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Removal of ammonia peaks from effluent wastewater using nitrifying biofilm on zeolite

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Removal of ammonia peaks from effluent wastewater using nitrifying biofilm on zeolite

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Abstract

Elevated levels of ammonia in discharged water leads to eutrophication and potential toxicity in water bodies. To combat nitrogen pollution, strict ammonium discharge limits of $1mgNH_4-N/L$ standard is set by the water framework directory. In many cases, current wastewater treatment facilities struggle to consistently meet this standard, particularly during peak concentration periods. For years now, the influent's peak pattern has been mirrored in the biologically treated water and currently, there lacks an effective solution to address this issue. This study explores use of zeolite in a biological filter, a potential technology to remove ammonia peaks from effluent wastewater. The fundamental concept of this technology involves combining zeolite with a nitrifying biofilm. In this process, the zeolite dampens the ammonia peak by adsorption, while the nitrifying biofilm regenerates the zeolite. Clinoptilolite, a natural zeolite of 1mm particle size and synthetic wastewater were chosen in this study. The impact of competing cations was investigated due to clinoptilolite's affinity for cations. It was found that the presence of other cations decreases ammonium removal capacity by 6.2 times of which potassium is the main competitor. But, percentage of potassium removed is much less than ammonium though it's concentration is 5 times higher. 44.2% of the total potassium was removed in 60 minutes compared to 70.9% ammonium removal. In the experiments with the nitrifying biofilm, it was found, that it does not affect rate of adsorption by zeolite, but enhances ammonium removal. Experimental results indicate that zeolite can be bio-regenerated effectively, and rate of conversion is faster than rate of desorption of adsorbed ammonium. The system of zeolite and biofilm has some buffer capacity, but cannot compensate for the bicarbonate anions needed for H^+ released. A BioWin model was designed to simulate the survival of biomass during extended periods of low concentration, and the results indicated that conversion capacity of the system reduces after 7 days of DWF concentrations. But the biomass can sustain longer periods of DWF concentrations, but it takes some time and exposure to higher concentrations to revive it's capacity. In conclusion this study confirms the potential in this technology and confirms effective bio-regeneration capabilities. The results from this research can built upon to answer further knowledge gaps with reactor operation and design. This paves the way for future studies to make it an industrially viable technology.

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Abbreviations

BAF - Biological aerated filter
ZBAF - Zeolite Biological Aerated Filter
WWTPs - Wastewater treatment plants
HRT - Hydraulic Retention Time
BOD - Biological Oxygen Demand
COD - Chemical Oxygen Demand
DWF - Dry Weather Flow
RWF - Rain Weather Flow
WFD - Water Framework Directory
PZC - Point Zero Charge
DO - Dissolved Oxygen
IC - Ion Chromatography
AOB - Ammonia Oxidising Bacteria
NOB - Nitrite Oxidising Bacteria

1

Introduction

During the summer months, certain lakes in the Netherlands continue to exhibit substantial blooms of blue-green algae, attributed to elevated temperatures that stimulate the heightened activity of these organisms, forming dense layers of algae. (van Algemene Zaken, 2017). Abundant ammonium in water streams results in eutrophication and potential toxicity of estuaries, rivers, lakes, and coastal seas (Widiastuti, Wu, Ang, & Zhang, 2011). Due to that, algae grows rapidly and reduces dissolved oxygen in water and thereby causes death of living organisms in water. It can cause undesirable environmental health effects and can cause a shift in biodiversity and ecosystem balance (European commission, 2023). One of the reasons why the surface water quality is not up to standards is the discharge of poorly treated wastewater (van Algemene Zaken, 2017). Consequently, the elimination of ammonium from wastewater is a crucial to control nitrogen pollution. The EU Water Framework Directory (WFD) has set a limit of 1 $mgNH_4 - N/L$ and daily average of total nitrogen not exceeding 10 mg N/L (Water framework directory, 2020). The ammonium discharge limit is based on the receiving water body, but 1 $mgNH_4 - N/L$ is a common target and is also chosen as a discharge limit in this study.

A requirement exists for technological solutions capable of providing superior effluent quality while concurrently minimizing capital and operational expenditures, as well as reduced demand for energy. Taking into account the money, time and effort that is associated with development of novel technologies, prior quantification of advantages is necessary before committing to subsequent investments. In Europe, the availability of undeveloped or "greenfield" sites for constructing new wastewater treatment plants (WWTPs) is quite limited. As a result, considerable attention is directed toward the integration of innovative technologies within established WWTPs (Soares, 2020)

In certain scenarios, relying solely on existing biological treatment solutions proves inadequate for efficiently addressing fluctuating and elevated influent ammonium concentrations. Consequently, it falls short of achieving the intended effluent quality standards (Baykal & Güven, 1997). In such cases, a polishing step is desired and a Biological Aerated Filter (BAF) is one such possibility. BAF functions as a flexible reactor, offering a compact footprint choice at different phases of wastewater treatment. Equipped with granular media that supports substantial biofilm growth owing to its large surface area-to-volume ratio, the BAF system also serves as a submerged filter for eliminating suspended solids. Operating as a fixed-film process, it enables maintenance of optimal conditions for applicable microorganisms, independently of hydraulic retention times (He, Xue, & Kong, 2007). The selection of a suitable BAF media is critical in the design and operation of the process, to enable the required effluent standards to be reached. Natural zeolite- Clinoptilolite as a media for BAF will not only support microbial growth but also assist in removal of ammonium by adsorption ion-exchange due to it's high affinity for the cation. Hence this research investigates the potential of the concept of removal of ammonium peaks from effluent wastewater using zeolite with a nitrifying biofilm.

Research on using zeolites for ammonium removal has been extensively done in the past few decades, but it has not materialised into an effective treatment solution. Some of the research gaps that hinders its application will be answered in this study. Major reasons for potential in this technology includes zeolite's high affinity for ammonium, ease of operation and low costs, small footprint, possibility to operate at low ammonium concentrations where it is difficult to maintain biomass and reliable performance at low temperature.

This is a research case for Waterschap- Rijn en IJssel, where the treatment capacity of an existing treatment plant is optimized to treat ammonium load to desirable effluent standards under dry weather conditions. But it is not possible to remove peaks of ammonium that occur due to rain weather flow. When long dry periods without rainfall let pollutants to build on land and in the sewer, during rain events, these non-point sources of nutrients run off with the rainwater and causes an initial flush of nutrients to the treatment plants (Gunaratne, Vogwill, & Hipsey, 2016). In such cases, the total pollution load is higher while treatment time is lower due to increased flow rate, resulting in a peak in ammonium concentration. This peak results in undesirable effluent water characteristics which does not abide by the water framework directory. An additional treatment technology is thus desired to reduce the ammonium peaks. Hence the proposed new treatment technology involves the use of zeolite as a support material and ammonium adsorber for nitrifying biofilm which will result in the overall conversion of peak ammonium loads to nitrate. For years now, the influent's peak pattern has been mirrored in the biologically treated water (Baykal & Güven, 1997) and currently, there lacks an effective solution— a broad, non-specific polishing treatment— to address this issue. Consequently, the development of the proposed technology could potentially serve as a valuable post-treatment method for wastewater treatment plant effluents, given its robust nature and straightforward operational simplicity.

An overview of the theoretical background for this research regarding application of zeolite as an ammonium adsorption medium, nitrifying biofilm and a combination of the two including past research on the topic and influencing parameters is discussed in chapter 2. After comprehending theory and prior literature, the unknowns regarding the technology and the resulting research questions will be addressed in chapter 3. After that an overview of materials and methods (including research setup) is given in chapter 4 . It is followed by results and discussion in chapter 5, a conclusion part in chapter 6 and concluding with recommendations in chapter 7.

2

Literature Review

Several solutions including but not limited to hybrid approaches have been proposed to remove ammonium from wastewater. They include oxidation, nano filtration, air stripping adsorption and precipitation (Vocciante et al., 2018). The biological removal method involves nitrification of ammonium to nitrite and nitrate followed by denitrification to nitrogen gas. But it is hard to maintain high biomass concentration when substrate concentration is less. Particularly, autotrophic bacteria like nitrobacter and nitrosomonas is more difficult to sustain (Kim, Lee, Choi, Zhu, & Lee, 2019). Zeolite with nitrifying biofilm is a potential treatment solution to tackle the issue of maintaining biomass concentration and dampening of ammonium peaks. High potential in this technology is due to

- Low cost natural zeolite's high affinity for ammonium (removal by ion exchange). Particularly, adsorption methods are acknowledged for their dependability and environmental friendliness, attributed to their minimal chemical usage and operating conditions.(Vocciante et al., 2018)
- Ion-exchange has a competitive advantage over biological methods and air-stripping when it comes to low temperature operations and low footprint. (Widiastuti et al., 2011)
- AOB populations thrive well in low concentrations of ammonia nitrogen with the assistance of zeolite media (Kim et al., 2019)
- The settling rate of bio-flocculated zeolite was found to be 2-3 times greater compared to the system lacking zeolite, as observed during experimentation. (Montalvo, Huiliñir, Borja, Sánchez, & Herrmann, 2020)
- Hybrid activated sludge systems, equipped with biofilm-supporting media, presents a viable and economical approach for retrofitting wastewater treatment plants to maintain nitrification. This can be accomplished without substantial increments in suspended growth concentration, thus avoiding the need for enlarging reactor or clarifier capacities. (Andraka, Dzienis, Myrzakhmetov, & Ospanov, 2016).
- Adsorption could serve as a substitute for ammonium removal in cases of low BOD/N ratio or in colder seasons at wastewater treatment facilities when nitrification and denitrification efficacy is diminished. (Hedström & Amofah, 2008)

But it is essential to understand the fundamentals of the process and parameters that affect it to determine the feasibility of the process in practical applications.

Thus, this background study is done to understand the processes individually and determine the necessary parameters to be studied. Moreover, this also gives insights into previous research on this topic to determine research gaps.

2.1 Zeolites theory

2.1.1 Adsorption

Ion exchange is an adsorption process in which equilibrium exists between a constant number of ions on the resin (solid phase) and ions in aqueous phase (Ramkumar & Mukherjee, 2012). The principle of ion exchange is that it is a process in which similarly charged ions are exchanged between an electrolyte solution in aqueous phase and an ion exchange material in solid phase. The reactions are based on stoichiometry and are reversible (Nasef & Ujang, 2012). Adsorption is the process where a substance accumulates at the interface between phases, either physically or chemically. Impurities in water accumulate at the solid-liquid interface. This phenomenon occurs when the adsorbate- the substance being removed from the liquid, prefers to reside on the surface of the adsorbent-the substance on which adsorption occurs, driven by a lower free energy state (Crittenden et al., 2012).
From a thermodynamic perspective, the adsorbate has lower free energy at the surface compared to being in solution. Therefore, during the process of equilibration, the adsorbate is driven onto the surface to achieve a lower energy state, which is favored according to the second law of thermodynamics. In a system at constant temperature and pressure that is not in equilibrium, it will spontaneously work to reduce its Gibbs free energy (Crittenden et al., 2012). In the case of ion adsorption, the most significant mechanism is electrostatic attraction, which is highly influenced by factors such as pH and ionic strength which will be discussed in detail in later parts of this report (Ramkumar & Mukherjee, 2012)

Adsorption isotherm At equilibrium, the system consisting of the solvent, adsorbate, and adsorbent reaches a state of minimum free energy (Crittenden et al., 2012). This necessitates the use of adsorption isotherms, which describe the equilibrium state of the adsorbate and adsorbent. Specifically, an adsorption isotherm describes the equilibrium concentration of the adsorbate on the adsorbent as a function of the bulk concentration of the adsorbate in the solution at a given temperature (Crittenden et al., 2012). The analysis of adsorption isotherms yields significant insights into essential parameters, such as the maximum adsorption capacity (mg/g) and the underlying adsorption mechanism. These findings hold great potential in the development and optimization of advanced adsorption systems aimed at wastewater treatment. (De Magalhães, De Sousa, & Peres, 2022)
They are used in the design of an adsorption system by providing information about capacity of the adsorbent - amount of adsorbent needed to eliminate a unit mass of pollutant under the given system conditions. (Kučić, Markić, & Briški, 2012) Of the numerous adsorption isotherm models available, commonly applied models for adsorption of ammonium on zeolite are the following 2 models.
Langmuir and Freundlich adsorption isotherms: The Langmuir isotherm is extensively utilized in the field of water treatment for describing the adsorption of compounds. It is favored due to its simplicity, physical foundation, and capability to effectively fit a wide range of experimental data. The model is based on several assumptions, including the independence of adsorption energy on the degree of surface coverage (although real surfaces are heterogeneous), reversibility of bonds, and the formation of a monolayer. (Crittenden et al., 2012) It is represented by the equation:

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \tag{2.1}$$

where C_e is the equilibrium concentration in mg/L
q_m is the maximum adsorption capacity in mg/L
K_L is the Langmuir constant in L/mg

and q_e is the equilibrium adsorption capacity in mg/g

On the other hand, the Freundlich isotherm attempts to address these assumptions by assuming an exponential decrease in the frequency of sites associated with the free energy of adsorption as the free energy increases. Although the Freundlich isotherm is empirical and lacks a theoretical basis for its underlying assumptions, it is widely employed for fitting observed data in practice. (Crittenden et al., 2012) It is represented by the equation:

$$q_e = K_F C_e^{1/n} \tag{2.2}$$

where C_e is the equilibrium concentration in mg/L
K_F is the Freundlich affinity parameter in $(mg/g) * (L/mg)^n$
n is the Freundlich constant and a function of adsorbetnn heterogeneity (-)
and q_e is the equilibrium adsorption capacity in mg/g
(De Magalhães et al., 2022).

Multi component adsorption Ideal scenario for adsorption where effluent water with just ammonium ions seldom occurs. There are competing cations with ammonium like potassium, sodium, calcium and magnesium. This complicates the application of the above theories of adsorption in practise as the real system now comprises of several adsorbates on a single adsorbent. Further elaboration on competing cations follows in the later sections.

Adsorption kinetics Thermodynamically, an equilibrium state exists between adsorbent and adsorbate, the removal of components in water treatment is determined by the rate of adsorption when in contact with the adsorbent (Lito, Cardoso, Loureiro, & Silva, 2012) Rate controlling step simplifies the kinetics of adsorption based on one of the operating parameters like temperature, bulk concentration of solute, etc. This is because in most cases, one phenomenon is much larger affects the rate much larger than the others and the other steps of kinetics can thus be neglected. In water treatment bulk transport is usually fast and thus the rate controlling step is mostly diffusion (Crittenden et al., 2012). All the theories for ion exchange commonly agree that it is a stoichiometric reversible reaction, it is an adsorption process, ion redistribution occurs through diffusion and the rate determining step is particle diffusion or film diffusion (Ramkumar & Mukherjee, 2012).

2.1.2 Desorption

The reuse of zeolite is heavily dependent on desorption of the adsorbed ammonium. Desorption can be induced by varying pH, temperature or by ion exchange processes. But these are complicated or energy intensive (Lu et al., 2019). Since this process is ion exchange, desorption of ammonium occurs when ammonium is exchanged with another cation from the bulk solution. Thus theoretically, desorption of ammonium will not occur in demi water.
A conclusion on ammonium desorption studies by different researchers over the years is presented below.

- Higher selectivity of zeolite for K^+ over $NH_4{}^+$ resulted in the desorption of $NH_4{}^+$ which was replaced by K^+ (Rivera-Utrilla, Aguilar-Armenta, González-Gutiérrez, Guerrero-Coronado, & Mendoza-Barron, 2004).
- On desorption with 1% NaCl, the new equilibrium was close to that of adsorption indicating that ion exchange on zeolite is reversible (Widiastuti et al., 2011).

- On using tap water in experiments to initiate desorption of adsorbed ammonium, larger water volumes and increased contact time resulted in increased desorption. 23% of adsorbed ammonium was desorbed with continuous tap water circulation for 48 hours whereas only 1% of the ammonium was desorbed with 0.15L of tap water that was changed every 24 hours initially and then after 35 hours and continued for 6 days (Hedström & Amofah, 2008)

(Lu et al., 2019) and (Lin et al., 2013) observed desorption of ammonium driven by concentration gradient when the concentration of ammonium in the influent was lowered. This is the scenario which will be used and studied in this research to regenerate zeolite. Zeolite will be loaded with ammonium during high ${NH_4}^+$ concentrations during RWF and desorption of ammonium is expected when concentration is lowered during DWF.

2.1.3 Properties, structure and types of zeolite

Zeolites are tectosilicates in which some Si^{4+} ions have been replaced by Al^{3+} ions, creating an unbalanced distribution of negative charges (Muscarella, Badalucco, Cano, Laudicina, & Mannina, 2021). Ion exchange properties displayed by these materials are due to the presence of permanent ionic sites attached to their framework, which is held together by lattice energy or chemical bonds. Ions with opposite charges, called counter ions (cations in this research case) migrate throughout the structure and can be replaced by ions with the same charge (Nasef & Ujang, 2012). Cations like sodium, potassium, ammonium, calcium, and magnesium balance out the overall negative charge on the zeolite (Hedström & Amofah, 2008). In fact, in natural zeolites, the exchange sites are occupied by the alkaline earth metal ions mentioned above that the chemical composition of even identical zeolite samples may be different (Boulinguiez, 2005). The porous structure of zeolite consists of interconnected cavities which contains water and cations.(Boulinguiez, 2005). The adsorption of ammonium on zeolite depends on ion exchange capacity, particle size and selectivity of the zeolite, and temperature and pH of the solution (Kučić et al., 2012). Selectivity refers to the ability of the ion exchanger to differentiate between the counter ions. This is dependent on factors such as electrostatic attraction between charged framework and counter ion - with focus on size and valance. Larger counter ions might be kept out of narrow pores of the resin (Nasef & Ujang, 2012). The cation exchange capacity (CEC), expressed as milliequivalents/g of exchangeable cations, is a function of the material's chemical and physical characteristics (De Magalhães et al., 2022). Theoretically calculated exchange capacities or those calculated by agitation experiments overestimates the capacity of the zeolite. Hence operating capacity or breakthrough capacity is a more appropriate value (Hedström & Amofah, 2008). .

Type of zeolite The three natural zeolites that are predominantly used in industrial applications are Clinoptilolite, mordernite and phillipsite. Natural zeolites tend to be irregular in structure and has loose micro pores and micro channels. Hence the possibility of structural damage is higher (Lu et al., 2019). Though phillipsite was discovered to be more efficient in removing ammonium, its weak structure made it undesirable.Moreover, most successful studies for ammonium removal using zeolite are on clinoptilolite (Boulinguiez, 2005). It is predominantly considered for the selective removal of ammonium due to it's high affinity for the ion. It has also been studied for use as a possible filter media for biological aerated filter (BAF) and equalize ammonia peaks in secondary effluent (He et al., 2007). Desired effluent ammonium concentration of 1 mg $NH_4 - N$/L was achieved by (Baykal & Güven, 1997) and (He et al., 2007) by dampening peak loads of ammonium using the Clinoptilolite filter. On the other hand, there are synthetic zeolites, manufactured to remove ammonium which have larger specific surface area, high density and are well structured. Resins which are highly cross-linked tend to be harder and highly resistant to mechanical breakdown, but less access to counter ions (Nasef & Ujang, 2012). There is a trade-off between performance and costs in this case, since natural zeolites tend to be cheaper. So weighing pros and cons for particular application is important.

Pretreatment of Clinoptilolite Pre-treatment is similar to regeneration of zeolite, where clinoptilolite in its desired form of sodium is achieved for effective removal of ammonium since sodium ions are exchanged with ammonium in solution (selectivity discussed in the following sections). Theoretically, for ammonium adsorption, the practical adsorption capacity of zeolite increases with pretreatment with Na-homoionic solution (Hedström & Amofah, 2008). Pretreatment is done with acid (HNO_3, HCl), NaOH and NaCl predominantly. The results of this pretreatment is not uniform in literature and contradicts each other where some see improvement in efficiency with acid treatment whereas some researchers found decrease in effectiveness for the same (Boulinguiez, 2005). This can be associated with the diversity in zeolite composition from place to place. Muscarella et al. (2021) studied the effects of acid and alkaline treatment on clinoptilolite and concluded that untreated & HCl-Na treated zeolite adsorbed highest amount of ammonium which was 27% higher than NaOH-Mg treatment. Pretreatment with $CaCl_2$ and $MgCl_2$ reduced adsorption, likely due to inefficient exchange between NH^{4+} and Ca^{2+} or Mg^{2+}. More on competitive cations is discussed in the further sections. Moreover, pretreatment with NaOH resulted in faster saturation compared to HCl treatment. This may be due to stronger ionic bond formation between O of clinoptilolite and Na^+ compared to the covalent bonds from alkaline treatments, hence resulting in lesser number of sites for ion exchange (Muscarella et al., 2021). Heating (also a form of pretreatment) of zeolite at $600°C$ for an hour does not increase removal capacity, but an increase in selectivity for ammonium was observed (Boulinguiez, 2005)

Ammonium can exchange with zeolite on the external surface as well as the internal pores (Widiastuti et al., 2011).Before delving deep into factors that influence the removal of ammonium by zeolite - Clinoptilolite, it is important to understand the removal mechanism. The following section explains in depth the process of adsorption - ion exchange.

Influencing parameters

Under particular conditions, clinoptilolite has a greater affinity for ammonium than for others and separation can be facilitated. The influencing factors are discussed below in detail. Chemical selectivity is desirable but is not a necessity for ion exchange.

2.1.4 Effect of contact time

In research by Mazloomi and Jalali (2016) the NH^{4+} removal by clinoptilolite increased with contact time up to 48 hours and then remained constant. 85% of the adsorption was complete in the first 30 minutes and only a slight increase in removal from 85% to 91.2% from 30-2880 minutes. So 24 hours contact time would be good for equilibrium studies analysis (Mazloomi & Jalali, 2016). Equilibrium may be achieved in the first few minutes in studies by other researchers because initially all adsorbent sites are empty, and the NH^{4+} concentration gradient is high, but then the decrease in adsorption sites and concentration gradient lead to decreased rate of ${NH_4}^+$ adsorption (Mazloomi & Jalali, 2016). Consequently, at lower flow rates ammonium removal is higher (Boulinguiez, 2005).

2.1.5 Effect of particle size

Research by Kučić et al. (2012) on variation of adsorption capacity with particle size concludes that capacity and removal efficiency increases with decrease in size of the zeolite particle. This is expected since adsorption is a surface phenomenon and surface area increases with decreasing particle size. This is only until particle size of 0.35mm, below which ammonium removal becomes ineffective due to increased pressure drop and thereby decreased permeation of water in the zeolite bed. Optimal adsorption was obtained for particle size between 0.3-0.7mm (Boulinguiez, 2005). Different particle sizes were evaluated and 1mm was best suited for use in fixed and fluidized bed reactors due to highest adsorption equilibrium and adherance of microbes. But population of nitrifiers were similar for all sizes and remained the dominant population among the communities discovered (Mery et al., 2012)

2.1.6 Effect of pH

Interpreting pH gives valuable insights into high purity water treatment systems.

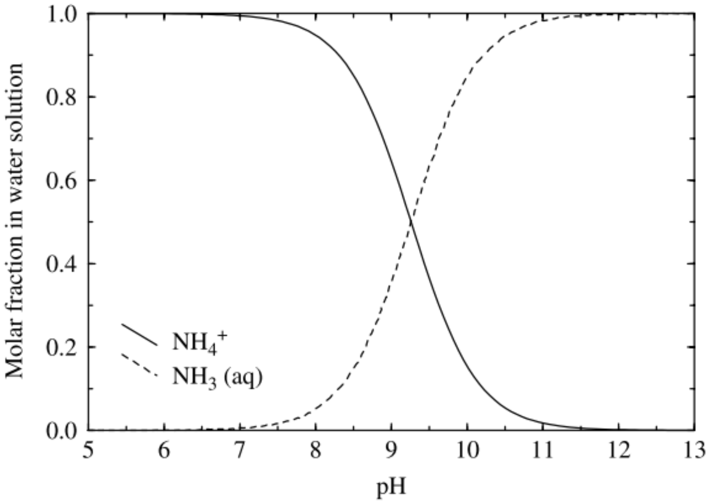


Figure 2.1: Speciation diagram of ammonia in water solution at 25°C.
Source: Rivera-Utrilla et al., 2004

From figure 2.1 we can see that below pH of 7 all the predominant form is ammonium. Moreover, the pH of effluent water that needs to be treated is between 7-8 and lowering the pH of that water and then again increasing pH to compensate the release of H^+ due to nitrification is not practically feasible. At pH above the point of zero charges, zeolite surface presents a negative charge. Zeolite can acquire a positive charge below Point Zero Charge (PZC), thereby making it inefficient in removing cations due to repulsion. For clinoptilolite PZC = 3 and in the pH range of 3-11 the clinoptilolite particles are negatively charged (Pavelić et al., 2017). Moreover, zeolite structure starts to collapse or dissolve with reducing pH in aqueous solutions, especially when pH is below 4 (Mazloomi & Jalali, 2016). Dealumination of zeolite (removal of Al^{3+} ions from zeolite, resulting in decreased exchange capacity with cations) occurs at pH 0 for clinoptilolite, but structural changes and dealumination were not observed between pH of 4-6 (Muscarella et al., 2021).

In literature, a trend on the effect of pH cannot be generalised for clinoptilolite. A conclusion on effect of pH from different studies is itemized below.

- Decline of $NH_4{}^+$ removal at acidic conditions of pH <5 was observed. This likely due to the increased number of H^+ ions in solution competing for the exchange sites of zeolite

(Mazloomi & Jalali, 2016). At pH of 3, lower adsorption of ammonium was observed probably due to competition with H^+ ions. Due to protonation reaction, the surface of the zeolite is stated to acquire a positive charge, thereby repulsing other cations due to electrostatic repulsion, which also reduces ammonium removal. (De Magalhães et al., 2022)

- The greatest removal of ammonium with natural clinoptilolite was found to be at pH range of 5-8 (Widiastuti et al., 2011).
- When varying pH for different initial concentrations of ammonium, maximum removal was observed at pH 7. Though the concentrations of ammonium used in this study are much higher (140-840 mg/L) when compared to the concentrations chosen in this research (1-20 mg/L) (Kithome, Paul, Lavkulich, & Bomke, 1998).
- Change in pH value from 6.5 to 9.5 did not affect ammonium removal efficiency significantly (Lu et al., 2019)

Invariably, a compilation of different studies on the effect of pH indicate that the best results can be obtained at a pH close to neutrality (De Magalhães et al., 2022), which is in favor for this study since the pH of effluent wastewater is between 7 and 8.

2.1.7 Effect of competitive cations

Cations compete with ammonium in terms of selectivity and concentration. (Vocciante et al., 2018). The selectivity sequence for removal of ions from wastewater by clinoptilolite is $K^+ > NH_4{}^+ > Na^+ > Ca^{2+}$, Mg^{2+} (Kithome et al., 1998). This is also supported in research by (Widiastuti et al., 2011) who found that presence of K^+, $SO_4{}^{2-}$, Na^+, Mg^{2+} and Cl^- has a negative effect on ammonium adsorption rate. The the order of selectivity presented is almost the same in most literature with interchanging of selectivity of K^+ and $NH_4{}^+$. This is because of similar size and equal charge of $NH_4{}^+$ and K^+ cations (Hedström & Amofah, 2008). When 2 ions are of similar charge and size, the selectivity of ion exchange resin arising from the material properties such as acidity, basicity and degree of cross-linking are not enough for effective removal of desired ion.

Appropriate complexing agents can be added to vary selectivity coefficients, but in the practical sense it is complicated and is not used in the design of an ion exchange system (Nasef & Ujang, 2012). These exchangeable cations are important in the functioning of zeolite as an ion exchanger for ammonium. The exchange process between the monovalent $NH_4{}^+$ ions and the divalent Ca^{2+} or Mg^{2+} ions is less effective. As the charge of the adsorbed cation increases, the ability of a cation to displace another adsorbed cation on the exchanger diminishes. This can be attributed to the amplified electrostatic interaction force between the divalent cation and the negatively charged surface sites on the exchanger (Muscarella et al., 2021).

A conclusion on effect of cations studied by different researchers over the years is presented below.

- Cationic competition was observed to reduce ammonium breakthrough capacity of a zeolite column by more than half when compared to pure synthetic ammonium solutions (Hedström & Amofah, 2008).
- When evaluating the effect of different compensation cations on $NH_4{}^+$ removal, highest ammonium removal potential was exhibited by Na^+ (Haji et al., 2016).
- Exchange capacity for ammonium reduced from 24mg/g to 10mg/g in the presence of competing cations under similar experimental conditions (Vocciante et al., 2018).

- Selectivity of ammonium is higher than hydrogen ion (Widiastuti et al., 2011). H^+ is released during the process of nitrification. But this release in H^+ will not affect ammonium removal by zeolite (It is not a competition unless pH ≤ 3 as discussed above)

Though the availability of exchange cites are reduced due to this competition, the interactions between cation-exchange sites and ammonium are stronger. (Vocciante et al., 2018).

2.1.8 Initial ammonium concentration and zeolite loading

The ammonium removal efficiency increases with increase in zeolite loading due to higher availability of sites for ion exchange. At a certain value of loading the equilibrium is attained, indicated by a plateau in the isotherm curve (Kučić et al., 2012). At constant initial concentration for different zeolite loading, the ammonium exchanges completely with the cations on the zeolite surface and reaches equilibrium. (Widiastuti et al., 2011). Zeolite's capacity to adsorb ammonium also increases with higher ammonium concentration in the influent solution. (Kučić et al., 2012). This is due to a greater driving force for migration of ammonium from solution to zeolite (Widiastuti et al., 2011).

2.1.9 Effect of Temperature

Temperature increase results in increased mobility of ions and promotes expansion of the zeolite's crystalline structure. This results in an increased adsorption rate (De Magalhães et al., 2022) Study on the effect of temperature on exchange isotherm reveals that the cation exchange capacity increased by 1.05 times when temperature is raised from $15 - 25°C$ and increases by 1.12 times when it was raised from $25 - 40°C$ (Rivera-Utrilla et al., 2004) However, (Hedström & Amofah, 2008) claims ammonium adsorption by natural zeolites is independent of temperature.

2.2 Nitrifying Biofilm

Theory of biofilms and factors that affect the growth and maintenance of biofilms as discussed in (Van Loosdrecht et al., 1995) are listed below.

- Dilution rate is the ratio of flow of medium into the reactor and the reactor volume. (Maier & Pepper, 2015) At lower dilution rates, the suspended microbes consume majority of the substrate that is fed to the reactor and maintains itself. Thus biofilm formation is not required for the biomass to stay in the system. Whereas at higher dilution rates, suspended growth occurs sometimes, but biofilms when formed are heterogeneous with large protuberances. This results in higher detachment due to shear, thereby increased sloughing. Thus dilution rate cannot be too low or high.

- Studies show that surface roughness enhances development of biofilm to an extent where some studies show that it is of higher importance than physicochemical surface characteristics.

- At higher temperature, activity is higher resulting in faster growth of attached biofilm. Roughness of particle helps with protection from detachment for longer duration to facilitate irreversible adhesion and eventually growth of the biofilm.

- Rate of biofilm growth depends on higher substrate surface loading and high yield of the associated organism. Biofilms with lesser density will not affect the transport rate of the substrate and thereby results in faster growth.

- Equilibrium biofilm thickness is the balance between growth rate and detachment rate as a function of biofilm thickness. Hence, the growth of biofilms fed with low substrate concentrations results in the formation of smooth structure without protuberances.
- To get a stable biofilm it is important to apply shear on the biofilm, else a thick heterogeneous biofilm may develop. Shear forces have a smaller effect on smooth biofilm than on a biofilm with protuberances. Moreover, increase in shear stress results in increase in density of pure culture biofilm (Vieira, Melo, & Pinheiro, 1993).

Biofilm thickness of 100-250 microns is desired for improved removal efficiency (Pak, Chang, & Hong, 2002). Excess biomass can slough from the biofilm and a clarifier might be needed to reach effluent quality in the later stages of developed biofilm on the carrier (Metcalf & Eddy, 2004)

2.2.1 Nitrifiers

The important microbial species responsible for nitrification are Nitrosomonas and Nitrobacter. They are autotrophic bacteria and hence consume inorganic carbon and oxidise inorganic nitrogen compounds to generate energy (Pak et al., 2002). The CO_2 that is used by the nitrifiers needs to be reduced which requires energy. Hence, when compared to heterotrophs, growth rate and yield of cell mass is lower. (Metcalf & Eddy, 2004) Nitrosomonas, which oxidises ammonium to nitrite obtains more energy per mole of nitrogen oxidised when compared to nitrobacter, which oxidises nitrite to nitrate. Hence greater amount of the former is expected when compared to the latter (Pak et al., 2002). Due to the above reasons, there is a possibility of retarded presence of Nitrobacter under conditions like limited oxygen, low temperature and elevated inlet ammonium loads. This leads to nitrite buildup in the system and process failure. Clinoptilolite has a additional benefit in this situation by regulating the initial nitrogen levels, thereby providing a protected environment for the growth of Nitrobacter (Pak et al., 2002). Theoretically, nitrification rate declines at a pH of water less than 6.5 as bacterial activity is inhibited by insufficient alkalinity (Qiu, Zhang, Wang, & Du, 2010). Optimum pH for growth of ammonia oxidisers is between 7.9 - 8.2 and that of nitrite oxidisers is 7.2 - 7.6 (Daalkhaijav & Nemati, 2013). Stable nitrification reaction is vital in ensuring the desirable nitrogen removal standards in the effluent water (Pak et al., 2002).

Nitrifying biofilm growth on zeolite Under similar reactor conditions of temperature and shear stress, nitrifiers form a denser (less porous) and stronger biofilm when compared to heterotrophs even though they are fast growing acidifiers. Density of a pure culture of nitrifying biofilm increases with increase in shear stress on the biofilm (Van Loosdrecht et al., 1995) & (Vieira et al., 1993). Slow growing organisms like nitrifiers form a stronger and less porous biofilm than fast growing organisms like heterotrophs (Van Loosdrecht et al., 1995). Favorable environment is created for Nitrobacter (which converts Nitrite to Nitrate) by zeolite by reducing ammonium toxicity resulting in outgrowth of Nitrobacter on zeolite (Pak et al., 2002) Additionally, on analysing the biomass in the biofilm of zeolites and expanded clay of 2 BAFs operated similarly in the work by (He et al., 2007), the authors claim that there is a more favorable environment for nitrifying bacteria in the biofilter with zeolite when compared to the expanded clay. This can be due to its affinity for ammonium.

A summary on effect of nitrifying biofilm on zeolite studied by different researchers over the years is presented below.

- Zeolite is perceived for its benefits of improved resistance to 2 inhibitors of nitrifying biomass - sulfide and organic matter. Better nitrification performance was observed in the presence of these inhibitors when compared to the control system at zeolite concentration of 15g/L (Huiliñir, Fuentes, Esposito, Montalvo, & Guerrero, 2019). Zeolite thus also exhibits catalyst characteristics to nitrification, by resisting sulfide and organic matter inhibition and also resisting free ammonia inhibition. (Montalvo et al., 2020).

- Cheng, Flavigny, Hossain, Charles, and Cord-Ruwisch (2018) studied the effect of salinity on nitrification in a BAF with zeolite and discovered that the NaCl had undesirable effect on ammonium adsorption and nitrification, but didn't lead to a system crash during the operational period. Hence a ZBAF can handle high saline content (which occurs sometimes during ice seasons in the Netherlands).
- Bio-regeneration by nitrification was achieved without prior desorption or liberation of the adsorbed ammonium from the zeolite's surface, but this was not the case with every research. This is due to the difference in the clinoptilolite used in the studies (Boulinguiez, 2005).
- Presence of zeolite resulted in robust biofilm (400-600μm thickness), resulting in enhanced settling property of the biomass. (Montalvo et al., 2020)
- In a fixed biofilm system, biological nitrification could lead to a localized pH reduction within the biofilm compared to the surrounding bulk water. This pH decrease at the biofilm's rear section might amount to approximately a 1 pH unit or more reduction in comparison to the bulk pH (Szwerinski, Arvin, & Harremoës, 1986)

Nitrification is difficult to sustain when ammonium concentration in the zeolite resin is low (Boulinguiez, 2005). This may be the case when the zeolite is emptied between 2 RWF periods and sustaining the biofilm during this interval is something to be considered.

Effect of temperature Research by (Kim et al., 2019) shows that nitrification by nitrifying biofilm over zeolite was maintained even at temperatures below $10°C$ and ammonium removal efficiency remained at 79% when there was sudden temperature decrease to $4.7°C$ from $20°C$. The water used in the study was pond water with low ammonium concentrations. However, the concentrations and effect of other cations present in the water were not evaluated. On the other hand, in the work by (He et al., 2007) at temperatures between $7 - 10°C$ it was observed that nitrification rate was reduced, but ammonium removal efficiency was maintained due to ion exchange with zeolite.
This technology is especially favorable in the cold climates, when clinoptilolite can adsorb excess ammonium while nitrifying activity is low and takes time to adapt to the lower temperatures.

Aeration Aeration of the effluent wastewater is required during the process since 4.57mg of O_2 is required to convert 1 mg of NH_3 to NO_3^- (Metcalf & Eddy, 2004). And supplying aeration to the system is highly energy intensive (about 65% of total energy consumption in wastewater treatment plant is from aeration) step because

- Air must be compressed and pressurised against the water column of the reactor
- Oxygen transfer efficiency is low (ranges from 4.8% to 34.1%)
- The poor solubility of oxygen in water at $25°C$ and 1 atm is only 8 mg/L. (Cheng et al., 2018)

Nitrification is limited by feed oxygen content, hence aerating feed to column is not sufficient. Direct oxygenation of column had better performance than supplying oxygenated feed to column, both of which performed better than non aerated feed. (Inan & Baykal, 2005)

2.3 Supplementary Insights

Zeolite can adapt to shock loads of ammonium. Effluent $NH_4 - N$ through the BAF column of zeolite remained stable when concentration of influent was doubled. This was compared to same experiment performed with expanded clay BAF which resulted in upto 15 times higher effluent $NH_4 - N$ when compared to the former (He et al., 2007).

In the experiments performed by (Baykal & Güven, 1997) it was concluded that bio regeneration in zeolite used as a column filter is not sufficient to regenerate the zeolite and hence chemical regeneration is required to sufficiently regenerate the zeolite. This is also due to columns not being aerated to sufficiently enhance biofilm activity. Moreover, chemical regeneration in combination with bio-regeneration is not a feasible solution since the formed biofilm will die in the process and will have to re-grow after the chemical regeneration step. These factors should be considered when designing columns for continuous experiments.

Standardised tests under different conditions for different zeolites is necessary to to identify the best suited zeolite for removal of ammonium. However this is hard since natural zeolites vary in composition and performance in different parts of the world, and characterizing clinoptilolite from one region does not necessarily guarantee it's similarity to clinoptilolite in another region. But standardised tests will help with framework to characterize the zeolite under consideration and evaluate it's performance against the standards.

3

Problem statement and Research questions

Long dry periods without rainfall let pollutants to build on land and during rain events, these non-point sources of nutrients run off with the rainwater and causes an initial flush of nutrients to the treatment plants. This peak in ammonium concentrations results in undesirable effluent water characteristics which does not abide by the WFD. Current treatment technologies used at Waterschap- Rijn en IJssel can treat ammonium loads to desirable effluent standards by optimisation of existing technology under dry weather conditions. Capacity of the water treatment plant is already optimized and it is not possible to remove peaks of ammonium that occur due to rain weather flow. An additional treatment technology is thus desired to reduce the ammonium peaks.

Table 3.1: Cation concentrations measured during dry and rain weather flow at Winterswijk Wastewater treatment plant.(n.d) signifies values that are not determined.

Ca^{2+} **(mg/l)**		Mg^{2+} **(mg/l)**		K^{+} **(mg/l)**		Na^{+} **(mg/l)**		**Q** (m^3/day)	**Flow type**
Not filterd	Filterd	Not filterd	Filterd	Not filterd	Filterd	Not filterd	Filterd		
n.d.	49	n.d.	13	n.d.	43	n.d.	170	6,164	DWF
49	42	14	13	70	69	160	150	5,788	DWF
55	51	18	17	92	90	190	190	6,211	DWF
47	41	11	10	46	45	130	110	6,485	DWF
44	42	10	10	57	56	140	130	8,310	DWF
38	31	9.9	9.1	52	52	94	93	14,040	RWF

The table above shows the concentration of Sodium, Potassium, Magnesium and Calcium cations measured at the Winterswijk wastewater treatment plant during different flows in the months of October and November of 2022. The ammonium concentration is about 0.5 - 1 mg $NH_4 - N/$L during Dry weather flow (DWF) and upto 18 mg $NH_4 - N/$L with an average concentration of 8 mg $NH_4 - N/$L during rain weather flow (RWF).

Biological removal cannot serve as the supplementary treatment step due to low conversion efficiency at low concentrations (owing to substrate limitation). Additionally, maintaining sufficient biomass during low ammonium concentrations in DWF for handling subsequent RWF peak concentrations is challenging. Ion exchange using natural zeolite is another possibility, but the main barrier in industrial scale is the regeneration of zeolite after saturation. It is possible to regenerate it with salt solutions like NaCl, but that results in a impure salt stream with high ammonium concentration, which cannot be discharged without purification, thus requiring additional expenditure on treatment.

This introduces a prospective technology that amalgamates the two aforementioned approaches. Zeolite could potentially function as an ion exchanger to mitigate ammonium peaks, while also providing a support for the nitrifying biofilm. The adsorbed ammonium can subsequently be digested by the biomass. Moreover, this could potentially serve as a concentrated ammonium source for the biofilm, enabling efficient conversion to nitrate. But existing research on this technology have not explored removal under low ${NH_4}^+$ concentrations and fluctuating flows, where increased flow rate is accompanied by higher concentrations. Moreover, studies focusing on the conversion of ${NH_4}^+$ by zeolite biological filters have not discussed the effect of competitive cations present in water on zeolite. This is an important factor in this research since the concentration of ammonium in effluent wastewater is much less when compared to other cations as can be seen in table 3.1. Additionally, there is also the question about the potential of zeolite regeneration and the associated time frame. Hence, the purpose of this research is to bridge the gaps regarding fundamental and operating aspects to determine the viability of this potential technology.

Research question

Can Zeolite with a nitrifying biofilm be used as a polishing step to remove ammonia peaks under different effluent flows?

The main research question can be divided into the following sub-research questions that cover different aspects of the research gap to effectively tackle the problem.

Sub-research questions:

- What is the impact of competitive cations, specifically varying ratios of ammonium and potassium, on ammonium adsorption by zeolite?
- Does biofilm influence rate of adsorption of ammonium by zeolite?
- Is it possible to completely regenerate the zeolite with the nitrifying biofilm?
- How is conversion impacted when the concentration fluctuates between DWF and RWF concentrations?
- What is the buffer capacity and oxygen requirements of the system?
- Does the biomass exhibit resilience over extended periods of low ammonium concentration, ensuring an adequate nitrification capacity during subsequent RWF concentration?

4

Materials and Methods

The experiments in this research are divided into the following parts :

- To characterize the performance of zeolite in ammonium removal the following batch experiments were performed
    - adsorption isotherm experiments for ammonium ions alone and for ammonium ions in the presence of competitive cations.
    - adsorption kinetics and fitting the kinetic data to kinetic models to form an equation that represents the kinetics of ammonium removal by clinoptilolite.
    - desorption of ammonium from clinoptilolite due to lowered concentration (in DWF) in the presence of competing cations.
- To grow a biofilm over the clinoptilolite
- To analyse performance of the combined technology in removing ammonium from effluent wastewater which includes
    - effect of biofilm on adsorption kinetics
    - buffer capacity of zeolite in solution during nitrification without addition of bicarbonates to feed
    - study of performance of the system of zeolite with biofilm under varying concentrations during DWF and RWF.
- A simulation on BioWin to predict the survival of biomass under prolonged periods of DWF concentrations.

4.0.1 Zeolite composition and properties

Clinoptilolite - a natural zeolite mineral, mined and supplied by *ZeolithKaufen*, Germany was used in this study. This was chosen because of it's higher affinity for ${NH_4}^4$ than K^+ and it's compressive strength as mentioned in the product description which is attached in the appendix A.4. Samples of diameter 1 mm were sieved from a size range of 0.3-1 mm and were washed with demi-water until the supernatent was clear. This is to remove the surface impurities present as dust. The washed sample was dried in an oven at $105°C$ for 2 hours (Muscarella et al., 2021). The compressive strength of the granule is 336.51 kg/cm^2 as given in data sheet provided by the producer. The composition of the mixture and chemical composition of clinoptilolite is given below in table 4.1 and 4.2. Particle size of 1 mm was chosen based on literature as mentioned in section 2.1.5. Moreover, this particle size is a good balance between high surface area, preventing resin carryover with product water and having increased head loss over column in real life applications.

Table 4.1: Mineralogical composition of zeolite sample used in this research(in %)

Clinoptilolite	**Cristobalite**	**Feldspar**	**Mica**	**Edisonite**	**Quartz**
86 - 90	5 - 8	2 - 4	2 - 4	0.1-0.3	traces

Table 4.2: Chemical composition of Clinoptilolite used in this research (in %)

SiO_2	Al_2O_3	CaO	K_2O	Fe_2O_3	Na_2O	MgO	$TiO2$	Si/Al
69.83 - 71.31	12.64 - 13.06	3.12 - 3.58	2.97 - 3.15	0.7 - 1.66	0.2 - 1	0.7 - 1.2	0.19 - 0.28	4.8 - 5.4

The bulk density of the clinoptilolite is also high (1600-1800 kg/m^3) which facilitated changing feed during experiments, but restricted fluidisation in reactor setups.

4.0.2 Synthetic wastewater composition

All the chemicals used in this experiment were of analytical grade of 99% purity procured from Sigma Aldrich. All the solutions and dilutions were made in de-ionized water. The synthetic wastewater used in the zeolite characterization experiments was prepared by dissolving K_2SO_4, $NaCl$ and NH_4Cl in tap water or demi-water. The concentration of salts were decided based on the average DWF and RWF concentrations provided by Waterschap- Rijn and IJssel as shown in table 3.1. The amount of salt was calculated based on stoichiometry and dissociation. These particular salts were chosen based on their pH in solution after dissociation. It is desired to maintain pH between 7 and 8 (preferably 7.5) to represent real life effluent water values. Tap water was used as base in multi-ion experiments since pH is already in desired range. A consolidation of different compositions is presented in the table below

Table 4.3: Composition of synthetic water for zeolite adsorption-desorption experiments.The ion concentration, alongside the salt concentration in the table, signifies the cation concentration based on average concentration during respective flows from table (3.1)

Sample	NH_4Cl **(mg/L)**	NH_4-N **(mg N/L)**	$NaCl$ **(mg/L)**	Na^+ **(mg/L)**	K_2SO_4 **(mg/L)**	K^+ **(mg/L)**
Dry weather flow	3.85	1	256.85	145	129.27	65
Rain weather avg flow	31.11	8	124.61	93	100.3	52
Rain weather max flow	68.28	18	124.61	93	100.3	52
Only $NH_4{}^+$ ion sample	31.11	10.5	-	-	-	-

The amount of salt mentioned in table 4.3 is corrected for the amount of respective the cation already present in tap water. The measured tap water of Delft already contains 44 mg/L Na, 7.4 mg/L of K and no NH_4. Ca and Mg concentrations in tap water were already in the range provided in table 3.1, hence it was not added. pH of the samples were adjusted by addition of 5 mol/L H_2SO_4 or NaOH solution prepared by dissolving 100 mg NaOH pellets in 1L of demi-water . All experiments were done at room temperature, which varied between $18-23°C$. Effect of temperature on removal was studied in literature in sections 2.2.1 and 2.1.9 and it was decided that this variation can be neglected.

A modified version of the synthetic growth medium used by (Daalkhaijav & Nemati, 2013) and trace elements solution of (Van De Graaf, De Bruijn, Robertson, Jetten, & Kuenen, 1996) is used in this study. The concentrations were adjusted based on ion concentrations used in this study as given in table 3.1. Table 4.4 shows the composition of synthetic waste water which was used as growth medium for the nitrifiers. The compounds were dissolved in demi-water for medium preparation to avoid the high hardness content of tap water.

Table 4.4: Composition of synthetic wastewater and trace elements solution used for growth and maintenance of nitrifiers as described by Daalkhaijav and Nemati (2013).

Compound	**RWF Concentration (g/L)**	**DWF Concentration(g/L)**
NH_4Cl	0.031	0.004
$NaHCO_3$	0.339	0.530
$CaCl_2.2H_2O$	0.114	0.165
KH_2PO_4	0.070	0.070
$KHCO_3$	0.082	0.102
$MgSO_4.7H_2O$	0.092	0.128
H_2SO_4	0.005	0.005
Trace Elements solution 1	1 mL	1 mL
Trace Elements solution 2	1.25 mL	1.25 mL

And the composition of trace elements 1 and 2 mentioned in table 4.4 is given below in table 4.5

Table 4.5: Composition of trace elements as described by Van De Graaf et al. (1996).

Trace Elements solution 1

Compound	**Composition (g/L)**
$FeSO_4.7H_2O$	9
EDTA	6

Trace Elements solution 2

Compound	**Concentration (g/L)**
EDTA	15
$ZnSO_4.7H_2O$	0.43
$CoCl_2.6H_2O$	0.24
$MnCl_2.4H_2O$	0.99
$CuSO_4.5H_2O$	0.25
$NaMoO_4.2H_2O$	0.22
$NiCl_2.6H_2O$	0.19
H_3Bo_3	0.014

4.1 Adsorption and Desorption Experiments

4.1.1 Experimental procedure

Isotherm - Solution with only ammonium ions Variable adsorbent dosages method is chosen over variable concentrations method to determine adsorption isotherm since data is more reliable (Ayoob, Gupta, Bhakat, & Bhat, 2008). The isotherm experiments were carried out by adding varying masses of zeolite to 100 mL of prepared synthetic wastewater solution as described in table4.3. 7 samples of Zeolite mass ranging from 0.1g to 2g (0.1, 0.4, 0.7, 1, 1.2, 1.5, 2) were chosen based on equilibrium adsorption values at low concentration found from literature (Baykal & Güven, 1997) and (Cyrus & Reddy, 2011). The pH of the solution was increased to 7.2 by addition of 13mL of 5.25 mmol/L of NaOH. Na^+ (which is a competitive cation) has negligible calculated concentration of 0.0681 mmol. The experiment was performed at room temperature of 16.9$°C$ for a duration of 24 hours (Cyrus & Reddy, 2011) & (Mazloomi & Jalali, 2016).

Isotherm - Solution with ammonium and competing cations The procedure was the same as mentioned above except - 1) A change in zeolite mass range was required due to lower removal of ammonium in the presence of competing cations. Hence, zeolite mass of 1, 1.2, 1.5, 1.7, 2, 2.2 and 2.5 g in 100mL feed each was used. 2) pH of the prepared solution 4.3 was decreased to 7.69 by the addition of 8 μL of 5M H_2SO_4. 3) Experimental temperature was 16.7$°C$

Kinetic experiments Zeolite loading of 20.5g/L was chosen from isotherm data for removal of 10.5mg/L of NH_4 for Rain weather average flow (RWF_{avg}) feed (100mL) with competing cations. Experimental temperature was 20.1$°C$ and pH was 7.83 with addition of 8 μL of 5 M H_2SO_4. The samples were collected at preset time intervals to determine concentration of ammonium in the solution at that time.

Desorption kinetics 2.1g zeolite was saturated with 100mL of (RWF_{avg}) concentration until equilibrium and then desorption was initiated by changing feed to DWF concentration. Experimental pH and temperature were 7.83 and 20.2$°C$. This was also done for (RWF_{max}) concentration to determine maximum ammonium desorbed during varying concentrations. The pH of feed in this case was 7.38. The zeolite sample was washed twice with demi water between change from DWF to RWF in order to ensure removal of residual ammonium from previous feed. The samples were collected at preset time intervals to determine concentration of ammonium in the solution at that time.

4.1.2 Experimental setup

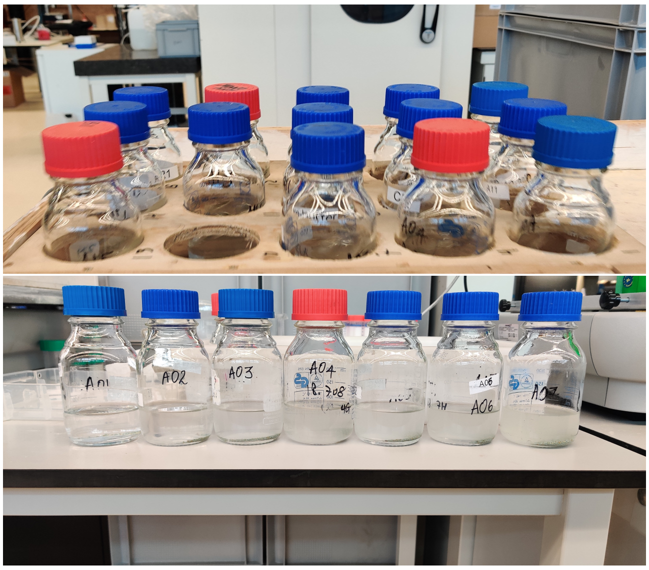


Figure 4.1: Experimental setup

All the above mentioned batch experiments were performed in the following setup. The samples were placed in 250 mL schott bottles which were closed at the top to prevent interference from surroundings. The bottles were placed in a shaker operated at 200 rpm. The samples from all the experiments were filtered through $0.45\mu m$ filter (Polyethersulfone) procured from Chromafil before analysing for ion concentration on ion chromatography (IC).

4.2 Biofilm experiments

Biomass adherence and microbial growth Nitrifying biomass was procured from B-stage sludge of sewage treatment plant of Dokhaven, Rotterdam. The biomass was cleared of heterotrophs by supplying with feed without organic carbon. The feed for nitrifiers was prepared as mentioned in 4.4. Excess biomass was refrigerated at $4°C$ by keeping it open to atmosphere (hence oxygen), thereby maintaining aerobic conditions. The conditions for growth of biofilm were optimised from literature as explained in section 2.2.1. The zeolite is then submerged in the nitrifying biomass for a week for microbial attachment. The zeolite is then aerated with feed with ammonium concentration of about 40mg/L to overcome substrate limitation and multiply at maximum growth rate to cover the surface of zeolite with nitrifying biomass. According to The doubling time for nitrifiers at this concentration and at a temperature of $20°C$ according to literature is 2.5 days (Metcalf & Eddy, 2004).

4.2.1 Experimental procedure

Effect of biofilm on adsorption Biofilm coated zeolite was regenerated by aerating with buffer solution (without ammonium). Regeneration was confirmed by verifying the absence of ammonium in the solution, while the nitrate concentration remained constant over time. Equal amounts of fresh zeolite and zeolite with biofilm were taken in a reactor and subjected to same feed and experimental conditions. The kinetics of ammonium removal was found through similar kinetic experiments as explained in the above sections.

Buffer capacity of zeolite The cation exchange capacity of the zeolite is put to test by testing its capacity to adsorb H^+ ions that are released during the process of nitrification. A modified feed solution is prepared by replacing sodium bicarbonate with sodium hydroxide and potassium bicarbonate with additional amount of mono potassium phosphate. The pH was balanced to 7.7 by the addition of H_2SO_4. Kinetics of ammonium removal was observed in the same way as discussed in the above sections while also recording the pH value at each time interval.

Varying concentration The kinetics of ammonium removal by zeolite coated with nitrifying biofilm is tested by exposing it to feed solution of DWF concentration for 1 hour and RWF concentration of 2 hours in cycles. A DWF cycle is followed by a RWF cycle and a DWF cycle. The time intervals are decided based on the kinetic experiments done of fresh zeolite. After each cycle the sample is completely removed from the reactor before replacing with next feed.

4.2.2 Experimental setup

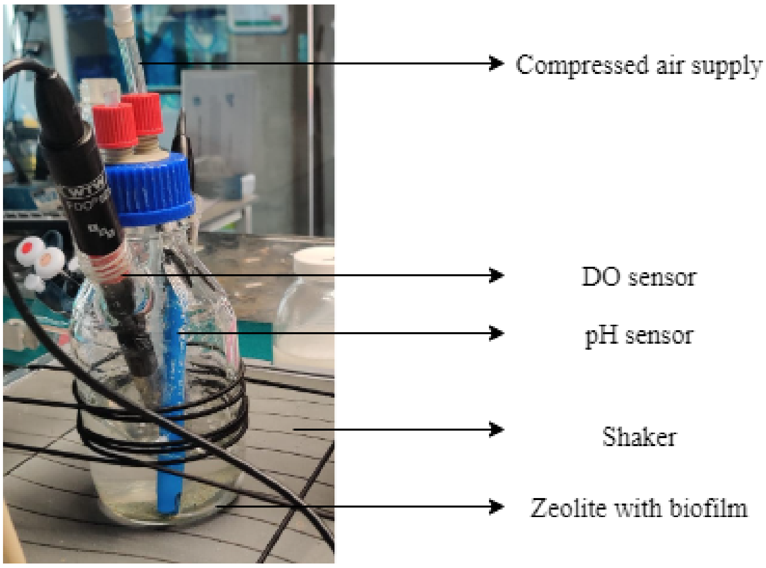


Figure 4.2: Experimental setup

250 mL of synthetic wastewater and zeolite were taken in 500 mL 3 neck schott bottle as seen in figure 4.2. A pH sensor and DO sensor were connected to monitor the pH of sample through experimental duration. Oxygen was supplied as compressed air such that oxygen concentration was always above 7 mg/L to avoid oxygen limitation. The bottle was placed in a shaker operated at 140rpm. The samples from all the experiments were filtered through $0.45\mu m$ filter before analysing for ion concentration on IC.

4.3 BioWin Modelling

BioWin software by EnviroSim Associates Ltd was used to simulate the concentration of biomass under varying conditions of DWF and RWF concentrations. The nitrifying biofilm in the above experiments was grown under continuous RWF conditions and the experiments are designed to investigate the performance of bacteria under different conditions independently. In practical scenarios, the bacterial population will typically not experience higher concentrations for most of its operational period. Therefore, it is essential to comprehend the survival of the bacterial population during extended periods of low $NH_4 - N$ concentration, and whether this amount survived is sufficient for converting RWF peak ammonium concentrations. Practical application of Biological filter with zeolite in continuous mode can be assumed to be similar to that of rapid sand filter due to the particle size and flow rate.

A theoretical column was designed based on this assumption and it was modelled on BioWin using 10 bioreactors (which will ultimately mimic a plug flow similar to that in column reactors). As the model encompasses numerous parameters, it becomes impractical to calibrate each one. However, studies have shown that using default parameter values can still yield acceptable predictions of the actual wastewater treatment process, producing results in the appropriate order of magnitude (Cao, Wah, Ang, & Raajeevan, 2008). Bioreactor with media controlled by air flow rate was used to represent the process. Media was assumed to be composed of 1mm sized spheres to approximately calculate the surface area and volume. The limits for biofilm formation was set between 100-250 μm as discussed in section 2.2. Since the adsorption of ammonium by zeolite cannot be simulated on BioWin, the kinetics of ammonium adsorption and desorption by zeolite is neglected. Adsorption of ammonium is represented by lower ammonium concentration (5mgN/L instead of 8mgN/L - which is the influent ammonium concentration). On the other hand, desorption of adsorbed ammonium is represented by a constant ammonium concentration post the influent ammonium peak, which is lower than the peak concentration, but higher than DWF concentrations.

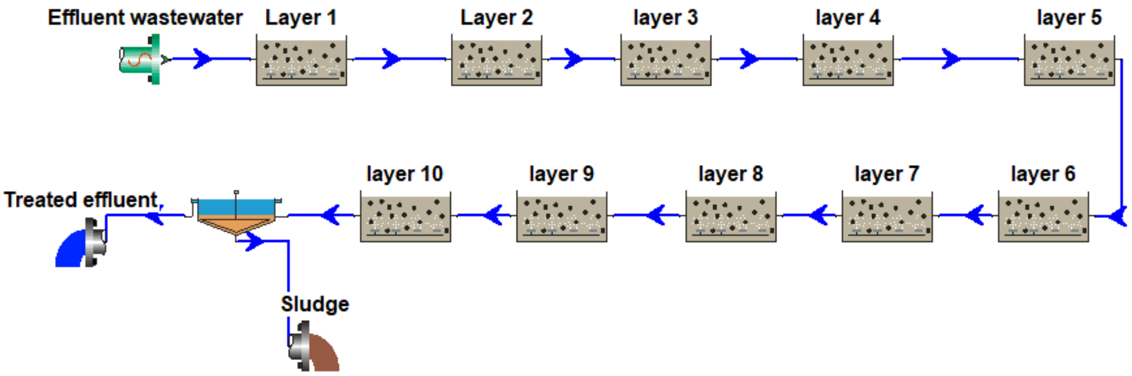


Figure 4.3: Flowchart of the fixed bed with nitrifying biofilm - where plug flow is represented by 10 bioreactors with media on BioWin

The influent wastewater parameters are changed according to data from table 3.1. Composition of synthetic wastewater sample used in experiments (4.2) was used to further adjust the pH of the model influent. The other parameters were set to default values. The filter was designed for a flow of 14040 m^3/d during RWF, and 6592 m^3/d as given in table 3.1. Length to width ratio of filter is taken as 1.25:1 (which is in the recommended range of 1.25-1.33 :1) and depth of 0.9 m which is based on standard design practises (Punmia, Jain, & Jain, 1994). Temperature was set at $20°C$.

4.4 Measurement and Analysis

Measurement of ion composition of samples was the major part of data collection in this research. Temperature, pH and DO of samples were measured using pH and DO sensors. The attachment and growth of biofilms were monitored on the microscope. The amount of biomass on zeolite was quantified by Gravimetric method.

4.4.1 Measurement equipment

Gravimetric method to measure volatile solids in Biofilm An overview of the process to measure volatile solids is given below.

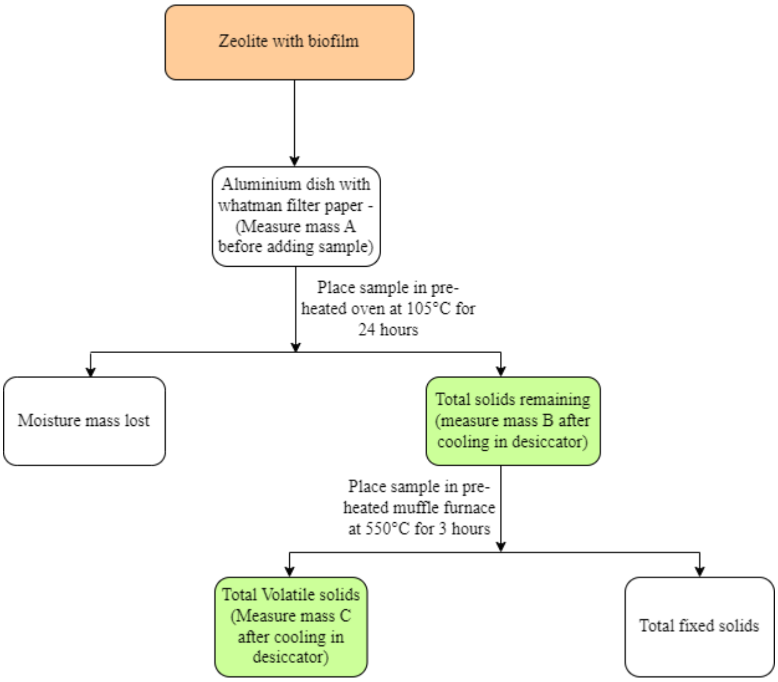


Figure 4.4: Procedure for determination of volatile solids in biofilm

The zeolite coated with biofilm from the experiments discussed earlier is taken in an aluminium dish. After removing excess water it is placed in another aluminium dish lined with Whatman filter paper (which is already weighed). The sample is placed in an oven at $105°C$ for 24 hours to ensure all the water (also from the pores of the zeolite) is evaporated. The sample after weighing is then placed in a muffle oven for 3 hours at $550°C$. This incinerates the volatile matter leaving behind non volatile matter and zeolite. The difference in weight is the amount of volatile solids present in the sample.

Ion Chromatography IC was used to measure the concentration of Sodium, Potassium, Magnesium, Calcium and Ammonium with respect to cations and Chlorine, Nitrite, Nitrate, Phosphate and Sulphate with respect to anions. It was used for standard deviation under 3% from the prepared standards. Hence this was preferred over measurement using HACH kits in the process of data collection. The samples were measured against standards of 100ppm, 50ppm, 10ppm and 1ppm which covered the range of expected values of concentrations used in this study. 3-5 mL of sample is filtered with $0.45\mu m$ filter for the IC. 6mL of 1 mol/L HNO_3 in 2L of ultra pure water is used by IC for cations measurement and 100 mL of 20 mM sodium bicarbonate and 64 mM sodium carbonate solution in 2 L of Ultra pure water is used for anions measurement.

Microscope VHX digital microscope was used to record images of the zeolite surface at 1000 μm size range. Microscopic images of fresh zeolite and zeolite with biofilm were taken for comparison. The biofilm could be seen as brown colonies on the surface of the zeolite. Refer to images in figure 5.9. Microbial staining was not necessary to observe the biofilm coating.

HACH kits HACH kits LCK303, LCK339 and LCK342 to measure NH_4, NO_3 and NO_2 were used to track the growth of the biofilm. Rate of nitrification was used as a indication to understand the rate of development of the biofilm. Though the values are not as accurate as the IC measurements, it gives a good and fast indication of nitrification. Also this was used to find oxygen limitation in the setup due by the amount of nitrite which is not converted to nitrate.

4.4.2 Kinetic models

Different kinetics models were utilized to describe the kinetics of adsorption of ammonium by zeolite (clinoptilolite). The value of regression coefficient and lowest difference between predicted adsorption value at different time intervals and experimentally determined values was used to finalise on a model to describe adsorption kinetics. High value of regression coefficient (r^2) indicates that the model successfully describes the process (Kithome et al., 1998). But since the equations are linearised, the error distributions tend to be altered (Kučić et al., 2012). The specific models considered in this study are as follows.

First order kinetic model The first order rate equation to model adsorption process can be written as (Sparks & Jardine, 1981)

$$q_t = q_e\left(1 - e^{-kt}\right) \tag{4.1}$$

In linearised form:

$$\ln\left(1 - F_{\mathrm{a}}\right) = kt \tag{4.2}$$

where,
F_a is the fraction of ammonium adsorbed on zeolite at time t. $F_a = \frac{X_t}{X_{eq}}$ (-)
X_t is the total ammonium adsorbed on zeolite at time t (mg/L)
X_{eq} is the total ammonium adsorbed on zeolite at equilibrium (mg/L)
and k is the adsorption rate coefficient (min^-1)
If the rate of adsorption follows first order kinetics, the graph of ln(1- F_a) against t should yield a straight line.

Pseudo first order kinetic model It is also called Lagrangian equation and is a popular choice to predict adsorption kinetics.

$$\frac{dq_t}{dt} = k_f\left(q_e - q_t\right) \tag{4.3}$$

Integrating equation 4.3 with boundary conditions t=0 to t=t and q_t=0 and q_t=q_t and In linearized form:

$$\log\left(q_e - q_t\right) = \log_e - \frac{k_f}{2.303} \cdot t \tag{4.4}$$

where
q_e and q_t are the amount of ammonium adsorbed at time t and at equilibrium (mg/L)
and k_f is the pseudo first order rate constant (min^-1)
The plot of log(q_e - q_t) vs time yields a straight line if the adsorption kinetics fits this model.

Pseudo second order kinetic model The pseudo second order kinetic equation is given by

$$\frac{dq_t}{dt} = k_s\left(q_e - q_t\right)^2 \tag{4.5}$$

On integrating the equation with limits t=0 to t=t and $q_t = 0$ and q_t= q_t and
In linearized form:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} \cdot t \tag{4.6}$$

where,
q_e and q_t are the amount of ammonium adsorbed at time t and at equilibrium (mg/L)
and k_s is the pseudo second order rate constant (g mg^-1 min^-1).
The plot of $\frac{t}{q_t}$ vs time yields a straight line if the adsorption kinetics fits this model.

Elovich model Elovich equation is written as (Chien & Clayton, 1980)

$$q_{\mathrm{t}} = (\frac{1}{\beta})\ln(\alpha\beta) + (\frac{1}{\beta})\ln t \tag{4.7}$$

where,
q_t is the amount of ammonium adsorbed at time t (mg/L)
α and β are constants (-)
If the process conforms to this model then the plot of q_t vs ln t will be linear. Slope of the curve is $\frac{1}{\beta}$ and intercept is $(\frac{1}{\beta})\ln(\alpha\beta)$

5

Results and Discussion

In this section, we will address the research questions introduced in Chapter 3. Each experiment builds on the previous one, contributing to the overall understanding of whether using a fixed-bed nitrifying biofilm on zeolite is a feasible approach for treating effluent wastewater. Note that throughout this chapter concentration is represented in mg/L, mg N/L and mmol/L as necessary to effectively represent and interpret the results. Desired effluent ammonium concentration post treatment with nitrifying biofilm on zeolite is 1 mgN/L or 1.3 mg/L. First zeolite's capacity is characterised by isotherm and kinetic experiments, and the data is fit to theoretical models to predict it's behaviour. Effect of competing cations on adsorption and adsorption kinetics is analysed, and concluded with an analysis on the effect of zeolite concentration. In the second part, data from experiments on nitrifying biofilm is used to assess the buffer capacity of the system, the bio-regenerability of the zeolite, the effect of biofilm on removal kinetics, and the system's ability with handling peak ammonium concentrations. The final part is also supplemented with a simulation on survival of biomass under prolonged DWF concentrations and it's ability to handle further RWF.

5.1 Adsorption - Desorption

5.1.1 Adsorption isotherm model

Adsorption isotherms are essential for designing adsorption systems. The experiment was performed with synthetic wastewater solutions with only ammonium and in the presence of competing cations. A summary of the experimental data can be seen in Appendix A.1 At equilibrium, the sorption capacity (q_e in mg/g) is determined as

$$q_e = \frac{(C_o - C_e)}{m}.V \tag{5.1}$$

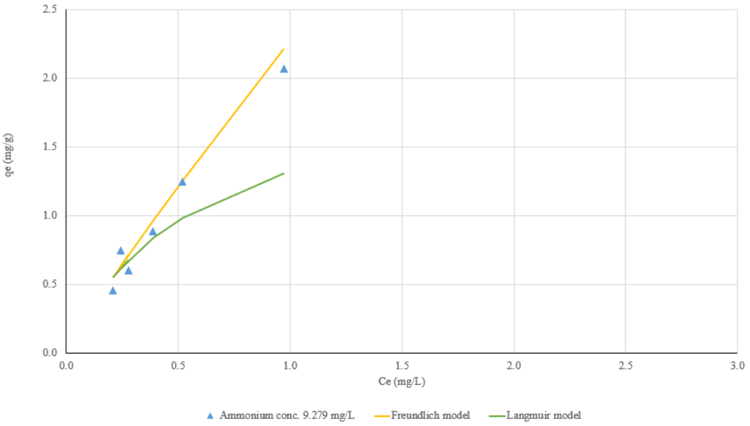
where,
C_o is the initial ammonium concentration in mg/L,
C_e is the final ammonium concentration in mg/L,
m is mass of zeolite in g,
V is volume of synthetic wastewater in L.

Different masses of zeolite were used and q_e was determined for respective C_e. The data was fit to Langmuir and Freundlich isotherm models to find the best model fit for the data. These models were selected because a significant number of fits for Ammonium adsorption on zeolite aligned with either the Langmuir or Freundlich isotherm, as documented in the literature

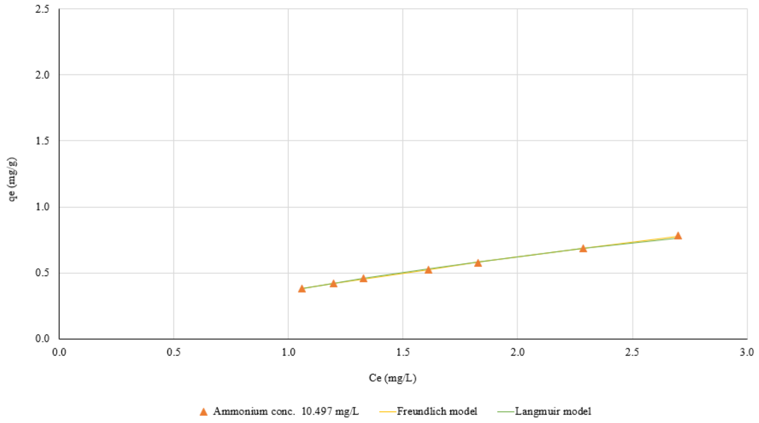
(De Magalhães et al., 2022). A summary of model equations and respective regression coefficients for fit of RWF ammonium concentration in the absence and presence of competing cations is provided in table 5.1.

Table 5.1: Equations for Langmuir and Freundlich isotherm models and correlation coefficients (r^2) for equilibrium ${NH_4}^+$ adsorption in solution with ${NH_4}^+$ alone and in the presence of competitive cations.

Sample	**Equation**	**Isotherm**	r^2 **value**
Only ammonium	$qe = 29.58 * 0.082 * Ce/(1 + 0.082 * Ce)$	Langmuir	0.8873
	$qe = 2.17 * Ce^{0.92}$	Freundlich	0.9420
With competing cations	$qe = 0.19 * 2.26 * Ce/(1 + (0.19 * Ce))$	Langmuir	0.9987
	$qe = 0.37 * Ce^{0.76}$	Freundlich	0.9992



(a) Solution with only ${NH_4}^+$



(b) Solution with ${NH_4}^+$ and other competing cations

Figure 5.1: Langmuir and Freundlich isotherm plots for ammonium adsorption from solution with only ${NH_4}^+$ ions (a) and from solution with ${NH_4}^+$ and other competing cations (b). The experimental data is represented as data points and Langmuir & Freundlich models are represented by green and yellow lines respectively

Figure 5.1 illustrates the comparison between model-predicted data and experimental data points for ammonium adsorption both in the absence and presence of competing cations. In both cases, q_m which represents maximum adsorption capacity of zeolite from Langmuir model as discussed in 2.1.1 is not reached. Moreover, Freundlich isotherm has slightly better r^2 values. Based on these 2 reasons, Freundlich isotherm was finalised for prediction of adsorption isotherm for ammonium adsorption by zeolite. Individual plots of adsorption isotherm models are available in appendix A.1.

Since the adsorption is represented by Freundlich isotherm, it can be inferred that it is a multi layer adsorption with non uniform distribution of sites for ion exchange. (Freundlich, 1907). Since the isotherm data fits Freundlich model, it can be inferred that, there is no limit on the amount of ammonium adsorbed and the strength of interactions between zeolite and ammonium depends on zeolite surface coverage (Agbovi & Wilson, 2021).

5.1.2 Effect of competing cations on ammonium adsorption

It was found that potassium is the major competition for ammonium adsorption which aligns with literature (2.1.7). Both K^+ and $NH_4{}^+$ exchanged with Na^+ hence sodium was not competing for adsorption sites at the investigated concentrations. From from Langmuir isotherm equations in table 5.1, we can see that, the value of q_{max} has reduced in the presence of cations, on the other hand, the value of b = 0.19 in the presence of competing cations is higher when compared to b = 0.0819 in its absence. q_{max} is the maximum amount of exchangeable ammonium which does reduce in the presence of competing cations. On the other hand, K_L indicates the strength of interaction between adsorbent (zeolite) and adsorbate (Ammonium), which in this case is higher in the presence of cations. Hence there is a stronger interaction between cation exchange sites and ammonium in the presence of competing cations, though it's availability towards ammonium is restricted due to competition. This was also observed by Vocciante et al. (2018) in their research on ammonium adsorption by zeolite in the presence of competing cations.

Using Freundlich isotherm, the exact amount of zeolite needed for adsorption of ammonium in the absence and presence of competing cations was determined. For a desired effluent $NH_4 - N$ concentration of 1 mgN/L, only 3.33 g/L of zeolite is needed to remove 9.2 mg/L (10.5-1.3) of ammonium, whereas in the presence of potassium the requirement increased to 20.59 g/L. Thus, in the presence of competing cations the zeolite requirement at equilibrium increases by 6.2 times.

Table 5.2: Percentage removal of Ammonium, Potassium and Sodium with increasing zeolite loading at concentrations of 0.582 mmol/L, 3.351 mmol/L and 1.299 mmol/L of $NH_4{}^+$ Na^+ and K^+ respectively. There was an increase in Na^+ concentration in the solution, hence negative value in the last column.

Sample ID	**Zeolite mass(g/L)**	**% $NH_4{}^+$ removed**	**%K^+ removed**	**%Na^+ removed**
A41	10	74.297	58.979	-6.154
A42	12	78.213	61.331	-5.859
A43	15	82.586	64.579	-5.428
A44	17	84.672	65.295	-5.291
A45	20	87.349	67.238	-4.260
A46	22	88.597	67.653	-4.277
A47	25	89.930	68.681	-3.573

But it can be observed from table 5.2 that, at equilibrium, even though Ammonium concentration in mmol/L is 2.23 times (approximately) lower than Potassium concentration, removal of ammonium is still higher. This indicates higher affinity of Clinoptilolite towards $NH_4{}^+$ when compared to K^+.

5.1.3 Adsorption kinetics - Application of data to kinetic models

Adsorption kinetic experiments were done to better understand the dynamics of ammonium adsorption in the presence of competing cations. The zeolite and ammonium concentration of different kinetic experiments E1, E2 and E3 are summarised below. The cation composition of all kinetic samples is provided in the appendix A.1.

Table 5.3: Summary of amount of zeolite (mg/100mL) and $NH_4{}^+$ conc (mg/L) used in performing kinetics experiments E1, E2 and E3 of synthetic wastewater volume of 100mL

Experiment	**Amount of zeolite (g/L)**	**Initial $NH_4{}^+$ conc. mg/L)**
E1	20	7.893
E2	21	8.806
E3	30	7.557

Different kinetic models were discussed in section 4 and individual fit of experimental data to these models are attached in appendix A.1.A summary of different models applied to data and its parameters and regression coefficients are given in table 5.4

Table 5.4: Equations and regression coefficients of determination for NH4 adsorption using the different models at initial NH4 concentration of 10.497 mg/L.

Model	**Equation**	r^2
First order kinetics	$q_t = q_e(1 - e^{0.0003t})$	0.9538
Pseudo first order kinetics	$q_t = (1 - e^{-1.0846t})$	0.9715
Pseudo second order kinetics	$\frac{t}{q_t} = \frac{1}{0.1766{q_e}^2} + \frac{1}{q_e}t$	0.9991
Elovich	$q_t = 0.6196\ln(0.6334) + 0.6196\ln t$	0.9942

The kinetics experiment data was observed to exhibit the best fit with the pseudo-second order kinetics model and Elovich model. Even though Elovich model has a high regression coefficient of 0.9942, there was notable variance between experimental and predicted removal values (an over-prediction of removal rate was observed). Moreover, q_e value predicted from kinetic data by the pseudo second order model is 0.444 which is close to the $q_e = 0.446$ determined by isotherm experiments. Hence, on the basis of regression coefficient and q_e determination, pseudo-second order model is finalised as the best fit. This was also the case with research by Kučić et al. (2012) and (Vocciante et al., 2018) (2018). The model was also applied to a duplicate experiment and predicted kinetic curve compared to experimental data is given in figure 5.2. While the initial deviation from experimental data is notably higher by 23%, effective prediction occurs from the 10-minute mark with a deviation of $0.85\% \pm 1.857\%$.

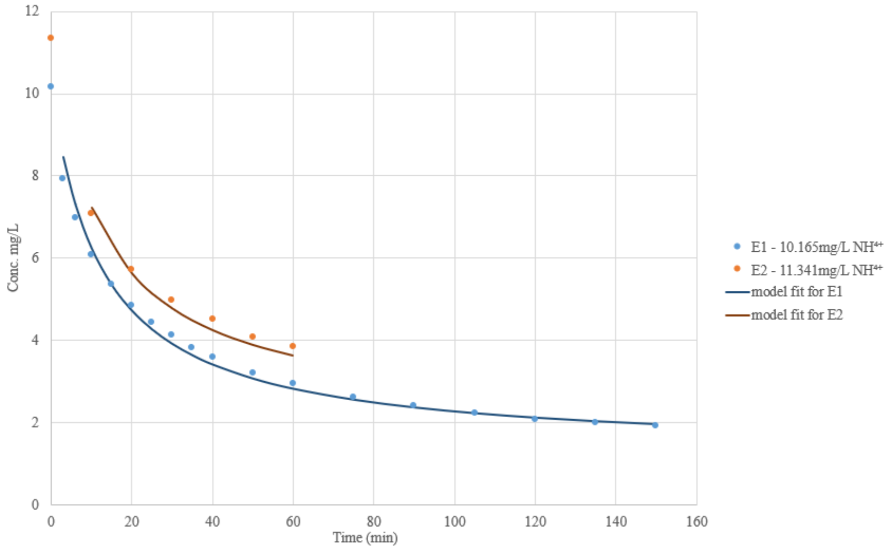


Figure 5.2: Kinetics of ammonium removal fit to pseudo second order kinetic model

5.1.4 Removal kinetics - Effect of zeolite concentration

The amount of zeolite used in different kinetic experiments along with corresponding initial ammonium concentration is presented in table 5.3.E1 and E2 have equilibrium capacity of zeolite as determined by Freundlich isotherm. E3 has 1.5 times higher zeolite than equilibrium value. E3 was an experiment performed in comparison to zeolite with biofilm discussed in the later sections. Due to the reduced biofilm volume on zeolite during the time of experiments, a higher amount of zeolite was taken for the study of biofilm experiments and an equal amount of fresh zeolite was also taken as the control experiment for comparison.
In graph 5.3, it is observed that E1 and E3 have a similar decrease in ammonium concentrations even though E3 has 1.5 times more zeolite concentration. Moreover, from table 5.5, it is evident that ammonium removed is the same in case of E1 and E3 at time of 30 minutes. Though the kinetic curves for each of these samples represent major differences in removal rate, the amount of ammonium removed with time has a very little difference as observed from the mean and standard deviation values in table 5.5.

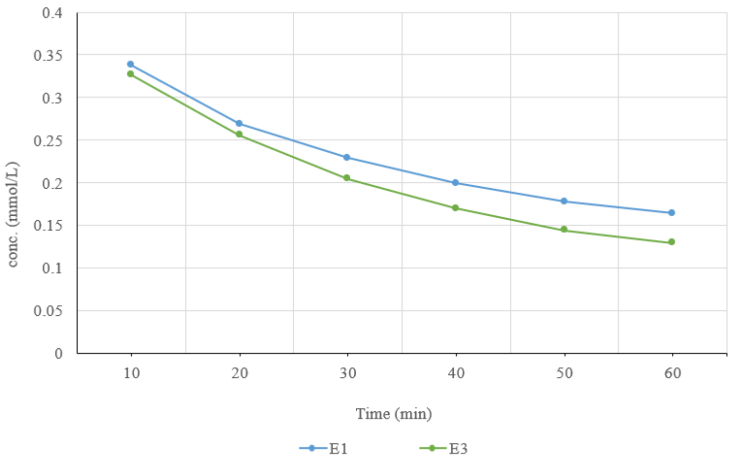


Figure 5.3: Concentration of ${NH_4}^+$ in mmol/L plotted against time for E1 and E3

Table 5.5: Comparison of ammonium removal in E1, E2 and E3 at times 10, 20, 30 and 40 minutes

Time (min)	**Removal E1 (mmol/L)**	**Removal E3 (mmol/L)**	**Mean (mmol/L)**
10	0.226	0.213	0.219 ± 0.006
20	0.295	0.284	0.289 ± 0.006
30	0.335	0.335	0.335 ± 0.000
40	0.364	0.370	0.367 ± 0.003

It can be inferred from graph 5.3 that higher zeolite amount results in overall higher removal of ${NH_4}^+$ with time due to higher availability of exchange sites. But for shorter contact time, removal rate might not be affected significantly as seen in table 5.5 where standard deviation between removal data of E1 and E2 close to 0. Factors that affect kinetics are concentration of solute (ammonium in this case), contact time and complexity of adsorbent surface (Saleh, 2022). It is in line with this result where amount of adsorbent (zeolite) concentration did not influence kinetics. It is also important to note that experiment E3 was performed with synthetic wastewater used in biofilm experiments as given in table 4.4 whereas E1 was with sample as described in table 4.3. Hence, the lower initial removal rate by E3 may be due to competition from various cations that is present in prepared synthetic solution. It is necessary to conduct tests using higher zeolite concentrations and same water sample in order to confirm the impact.

5.1.5 Removal kinetics - Ammonium vs Potassium

On comparison of amount of ${NH_4}^+$ and K^+ in mg/L removed from bulk solution, it can be seen that higher amount of potassium is removed. But when looking at the amount of potassium removed in comparison to initial concentration, it can be noted that 44.2% of the total potassium was removed in 60 minutes compared to 70.9% ammonium removal. Since exchange of ions is taking place, a comparison of mass in mg might not effectively convey the difference in removal efficiency. Thus, when removal is looked at from mmol perspective, potassium removed in 60 mins was 0.56 mmol/L (22.07 mg/L) and ammonium was 0.4 mmol/L (7.2 mg/L). Hence, figure 5.4 provides a more precise representation of removal comparison where it can be noted that the slope of ammonium removed is steeper than that of potassium though the concentration of the former is 2.23 times lower.

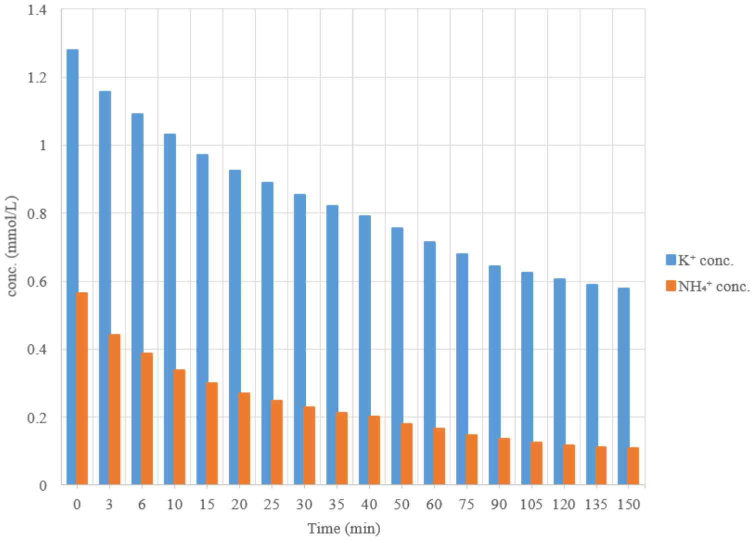


Figure 5.4: Removal of ${NH_4}^+$ and K^+ with time.

5.2 Nitrifying biofilm Experiments

5.2.1 Buffer capacity

The experimental data for buffer capacity determination is provided in the appendix A.1. The experiment was performed by modifying the synthetic wastewater as described in 4.4 - removing the bicarbonate buffer. From the graph in figure 5.5, it can be seen that pH drop is almost linear with linear increase in conversion of ammonium. This indicates that though zeolite is a cation exchanger, does not remove H^+ effectively to act as a buffer system for nitrification. This is also in line with theory where zeolite has a low affinity for H^+ ions.

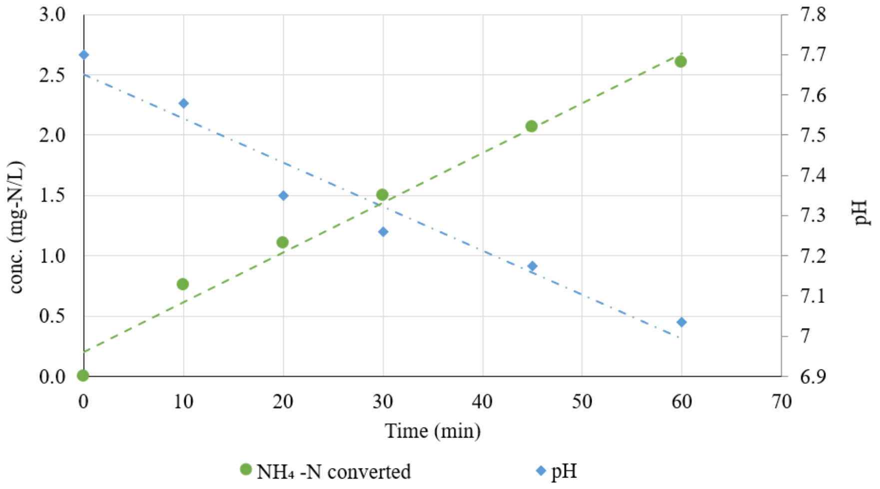


Figure 5.5: Variation of pH with time and corresponding conversion of ammonium to nitrite and nitrate

The oxidation of ammonia to nitrate by biological nitrification is as follows:

$$NH_4{}^+ + 2O_2 \rightarrow NO_3{}^{2-} + 2H^+ + H_2O \tag{5.2}$$

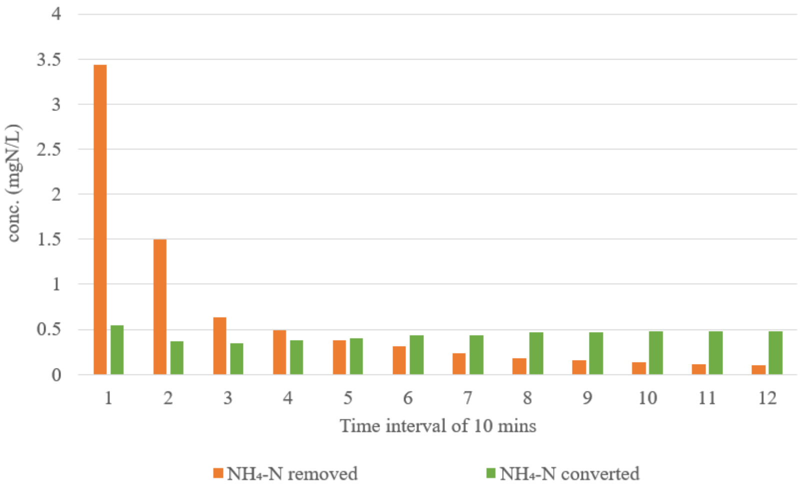
According to equation 5.2, 1mmol of H^+ is released for every 9.015mg of ammonium nitrified. Thereby the calculated pH value corresponding release of H^+ would've been much lower. But ammonium oxidation is inhibited below pH 5 and in reality this wouldn't occur (Le, Fettig, & Meon, 2019). Hence, without some buffer, nitrification wouldn't have proceeded at a constant rate as seen in figure 5.5. Even though an external buffer was not added to the synthetic solution, buffering could've occurred in the form of

- Dissolved CO_2 from compressed air.
- Some amount of ammonium in the ammonia form can lead to an increased pH in the beginning as can be seen from the ammonia-ammonium equilibrium graph 2.1. Although, reduction in pH due to ammonium removal is almost negligible
- Neutralisation capacity due to the presence of OH^- ions in the solution. It is from the addition of NaOH to increase pH of prepared synthetic wastewater, and also as a source of Na^+ ions of representative RWF concentration.
- Biofilm in itself acts as a buffer and $PO_4{}^+$ concentrations, though low has some buffer effect at low alkalinities. (Szwerinski et al., 1986)
- Possible buffer capacity of zeolite by adsorbing the H^+ ions that are produced on it's surface.

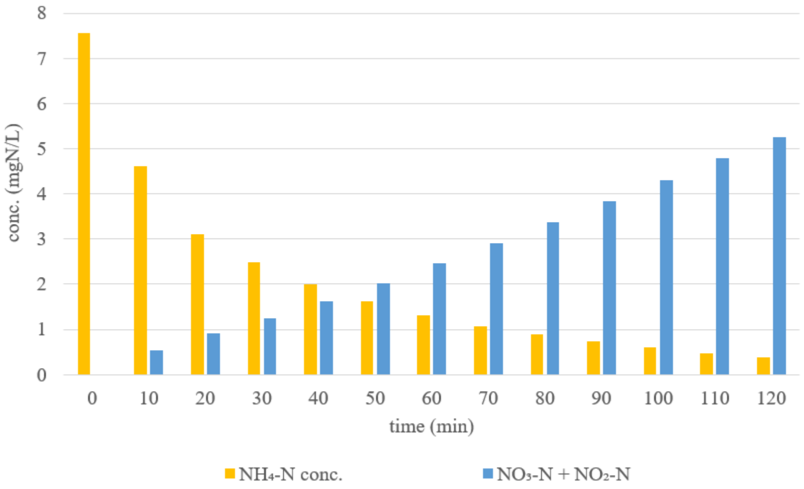
The above information cannot be used as a conclusion on the extent of buffer capacity of zeolite. But it can be concluded that pH of the solution cannot be maintained by this system of biofilm and zeolite as there is a significant pH drop from 7.7 to 7.035. Hence, buffer capacity of the incoming wastewater is also an important parameter to be considered during the design of the reactor.

5.2.2 Bio-regeneration of zeolite

Nearly complete regeneration of zeolite was first proved from samples taken during the growth phase of the biofilm where 38.441 $mgNH_4 - N/L$ was fed to the zeolite with biofilm sample and in 24 hours an effluent concentration of 38.477 $mgNO_3 - N/L$ and 0.128 $mgNO_2 - N/L$ was observed, adding up to 38.605 mgN/L. It can also be observed in the kinetic experiments as shown in example in figure 5.6.



(a) The amount of $NH_4 - N$ removed and converted in time intervals of 10 minute time intervals. X-axis represents the interval number



(b) Concentration of $NH_4 - N$, $NO_3 - N$ and $NO_2 - N$ plotted against time

Figure 5.6: Graph (a) shows that after the 5^{th} time interval the amount of ammonium converted is more than the amount of ammonium removed, indicating conversion of desorbed ammonium. Graph (b) shows the linear increase of nitrate and nitrite with time and at 120 minutes $NO_3 - N + NO_2 - N$ is not equal to initial $NH_4 - N$ concentration at time t= 0 min.

It can be seen from figure 5.6 (a) that, in the beginning there is a removal of 42.6% of $NH_4 - N$ but only 15% of it is converted. The rest is adsorbed by the zeolite. But after the 5th interval, the amount of $NH_4 - N$ converted is greater than that removed, indicating the conversion of ammonium released by the zeolite. The amount of nitrate and nitrite produced is not equal to the initial amount of ammonium as seen in figure 5.6 (b), indicating storage in zeolite, thereby complete regeneration is not achieved in 2 hours.

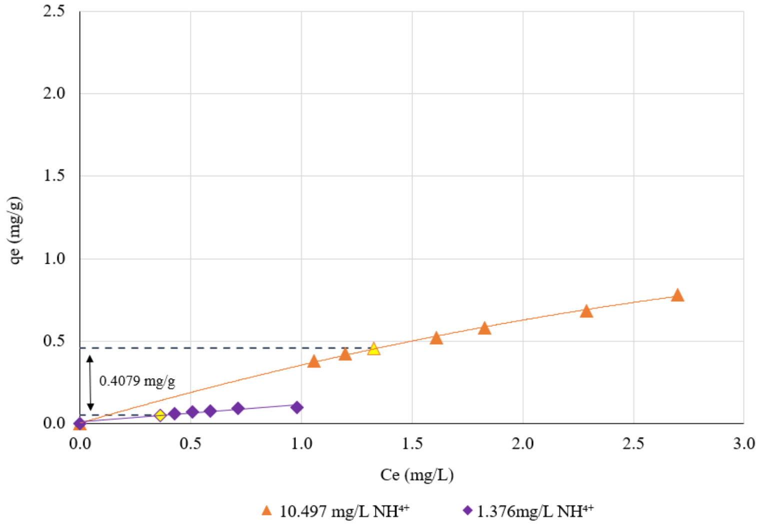


Figure 5.7: Adsorption isotherm determined at constant $NH_4{}^+$ concentrations of 10.497 mg/L and 1.376 mg/L and varying zeolite loading ranging from 1-25 g/L

Moreover, from figure 5.7 it can be inferred that maximum desorption (at equilibrium) due to the reduction in concentration from RWF to DWF is 0.41 mg $NH_4{}^+$/g zeolite. It was found that equilibrium loading is 0.446 mg/g and that implies, at equilibrium 91% of the adsorbed ammonium should be desorbed. But from desorption kinetic experiments it was observed that in a 3 hour time period, average desorption observed was 0.1924 mg/g. It may take a very long time to reach the theoretical equilibrium. Hence, from the conclusions based on desorption isotherm and removal - conversion data, it can be concluded that zeolite can be effectively regenerated.

5.2.3 Effect of nitrifying biofilm on ammonium adsorption

The results of ammonium removal with fresh zeolite and regenerated zeolite with nitrifying biofilm is depicted in the graph 5.8. With only zeolite, desired effluent concentrations are barely reached in the 2 hours of operation, whereas with biofilm, it is reached after 70 minutes. It is evident that with biofilm, the amount of ammonium removed as well as rate of removal is faster. This maybe attributed to focused source of ammonium for the biofilm as well as persisting gradient in ammonium concentration due to conversion of ammonium by the biofilm.

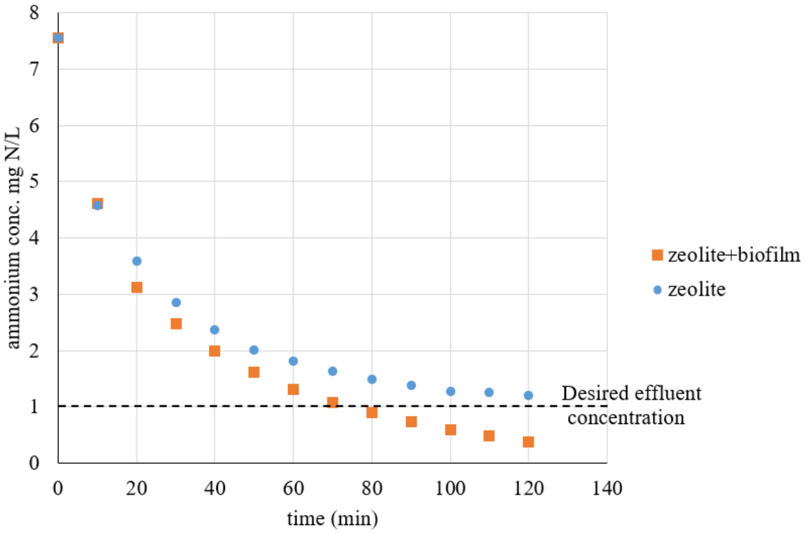
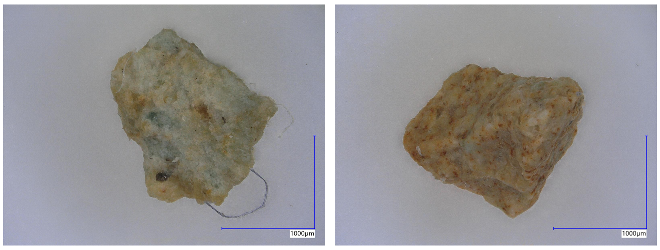


Figure 5.8: Performance of regenerated zeolite with biofilm in comparison to fresh zeolite

(a) Fresh zeolite (b) Barely covered (c) Minimal coverage



(d) Minimal coverage (e) Completely covered

Figure 5.9: Microscopic pictures of zeolite with biofilm (except image a which is fresh zeolite) taken on 31.07.2023 at the end of the above-mentioned experiment. The nitrifying biofilm can be spotted by the brown tint on the zeolite surface which is otherwise greyish-white in color.

Image (a) in figure 5.9 depicts fresh zeolite and serves as a reference for comparison with biofilm-coated zeolite to identify the distinctive brown spots indicative of the biofilm presence. These microscopic images, derived from a random sample of the experimental zeolite volume, illustrate the range of surface coverage observed across the zeolite particles. While some surfaces exhibit complete biofilm coverage, as evidenced in image (e), others display less coverage, as evident in image (b).

From the experimental data depicted by graph 5.8, it can be concluded that biofilm does not affect adsorption of ammonium by zeolite (atleast with this amount of surface coverage). This is a suitable indicative conclusion since, from literature it is known that nitrifiers don't form thick biofilm layers (Van Loosdrecht et al., 1995). Moreover, when ammonium substrate concentrations are low, biomass concentrations will also remain limited.

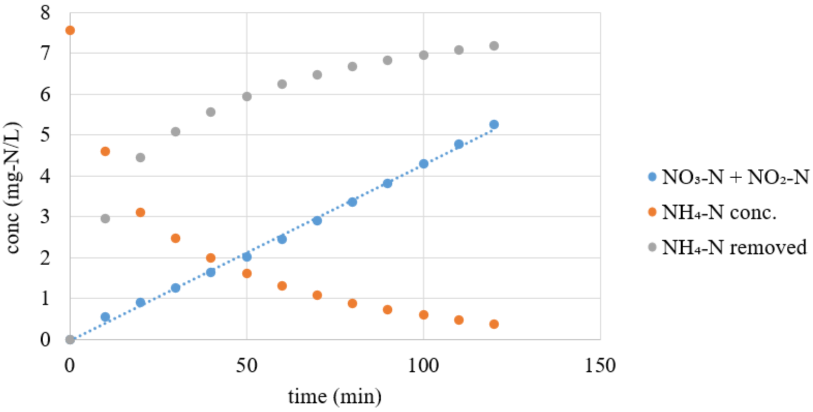


Figure 5.10: Reduction of ammonium concentration with time compared to the amount of nitrate and nitrite produced

From the above graph 5.10 it can be seen that conversion is linear which indicates there are no limiting factors for nitrification. One of the main issues with biological removal in effluent wastewater is substrate limitation that occurs at lower concentration, which is not observed in case of combination of biofilm with zeolite. Removal rate is much higher as seen in the first half of the grey curve. And as discussed in the above subsection 5.2.2, zeolite helps with the initial adsorption of bulk ammonium. Hence, in this combined technology zeolite helps with the dampening of the peak while biofilm contributes by regenerating the zeolite.

Oxygen requirements Calculating the slope of the curve which is indicative of the nitrification rate of the experimental system results in 0.043 mg $NH_4 - N/L.min$ which is 62.06 $mgNH_4 - N/L.day$

According to stoichiometery, 4.57g O_2 is required to oxidise 1 g of NH_4. Therefore, 0.25 mg/L.min of O_2 is consumed at this rate. For a HRT of 10 minutes, the amount of oxygen required will be 2.5 mg/L.

Determination of amount of biomass The amount of biomass was determined as described in section 4.4.1. It was found to be 0.2426 g. The amount of biomass was determined as described in section 4.4.1. The mass of volatile solids was found to be 0.2426 g. The measured mass is much higher than the expected amount of biomass for a water volume of 200 mL with an ammonium concentration of 8 mgN/L (which was the sample volume taken during experiments and during the growth of biofilm). The amount of biomass expected for this substrate concentration is about 0.15 mgCOD/L (0.105 mg VSS/L) as determined using BioWin simulations discussed in section 5.3. One of the major reasons for this discrepancy in value is due to mass loss of zeolite caused by exposure to elevated temperatures. A mass loss of about 10% was observed by De Souza, Villarroel-Rocha, De Araújo, Sapag, and Pergher (2018) when zeolite was heated to 550$°C$. The mass loss might be due to the loss of hydroxyl groups due to condensation.

5.2.4 Adaptation of system of zeolite + biofilm to varying concentrations

The ammonium concentration was altered between DWF and RWF concentrations to assess zeolite's efficacy under different concentration scenarios.

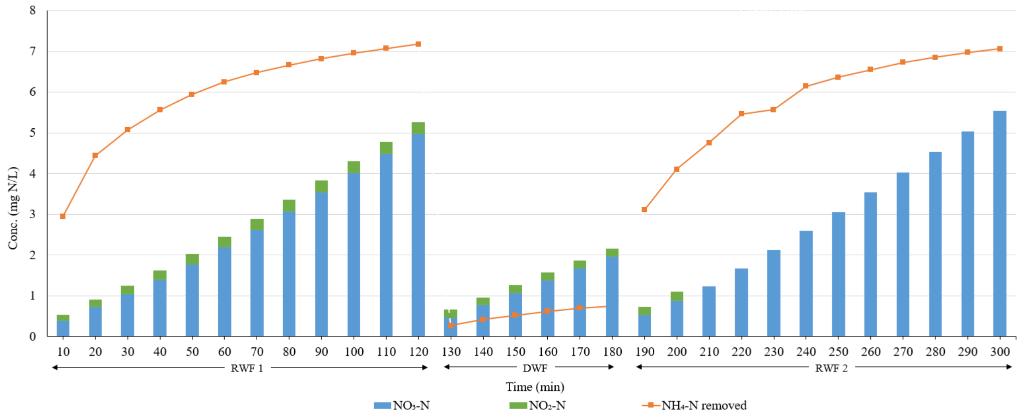


Figure 5.11: Experimental data of variation in flow from RWF - DWF - RWF concentrations indicating adsorption, desorption-regeneration and adsorption. $NH_4 - N$ removed is plotted as a line graph with $NO_3 - N$ and $NO_2 - N$ as a stacked bars indicating total ammonium converted.

The observed results indicate that the zeolite's removal capacity remained unaffected even after consecutive exposure to RWF concentrations. The ammonium concentration remains well below the stipulated effluent requirements across all three cycles. Additionally, the quantity of ammonium stored as adsorbed ammonium in the zeolite is slightly lower following the second exposure - indicated by smaller difference between $NH_4 - N$ removed vs. converted in RWF 2 when compared to RWF 1 (gap between orange line and stacked bar at the end of RWF cycles). Furthermore, a noteworthy observation is the complete conversion of nitrite to nitrate during the second RWF cycle, signifying the absence of oxygen limitation.

From figure 5.12 it can be inferred that, while the slope during DWF is approximately 25% lower than the slopes observed during RWF, the noteworthy point is that a linear nitrification rate persists even during low ammonium concentrations in the DWF scenario. This observation implies the absence of substrate limitation in nitrification, addressing a significant shortcoming associated with employing biological removal for effluent wastewater treatment.

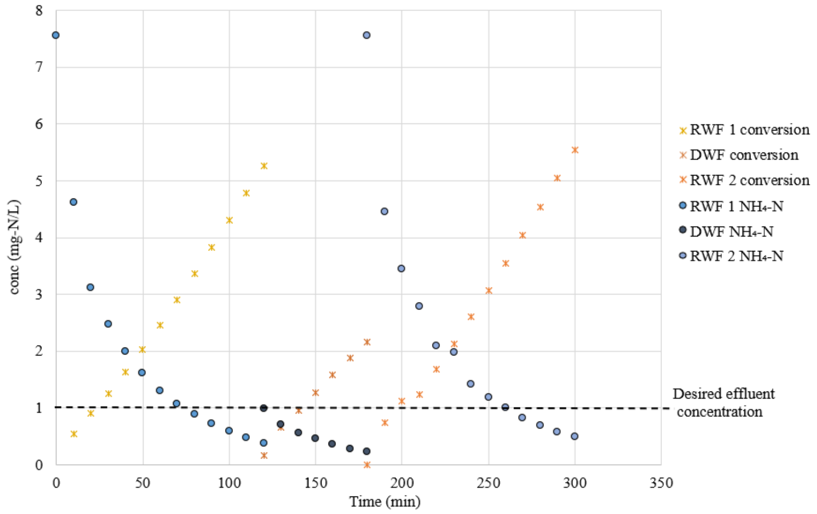


Figure 5.12: The variation of influent ammonium concentration from RWF to DWF to RWF concentrations. The dots represent reduction of $NH_4 - N$ concentration with time and the 'x's denotes the converted $NH_4 - N$ to $NO_3 - N$ and $NO_2 - N$

Moreover, the slope (nitrification rate) during RWF 2 is about 4% higher than slope during

RWF 1. Since the difference is marginal, it can be attributed to inconsistencies while performing experiments resulting in better aeration and mixing during the RWF 2 cycle.

5.3 Modelling biomass concentration

As discussed in chapter 4 the model dimensions were based on that of a rapid sand filter and zeolite amount to adsorb peak ammonium concentration. The filter calculations were made for 1 day capacity of peak concentration. Assuming a RWF flow rate of 14040 m^3/day as given in table 3.1, an influent contact time of 10 minutes, a filter depth of 0.9m, peak ammonium concentration of 8 mgN/L and zeolite parameters as given in table 5.6, the following calculations were made regarding dimensions of the filter to predict growth and maintenance of biomass.

Table 5.6: Calculation of zeolite volume and bioreactor dimensions for modelling on BioWin

For ion exchange					
$NH_4{}^+$ concentration	10500	mg/m^3			
Total $NH_4{}^+$ per day	1.47E+08	mg/day			
Equilibrium zeolite capacity	0.446	mg $NH_4{}^+$/g zeolite			
Zeolite required	3.31E+08	g of zeolite for a day			
Zeolite parameters			**Reactor dimensions**		
Diameter	0.001	m	Area	682.18	m^2
Surface area of 1 particle	3.14E-06	m^2	width	23.36	m
Volume of 1 particle	5.23E-10	m^3	length	29.20	m
Mass of 1 in g	8.37E-04	g	depth	0.9	m
No. of particles	3.95E+11	-			
Total volume	206.6	m^3	HRT	10	min
Total area	1.24E+06	m^2	Corresponding water volume	97.5	m^3
Biofilm					
BF thickness (max)	0.00025	m			
Volume	309.8795				

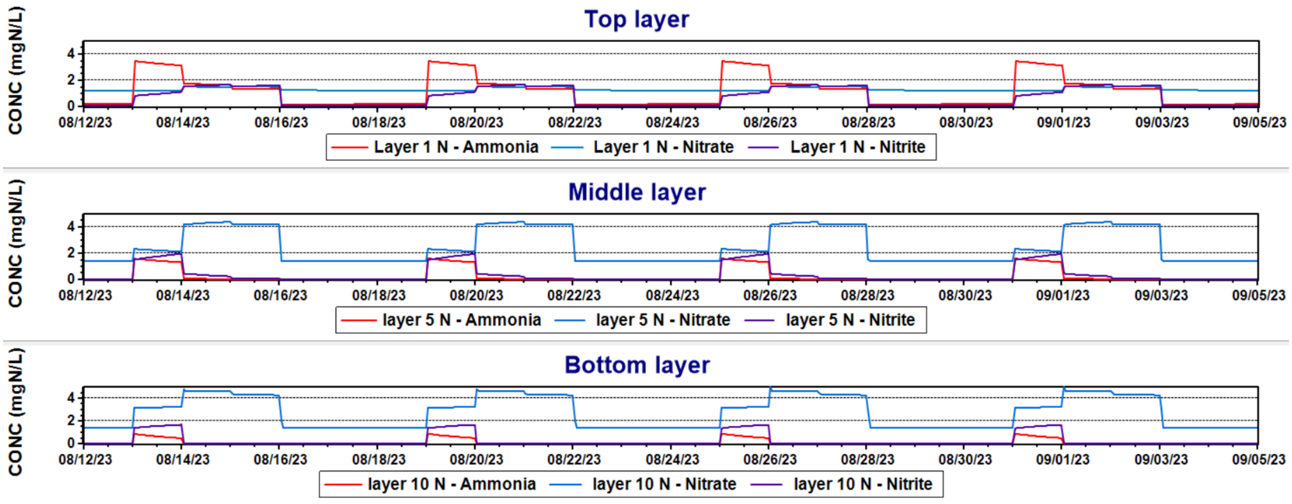
Total reactor volume = Volume of zeolite + max. Biofilm volume + volume of water = 614.38 m^3

From experimental data, the rate of oxygen requirement is determined in section 5.2.3. For this model, this oxygen requirement will not suffice since adsorption by zeolite is ignored. Hence, the aim was to simulate a system without oxygen limitations to understand the distribution and activity of the bacteria. It does not depict the actual removal mechanism since the effect of zeolite is ignored. Moreover, the focus of the model is to understand the biomass distribution throughout the filter and survival of biomass during periods of DWF conditions, which will provide insights on practical operation of the filter.

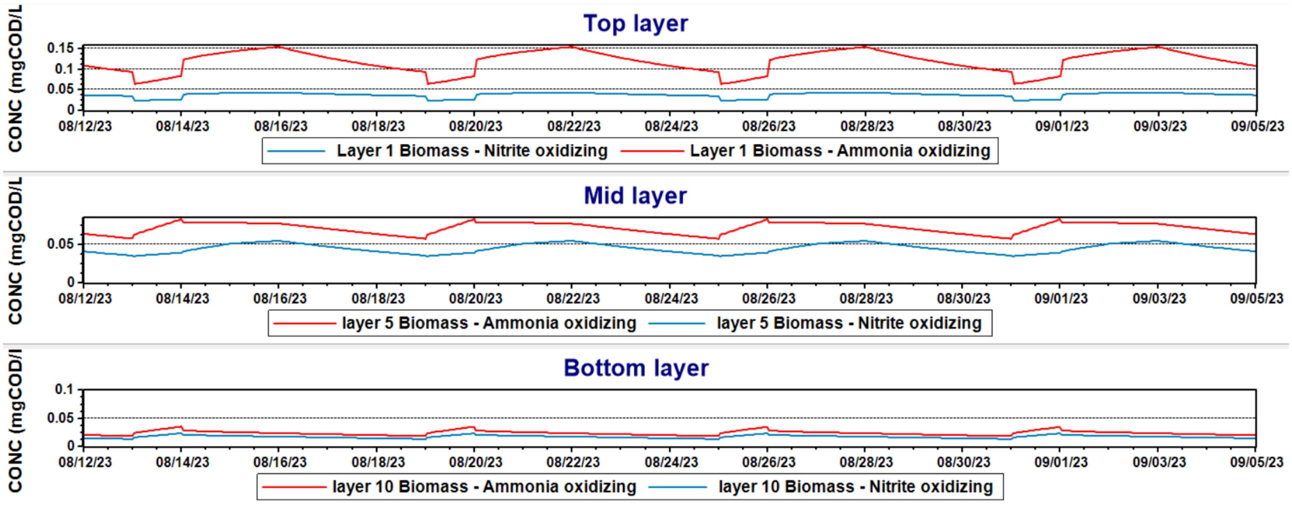
Table 5.7 summarises different cases of simulation done with the model. Peak ammonium concentration during RWF first flush is dampened to simulate the effect of zeolite. Without peak dampening effect, ammonium concentration is not reduced to desired effluent concentration of 1 mgN/L as seen in case 5 from table 5.7 for this contact time.

Table 5.7: This table summarises different cases that were simulated with the model described above. In cases 1-4 the peak ammonium concentration was dampened whereas in case 5 it was not. Simulation period signifies the duration of DWF concentration between subsequent RWF concentrations. Column 3 and 4 describes the ammonium and biomass curves. All the simulation graphs are attached in appendix A.3

Case No.	Simulation period	Effluent ammonium concentration	Biomass concentration
Case 1	ammonium peak concentrations every 10 days followed by peak in 5 days	Desired level remains unattained when the peak occurs every 10 days, whereas it is achieved when the peak frequency is once every 5 days.	Remains consistent when peaks occur every 10 days, whereas it experiences an increase with peaks every 5 days.
Case 2	ammonium peak concentrations every 5 days	Desired value reached consistently	Remains consistent with every peak throughout the simulation period
Case 3	ammonium peak occurs 20 days after reaching a constant value as described in case 2	stays above 2mgN/L at the end of the day.	Recovery post long DWF concentration is low, especially in the bottom layer
Case 4	ammonium peak occurs 7 days after reaching a constant value as described in case 2	Reached desired values few hours into operation under peak concentration	Recovered after a few hours of operation in RWF concentrations
Case 5	ammonium peak concentrations every 5 days without dampening effect	effluent conc of about 2.37mgN/L	NOB concentration in bottom layer is less compared to dampened peak cases, possibly due to concentration with AOB.



(a) $NH_4 - N$,$NO_3 - N$ and $NO_2 - N$ concentrations



(b) Biomass concentration

Figure 5.13: Case 2 simulation curve. 5 days of DWF concentration followed by RWF $NH_4 - N$ peak.

All simulation curves containing graphs of concentration variation of biomass, $NH_4 - N$,$NO_3 - N$ and $NO_2 - N$ concentrations are attached in appendix A.3. To discuss results of simulations, an example simulation case is given above in figure 5.13. The conclusions derived from the simulation cases discussed above are:

- Maximum AOB concentration is about 0.15 mgCOD/L and maximum NOB concentration is about 0.05 mgCOD/L. Biofilm thickness varied between 0.1 to 0.12 mm.
- Peak of 8mgN/L was dampened as 5mgN/L on the RWF day, 3.38 mgN/L and 3 mgN/L on the subsequent days. The concentrations on second and third day were effectively removed post the higher concentration on the day of RWF peak.
- AOB concentration is the highest in the top layer and decreases along the depth of the filter. This is due to decreasing concentration of $NH_4 - N$ along the depth.
- NOB concentration is highest in the middle layer, followed by the top layer and then the bottom layer. This is due to $NO_2 - N$ produced by AOB in the top layers. In the bottom layer though there is enough nitrite NOB concentration is low, possibly due to oxygen limitations.
- In the top layer, the biomass concentrations peaks 2 days after the first peak. For example, in figure 5.13, ammonium peak in layer 1 is on 08/25/23 in graph (a) whereas the biomass in layer 1 in graph (b) begins increasing on 08/25/23, and reaches maximum on 08/28/23, and then begins decreasing when DWF concentration begins.
- In the middle layer, NOB exhibits the same behaviour as biomass in layer 1. But AOB in layer 5 (middle layer) peaks at the end of the RWF peak (i.e. 08/25/23 as discussed in the previous point). This is due to higher ammonium reaching the bottom layers on the first day when compared to subsequent days where the concentration is already consumed by biomass in layer 1. This is also similar in the presence of zeolite where ammonium concentration is lower in the middle and bottom layers, thereby adsorption and subsequent desorption of the adsorbed ammonium is also lower, limiting the substrate availability in the lower layers, especially during times after the first flush event. The AOB and NOB fluctuation in the bottom layer is similar to the AOB in the middle layer.
- Desired effluent concentration is reached without any disturbance in system performance when DWF period lasts for 5 days.
- During DWF concentrations for periods of 7-10 days the biomass activity is regained at the end of day in which concentration peaks, (i.e.) the activity is regained in a few hours.
- For periods of 20 days of DWF the removal of ammonium decreases by 200% as seen in case 3 graph in appendix A.3. But capacity can be regained by subsequent days of exposure to higher concentrations.
- Though the peak was dampened, longer periods of DWF cannot be sustained by the system as shown in the simulations above. Adsorption of ammonium by the zeolite might provide longer time for the biomass to regain its activity and then regenerate the zeolite.

Hence regular (once in 6 days in this modelling case) supply of peak concentration of influent ammonium is necessary to run the system at peak capacity. It is possible to run at longer periods of DWF, but it takes longer time for the bacteria to recover, and it is necessary to have enough zeolite in the system to compensate for this delay in regeneration without compromising on the effluent quality.

6

Conclusion

The findings of this study have shed a light on several important aspects regarding the feasibility of using zeolite with a nitrifying biofilm as a polishing step to remove ammonium.
Freundlich isotherm fit the adsorption data well and equilibrium ammonium adsorption capacity in the absence of cations was found to be 2.764 mg ${NH_4}^+/$ g zeolite for the clinoptilolite used in this study. And in the presence of competing cations, the equilibrium adsorption capacity for the same was 0.44 mg/g. This brings the amount of zeolite to lower ammonium peak concentration from 10.5 to 1.3 mg/L (i.e. 8 mgN/L to 1 mgN/L) to be 20.59 g/L whereas without cations the amount needed would be 3.33 g/L. Thus the ammonium removal capacity decreases by 6.2 times due to competing cations in the wastewater. Kinetics of ammonium removal is fit to pseudo second order kinetic model which predicts the kinetics effectively from 10 minutes of operation. It was also observed from experimental data that increasing zeolite concentration (by 1.5 times) does not necessarily increase the kinetics of removal. It can also be concluded that, though potassium competes with ammonium for ion exchange sites, but only 44.2% of the total potassium was removed in 60 minutes compared to 70.9% ammonium removal. This is in spite of the fact that potassium concentration is about 5 times higher than that of ammonium on mass basis.
The system of zeolite and biofilm has some buffer capacity, but cannot compensate for the bicarbonate anions needed to balance pH. But, contact time of water with the filter is an important factor when it comes to amount of nitrification that occurs in a particular volume of water, thereby reducing it's pH. Hence, pH and O_2 requirements for the process can be controlled by mode of operation.
The ideal outcome of this research is the successful regeneration of zeolite through this technology. Analysing desorption at equilibrium and rate of ammonium conversion it was concluded that zeolite can almost be completely regenerated. Comparing desorption against conversion, it was also seen that rate of conversion is faster than rate of desorption of adsorbed ammonium. But the mechanism of regeneration was not clear - whether the biofilm can take the ammonium from the surface or adsorbed ammonium was desorbed and then digested by the biofilm. The performance of zeolite with biofilm was compared against fresh zeolite and it was found to remove more ammonium overall and also at a faster rate. Also, no substrate limitation was observed even at bulk ammonium concentration of less than 1mgN/L. Additionally in this stage of biofilm growth, adsorption rate and capacity of the zeolite was not affected.
Nitrification rate was determined to be 0.04 mg $NH_4 - N/L.min.$ The zeolite with biofilm was subjected to varying RWF and DWF concentrations and the peaks were dampened in the batch system in 70-80 minutes. The buffer capacity of the zeolite is not enough to maintain the pH in the absence of buffers like bicarbonates. Operating as a fixed bed technology will result in oxygen limitations at longer contact times. Hence it is important to optimize the oxygen and pH requirements of this system for real scale applications.

Moreover, the BioWin model reveals that at inlet concentration of 8mg-N/L, it is not possible to reach effluent standards in a bioreactor with media, without peak dampening for a shorter contact time. It can also be seen that biomass can sustain longer periods of DWF concentrations, but it takes some time and exposure to higher concentrations to revive it's capacity. Hence, supply of nutrients to the setup during long periods of low concentrations is essentially to keep it functional.

Overall, it can be concluded that there is potential in the technology and further studies regarding pilot scale and full scale applications are necessary.

7

Recommendations

Some of the research gaps in using zeolite with nitrifying biofilm as a biological filter in the treatment of effluent wastewater has been answered through this research. There is still a long way to go before this technology can be implemented in full scale. The following section discusses some considerations and drawbacks found through this research and some recommendations for future work.

- The BioWin model represented activity of nitrifiers in a biofilm and effect of zeolite was neglected. Hence a model encompassing the adsorption-desorption effect of zeolite in combination with the activity of biofilm is important to analyse this technology under various flows, concentrations and temperatures, as well as optimisation of the process. This model can be validated by the column experiments performed on lab scale.
- Amount of biofilm on zeolite could not be determined by Gravimetric method. A plan to measure biomass before beginning experiments is necessary.
- The continuation of this work would be to interpret these results and build a lab scale column of a biological filter made of zeolite. The findings from this research can be used as a basis to design a column which will answer the following questions regarding the implementation of this technology in real scale.
  - Optimisation of DO and buffer requirements of the system with mode of operation.
  - Validation of BioWin model results from this study regarding the survival of nitrifiers for long periods of low concentration.
  - Testing the system with real effluent wastewater to understand fouling and effect of biofilm with aerobic and anaerobic microbes (other than nitrifiers).
  - Influence of thicker biofilm (especially in the top of the filter) on adsorption of ammonium by zeolite.
  - How long does it take for the biomass to regain its activity after long periods of DWF?
- The BioWin model is built for ideal breakthrough curve and equilibrium removal. Practical values based on kinetics and zeolite capacity needs to be considered.
- Though nitrate is less harmful to the environment when compared to ammonia, the release of nitrate is not favorable. A possible solution is to recycle water after polishing step back to the biological removal process, to remove nitrate during denitrification cycle. Alternatively, this process can be expanded to anoxic zone in the filter after the nitrification zone. But organic carbon source and low nitrate concentrations can pose as an issue.

- Nitrite accumulation is possible in the system (Montalvo et al., 2020) which can be used to build an annamox biofilm system thereby reducing oxygen requirement in the system. This can be an energy saving and economical treatment alternative for the current research.

Design considerations for lab scale and full-scale systems

As for designing the reactor, adsorption capacity, regeneration time, volume of biomass and volume of water treated in particular residence time must be points of consideration.

- As discussed in section 5, aeration of 2.5 mg/L was enough for the nitrification rate obtained from experimental data under shorter HRT of 10 minutes. But it is important to remove the ammonia peak by adsorption in this time period. Additionally effective aeration can also be achieved by pre-aerating the water before entering the reactor or dividing the entire reactor into 2 and implementing aeration in between. In these cases buffer capacity of water for higher conversion (due to more oxygen) must also be considered. Since buffer capacity of existing effluent wastewater was unknown, this research only covered the buffer capacity of the system with synthetic wastewater and without addition of bicarbonate ions.

- To facilitate the ease of operation zeolite of higher particle size can be considered. This research considers particle size of 1mm which is practically usable, but has a increased chance of filter clogging and increased head loss. Using higher particle size will result in decreased ammonium removal due to decreased surface area. Hence higher volume of zeolite would be required in case of bigger particle size, which wouldn't be a problem since for 1mm particle size only 207 m^3 of zeolite was required at equilibrium to remove peak ammonium value for a day. This results in increased capital cost which can be balanced by potential reduction in operational cost due to decreased head loss and ease of operation.

- Filter clogging can be prevented by employing a clarifier before treatment with zeolite biological filter. Alternatively, the filter bed can be constructed similar to a rapid sand filter with sand layer on top and zeolite layer in between followed by bigger particles in the bottom. This will result in higher HRT to accommodate larger volumes as well as prevent clogging in the zeolite layer.

- The distribution of biomass across filter is uneven as seen in section 5.3. This may result in lower regeneration (due to less biofilm) in the bottom of the column. A possible solution is to reverse water flow direction, but pumping difficulties and possible release of ammonium from top of the filter are to be considered.

- During longer periods of DWF concentrations between RWF peaks, the filter can be supplemented with ammonia from partially treated secondary treatment feed to sustain the biomass concentrations

A

Appendix

A.1 Appendix A: Zeolite and Adsorption experiments

Zeolite pre-treatment Washing the zeolite with demi-water multiple times till supernatant is clear liquid.

Figure A.1: Zeolite before cleaning (left) and after cleaning (right)

Ion exchange experiments

Adsorption Isotherm

Table A.1: Experimental data of adsorption of ammonium only on zeolite

Samples	$NH_4{}^+$ **ini**	**Na ini**	**Temperature** $^\circ C$	**pH**			
A01-A07	3.9565	2.131	16.9	7.205			
A11-A17	9.2795	2.0485	16.9	7.15			
Sample ID	**Zeolite mass (g/100ml)**	**Zeolite mass(g/L)**	**water (mL)**	$NH_4{}^+$ **final (mg/L)**	**Na final (mg/L)**	**K final (mg/L)**	**qe**
A01	0.103	1.03	100	0.96	4.332	0.364	2.90
A02	0.4	4	100	0.291	5.538	0.289	0.91
A03	0.703	7.03	100	0.201	5.943	0.236	0.53
A04	1.001	10.01	100	0.196	6.065	0.282	0.37
A05	1.205	12.05	100	0.069	6.154	0.247	0.32
A06	1.501	15.01	100	0.12	6.534	0.227	0.25
A07	2	20	100	0.068	6.851	0.275	0.19
A11	0.104	1.04	100	3.45	4.848	0.994	5.60
A12	0.402	4.02	100	0.972	8.148	0.781	2.06
A13	0.701	7.01	100	0.521	9.163	0.594	1.24
A14	1	10	100	0.389	9.786	0.604	0.89
A15	1.204	12.04	100	0.245	9.989	0.602	0.75
A16	1.5	15	100	0.277	10.258	0.599	0.60
A17	1.999	19.99	100	0.21	10.577	0.523	0.45

Adsorption isotherm

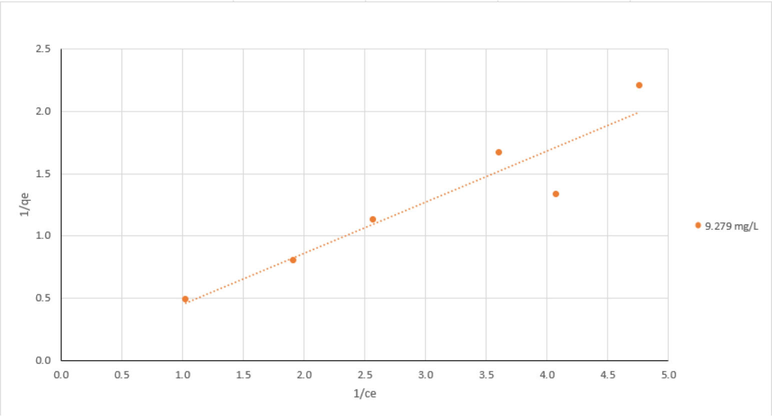


Figure A.2: Langmuir isotherm for solution with only ammonium ions

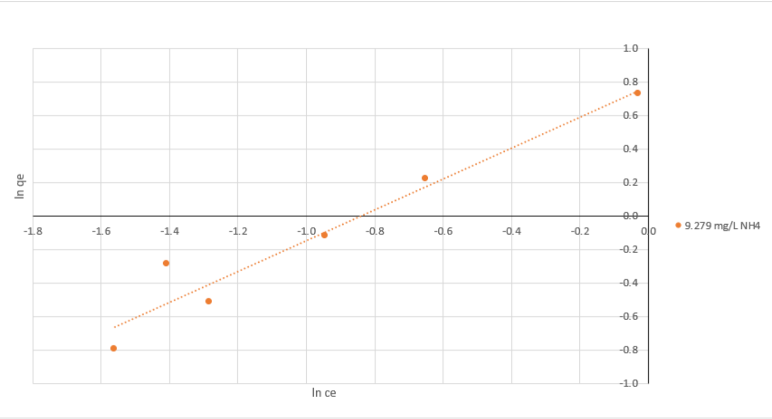


Figure A.3: Freundlich isotherm for solution with only ammonium ions

Table A.2: Experimental data of adsorption of ammonium on zeolite in the presence of competing cations

Samples	$NH_4{}^+$ **ini**	Na^+ **ini**	K^+ **ini**	**Temperature** $°C$	**pH**			
A21-A27	1.376	141.037	50.99	16.6	7.82			
A31-A37	4.765	122.864	20.911	16.7	7.72			
A41-A47	10.497	77.043	50.803	18.7	7.69			
Sample ID	**Zeolite mass (g/100ml)**	**Zeolite mass(g/L)**	**NH4 final (mg/L)**	**Na final (mg/L)**	**K final (mg/L)**	**qe**	$NH_4{}^+$ **removal**	
A21	0.103	1.03	1.392	137.365	16.902	-0.015	-1.163	
A22	0.4	4	0.98	136.103	12.185	0.099	28.779	
A23	0.703	7.03	0.715	134.036	9.868	0.094	48.038	
A24	1.001	10.01	0.59	131.498	8.726	0.078	57.122	
A25	1.205	12.05	0.509	129.951	8.41	0.072	63.009	
A26	1.501	15.01	0.428	127.586	7.801	0.063	68.895	
A27	2	20	0.364	124.144	7.275	0.050	73.547	
A31	0.1	1	4.053	122.91	17.869	0.712	14.942	
A32	0.403	4.03	2.597	122.744	12.72	0.538	45.498	
A33	0.701	7.01	1.81	121.159	10.309	0.421	62.015	
A34	1.001	10.01	1.395	118.973	9.076	0.336	70.724	
A35	1.201	12.01	1.177	118.01	8.468	0.298	75.299	
A36	1.5	15	0.98	116.15	7.835	0.252	79.433	
A37	2	20	1.805	113.403	7.196	0.148	62.120	
A41	1	10	2.698	81.784	20.84	0.779	74.297	
A42	1.2	12	2.287	81.557	19.645	0.684	78.213	
A43	1.5	15	1.828	81.225	17.995	0.577	82.586	
A44	1.7	17	1.609	81.119	17.631	0.522	84.672	
A45	2	20	1.328	80.325	16.644	0.458	87.349	
A46	2.2	22	1.197	80.338	16.433	0.422	88.597	
A47	2.5	25	1.057	79.796	15.911	0.377	89.930	

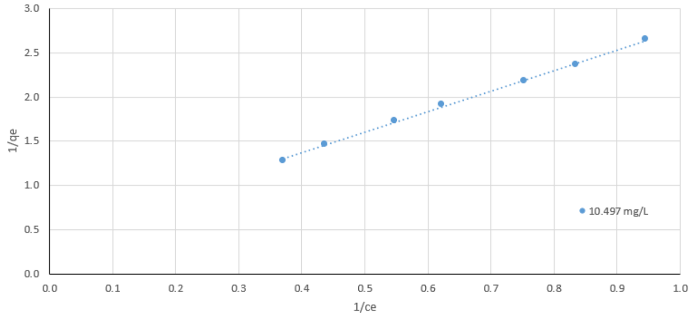


Figure A.4: Langmuir isotherm for solution with with competing cations

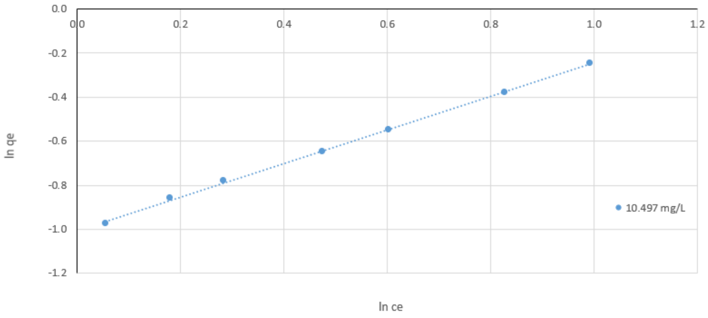


Figure A.5: Freundlich isotherm for solution with competing cations

Adsorption kinetics

Table A.3: Data from kinetics experiment E1 at temperature of 20.1°C and pH of 7.83

Sample ID	**Zeolite mass (g/150mL)**	$NH_4{}^+$ **ini**	K^+ **fin (mg/L)**	Na^+ **fin (mg/L)**	**Time (min)**
Initial Sample		10.165	49.974		0
K1.3	3	7.947	45.195	83.735	180
K1.6	3	6.973	42.618	85.654	360
K1.10	3	6.095	40.263	87.034	600
K1.15	3	5.375	37.931	88.111	900
K1.20	3	4.846	36.093	88.642	1200
K1.25	3	4.449	34.686	89.012	1500
K1.30	3	4.125	33.335	89.245	1800
K1.35	3	3.831	32.088	89.267	2100
K1.40	3	3.598	30.892	89.286	2400
K1.50	3	3.208	29.45	89.055	3000
K1.60	3	2.956	27.904	88.849	3600
K1.75	3	2.63	26.54	88.241	4500
K1.90	3	2.414	25.098	87.738	5400
K1.105	3	2.244	24.362	87.163	6300
K1.120	3	2.072	23.641	86.729	7200
K1.135	3	1.995	23.026	86.221	8100
K1.150	3	1.929	22.554	85.826	9000

Kinetic model graphs

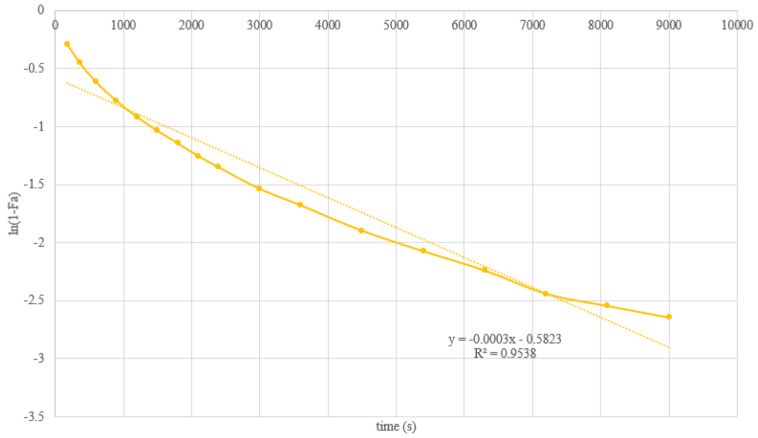


Figure A.6: First order kinetic model

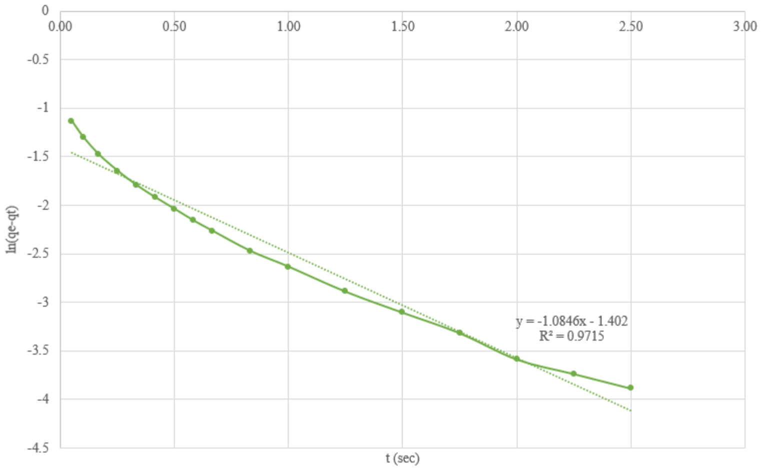


Figure A.7: Pseudo first order kinetic model

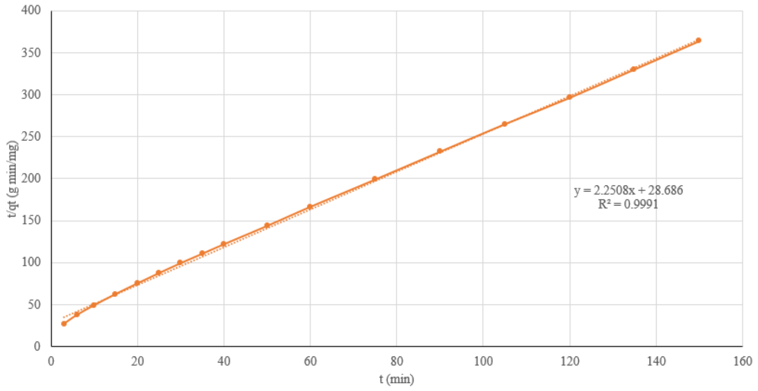


Figure A.8: Pseudo Second order kinetic model

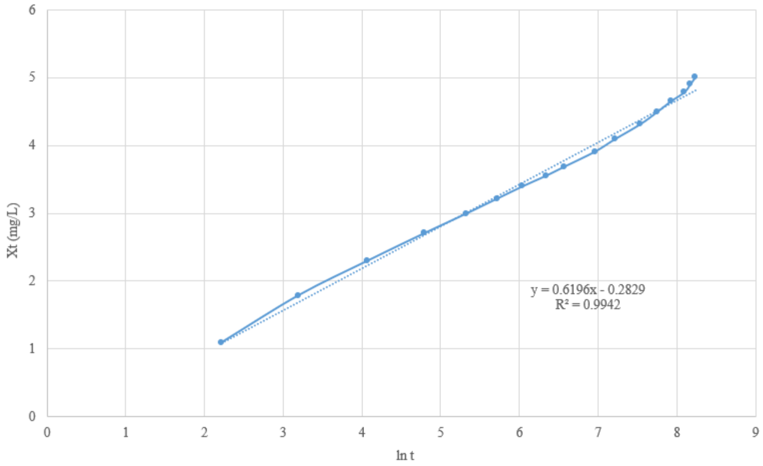


Figure A.9: Elovich model

Other kinetics experiment data

Table A.4: Data from kinetics experiment E2 at temperature of 22.8°C and pH of 7.76

Sample ID	**Time (min)**	NH_4 **fin (mg/L)**	**K fin (mg/L)**	**Na fin (mg/L)**
Ak0	0	11.341	51.242	87.122
AK10	10	7.096	41.298	95.193
AK20	20	5.731	37.303	96.524
AK30	30	4.979	34.414	97.052
AK40	40	4.519	32.206	97.202
AK50	50	4.095	30.922	97.113
AK60	60	3.859	29.728	96.968

Table A.5: Data from kinetics experiment E3 at temperature of 21°C and pH of 7.58

Sample ID	**Time (min)**	Na^+	NH_4^+	K^+
Feed	0	88.989	9.732	48.835
Zt10	10	95.359	5.888	38.219
Zt20	20	96.595	4.614	33.775
Zt30	30	97.167	3.685	29.961
Zt40	40	97.322	3.059	27.933
Zt50	50	97.045	2.595	25.942
Zt60	60	96.767	2.332	24.427
Zt70	70	96.203	2.105	23.202
Zt80	80	95.665	1.922	22.394
Zt90	90	95.247	1.782	21.858
Zt100	100	92.277	1.635	20.827
Zt110	110	94.307	1.607	20.755
Zt120	120	93.709	1.542	20.671

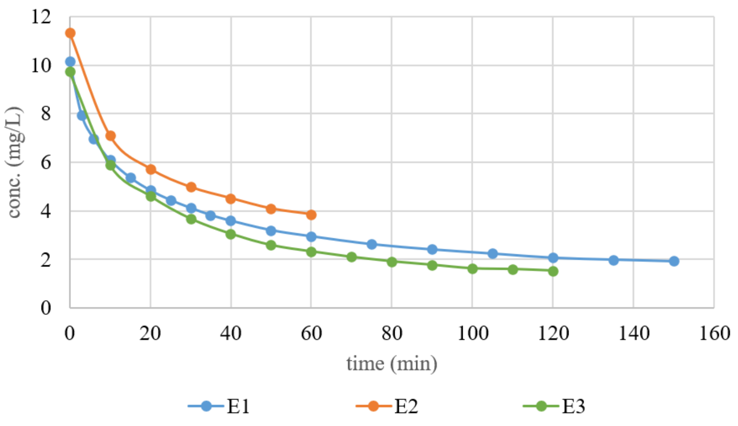


Figure A.10: Comparison of kinetic curves of E1,E2 and E3

Desorption

Table A.6: Experiment as described in section 4.1.1. Different zeolite samples are exposed RWFavg and RWFmax concentrations till equilibrium and then subjected to DWF feed. Desorption for both average and max cases are noted below.

Water sample	**Na (mg/L)**	**NH4 (mg/L)**	**K (mg/L)**
RWF avg	102.897	11.085	45.014
RWF max	64.637	20.404	42.018
DWF	140.151	2.848	58.327
RWF avg final	79.907	2.084	15.915
RWF max fin	71.309	2.643	15.339

Sample ID	**Time (min)**	**Na (mg/L)**	**NH4 (mg/L)**	**K (mg/L)**
avg5	5	138.519	3.493	48.533
avg10	10	138.407	3.351	45.053
avg20	20	138.113	3.168	41.347
avg30	30	137.408	3.119	39.394
avg45	45	136.831	3.269	36.752
avg60	60	136.055	3.307	34.734
avg90	90	134.816	3.24	32.573
avg120	120	133.877	3.246	31.475
avg155	155	132.698	3.139	29.536
avg180	180	132.092	2.997	28.791
max5	5	137.582	3.928	48.19
max10	10	137.173	4.281	44.638
max20	20	136.45	4.542	41.408
max30	30	136.016	4.829	38.708
max45	45	134.963	4.807	36.208
max60	60	134.205	5.029	35.042
max90	90	132.94	4.851	31.737
max120	120	131.7	4.806	30.783
max155	155	130.607	4.903	30.301

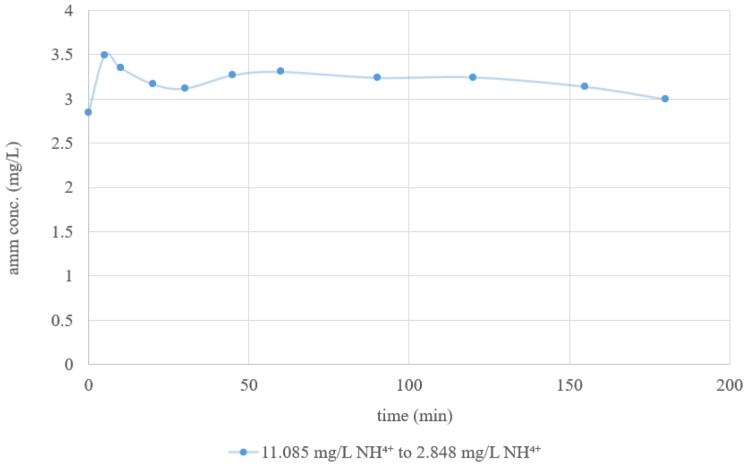


Figure A.11: Increase in $NH_4{}^+$ concentration with time due to desorption. Zeolite was subjected to RWF concentration of 11.085 mg/L $NH_4{}^+$ and then exposed to concentration of 2.848 mg/L $NH_4{}^+$ which resulted in desorption

A.2 Appendix B: Nitrifiers and Biofilm experiments

Preparation of biomass B-stage sludge from Dokhaven is taken and grown in the continuous reactor in the lab to have only nitrifiers.

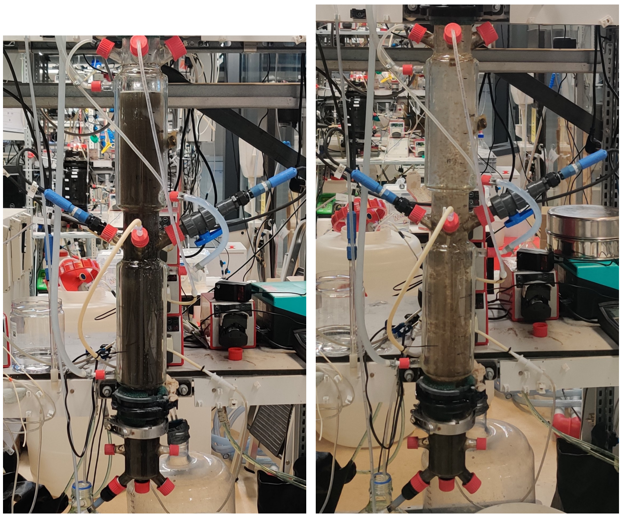


Figure A.12: Clearing up biomass to have only active nitrifiers. Can be seen from change in colour from dark brown to light brown

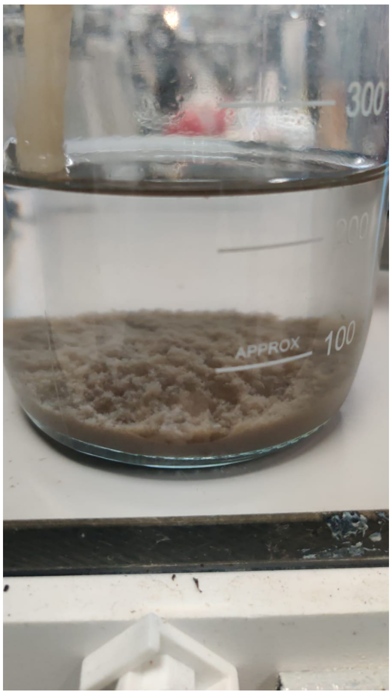
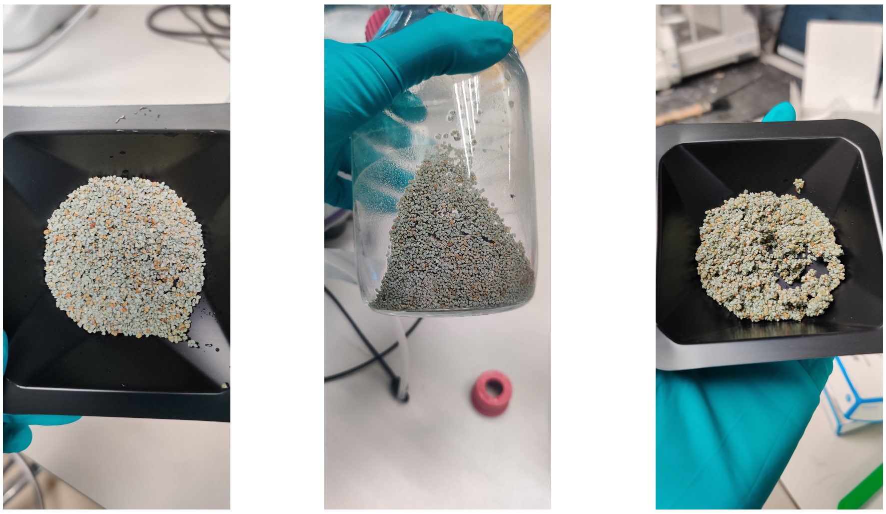


Figure A.13: Submerging zeolite in biomass for biofilm attachment



(a) Fresh wet zeolite (b) Zeolite with biofilm (c) Zeolite with biofilm

Figure A.14: Biofilm over zeolite can be seen from the brownish tinge in images b and c

Biofilm experiments

Zeolite only vs Zeolite with biofilm

Table A.7: Experimental data for experiment described in 4.2.1. The Bt samples represent the kinetic data of experiment with biofilm and the Zt samples in the second half of the table represent th ekinetic data of experiment with fresh zeolite (no biofilm)

Sample ID	**Time (min)**	Cl^- **(mg/L)**	NO_2^- **(mg/L)**	NO_3^- **(mg/L)**	Na^+ (mg/L)	NH_4^+ **(mg/L)**	K^+ **(mg/L)**
Feed BZ	0	74.235			88.989	9.732	48.835
Bt10	10	72.892	0.474	1.755	100.558	5.938	42.777
Bt20	20	73.418	0.61	3.207	105.838	4.013	39.544
Bt30	30	73.539	0.691	4.622	108.281	3.196	37.692
Bt40	40	73.722	0.753	6.197	110.069	2.566	36.398
Bt50	50	73.84	0.807	7.876	111.489	2.079	35.605
Bt60	60	73.925	0.861	9.715	112.547	1.681	34.7
Bt70	70	74.067	0.894	11.613	113.317	1.381	34.058
Bt80	80	74.203	0.93	13.625	113.825	1.149	33.648
Bt90	90	74.316	0.953	15.668	114.394	0.941	32.794
Bt100	100	74.421	0.959	17.755	114.722	0.764	32.416
Bt110	110	74.615	0.961	19.865	115.082	0.617	32.22
Bt120	120	74.738	0.95	22.018	115.514	0.484	32.042
Zt10	10				95.359	5.888	38.219
Zt20	20				96.595	4.614	33.775
Zt30	30				97.167	3.685	29.961
Zt40	40				97.322	3.059	27.933
Zt50	50				97.045	2.595	25.942
Zt60	60				96.767	2.332	24.427
Zt70	70				96.203	2.105	23.202
Zt80	80				95.665	1.922	22.394
Zt90	90				95.247	1.782	21.858
Zt100	100				92.277	1.635	20.827
Zt110	110				94.307	1.607	20.755
Zt120	120				93.709	1.542	20.671

Buffer capacity experiment

Table A.8: Modified synthetic wastewater sample used in the buffer capacity experiment

Water sample	**g/L**	
NH_4Cl	0.031	
$NaHCO_3$	0	
$CaCl_2.2H_2O$	0.114	
KH_2PO_4	0.181	
$MgSO_4.7H_2O$	0.092	
$NaOH$	0.1617	
H_2SO_4	520	μL of 2.5M
Trace 1	1	mL
Trace 2	1.25	mL

Table A.9: Experimental data for determining buffer capacity of the system as described in section 4.2.1

Sample ID	Time (min)	pH	NO_2^-(mg/L)	NO_3^- (mg/L)	Na^+ (mg/L)	NH_4^+ (mg/L)	K^+ (mg/L)
Feed	0	7.7	0.738	4.877	92.255	10.832	41.38
P1t10	10	7.58	0.562	8.483	91.862	7.045	35.442
P1t20	20	7.35	0.705	9.795	92.024	6.605	37.479
P1t30	30	7.26	0.836	11.372	92.193	6.056	35.291
P1t45	45	7.174	0.957	13.716	91.985	5.488	32.876
P1t60	60	7.035	0.998	16.043	91.853	5.062	29.745

Flow variation experiment

Table A.10: Experimental data of variation in flow from RWF - DWF - RWF concentrations indication adsorption, regeneration and adsorption again.

Sample ID	Time (min)	NH_4-N (mgN/L)	NO_3-N (mgN/L)	NO_2-N (mgN/L)	NH_4-N removed (mgN/L)	Total converted (mgN/L)
RWF feed	***0***	***7.557***	***0***	***0***		
R1Bt10	10	4.611	0.396	0.144	2.946	0.541
R1Bt20	20	3.116	0.724	0.186	4.441	0.910
R1Bt30	30	2.482	1.044	0.210	5.075	1.255
R1Bt40	40	1.992	1.400	0.229	5.564	1.629
R1Bt50	50	1.614	1.779	0.246	5.942	2.025
R1Bt60	60	1.305	2.195	0.262	6.251	2.457
R1Bt70	70	1.072	2.623	0.272	6.484	2.896
R1Bt80	80	0.892	3.078	0.283	6.665	3.361
R1Bt90	90	0.731	3.539	0.290	6.826	3.830
R1Bt100	100	0.593	4.011	0.292	6.963	4.303
R1Bt110	110	0.479	4.488	0.293	7.078	4.780
R1Bt120	120	0.376	4.974	0.289	7.181	5.263
					amount stored in zeolite	1.918
DWF feed	***120***	***0.985***	***0.157***	***0***		***0.157***
D1Bt10	130	0.712	0.512	0.150	0.273	0.662
D1Bt20	140	0.567	0.788	0.176	0.419	0.963
D1Bt30	150	0.459	1.074	0.190	0.526	1.264
D1Bt40	160	0.360	1.381	0.198	0.625	1.579
D1Bt50	170	0.285	1.674	0.200	0.700	1.874
D1Bt60	180	0.235	1.966	0.197	0.750	2.163
					excess conversion	1.255
RWF feed	***180***	***7.557***	***0***	***0***		***0***
R2Bt10	190	4.449	0.542	0.193	3107	0.735
R2Bt20	200	3.445	0.880	0.232	4.111	1.113
R2Bt30	210	2.795	1.236	0	4.762	1.236
R2Bt40	220	2.092	1.681	0	5.465	1.681
R2Bt50	230	1.986	2.124	0	5.570	2.124
R2Bt60	240	1.411	2.602	0	6.164	2.602
R2Bt70	250	1.192	3.064	0	6.365	3.064
R2Bt80	260	1.004	3.546	0	6.553	3.546
R2Bt90	270	0.826	4.039	0	6.731	4.039
R2Bt100	280	0.698	4.539	0	6.859	4.539
R2Bt110	290	0.579	5.044	0	6.977	5.044
R2Bt120	300	0.489	5.547	0	7.068	5.547
					amount stored in zeolite	1.520

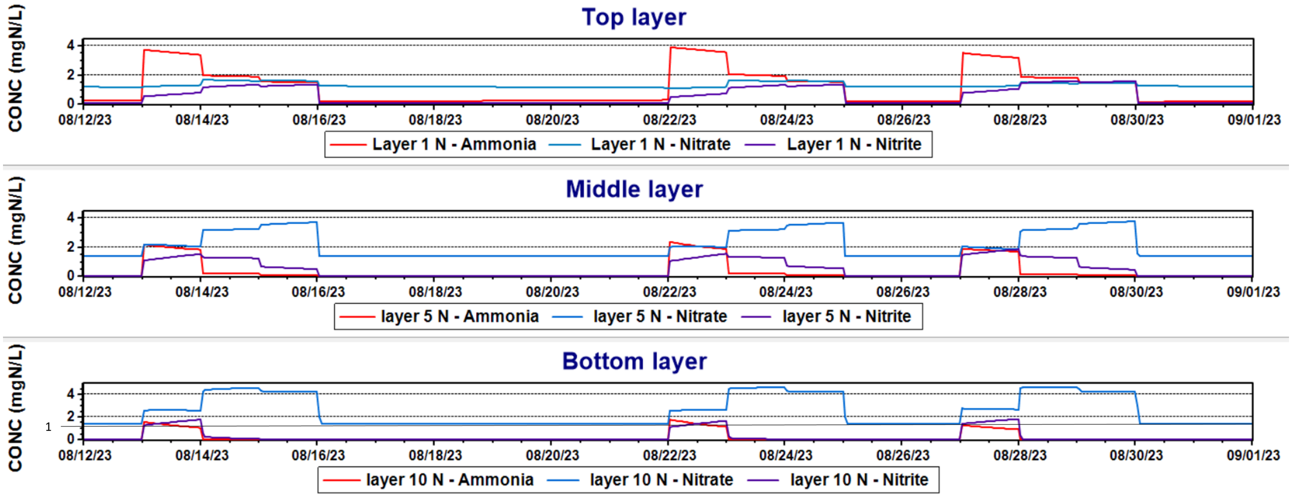
Gravimetric method experiment for measurement of volatile solids on zeolite

(a) Before treatment in muffle oven

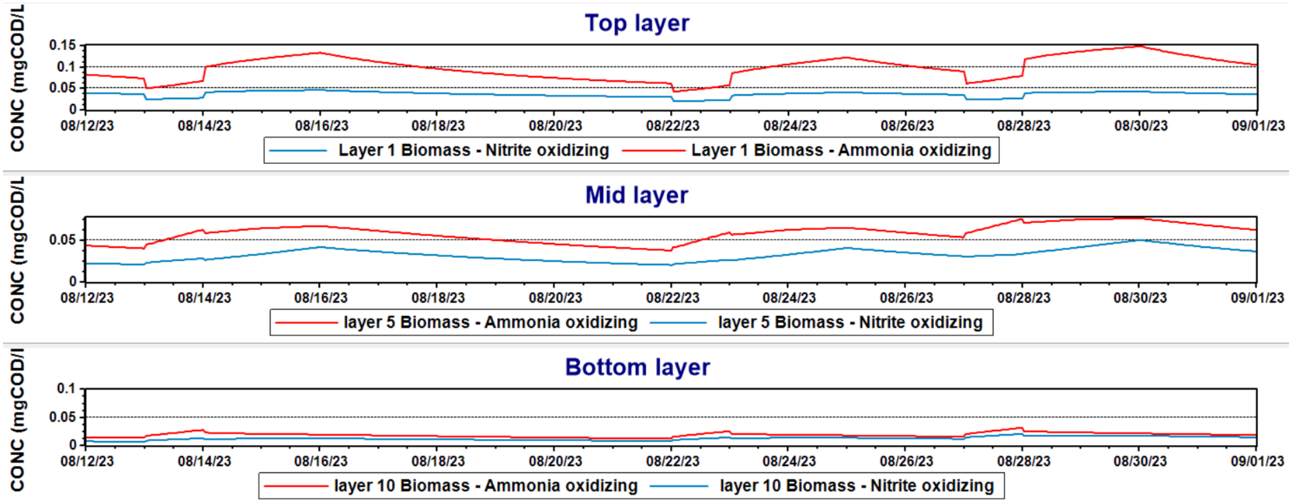
(b) After treatment in muffle oven

Figure A.15: Zeolite samples from gravimetric method to determine Volatile solids on zeolite

A.3 Appendix C : BioWin Modelling

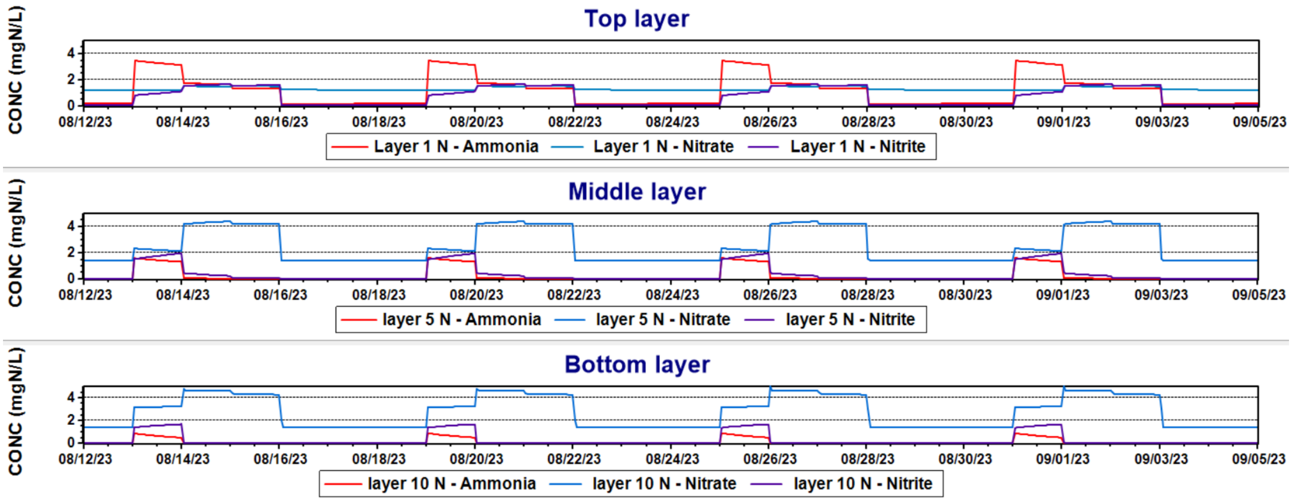


(a) NH_4-N,NO_3-N and NO_2-N concentrations

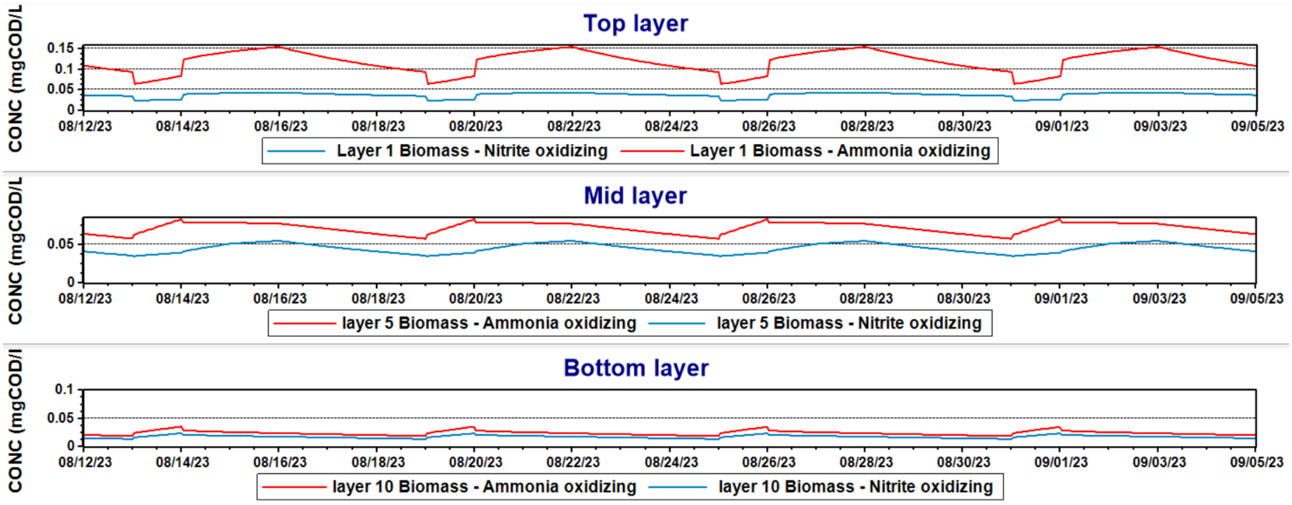


(b) Biomass concentration

Figure A.16: Case 1

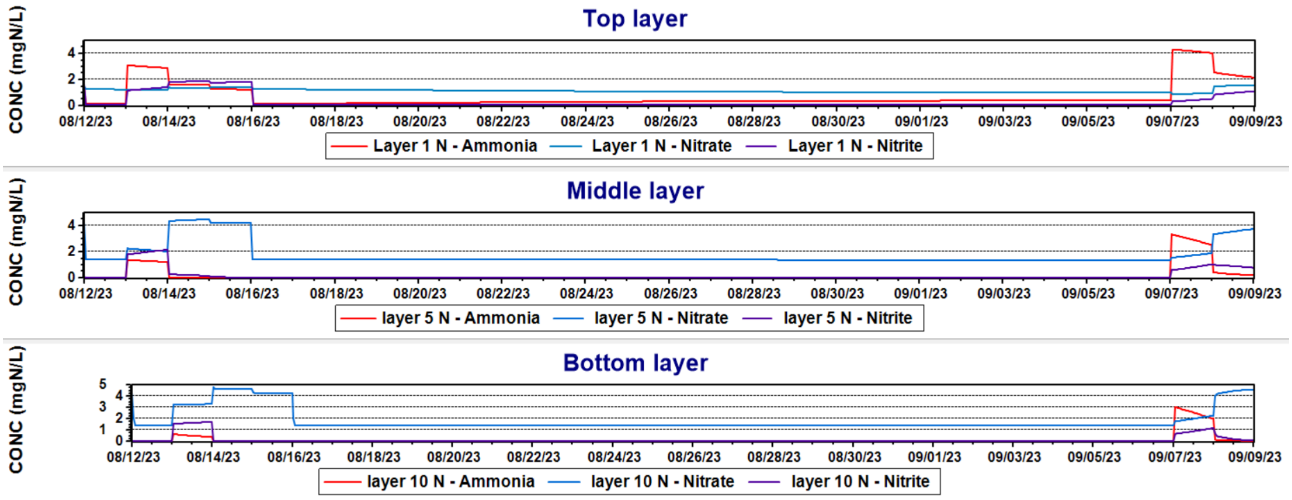


(a) $NH_4 - N$,$NO_3 - N$ and $NO_2 - N$ concentrations

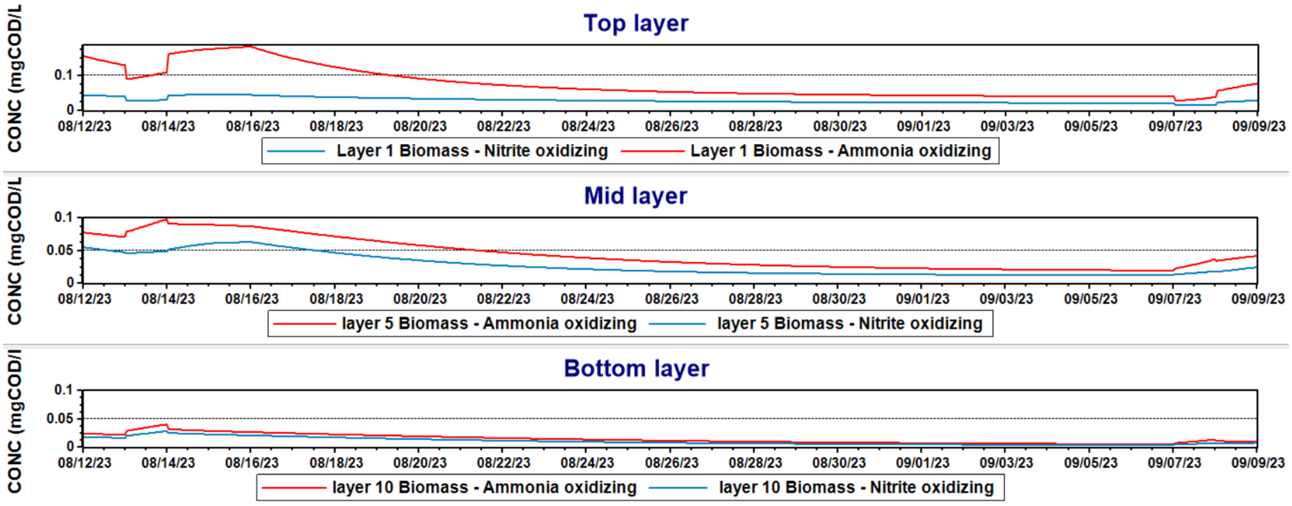


(b) Biomass concentration

Figure A.17: Case 2

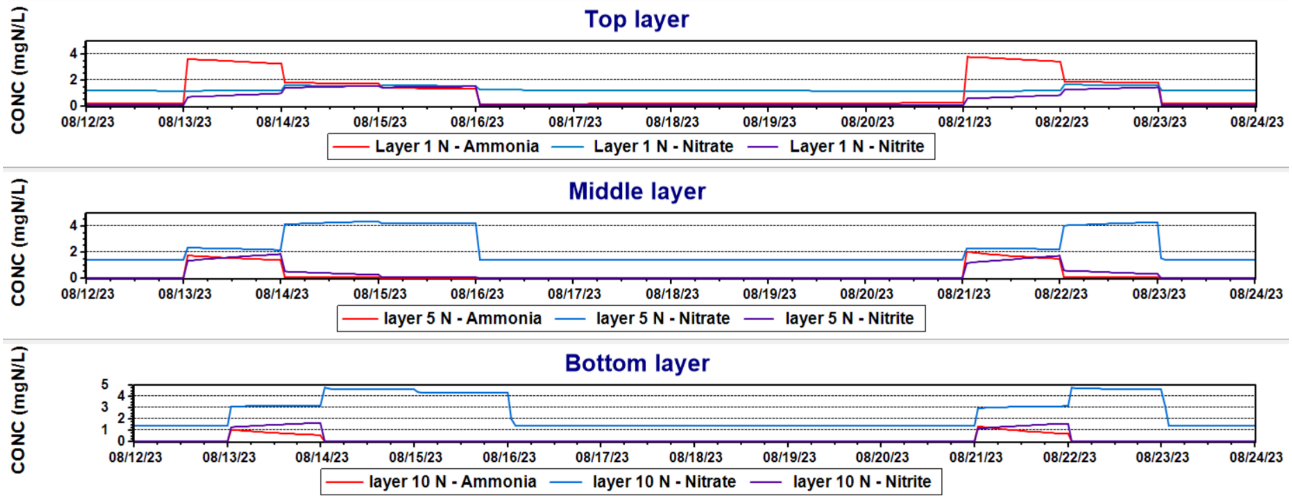


(a) $NH_4 - N$,$NO_3 - N$ and $NO_2 - N$ concentrations

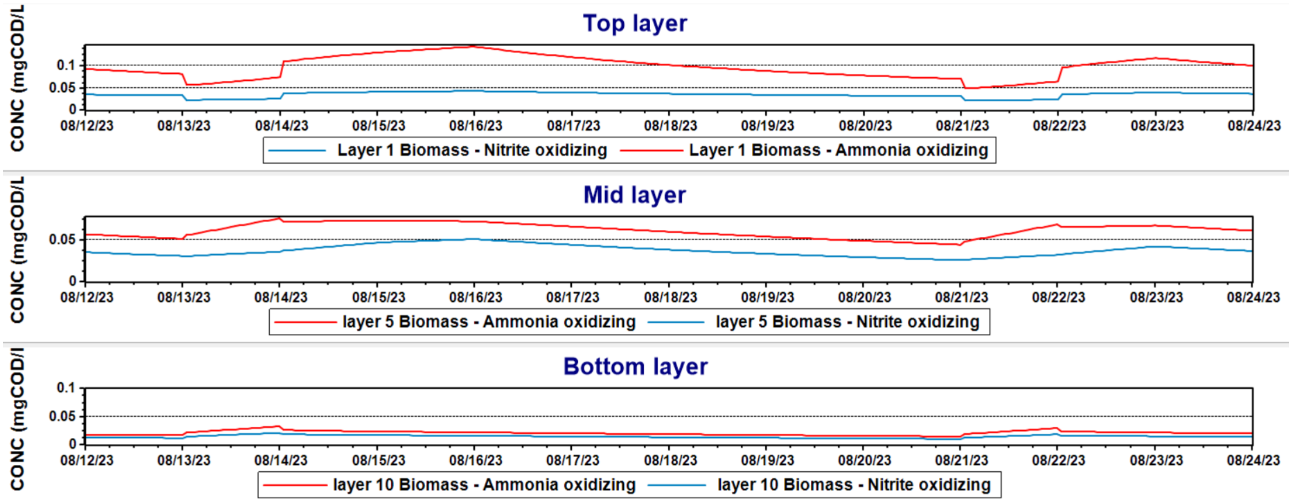


(b) Biomass concentration

Figure A.18: Case 3

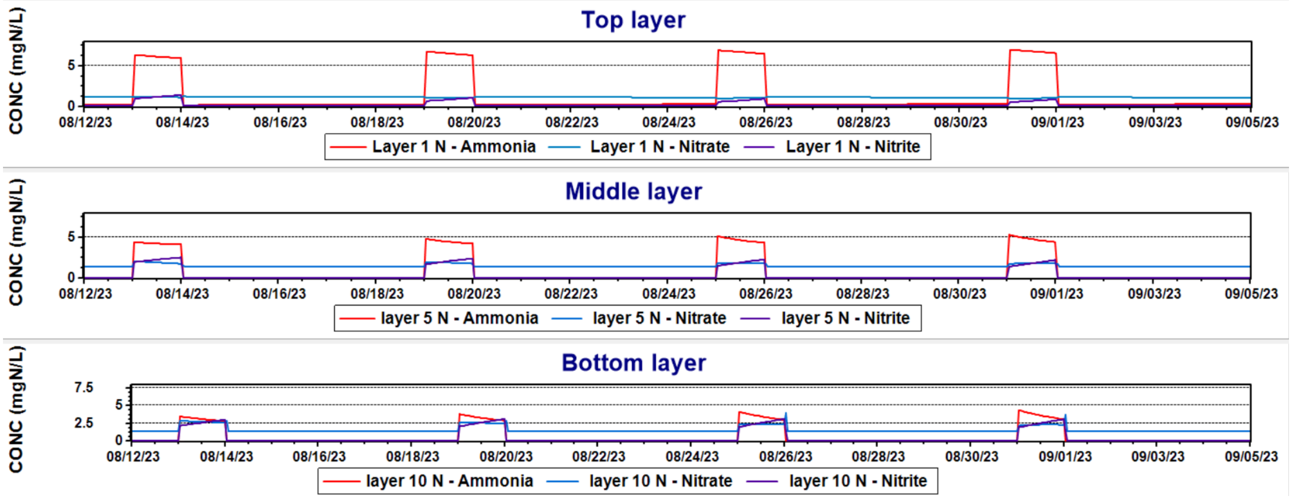


(a) $NH_4 - N$,$NO_3 - N$ and $NO_2 - N$ concentrations

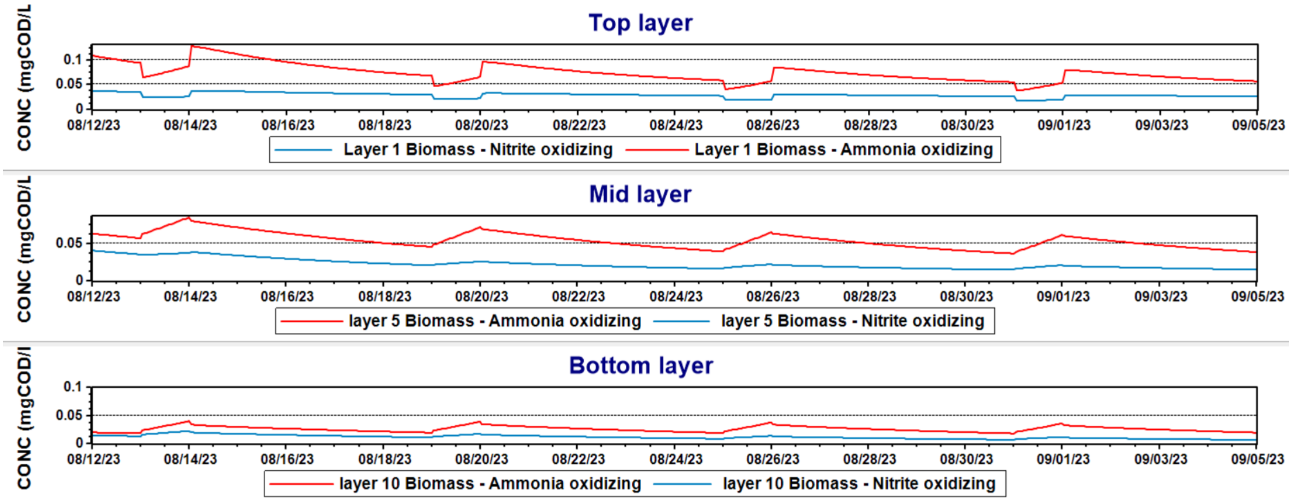


(b) Biomass concentration

Figure A.19: Case 4



(a) NH_4-N,NO_3-N and NO_2-N concentrations



(b) Biomass concentration

Figure A.20: Case 5

A.4 Appendix D: Zeolite product information

MATERIALBEZEICHNUNG

Materialname	Naturzeolith
Chemischer Name	Hydratisiertes Alumosilikat der Alkali- und Erdalkalimetalle
Mineralogische Form	Klinoptilolith
Chemische Art	Molekularsieb
Empirische Formel	Ca1,8K1,8Na0,2Mg0,2Al6Si30O72.24H2O [1] Na20.21K.74) (Ca1.71Mg0.31) (H20)18.28| [Al6.11 Si2990O722] [2] (Na0.08K0.35) (Ca0.44Mg0.08) [Al1.47 Si7.53O18] .4,34 H2O [3]
Allgemeine Formel	(Ca, K2, Na2, Mg)4al8Si40O96.24H2O

MINERALOGISCHE ZUSAMMENSETZUNG (in %)

Klinoptilolith	86 - 90	Cristobalit	5 - 8	Glimmer	2 - 4
Feldspat	2 - 4	Edisonite	0,1 - 0,3	Quarz	Spuren

CHEMISCHE ZUSAMMENSETZUNG (in %)

SiO_2	69,83 - 71,31	Al_2O_3	12,64 - 13,06	CaO	3,12 - 3,58	K_2O	2,97 - 3,15	Fe_2O_3	0,70 - 1,66
Na_2O	0,20 - 1,0	MgO	0,70 - 1,20	TiO_2	0,19 - 0,28			Si / Al	4,80 - 5,40

IONENAUSTAUSCHEIGENCHAFTEN

CA^2+	0,64 – 0,98 mol.kg-1	Mg^2+	0,06 – 0,19 mol.kg-1	K+	0,22 – 0,45mol.kg-1	Na+	0,01 – 0,19 mol.kg-1

Gesamtaustauschkapazität	1,20 – 1,50 mol.kg-1
Wasserdampfabsorption durch dehydriertes Gestein	
bei 20°C und relativer Feuchte von 52%	7,50 – 8,50 g H2O.100g-1
bei relativer Feuchte von 98%	13,50 – 14,50 g H2O.100g-1

PHYSIKALISCHE UND CHEMISCHE EIGENSCHAFTEN

Spezifisches Gewicht	2200 - 2440 kg/m^3	Porosität	24 - 32 %
Rohdichte	1600 - 1800 kg/m^3	Effektiver Porendurchmesser	0,4 nm
Aussehen und Geruch	graugrün - ohne G.	Dichte	70%
Härte nach Mohs	1,5 - 2,5	Druckfestigkeit	336,51 kg/cm^2
Erweichungstemperatur	1260° C	Weißgrad	70%
Schmelztemperatur	1340° C	Mahlbarkeit nach VTI	kVTI = 1.628
Fließtemperatur	1420° C		

REAKTIONSFÄHIGKEITSDATEN

Säurestabilität	79,50 %	Gefährlicher Zerfall	nicht vorh.
Thermische Stabilität	bis 400° C	Gefährliche Polymerisation	nicht vorh.
Wasserlöslichkeit	nein	Spezifische Oberfläche (BET)	30 – 60 m^2/g

SELEKTIVITÄT

Cs+ > Pb2+ > NH4+ > Cu2+ > Zn2+ ,Sr2+,Cd2+ > Ni2+ > Co2+ [4]

NH4+ > K+ > Mg2+ > Ca2+ [4]

Cs+ > NH4+ > Pb2+ > K+ > Na+ > Ca2+ > Mg2+ > Ba2+ > Cu2+ > Zn2+

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