protect against osmotic pressure was found when cultures were grown in NaCl solutions of 1.5 M and 2.8 M, respectively (Ben-Amotz and Avron, 1973; Wegmann, 1971). Borowitzka and Brown (1974) reported very high intracellular concentrations

of glycerol in *D. viridis* grown in 4.25 M NaCl. One of the most well known and well adapted of the genus is *D. salina*, which has been shown to grow in up to 5 M NaCl solution and produce glycerol at concentrations of 7 M, 5 times greater than the glycerol produced by *D. tertiolecta* in 1.4 M NaCl (Ben-Amotz and Avron, 1981).

Surviving and thriving in hypersaline conditions are considerably different notions. Production of glycerol is a response to osmotic pressure, which is usually linear with increasing salt concentrations. However, this does not mean that growth rate will follow the same trend. Johnson et al. (1968) found that *D. viridis* grows best between 0.8 and 2.0 M NaCl solutions, though growth at 3.75 M NaCl can lead to high glycerol production. The authors also determined that the alga required sodium salts to remain viable. Other salts, like potassium and lithium, showed signs of growth inhibition. Although the microalga *D. salina* can grow at NaCl concentrations up to 5 M, the rate of chlorophyll production, which corresponds to growth, is significantly reduced when compared to growth in optimal conditions (Ben-Amotz et al., 1982). Similarly, Hellebust (1985) showed that specific growth rates of *D. tertiolecta* increase rapidly with salt concentration up to 0.5 M NaCl, and then gradually decline at higher concentrations. Of course, nutrient availability also plays an important role in the growth of these unique algae. Herrero et al. (1991) compared growth and protein formation of *D. tertiolecta* using four nitrogen sources and determined that urea produced the highest cell density at low N concentrations in seawater. *Dunaliella* can also serve wastewater treatment needs because it can accumulate and remove common nutrients like ammonium, phosphorous and nitrate as well as some metals like copper, chromium, and aluminum (Thakur and Kumar, 1999; Santos et al., 2001; Raja et al., 2004; Dönmez and Aksu, 2002). However, the use of *Dunaliella* for the treatment of municipal or agricultural wastewater is limited because of its salt requirement. The only practical applications for using this alga are for saline types of wastewaters. Although, if the constituents in wastewater could be separated and treated in side stream processes, the possibility of utilizing marine algae may then become a viable alternative that could provide additional benefits and control.

2.1.3.4. Algae for Valuable Products

Adaptation to hypersaline conditions causes *Dunaliella* to produce glycerol and some other biochemicals. Also, in response to high irradiance and under certain conditions the alga can produce beta carotene and other carotenoids (Mendoza et al., 1999; Capa-Robles et al., 2009). These biochemicals are highly sought after products for food, cosmetics, and pharmaceuticals. The molecular pathway for the formation of intracellular glycerol in *Dunaliella* sp. is described in several studies (Wegmann, 1971; Borowitzka and Brown, 1974; Ben-Amotz and Avron, 1973). Glycerol production in some cells of *Dunaliella* can reach as high as 50% of the dry weight (Ben-Amotz et al., 1982). Under specific nitrogen and irradiance conditions *Dunaliella* can also produce large amounts of beta-carotene, vitamin C and vitamin E (Ben-Amotz and Avron, 1981; Herrero et al., 1991). *D. salina* is known for being the one of the most effective natural producers of beta-carotene because it can synthesize and accumulate concentrations up to 8% of dry weight (Ben-Amotz and Avron, 1981). For this reason, *Dunaliella* has been cultivated heavily for commercial production of these biochemicals. The glycerol content of some species has led some to suggest *Dunaliella* as a potential biofuel feedstock (Ginzburg, 1993; Hosseini Tafreshi and Shariati, 2009). However, the market price for fuel oil has always been considerably less than that of other high-value-products (HVP) like beta-carotene (Borowitzka et al., 1984). A number of companies from India, Australia, Russia, U.S., Israel, and Azerbaijan have been cultivating and selling *Dunaliella* since the 1960's mainly as a vitamin supplement. The number of *Dunaliella* biofuel producers is far fewer and mostly in experimental stages. Algae have been given much attention in recent scientific literature for their unique potential to become the next generation biofuel. Though most species of algae do not produce the high-value-products found in *Dunaliella*, faster growth rates and higher cellular lipid concentrations makes some algae suitable for oil production.

2.1.4. Recovery of Ammonium from Wastewater

The remainder of this chapter discusses a novel concept for treating ammonium in wastewater by means of separation and biological uptake. A review of relevant literature has outlined the prospects and limitations two alternatives for treating ammonia wastewaters, natural ion exchange and algae-based remediation. The objective of this current study is to

demonstrate that a clever combination of these two methods of treatment can offer synergistic benefits that may help to overcome some of the individual limitations and improve upon conventional ammonium treatment practices.

A hypothetical treatment system is proposed as an alternative to nitrification in municipal sewage treatment. Figure 2.5 outlines the key features of the proposed system. A column of ammonium selective ion exchanging clinoptilolite (a.) serves as the main removal mechanism for inorganic ammonium nitrogen after primary clarification. Wastewater is pumped upflow through the column with a relatively short empty bed contact time (EBCT) of 25 minutes. The effluent from the column is then considered treated and the ammonium-free water will continue on for further treatment. As breakthrough occurs and ammonium concentrations begin to increase in the effluent, the column is taken offline for regeneration (dashed lines). A hypersaline solution is used to regenerate the column with the smallest volume possible, restoring the ion exchange sites to sodium phase. Once all or most of the capacity is restored to the material, the column can begin treatment. The ammonium laden brine (e.) is rejuvenated by feeding the brine directly to halotolerant algae, *Dunaliella*. The algae (b.) will assimilate nitrogen into biomass, removing dissolved inorganic ammonium from the brine. The cells are then separated by filtration (c.) and the brine is considered viable for further use as a regenerant (d.). Biosolids from the algae can be further processed offsite or anaerobically digested for biogas.

This proposed process has several advantages over other methods of ammonium treatment.

1. Ion exchange can remove ammonium much faster and more reliably than nitrifying bacteria can convert. Ion exchange responds and adapts quickly to surges in influent ion concentration, whereas bacteria need more time to adjust to new conditions, which may sometimes be fatal.
2. The environmental and water quality impact of controlled algae growth is more beneficial than growth of nitrifiers. See Figure 2.4.

3. Separating ammonium from the main wastewater stream eliminates the formation of nitrate and nitrite, and eliminates the need for denitrification.
4. Regenerating the clinoptilolite with cheap salt solutions at high concentrations reduces the volume of brine needed, which minimizes the amount of time that the column is offline. Also, high salt concentrations may prevent unwanted growth in the system and reduce instances of contamination or biofilms.
5. Using algae to rejuvenate the brine for reuse lowers input costs and offers an elegant and simple solution to disposal of the recovered ammonium.
6. Halotolerant algae are an ideal candidate for this process because they can grow well in hypersaline conditions, allowing the use of more effective regenerant concentrations. Also, the algae's natural biochemical response to these conditions may provide an opportunity for cost recovery by harvesting some high value products. Algal biomass, nonetheless, is still valuable as a biofuel feedstock or for animal feed.

Bench scale experiments were designed to test the core elements of this proposed treatment process and address key questions:

1. How might the ion exchange material perform with primary clarifier effluent as the feedwater? What level of treatment can be expected over several loading cycles?
2. How effectively can the material be regenerated, and how can regeneration be optimized to reduce brine usage and time offline?
3. Does the ammonium laden brine offer substantial support for growth of halotolerant algae? Can the algae effectively rejuvenate the brine for further reuse and is there any loss of regeneration efficiency?

Original data reveals that the combination of these two processes, with the selection of an appropriate algae species, not only can achieve effluent quality standards, but offers addition benefits that are not realized when the processes are used alone.

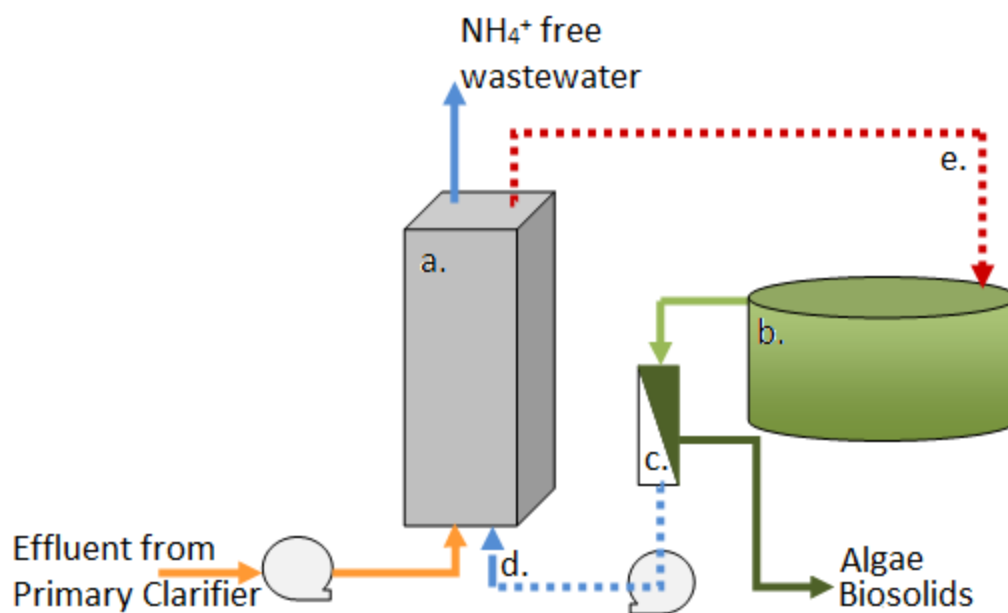


Figure 2.5. Overview of proposed ammonium recovery process. Dashed lines represent regeneration mode. a.) Clinoptilolite ion exchange column, b.) Halotolerant Algae Bioreactor, c.) Filter for separating and thickening solids, d.) Rejuvenated ammonium free brine, e.) Ammonium laden brine fed into algae reactor.

2.2. Methods and Materials

2.2.1. Clinoptilolite

The clinoptilolite was obtained from St. Cloud Mine (St. Cloud Zeolite, Winston, NM). The material arrived preprocessed into a standard mesh size 14 x 40, pictured in Figure 2.6. Before use, the material was rinsed thoroughly with deionized water (DI) until the wash water was clear. For conditioned samples, clinoptilolite was then soaked in 10% saltwater overnight and rinsed once more with DI before use.



Figure 2.6. Photograph of clinoptilolite from St. Cloud Mines, mesh size 14x40.

2.2.2. Feedwater

The feedwater used in the study was obtained from the Urbana-Champaign Sanitary District primary clarifier effluent. The water was then filtered by a 40 micrometer flat sheet filter and the filtrate was stored in a 5°C cold room until needed. Concentrations of ammonium in the feedwater did not change after filtration and ranged from 20 – 25 mg N/L depending on when the water was retrieved.

2.2.3. Determination of Ammonium Concentrations

Ammonium concentrations for the all samples throughout the study were determined by Nesslerization using a Hach-2010 Spectrophotometer (Hach Company, Loveland, CO). The detection range of this method (#380) is 0.01 – 2.50 mg NH₄-N/L. Most samples were diluted at least 1:25 to be within the detection range.

2.2.4. Column Tests for Breakthrough Study

The initial breakthrough test used 10 mL clinoptilolite, conditioned as described above and packed into glass columns. Feedwater was pumped upflow through the column at 0.4 ml/min (2.4 BV/hr), with an empty bed contact time (EBCT) of 25 minutes. A larger volume column holding 50 mL unconditioned clinoptilolite was operated in upflow at 1.5 BV/hr, with an

EBCT was 40 minutes. Effluent ammonium concentrations were tracked periodically until steady state was achieved at or near $C_{in} = C_{out}$.

2.2.5. Regeneration Tests with Fresh and Biologically Treated Regenerant

Regenerating the capacity of the clinoptilolite is essential to improving the economics of ion exchange treatment. Concentrated seawater was chosen as a regenerant because of its effectiveness, availability, and low cost. Other benefits of using concentrated seawater are described in the following section. For this study, concentrated seawater brine was synthesized by dissolving Instant Ocean sea salt in 1 L deionized water to achieve desired salt concentrations. Regeneration of the clinoptilolite in the column was carried out after each loading cycle with either fresh or biologically rejuvenated brine. Consecutive batches of 2 bed volumes of regenerant were recirculated through the column at a flowrate of 2.4 BV/hr until nearly all ammonium was accounted for in the regenerant solution. Batches of 4 bed volumes were used when comparing fresh and biologically regenerated brine.

2.2.6. Batch Growth of Marine Algae and Brine Regeneration

After regenerating the column of clinoptilolite, the spent brine contains high concentrations of ammonium and has no more regenerative ability. Treatment of the spent brine is not only necessary, but offers cost savings if the brine can be reused for further regenerations of the clinoptilolite.

2.2.6.1. Halotolerant Algae Growth in Brine

Halotolerant algae offer several advantages in the proposed treatment scheme. As stated previously, some species of *Dunaliella* can grow in salt concentrations as high as 20% and some may even be optimized for growth in 5 – 15% salt concentrations. The ammonium is removed by algae assimilating the nitrogen into new cells, removing it from solution and placing into a separable biomass. Two species of halotolerant algae were examined for optimal growth conditions within the practical range of the experiments. *Dunaliella parva* and *Dunaliella salina*, obtained from the University of Texas Algae Culture Collection (UTEX), were grown in 250 ml erlenmeyer flasks containing 125 mL of 35, 50, or 100 g sea salt/L and 10 mL of algal seed. The initial ammonium concentrations were 27 - 29 mg $\text{NH}_4\text{-N/L}$, diluted from spent

100 g/L solution. For comparison, *D. parva* and *D. salina* were also grown in 100 g/L solution and fed F/2 media described in (Guillard, 1975) with no ammonium. Flasks were placed on magnetic stirrers in a climate controlled room at 28 degrees Celsius and CO₂ concentration of 3-4%. Chlorophyll-*a* concentration was used a marker for algae growth and was monitored by measuring optical density at 680nm (OD680) by using a Tecan i200 (Tecan Group Ltd., Männedorf, Switzerland).

2.2.6.2. Ammonia Removal Rate

Ammonia concentrations were monitored in each of the flasks during the growth periods. Small volume samples (less than 1 mL) were taken from the flasks and filtered with 0.2 micrometer nylon filter. The filtrate was analyzed for ammonium by the method described above. Once the concentration of ammonium in solution fell below detection limit, 100 mL from the flask could be filtered. The filtrate could then be reused as a regenerant by the method described above.

2.3. Results

2.3.1. Breakthrough Tests on Clinoptilolite

To determine the effect of preconditioning on the performance of clinoptilolite, two columns were operated upflow using effluent from the primary clarifier of the local wastewater treatment facility. One column (BV = 50 mL) of unconditioned clinoptilolite was operated with a flowrate of 1.5 BV/hr until breakthrough reached a plateau near $C_{in} = C_{out}$. Another column (BV = 10 mL) contained clinoptilolite that had been preconditioned by soaking in a solution of 100 g/L sea salt. The preconditioned material had an ammonium capacity that was actually about 8% less than the unconditioned clinoptilolite. However, Figure 2.7 shows the fractional breakthrough for each column during the first loading. The two breakthrough profiles overlay, which indicates that the rate of column exhaustion is essentially the same. The decreased capacity measured in the preconditioned material, therefore, is likely due to the slight variation in operational parameters; flowrate, column size, influent ammonium concentrations. Nonetheless, it can be concluded that clinoptilolite preconditioned with highly concentrated sea salt did not offer any significant advantages over unconditioned samples.

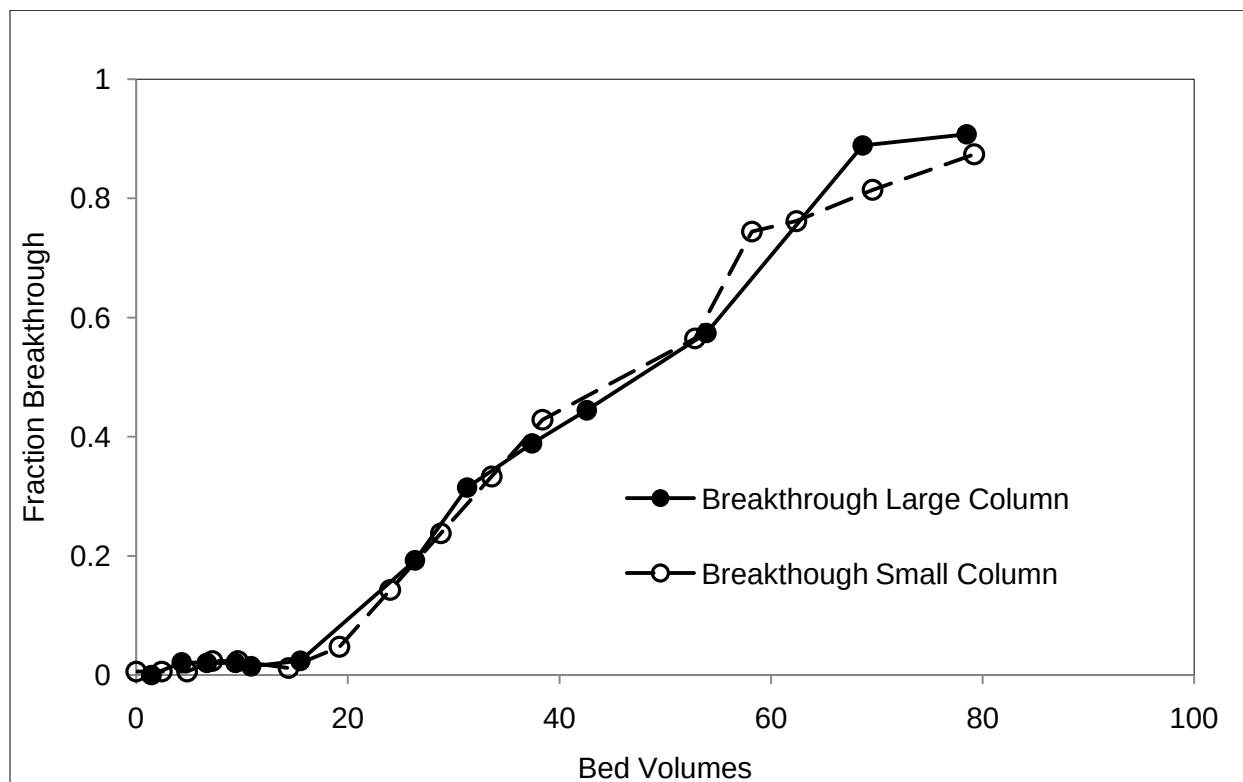


Figure 2.7. Comparison of breakthrough on two columns: 50mL BV, 1.5 BV/hr; 10mL, BV 2.4 BV/hr. Only the small column was preconditioned with 100 g/L sea salt solution before use.

Though preconditioning did not increase capacity of the clinoptilolite, several studies have reported that site ‘activation’ can occur, where the material gains capacity over several loading and regeneration cycles (Jorgensen et al., 1976; Rahmani et al., 2004). The two columns operated in the present study experienced this type of serial increase in capacity. Even though the regenerant salt concentrations were different, Figure 2.8 shows that both columns experienced very similar increases in total capacity. Both columns had a 48% increase in capacity after the first regeneration. Further, over three loading cycles for each column, the total ammonium capacity nearly doubled. The shape of the breakthrough curves did not change for the three loading cycles. Instead, the period of complete ammonium removal was extended in both cases. For the smaller column, the amount of wastewater treated to below 2 mg-N/L was increased from about 35 BV to nearly 90 BV. When this column was operated for an

additional two loading cycles, the capacity did not appear to increase significantly (Figure 2.9), indicated a steady working capacity of the clinoptilolite at a level more than twice as high as the initial capacity. In the fifth loading of the small column some ammonium leakage occurred due to residual concentrations leftover from the previous regeneration. The fact that the effluent concentrations quickly decreased after this sample verifies that the column was regenerated adequately and with proper rinsing of the column between regeneration and loading cycles this point would have been low or the below detection limit.

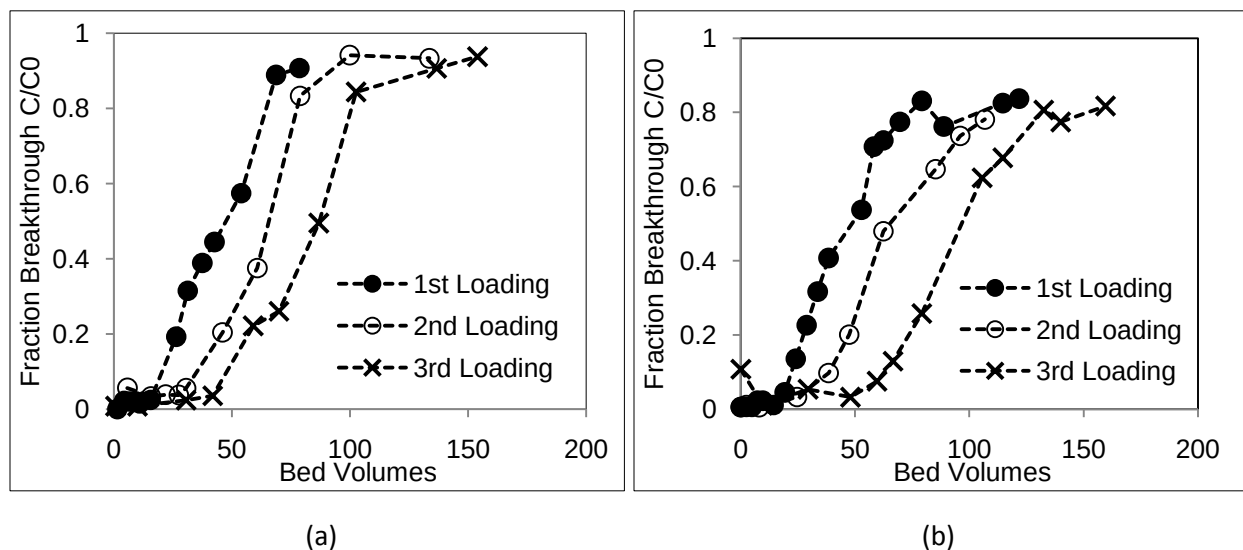


Figure 2.8. Capacity increase over subsequent loading and regeneration cycles. (a) BV = 50 mL, 1.5 BV/hr, 60 g/L sea salt regenerant; (b) BV = 10 mL, 2.4 BV/hr, 100 g/L sea salt regenerant.

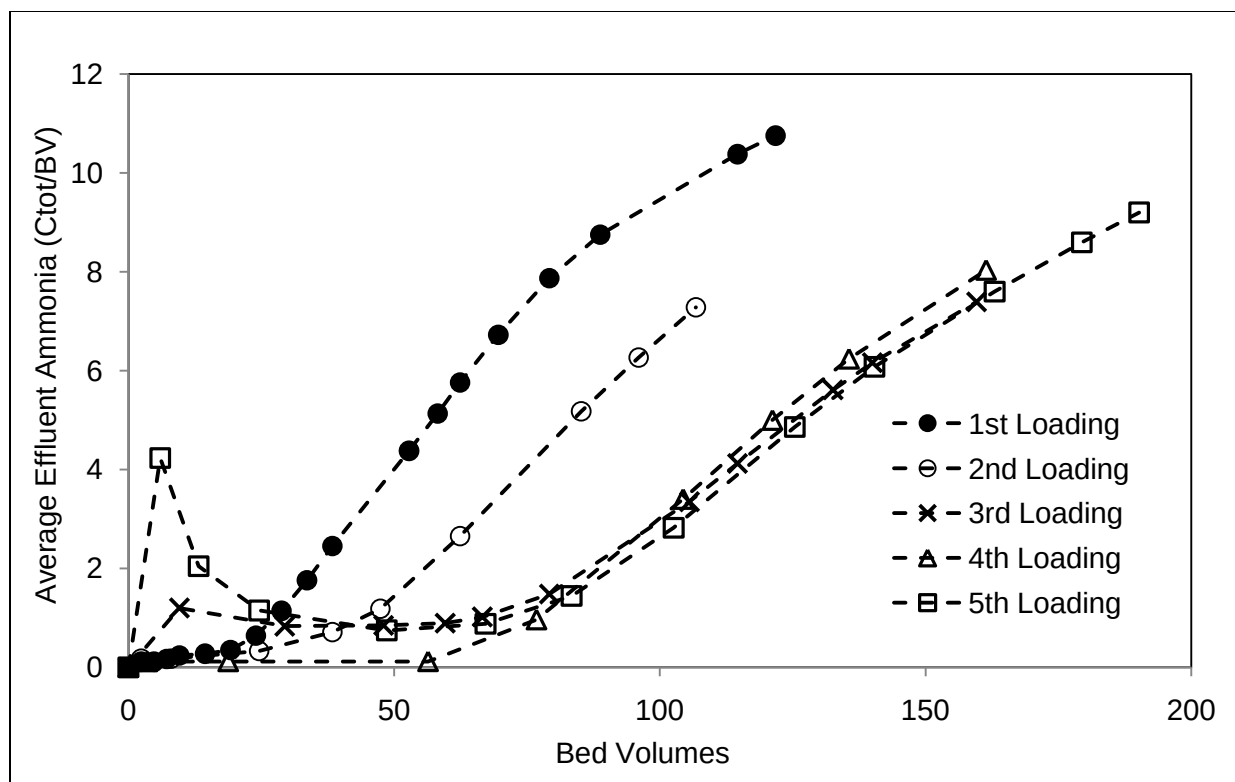


Figure 2.9. Breakthrough in terms of total average ammonium concentration over 5 loading cycles. BV = 10 mL.

2.3.2. Regeneration of the Clinoptilolite

The data presented in Figure 2.8 and Figure 2.9 indicates that the regeneration of clinoptilolite with high concentrations of sea salt is possible. Most of the studies reviewed in the previous section discuss lower concentration salt solutions used in regeneration of spent clinoptilolite, which may not offer the benefit of concentrating the ammonium and reducing the volume of brine used for regeneration. However, in a wastewater treatment situation, it is ideal to minimize the volume of water needed in order to reduce cost. Optimization of column regeneration requires that each volume of water is used as efficiently as possible. Recirculating regenerant solution through the column can ensure that the maximum amount of ammonium is eluted from the spent material per volume of regenerant. This is a common industrial practice that can significantly reduce the total volume of regenerant solution needed. Also, increasing ionic strength of the regenerant solution causes the material to elute more ammonium. Since the regenerant solution in this study is being used as a carrier of nitrogen to

halotolerant algae, higher concentrations of salt may be used. This has several advantages –

1. Higher ionic strength minimizes the amount of regenerant needed,
2. Less time that a column must spend offline due to regeneration,
3. High salt concentrations can support the growth of potentially high value algae,
4. Hypersaline solutions provide an element of selectivity and suppresses the likelihood of contamination by unwanted species.

Figure 2.10 compares the regeneration efficiencies of two different concentrations of regenerant solutions. The experiments were carried out by recirculating small batches of 2 BVs upflow through a spent clinoptilolite column until the concentration in the solution leveled off. The solution was then replaced with a fresh 2 BV batch and repeated until nearly all of the ammonium was recovered from the clinoptilolite. By reducing the concentration of sea salt in the regenerant solution from 100 to 60 g/L, the volume required for regeneration increased by 40%. Though the total amount of salt used was similar for each case, the lower concentration solution would require longer regeneration times and larger storage containers, which leads to higher costs. Even though some studies report that normal seawater concentrations are sufficient for clinoptilolite regeneration, the volume of regenerant and the time needed would most likely inhibit the treatment process.

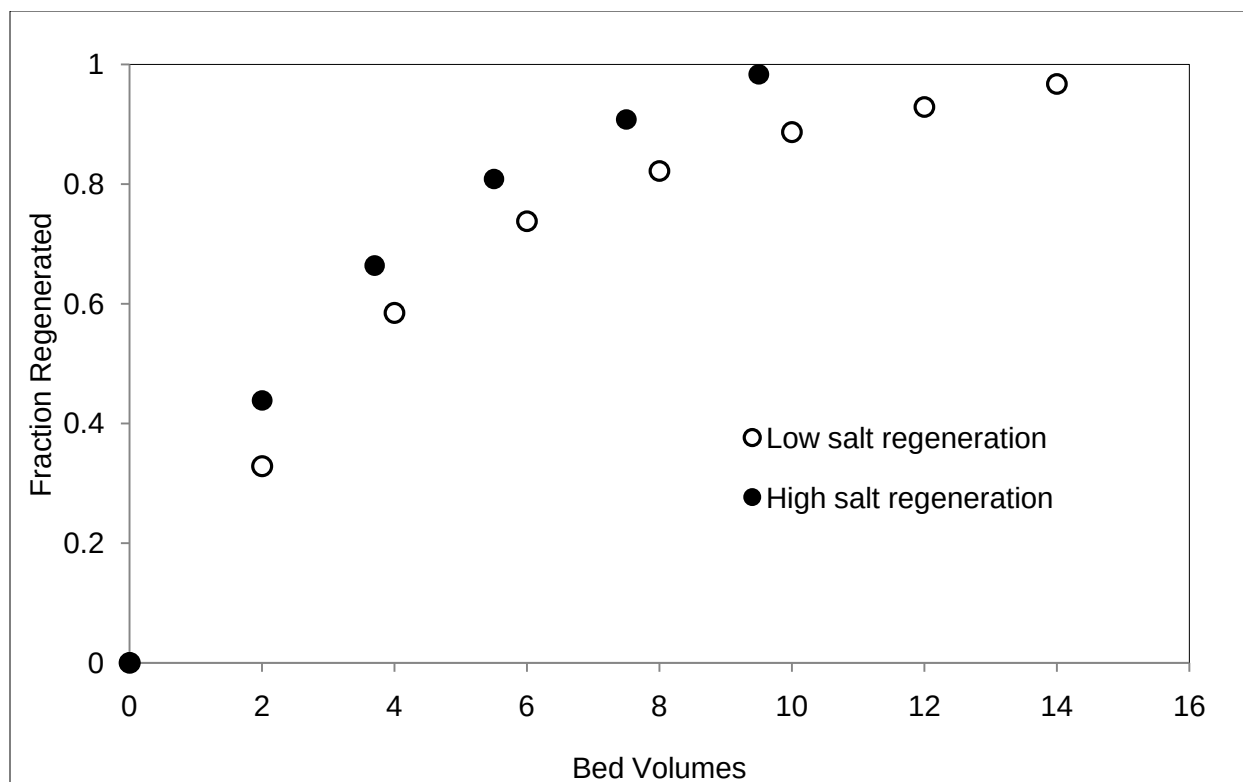


Figure 2.10. Comparison of regeneration efficiencies using different salt concentrations (open circles = 60 g/L, filled circles = 10 g/L).

In Figure 2.8 it is clear that the capacity of the clinoptilolite was increased over subsequent loading and regeneration cycles. However, Figure 2.11 shows that the increasing capacity for ammonium during the loading cycles did not affect the total amount of brine needed for regeneration. The data on the left of Figure 2.11 shows that if more ammonium was loaded onto the clinoptilolite surface, a proportionate increase in eluted ammonium was observed in the regenerant brine. A second look at the data (right) normalized to the total amount of ammonium sorbed in the previous loading cycle reveals that the efficiency of regeneration is essentially the same for all three cycles, regardless of the increase in loading capacity. The amount of regenerant needed to recover more than 98% of the ammonium from the material was only 10 BV, approximately one-sixteenth of the total volume of water treated in the third loading. Note that the columns in this study were operated to the point where C_{out} approached C_{in} for comparison and mass balance purposes. If a similar treatment scheme were

employed at a wastewater treatment facility, effluent ammonium standards would require more frequent regenerations and shorter loading cycles. It can be expected, therefore, that regenerant requirements may also decrease since there is less ammonium to elute from the material.

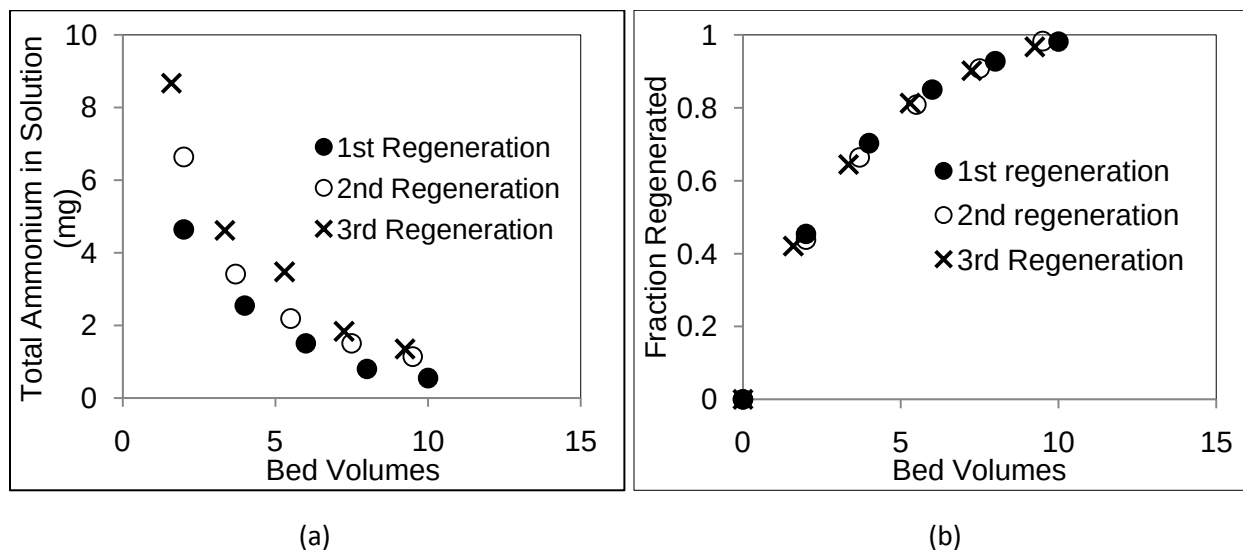


Figure 2.11. First three regenerations of small column using 100 g sea salt/L. (a) Total ammonium recovered from material in mg-N. (b) Total ammonium recovered as a fraction of total amount sorbed onto the material.

In the proposed system, however, the cost of regenerants can be dramatically reduced since the brine will be reused for multiple regenerations. Direct biological growth in the ammonium saturated regenerant brine will consume all or most of the inorganic nitrogen, rejuvenating the solution and allowing for repeated use of the brine. To test the effectiveness of using biologically rejuvenated regenerants, after the forth loading of the 10 mL column, the clinoptilolite was divided amongst two 5 mL columns. One column was regenerated with fresh 100 g/L sea salt regenerant brine and the other column was regenerated with a solution that had been biologically rejuvenated by *Dunaliella parva*. As seen in Figure 2.12, the efficiency of regeneration was essentially the same for the fresh and reused regenerants. After regenerating the clinoptilolite, the columns were recombined and another loading cycle revealed that no

capacity was lost (Figure 2.9), even though a portion of the regeneration was done with reused brine.

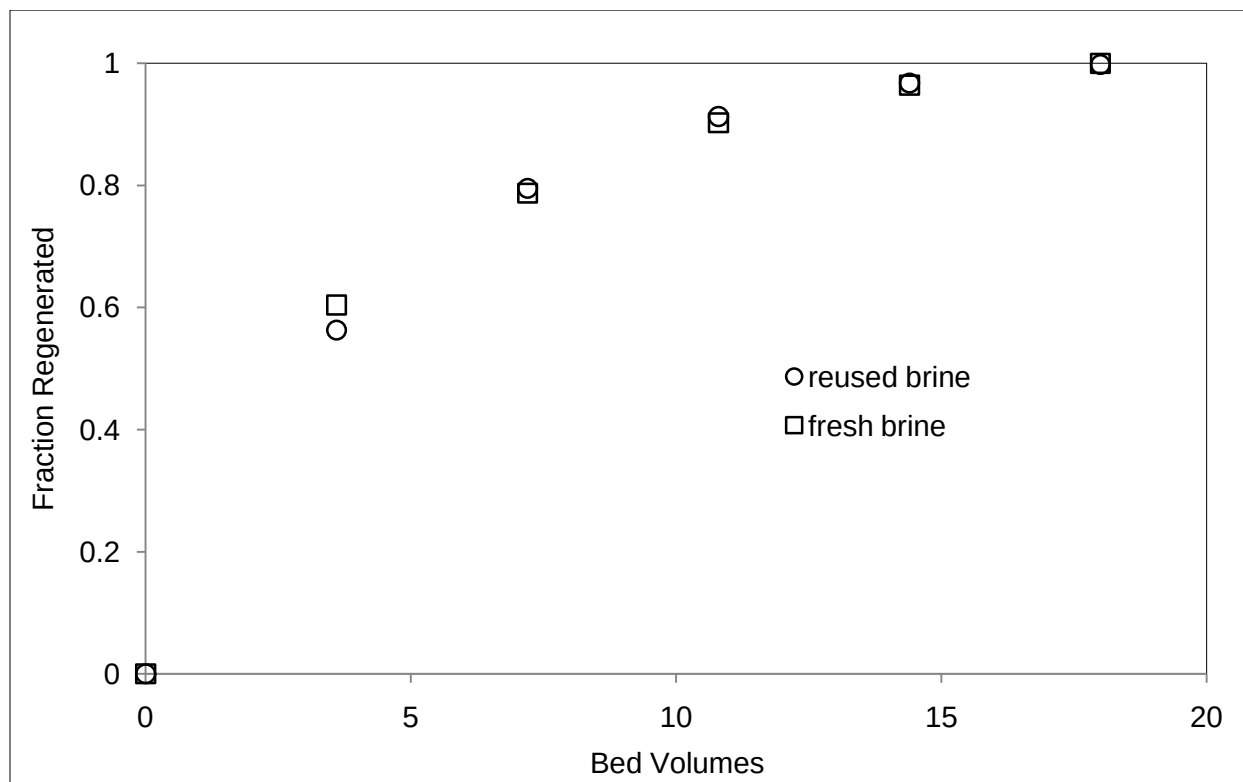


Figure 2.12. Regeneration of clinoptilolite column with fresh (squares) and algal-rejuvenated (circles) brine.

2.3.3. Algae Growth in Ammonium Brine

The algae selected for this study are popular halotolerant species of *Dunaliella*, which can grow in concentrations up to 5 times greater than seawater. The regenerant solution used here was made from 100 grams of sea salt dissolved into 1 liter of deionized water, which is equivalent to approximately 3 times the salinity of normal seawater. As shown in Figure 2.10, the sea salt solution can effectively and efficiently regenerate a column of clinoptilolite and concentrate the ammonium into a relatively small volume. The total average ammonium concentration in the sea salt solution after regeneration was between 5 and 10 times more concentrated than the initial wastewater sample. Though some species of algae would have no

problem growing in these concentrations, *Dunaliella* is not known for its ability to thrive in high nitrogen concentrations and in this study the solutions were diluted to more appropriate levels for growth in batches.

Two algae were grown in various concentrations of saltwater and their growth rates and nitrogen consumption were compared to determine optimal salinity conditions for each species. *Dunaliella salina* is the most glycerol-accumulating of the halotolerant algae and has been shown to grow in very high salinities, but with a compromise in growth rate (Ben-Amotz and Avron, 1981). *Dunaliella parva* can also accumulate high concentrations of intercellular glycerol, but its growth rate is less affected by increasing salt concentrations (Ben-Amotz and Avron, 1973). Figure 2.13 compares the growth of these two algae in 3 different concentrations of sea salt; 35, 50, and 100 g/L. The media was provided by diluting used regenerant solution to 26 – 29 mg NH_4^+ -N/L as well as the target salt concentration. In this study, increasing cellular chlorophyll *a* (chl-*a*) concentration was tracked by measuring the optical density of the algal cultures at 680 nanometers (OD680) by spectrophotometry. Out of all the cultures grown in this test, *D. salina* in 50 g/L sea salt solution (Figure 2.13d) grew the best during the 10+ days of culture time and had the highest ammonium consumption rate. The average chl-*a* increase at this concentration was 27% higher than at the lower concentration (Figure 2.13f) and 122% higher than growth at 100 g/L (Figure 2.13b). This suggests that the optimal salt concentration for growth of *D. salina* is within the region tested, but maybe not exactly at 50 g/L. This result is not in agreement with the findings of Ben-Amotz et al. (1982), which reports an inverse relationship between chl-*a* content and salt concentration. This may be attributed to the fact that the researchers in that study had different growth conditions, and were not culturing the cells with high ammonium concentrations.

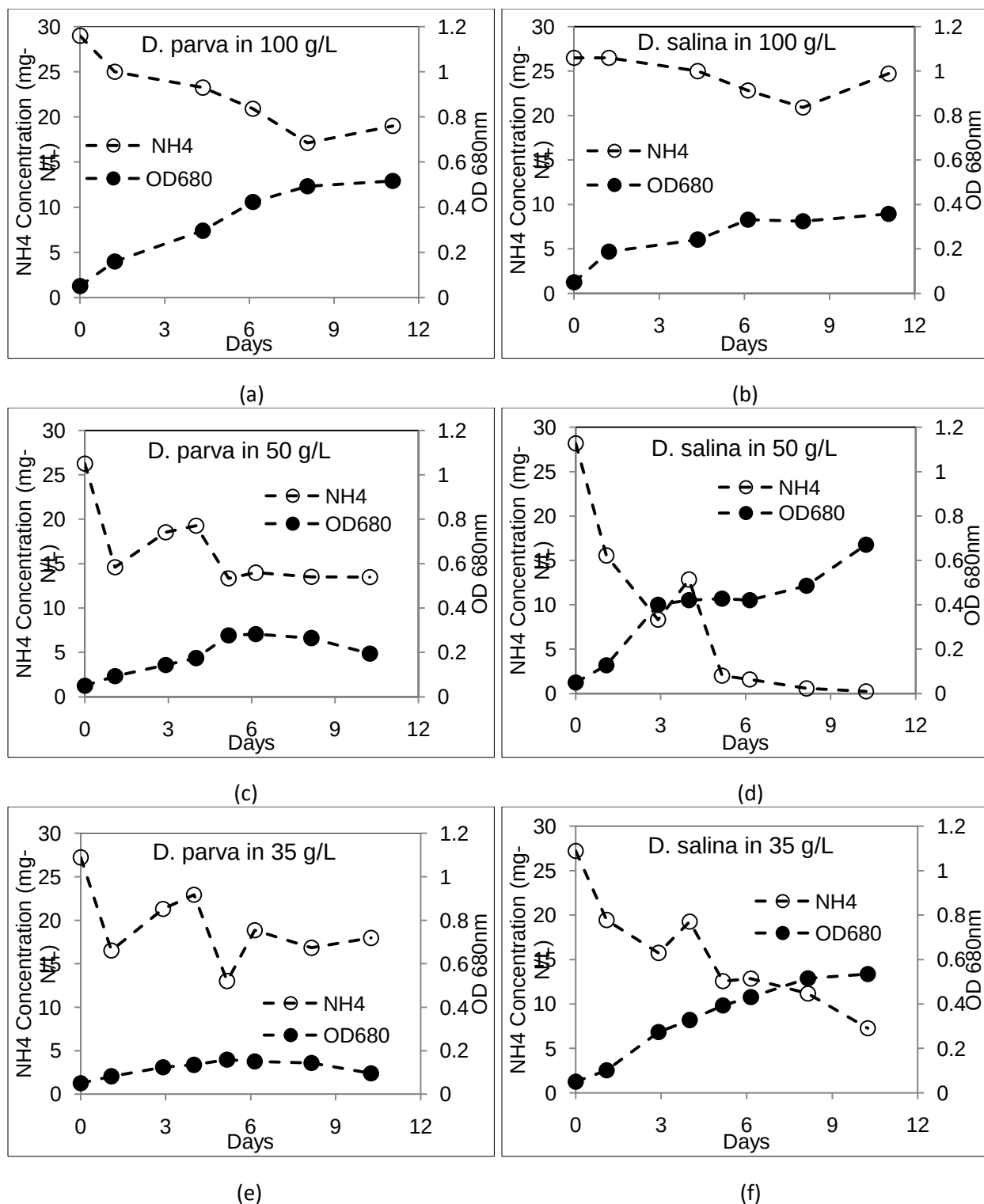


Figure 2.13. Optical density (680 nanometers) and ammonium consumption in *D. parva* and *D. salina*. Starting ammonium concentration 26-29 mg-N/L. (a) *D. parva* in 100 g Sea salt/L, (b) *D. salina* in 100 g Sea salt/L, (c) *D. parva* in 50 g Sea salt/L, (d) *D. salina* in 50 g Sea salt/L, (e) *D. parva* in 35 g Sea salt/L, (f) *D. salina* in 35 g Sea salt/L.

Compared to the *D. parva* grown in the 50 g/L (Figure 2.13c), *D. salina* exceeded by more than three times. As mentioned previously, *D. parva* is considered halophilic, meaning that there is preferential growth in extremely salty waters. By increasing the salt concentration from 35 g/L (Figure 2.13e) to 100 g/L (Figure 2.13a), *D. parva* experienced an order of magnitude increase in chl-*a* production rate. This gives further validation to the suggestion that *D. parva* may be growth inhibited at lower salt concentrations. However, the total average ammonium consumption rate over this period did not follow the same trend for *D. parva*. Cultured in 50 g/L sea salt solutions, both *D. parva* and *D. salina* had the highest rates of ammonium consumption, 1.25 and 2.73 mg-N/L/day, respectively. The ammonium consumption rate for *D. parva* in 100 g/L sea salt solution was actually about 30% lower, at 0.9 mg-N/L/day. This suggests that there is not a linear relationship between chlorophyll *a* concentration and ammonium uptake for cells grown in different salt concentrations. Herrero et al. (1991) similarly concluded that the relationship between chlorophyll *a* and cell growth changed for varying growth conditions. There is, however, a clear trend in Figure 2.13 between ammonium uptake and chlorophyll *a* within any individual culture.

None of the data, except Figure 2.13d, show complete reduction in ammonium concentrations within the culture period. Since none of the flasks received growth media commonly used in algal culture, it is likely that at some point, cell growth (or chl-*a* production) became limited by lack of micronutrients. Figure 2.14 compares chlorophyll *a* content for both species grown at high salt concentrations spiked with common F/2 growth media and without the presence of ammonium. In both cases, longer culture times were required to reach stagnation phase, which indicates that the rate of chl-*a* formation was slower in cultures that had low nitrogen content. Since *D. parva* exhibited the most potential for growth in 100 g/L sea salt solution (the concentration used for regenerating the clinoptilolite) containing ammonium, it was chosen for further study. After 11 days of initial growth period in ammonium laden brine (Figure 2.13a), the culture was spiked with F/2 growth media. Though the media contains small amounts of nitrate, this did not affect the measurement of ammonium in solution. Figure 2.15 shows that *D. parva* was able to completely remove the remaining ammonium from the

solution in as little as 8 days after the addition of F/2, with an ammonium removal rate for that period of 2 mg-N/L/day, more than twice the rate during the previous 11 days. At the end of the growth cycle, once all inorganic ammonium was removed by algae, the solution was considered rejuvenated and filtered to remove suspended solids so that the brine could then be reused for clinoptilolite column regeneration (Figure 2.12). The ammonium laden brine obtained from that regeneration cycle was again used in cultivating cells of *D. parva* in the same manner described in Figure 2.15. An equivalent addition of F/2 after the 11 days of initial growth yielded very similar results. In fact, the overall ammonium removal rate after media addition was exactly the same for both experiments. All of the ammonium removed in the experiments was assumed due to algal cell uptake and assimilation. Volatilization as ammonia gas was not likely since pH was consistently below 8.5. Also, sterile growing conditions and high salt concentrations reduce the possibility that bacteria such as nitrifiers played a role. Clearly, the ability for cells of *D. parva* to uptake ammonium from the regenerant brine is possible, but the rates and completeness of removal are dependent on the availability of essential nutrients not present in the brine alone. Further, a higher concentration of nitrogen, with the addition of F/2 media, appears to positively influence the formation of chl-*a* when compared to culturing with only F/2 media.

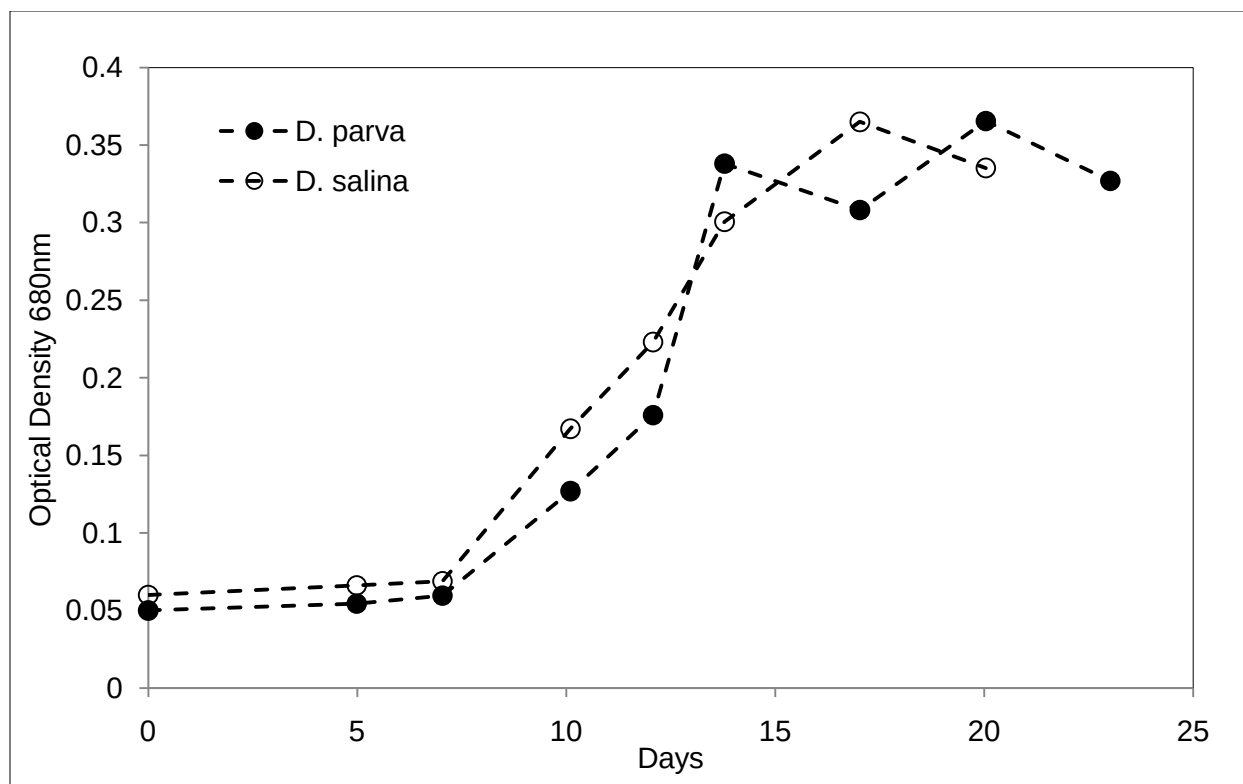


Figure 2.14. *D. parva* and *D. salina* in 100 g/L sea salt solution with F/2 media, no ammonium.

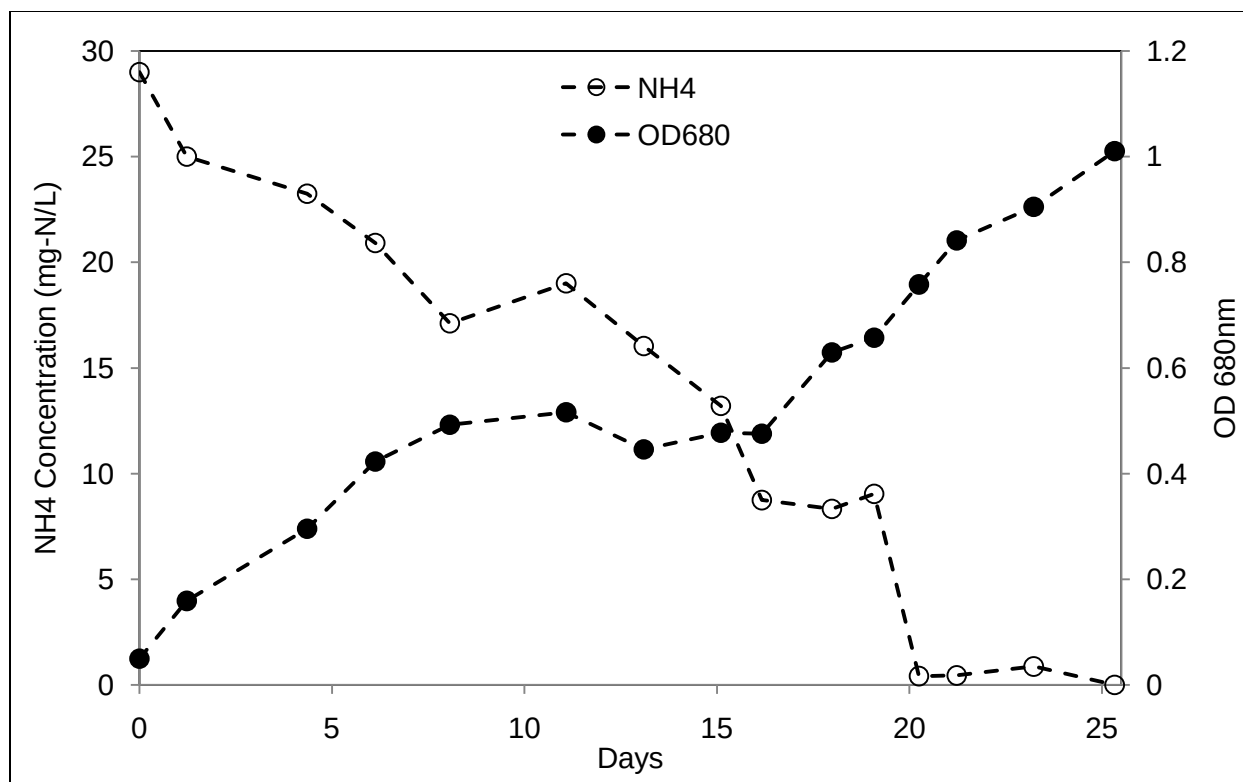


Figure 2.15. *D. parva* in 100 g/L sea salt solution and dosed with F/2 media on day 12.

2.4. Conclusion

A novel concept for treating wastewater ammonium was proposed in this study. The concept combines the application of natural ion exchange and halotolerant algae into a system that not only offers definite process advantages over nitrification, but has the potential to produce significant cost savings and possibly make treating ammonium profitable. The combination of ion exchange and biological treatment allows ammonium removal to become more reliable and complete, especially under conditions that could impair nitrification. The synergistic relationship formed by the marriage of these two treatment alternatives allows us to overcome some of the key limitations that impede the widespread use of either technology, such as brine disposal for ion exchange, and contamination issues for algae-based remediation. The experiments conducted in this study were targeted to answering a few key questions regarding the proposed process. The data has shown that not only can the clinoptilolite offer fast and continuous removal of ammonium to levels under the effluent standards, but also that

the capacity of the material increases over the first several loading cycles. Additionally, regeneration of the spent material can be improved through the use of highly concentrated salt solutions (about 10% w/v). This ammonium laden brine was shown to support the growth of specific halotolerant algae, *Dunaliella*, which were able to rejuvenate the brine by uptaking ammonium in solution. Further, this brine was able to be reused for additional column regeneration without significant loss of regeneration efficiency. The findings of this study are an important first step in proving that the proposed treatment concept can be a viable alternative to nitrification and possibly applicable to many other types of ammonia wastewaters. Further investigation is needed to optimize specific operational parameters and identify energy requirements and possible limitations, such as metals interference during ion exchange or long term deterioration of the material. The parameters for algae growth, such as light intensity, mixing rates, and nutrient availability need much more intense investigation if cells are to be optimized for production of high value products, like beta-carotene or glycerol. Some contradiction exists in that a low nitrogen environment is associated with maximal glycerol production in *Dunaliella*, but the brine used to culturing the cells is highly concentrated with ammonium. However, the correct bioreactor configuration and dilution rate should be able to offer some control over the algae's physiological responses.

3. NOVEL PROCESS FOR TREATMENT OF PERCHLORATE WASTEWATER

3.1. Introduction

3.1.1. A Novel Reactor Concept

Membrane bioreactors (MBRs) are an increasingly important wastewater treatment technology that can deliver a better quality effluent with a smaller treatment footprint because the integrated membrane allows for very high suspended biomass concentrations, better particulate removal, and they avoid the need for downstream solids separation equipment. Thus, MBRs are advantageous where space is constraining and water quality standards are more stringent, which justifies the slightly higher cost of current MBR technology for some applications. However, additional process advantages or lower costs are needed to facilitate more widespread use of MBR systems. Process consistency and reliability is one area where significant enhancements are possible. While all biological treatment processes are subject to upset because of variations in process influent conditions, the smaller size and hydraulic retention time (HRT) of MBR processes make them generally even more sensitive to influent spikes of incoming substrates or inhibitory compounds. This paper introduces a novel treatment process, the hybrid adsorption-membrane biological reactor (HAMBgR), that enhances MBR performance and stability, thus offering the potential to improve cost-effectiveness and significantly expand the application of MBR technology. This study focuses on one potential application, the cleanup of perchlorate laden wastewaters, to demonstrate some key features of the HAMBgR process that are also applicable to a variety of other wastewater treatment needs.

3.1.2. Perchlorate Contamination and Treatment

3.1.2.1. Impacts of Perchlorate Contamination

Perchlorate is an important emerging contaminant because it can impair proper thyroid function at low $\mu\text{g/L}$ concentrations and has widespread occurrence in environmental water sources (Greer et al., 2002; Gullick et al., 2001; Tikkanen, 2006). Although there are some

natural sources, perchlorate is most commonly associated with explosives manufacture and military applications, where it serves as an oxidizer for munitions and solid rocket fuel. It is necessary to have efficient and reliable treatment techniques that can remove perchlorate from both high-concentration process wastewaters and low-concentration drinking water sources to mitigate the potential environmental and health effects associated with the widespread use of perchlorate.

3.1.2.2. Perchlorate Treatment Methods

In past research, the removal of perchlorate from water is generally achieved either by anoxic biological reduction (Miller and Logan, 2000; McCarty and Meyer, 2005; Nerenberg et al., 2002) or physicochemical adsorption on ion exchange resins (Tripp and Clifford, 2006). Most of the previous work on biological perchlorate removal has focused on fixed-film processes using biologically active granular media filters or membrane diffuser reactors that use a membrane to feed hydrogen gas to a biofilm that grows on the membrane surface (Logan and LaPoint, 2002; Nerenberg and Rittmann, 2004). Past studies have shown that perchlorate can be biologically converted to a harmless chloride ion form under anaerobic conditions using both organic electron donors like acetate and inorganic ones like hydrogen (Xu et al., 2003). Microbiological treatment processes can provide very cost-effective removal of perchlorate and simultaneous removal of other target contaminants, but their use is hindered by concerns about process reliability (Kim and Logan, 2001; Roquebert et al., 2000), especially in the face of natural variations of influent concentrations, temperature, pH, etc. .

Alternatively, ion exchange processes with both strong and weak base anion resins have also been shown to effectively remove perchlorate. Many resins used for perchlorate removal can be at least partially regenerated with a salt brine, but disposal of concentrated perchlorate brines merely transfers the contaminant from one location to another and becoming an increasingly restrictive regulatory hurdle (Lehman et al., 2008). Perchlorate-specific, single-use resins are another option, but they suffer a similar disposal problem for the spent resin. Some recent work has developed a multistage regeneration technique for perchlorate-specific resin using tetrachloroferrate and hydrochloric acid (Gu et al., 2001), which should make single-use

resins more attractive. The major advantage of these adsorptive physicochemical processes is robust and reliable treatment, but they are expected to have higher costs, especially when ultimate disposal costs are included or when influent concentrations are higher. The needs for an acceptable disposal venue or further treatment remain as key limitations.

3.1.2.3. HAMBgR Process for Treating Perchlorate

To address the key limitations of currently available perchlorate treatment processes, a novel treatment process is introduced, the hybrid adsorption-membrane biological reactor (HAMBgR). The HAMBgR process integrates a granular ion exchange media directly into the mixed liquor of a MBR, which can be done without increasing size or number of membrane tanks. With this hybrid process, the ion exchange resin provides a temporary physicochemical sink for contaminants that maintains low effluent contaminant concentrations even during microbial upsets or adaptation to changing reactor conditions, which addresses the biological instability problem of conventional biological treatment systems. The process combination also provides continuous biological adsorbent regeneration, which avoids the cost, effort and undesirable environmental impacts of the concentrated brines that typically accompany ion exchange treatment of perchlorate. Finally, the membrane used in the HAMBgR process serves to retain the both the ion-exchange media and all microbes, which avoids any problems associated with microbial carryover.

Other process combinations have been proposed that utilize both biological and abiotic treatment components for perchlorate removal. For instance, Lehman et al. (2008) introduced a method for treating perchlorate ion-exchange regeneration brine using salt-tolerant perchlorate-reducing bacteria. Wang et al. (2008b) later reported that perchlorate laden ion exchange resin could regain significant capacity by direct biological regeneration without the use of a chemical brine. In this study, we build on the findings of these recent studies by demonstrating that in fact, these processes can be combined into a single-tank simultaneous process with synergistic benefits to complement both treatment components. Some key questions related to this novel process are as follows: (1) How effective is the resin for shaving effluent peaks during dynamic loading conditions; (2) How well is the resin regenerated when

integrated into the routine operation of an MBR (3) Is there a gradual irreversible loss of resin capacity when it is kept in contact with MBR biomass continuously over multiple potential loading cycles? This paper presents original bench- and pilot-scale experimental work that addresses these questions and compares the novel HAMBgR process with a conventional MBR treatment concept as it was developed and applied for the removal of aqueous perchlorate (ClO_4^-) from the wastewaters associated with the munitions manufacture for military activities.

3.2. Methods and Materials

3.2.1. Ion Exchange Resins

Three different types of commercial anion exchange resin manufactured by Rohm and Haas (Philadelphia, PA) or by Purolite (Bala Cynwyd, PA) were selected for this study. Amberjet-4400 is a strong base anion (SBA) resin with a quaternary ammonium functional group, initially in the hydroxide form. Amberlite IRA-92, pictured in Figure 3.1, has a macroporous polystyrene matrix and a binary amine functional group that results in a weak base anion exchange (WBA) resin, which is generally easier to chemically regenerate. For this resin, the amine functional group is in the free base form, which means that it has reduced capacity above neutral pH. In contrast, SBA resins can generally operate effectively over a wide range of pH. The third resin used in this study was Purolite's A532E, a perchlorate specific anion exchange resin with dual amine bi-functional groups, which make it highly selective for the relatively hydrophobic perchlorate ion. A comparison of key resin characteristics is provided in Table 3.1.

Table 3.1. Summary of characteristics for three resins.

Resin Model & Type	Manufacturer	Matrix	Functional group	Ionic form	Capacity ^[a]	Particle Size ^[b]
Amberjet® 4400 OH-Strong Base Anionic	Rohm & Haas	styrene-DVB	quaternary ammonium	hydroxide	1.33	0.58-0.68
Amberlite® IRA-92-Weak Base Anionic	Rohm & Haas	macroporous polystyrene	Secondary amine	free base	>1.55	0.60-0.80
Purolite® A532E-Perchlorate Selective	Purolite	styrene-DVB	bifunctional quaternary amines	chloride	0.75	0.55-0.65

^[a] Particle size expressed in millimeters.

^[b] Capacity expressed in meq/mL.

Note- Information in this table was provided by manufacturers' product data sheets and was not independently verified.



Figure 3.1. Photographs of Amberlite® IRA-92 anion exchange resin.

3.2.2. Batch Isotherms

To quantify and compare resin capacity over multiple cycles of biological regeneration, batch isotherm tests were conducted with fresh resins and biologically regenerated resins over with repeating cycles of abiotic loading followed by biological regeneration. For these tests, serum bottles were first loaded with varying amounts of ion-exchange resin (30 – 650 mg) and 100 mL of influent perchlorate wastewater solution with a target ClO_4^- concentration of 100 mg/L. The bottles were then placed on a shaking table at a mixing rate of 240 rpm and effluent samples were analyzed periodically for perchlorate concentration until an aqueous-phase concentration plateau was reached, which was operationally defined as equilibrium. Aqueous perchlorate samples were analyzed by ion chromatography using a Dionex ICS-2000 Analyzer with an AS-16 column, and the resulting analysis had a perchlorate detection limit of 5 mg/L. The pH of the batch isotherm solutions generally ranged between 7.2 to 7.7, but the first loading of the Amberjet 4400-OH resin was an exception. With this resin much higher pHs levels

ranging from 8.4 to 10.5 occurred during the first abiotic loading due to exchange of the original hydroxyl ions initially loaded on the resin surface.

After the resins reached abiotic equilibrium, active perchlorate reducing bacteria (PRB) were added to each serum bottle to induce biological regeneration. The PRB were supplied from an operating pilot MBR system, which is described below. Hydrogen was added to the headspace of each bottle up to a gas pressure of 172 kPa (25 psi), which served as the primary electron donor for the autotrophic PRB used in this study. The bottles were replaced back on the shaking table and temperature was controlled at 34°C to allow the PRB to degrade the perchlorate until the liquid-phase concentrations were below detection limit. Bottles were then decanted of the liquid and biomass, leaving behind the biologically regenerated resin for another abiotic loading cycle as described in the previous paragraph. Note that the resin was not rinsed between cycles to ensure all regeneration was strictly biological. The abiotic loading cycles were repeated up to six times with a fresh 100 mL of influent perchlorate solution added to each serum bottle. Although a small amount of residual PRB biomass could be carried over into the subsequent abiotic loading steps, no hydrogen electron donor was added to the headspace during this phase to avoid any significant biological perchlorate removal during the resin loading phase.

To assess longer term effects of continuous contact between ion exchange resins and MBR biomass, a batch isotherm test was also conducted using resin that had been exposed to the MBR biomass for at least 105 days in the pilot MBR system described below. For Amberjet 4400-OH, the resin contacting period was extended to 150 days. For these tests, the various resin quantities were weighed, added to a tea bag, and then installed into the MBR system. At the end of the desired contacting period, the tea bags were removed and the known resin amounts were placed into serum bottles with perchlorate spiked wastewater for an abiotic loading cycle as described previously.

3.2.3. Pilot Scale Operations

3.2.3.1. Reactor Setup and Normal Operation

A pilot-scale membrane bioreactor (Figure 3.2) was operated for 15 months-- switching back and forth between a conventional MBR mode and a HAMBgR mode by the addition of an anionic exchange resin to the microbial suspension and subsequent resin removal by sieving the reactor contents. The total reactor capacity was 12 L, but during operation the liquid volume was maintained at 10 L. At startup, the reactor was seeded with anaerobic digester sludge from the local municipal wastewater treatment plant, which was allowed to grow and evolve naturally over time. Anaerobic conditions were maintained in the MBR by feeding gaseous hydrogen and carbon dioxide to a coarse bubble diffuser stone installed at the bottom of the reactor and then recirculating gasses in the reactor headspace back to the diffuser stone at a rate of 1.5 standard L/min. The hydrogen gas served as the electron donor, and the carbon dioxide provided both pH control and a carbon source for the autotrophic perchlorate reducing bacteria. The membrane module used in the MBR, which was a Zee-Weed 1000 Jr hollow-fiber microfiltration module made by GE-Zenon with a surface area of 1 m². The hollow fibers are made from a hydrophilized polyvinylidene fluoride (PVDF) material with a nominal pore size of 0.04 µm, which is the same fiber used in many large-scale water purification applications. The membrane module was operated in a submerged mode with suction applied to the downstream side of the membrane and gas scour on the upstream external side of the membrane to control fouling. This configuration allows for operation with increased biomass concentrations and provides efficient use of the recirculating hydrogen and carbon dioxide gases for simultaneous reactor mixing, gas mass transfer, and membrane surface scouring.

The reactor was operated with a synthetic wastewater influent fed at different rates as needed to achieve HRTs in the range of 2 to 24 hours. Various influent perchlorate concentrations were used ranging from 100 - 1000 mg/L, and the influent also contained bicarbonate and phosphate buffers as well as a mixture of trace minerals shown in past studies to support PRB growth (Miller and Logan, 2000; Van Ginkel et al., 1995). The specific recipe of the influent solution is provided here: NaClO₄ (123.1 or 1231 mg/L), NaHCO₃ (793 mg/L),

$\text{NH}_4\text{H}_2\text{PO}_4$ (166.7 mg/L), $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ (33.3 mg/L), K_2HPO_4 (501.5 mg/L), $\text{NaH}_2\text{PO}_4 \times \text{H}_2\text{O}$ (254 mg/L), $\text{MnCl}_2 \times 2\text{H}_2\text{O}$ (0.66 mg/L), $\text{NiCl}_2 \times 6\text{H}_2\text{O}$ (0.066 mg/L), $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ (0.134 mg/L), $\text{CaCl}_2 \times 2\text{H}_2\text{O}$ (0.66 mg/L), $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ (0.334 mg/L), $\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$ (0.134 mg/L), $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ (0.26 mg/L), $\text{CoCl}_2 \times 6\text{H}_2\text{O}$ (0.26 mg/L), $\text{Na}_2\text{SeO}_3 \times 5\text{H}_2\text{O}$ (0.066 mg/L), and EDTA (3 mg/L). This same recipe with the lower perchlorate concentration was used in the batch isotherm tests discussed earlier.

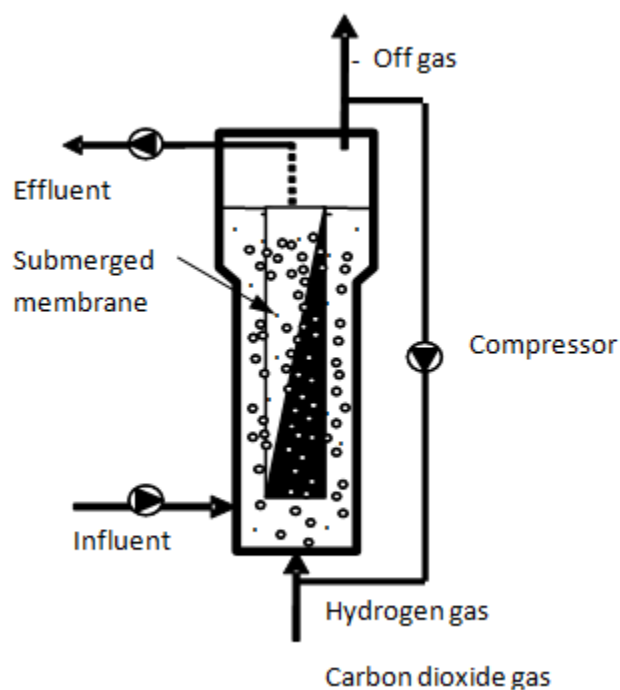


Figure 3.2. Schematic diagram of the membrane bio-reactor system.

3.2.3.2. MBR and HAMBgR Under Dynamic Loading

To assess and compare the response of the conventional MBR and HAMBgR process modes to sudden temporary changes in the influent contaminant concentration, the reactor was occasionally given an instantaneous pulse dose of perchlorate and the effect on effluent perchlorate concentration was monitored. In one case reported in this study, the reactor was operating steadily with a 24 hour HRT and 100 mg/L of perchlorate in the influent when a pulse dose of 500 mg of perchlorate (50mg/L) was injected directly into the reactor. This pulse dosing

experiment was repeated multiple times over a one week period both with and without resin in the reactor. IRA-92 weak base anion resin was used in this experiment at a concentration of 22 g/L of reactor volume, which accounts for approximately 2% of the total reactor volume. The reactor biomass concentration during these tests was 3.4 g/L (+/- 10%).

A second test was designed to compare the response to a continuous step increases in the loading of perchlorate during the two modes of operation. Preceding the test, the reactor was operated with complete perchlorate removal at 4 hr HRT, 100 mg/L influent perchlorate concentration and steady biomass concentrations. At the beginning of the test, the MLSS concentration was reduced to 0.68 g/L with the same loading rate. Measurements of effluent perchlorate and biomass concentrations were taken for 2 – 3 days until the loading rate increased by increasing the influent perchlorate concentration. Three target loading rates were testing under each mode of operation – 25, 125 and 250 mg $\text{ClO}_4^-/\text{L-hr}$. For this test, perchlorate selective A532E strong base anion resin was added to the reactor at a concentration of 4 g/L during the HAMBgR process mode.

3.3. Results

3.3.1. Comparison of Resin Isotherms

3.3.1.1. Initial Loading and Isotherm Shape

Figure 3.3 presents the results of a batch isotherm test with the three types of fresh ion exchange resin used in this study. This figure indicates that all three resins had significant capacity for perchlorate, but not surprisingly, the perchlorate specific resin (Purolite A532E) generally exhibited the highest capacity, followed by the strong base anion resin (Amberjet 4400-OH), and the weak base resin (Amberlite IRA 92) had the lowest capacity. Note that the WBA resin requires its functional group be protonated to most effectively exchange anions. By operating the IRA-92 batch tests at a pH between 7.3 and 7.7, which is beneficial for biological perchlorate removal, the WBA resin capacity is somewhat reduced. SBA resins, on the other hand, are fully effective over a wide range of pH from 0-13, according to manufacturers' literature. The isotherm for the Purolite resin has two distinct regions, a horizontal line on the

right side corresponding to resin saturation and a Freundlich form portion on the left side, where the log of the surface loading (q_e) increases linearly with the log of the equilibrium aqueous-phase concentration (C_e). The other two resins had a Freundlich form over the entire tested concentration range. The A532E resin is most advantageous at low equilibrium perchlorate concentrations ($C_e < 2\text{mg/L}$), where it showed more than 6 times the capacity of the other two resins.

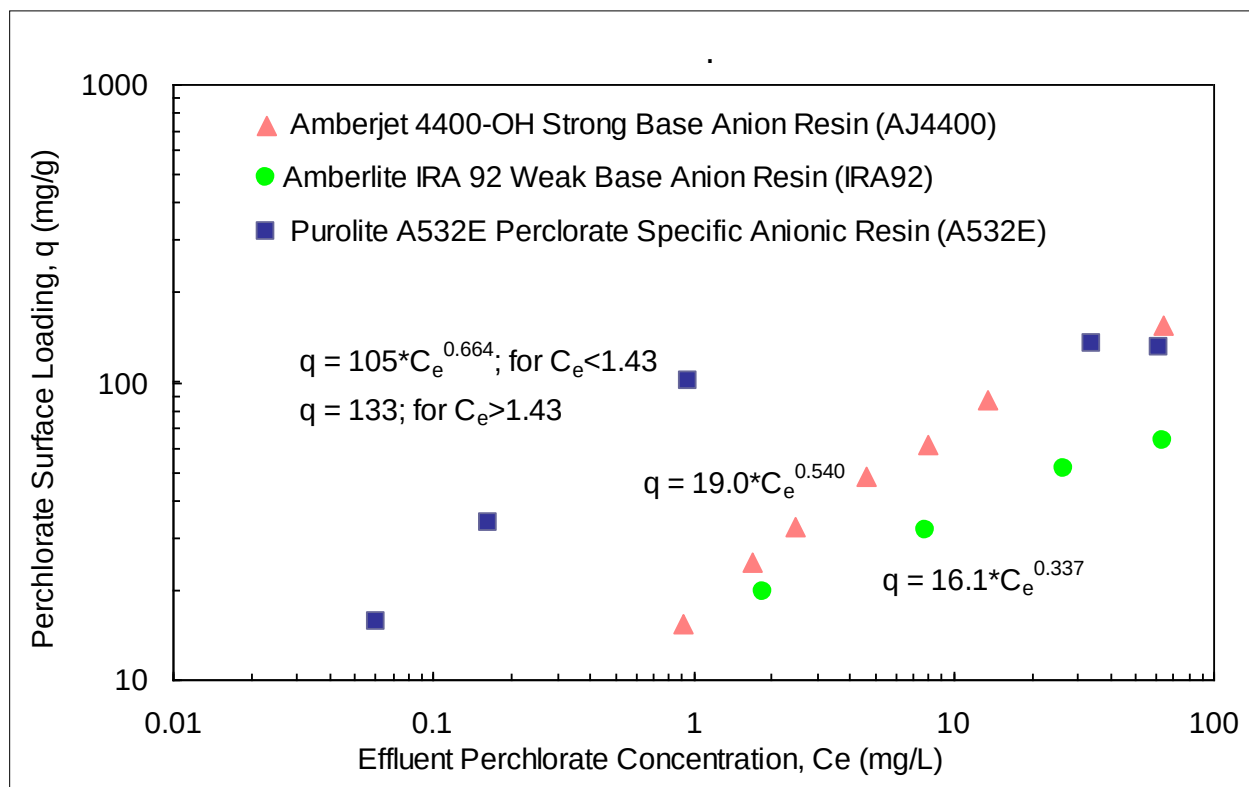


Figure 3.3. Comparison of isotherms for virgin anionic exchange resins.

3.3.1.2. Biological Regeneration of Resin

After the abiotic isotherm test with fresh resin, each of the resin bottles was dosed with hydrogen and PRB biomass from the MBR pilot reactor. After the PRB biomass degraded aqueous perchlorate concentration below detection, the biomass was decanted off and another abiotic loading cycle ensued. This process was repeated multiple times and results from successive abiotic loading cycles after biological regeneration are shown in Figure 3.4 – Figure 3.6. As shown in Figure 3.4, the resin capacity for the strong base resin (AJ-4400)

declined by an average of 35% over the first two biological regeneration cycles (range = 27% to 43% loss), but then it approached a stable working capacity that was maintained through a total of 5 biological regeneration cycles. Figure 3.4 also shows isotherm data for AJ-4400 resin after long-term (5 months) exposure to PRB in the MBR system. These data overlay the other biological regeneration data, indicating there was no additional capacity loss during longer-term contacting of resin with PRB.

The IRA-92 weak base resin, was also subjected to alternating cycles of abiotic loading and biological regeneration to measure the effects on resin working capacity. These data are shown on Figure 3.5. IRA-92 decreased in capacity by about 23% on average (range of 12 to 25%), which was slightly less than AJ-4400. As presented in Figure 3.6, the perchlorate specific resin was also biologically regenerated in the same type of cycling batch tests. The A532E resin showed an average capacity loss of 47 % (range of 40 to 57%). An isotherm after long-term exposure (3 months) contact with the PRB from the MBR system is shown for each of the Resins in Figure 3.5 and Figure 3.6. In both these cases, the working resin capacity after 2 biological regeneration cycles was approximately the same as resin samples that had been put in long-term. Thus, additional sequencing regeneration cycles were not considered necessary.

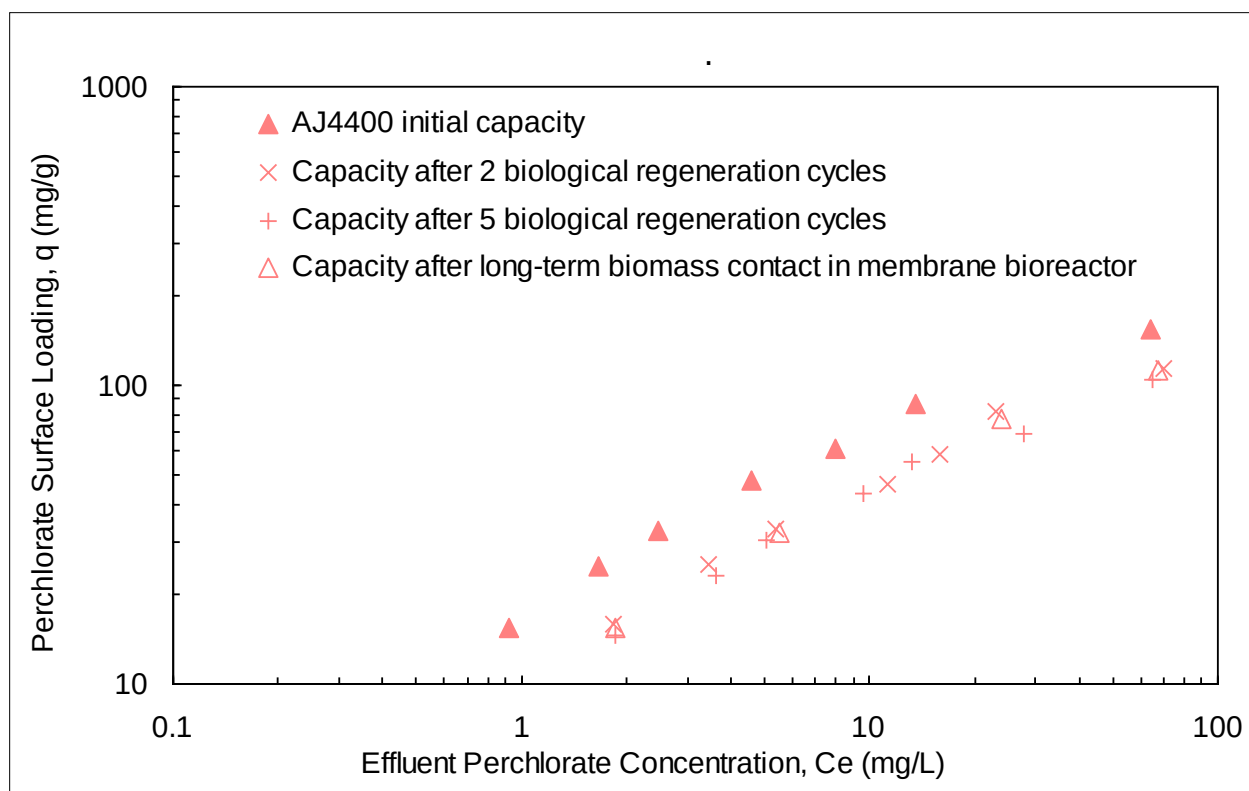


Figure 3.4. Comparison of AJ-4400 resin isotherms over multiple biological regeneration cycles.

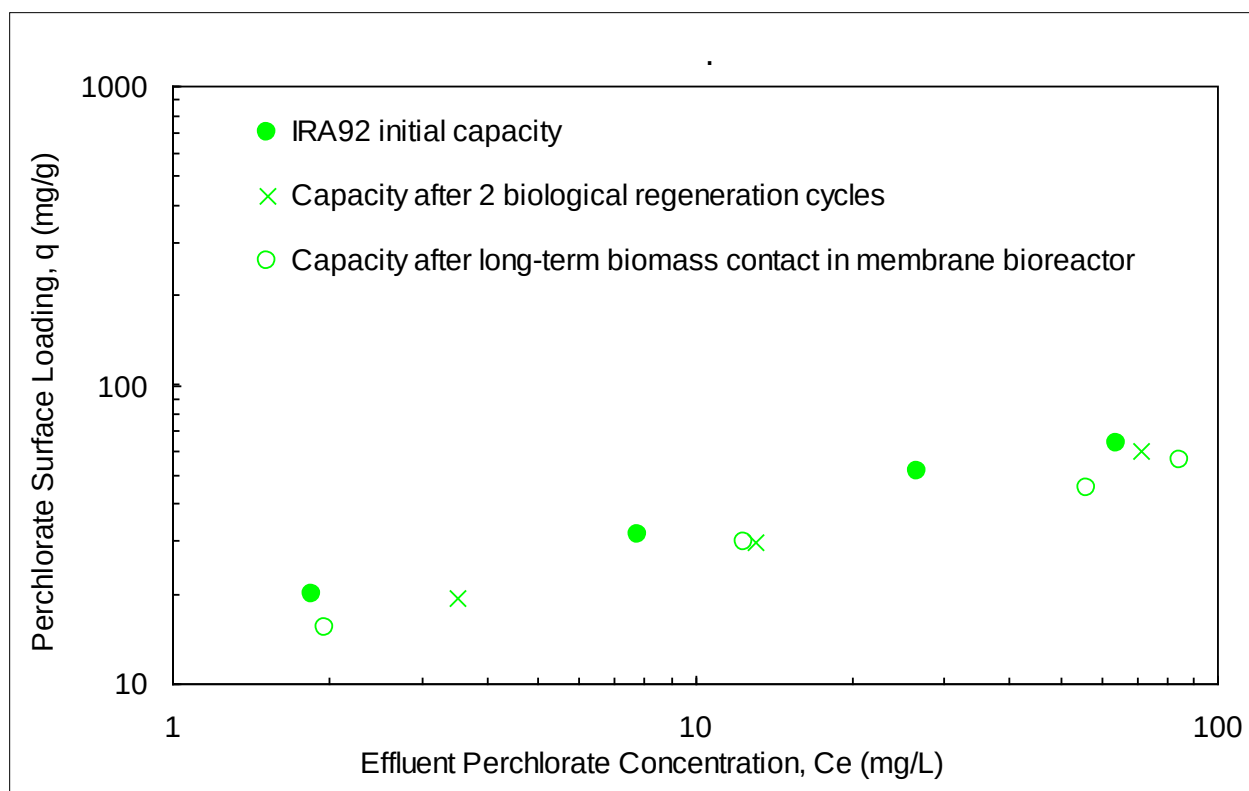


Figure 3.5. Comparison of IRA-92 resin isotherms over multiple biological regeneration cycles.

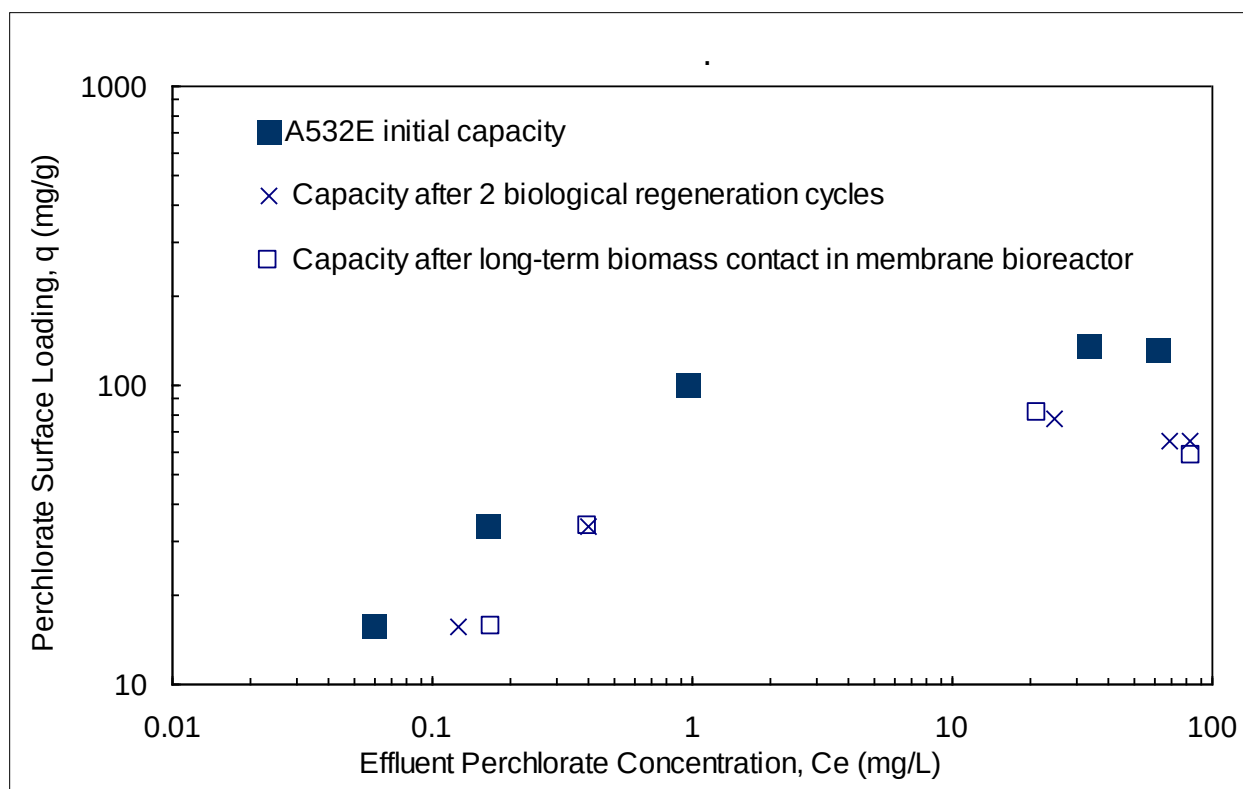


Figure 3.6. Comparison of A532E resin isotherms over multiple biological regeneration cycles.

Wang et al. (2008a) described a similar sequential biological regeneration scheme for perchlorate loaded resins, but included extra steps of chemically washing the resin with bleach and rinsing with distilled water rinse to inactivate and washout any bacteria. This previous study showed a loss of virgin resin capacity of 0 to 20% for 3 different resins over multiple regeneration cycles. Overall, the amount of resin capacity loss found in this previous study was lower than those observed in the present study. This could be due to different resin properties, lower surface loadings, or to the bleach wash and rinse cycles used in the previous study. For this study, we decided not to use a disinfectant cleaning step for two reasons. First, the bleach wash can serve a chemical regenerating solution for the resin due to significant anion concentrations, and this can make it more difficult to delineate strictly biological resin regeneration. Secondly, the HAMBgR process is intended to be a single reactor continuous process where the resin stays in contact with the PRB biomass for long periods of time. Thus, chlorine or other chemical washing of a resin would be disruptive to routine HAMBgR

operations, although it could be accommodated by occasionally removing the resin from the main reactor by sieving and then returning it after the chemical regeneration is completed.

3.3.1.3. Long Term Exposure of Resin to Bacteria

After the long term exposure of Amberjet 4400 resin to PRB in the MBR was done, a sample of the resin was viewed under the microscope to look at biofilm formation on the surface. The resin surface was smooth and there was no discernable buildup of bacterial biofilm on the resin surface. This is consistent with the findings of Wang et al. (2008), who also found no discernable biofilm on an ion exchange resin that was biologically regenerated.

All in all, these batch isotherm results suggest that the HAMBgR process could be an attractive alternative for continuous treatment of perchlorate contaminated water. The sequential nature of the tests clearly showed that the biomass could degrade previously adsorbed perchlorate and effectively regenerate a substantial working capacity for the resins. The working capacity decreases over the first few loading cycles, but then achieved a plateau value that remained consistent even during continuous exposure to PRB biomass for several months and multiple spike loading events.

So while biofouling of the resins on the timescales of few months was not found to be overly problematic, the question of slower long-term decline in ion exchange resin capacity remains an open issue that needs future attention. If it does occur, one mitigation strategy would be to provide occasional chemical regenerations/cleanings. Depending on the resin and membrane used in a HAMBgR process, it may be possible to clean/regenerate both of these process components at the same time and perhaps even with the same chemicals. This of course would help to minimize the net costs of the HAMBgR process. If infrequent chemical regenerations are needed to maintain long-term, multi-year usage of the resin, we found that the resin can be readily separated from the active biomass in the reactor, by sieving or screening the reactor contents.

3.3.2. MBR and HAMBgR Under Dynamic Loading Conditions

3.3.2.1. Response to Pulse Perchlorate Loading

In a conventional MBR and other biological reactors in general, there can be a period of poor performance in response to changes in influent conditions while the microorganisms grow or otherwise adjust to new conditions. In such cases, the HAMBgR process provides a physicochemical backup to the biological process that can attenuate or eliminate the spike in effluent contaminants that would normally occur while the biological process adjusts. To demonstrate this feature, the continuous flow pilot MBR system was first operated without any resin at pseudo-steady state and then perturbed with an instantaneous spike load of 500 mg of perchlorate (50 mg/L of reactor). Before this spike the MBR was operating with full removal of 100 mg/L of influent perchlorate at an HRT of 24 hours. Thus, the instantaneous spike contained the same amount of perchlorate that would normally have been delivered to the reactor in 12 hours (720 minutes). Figure 3.7 shows a dashed line that would correspond to the washout of the perchlorate spike if the biological perchlorate degradation rate remained the same as before the spike. However, the actual measured perchlorate effluent data after the spike, as shown with a solid line on Figure 3.7, indicated that the MBR biomass rapidly increased their uptake of perchlorate in response to the spike. The resulting effluent spike of perchlorate from the MBR peaked quickly at above 43 mg/L and took about 300 minutes to return to baseline conditions. Thus, in comparison to the simple washout scenario, the PRB biomass reduced the peak effluent level by 14%, but made a more significant reduction of 96% in the total amount of perchlorate that escaped the reactor.

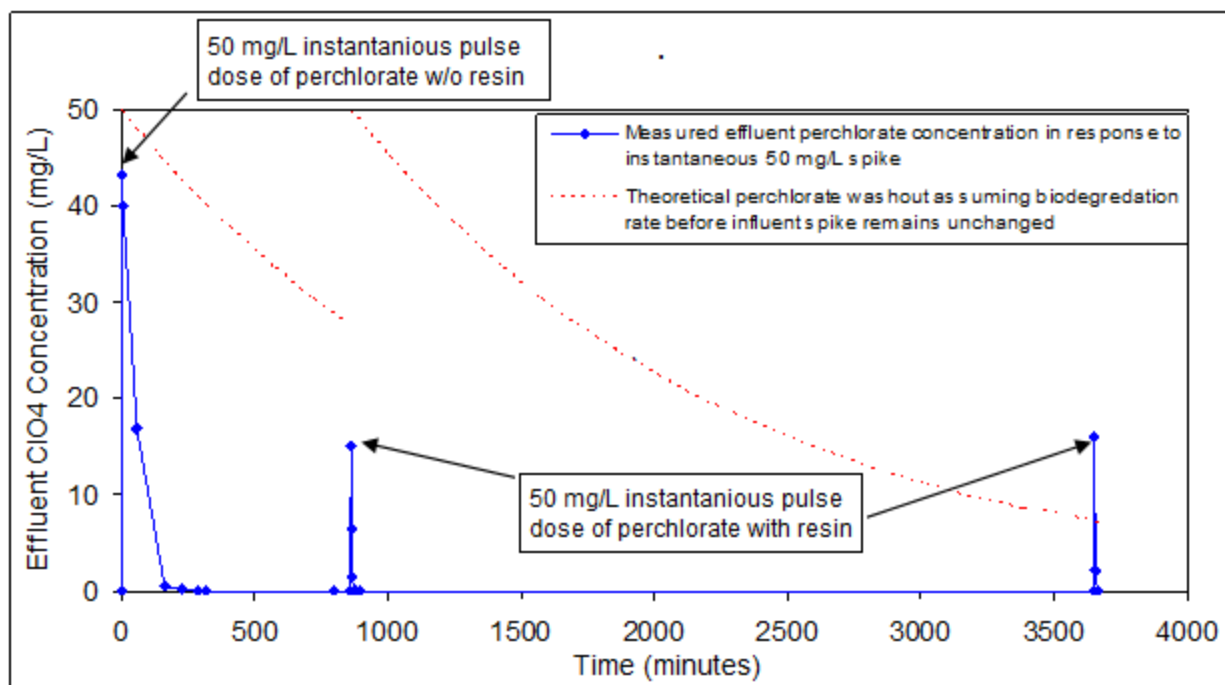


Figure 3.7. Comparison of perchlorate removal for MBR and HAMBgR processes in response to a spike load of perchlorate (50 mg/L).

A few hours after this spike had been attenuated, the reactor was switched over to HAMBgR mode by adding 225 g of IRA-92 WBA resin to the MBR (22.5 grams per L of reactor), and then was dosed with another instantaneous spike of perchlorate at 50 mg/L. Note, that the WBA resin was selected to provide a lower bound example of HAMBgR process performance because it had the lowest capacity of the resins tested. Even so, the HAMBgR system was able to significantly reduce both the maximum effluent pulse of perchlorate and the amount that escaped the reactor in comparison to the conventional MBR mode of operation. Figure 3.7 shows that following the same 500 mg pulse dose of perchlorate, the effluent concentration peaked at 16 mg/L for the HAMBgR process and returned to baseline levels in only 15 minutes. Thus, in comparison to the theoretical washout scenario, the HAMBgR process reduced the maximum effluent peak by 78% and only allowed 0.1% of the incoming spike to escape the reactor. This performance also represents a significant improvement over the conventional MBR. Directly comparing HAMBgR operation to the MBR without resin, shows that the maximum effluent peak was reduced by 63%, the spike was attenuated to background levels

more than 20 times faster, and the total amount of perchlorate that escaped the reactor was 96% less than the conventional MBR. The perchlorate spike with the HAMBgR operating mode was repeated two days later and yielded essentially the same result, which is also shown on Figure 3.7.

3.3.2.2. Response to Step Increases in Perchlorate Loading Rate

The shock test shows how the HAMBgR process can dramatically improve reactor effluent during an instantaneous influent spike. To further demonstrate the advantages of a physicochemical backup, a continuous stress test was performed under the two modes of operation. Influent perchlorate concentrations were increased from about 100 to 500 to 1000 mg/L with an HRT of 4 hours. Bacterial solids concentrations (MLSS) were reduced to the same level at the beginning of each test and measured throughout the tests. Each loading condition was maintained for 2 – 3 days except for the highest loading condition in the MBR, which needed more time to reduce effluent concentrations.

During MBR mode, the reactor effluent perchlorate peaked during each of the three loading conditions, shown in Figure 3.8, until biomass adapted and brought the concentrations to nearly zero. During HAMBgR mode, with only 4 g/L of A532E perchlorate selective resin, these effluent peaks were nearly eliminated. Operating in HAMBgR mode reduced the total amount of perchlorate released into the effluent by more than 99%. This is because of the temporary perchlorate sink that the resin provides, retaining more food in the reactor and allowing the biomass to feed more easily. The inclines of the peaks during MBR mode occur within the first few hours of feeding as the reactor undergoes hydraulic change and biomass begins to respond. This pattern is very clear in the first two peaks of Figure 3.8. The only significant peak during HAMBgR mode occurred at more than 20 hours after start to feed 90 mg/L influent. This indicates that the resin was uptaking excess perchlorate for a period of time, but then capacity exhaustion grew quicker than biological regeneration could replenish the ion exchange sites. At the end of the peak, biomass concentrations in HAMBgR mode were more than 25% higher than they were for the same loading condition of MBR mode, which supports the hypothesis that the resin-bacteria environment can assist biological growth by retaining

more electron acceptor. The increased biomass concentration during the first loading condition of HAMBgR mode allowed the second loading condition, 470 mg ClO_4^-/L influent, to be managed much more easily and there was no significant effluent perchlorate. Note that biomass concentration during this condition increased nearly 4 fold, compared to a 2 fold increase measured during MBR mode. The biomass concentration after the third loading condition during HAMBgR mode was 10 times greater than at the beginning of the test and appeared to be increasing further, but the experiment was stopped based on zero effluent perchlorate measurement. The total increase in biomass concentration during MBR mode was less than 6 fold, which appeared to be a temporary maximum. The tests shown in Figure 3.8 demonstrate that the HAMBgR process works in two ways to improve effluent quality during periods of sustained stress, with step increases in contaminant loading rate. The capacity of the resin alone can offer temporary relief while the organisms adjust. Also, by retaining more of the would-be-lost electron acceptor, biomass concentrations can increase faster, which further enhances the contaminant removal rate.

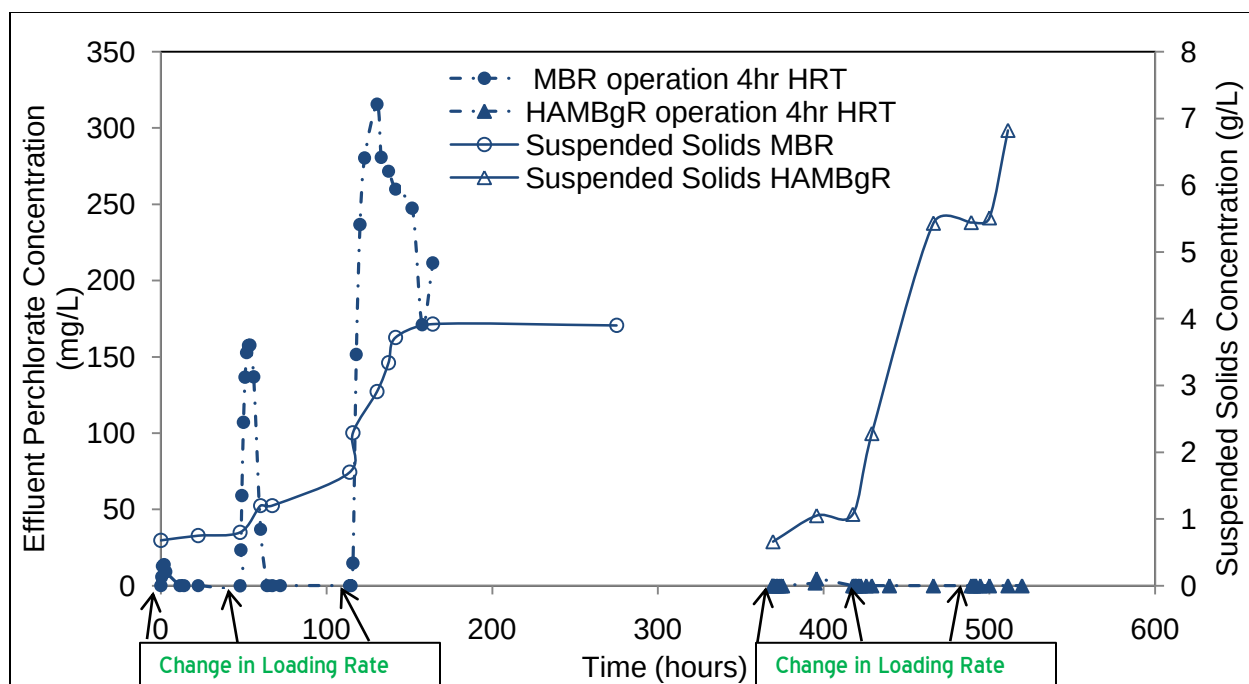


Figure 3.8. Comparison of perchlorate removal and biomass growth for MBR and HAMBgR processes in response to stepwise increases in loading rate – 25, 125 and 250 mg/L-hr.

Of course the performance of the HAMBgR process can be further improved by using more resin or a resin with a higher working capacity. This gives an MBR system designer a flexible tool for providing the amount of process redundancy and reliability that suits a particular situation. For instance, if a desired maximum effluent concentration criteria is set, and the biological process is assumed to have a total failure for a certain period, the resin isotherm (preferably after a couple cycles of biological regeneration) can be used to estimate the amount of resin needed to cover the biological process downtime. Furthermore, the HAMBgR process provides some opportunities to reduce the overall costs of biological treatment systems. For instance, biological processes are often designed with a certain level of safety factor in sizing and/or with large attenuation basins to smooth out variations in flow and other influent conditions. Providing redundancy in this way can be quite capital intensive as they require large heavy-duty hydraulic structures that are designed for significant structural loads. Additionally there can be extra operating costs associated with the energy to pump wastewater that is stored in certain peak shaving attenuation basins. The Deep Tunnel projects for combined sewer overflow in several major municipalities are an example of this kind of extra expenditure. The HAMBgR process can provide this kind of protection against variable influent conditions without the need to upsize or attenuate short-term peak load conditions. Instead it can be done in the main process reactors which have the ability to soak up extra pollutants on the adsorbent surface and release them slowly over a few days as the biomass adjusts to the dynamic conditions. This novel approach provides the potential for significant savings in many types of wastewater treatment systems.

3.4. Conclusion

This study introduced a novel process configuration for more reliable and potentially more cost-effective systems to provide biological treatment of wastewaters. Specifically, the novel process is referred to as HAMBgR (Hybrid adsorption-membrane biological reactor) and involves the addition of an ion-exchange resin directly into the mixed liquor of a membrane bioreactor (MBR) system. In this study we demonstrated the use of such a process for removal of perchlorate, a contaminant used in explosives and propellants that is commonly associated with a variety of military activities. Using sequential batch studies, we clearly showed that it is

possible to biologically regenerate the ion exchange resin and thus the HAMBgR process provides an efficient, in-situ, physicochemical backup to microbiological treatment processes. It allows them to provide consistent removal even during fluctuations in contaminant loadings and other factors that would otherwise result in decreased performance or failure of a conventional biological perchlorate removal system. By having adsorptive media acting within a biological reactor, target contaminants can be trapped until the microorganisms can adjust the dynamic influent conditions. The result, presented in this study, is more electron acceptor availability in the reactor and increased biological activity. At resin concentrations of only a few grams per liter of reactor, HAMBgRs can be a very cost effective improvement to conventional MBRs. Moreover, this study has also shown that spent perchlorate ion exchange resin can be regenerated without using potentially expensive or difficult to dispose of chemicals.

4. SUMMARY OF WORKS

Environmental water quality and water security are issues of increasing concern that are leading to inevitable adaptation and advancement of treatment technologies. As regulations become more stringent, an increasing number of facilities are finding it difficult to meet the required treatment goals with limited technological and economic resources. Biological treatment of contaminants such as ammonia and perchlorate is effective and well established, but is highly sensitive to temperature, loading rate, and aeration and can require longer reaction times than other physical or chemical methods of treatment. Separation technologies, like ion exchange and sorption, offer the ability to quickly and effectively remove targeted contaminants and concentrate them into brine. However, the cost and complexity of concentrated brine disposal is often restrictive.

Two original studies were presented in the previous chapters that demonstrate the prospects of combining ion exchange and biological treatment processes. Ion exchanging clinoptilolite was used to separate ammonium from municipal sewage in a small column reactor with a contact time of only 25 minutes. The capacity of the clinoptilolite increased over three loading cycles to nearly twice its original capacity, which was consistent with results from literature. Concentrated sea salt solutions were used to efficiently regenerate the column and concentrate all of the sorbed ammonium.

Avoiding expensive and complicated disposal tactics, the ammonium-laden brine was fed to halotolerant algae to remove the ammonium from solution. *Dunaliella salina* was able to best uptake ammonium in a solution of 50 g sea salt/L and without the addition of supplemental micronutrients. *Dunaliella parva*, on the other hand, grew best in 100 g/L and consumed all the ammonium within 25 days. The ammonium laden 100 g/L brine needed to be supplemented with micronutrients in order to support adequate algae growth. The limiting nutrient was not determined, but seems to be related to the alga's mechanism for surviving in high salt concentrations. Brine rejuvenation allowed for repeated use of the same regenerant solution and also generated algal biomass, which has a potentially high market value. The novel

ammonium treatment process needs further development, but has already shown signs of significant improvement over conventional nitrogen removal processes.

Secondly, a novel hybrid absorptive membrane biological reactor (HAMBgR) process was developed to effectively and consistently remove perchlorate from concentrated synthetic wastewater. Batch and continuous studies verified that perchlorate reducing bacteria were able to biologically regenerate three types of ion exchange resins, including a selective type prescribed as a single use resin, without the use of chemical brines. Though each resin experienced some loss in capacity over the first few loading regeneration cycles, a long-term working capacity was reached for each resin.

By augmenting a conventional MBR with anionic exchange resin, continuous and reliable removal of perchlorate was possible with improved responses to dynamic loading conditions, reducing effluent peaks by up to 99%. By retaining more electron acceptor in the reactor, biomass growth was stimulated and concentrations increased faster. Also, when perchlorate was instantaneously spiked to the reactor under HAMBgR mode, the effluent peak was reduced by 76% and completely eliminated in only 15 minutes, compared to 300 minutes under MBR mode. The results of this study show that the novel reactor concept can improve biological performance and possibly reduce the cost of treating perchlorate wastewater.

5. FUTURE WORK

Develop Ammonium Removal Concept

- Optimize specific operational parameters like contact time and column size and identify energy requirements for ion exchange separation in order to compare the proposed process to conventional nitrification and denitrification.
- Investigate parameters for halotolerant algae growth such as light intensity, mixing rates, and nutrient availability. Optimize those parameters for production of high value products, like beta-carotene or glycerol. Identify additional purification steps needed in order to use the biomass for commercial products and how that affects an overall cost balance.
- Apply the concepts developed in this study to other ammonium waste streams, like agricultural and industrial wastewater.

Apply Hybrid Adsorption-Biological Treatment to Other Contaminants

- Many metal contaminants are removable by cation exchange methods and are able to be uptaken by specific organisms. A combination of two effective technologies could produce results similar to those shown in the HAMBgR process, which could improve removal efficacy and reduce cost.
- Bacterial oxidation of many organics is possible, but not achieved in most wastewater treatment by the dominant species. Separation of certain organic contaminants by specialized adsorbents, like activated carbon or synthetic resins, can allow for sidestream biological treatment.

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