CRANFIELD UNIVERSITY

JUDIT CANELLAS-GARRIGA

TERTIARY AMMONIUM REMOVAL WITH ZEOLITES

School of Water, Environment and Energy
Research Degree

Ph.D.
Academic Year: 2014 - 2018

Supervisor: Prof. Bruce Jefferson and Dr. Ana Soares
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This thesis is submitted in partial fulfilment of the requirements for the degree of Ph.D.

ABSTRACT

Ammoniacal nitrogen (NH_4-N) can accelerate eutrophication in rivers and lakes and thus needs to be removed from domestic wastewater before discharging the effluent into a fresh water or a seawater. Currently, biological processes are used to oxidise the reactive nitrogen into N_2, but these processes are highly energy intensive and have difficulties to reach the required effluent concentrations lower than 1 mg L^{-1}. Zeolites have the ability to selectively remove NH_4^+ ions even in the presence of competing species such as calcium. This thesis investigated and compared the properties of natural and synthetic zeolites to determine their suitability for removing nitrogen in a tertiary treatment. Overall the synthetic zeolite MesoLite showed the highest capacity (4.6 meq g^{-1}) and selectivity towards NH_4^+ when compared to other zeolites. Dynamic experiments also showed MesoLite to achieve the highest operational capacity at 27 mg g^{-1}, while other commonly used zeolites like Mordenite and US-Clinoptilolite achieved 25 and 22 mg g^{-1} respectively. One of the most prominent knowledge gaps in literature concerns regeneration of zeolites. Regeneration is the biggest obstacle to wide spread use of zeolite based wastewater treatment on full scale in a way that is economically feasible. The results showed that when the regeneration occurs at pH 12, brine reuse was possible for 5 consecutive cycles. Brine reuse was also found to be one of the key factors determining overall economical feasibility of the process. Specifically, operational expenses were found to be reduced by 50 % when the brine was reused during three consecutive cycles. When the whole life cycle was compared to a solution based on a Nitrifying Submerged Aerated Filter (N-SAF) the process became cheaper for empty bed contact times (EBCT) of 1, 2.5 and 4 min for a 20,000 popular equivalent (PE) business case and for 1, 2.5, 4 and 8 min EBCT for a 2,000 PE business case. The option of recovering reactive nitrogen through a hollow fibre membrane was considered for the 20,000 PE business case. This last setup was found to be more economical than a solution based on the N-SAF process for every one of the tested EBCT (1, 2.5, 4, 8 and 15 min EBCT). In summary, this thesis identified configurations of zeolites and process parameters that were shown to be effective at removing ammoniacal nitrogen from both synthetic and real wastewater and economical analysis showed that zeolite based processes can compete with state of the art approaches.

Keywords:

Reactive nitrogen, zeolite, ion exchange, ammonia, capacity, selectivity, OPEX, CAPEX, WLC

ACKNOWLEDGEMENTS

This has been one of the most challenging and exciting times of my life. I am utmost grateful that I have been able to share this experience with a group of wonderful friends and colleagues who supported me through the more difficult hours of this journey.

First and foremost, I would like to thank my supervisor Prof. Bruce Jefferson. Thank you for choosing me for doing this research, for when you barely knew me you sensed that this project was just perfect for me. Thank you for trusting me during all these years and for helping me to grow and to think about the science behind our work! You have been a “super good” supervisor and I greatly enjoyed (most of the days of) my Ph.D. project. I maintain that without you as my supervisor I could have never evolved into the scientist and person I am today.

Special thanks also to Ana Soares. While we did not have much chance to work together for this research project, you have been in many ways a role model for me – not only in terms of how to conduct research by the most rigorous and professional standards, but also for how to empathetically and professionally lead students so they can unleash their full potential.

I truly hope that these four years have been as rewarding for my other friends and colleagues at the Cranfield Water Science Institute as they have been for me. You all provided a great environment for me to grow as a researcher.

I would like to particularly thank Andre R. for all the great laughs and cheerful conversations we had. Thanks also to Ewan McAdam because every time I talked to you about my research you challenged me to think outside the box. A great thank you also to Tania Rice for providing help whenever I needed it. Without you everything would have been much harder.

Importantly, to my Ph.D. sisters Edwina and Joana: Girls, I am not sure if I could have done it without you. Your generosity, your friendship, and all the fun things we have done together made the difference. You made these years at Cranfield an unforgettable experience. We all now have made it! This is only the beginning of an incredibly exciting journey ahead of us. I truly love you girls.

A mi Pablito e Irene, mis amores! Muchas gracias por todos esos cafés, conversaciones en lab, y estar ahí cuando lo he necesitado. Sois un modelo a seguir para mi y no imagináis lo feliz que soy de que Cranfield me haya dado la oportunidad de tenernos como amigos.

A la meva mare i el meu germà per ser vosaltres. Gràcies Tete per ser qui ets, no imaginària tenir un millor germà que tu, ets increïble i només saber que tinc el teu recolzament em dona molta tranquilitat. A tu mami, per haver lluitat tant per nosaltres, ho has fet increïble! Sense tu, no estaria aquí. Aquest doctorat es també vostre, us estimo.

And of course to you…

Worte können nicht ausdrücken wie dankbar ich meinem Partner bin, der mir in den letzten 2 Jahren so sehr geholfen hat. Du hast mich unterstützt, mich motiviert, mir immer das Gefühl gegeben gute Arbeit zu leisten und mir geholfen eine positive Einstellung zu behalten... Und natürlich die vielen Stunden die du mit Korrekturlesen verbracht hast und dabei Spass an meinem Englisch hattest. Ich liebe dich so sehr und ein Teil dieser Doktorarbeit gehört auch dir..

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NH_4-N	Ammoniacal nitrogen
Å	Angstroms
Al	Aluminium
ASP	Activated sludge processes
Bv	Bed Volume
BOD	Biological Oxygen Demand
C_t	Concentration at time t
C_o	Initial concentration
Ca^{2+}	Calcium
CAPEX	Capital expenditure
CEC	Cation exchange capacity
CO_2	Carbon dioxide
DI	Deionised water
EBCT	Empty bed contact time
FFT	Full flow treatment
F:M	Food to Microorganism ratio
HF	Hollow fibre
IEC	Ion exchange capacity
IEX	Ion exchange
K	Thousand
K_T	Thomas constant
K_{YN}	Yoon and Nelson constant
M	Million
MBR	Membrane Bio-Reactor
Meq	Milliquivalents
N_2	Nitrogen gas
NH_4^+	Ammonia in ionized form
NH_3	Ammonia in a molecular form
N_2O	Nitrous oxide
NH_4Cl	Ammonium Chloride
$(NH_4)_2SO_4$	Ammonium sulphate
N-SAF	Nitrifying Submerged Air Filter

OPEX	Operational expenditure
PE	Popular equivalent
PBU	Primary building unit
PST	Primary settlement tank
Q	Capacity
Re	Reynolds number
TF	Trickling filter
Si	Silica
SBU	Secondary building unit
TGA	Thermogravimetric analysis
US	United States
UK	United Kingdom
WLC	Whole life cycle
WWTW	Wastewater treatment works

1 INTRODUCTION

1.1 Background

Reactive nitrogen, such as ammoniacal nitrogen (NH_4-N) reaches the wastewater treatment works (WWTW) from sources such as fertilisers, faeces or urea (Maurer *et al*., 2003). Nitrogen is an essential nutrient for living species and thus a valuable resource. However, elevated discharges of nitrogen and nitrates into lakes or rivers can have detrimental effects on these ecosystems as nitrogen accelerates eutrophication and deteriorates the water sources (Canfield *et al*., 2010; Fernández *et al*., 2008). To address this problem, the Water Framework Directive 2000/60/EC and urban wastewater treatment Directive 91/271/EC (Directive 1991; European parliament 2000) require strict discharge consents with levels below 1-5 mg NH_4-N L^{-1} and 10-30 mg NO_3-N L^{-1} for discharge into fresh water and 50 mg NO_3-N L^{-1} into seawater. The directive also requires different total nitrogen concentrations depending on the popular equivalent, specifically 15 mg N L^{-1} for 10,000 to 100,000 PE and 10 mg N L^{-1} for over 100,000 PE (Directive 1991; European parliament 2000).

The most common approach to remove reactive nitrogen is through reaction by means of aerobic biological processes, such as the activated sludge process (ASP) or trickling filters (TF). Whilst these processes are effective at the conversion of ammonia into nitrate, delivery of very low ammonia discharge concentrations (lower than 1 mg L^{-1}) remain challenging, especially to TFs. The challenge relates to overall removal capacity and management of instabilities caused by overloading, shock loadings and temperature changes (Almutairi *et al*., 2015; Mery *et al*., 2012; Miladinovic and Weatherley, 2008). These are most commonly encountered at smaller remote works where load variations are larger (seasonally and daily) and passive biological processes such as TFs predominate. In situations where discharge consents have been lowered it is common to replace the TFs with ASP processes as they have greater levels of control and capacity adaptation.

Both processes oxidise the available ammonia into nitrate and then convert this to nitrogen gas when adapted to include denitrification. Accordingly, the process exerts environmental cost through the use of energy in the ASP process and process emissions such as N_2O for both ASP and TF (Huijie and Chandran, 2010). For instance, the estimated energy demand to deliver nitrification is 40 MJ KgN_{rem}^{-1} [13-24 kWh MJ KgN_{rem}^{-1}] (Canfield *et al*., 2010; Mulder, 2003). In addition, biological processes are destructive offering limited potential for recovery. Whilst nitrogen is not a limiting resource, like phosphorus, the production of ammonia is accomplished through the Haber-Bosch process which is directly responsible for 1 to 2 % of the global energy demand and associated with 4 to 8 tons of CO_2 per ton of fertiliser produced (Hargreaves, 2014; Matassa *et al.,* 2015).

Consequently, there is growing interest in finding alternative approaches that offer the possibility to remove and recover reactive nitrogen form wastewater. Ammonia exists in either a molecular (NH_3) or an ionic form (NH_4^+) depending on pH such that it can be removed through physicochemical processes such as stripping or ion exchange (Koon and Kaufman, 1975; Saracco and Genon, 1994). At the normal pH levels of wastewater, 6-8, the ionic form will predominate such that removal through ion exchange pathways is possible. The process works by flowing the wastewater over a media that contains charged sites, balanced by a presaturant ion, typically Na^+. The ammonium ion is preferred by the charged sites within the media and so exchanges with the Na^+ ion. When saturated the media can be regenerated by flushing with a high concentration of the presaturant ion. The ion exchange process operates with relatively low energy demands and is resilient to shock loading and low temperatures, while being able to reach very low effluent concentrations (< 1 mg L^{-1}) (Thornton *et al*., 2007). The main challenges with the process are the selectivity of the media and the generation of large quantities of regenerant liquid that needs managing. One option is to clean up the liquid and recover the captured ammonia providing a route to generating an added value aligned to the circular economy.

The most commonly reported ion exchange media used for ammonium removal are zeolites which are hydrated aluminosilicate materials where substitution of Al^{3+} into the lattice in place of Si^{4+} leads to a charge imbalance that drives uptake of cations (Wang and Peng, 2010). The most commonly reported is Clinoptilolite whose efficacy for ammonium removal has been demonstrated in synthetic and real wastewaters in both batch and continuous trials (Hedström, 2001). In recent years, a synthetic zeolite, MesoLite, has been shown to be potentially more effective than Clinoptilolite offering better capacity and selectivity (Thornton *et al.,* 2007). However, considerably less attention has been given to this material with no reported studies directly comparing MesoLite to natural zeolites or applying it to low strength feed waters such as those associated with tertiary ammonium polishing. The successful work on Clinoptilolite has led to a number of full scale systems over the last fifty years and this has highlighted three main issues that limit wider implementation (Liberti *et al.,* 1981).

(1) The need to pretreat the wastewater to limit solids in the feed to the zeolite filters
(2) The cost associated with regeneration of the media
(3) Management of the spent regeneration liquids

1.2 Aim and objectives

The overall aim of the thesis is to understand and critically evaluate the technical and economic challenges associated with using a zeolite media for removing ammonia from wastewater. To deliver against the overall aim the following objectives were set:

1- **Objective 1:** To establish the optimum pre-treatment to increase zeolites' capacity
2- **Objective 2:** To establish the impact of zeolite selection on the efficacy of a zeolite for ammonium removal.
3- **Objective 2:** To understand the impact that Empty Bed Contact Time (EBCT), feed ammonia concentration, and the presence of competing ions and suspended solids have on the capacity and selectivity of zeolites.

4- **Objective 3:** To establish the requirements to ensure effective media regeneration.

5- **Objective 4**: To understand the key parameters that influence the overall economic viability of using zeolites for ammonia removal from wastewater.

In doing so the thesis aims to provide a basis for a suggested design of a zeolite contactor for tertiary ammonium polishing.

1.3 Thesis Plan

Each chapter is presented as a series of papers for publication which altogether constitute the Ph.D. thesis. All experiments were designed and conducted by Judit Canellas-Garriga at Cranfield University with support provided during Chapter 2 and Chapter 6 by Bastien Jego and Nina Huynh under supervision of Judit Canellas-Garriga. Each chapter was entirely written by the first author Judit Canellas-Garriga and edited by Prof. Bruce Jefferson.

A literature review (Chapter 2) was completed to review zeolite properties and their application to wastewater treatment. The review provides the bench mark of existing zeolite data and highlighted the key challenges that needed to be addressed when considering the use of zeolite contactors for tertiary ammonium polishing.

The experimental work then assessed the impact of zeolite properties on the efficacy of ammonia removal in terms of capacity and selectivity towards NH_4^+ in synthetic solutions (Chapter 3, Objective 1). The zeolites tested were the natural zeolite Clinoptilolite (from 3 different sources), Mordenite, two different types of Chabazite and the synthetic zeolite MesoLite. The work then proceeded with three zeolites to assess their performance during dynamic operation (Chapter 4, Objectives 1, 2). The impact of the empty bed contact time and the inlet concentration was evaluated and two mathematical models were applied to verify the experimental data.

The assessment of the zeolites combined both removal (Chapters 3, 4) and regeneration (Chapter 5, Objective 3) to understand the underlying mechanisms and to assess the potential for long term operation. The impact of water chemistry (pH, ionic strength and ion selection) was assessed in terms of regeneration efficacy and re-use through multiple regeneration cycles.

The findings from the previous chapters were then utilised during testing with real wastewater to translate the findings to real applications (Chapter 6). Comparison with the previous finding using synthetic solutions was used to reveal the impact wastewater has on the selectivity, capacity and regeneration. The overall findings from chapters 3, 4, 5 and 6 were then used to design a fixed bed system for (1) wastewater treatment works (WWTW) treating 2,000 popular equivalent (PE) effluent and (2) WWTW treating 20,000 PE with a nitrogen recovery facility. (Chapter 7, Objective 4). Economic analysis of the systems was compared to a bench mark case of a tertiary nitrifying submerged aerated filter to establish the conditions under which the new process is economically plausible.

The technical and economic analyses were then discussed overall (Chapter 8). This will incorporate a proposed design basis for a zeolite based ammonia removal systems as a tertiary process for use in wastewater treatment.

Chapter 9 then describes the key overall conclusions from the work and makes suggestions for further work to further enhance understanding or applications of zeolites for wastewater treatment.

This Ph.D. project was sponsored by the following water utilities: Thames Water, Anglian Water, Scottish Water, Severn Trent and Yorkshire Water.

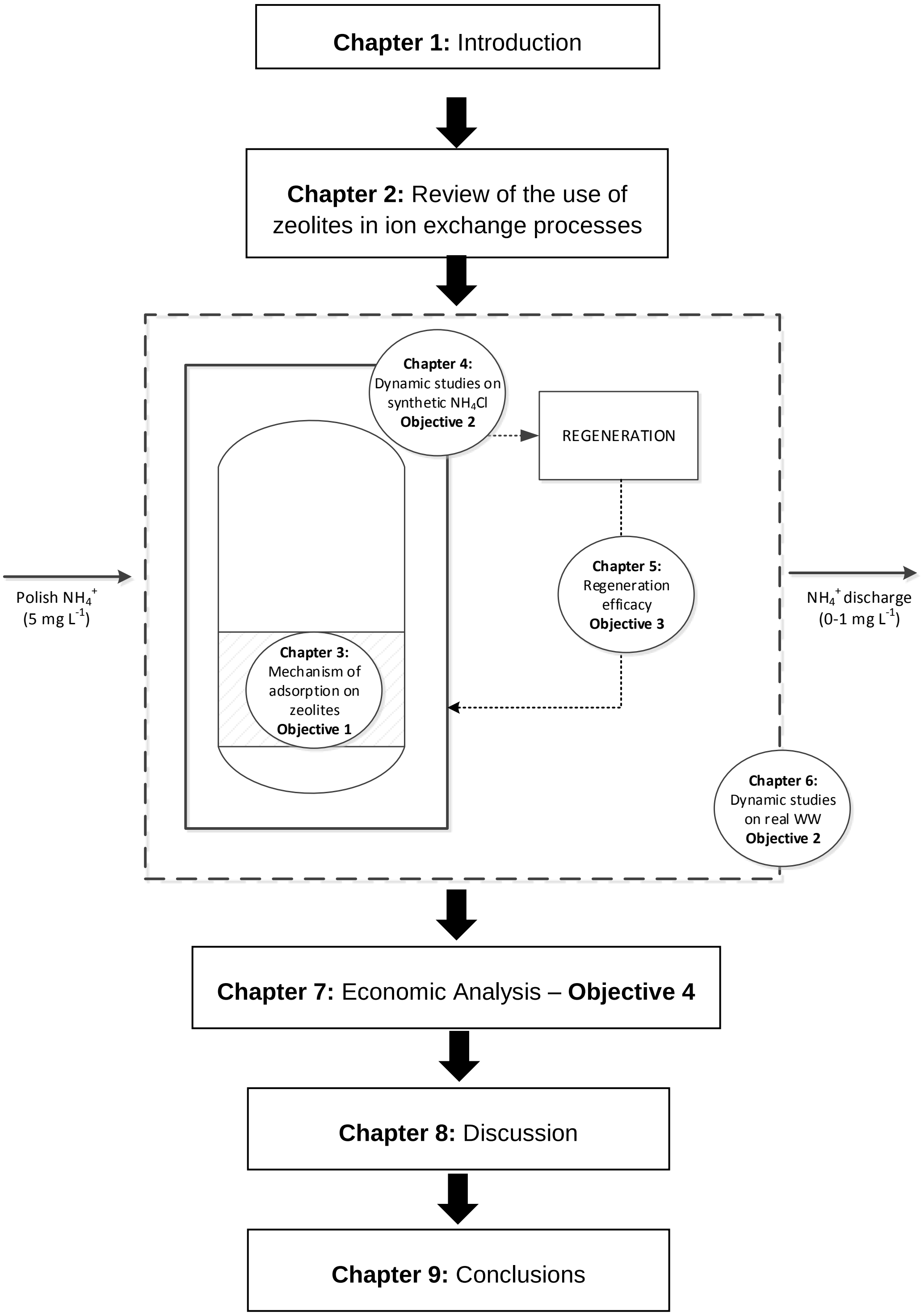

Figure 1-1 Schematic diagram of the thesis structure

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2 ZEOLITES AS A MEDIA FOR AMMONIA REMOVAL FROM MUCNIPIAL WASTEWATER – A REVIEW

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Abstract

The removal and recovery of ammonium from wastewater is a current and global challenge. This challenge requires technology that can substantially reduce ammonium concentration in wastewater effluents to potentially less than 1 mg L^{-1} in a way that later allows to recover the captured material. There is increasing interest in the use of zeolites as adsorbent material to achieve this due to their high selectivity and capacity for NH_4^+. A range of available zeolites exist, both natural and synthetic, that exhibit differences in capacity and selectivity towards ammonium. The difference are related to the Si:Al which controls the total number of available exchange sites and hence the cation exchange capacity (CEC). The Si:Al ratio for natural zeolites is in the range 4:1 to 5:1 compared to 1:1 for the synthetic zeolite, MesoLite resulting in reported capacities of up to 4 meq g^{-1} in comparison to 0.05 and 2.84 meq g^{-1} for Clinoptilolite. Overall these experiments suggest MesoLite's suitability for ion exchange applications.

Key Words: zeolites, ammonium, selectivity, capacity

2.1 Introduction

The discharge of ammoniacal nitrogen (NH_4-N) and nitrates (NO_3^-) into rivers or lakes can detrimentally affect their ecosystems by accelerating eutrophication (Canfield *et al*., 2010; Fernández *et al.*, 2008). As a consequence, more strict consent limits have been stipulated in the Water Framework Directive 2000/60/EC and Council Directive 91/271/EEC which can see wastewater treatment works required to discharge ammonia concentration as low as 1 mg L^{-1} and between 10 and 30 mg NO_3-N L^{-1} for discharge to fresh water and 50 mg NO_3-N L^{-1} into seawater (Directive 1991; European parliament 2000).

Currently, NH_4-N is oxidised to nitrate (nitrification) and then potentially reduced to nitrogen gas (denitrification) through the action of microorganisms using processes such as the activated sludge processes (ASP) (Hyungseok *et al.*, 1999). However, aerobic biological processes can struggle to reach such levels especially on smaller works and with passive biological processes such as trickling filters. This is mainly due to their sensitivity to changes in NH_4-N loading and temperature (Almutairi *et al*., 2015; Mery *et al.,* 2012; Miladinovic *et al*., 2008). In the case of ASP, a large amount of energy is required due to the need for aeration and pumping which can account for 50 % of the total electrical demand of the process (McAdam *et al.*, 2011). Further, the process enables alternative biological pathways to co-exist which can lead to the emission of nitrous oxide which is a greenhouse gas with an impact which is 310 times that of carbon dioxide (Huijie and Chandran, 2010). Accordingly, there is increasing interest in alternative approaches that can increase the resilience of meeting low ammonia discharges whilst not increasing energy demand.

Ammonia is a highly soluble gas defined by a Henry's law constant of 5.53 x 10^{-4} mol L^{-1} Pa^{-1} such that its solubility is around 900 g L^{-1} at 0 ºC and around 400 g L^{-1} at 300 ºC. In addition, ammonia is a weak base that dissociates in water to form a pH dependent equilibrium with its ionic form, ammonium:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$ **Equation 2.1**

At pH 9.2 the mole fraction is 50 % of each species with increasing amounts of the molecular form (NH_3) as the pH increases up to pH 11 where it become 100 % ammonia. Conversely, as the solution becomes more acidic, the ionic form predominates such that at pH 9, 66 % is in the ionic form rising to almost 100 % at pH 7. Accordingly, in wastewater the predominate form will be ionic ammonium since the pH is found between 6.5 and 8 (Metcalf and Eddy, 2003) which enables removal through ion exchange pathways.

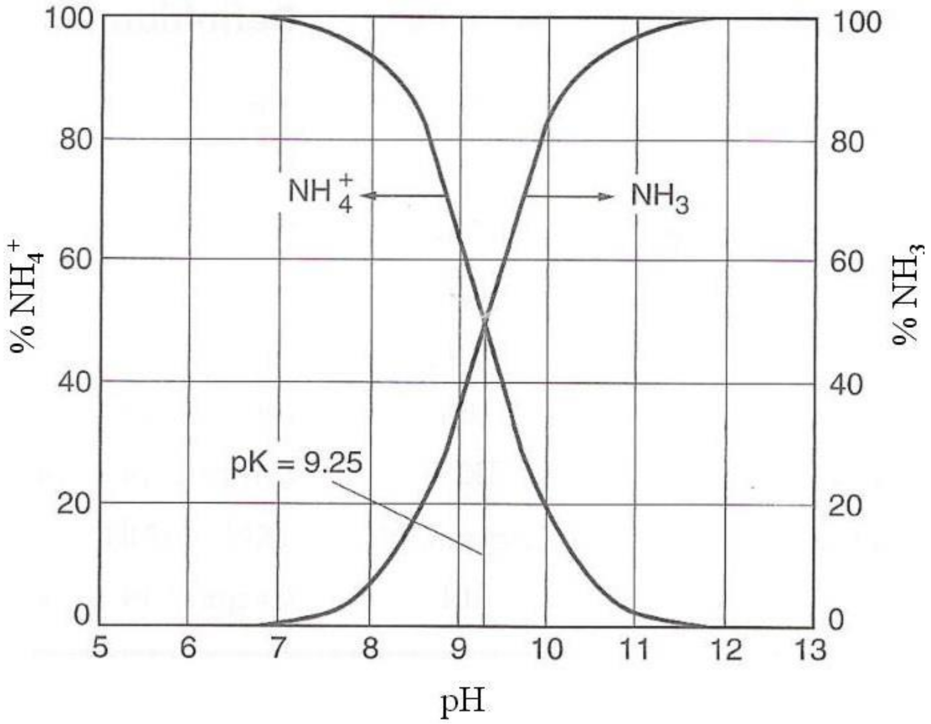


Figure 2.1 Ammonium and ammonia distribution as a function of pH (Metcalf and Eddy, 2003).

Ion exchange is a physicochemical process where dissolved ammonium ions (NH_4^+) are selectively removed from the wastewater by substitution with ions residing within the media (e.g. sodium, Na^+); thereby maintaining an overall charge balance (Equation 2.2).

$$Z.NH_4^+ + Na^+ + Cl^- \leftrightarrow Z.Na^+ + NH_4^+ + Cl^- \qquad \textbf{Equation 2.2}$$

Where; Z. NH_4^+ is the ammonium in the solid, Na^+ is the sodium released from the solid, Cl^- chloride in the liquid, Z. Na^+ the sodium in the solid and NH_4^+ the ammonium in the liquid.

Selectivity, understood as the affinity that certain ions have towards certain materials, enables ammonium to be removed preferentially over other species such as Ca^{2+} or Mg^{2+}. Once the media has become saturated, it must be regenerated so that it can be reused. Regeneration is commonly achieved using high strength ionic brines, e.g. aqueous sodium chloride (NaCl), where Na^+ ion the liquid replaces the NH_4^+ adsorbed in the solid liberating it into the liquid phase *(*Deng *et al., 2014;* Mackinnon *et al.,* 2003*;* Mackinnon *et al.*, 2010a).

2.2 Zeolites

A number of different materials have shown promise for ammonium removal including hydrogels (Zheng *et al.,* 2011), fly ash (Uurlu and Karalu, 2011) and attapulgite (Yin and Kong, 2014). However, the most common are the use of zeolites which are crystalline, alumino-silicate minerals that occur naturally or can be formed synthetically. Natural zeolites can be found across the world and are formed by the interaction of volcanic rocks and ash with alkaline underground water (Shoumkova and Stoyanova, 2013). This natural process leads to inconsistency and variability in terms of purity, chemical composition, crystal size, porosity and pore diameter leading to variability in selectivity and capacity commonly reported throughout all natural zeolites (Wang *et al*., 2008).

Synthetic zeolites can be formed through alkali treatment of clays such as Kaolinite (Basaldella *et al*., 1998). Zeolites were first made using strong salt concentrations and high temperatures (Barrer and Meier, 1959) and then with reactive materials and milder conditions leading to the discovery of Zeolite A (Milton, 1959). However, it was not until 2010 that the industrial production of synthetic MesoLite was possible using lower temperatures ($< 100\ ^0C$) in a continuously stirred, mixed reaction (Mackinnon *et al.*, 2010). The benefit of synthetically produce zeolites is increased consistency and more targeted selectivity.

2.2.1 Structure of zeolites

The primary framework structure of a zeolite is a tetrahedron (Figure 2-1), which is formed by four oxygens surrounding a central ion. Each tetrahedron shares every oxygen with an adjacent tetrahedron, creating infinite lattices of identical building blocks (Table 2-1) (Dyer, 1998). The central tetrahedron ion can be either a Si^{4+} or Al^{3+}. Since Al has valence 3+, every time that the central ion is formed by an Al, a negatively charged tetrahedron results ($[AlSi_3O_8]^{1-}$). Therefore, monovalent cations like Na^+, K^+ or even Ca^{2+} are needed to balance the negative charge (presaturant ion) (Armbruster and Gunter, 2001; Dyer, 1998).

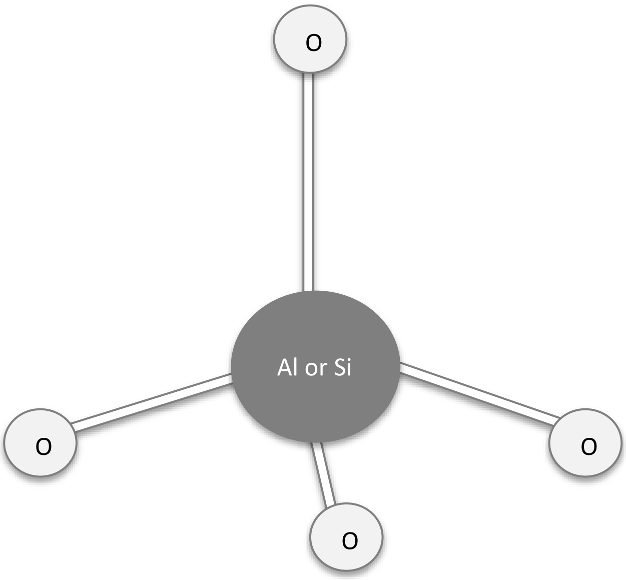


Figure 2-2 Primary structure of a Zeolite

The number of rings within the zeolite structure sets the internal pore sizes:

(i) small pore zeolites consist of 8-ring channels with diameters of 0.30 to 0.45 nm,

(ii) medium pore zeolites consist of 10-ring channels with diameters of 0.45 to 0.60 nm or

(iii) large pore zeolites consist of 12-ring channels with diameters of 0.6 to 0.8 nm.

Material in which pores are formed as windows defined by six T-atoms or less (six rings) are not considered to be zeolites and materials with polyhedral structures where at least one face is larger than a six-ring are called cavities (Kaduk and Faber, 1995; Mitchell *et al*., 2012).

The voids in these materials are an essential part of their structure. The flexibility of the structures and size of cavities allows molecules such as water and cations to pass through them. The cations undergo the exchange and keep the neutrality of the framework when an Al central ion is present. For instance, Na^+ will be exchanged by another highly selective cation, in this case NH_4^+ (Equation 2-2).

Since neutrality needs to be satisfied, it can be stated that the sum of Al centre ions will equal to the sum of exchangeable cations defined as the cation exchange capacity (CEC) (Palaban, 2001). The maximum Si:Al ratio is defined by the Loewenstein rule to be 1:1 (Armbruster and Gunter, 2001). This is realised in the synthetic zeolite, MesoLite, which has a corresponding CEC of 4.9 meq g^{-1} compared to 2.0 meq g^{-1} for Clinoptilolite which has a Si:Al ratio of 4:1.

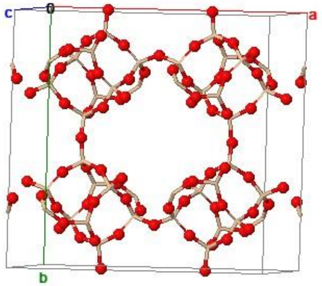
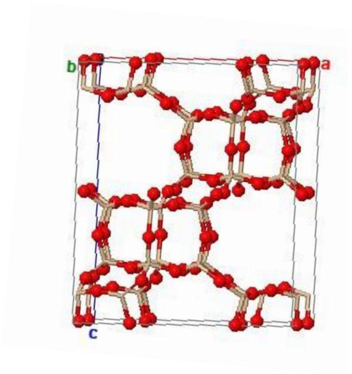
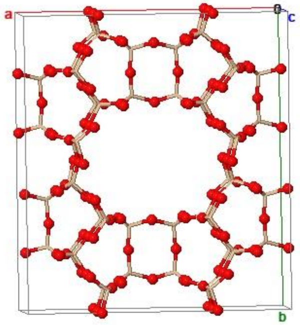
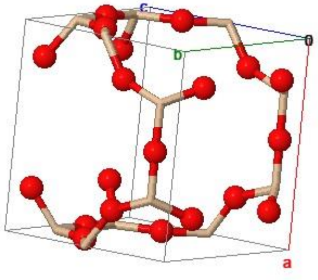
2.2.2 . Selectivity in zeolites

Selectivity is defined as the affinity or preference that certain types of materials have to certain ions (Semmens and Martin, 1988). To illustrate, from over 200 known zeolites less than five have proven to be selective towards NH_4^+ ions. Explanation of selectivity is based on combinations of material and ion interactions in relation to ion radii (molecular sieving), ion hydration energies and electrostatic bond energies (Cooney *et al.* 1999; Hankins *et al*., 2004; Metropoulos *et al*., 1993).

Traditionally, it was assumed that molecular sieving was the main mechanism responsible for the selectivity of certain cations towards certain zeolites (Wang *et al.,* 2008). Ions that are bigger than the effective windows within the zeolites structures will be excluded (sieved) enabling only smaller ions to pass.

Table 2-1 Characteristics of Natural zeolites: Clinoptilolite, Chabazite, Mordenite and the synthetic zeolite MesoLite

Zeolite	**Clinoptilolite**	**Chabazite**	**Mordenite**	**MesoLite**
Primary	HEU	CHA	MOR	EDI
Secondary Building Unit	4-4-1	D6R	5-1	4-1
Membered Rings	10 ring-channel – 7.5 x 3.1 Å “parallel to the c-axis” 8 ring-channel - 3.6 x 4.6 Å ”parallel to the c-axis” 8 ring-channel 2.8 x 4 Å ”parallel to the c-axis”	8-membered ring – 3.8 x 3.8 Å “parallel to the c-axis”	12-membered ring – 6.5 x 7.0 Å ”parallel to the c-axis” 8-membered ring – 2.6 x 5.7 Å ”parallel to the c-axis”	8-membered ring – 2.8 x 3.8 Å ”parallel to the b-axis” 8-membered ring – 2.3 x 3.1 Å ”parallel to the c-axis”
Unit Cell Content	$(Na)_6[Al_6Si_{30}O_{72}].\ 20H_2O$	$(Na)_4[Al_4Si_8O_{24}].\ 12H_2O$	$(Na_2)_4[Al_8Si_{40}O_{96}].\ 28H_2O$	$(Na, K)\ [Al_4Si_6O_{20}].\ 8H_2O$

Zeolite	Clinoptilolite	Chabazite	Mordenite	MesoLite
Unit cell 3D				
Topological Symmetry	Monoclinic (C2/m)	Trigonal (R3/m)	Orthorhombic (Cmm2)	Orthorhombic (P 222)
Atoms Unit Cell	108	108	144	15
Channels/ Unit Cell	24 Channels 3% pore volume= 2 Å 7% pore volume= 7 Å	42 Channels 5% pore volume >4 Å 4% pore volume 4-6 Å	24 Channels 16% pore volume= <4 Å 48% pore volume= >6 Å 36% pore volume= <6 Å	7 Channels 18% pore volume= <4 Å 2% pore volume= 4-6 Å

Zeolite	**Clinoptilolite**	**Chabazite**	**Mordenite**	**MesoLite**
***Occupiable Volume (%) for (<1.41 Å)**	9.42	17.27	12.57	9.52
Effective window size (Å)	4.6	7.37	6.70	5.72
Pore Limiting (Å)	4.3	4.2	6.5	4.1
Largest Cavity(Å)	6.6	8	6.5	6.4
Unit Cell Volume (Å^3)	2,055	2,391	2,827	307.48
Unit Cell Volume Calculation	a=17 b=17.6 C=7.4 β=116.1^{o} $v = abc\ sin116.1$	a=13.7 C=14.8 $v = a^2\ c\ sin90$	a=18.1 b=20.5 C=7.5 $v = a\ b\ c$	$\mathrm{a} = 6.9\ \mathrm{C} = 6.4$ $v = a^2\ c$
Si:Al	>4	4:1	5:1	1:1
Density (g.cm^{-3})	0.845	0.573	0.638	0.715

Wang *et al.* (2007) demonstrated this fact by studying two zeolites. One was Clinoptilolite synthetically modified (Zeolite Y-Na) and the other natural Clinoptilolite. The former had the following sequence $Mg^{2+} > Ca^{2+} > K^+$ while the sequence found on the natural zeolite was $K^+ > Na^+ > Ca^{2+}$. The reason of this difference was associated to the size of the window within the lattice of the zeolites, at 7.4 and 4.6 Å for the synthetic and the natural zeolite respectively.

Clinoptilolite consists of two 10-ring channels and one 8-ring channel with an effective window of 4.6 Å (Table 2- 1) (Armbruster, 2001; Dyer, 1998). Whereas the hydrated size for Ca^{2+}, Na^+, K^+ and NH_4^+ are 4.12, 3.58, 3.31 and 3.31 Å respectively (Nightingale, 1959). Hankins *et al., (*2004) compared the relative sizes to show that the ions can pass through all the channels and hence refuted the concept of molecular sieving being the primary or unique mechanism to explain selectivity of NH_4^+ on Clinoptilolite. The alternative idea is that the selectivity sequence is related to the bonding energies with the material surface in relation to the free energy of hydration of the ions. The free energy of hydration is the energy released or required as the hydration state of the ion is and hence influences the type of bonding that can occur with the zeolite material (Hunger *et al*., 1997; Jeffroy *et al.,* 2011). For instance, ions with a lower free energy of hydration are more likely to shed water molecules and form inner complex bonds with the base material. Whereas ions with a higher free energy of hydration are more likely to stay fully hydrated and thus form only outer sphere complexes, reducing the likelihood of preference. A number of authors have used this idea and compared the free energies of hydration of the competing ions to show that they followed the same sequence as uptake: -103.94, -111.80 and - 403.60 kJ mol^{-1} for $NH_4^+ > Na^+$ and Ca^{2+} respectively (Cooney *et al.,* 1999; Hankins *et al.,* 2004; Koon and Kaufman, 1975).

Whilst free energy of hydration is effective in understanding selectivity of different ions to a single material, it does not help explain the difference in selectivity between materials. In such cases, the properties of the different zeolites need to be considered with emphasis given to Si:Al ratio, Al distribution, type of neutralising alkaline cations and zeolites' hydration (Armbruster, 2001; Barrer, *et* *al*.,1967; Cooney *et al.*, 1999; Gedik and Imamoglu, 2008; Jae *et al*., 2011; Koon and Kaufman, 1975; Marinsky and Reddy, 1973; Pabalan and Bertetti, 2001; Semmens and Martin, 1988).

2.2.2.1 Si:Al ratio

Theoretically, the capacity of a zeolite increases with the number of Al central ions as these generate the charge deficit within the material. For instance, Si-O bonds have an electrostatic bond of 1 and Al-O bonds have an electrostatic bond of 0.75 (Armbruster, 2001). Therefore, when an oxygen is linked to two Si tetrahedra (Si-O-Si), the sum of bonds is (+2), which balances the oxygen valence (-2). However, when one of the tetrahedral cations is Al (Al-O-Si), the total sum of bonds is 1.75. Accordingly, the relative ratio of Al:Si impacts the overall charge density within the zeolite structure with it increasing as the Al:Si ratio decreases. Zeolites with a low charge density (high Si:Al ratio) will show higher selectivity towards cations of lower charge such as Na^+ and NH_4^+ and vice versa (Wang *et al.,* 2008). For instance, the selectivity of caesium (Cs^+) decreased with respect to Na^+ (lower charge density ion than Cs^+) as the Si:Al ratio decreased (Nakamura *et al.*, 2013). The amount of Al in a zeolite has an impact on the hydrophobicity of the zeolite, becoming more hydrophobic as the Si:Al ratio increases (Li *et al*., 2013; Ockwig *et al*., 2008).

2.2.2.2 Location of Al central cations

In addition to the quantity, the distribution of Al within the zeolite can impact selectivity. For instance, Nakamura *et al*., (2013) studied the effect that Al distribution has onto selectivity of Na^+ and Cs^+ on Mordenite. Uniform distribution of the Al atoms increases the relative selectivity towards Cs^+ through changing the relative stability of the ions within the zeolite lattice.

Channon *et al*., (1998) modelled the free energy when Na^+, K^+ or Ca^{2+} were introduced in the framework at different Al positions. For each ion, the minimum overall energy was achieved when the ions were located at different positions. The lower energy obtained from the lattice energy simulations was achieved when Na^+ was sat on M (1) position and Al sitting at T (II). Whereas, in the case of K^+, the lowest energy and hence the most stable position for Al was when it was located on T (I) and K$^+$ on M (1), and for Ca^{2+} the Al was located on T(III) and M (1) (Figure 2-3). Accordingly, depending on the relative position of the Al atoms within the structure, different ions will lead to a lower free energy and hence be preferred.

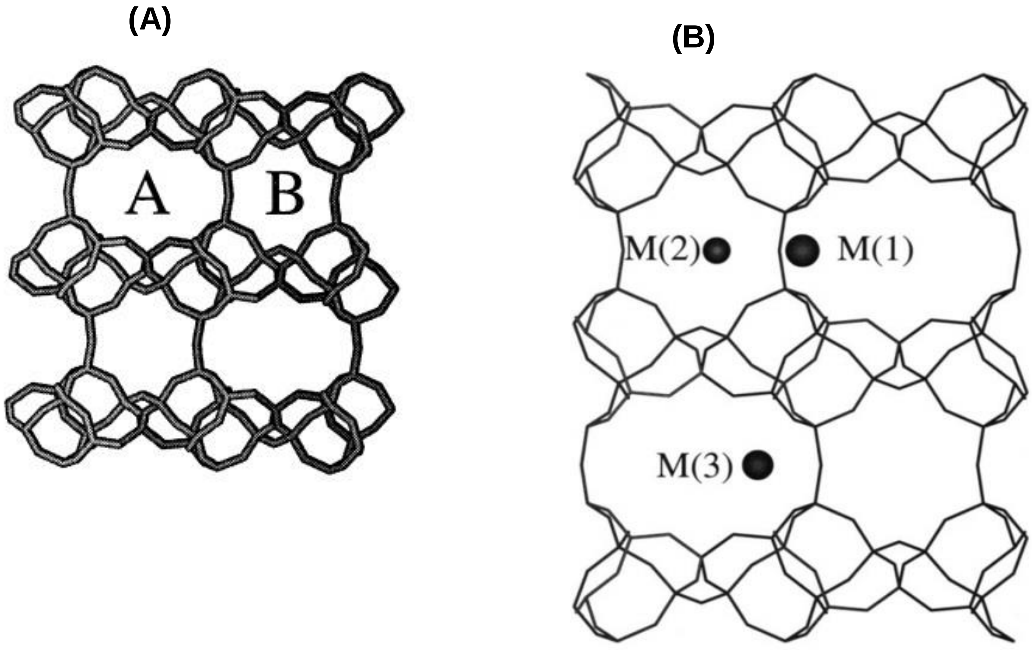


Figure 2-3 Channel structure of natural zeolite Clinoptilolite (A) and extra-molecular cation position on Clinoptilolite (B) Channon (1998).

2.3 Application of zeolites for removal of ammonia from wastewater

The most common zeolite studied for ammonium removal from wastewater is Clinoptilolite with a reported capacity between 0.05 and 2.84 meq g^{-1} (Table 2-2). The variation observed reflects differences in the make-up and purity of the materials sourced from different locations around the world. The capacity is also influenced by competition from other ions which varies based on the presaturant ion. For instance, Hankins *et al., (*2004) observed that K$^+$ ions had a major impact onto NH$_4^+$ uptake, and hence capacity was reduced in its presence. However, Weatherley and Miladinovic (2004) observed that the capacity was highly reduced in presence of Ca^{2+}. A general selectivity sequence for zeolites is reported to be $Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Na^+ > Ca^{2+} > Li^+$ (Wang and Peng, 2010) with specific studies showing differences (Table 2-2). For instance, Hankins *et al.,* (2004), reported a sequence specifically for Clinoptilolite as $K^+ > NH_4^+ > Na^+ > Ca^{2+}$. Whereas, for Chinese Clinoptilolite a sequence of $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ was reported (Lin *et al.,* 2012). Studies looking into different zeolites have shown different selectivity sequences such that competition from back constituent is likely to be different depending on the choice of zeolite. To illustrate, a comparative study of Clinoptilolite and Mordenite revealed respective selectivity sequences of $NH_4^+ > Ca^{2+} > K^+ > Na^+$ and $NH_4^+ > K^+ > Ca^{2+} > Mg^{2+}$ (Weatherley and Miladinovic, 2004).

In comparison, reported studies on the use of synthetic zeolites are more limited. Comparisons between natural and synthetic zeolites commonly conclude that the former have the higher selectivity and capacity (Fletcher, 1982; Weatherley and Miladinovic, 2004). However, many of the synthetic zeolites tested to date have been made for applications not requiring selectivity towards ammonium such as those used in detergent powders (Aarts *et al*., 2004; Dyer, 1998; Milton, 1959). The exception is MesoLite (Zeolite-N) which has been shown to have high capacity and selectivity towards ammonium (Barrer and Meier, 1959). The zeolite has a cation exchange capacity of 4.9 meq g^{-1} (Mackinnon et al, 2010) and an operational capacity of 72 mg g^{-1} (4 meq g^{-1}) when treating a mono component solution containing 1000 mg L^{-1} of ammonium (Thornton *et al.,* 2007).

Two studies have reported the use of MesoLite in continuous column experiments, both looking at sludge liquid treatment to reduce return flows of ammonium to the main biological treatment stage of the works. (Mackinnon *et al*., 2003;Thornton *et al*., 2007b). The feed contained between 500 and 1000 mg NH_4^+ L^{-1} and was treated in columns operated at empty bed contact times between 12 and 60 minutes. In both cases the effluent was treated down to low residual ammonium concentrations (90 % removal) resulting in operating capacities of 45 to 50 mg g^{-1} (Mackinnon *et al*., 2003) and 39 to 27 mg g^{-1} (Thornton *et al*., 2007). To date, there are no reported studies exploring the use of MesoLite for low concentration effluent polishing in continuous columns and as such this represents a clear area for development. Equivalent studies with Clinoptilolite have looked at feed concentrations between 17 and 100 mg L^{-1} operating at EBCTs of 0.56 to 8 minutes (Table 2-3). For instance, Cooney *et al.,* (1999) used natural Australian Clinoptilolite to treat secondary effluents with initial concentrations from 25 to 45 mg L^{-1}. The maximum observed capacity obtained was 2.8 mg g^{-1} resulting in an effluent concentration of 5 mg L^{-1}. The observed efficacy of zeolites for ammonium removal has led to a number of full scale plants based on Clinoptilolite in the UK, US and Australia over the last fifty years (Liberti *et al.,* 1981). Long term operation has thus been proven with one site operating for 500 cycles each lasting 80 BV (Liberti *et al*., 1981). The analysis from the sites has confirmed that the key challenges for wider scale implementation of the technology are: The need to reduce solids concertation onto the beds to avoid frequent clogging, the high cost of regeneration and management of the spent regeneration solutions (Hedström, 2001; Liberti *et al.,* 1981).

Overall, the option to use zeolites for ammonium polishing looks plausible although confirmation is required as to the most effective zeolite to use and the likely operating cycles that can be achieved. Further, there is a lack of optimisation work on regeneration and this needs investigation given that it is estimated to account for up to 80 % of the total operating cost of using zeolites (Miladinovic and Weatherley, 2008).

Table 2-2 Literature on batch equilibrium studies.

Reference	Material	Source of water	Equilibrium Capacity (meq NH_4^+ g zeolite^{-1})	Initial concentration (mg NH_4^+ L^{-1})	Total salinity (meq NH_4^+ L^{-1})	Selectivity sequence
(Hankins et al. 2004)	Natural Clinoptilolite	Mono-component: NH_4^+ synthetic solution	0.22	200	11.11	—
	Natural Clinoptilolite	Two-component (NH_4^+, and Na^+) synthetic solution	0.54	2,880	160	—
	Natural Clinoptilolite	Multi-component (NH_4^+, Ca^{2+} and Na^+) synthetic solution	0.47	2,880	160	$K^+ > NH_4^+ > Na^+ > Ca^{2+}$
(Erdoğan 2011)	Clinoptilolite	Mono-component: NH_4^+ synthetic solution	0.05 to 0.5	10 to 300	0.71 to 21.43	—
(Karadag et al. 2006)	Clinoptilolite	Mono-component: NH_4^+ synthetic solution	0.05 to 0.26	25 to 150		—
(Weatherley and Miladinovic 2004)	Clinoptilolite	Mono-component: NH_4^+ synthetic solution	0.66	200	11.11	$NH_4^+ > Ca^{2+} > K^+ > Mg^{2-}$
		Two-component: synthetic solution (NH_4^+, Ca^{2+})	0.57	200	13.1	

Reference	Material	Source of water	Equilibrium Capacity (meq NH_4^+ g zeolite^{-1})	Initial concentration (mg NH_4^+ L^{-1})	Total salinity (meq NH_4^+ L^{-1})	Selectivity sequence
	Mordenite	Two-component: synthetic solution (NH_4^+, Mg^{2+})	0.61	200	14.4	$NH_4^+ > K^+ > Ca^{2+} > Mg^{2-}$
		Two-component: synthetic solution (NH_4^+, K^+)	0.60	200	12.1	
		Mono-component: NH_4^+ synthetic solution	0.80	200	11.1	
		Two-component: synthetic solution (NH_4^+, Ca^{2+})	0.78	200	13.1	
		Two-component: synthetic solution (NH_4^+, Mg^{2+})	0.79	200	14.4	
		Two-component: synthetic solution (NH_4^+, K^+)	0.77	200	12.1	
(Lei *et al.*, 2008)	Chinese natural zeolite	Mono-component: NH_4^+ synthetic solution	0.39	50	2.7	
	Thermal-treated zeolite		0.58	50	2.7	

Reference	Material	Source of water	Equilibrium Capacity (meq NH_4^+ g zeolite^{-1})	Initial concentration (mg NH_4^+ L^{-1})	Total salinity (meq NH_4^+ L^{-1})	Selectivity sequence
	Microwave-treated zeolite		0.61	50	2.7	
	Microwave-treated zeolite	Two-component: synthetic solution (NH_4^+, Ca^{2+})	0.42	50	2.7	$Na^+ > K^+ > Ca^{2+} > Mg^{2+}$
		Two-component: synthetic solution (NH_4^+,Mg^{2+})	0.53	50	2.7	
		Two-component: synthetic solution (NH_4^+,K^+)	0.32	50	2.7	
		Two-component: synthetic solution (NH_4^+,Na^+)	0.28	50	2.7	
(Lin et al. 2012)	Chinese Natural	Mono-component: NH_4^+ synthetic solution	0.61	1000	55.5	$Na^+ > Ca^{2+} > K^+ > Mg^{2+}$
	Na- Natural	Mono-component: NH_4^+ synthetic solution	0.94	1000	55.5	
(Sprynskyy et al. 2004)	Transcarpathian Clinoptilolite	Mono-component: NH_4^+ synthetic solution	0.37	100	5.5	

Reference	**Material**	**Source of water**	**Equilibrium Capacity ($meq\ NH_4^+\ g\ zeolite^{-1}$)**	**Initial concentration ($mg\ NH_4^+\ L^{-1}$)**	**Total salinity ($meq\ NH_4^+\ L^{-1}$)**	**Selectivity sequence**
(Mc Veigh and Weatherley 1999)	Clinoptilolite	Mono-component: NH_4^+ synthetic solution	0.2 to 0.6	10 to 24		
		Multi-component: Real wastewater (secondary effluent)	0.2 to 0.5	7 to 40		$K^+ > NH_4^+ > Na^+ > Ca^{2+}$
(Thornton et al. 2007)	Synthetic zeolite MesoLite	Mono-component: NH_4^+ synthetic solution	4	1000	—	—
		Multi-component: NH_4^+ synthetic solution	0.16 to 2.61	20 to 2000	—	—
(Metropoulos et al. 1993)	Zeolite A (Na-A, K-A and Ca-A)	Mono-component: NH_4^+ synthetic solution	2.85, 2.62, 2.013	1,800	100	$Ca^{2+} > K^+ > Na^+ > NH_4^+$
	Natural Zeolite (Clinoptilolite, Mordenite, Ferrierite)		1.2, 1 and 0.9	1,800	100	

Table 2-3 Literature on dynamic studies.

Reference	Material	Source of water	Operational capacity (mg g^{-1})	Initial concentration (mg L^{-1})	Breakthrough concentration (mg L^{-1})	Flow Rate (L h^{-1})	Empty bed contact time (min)
(Mackinnon et al. 2003)	Synthetic zeolite: MesoLite	Real side streams from anaerobic digesters	45-50	500 - 1000	50	290	60
(Svetich R. 1993)	Clinoptilolite	Real wastewater					
(Mc Veigh and Weatherley 1999)	Clinoptilolite	Mono-component (synthetic solution)	32	25 to 32	Saturation	1.2	12 to 15
		Two-component (NH_4^+, and Ca^{2+}) synthetic solution	28	29 NH_4^+ 15 Ca^{2+}	Saturation	1.2	12 to 15
		Two-component (NH_4^+, and K^+) synthetic solution	25	29 NH_4^+ 29 K^+	Saturation	1.2	12 to 15
(Thornton et al. 2007b)	Synthetic zeolite: MesoLite	Real side streams from anaerobic digesters	51	500 to 605	Saturation	~ 500	12
			39 to 27	~650	50	~ 500	12
		Synthetic wastewater	4.4	40	2	0.85	0.56

Reference	**Material**	**Source of water**	**Operational capacity (mg g^{-1})**	**Initial concentration (mg L^{-1})**	**Breakthrough concentration (mg L^{-1})**	**Flow Rate (L h^{-1})**	**Empty bed contact time (min)**
(Malovanyy et al. 2013)	Natural zeolite (70 to 75 % Clinoptilolite)	Mono-component NH_4^+ (synthetic solution)	9.0	40	2	0.85	0.56
		Synthetic wastewater	6.4	40	2	0.83	0.56
	Synthetic zeolite	Mono-component NH_4^+ (synthetic solution)	17.5	40	2	0.83	0.56
(Hlavay et al. 1982)	Clinoptilolite (Hungarian)	Wastewater	For 0.5 to 1 mm particle size: 9.1 For 0.2 to 1 mm particle size: 6 For 1.6 to 4 mm particle size: 1.4	25	2	0.4	6
		Wastewater	4.13 to 4.17	17 to 45	2	0.2 to 0.28	12 to 8.6

Reference	Material	Source of water	Operational capacity ($mg\ g^{-1}$)	Initial concentration ($mg\ L^{-1}$)	Breakthrough concentration ($mg\ L^{-1}$)	Flow Rate ($L\ h^{-1}$)	Empty bed contact time (min)
(Sprynskyy et al. 2004)	Transcarpathian Clinoptilolite	Mono-component NH_4^+ (synthetic solution)	For particle from 0.5 to 0.71 to 1.4 to 2 mm: 21.52 to 18.51	100	2	0.54	1.5
			17.61 to 13.56	100	2	0.36 to 0.11	2.3 to 7.7
(Cooney et al. 1999)	Australian Clinoptilolite	Real secondary effluents	2.3 to 2.8	25 to 45	5	291	6.4

2.4 Conclusions

Zeolites are a suitable material for ammonium removal from wastewater with both natural zeolites such as Clinoptilolite and synthetic zeolites such as MesoLite shown to be effective in removing ammonium in synthetic and real wastewater during both batch and continuous column experiments. Both types of zeolites appear to offer reasonable selectivity towards ammonium although the selectivity sequences vary across the different zeolites and sources of any specific type. The key zeolite property is related to the SI:Al ratio which controls the cation exchange capacity of the materials as well as the operational capacity observed during experimentation.

Key knowledge gaps were revealed in relation to the need for a direct comparison between MesoLite and the natural zeolites to understand the true difference in performance. Importantly, more work is required looking at low strength solutions that mirror those associated with tertiary treatment as there is a genuine paucity of information that covers this ammonium concentration range. This includes optimisation of the regeneration system as it is known to be a key component in the economic appropriateness of the use of zeolites.

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3 REMOVAL OF AMMONIA FROM WASTEWATER USING ZEOLITES: A COMPARISON OF NATURAL AND SYNTHETIC ZEOLITES – AN EQUILIBRIUM STUDY

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Abstract

The removal of ammonium from wastewater by ion exchange onto zeolites offers potential in cases where biological processes struggle, such as high load variations and low temperatures. A range of zeolites exist that provide reasonable capacity and selectivity towards ammonium including natural and synthetic media. The current work compared seven available zeolites (US-Clinoptilolite, UK-Clinoptilolite, thermally modified US-Clinoptilolite, Mordenite, Ca-Chabazite, Na-Chabazite and MesoLite) in a series of batch tests with synthetic and real wastewater solutions. The synthetic zeolite, MesoLite, provided the highest capacity at 4.6 meq g^{-1} compared to between 1.1 and 2.1 meq g^{-1} for the natural zeolites when presaturated with sodium ions. For MesoLite, the capacity in real wastewater was between 74 and 97 % of that observed in a mono component synthetic solution set at approximately the same ionic load. This was much higher than the equivalence for the natural zeolites indicating that the synthetic zeolite was an appropriate media for use in wastewater polishing applications.

Key Words: ammonium, ion exchange, zeolite, capacity, selectivity

3.1 Introduction

The removal of ammonia is a key component of most wastewater treatment works with anticipated new targets requiring a large number of sites to meet discharge consents between 1-3 mg L^{-1}. Whilst this is commonly achieved in biological systems such as the activated sludge process, it comes with a substantial energy cost which can account for 50 % of the total energy demand of the process (Canfield *et al.*, 2010; McAdam *et al*., 2011) as well as potentially emitting the greenhouse gas nitrous oxide which is 310 more potent than carbon dioxide (Huijie and Chandran, 2010). On smaller sites, especially those based on low energy biological processes such as trickling filters, resilient compliance to the new standards is thought to be challenging due to limitations related to controlling even distribution and mass transfer (Miladinovic and Weatherley, 2008).

Under the normal pH range of wastewater, the ammonia exists predominately in its reactive ionic form, ammonium (NH_4^+). Accordingly, it can be removed by ion exchange processes where the wastewater is contacted with an ion exchange material that is presaturated with an alternative cation, commonly (Na^+). The materials have a thermodynamic preference for the ammonium ion such that it exchanges with the Na^+ ion and is removed. Once the media becomes saturated it can be regenerated and the captured ammonia recovered. The process works for all available cations and so there is competition with the other constituents within the water, mainly Ca^{2+} and Mg^{2+}. A range of different materials provide this capability including polymer ion exchange resin as well as natural and synthetic zeolites. All exhibit different capacities and selectivities towards the target ion and so selection of the most appropriate media is important.

The capacity and selectivity of the different zeolites is influenced by a combination of the internal pore sizes of the lattice structure, the ratio of Si:Al and the distribution of Al within the lattice frame. The properties can be modified by pretreatment with different cations, temperature or microwave techniques or the most used, activation agents, which consists on putting the zeolites in contact with high concentrations of KOH or NaOH for a certain amount of time (Barrer and Meier, 1959; Klieve and Semmens, 1980; Lei *et al.,* 2008; Mackinnon *et al.,* 2010;

Querol *et al*., 2002; Shoumkova and Stoyanova, 2013). Zeolites can be natural or synthetic. Natural zeolites are formed across the world by interaction of volcanic rocks and ash with alkaline underground water (Shoumkova and Stoyanova, 2013). Consequently, the purity, chemical composition, crystal size, porosity, pore diameter vary and this impacts on their efficacy for wastewater treatment in terms of their capacity and selectivity towards ammonium (Table 3-1). Modern synthetic zeolites are made by alkali treatment of raw materials rich in silica and alumina such as clays like montmorillonite and kaolinite (Basaldella *et al*., 1998).

Comparison of possible zeolites is commonly conducted in equilibrium batch trials to assess capacity and selectivity against synthetic and real systems (Table 3-1). A wide range of material have been previously tested for ammonium removal using natural zeolites with the majority based around Clinoptilolite due to its high relative selectivity towards ammonia and wide spread availability. In fact, full scale Clinoptilolite filters were used in California from 1978 to 1993 (Svetich, 1993). Comparison with synthetic zeolites is less common and often based on synthetic zeolite not intended for ammonia removal such as zeolite A, which is applied as a builder in detergent powders and tablets for water softening (Aarts *et al.*, 2004; Dyer, 1998; Milton, 1959). Consequently, such studies tend to show better efficacy with the natural zeolites (Fletcher and Townsend, 1982; Hankins *et al*., 2004; Weatherley and Miladinovic, 2004). However, work has also shown the benefits of MesoLite or zeolite N, a synthetic zeolite made from Kaolinite (Kingwhite 65 and Kingwhite 80) dissolved with potassium or sodium reagents heated to between 65 and 100^{0}C.

Table 3-1 Batch equilibrium capacities on mono and multicomponent waters

Zeolite	Initial Concentration (mg L^{-1})	Mono-component: NH_4^+ synthetic solution - Equilibrium capacity (meq g^{-1})	Reference
Clinoptilolilte	200	0.22	(Hankins *et al.,* 2004)
Clinoptilolilte	10	0.04	(Erdoğan and Ülkü, 2011)
Clinoptilolilte	25 to 150	0.05 to 0.25	(Karadag *et al*., 2006)
Clinoptilolilte	10 to 200	0.07 to 0.66	(Weatherley and Miladinovic, 2004)
Mordenite		0.07 to 0.80	
Clinoptilolite	50	0.30	(Lei *et al.,* 2008)
Clinoptilolite	1000	0.95	(Lin *et al.2012),*
MesoLite	1000	4	(Thornton *et al., 2007)*

To the authors knowledge no study has conducted a direct comparison of MesoLite with natural zeolites (both parent and modified) for the removal of ammonia. Accordingly, the current work investigates adsorption, desorption, selectivity, cation exchange capacity (CEC) and performance of 6 natural zeolites (US-Clinoptilolite, UK-Clinoptilolite, thermally modified US-Clinoptilolite, Mordenite, Ca-Chabazite, Na-Chabazite) and the synthetic zeolite MesoLite in mono and multicomponent systems in order to evaluate the use of zeolites for tertiary ammonia removal from wastewater.

3.2 Materials and methods

Natural UK Clinoptilolite (RS Minerals, UK), Mordenite (Newstone international, Japan), synthetic MesoLite (Nanochem Pty Ltd. Australia), US Clinoptilolite, Chabazite (in sodium and calcium forms), and thermally modified US Clinoptilolite (St. Cloud, USA) were sieved to achieve uniform media range (1 to 1.7 mm) and washed in distilled water to remove particulate impurities. The zeolites were preconditioned prior to testing using 1 M NaCl and 1 M $CaCl_2$ (stated purity >99 %; Fisher Scientific, UK) dissolved into de-ionised (DI) water (15 MΩ cm^{-1}). The test solution was prepared using ammonium chloride (NH_4Cl) (stated purity > 99 %; Fisher Scientific, UK) dissolved into DI water.

3.2.1 Experimentation

3.2.1.1 Batch Equilibrium

Experiments were conducted in batch using 250 mL Erlenmeyer flasks for each of the zeolites. Different amounts of the zeolites (from 0.1 to 0.5 g) were contacted with 100 mL of the test solution. The synthetic solution was set at a concentration of 16 mg NH_4^+ L^{-1} (0.89 meq NH_4^+ L^{-1}, pH between 7 and 8) for the mono component experiments and compared to real wastewater from Cranfield University's sewage work with an average concentration of 16 mg NH_4^+ L^{-1}. The sample was taken post biological treatment (trickling filter) and then filtered through a 0.2 μm filter to remove solids. The tested ammonium concentration of the real wastewater varied between 11.9 and 16.2 mg NH_4^+ L^{-1} at a pH of 7 equating to 0.9 and 0.66 meq NH_4^+ L^{-1}. The flasks where then agitated at 125 rpm for up to 48 hours with samples taken at 0, 20, 40 minutes and 1, 2, 4, 6, 8, 12, 24 and 48 hours. It was observed that all the zeolites reached equilibrium within 24 h.

Equilibrium data for each of the zeolites was then compared to both Freundlich and Langmuir isotherm models (Almutairi *et al.,* 2015; Karadag *et al*., 2006; McAdam *et al*., 2011). The ammonium concentration was determined spectrometrically by cell test (Merck, Germany) using a spectrophotometer (Merck, Spectroquant Nova 60, Germany). With this method there is no interference by other dissolved species (e.g. cations, anions) in the liquid phase. The concentration of Na^+, Ca^{2+}, K^+ and Mg^{2+} were analysed by atomic absorption spectroscopy (AAS) (Aanalyst 800, PerkinElmer, UK). The concentration of ions in the solid phase, and hence the capacity of the zeolite, was calculated using the following mass balance equation (Jorgensen *et al*., 1976). The experiments were conducted in duplicate.

$$Q_e = \frac{(C_o - C_e)V}{M}$$ **Equation 3.1**

Where Q_e is the amount of ions in the solid phase (mg g^{-1}) or [meq g^{-1}], C_o is the initial ion concentration in solution (mg L^{-1}) [meq L^{-1}], C_e is the ion remaining in solution at equilibrium (mg L^{-1}) [meq L^{-1}], V is the solution volume (L) M is the mass of zeolite introduced (g).

3.2.1.2 Regeneration

Following the adsorption process, the zeolites were contacted with 1 M NaCl for 24 h and the amount of ammonium released into solution was measured. The recovered capacity was then determined for both synthetic and real wastewater solution throughout a subsequent testing phase of 24 h with a fresh solution of the test liquid to assess the new capacity and this was compared to the previous value.

3.2.1.3 Saturation ammonium Capacity

The saturation capacity of the test zeolite was established through a fed batch experiment using 0.3 g of zeolite (Cooney, 1999). The zeolites were prepared in 100 mL test solution that contained NH_4Cl at a concentration of 600 mg L^{-1} and were then agitated for 24 hours. After this time, 50 mL of the solution was withdrawn and replaced with a fresh 50 mL of test solution. These steps were repeated until no more exchange of NH_4^+ was measured.

3.2.1.4 Cation Exchange Capacity (CEC)

The CEC was evaluated for the following ions: Ca^{2+}, Na^+, K^+ and Mg^{2+} following the ammonium acetate method number 16 of the MAFF Reference Book RB427. 20 ml of 1 M ammonium acetate solution (stated purity > 99 %, Fisher Scientific, UK) was contacted with 5 g of zeolites sieved to a size between 1 and 1.7 mm after being pre-conditioned with NaCl. After 24 h of contact, the solution was filtered and the zeolite was leached with 1 M ammonium acetate until 250 ml were collected (Faithful ,1986).

To determine the CEC of Ca^{2+} and Mg^{2+}, 2.5 mL of strontium chloride (stated purity > 99 %; Fisher Scientific, UK) were added to 10 mL volumetric flask. The volume was increased up to 25 ml using 1 M of ammonium acetate. The capacity for Ca^{2+} and Mg^{2+} of each zeolite was calculated through the equations below:

$$meq\ Ca/100g = \frac{(Ca_s - Ca_b)\ x\ 6.25}{v} \qquad \textbf{Equation 3.2}$$

$$meq\ Mg/100g = \frac{(Mg_s - Mg_b)\ x\ 10.3}{v} \qquad \textbf{Equation 3.3}$$

Where Ca_s is the concentration of calcium in the sample extract (µg mL^{-1}), Ca_b is the concentration of calcium in the blank extract (µg mL^{-1}), Mg_s is the concentration of magnesium in the sample extract (µg mL^{-1}), Mg_b is the concentration of magnesium in the blank extract (µg mL^{-1}) and v is the aliquot volume (mL).

To determine the CEC of Na^+ and K^+ 10 ml of the extract were diluted to 25 ml using 1 M ammonium acetate. Equation 3.5 and 3.6 were used to calculate the capacity for Na^+ and K^+ for each zeolite respectively.

$$meq\ Na/100g = \frac{(Na_s - Na_b)\ x\ 5.4375}{v} \qquad \textbf{Equation 3.4}$$

$$meq\ K/100g = \frac{(K_s - K_b)\ x\ 3.2}{v} \qquad \textbf{Equation 3.5}$$

Where Na_s is the concentration of sodium in the sample extract (µg mL^{-1}), Na_b is the concentration of sodium in the blank extract (µg mL^{-1}), K_s is the concentration of potassium in the sample extract (µg mL^{-1}), K_b is the concentration of potassium in the blank extract (µg mL^{-1}) and v is the aliquot volume in ml, of the sample used.

3.2.2 Isotherm modelling

Batch equilibrium data is commonly analysed with respect to empirical isotherm models such as the Langmuir or Freundlich models. Both were originally developed for gas adsorption in mono component systems but are now widely applied to liquid adsorption, ion exchange in mono-, binary- and multicomponent systems (Karadag *et al.,* 2006; Mohan and Singh 2002; Thornton *et al*., 2007).

The Langmuir model is based on the concept of constant site energy that assumes one solute molecule per site and constant cation capacity for each exchangeable site (monolayer adsorption), (Wang *et al.,* 2007; Mohan and Singh, 2002) and is expressed as:

$$q_e = \frac{q_{max} b C_e}{1+bC_e}$$ Non-linear form, **Equation 3.6**

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max} b}\right) + \left(\frac{1}{q_{max}}\right) C_e$$ Linear form **Equation 3.7**

Where q_e is the amount of solute adsorbed per unit of weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), q_{max} is the monolayer adsorption capacity (mg g^{-1}) and b is the constant related to the free energy of adsorption ($b \sim e^{-\Delta G/RT}$). It is reciprocal to the concentration at which half the saturation of the adsorbent is attained.

The Freundlich model describes a logarithmic relationship between solid and solution concentration assuming that the adsorbent has a heterogeneous surface with non-uniform distribution of adsorption sites (Mohan and Singh, 2002; Lin *et al.,* 2012). The Freundlich equation can be written as:

$$q_e = K_F C_e^{1/n}$$ Non-linear form **Equation 3.8**

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$ Linear form **Equation 3.9**

Where q_e is the amount of solute adsorbed per unit of weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and 1/n is the constant indicative of the intensity of the adsorption (Mohan and Singh, 2002). Strictly, the models should only be applied to mono component systems and when used beyond that it is customary to compare the model constant as an indication of the impact of competing species rather than for prediction.

3.3 Results and Discussion

3.3.1 Comparison of mono component capacity

The equilibrium capacity of the different zeolites ranged from 1.15 to 4.6 meq g^{-1} when in the sodium form and 0.15 to 1.45 meq g^{-1} when in the calcium form with an initial NH_4Cl of 600 mg L^{-1} (33.3 meq L^{-1}) (Figure 3-1). Importantly, the synthetic zeolite, MesoLite, delivered a higher equilibrium capacity and selectivity than all the natural zeolites with both pre-treatments. The difference due to pretreatment (Na^+ or Ca_{2+}) in all zeolites is in accordance with previous studies of both natural and synthetic zeolites (Metropoulos *et al.,* 1993; Lei *et al.,* 2008). The capacity reduction associated with calcium pretreatment is congruent with the known selectivity coefficient for the zeolites of 5.37 for $\alpha_{NH4+,Na+}$, 2.2 for $\alpha_{NH4+,Ca2+}$ and 1.97 for $\alpha_{Na+,Ca2+}$ (Hankins *et al.,* 2004; Jama and Yocel, 1989; Watanabe *et al.,* 2004). The results highlight the significance of the presaturant ion initially associated with the zeolite and aligns to simulations that have shown that Na^+ yields a lower energy state within the lattice than Ca^{2+} (Channon *et al*., 1998).

The thermally modified US-Clinoptilolite and Mordenite were affected most negatively by pretreatment with Ca^{2+} with a reduction in capacity of 91 and 88 % compared to pretreatment with Na^+ respectively. In comparison, the capacity of MesoLite only reduced by 68 % indicating a more resilient selectivity towards ammonium ions. Interestingly, the three Clinoptilolite materials showed significant variation with capacities in the sodium form of 1.72, 1.19 and 1.15 meq g^{-1} for the US, thermally modified US and the UK samples, a variation of 35 %. This confirms previous reports about the potential variability in the properties of natural zeolites such that capacities need to be confirmed when switching the origin of the material (Almutairi *et al*., 2015; Erdoğan and Ülkü, 2011).

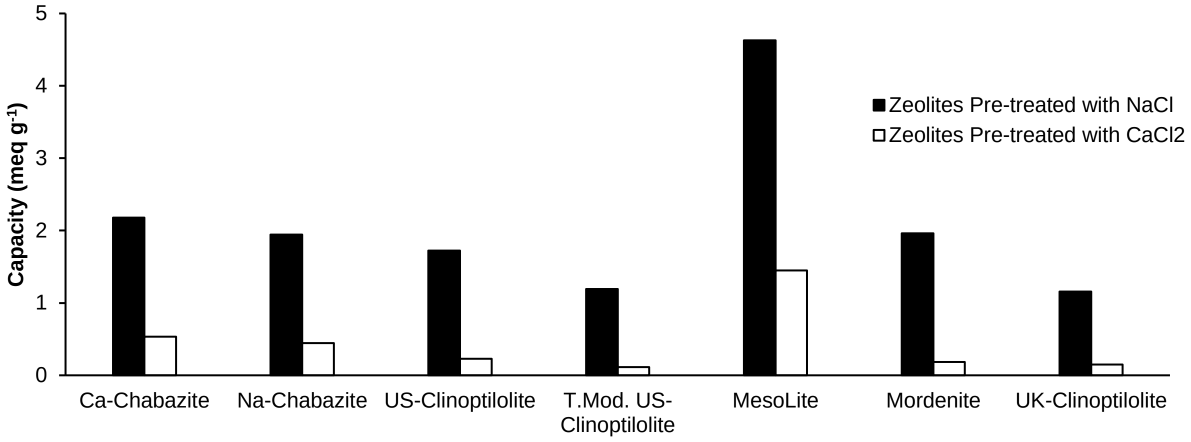

Figure 3-3-1 Equilibrium batch saturation capacity against a synthetic mono component solution (125 rpm; C_0 = 600 mg L^{-1} (33.3 meq L^{-1}) during 5 cycles to ensure completely saturation; pH = 7) using 1 M of NaCl and $CaCl_2$ as a pre-treatment for seven different zeolites (1 g of zeolite).

Comparison to the base properties of the different zeolites indicates that the Si:Al ratio may account for the difference between the observed capacity of MesoLite and the natural zeolites. To illustrate, the Si:Al ratio is > 4:1, 4:1, 4:1, 5:1 and 1:1 for Clinoptilolite, Na-Chabazite, Ca-Chabazite, Mordenite and MesoLite respectively. Whereas the effective window size was 4.6, 7.4, 7.4, 6.7 and 5.7 Å respectively for the same zeolites. The hydrated size of the ions are; 4.12, 3.58. 3.31 and 3.31 for Ca^{2+}, Na^+, K+ and NH_4^+ respectively such that size exclusion is unlikely to be significantly different between the zeolites (Hankins *et al.*, 2004). Instead the much lower Si:Al indicates a lattice structure with more exchange sites and hence an increased overall capacity (Armbruster and Gunter, 2001; Channon *et al*., 1998; Ruiz-Salvador *et al*.,1998).

3.3.2 Comparison of capacity in real wastewater

The seven zeolites were then compared in terms of their equilibrium capacity when treating a real wastewater effluent. Two different samples were required to test the full range of zeolites and the properties of the wastewater changed between the two samples (Table 3-2). The effluent was sourced post a trickling filter with a pH of 7.2 for the first sample and 7.3 for the second sample indicating that ammonium ions are likely to predominate. The actual concentration of ammonium ions within the sample was 16.2 and 11.7 mg L^{-1} (0.9 and 0.65 meq L^{-1}) compared to calcium concentrations of 62.8 and 51.4 mg L^{-1} (3.14 and 2.57 meq L^{-1}) and sodium of 100 and 67.16 mg L^{-1} (4.366 and 2.92 meq L^{-1}). To adequately compare capacity for the real wastewater, a synthetic solution was made up using the average secondary effluents NH_4-N concentration of 16 mg L^{-1} (0.8 meq L^{-1}).

Table 3-2 Characterization of the real effluent.

Aerobic effluent	Zeolites	Total (meq L^{-1})	NH_4^+ (meq L^{-1})	Ca^{2+} (meq L^{-1})	Na^+ (meq L^{-1})	K^+ (meq L^{-1})	Mg^{2+} (meq L^{-1})
Day 1	MesoLite, US-Clinoptilolite, Na and Ca-Chabazite	9.61	0.90	3.1	4.4	0.47	0.74
Day 3	T. Mod. US-Clinoptilolite, Mordenite and UK-Clinoptilolite	7.43	0.66	2.6	3	0.46	0.71

Comparison of the zeolites revealed that for all zeolite masses tested, MesoLite was able to remove more ammonium than the other zeolites. To illustrate, the removal efficiency of ammonium with MesoLite increased from 67 to 93 % when the mass of zeolite added increased from 0.1 to 0.5 g (Figure 3-2). In comparison, the worst performing zeolite was the UK Clinoptilolite where the removal efficiency increased from 10 to 73 % for the same increase in zeolite mass. The best performing zeolite in this aspect was the thermally modified Clinoptilolite where removal efficiency increased between 36 and 84 % over the range of added masses tested. Whilst removal increased with the added mass, the capacity decreased with MesoLite the most affected in absolute capacity terms. In fact, the capacity of UK Clinoptilolite did not vary much with added mass with capacities between 0.115 and 0.166 meq g^{-1} compared to MesoLite where the capacity varied between 0.16 and 0.78 meq g^{-1} for 0.5 g and 0.1 g of zeolite respectively (Figure 3-3).

Overall, MesoLite demonstrated the highest capacity for ammonium and the least impact from competing species in terms of the relative reduction in ammonium capacity. For instance, the reduction in capacity from switching from the mono component system to the real wastewater ranged from 3 to 26 % for 0.5 g to 0.1 g of zeolite. In comparison, the natural zeolites demonstrated a greater impact as a result of competition ranging between 40 and 80 % for 0.1 g of zeolite and between 16 and 50 % for 0.5 g of zeolite (Figure 3-3). Therefore, the higher capacity numbers are associated with the smaller masses of added zeolite where there are less total available exchange sites. This occurs when the actual levels of ammonium removal are low with values ranging between 10 and 40 % (Figure 3-2). Increasing the removal efficiency by adding more zeolite then reduces the percentage of the capacity associated with ammonium reflecting an inefficiency which is much less pronounced in the case of MesoLite.

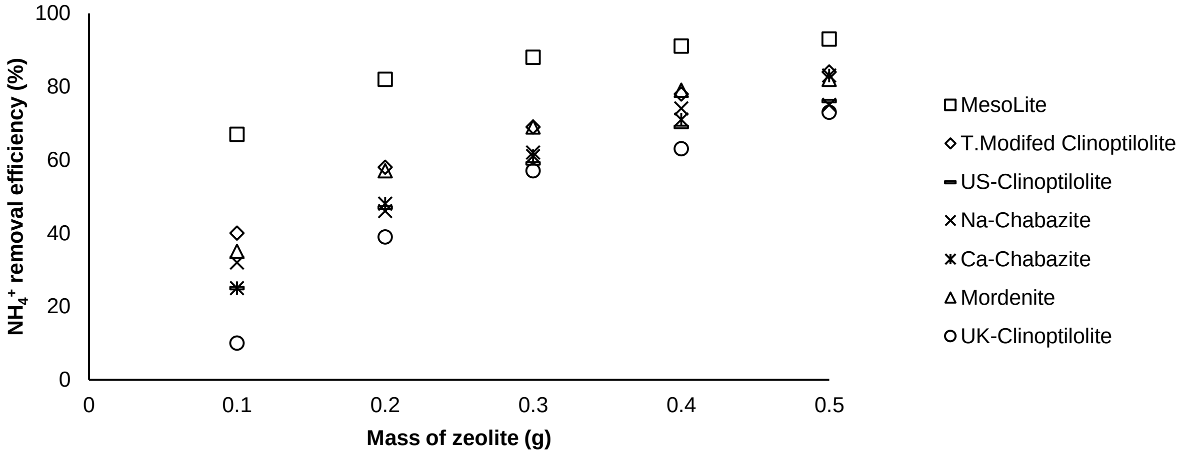

Figure 3-2 Removal efficiency of ammonium for different masses of adsorbent in real wastewater effluent.

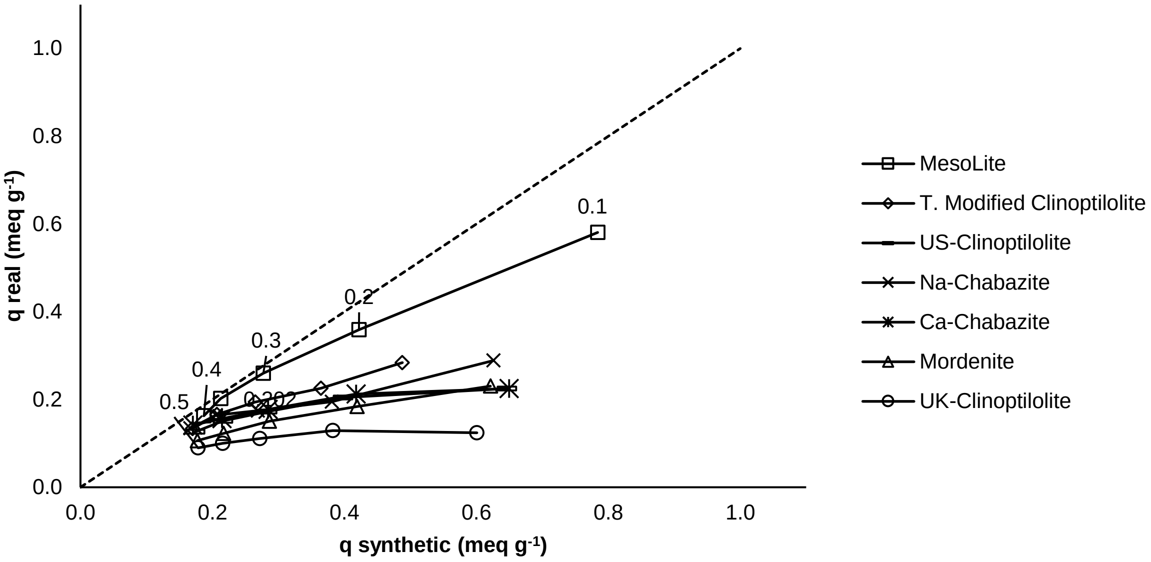

Figure 3-3. Comparison of batch capacity in real and synthetic effluents at 5 different zeolite weights (0.1 to 0.5 g). [125 rpm; C_o = 16 mg L^{-1} (0.8 meq L^{-1}); pH=7]

Further analysis of the removal of the different ions from the real wastewater revealed substantial uptake of Ca^{2+} with additional removal of K^+ and Mg^{2+} with some of the natural zeolites (Figure 3-4). To illustrate, when adding 0.1 g of zeolite the capacity with respect to Ca^{2+} was 0.25, 0, 0.35, 0.97, 1.01, 0.25 and 0.24 meq g^{-1} for MesoLite, thermally modified US Clinoptilolite, US Clinoptilolite, Na-Chabazite, Ca-Chabazite, Mordenite and UK Clinoptilolite respectively. This represented 30 %, 0, 55 %, 72 %, 78 %, 46 % and 60 % of the total uptake. Even though the thermally modified Clinoptilolite does not adsorb any Ca^{2+}, MesoLite has better capacity and selectivity towards ammonium (Figure 3-4 (A)). When increasing the mass of zeolite to 0.5 g, five times as many exchange sites were available. This decreased overall capacity indicating that a significant number of sites were still available which made it possible for other ions to be captured. For instance, a measured uptake capacity for K^+ was observed for all natural zeolites in comparison to just for thermally modified US Clinoptilolite, Na-Chabazite and Ca-Chabazite when only 0.1 g of zeolite was added. Further, when the higher mass of 0.5 g of zeolite was added, Mg^{2+} was also taken up by all the zeolites with the exception of thermally modified US Clinoptilolite (Figure 3- 4(B)). The corresponding percentage of the capacity associated with ammonium was 38 % for MesoLite which removed 93 % of the available ammonium from the water. The equivalent percentage of the uptake associated with ammonium was lower for all the natural zeolites and ranged between 24 and 40 %. The fact that when using 0.5 g of zeolite, the reduction in ammonium capacity (14 to 50 %) and the percentage of the total capacity associated with ammonium (41 to 25 %) were different indicates that the systems are not utilising all the available sites. For instance, the overall saturation CEC of MesoLite for NH_4^+ is 4.6 meq g^{-1} indicating that the experiments conducted here were utilising around 13 and 3.5 % of the total available active sites for 0.1 and 0.5 g respectively.

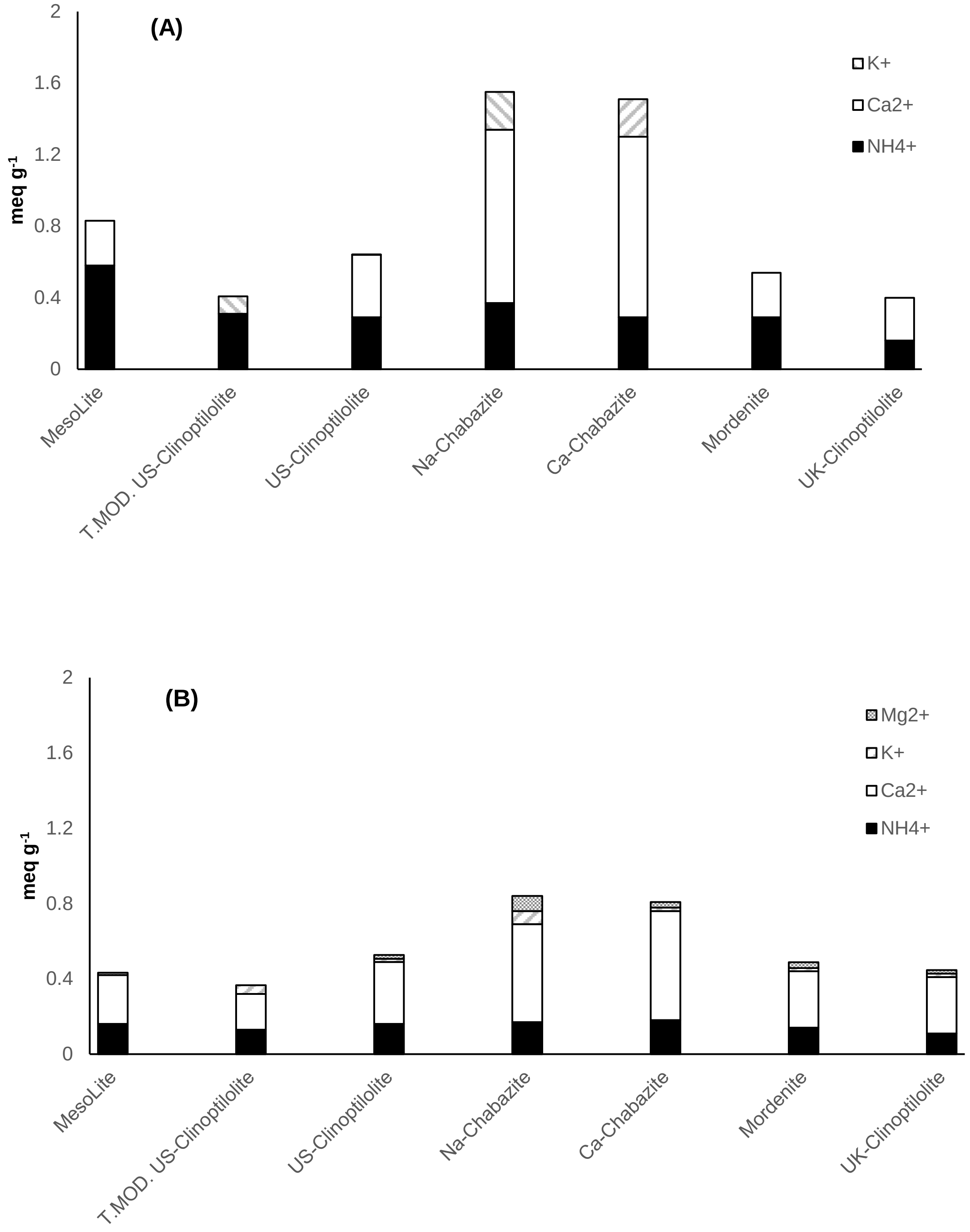

Figure 3-4 Comparison of adsorbance of competing cations (Ca^{2+}, Mg^{2+} and K^{+}) with the adsorbance of NH_4^+ for (A) 0.1 g of zeolite and (B) 0.5 g of zeolite

The results support previous trials with Clinoptilolite where a selectivity sequence of $Ca^{2+} > K^{+} > Mg^{2+}$ was reported during synthetic trials (Metropoulos *et al.,* 1993;

Weatherley and Miladinovic, 2004). This was extended to include ammonium with a sequence of NH_4^+ >Na^+ > Ca^{2+} during investigation into the use of Clinoptilolite for the treatment of landfill leachate (Hankins *et al.,* 2004). However, it has been previously suggested that calcium will not adversely affect uptake of most metallic ions onto Clinoptilolite and Chabazite when the concentration is below 10 meq L^{-1} with a dramatic reduction in ammonium removal expected once the Ca^{2+} concentration exceeds 25 meq L^{-1} (Ouki and Kavannagh, 1997). In contrast, in the present study Ca^{2+} concentrations were lower than that and showed a substantial impact. This is similar to previous work on landfill leachate where an addition of calcium reduced ammonium capacity by 21 % in a 0.16 N ionic solution (Hankins *et al.,* 2004).

The relative impact of competing ions on the uptake of ammonium for the different zeolites reflects a combination of the different concentrations of each component and the differences in the ion (size and energy of hydration) and zeolite (aluminium distribution and Si:Al ratio) properties (Channon *et al., 1998)*. The fact that uptake of calcium was maximised for the zeolite Chabazite is in line with this idea as the zeolite has a relatively low charge in the framework (Si:Al = 4) and the largest effective window size of the tested zeolites at 7.37 Å compared to 5.97 Å, 6.7 Å and 5.7 Å for Clinoptilolite, Mordenite and MesoLite respectively (Chapter 2; Table 2-1). The other feature is the properties of the ions themselves in relation to the free energy of hydration. If all other features are fixed, the selectivity sequence in low concentration systems is reported to mirror the free energy of hydration with lower free energies reducing preference (Kantiranis *et al*., 2011a). This is because ions with higher free energy of hydration are more likely to shed water molecules and form inner sphere complexes with the zeolite structure (Kantiranis *et al*., 2011b). Further, uptake of Mg^{2+} and K^+ became significant only when the total number of sites was increased reflecting their position further down the selectivity sequence which is consistent with their lower free energy of hydration and their larger effective ionic size (Eisenman, 1962; Sherry, 1966).

3.3.2 Isotherm models

Both isotherm models appropriately represented the equilibrium data although in the cases of UK Clinoptilolite and Na-Chabazite, the Freundlich model was seen to be a more representative fit to the data (Appendix A). The Freundlich constant (K_f) for MesoLite decreased from 7.2 mg g^{-1} in the mono component system to 2.7 mg g^{-1} in the multicomponent batch test (Figure 3-5 and Figure 3-6). The equivalent decrease in K_f for the natural zeolites were 70, 69, 61, 64, 40, and 50 % for US-Clinoptilolite, Mordenite, UK-Clinoptilolite, Ca-Chabazite, Na-Chabazite and thermally modified US-Clinoptilolite respectively. Comparison to previously reported values for Clinoptilolite show a large range of values (Table 3- 4) reflecting the limitation of the models for comparison between studies. Accordingly, Inglezakis (2005) suggests that the isotherm coefficients are only true for the specific experimental conditions used such that comparison across different studies should be done very carefully.

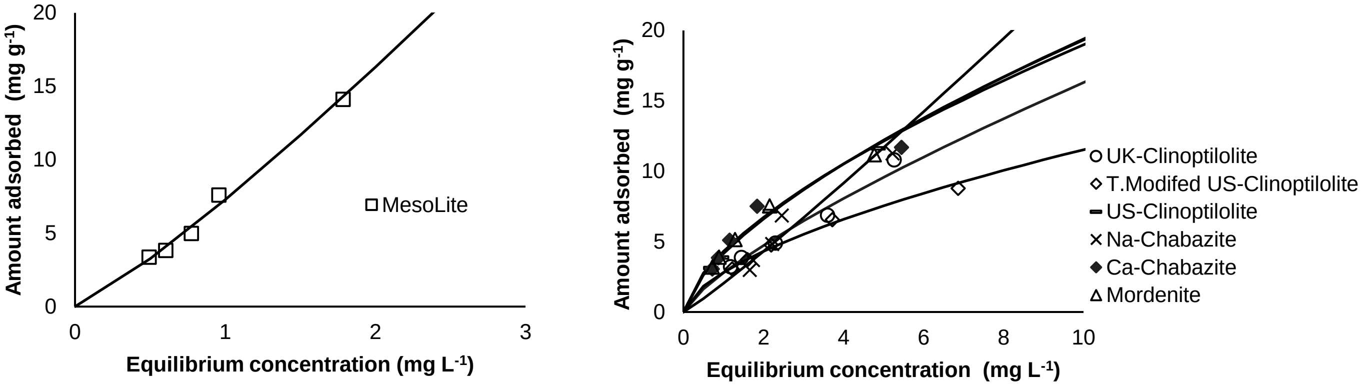

Figure 3-5 Comparison of the isotherm curves for the different zeolites fitted with a Freundlich model when treating a mono-component synthetic solution at an initial concentration of 16 mg L^{-1} and a pH of 7.5. (A) For MesoLite and (B) for the natural zeolites

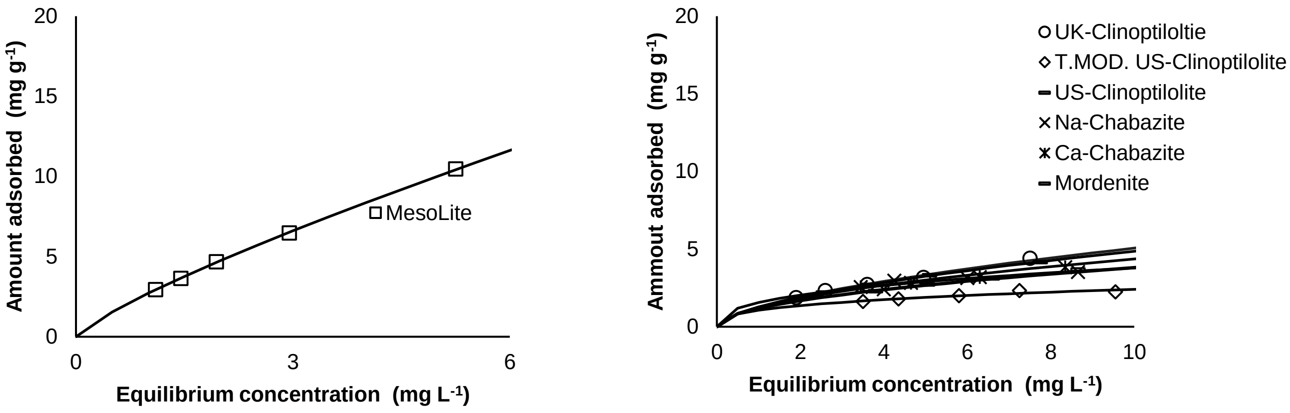

Figure 3-6 Comparison of the isotherm curves for the different zeolites fitted with a Freundlich model when treating a multi-component real wastewater at an initial concentration of 11.7 to 11.2 mg L^{-1} and a pH of 7. (A) For MesoLite and (B) for the natural zeolites

Table 3-3 Langmuir (q_m) and Freundlich (K_F) constants for different experimental setups.

Material	Experimental conditions	q_m	K_F	Reference
Clinoptilolite	Concentration range of NH_4^+ (23 to 113 mg L^{-1}) in three different particle sizes	2.128	0.428	(Wang *et al.,* 2006)
		2.375	0.596	
		2.469	0.432	
Clinoptilolite	Concentration range (50 to 250 mg L^{-1})	11.2	2.71	(Wang *at al.* 2007)
and modified Zeolite		22.64	3.639	
Natural Clinoptilolite	Three temperatures (25, 40 and 55°C)	6.05	6.62	(Karadag *at al.,* 2006)
	Concentration range (25 to 150 mg L^{-1})	4.75	5.50	
		3.76	4.01	
Clinoptilolite	Concentration range (0 to 200 mg L^{-1})	6.54	10.66	(Weatherley and Miladinovic, 2004)

The Freundlich model fits better the experimental data because this model assumes non-distribution of adsorption and it assumes heterogeneous surface.

3.3.3 Regeneration studies

The regeneration efficiency of the natural zeolites was significantly higher than that for the synthetic zeolite, MesoLite (Figure 3-7). For instance, the regeneration efficiency of MesoLite was 68 % during the synthetic trials and 50 % during the real wastewater trials. In comparison, the regeneration efficiency of the natural zeolites ranged from 90 to 100 %. As such, whilst MesoLite provided a higher operational capacity the ability to utilise the available capacity over prolonged periods may be challenging. It is suggested that this may be due to strong Ca^{2+} binding with the MesoLite as a consequence of its much lower Si:Al ratio. The higher proportion of Al substitution within the lattice structure enables the Ca^{2+} ion to potentially bind with two Al ions and form a stable inner sphere complex that is difficult to exchange (Ruiz-Salvador *et al.,* 1998). As a consequence regeneration for MesoLite needs to be optimised to ensure that the improved capacity can be maintained over multiple cycles for the material to be usable in practice.

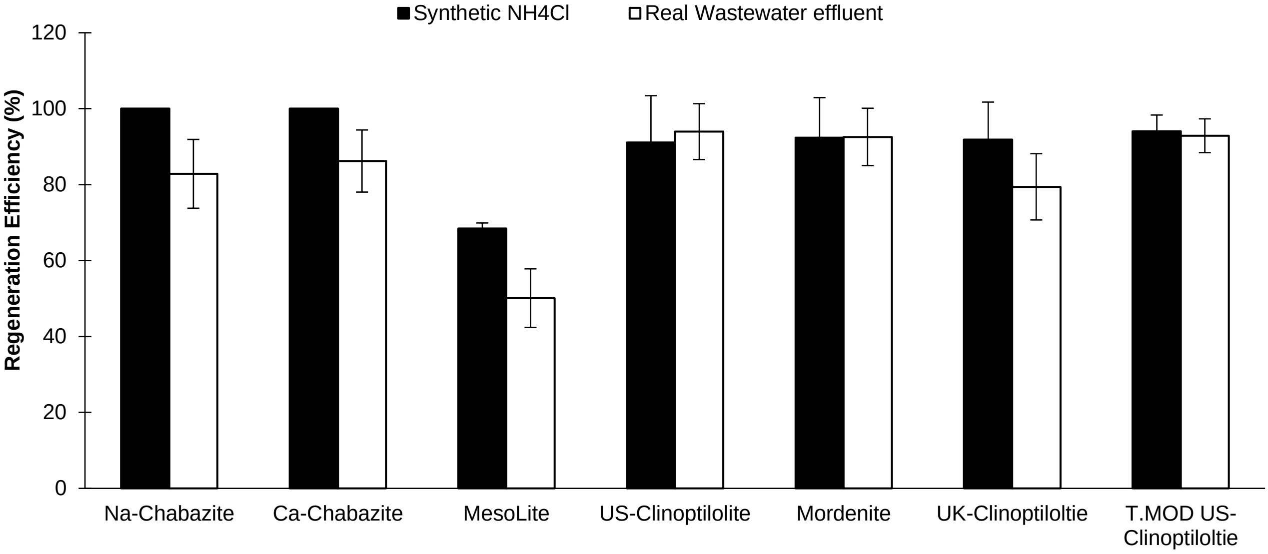

Figure 3-7 Comparison of the average regeneration efficiency over a five cycle sequence for the seven different zeolites treating synthetic and real wastewater

3.4 Conclusions

The synthetic zeolite MesoLite showed higher capacity and higher removal efficiency than the natural zeolites, reaching a saturation capacity of 4.6 meq g^{-1} relative to an average of 1.5 meq g^{-1} for the natural zeolites. The capacity of all zeolites was significantly reduced when pre-treated into the calcium form with Chabazite being most heavily impacted. The natural zeolites were more effectively regenerated with a 1 M NaCl solution with restricted regeneration efficiency observed for MesoLite. Finally, it was found that the Freundlich model adjusted better to the experimental data than the Langmuir model, with MesoLite being the zeolite with the highest K_F coefficient of 7.28.

3.5 Acknowledgements

The authors acknowledge the financial support of the project sponsors; Thames Water, Severn Trent, Anglian Water, Yorkshire Water and Scottish Water.

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4 REMOVAL OF AMMONIA FROM WASTEWATER USING ZEOLITES: A COMPARISON OF NATURAL AND SYNTHETIC ZEOLITES IN CONTINUOUS COLUMN EXPERIMENTS

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Abstract

Comparison of three zeolites (Clinoptilolite, Mordenite and MesoLite) was undertaken in continuous column trials with a synthetic ammonium solution set to 5 mg L^{-1} to mimic the potential application for tertiary wastewater treatment ammonium polishing. MesoLite cycle times were substantially longer than observed with the other two zeolites and ranged between 3 and 40 days at empty bed contact times (EBCT) of 1.2 minutes and 15 minutes respectively. The resultant capacities to breakthrough of 1 mg L^{-1} were 22, 25 and 47 mg g^{-1} for Clinoptilolite, Mordenite and MesoLite. Operating the MesoLite column at higher initial ammonium concentration decreased the cycle time at an EBCT of 1.2 minutes from 3672 BV when treating 5 mg L^{-1} to 255 BV when treating 30 mg L^{-1}. Overall the data fit well to the Thomas second order reaction model indicating that the impact of concentration would continue at that EBCT up to a maximum concentration of 42 mg L^{-1}.

Key Words: ammonium, MesoLite, EBCT

4.1 Introduction

Ion exchange is considered a potential alternative to conventional biological processes for nitrogen removal from wastewater when the conditions are less favourable for effective biological treatment. These include low BOD:N ratio, wastewater temperatures or discharge standards as well as wastewater that contains inhibitors through industrial input or large flow and load variations including seasonal variations encountered with tourist locations (Hedström, 2001; Verkerk and Van der Graaf, 1999). An added benefit of using ion exchange processes is the ability to recover the captured ammonium such that use of ion exchange systems enables realisation of the aspirations of the circular economy. Indeed, recent developments in anaerobic membrane bioreactors have indicated that non-biological nitrogen removal is likely to be needed if flowsheets that incorporate an MBRs are to effectively deliver energy neutral resource factories (Jefferson *et al.,* 2018).

In the case of ammonium, the most effective exchangers tend to be natural zeolites (Hedström, 2001; Wang and Peng, 2010) as they exhibit high capacity and selectivity towards the target cation (Kithome *et al.,* 1999). There are many natural zeolites found all around the world including Clinoptilolite, Mordenite and Chabazite with Clinoptilolite being the most commonly available and the leading option (Chapter 2; Fletcher and Townsend, 1982; Gedik and Imamoglu, 2008). As with all natural materials, the specific characteristics vary due to natural differences in their formation, the purity of the materials and the presence of clay which can limit diffusion and block pores (Mondale *et al.,* 1995). The cation exchange capacity (CEC) is generated through substitution of Al^{3+} in place of Si^{4+} within the zeolite framework thereby forming a negative charge within the mineral lattice. This is balanced by cations such as sodium, calcium and potassium that are exchangeable with other cations, notably ammonium (Curkovic *et al.,* 1997). The CEC represents the theoretical quantity of cations that can be exchanged per mass of zeolite and is reported to range between 0.6 and 2.3 meq g^{-1} (Wang and Peng, 2010). However, such levels can never be reached in practice with operational capacity expected to approach up to 50 % of the CEC (Hedström, 2001). The specific operational capacity depends on a number of factors such as initial ammonium concentration, media size, contact time (empty bed contact time in continuous column experiments – EBCT), temperature and the concentration of competing species such as calcium, magnesium and potassium as well as organic molecules. Consequently, reported capacities have a wide range between 2.7 and 30.6 mg g^{-1} (Wang and Peng, 2010) with reported operational capacities at a breakthrough concentration in a mono-component low strength ammonium trials in the range of 9 to 21.52 mg g^{-1} (Hlavay *et al.,* 1982; Malovanyy *et al.,* 2013; Sprynskyy *et al.,* 2005).

The use of MesoLite, a synthetic zeolite made by modification of clay and other aluminium bearing minerals, shows promise offering potentially higher operating capacities than the natural zeolites. The material has a CEC of 4.9 meq g^{-1} with reported operating capacities when treating sludge liquors of 45 to 55 mg g^{-1} (Mackinnon *et al.,* 2003; Thornton *et al.,* 2007b). Further, batch trials have shown MesoLite to be less influenced by the surrounding ions making it potentially more effective for tertiary ammonium polishing (Chapter 3). However, there is a paucity of reported data on the use of MesoLite, it has not been tested at low ammonia concentrations (lower than 10 mg L^{-1}) and there is no direct comparison against natural zeolites to establish whether it provides additional benefit. Accordingly, the current paper provides the first direct comparison of MesoLite and two natural zeolites (Clinoptilolite and Mordenite) in a series of column experiments to assess the impact of empty bed contact time and initial ammonium concentration on the efficacy of removal.

4.2 Materials and Methods

Three zeolites were selected for the experiments based on a previous study exploring the capacity, selectivity and regeneration properties of a range of zeolites (Chapter 3). Natural Mordenite (Newstone International, Japan), natural US-Clinoptilolite (St. Cloud, NM, USA) and synthetic MesoLite (Nanochem Pty Ltd., Australia) were sieved to generate a size range between 1 and 1.7 mm. Continuous bed experiments were performed using Polyvinyl Chloride (PVC) columns with an internal diameter of 52 mm and a media bed volume of 100 mL, corresponding to 69.6 g, 84.94 g and 76.84 g for Mordenite, US-Clinoptilolite and MesoLite respectively. Prior to the experiments, the columns were back flushed with de-ionised (DI) water (15 MΩ cm^{-1}) at 50 BV h^{-1} for 1 h and regenerated using 1 M NaCl (> 99 % stated purity; Fisher Scientific, UK) at 4 BV h^{-1} for 24 h to ensure mono ionic exchangeable cations were standardised across all three zeolites. The beds were fed with a synthetic ammonium solution (NH_4Cl in DI water) set to 5 mg L^{-1} to mimic typical effluent requiring polishing (Figure 4-1) and to avoid competition with other ions. Each column was operated at a series of downward flow rates corresponding to EBCT of 1.2, 2.5, 4, 8 and 15 minutes (85, 40, 25, 12.5 and 6.6 mL min^{-1} respectively). In addition, the impact of influent concentration was tested with the MesoLite columns at 5, 10, 20, 30 mg L^{-1} at a fixed EBCT of 1.2 minutes.

The total amount of ammonium exchanged (total capacity) was calculated as the area between the influent and the effluent curve as a function of time:

$$q = \frac{Q}{1000\,m}\int_{t_o=0}^{t_s} (C_0 - C_t)\,dt$$

Equation 4.1

Where Q is the influent flow (ml min^{-1}), C_0 the influent concentration (mg L^{-1}), m the mass of adsorbent (g) and t_s the saturation time (min).

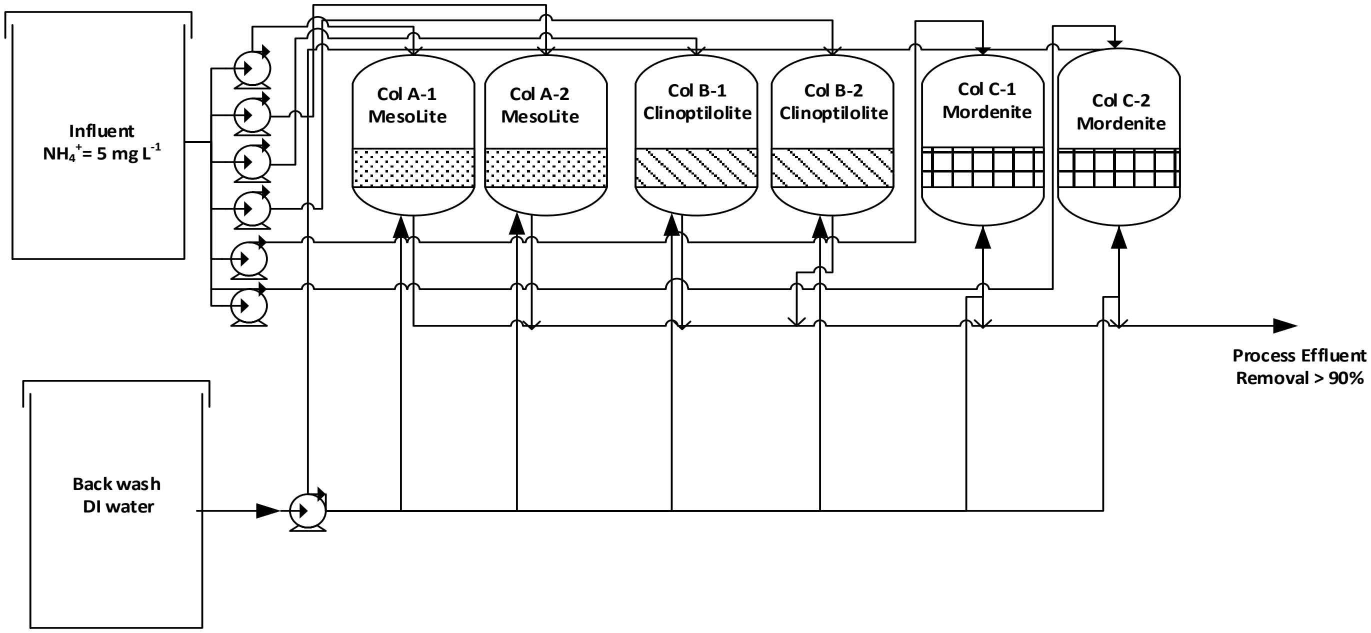


Figure 4-1 Schematic process diagram of the lab scale columns

4.2.1 Uptake models

The experimental data was fit with two different second order reversible kinetic reaction models that assume no axial dispersion (Malovanyy *et al*., 2013; Singh *et al.,* 2017; Soto *et al.,* 2017; Zou *et al*., 2011). The linear form of the models was:

Thomas: $\ln\left(\frac{C_0}{C_t}-1\right)=\frac{m\,q_{o(Th)}K_{Th}}{Q}-\ C_oK_{Th}t$ **Equation 4.2**

Yoon and Nelson: $\ln\left(\frac{C_t}{C_o-C_t}-1\right)=K_{YN}t-t_{1/2}\,K_{YN}$ **Equation 4.3**

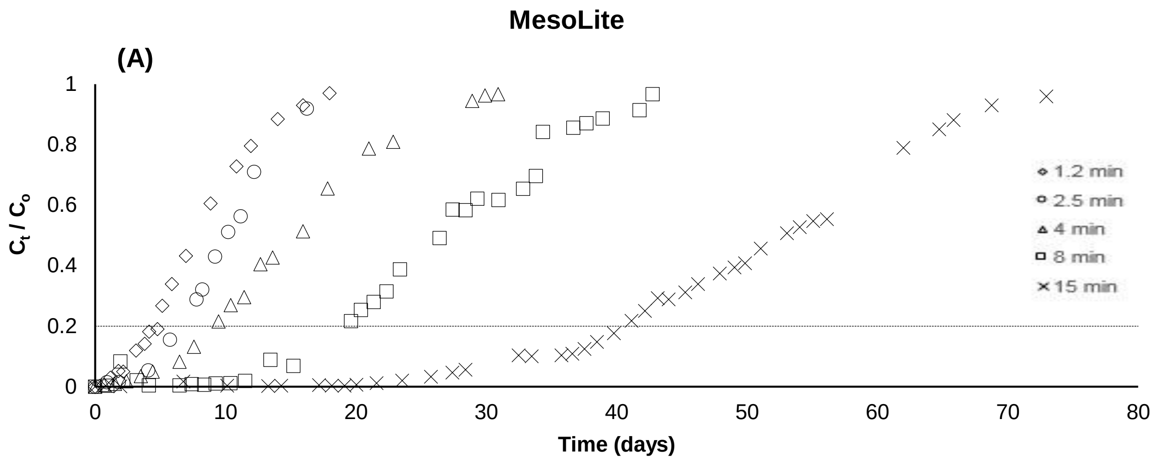
where C_o is the influent concentration (mg L^{-1}), C_t the effluent concentration at time t (mg L^{-1}), m the mass of adsorbent (g), K_{Th} the Thomas constant (mL min^{-1} mg^{-1}), q_o the maximum adsorption capacity at equilibrium (mg g^{-1}), Q the influent flow rate (mL min^{-1}) and V the effluent volume (mL). K_{YN} the Yoon and Nelson constant (min^{-1}) and $t_{1/2}$ the time at which 50 % adsorbate is adsorbed (min).

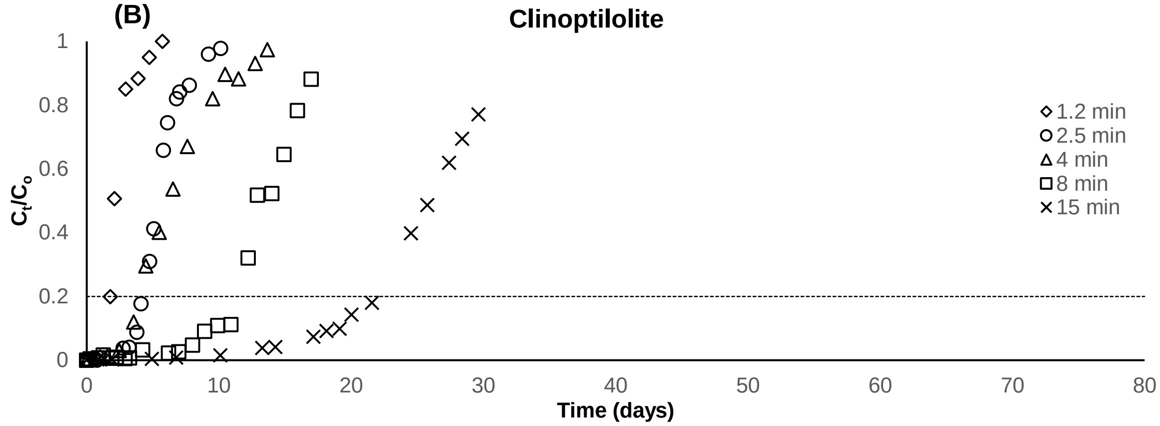
4.3 Results and Discussion

4.3.1 Effect of the Empty Bed Contact Time

Operation at longer EBCTs extended the run time to breakthrough for all three zeolites (Figure 4-1). For example, in the case of MesoLite and a breakthrough concentration of 1 mg L^{-1} (C_t/C_0 = 0.2), the run time increased from 3 days at an EBCT of 1.2 minutes to 40 days at an EBCT of 15 minutes. In comparison, the run times of the two natural zeolites were much shorter across all EBCTs. For instance, at an EBCT of 15 minutes, run times of 22 and 26.8 days were reported for Clinoptilolite and Mordenite respectively. The extended run time when using MesoLite compared to the others reflects the difference in batch capacity measured for the three zeolites at 1.72, 1.96 and 4.63 meq g^{-1} for Clinoptilolite, Mordenite and MesoLite respectively (Chapter 3). However, the difference observed in run time is much larger than the 24h required to reach equilibrium observed in batch capacity reinforcing the importance of column trials to establish operational comparisons. The equivalent saturation capacity during the column experiments reached a maximum of 22, 25 and 47 mg g^{-1} [1.2, 1.4 and 2.6 meq g^{-1}] (Table 4-1). This compares to a range of 2.7 to 30.6 mg g^{-1} previously reported for natural zeolites (Wang and Peng. 2010) and 27 to 51 mg g^{-1} for MesoLite (Thornton *et al.,* 2007b).

Further, as the EBCT increased (the flow rate decreased), the saturation capacity decreased with the respective values for Clinoptilolite, Mordenite and MesoLite being 14, 14.2 and 32.2 mg g^{-1} at an EBCT of 15 minutes. This supports previous reports at different concentrations (Sprynskyy *et al.,* 2005) or with different target species (Soto *et al.,* 2017) working with Clinoptilolite. For instance, an increase in ammonium capacity from 13.6 to 21.5 mg g^{-1} was reported for a change in flowrate from 1.8 to 9 mL min^{-1} equating to EBCTs of 7.7 and 1.5 minutes respectively when treating an ammonium solution with an initial concentration of 100 mg L^{-1} (Sprynskyy *et al.,* 2005). Similarly, phenol capacity increased from 7.7 mg g^{-1} to 32.7 mg g^{-1} as the flowrate increased from 1 mL min^{-1} to 5 ml L^{-1} equating to EBCTs of 16 and 3.2 minutes (Soto *et al.,* 2017).





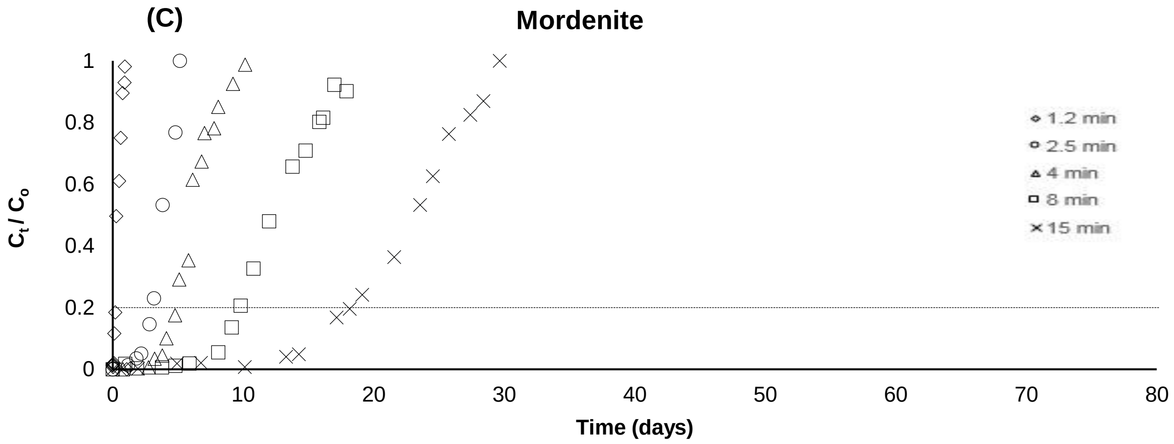


Figure 4-2 Breakthrough curves, ran until saturation at fixed concentration (5 mg L^{-1}, Z=5cm) at 5 different EBCT [1.2(◇), 2.5(○), 4(△), 8(□) and 15(X) minutes], run for three different zeolites: MesoLite (A), Clinoptilolite (B) and Mordenite (C) from top to bottom panel.

The capacity changes in the current study are consistent with the change in the shape of the C_t/C_o vs time curves which become steeper at shorter EBCTs indicating better mass transfer profiles at shorter EBCTs. The range of EBCTs operated in the current study equates to Reynolds (Re) numbers between 0.1 and 1.6 such that flow is laminar and boundary layer thicknesses are expected to be relatively large. This is consistent with previous work investigating mass transfer effects with Clinoptilolite where the overall mass transfer coefficient was reported to be film diffusion controlled (Yuan *et al.,* 2008). The fact that the capacity increased with Re supports this and is in contrast to previous column studies with hybrid ion exchange media where intra particle diffusion was seen to dominate (Muhammad *et al*, 2018). When viewed in terms of bed volumes treated (Figure 4-2) a reasonable degree of self-similarity in the curves is observed due to the common underpinning mechanisms of operation. The observed difference between the zeolites therefore relates to the overall capacity of the zeolites and the diffusion of the captured ions within the zeolite structures as the boundary layer thickness can be assumed to be similar for all three zeolites as the Re is fixed during the comparison (Sprynskyy *et al.,* 2005).

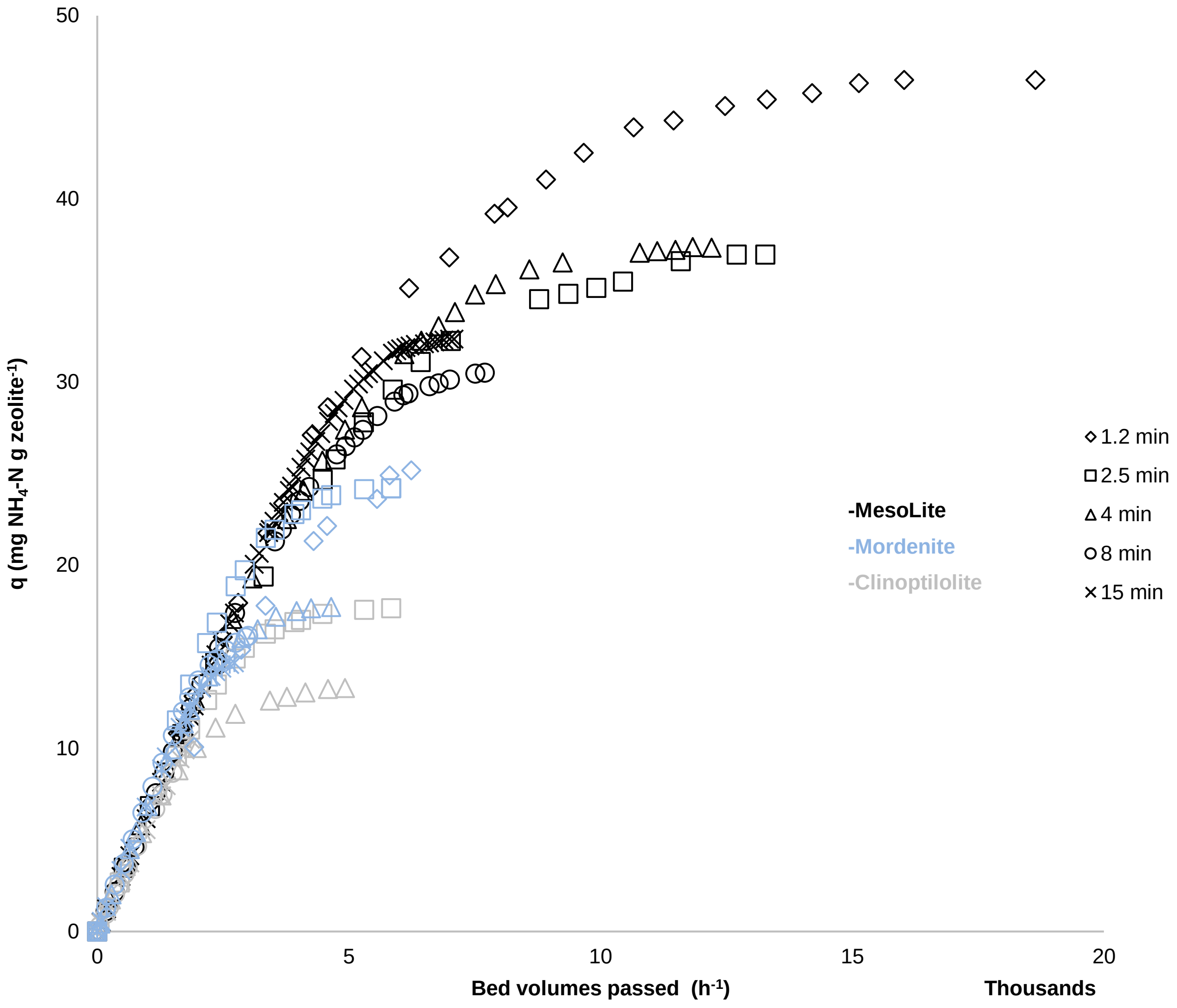


Figure 4-3 Study of the effect of capacity against bed volumes passed through the columns (Z= 5 cm, C_o= 5 mg L^{-1}) [1.2(◇), 2.5(○), 4(△), 8(□) and 15(X) minutes].

Importantly, the systems show prolonged operation and the ability to meet low effluent concentrations across a range of EBCTs from 1.2 to 15 minutes (Table 4-1). Previous studies on ammonium uptake onto Clinoptilolite have recommended an EBCT of 5 minutes and not less than 3 minutes as breakthrough would occur too fast (Baykal and Guven, 1997). The EBCT levels used in the current study equate to flow rates between 4 and 51 BV h^{-1} (Figure 4-3) and can be compared to previously reported values between 1 and 24 BV h^{-1} for Clinoptilolite (Hedström, 2001) and MesoLite (Mackinnon *et al.,* 2003).

Operational capacities as a function of BV h^{-1} varied between 22.6 and 26.6 mg g^{-1} for MesoLite compared to between 11.8 and 16.6 mg g^{-1} for Mordenite and between 11.4 and 16 mg g^{-1} for Clinoptilolite (Figure 4-3). Comparison to the saturation capacity suggests operating levels of 57 to 84 % for MesoLite, 64 to 83 % for Mordenite and 74 to 86 % for Clinoptilolite indicating better utilisation of the available capacity for the natural zeolites.

Table 4-1 Experimental results obtained from 5 different EBCT with an initial concentration of 5 mg L^{-1} (Z=5 cm).

	EBCT (min) **Flow rate (Bv h^{-1})**	**1.2** **51**	**2.5** **24**	**4** **15**	**8** **7.5**	**15** **4**
MesoLite	**t_b (days)**	4.8	6.4	9	19	40
	q_b (mg/g)	27	23	24	23	27
	q_s (mg/g)	47	37	37	30.5	32
US-Clinoptilolite	**t_b (days)**	2	4.2	4.3	11	22
	q_b (mg/g)	16	13	10.5	11.4	11.9
	q_s (mg/g)	21.7	17.6	13.3	15	14
Mordenite	**t_b (days)**	2.9	4.3	5.2	9.7	26.8
	q_b (mg/g)	16.6	15.8	12.4	12	11.8
	q_s (mg/g)	25	24.2	18	16.2	14.2

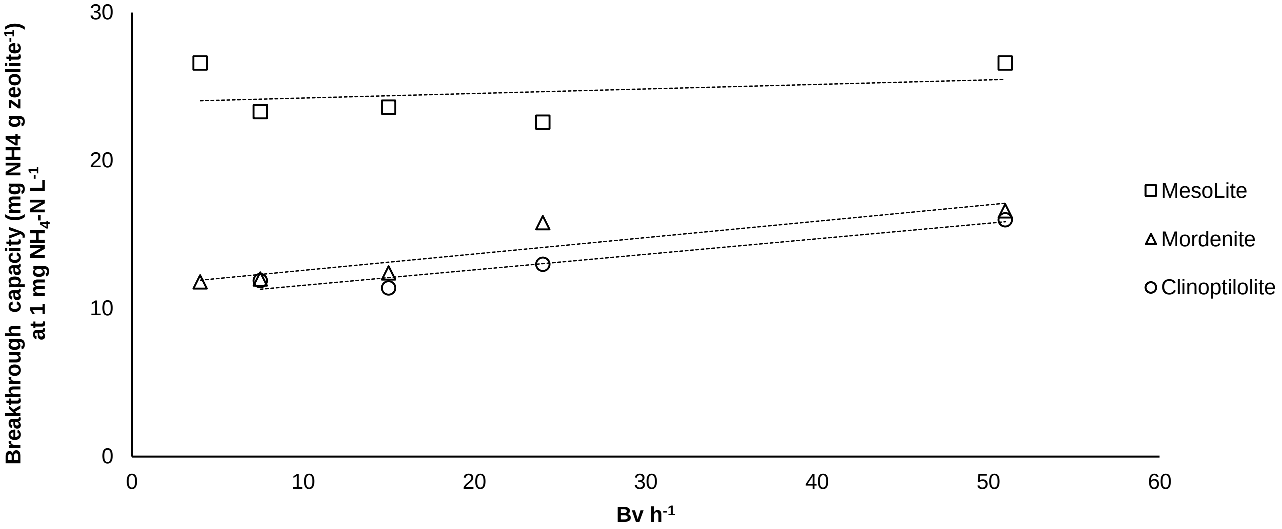


Figure 4-4 Relationship between flow rate (Bv h^{-1}) and breakthrough capacity of 1 mg L^{-1}.

4.3.2 Impact of inlet concentration on the performance of MesoLite

The efficacy of MesoLite was further examined through testing different initial ammonium concentrations between 5 and 30 mg L^{-1} (Figure 4-4). Steeper breakthrough curves and faster adsorption was observed as the concentration increased such that the breakthrough time to reach $C/C_o = 0.2$ decreased from 2.15 days when treating a 5 mg L^{-1} solution to 5.5 h for the 30 mg L^{-1} influent. Similar findings have been reported for Clinoptilolite where the breakthrough time changes from 5.2 to 3 days as the influent concentration increased from 30 to 50 mg L^{-1} (Singh *et al.,* 2017). Represented in terms of Bv treated the impact of feed concentration is seen in a decreased to a tenth in the Bv treated from 2662 to 284 as the feed concentration increased from 5 to 30 mg L^{-1}.

Data fit by the linear form of second order rate expressions resulted in regression fits (R^2) of between 0.89 and 0.97 confirming the suitability of the use of the models to describe ammonium uptake onto these zeolites. The impact of concentration is seen in the Thomas model through a reduction in K_T of 0.008 to 0.003 mL mg^{-1} min^{-1} as the concentration increased from 5 to 30 mg L^{-1} (Table 4-2). The equivalent is seen in the Yoon and Nelson model through the time to reach half of the saturation ($t_{1/2}$) that decreases from 92 h to 20 h, as the inlet concentration increases from 5 to 30 mg L^{-1} (Table 4-2).

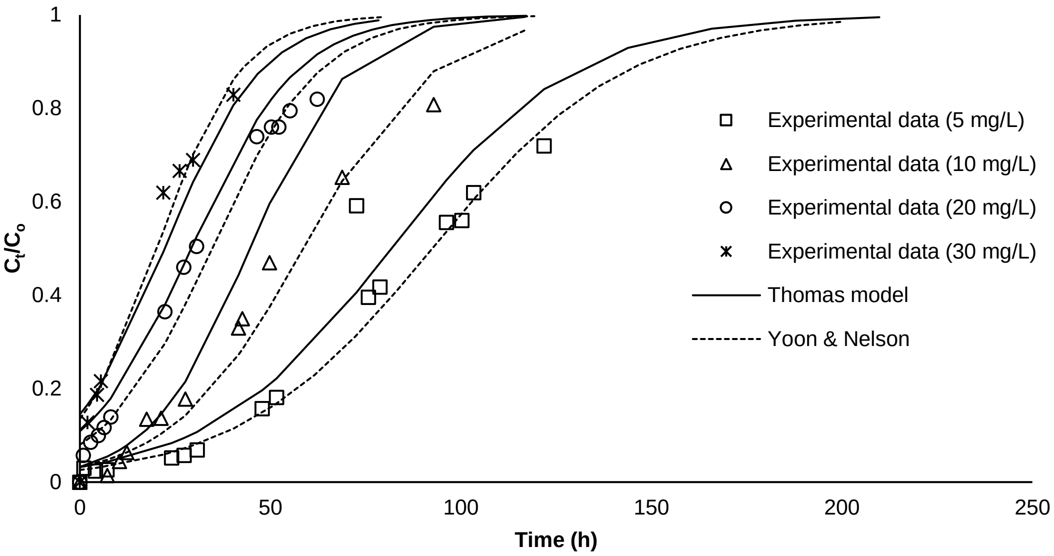


Figure 4-5 Breakthrough curves at four different concentrations for a fixed bed height (5 cm) and a fixed EBCT of 1.2 min.

A comparison of the models indicates that the Yoon and Nelson model fits the data better, especially at the lower feed concentrations that are more pertinent to the application of ammonium polishing. However, the Thomas model is mathematically more correct, since it offers two different mathematical parameters (K_{Th} and $q_{0(Th)}$). Importantly, both models predicted the breakthrough point observed experimentally and work effectively at higher feed concentrations. To illustrate this, the Thomas model was utilised for the case of 100 BV at an EBCT of 1.2 minutes to establish the impact of feed concentration (Figure 4-5). Estimation of the likely maximum capacity can be obtained by calculating the ammonia concentration at the point where the kinetic parameter becomes zero such that the bed will be fully utilised. Predictions based on the current data suggest a limiting concentration of 42 mg L^{-1} resulting in a capacity of 56.8 mg g^{-1}. Further, at this concentration, the 100 ml bed will become instantly saturated and that way much greater bed depths will be required. In the current experimental case, the capacity increased from 28.1 mg g^{-1} when treating 5 mg L^{-1} to 44.6 mg g^{-1} when treating 30 mg L^{-1}. Comparison to the literature reveals that the capacity increases to a range between 47 and 51 mg g^{-1} for when treating with ammonia concentrations between 500 and 700 mg L^{-1} (Thornton *et al.,* 2007b). Overall, this supports the idea of film diffusion control with the increased feed levels generating greater concentration gradients between the solid and the liquid phase (Huang *et al.,* 2015; Uddin *et al.,* 2009).

The impact appears only significant for relatively low feed ammonia concentrations and hence is particularly important when considering polishing applications where the small changes in concentration will have a big impact on capacity. However, this was conducted at a very short EBCT and so extending the work to other EBCT is a critical step going forward.

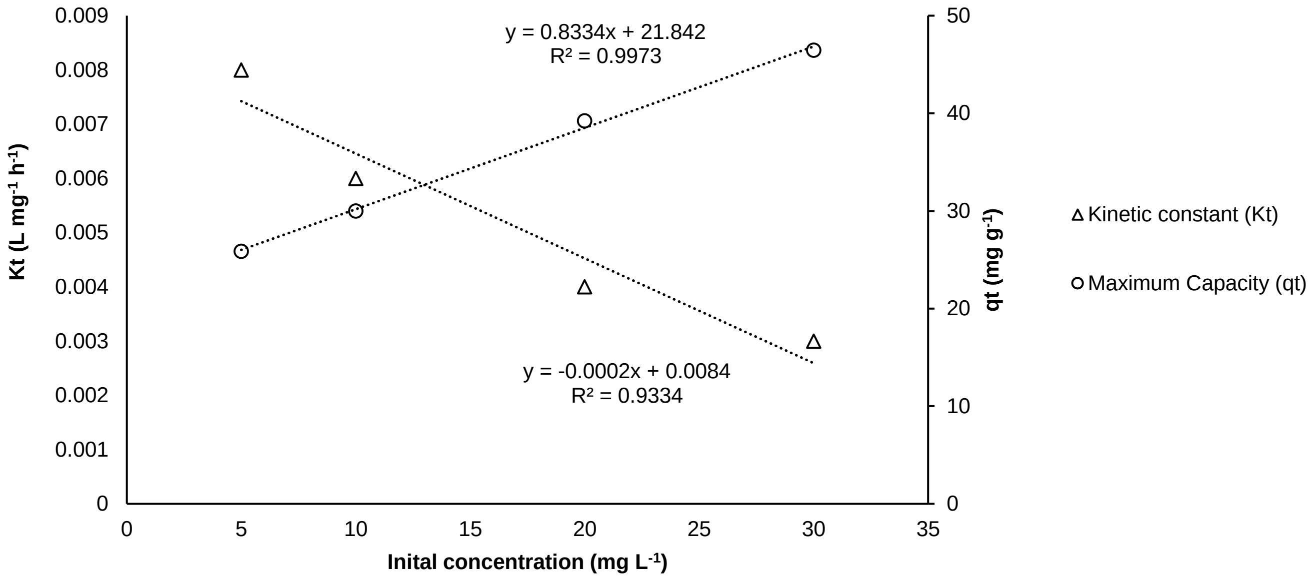


Figure 4-6 Relationship between initial inlet concentration and both Thomas constants, kinetic constant, K_T (L h^{-1} mg^{-1}) and maximum, q_T (mg g^{-1}).

Table 4-2 Experimental data compared to both models (1) Thomas and (2) Yoon and Nelson, fitting the data at R^2 > 89 %.

Experimental data							Thomas Model			Yoon and Nelson		
C ($mg\ L^{-1}$)	Q (ml min^{-1})	EBCT (min^{-1})	Z (Cm)	M (g)	Saturation capacity ($mg\ g^{-1}$)	t ½ (h)	K_T ($L\ h^{-1}\ mg^{-1}$)	q_T ($mg\ g^{-1}$)	R^2	K_{YN} (h^{-1})	$t_{1/2}$ (h)	R^2
5	86	1.16	5.09	76.8	28.16	67.92	0.008	25.87	0.93	0.04	92.50	0.95
10	86	1.16	5.09	76.8	38.53	52.80	0.006	30.0	0.93	0.06	58.56	0.89
20	86	1.16	5.09	76.8	42.82	30.48	0.004	39.21	0.89	0.07	34.56	0.97
30	86	1.16	5.09	76.8	44.65	17.52	0.003	46.46	0.97	0.09	20.31	0.97

4.4 Conclusions

MesoLite cycle times were substantially longer than with the two natural zeolites Clinoptilolite and Mordenite and ranged between 3 and 40 days at EBCTs of 1.2 minutes and 15 minutes respectively. The resulting capacities to breakthrough of 1 mg L^{-1} were 22, 25 and 47 mg g^{-1} for Clinoptilolite, Mordenite and MesoLite respectively. The operating cycle of all three zeolites decreased with increasing EBCT but the capacity increased as the mass transfer front became sharper at shortened EBCTs. The operating cycle time was found to decrease as a function of initial ammonium concentration from 3672 BV at a feed concentration of 5 mg L^{-1} to 255 BV when the feed concentration of 30 mg L^{-1}. Overall the data fit by the Thomas second order reaction model indicates that the impact of concentration would continue at that EBCT up to a maximum concentration of 42 mg L^{-1}.

4.5 Acknowledgements

The authors acknowledge the financial support of the project sponsors Thames Water, Severn Trent, Anglian Water, Yorkshire Water and Scottish Water.

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5 IMPACT OF IONIC SPECIES AND CONCENTRATION ON THE EFFICACY OF REGENERATION OF ZEOLITES FOR AMMONIUM REMOVAL

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Abstract

Regeneration of the media is the biggest challenge to implementing ion exchange processes in full scale at wastewater treatment works. Regeneration efficiency as a function of brine type, brine reuse, molarity and pH was investigated for the zeolite MesoLite treating synthetic solutions of ammonium. When pretreating the zeolite with KCl rather than NaCl a 30 % improvement in regeneration efficiency was found in the first cycle, which dropped to a 10 % improvement in the fifth cycle. For both systems, the uptake capacity observed during the load cycle remained constant indicating that both were effective and that the brine could be reused five times without deterioration in the performance of the zeolite. The use of KCl was more effective at lower molarities than NaCl such that equivalent regeneration efficiencies were observed at 1.0 M and 0.1 M for NaCl and KCl respectively. Alteration of the pH between 9 and 12 had no impact on the regeneration efficiency. However, operation at pH 12 was possible without brine.

Key Words: Ammonium, MesoLite, regeneration

5.1 Introduction

Ion Exchange is a promising alternative to biological processes due to its capability to selectively adsorb NH_4^+ ions achieving < 1 mg NH_4-N L^{-1} in the effluent using comparably little energy (Hedström, 2001). Relative to biological processes, ion exchange is also attractive as it is more resilient to shock loadings and low temperatures (Aiyuk *et al.,* 2004; Svetich, 1993). In addition, it provides a route to recover nitrogen for further use for fertilisers or livestock feed through microbial protein production (Matassa *et al.,* 2015). This decreases the need to synthetically fix N_2 into reactive nitrogen (NH_4-N) through the Haber-Bosch process (Erisman *et al.,* 2008). A particularly effective combination has been reported in relation to downstream nutrient recovery following anaerobic sewage treatment in membrane bioreactors (Deng *et al.,* 2014; Jefferson *et al.,* 2018).This responds to renewed interest in delivering resource factory thinking (seeing waste as a resource and recover the valuable materials from it) into wastewater treatment and as such offers a new application area for the use of zeolites.

The potential advantages of using zeolites as exchangers to adsorb NH_4-N has seen a number of demonstration and full-scale schemes across the world over the last fifty years (Liberti *et al*., 1981) including a 22,500 m^3 d^{-1} plant in California for the removal of ammonium from domestic wastewater (Svetich, 1993). Wider implementation has been restricted by the relative ease of adaption of biological processes for ammonia removal and process limitation with ion exchange including (1) the requirement for pretreatment to avoid clogging, (2) high cost of the chemical regenerant and (3) disposal of the spent brine.

Regeneration is needed once the effluent concentration exceeds the target (breakthrough) concentration. At this point the media is typically backwashed to remove solids and then a brine solution pumped through the media column. During regeneration, previously adsorbed NH_4^+ ions within the framework of the zeolite are exchanged for an alternative cation, such as sodium (Equation 5-1).

$$Z.NH_4^+ + Na^+ + Cl^- \leftrightarrow Z.Na^+ + NH_4^+ + Cl^- \qquad \textbf{Equation 5.1}$$

Since the used zeolite is highly selective toward NH_4^+, a sufficient strength and quantity of brine is required (Table 5-1). This requirement is defined through the regeneration ratio which is calculated as the total amount of regenerant (meq) divided by the total ionic load (meq) and is set at a level to ensure maximum replenishment of the available exchange sites (Table 5-1).

Once spent, the brine has to be disposed as hazardous waste, with typical prices of 65 £ t^{-1} (Martin e*t al*., 2009) which can constitute approximately 80 % of the total cost (Miladinovic and Weatherley, 2008). A number of approaches to cleaning up the brine in order to enable reuse have been considered including air stripping (Mercer *et al.*, 1970; Svetich,1993), membrane degassing (Verrecht *et al.,* 2010), evaporation-condensation (Ukwuani and Tao, 2016) and biological regeneration (Lahav and Green, 1998). In addition, operation at elevated pH converts the released ammonium into the molecular form and hence the ammonium no longer exchanges. As such, the regeneration liquids can potentially be reused for multiple cycles prior to recovery to maximise the available ammonia and hence reduce the operational costs of regeneration clean up and nitrogen recovery.

Table 5-1 Example regeneration characteristics when using zeolites for ammonium removal.

	(Koon and Kaufman, 1975)	(Liberti *et al.,* 1981)	(Semmens and Porter 1979)	(Thornton *et al.,* 2007b)	(Mackinnon *et al.,* 2003)
Zeolite	Clinoptilolite	Clinoptilolite	Clinoptilolite	MesoLite	MesoLite
Capacity (meq g^{-1})	0.69	2	0.30	3.6	3.93
Brine	NaCl	NaCl	NaCl $NaNO_3$	NaOH	Na_2CO_3
Brine concentration (M)	0.21 to 0.34	0.6	0.3	1.25	0.5 to 2.0
Regeneration flow (BV h^{-1})	15	30	12 to 20	5	0.5
Duration (h)	0.7 to 1.3	0.7	1	4	4
Brine volume passed (BV)	20	20	12 to 20	-	22 to 24
pH	11.5 to 12.5	7	7 to 8.4	-	-
Regeneration ratio	304:1 to 493:1	300:1	1,077:1	417:1	254:1 to 1,018:1
RE (%)	100	100	90-97	> 95	60-80

There is a paucity of studies exploring the optimisation of regeneration and to the authors knowledge no studies have focussed on the regeneration of MesoLite or directly compared regeneration of natural and synthetic zeolites. Accordingly, the current work aims to investigate the impact of regeneration liquid characteristics (ionic type, strength, and pH) on the efficacy of regeneration of Clinoptilolite, Mordenite and MesoLite when used for the removal of ammonia.

5.2 Materials and Methods

Three zeolites were used throughout the experiments, selected from previous batch trials as the most promising options (Chapter 3): Mordenite (Newstone International, Japan), US-Clinoptilolite (St. Cloud, NM, USA) and MesoLite (Nanochem Pty Ltd., Australia). All zeolites were sieved into a uniform size fraction of between 1 and 1.7 mm before being washed with de-ionised (DI) water (15 MΩ cm^{-1}) to remove dust particles and regenerated using 1 M NaCl (purity stated > 99 %; Fisher Scientific, UK) for 24 h.

Experiments were conducted in batch using 250 ml Erlenmeyer flasks adding different amounts of zeolites (from 0.1 to 0.5 g) into 100 mL of synthetic ammonium solution (5 and 16 mg L^{-1}). The experiments involved five cycles of loading and regeneration with 100 mL of either KCl or NaCl (purity stated > 99 %, Fisher Scientific, UK). Each load and regeneration cycle lasted 24 hours with the sample agitated at 125 rpm on an orbital shaker (Stuart Orbital Shaker, Bibby Scientific Ltd., Staffordshire, UK). Required changes in pH were accomplished by dropwise addition of a solution of 10 % NaOH solution (purity stated > 99 %; Fisher Scientific, UK).

The concentrations of NH_4^+ in the liquid phase were determined spectrometrically by cell test (Merck, Germany) using a spectrophotometer (Merck, Spectroquant Nova 60, Germany) method that is insensitive to interference by other dissolved species (e.g. cations, anions) in the liquid phase. The pH was measured using Jenway 3510 pH Meter (Camlab, UK).

The capacity (*q*) for each zeolite was calculated as indicated in equation 5-2 and the regeneration efficiency was calculated as indicated in equations 5-3 to 5-5.

$$q\ (meq\ g^{-1}) = \frac{\left([NH_4]_{inital} - [NH_4]_{post\ adsorption}\right) x\ Volume\ x\ valence}{atomic\ weight}$$

Equation 5.2

$$Adsorption_{NH_4}\ (mg\ L^{-1}) \quad = [NH_4]_{inital} - [NH_4]_{post\ adsorption}$$

Equation 5.3

$$NH_4\ retained\ in\ solid\ phase \quad = [NH_4]_{adsorbed} - [NH_4]_{Regenerant}$$

Equation 5.4

$$Regen\ efficiency \quad (\%) = \frac{Adsorption \quad - NH_4\ retained\ in\ solid\ phase}{Adsorption}\ x\ 100$$

Equation 5.5

5.2.1 Thermogravimetric analysis

Four 250 mL Erlenmeyer flasks containing 1 g of MesoLite were used to presaturate the zeolite with 100 mL of either 1 M NaCl (> 99 % purity stated, Fisher Scientific, UK) or 1 M KCl (> 99 % purity stated, Fisher Scientific, UK). After contacting the zeolites with the regenerant solution for 24 hours at 125 rpm on an orbital shaker (Stuart Orbital Shaker, Bibby Scientific Ltd., Staffordshire, UK) the samples were rinsed in deionized water (15 MΩ cm^{-1}) to remove excess of salt (control). Two of each set of four samples were then contacted with 100 mL of 800 mg L^{-1} NH_4Cl (> 99 % purity stated; Fisher Scientific, UK) to make sure that saturation would occur.

The zeolites were dried and thermogravimetric analysis was performed (TGA/Pyris 1, Perkin Elmer, UK). The temperature started at 25^oC and ended at 500^oC, using a heating rate of 20^oC min^{-1}. The gas oxidant was set as air with a flow rate of 20 mL min^{-1}. The amount of volatilised NH_4-N was measured as the difference between the absolute weight loss of the zeolite that only contained NaCl or KCl and the weight loss of the equally prepared zeolites which were saturated with NH_4-N.

5.3 Results and Discussion

5.3.1 Impact of regenerating ion

Regeneration efficiency across the five cycles was observed to remain effectively stable in the case of NaCl with levels for the progressive cycles of 68.6 %, 64.3 %, 65.9 %, 64.8 % and 67.2 %. The corresponding regeneration efficiencies with KCl were 94.4 %, 90.7 %, 89.3 %, 72.2 % and 76.5 % (Figure 5-1). Overall the use of KCl generated a higher regeneration efficiency although its efficacy decreased in the last two cycles such that the regeneration efficiency approached that of NaCl with only a 10 % improvement at cycle 5 compared to a 30 % difference in cycle 1. Previous work has been based on Clinoptilolite with a NaCl solution where regeneration efficiencies in batch studies were shown to increase from 38 % to 64 % as the concentration increased from 5 to 30 g L^{-1} [0.08 M to 0.51 M] and hence were similar to the results for MesoLite at the higher salt concentration (Deng *et al.,* 2014). Similar findings have also been reported in continuous column trials with both low (Deng *et al.,* 2014) and high salt concentrations (Milán *et al.*, 2011) supporting the observations in the present study. Further, repetitive use of a NaCl solution to regenerate Clinoptilolite revealed a decrease in operational capacity of 50 % after 10 cycles and 80 % after 24 cycles (Deng *et al.,* 2014). Others have suggested no detrimental impact if the regenerant solution was used four (Milán *et al.,* 2011) or six (López-Vigil *et al.,* 2006) times. However, previous work with MesoLite showed a reduction in ammonia removal of less than 10 % with a single reuse of Na_2CO_3 solution (Mackinnon et al., 2003).

The improvement observed when using KCl is congruent with the zeolite being originally made with potassium as the main exchangeable ion (Mackinnon *et al.*, 2003). At the same time, the presence of the negative charge due to the presence aluminium , as explained in chapter 2, affects not only the structure of the zeolite but also its chemistry. For instance, as higher is the negative charge higher is the hydrophilicity and hence the hydration. Further, recent modelling work has identified that potassium becomes favoured over sodium when the lattice structure is sufficiently hydrated (Ruiz-Salvador *et al.*, 1998). Such conditions are more likely in zeolites, such as MesoLite which has a low Al:Si ratio (Channon *et al*., 1998; Futalan *et al*., 2011; Yang and Armbruster, 1996). In addition, the selectivity sequence for most zeolites can be approximated to $Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Na^+ > Ca^{2+} > Li^+$ (Wang and Peng, 2010). Overall this leads to a preference for K^+ as it provides a higher stability to the zeolite framework.

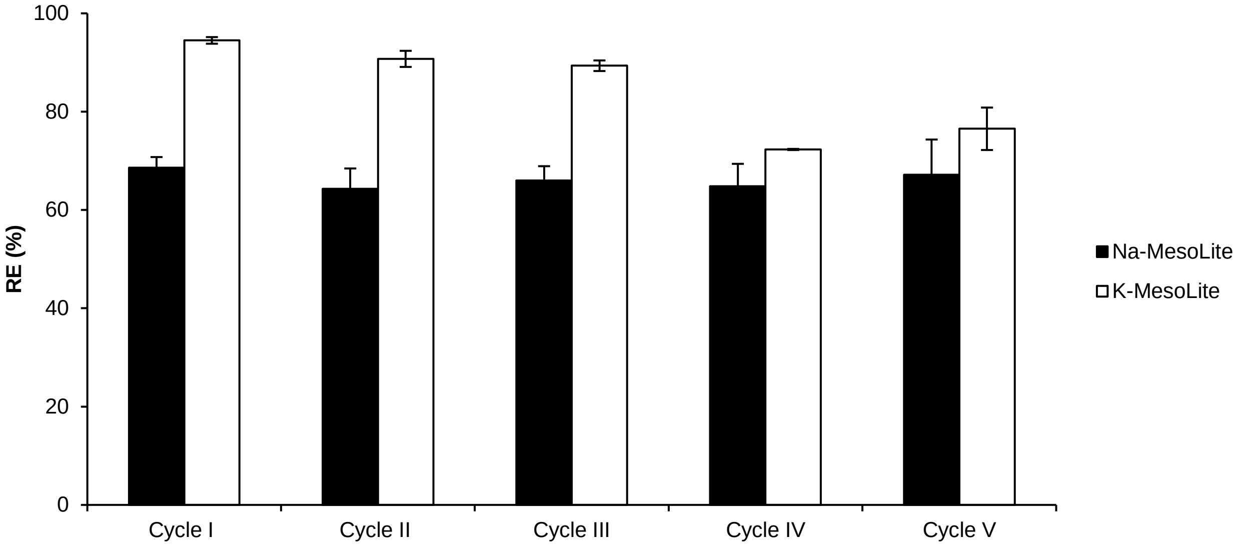

Figure 5-1 Batch regeneration of MesoLite using 1 M NaCl (1000 meq L^{-1}) compared to 1 M KCl (1000 meq L^{-1}). Initial experimental concentration of NH_4^+ was set at 16 mg L^{-1} (1.14 meq L^{-1}) for Na-MesoLite and 20 mg L^{-1} (1.43 meq L^{-1}) for K-MesoLite. The weight of the zeolite used was 0.3 g. The pH of the regeneration solution was 7.

The equilibrium capacity after each cycle was 5, 5.3, 5.31, 5.23 and 5.25 mg g^{-1} in the case of NaCl and 5.2, 5.7, 5.7, 5.7 and 5.6 when KCl was used (Figure 5-2). So when low ammonium concentration was used, capacity was not affected by low regeneration efficiencies. This is because the remaining NH_4^+ ions in the lattice are not sufficient to completely saturate the active sites of the zeolite. Accordingly, the utilisation of the zeolite can be maintained over multiple cycles. Hedström (2001) reported capacity recovery levels that range between 98 and almost 100 % for Clinoptilolite.

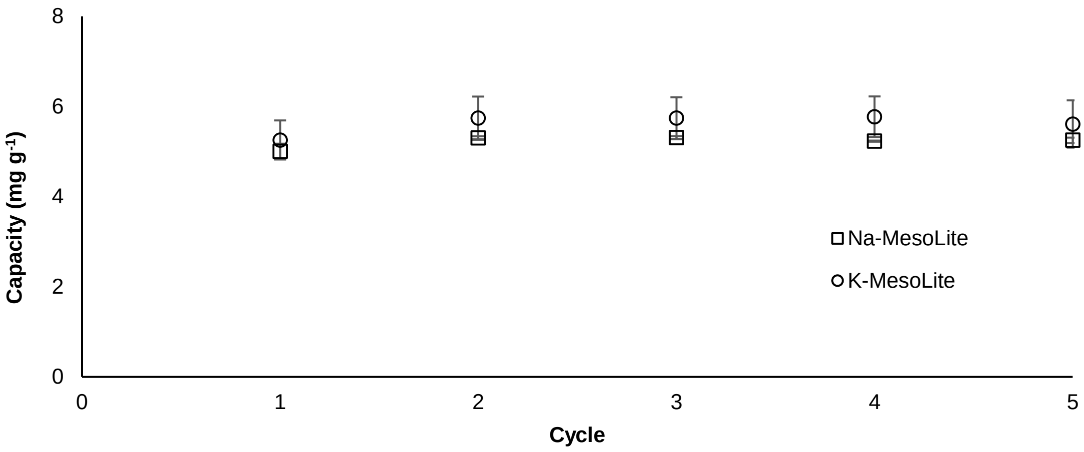

Figure 5-2 Batch Capacity of MesoLite using 1 M NaCl (1000 meq L^{-1}) compared to 1 M KCl (1000 meq L^{-1}). Initial experimental concentration of NH_4^+ was set at 16 mg L^{-1} (0.8 meq L^{-1}) for Na-MesoLite and 20 mg L^{-1} (1.1 meq L^{-1}) for K-MesoLite. The weight of the zeolite used was 0.3 g. The pH of the regeneration solution was 7.

Alteration of the molarity of the salt solution had a significant impact on the regeneration efficiency of the zeolite (Figure 5-3). To illustrate, in the case of NaCl, the regeneration efficiency decreased from a maximum value of 71 % when using a molarity of 2 M (2000 meq L^{-1}) down to 34.6 % using a molarity of 0.2 M (200 meq L^{-1}) (Figure 5-3-(A)). Such levels are higher than those reported for Clinoptilolite where a 60 % regeneration efficiency was observed when utilising a 2 M NaCl solution (Milán *et al.,* 2011). In that study, the efficiency increased further to 80 % when using a 4 M solution with an 8 hour operating time in a continuous column operated at a flow rate of 4 BV h^{-1}. In comparison, the regeneration efficiency of KCl was 83 % at a molarity of 0.2 M. Indeed, regeneration efficiency remained comparable to that of NaCl even at lower salt concentrations with regeneration efficiencies of 55 %, 60 % and 74 % at molarities of 0.025, 0.05 and 0.1 M respectively (Figure 5-3 (B)) such that with KCl substantially lower concentrations can be used for the brine solutions.

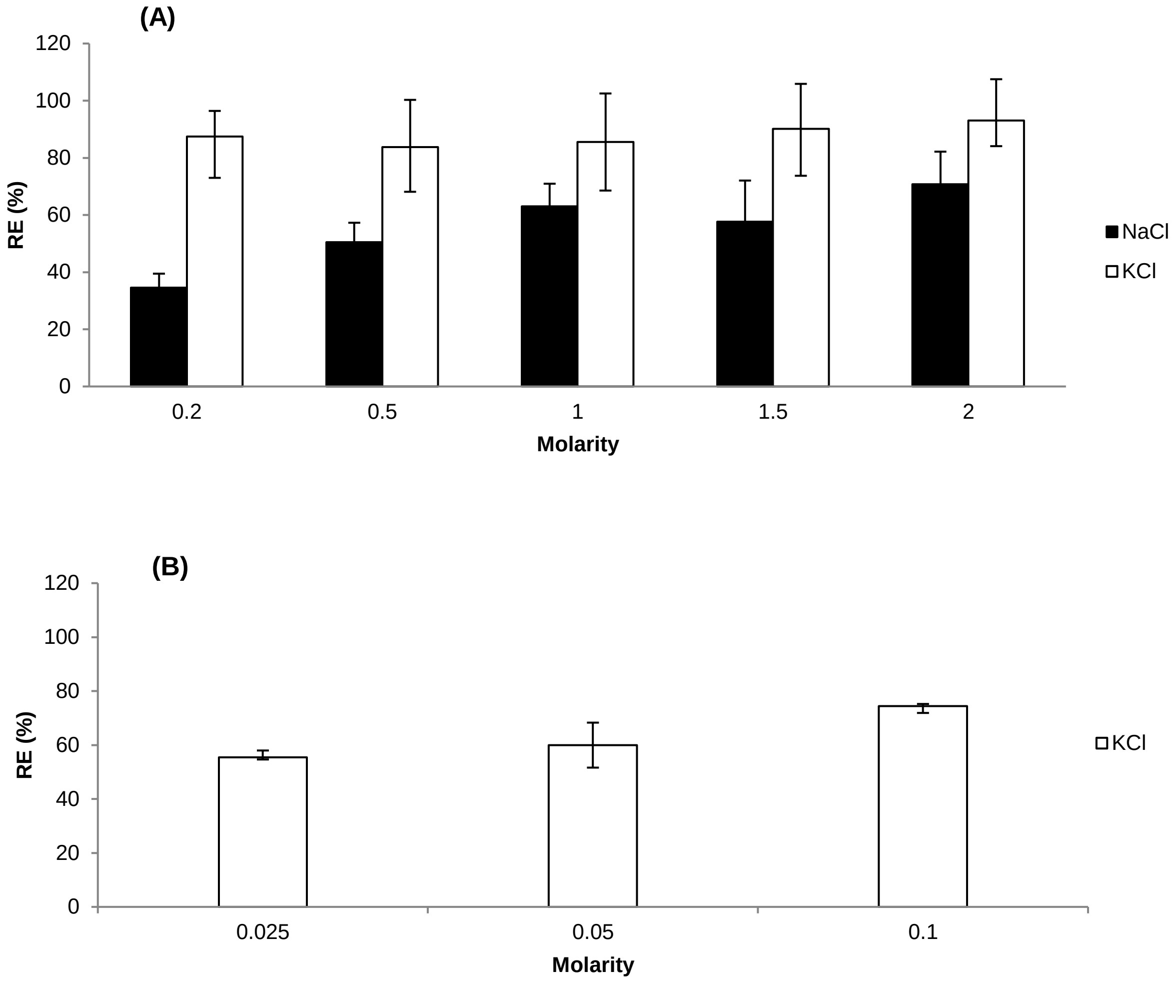

Figure 5-3 Average of 5 batch cycles at 125 rpm. (A) Comparison of regeneration at 5 different salinity concentrations. (B) Regeneration efficiency below 0.1 M KCl. The initial NH_4Cl used was 16 mg L^{-1} [0.8 meq L^{-1}], pH of the regeneration solution was set at 7.

5.3.2 Effect of high ammonium concentration on regeneration

The impact of fully saturating the active sites of the test zeolites was assessed by initially operating a batch cycle with an initial ammonium concentration of 900 mg L^{-1} [50 meq L^{-1}]. Thereafter the operating cycle returned to a load cycle with 800 mg L^{-1} [44.4 meq L^{-1}] followed by regeneration with either 1 M NaCl (Na form) or KCl (K form) (Figure 5-4). Comparison of the last four cycles shows relatively stable but low regeneration efficiency with all four zeolite trials. For instance, the regeneration efficiency with the two natural zeolites ranged between 23.5 and 22 % for Clinoptilolite and between 26 and 27 % for Mordenite. In comparison, MesoLite regenerated with NaCl demonstrated similar regeneration efficiencies compared to Mordenite ranging between 31 and 26 % (Figure 5-4). However, regeneration with KCl generated better regeneration efficiencies as seen before with a range between 50 and 43 %. The relatively low regeneration efficiency was explained by the regeneration ratio which ranged from 92 to 309 meq(Na):meq(NH_4^+) which was around 50 % less than the recommended ratio to obtain high regeneration efficiencies (Table 5-1; Koon and Kaufaman, 1975; Liberti *et al.,* 1981; Semmens and Martin, 1988).

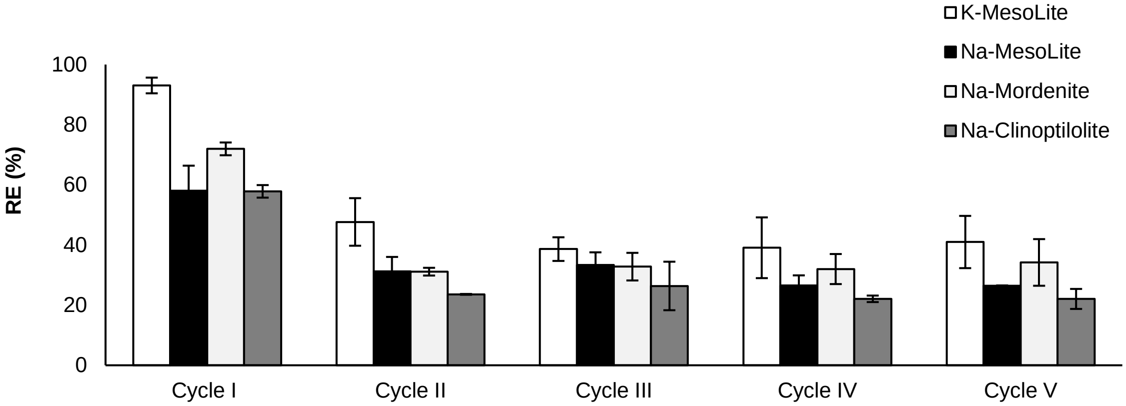

Figure 5-4 Batch regeneration of MesoLite using 1 M NaCl compared to 1 M KCl. 125 rpm, pH = 7. A clean regenerant was used for each cycle and zeolite. Initial concentration of NH_4^+ was set at 900 mg L^{-1} [50 meq L^{-1}].

The total concentration of ammonia in the regeneration liquid was 813, 679, 300 and 405 mg L^{-1} for K-MesoLite, Na-MesoLite, Clinoptilolite and Mordenite respectively. Previous work in continuous flow using Clinoptilolite reported ammonia concentrations in the regenerant of 280 mg L^{-1} (Liberti *et al.*, 1981) although it was suggested that this could be increased to between 300 and 1000 mg L^{-1} (Verkerk and Van deer Graaf, 1999). These levels have been exceeded when MesoLite was used to treat sludge liquors where concentrations up to 10,000 mg L^{-1} have been reported (Mackinnon *et al.,* 2003).

5.3.3 Effect of the pH on the regeneration of MesoLite

Alteration of the pH between 9 and 12 had no significant impact on the regeneration efficiency of MesoLite using either NaCl or KCl (Figure 5-5). To illustrate, the regeneration efficiency ranged between 75.5 and 85 % for NaCl and between 86.5 and 92 % for KCl. In comparison, regeneration with just pH adjustment resulted in regeneration efficiencies of 10.3, 8.9, 13.6 and 75.8 % at pH levels of 9, 10, 11 and 12 respectively. Accordingly, MesoLite can be effectively regenerated solely with NaOH. The significance of this is that equivalent removal of phosphorus is effectively achieved with a hybrid ion exchange resin that contains iron nanoparticles (Martin *et al.,* 2013). Importantly, the media is regenerated with a caustic soak at pH 12 or above such that both resins could be potentially regenerated with the same solution thus improving economic efficiency.

The use of alkaline pH values drives the equilibrium of ammonium into the molecular form where no further exchange occurs as only about 1 % of ammonium remain in ionized form at pH 11 (Langwaldt, 2008) compared to 100 % at a pH of 7 or less. Accordingly this offers two potential pathways in which pH adjustments assist regeneration. The switch to the unionized form may enhance desorption rates (Lin *et al.,* 2012). However, addition of NaOH provide a source of exchangeable ions with the different pH levels representing concentrations of 0.01, 0.1, 1 and 10 meq L^{-1} for pH 9, 10, 11 and 12 respectively. Accordingly, it is likely that the shift in equilibrium is the predominate feature.

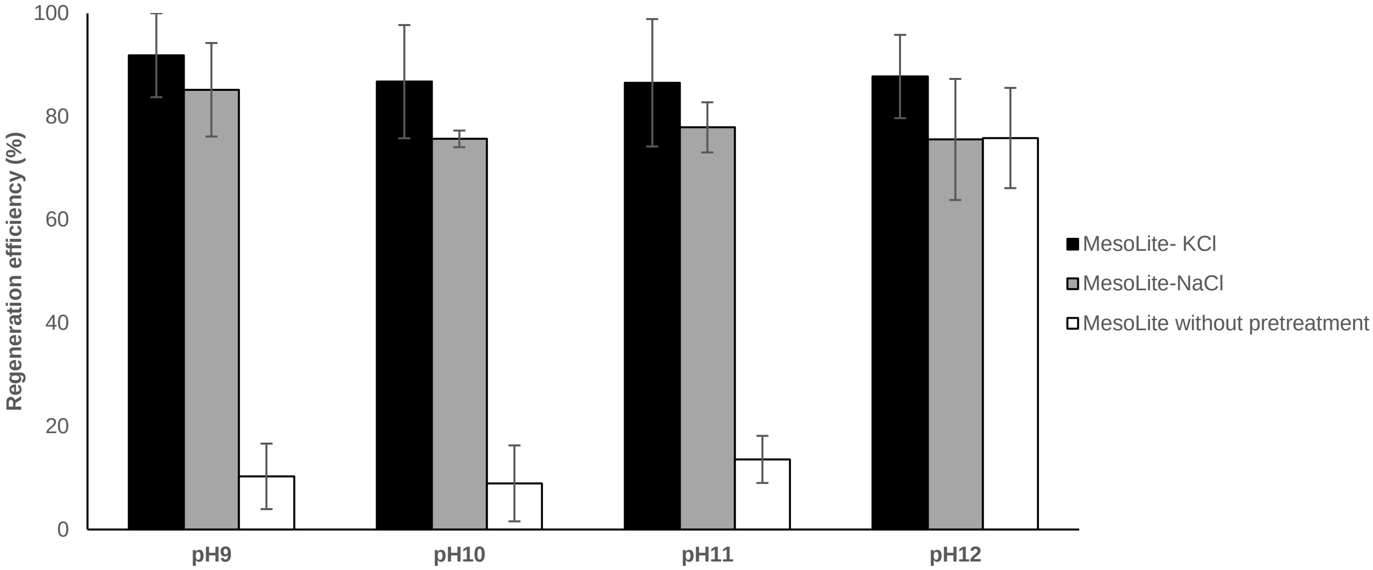

Figure 5-5 Impact of pH on the regeneration efficiency of MesoLite across 5 batch cycles using KCl, NaCl. Initial NH_4^+ concentration was set at 16 mg L^{-1} [0.8 meq L^{-1}].

5.4 Thermogravimetric analysis on synthetic zeolite MesoLite

KCl was consistently observed to be a more effective regenerant solution than NaCl when regenerating MesoLite. Thermogravimetric analysis (TGA) was used to analyse the strength of the bonds between the ions and the extra molecular framework (Alshameri *et al.,* 2014; Su *et al*., 2004). Across the whole temperature range, around 4 % of the volatilised ammonia, out of a maximum of 10%, was released when the 0.02 g of MesoLite was pretreated with potassium, indicating that the bond between K-Zeolite and NH_4^+ is weaker than the bond between Na-Zeolite and NH_4^+. This difference may be of practical significance, since the deviation by 4% is large relative to the dynamic range of around 0 to around 10 for the volatilisation of K-Mesolite (Figure 5-6(A)). In the case of the samples without ammonium, significant weight loss was observed from temperatures between 100 to 150 ^oC, followed by further gradual decrease until it reached a stable level of 86 % (Figure 5-6(B)). This was not observed in the case where the zeolite contained ammonium or when the samples were pretreated with potassium. This indicates that extra molecular ions may have changed the properties of the material itself. Support can be found from previous studies investigating the catalytic properties of zeolites which identified that the acidity and acid strength of the lattice could be modified (Haller, 1981; Ward, 1970).

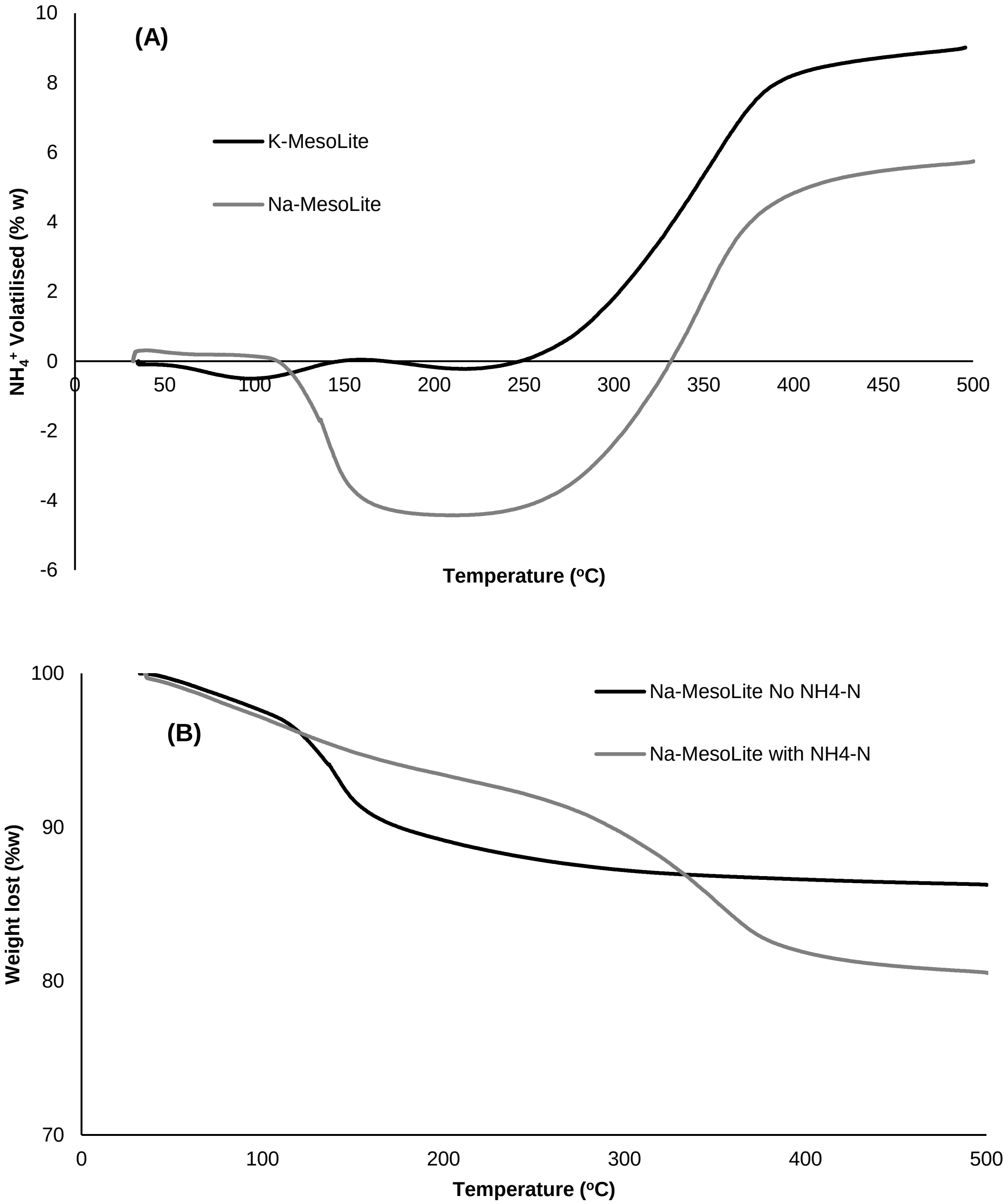

Figure 5-6 Thermogravimetric analysis performed to K-MesoLite and Na-MesoLite showing (A) volatilised NH_4^+ and (B) overall lost weight.

5.5 Conclusions

Potassium chloride is a more effective regenerant than sodium chloride when using MesoLite. The corresponding regeneration efficiencies were between 72 to 94 % for potassium chloride and between 64 and 68 % for sodium chloride. Stable capacities were obtained with both regeneration liquids over five cycles and no substantial deterioration in performance was observed. Potassium chloride remained effective down to low molarities (0.1 M) generating the same regeneration efficiency as 1.0 M sodium chloride. pH levels between 9 and 12 did not impact the regeneration efficiency of either solution but at pH 12 effective regeneration occurred without inclusion of a brine.

5.6 Acknowledgements

The authors acknowledge the financial support of the project sponsors Thames Water, Severn Trent, Anglian Water, Yorkshire Water and Scottish Water.

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6 IMPACT OF SOLIDS AND COMPETING IONS ON AMMONIA REMOVAL USING MESOLITE

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Abstract

The use of zeolites in an ion exchange filter for tertiary ammonium polishing is considered as an alternative to tertiary biological nitrification processes. Ion exchange systems promise advantages under conditions like low temperatures or load variations and can achieve very low ammonium concentrations to meet more strict discharge standards. Application in real wastewater is limited by concerns over the impact of solids and the use and management of the regeneration liquids. This work investigated these issues for the synthetic zeolite MesoLite by conducting column experiments that were fed directly from Cranfield University's sewage works. The trial enabled an 80 % removal of ammonium over a 876 BV cycle, equivalent to 4.8 days of operation between regenerations. Reuse of brine reduced cycle times due to the accumulation of ammonium ions in the liquor and this was more evident at lower pH. Accordingly, it is recommended that a pH 12 brine be used and that the brine is reused at least three times. Solids were also seen to impact operation in terms of capacity with a reduction of 37 and 75 % when the concentration of solids in the wastewater was increased from 0 to 29 and 45 mg L^{-1} respectively.

Key Words: Ammonium, zeolite, real wastewater, regeneration, re-use regenerant

6.1 Introduction

Zeolites are hydrated alumina-silicate materials that are known to have a high affinity for ammonium as it can be found in municipal, industrial and aquacultural wastewater (Baykal and Guven, 1997; Liberti *et al.,* 1981). The actual levels of removal are influenced by the type of zeolite, zeolite size and the composition of the wastewater in terms of both competing species (Ca^{2+}, Mg^{2+}) as well as suspended solids. The cation exchange capacity (CEC) of natural zeolites, such as Clinoptilolite, are between 0.6 and 2.3 meq g^{-1} with variation due to specific content and the purity of the material (Wang and Peng, 2010). In addition, a synthetic zeolite, MesoLite, has also been considered. It's CEC lies at 4.9 meq g^{-1} (Mackinnon *et al.,* 2003). Operational capacities are considerably lower than that resulting in uptake capacities of between 2.7 and 30.6 mg g^{-1} for the natural zeolites and up to 55 mg g^{-1} for MesoLite.

The ability of zeolites to manage shock loading, polish wastewater effluents to low ammonia concentrations or recover nitrogen has led to a number of full scale Clinoptilolite plants over the last fifty years (Liberti *et al.,* 1981; Svetich, 1993). In comparison, there is a paucity of investigation into the use of MesoLite (Mackinnon *et al.,* 2010; Mackinnon *et al.,* 2003; Thornton *et al.,* 2007b), which thus far has been used to remove high concentrations of ammonium from sludge liquor lines. Specifically in one of these studies, MesoLite was used in a pilot plant operating for 11 full cycles reducing the concentration of NH_4-N from over 500 to 50 mg L^{-1} (Thornton *et al.,* 2007b). However, no studies have been reported on its use for sewage effluent polishing although it has been demonstrated to have an elevated capacity and selectivity compared to Clinoptilolite in treating synthetic solutions during batch and continuous trials (Chapter 3, 4).

Previous applications of zeolite filters for real wastewater have identified three major obstacles to more wide spread use: The need to reduce concentration of solids onto the beds to avoid frequent clogging, the high cost of regeneration and management of the spent regenerant solutions (Hedström, 2001; Liberti *et al.,* 1981). Typical media sizes of the zeolites used are between 0.5 and 9 mm with the majority between 1 and 2 mm, equivalent to mono media depth filters (Table 6-1) (Metcalf and Eddy, 2003). Media size is known to impact capacity with reported reductions from 9.1 mg g^{-1} for a size of 0.5 to

1.0 mm to 1.37 mg g^{-1} when using a size of 1.6 to 4.0 mm (Hlavay *et al.,* 1982). However, clogging risk increases with decreasing media size such that recommended minimum size limits of 0.25 to 0.5 mm have been reported (Hlavay *et al.,* 1982; Gisvold *et al.,* 2000). Solids concentrations during previous trials have varied with levels typical of sewage effluent up to higher concentrations. Many of the plants have incorporated pretreatment filters to reduce solid loading although others have operated with the filter directly and backwashed frequently to maintain hydraulic conductivity (Liberti *et al.,* 1981). In such cases the flow rate is reduced to that common for depth filtration at around 4 to 12 $m^3\ m^{-2}\ h^{-1}$.

Table 6-1 comparison of previous studies treating real wastewater with zeolites

Material	**Size (mm)**	**Flow rate (BV h^{-1})**	**Influent NH_4-N (mg L^{-1})**	**Influent SS (mg L^{-1})**	**Pre treatment**	**Ref**
Clinoptilolite	0.87	8	25 to 44	20	Filter coal layer	(Booker *et al.,* 1996)
Clinoptilolite	0.5 to 1.0	5-7.5	12 to 45	178	none	(Hlavay *et al.,* 1982)
Clinoptilolite	-	24	3.7	10 to 20	none	(Liberti *et al.,* 1981)
MesoLite	3 to 9	6-24	500 to 1000	1500	Sand filter	(Mackinnon *et al.,* 2003)
MesoLite	1.4 to 2.5	4-5	500 to 700	-	Ceramic filter	(Thornton *et al.,* 2007b)
MesoLite	1 to 1.7	4	6 to 20	14	Sedimentation and filtration	Current

This work aims to build on the previous studies in MesoLite and to extend it to applications related to sewage effluent polishing, exploring the impact of wastewater constituents (calcium and solids) as well as the opportunity of brine reuse which was previously highlighted (Chapter 5).

6.2 Materials and Methods

MesoLite (Nanochem Pty Ltd., Australia) was sieved to a uniform size range of 1 to 1.7 mm and placed into duplicate PVC columns, internal diameter of 52 mm to regenerate a bed volume of 100 mL (76.84 g). Before the experiments started, the columns were flushed with deionised (DI) water (15 MΩ cm^{-1}) in an upflow direction at 50 BV h^{-1} for 15 minutes to remove possible dust present in the media. Afterwards, the zeolite was regenerated using 1 M NaCl (> 99 % stated purity; Fisher Scientific, UK) for Na-MesoLite and 1 M KCl (> 99 % stated purity; Fisher Scientific, UK) for K-MesoLite at 4 BV h^{-1} in a down flow orientation for 24 h. Where required, the pH was adjusted through droplet addition of 1 M of NaOH (> 99 % stated purity; Fisher Scientific, UK) until the desired pH was reached. The columns were fed from wastewater from the Cranfield University sewage works post lamellar clarification. The average concentration of suspended solids was 50 mg L^{-1} and the wastewater was further clarified through additional sedimentation and/or filtration through a rotary filter with 60- micron stainless steel screen, (Aqua Forte drum filter, UK) (Figure 6-1).

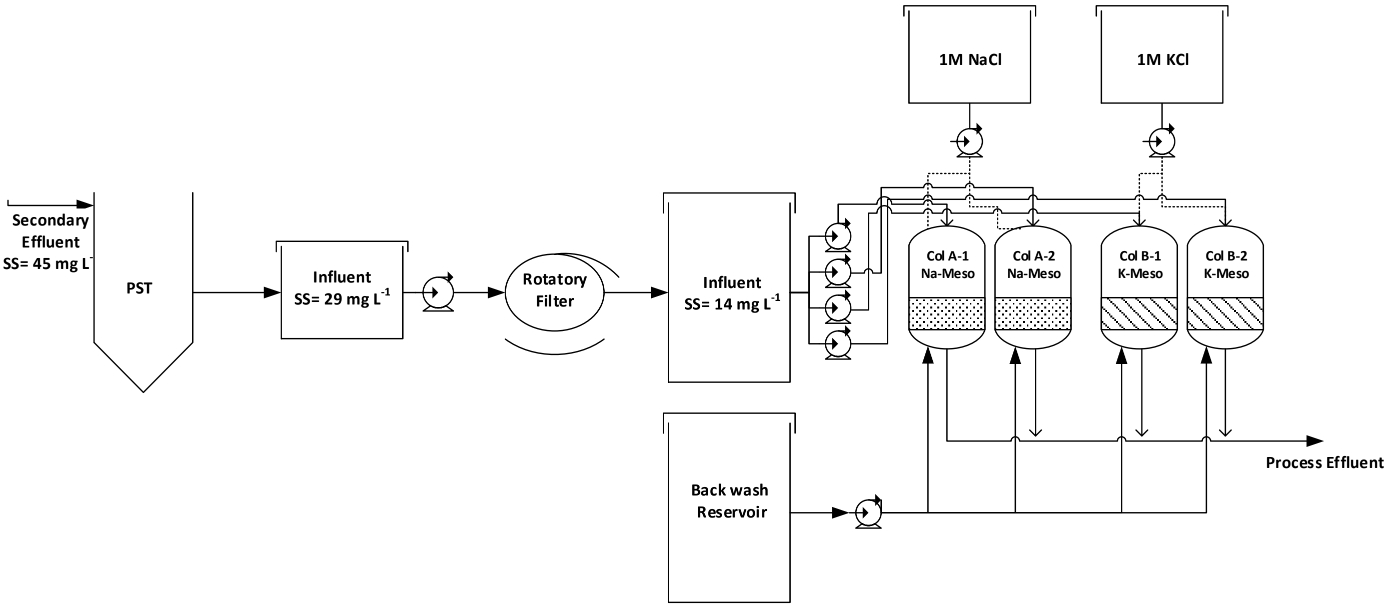

Figure 6-1 Schematic process diagram of the lab scale columns installed at Cranfield Wastewater treatment works.

The ammonium concentration in the solution was determined spectrometrically by cell test (Merck, Germany) using a spectrophotometer (Merck, Spectroquant Nova 60, Germany). Using this method there was no problem with interference by other dissolved species (e.g. cations, anions) in the liquid phase. The amount of suspended solids was measured by filtration through a 0.2 µm Whatman filter paper (Sigma Aldrich, UK) and subsequent drying at 105^{o}C for 24 h using a lab oven (Genlab Limited, OV/100/F, Cheshire, UK). The ammonium capacity was determined by the area under the breakthrough curve:

$$q = \frac{Q}{1000\,m}\int_{t_o=0}^{t_b} (C_0 - C_t)\,dt$$

Equation 6.1

Where q is capacity, Q is the influent flow (mL min^{-1}), C_o the influent concentration (mg L^{-1}), m the mass of adsorbent (g), t_0 is the start time of the process and t_b is the breakthrough time (min). Regeneration efficiency was calculated as in equations 5.2 and 5.3. However, it is important to consider that re-using the regenerant means that a certain NH_4- N concentration remains from previous regeneration cycles. To accurately calculate the regeneration efficiency, the ammonium concentration from previous cycles was taken into account.

$$Adsorption_{NH_4}\ (mg\ L^{-1}) \quad = [NH_4]_{inital} - [NH_4]_{post\ adsorption}$$

Equation 6.2

$$NH_4\ retained\ in\ solid\ phase \quad = [NH_4]_{adsorbed} - [NH_4]_{Regenerant}$$

Equation 6.3

$$Regen\ efficiency \quad (\%) = \frac{Adsorption \quad - NH_4\ retained\ in\ solid\ phase}{Adsorption}\ x\ 100$$

Equation 6.4

6.3 Results and Discussion

6.3.1 Comparison of Na-MesoLite and K-MesoLite during five cycles with brine reuse at pH 7 and 12.

The average ammonium concentration in the feed wastewater varied considerably across the trial. In the case of the trials with neutral pH, the average ammonium concentration was 6 ± 3, 13 ± 5, 11 ± 2, 20 ± 2 and 8 ± 3 mg L^{-1} for cycles 1 to 5. The equivalent concentrations at pH 12 were 7.3 ± 2, 6.4 ± 3, 13 ± 1, 14 ± 1 and 16 ± 1 mg L^{-1} respectively. The columns were operated to a fixed removal efficiency of 80 % and then regenerated, reusing the brine each time. In the case of the trials at pH 7, the first cycle ran for 4.8 days equating to 876 BV for both Na-MesoLite and K-MesoLite. However, the Na-MesoLite generated a slightly lower concentration resulting in a capacity for the first cycle of 6.90 mg g^{-1} compared to 6.68 mg g^{-1} for K-MesoLite. The impact of the varying and relatively high ammonium concentration coupled to the reuse of the brine reduced the run time of the subsequent cycles. For instance, in the case of Na-MesoLite, the subsequent run times were 1.7, 2.4, 0.92 and 0.12 days (Figure 6-2). The impact was more pronounced with K-MesoLite with the total run time for the five cycles during the pH 7 operation being 9.3 days and compares to 11.6 days for Na-MesoLite. The regeneration efficiency of the four operations were 57 %, 8 %, 4 % and 16 % for KCl and 20 %, 2 %, 4 % and 8 % for NaCl. The final ammonium concentrations retained in the liquid phase were 499 and 274 mg L^{-1} respectively which would inhibit ammonium desorption as it would exist in its ionic form at the solution pH indicating that brine reuse at neutral pH limits operational run times.

Elevating the pH of the regeneration solution increased the regeneration efficiency between cycles to 34 %, 29 %, 12 % and 8 % for NaCl and 64 %, 41 %, 31 % and 5 % for KCl (Figure 6-2). Thus it was possible to reuse the brine for five cycles with run times of 3, 3, 1.8, 1.2 and 0.3 days for Na-MesoLite compared to 3, 3, 1.7, 1.1 and 0.97 days for K- MesoLite. Therefore, the ammonium concentration in the final regeneration liquid increased to 466 and 579 mg L^{-1} for Na-MesoLite and K-MesoLite respectively, representing 18 and 30 % of the observed removed capacity.

The overall operational capacity over the five cycles was 12.5 and 19 mg g^{-1} [0.69 meq g^{-1}, 1.05 meq g^{-1}] at pH 7 for K-MesoLite and Na-MesoLite respectively. These decreased to 10 and 12.8 mg g^{-1} [0.5 meq g^{-1}, 0.71 meq g^{-1}] at pH 12 due to the lower feed concentrations. This compares to capacity levels during the synthetic column experiments at an EBCT of 8 minutes of 30 mg g^{-1} indicating a reduction of 36 % at pH 7 and 57 % at pH 12 during treatment of wastewater. This aligns to previous reports for Clinoptilolite where a reduction of 50 % was reported comparing real and synthetic trials (Hlavay *et al.,* 1982; Malovanyy *et al.,* 2013). However, this is greater than the 20 to 30 % reduction seen during the filtered wastewater batch trials (Chapter 3) confirming the need for continuous bed trials when assessing the potential of zeolites to a specific application. The run time of the first cycle (876 BV) compares to 80 BV previously reported for Clinoptilolite when operated at a flow rate of 24 BV h^{-1} (Liberti *et al.,* 1981) indicating the efficacy of MesoLite as an ammonium exchanger. Previous trials with MesoLite on high ammonium concentration sludge liquors (500 to 700 mg L^{-1}) reported operational capacities at 50 mg L^{-1} breakthrough between 27 and 39 mg g^{-1} [1.5 - 2.2 meq g^{-1}] with cycle times between 29 and 50 BVs (Mackinnon *et al.,* 2003; Thornton *et al.,* 2007b). The extended cycle times observed when using MesoLite for low ammonium concentration polishing offer the possibility to use the media for small, rural sewage works as passive barriers utilising mobile regeneration systems that limit the embedded infrastructure required. A similar observation was previously made with respect to phosphorus removal using hybrid ion exchangers (Muhammad *et al.,* 2018). In these cases, the cost of regeneration is reduced and recovery enabled by using a mobile regeneration system that can service multiple small works.

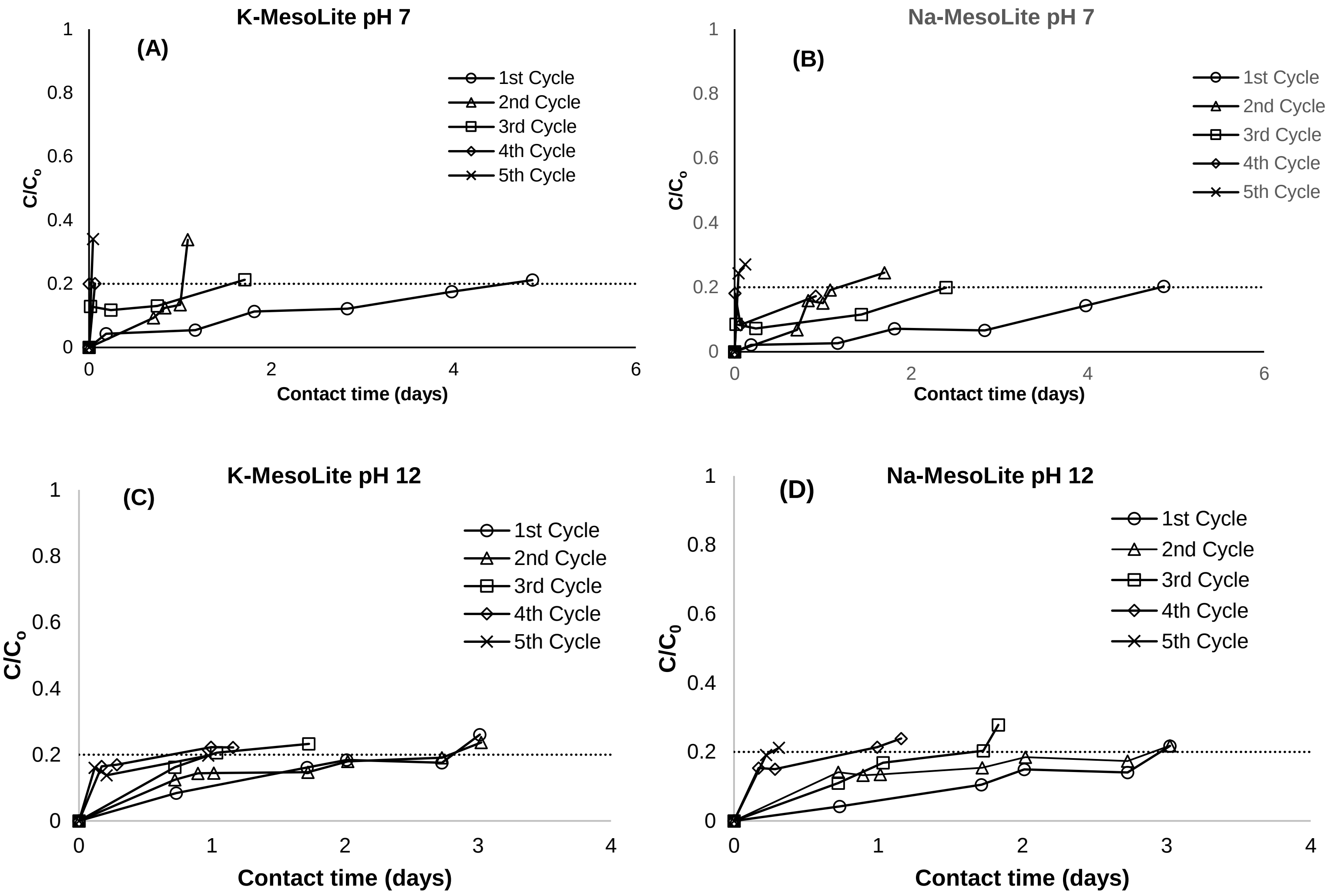

Figure 6-2 Dynamic studies using 8 min EBCT (12.5 mL min^{-1}) and 5 consecutive cycles (adsorption and regeneration). (A) Cycles using K-MesoLite under pH 7, (B) Na-MesoLite under pH 7 (C) Cycles using K-MesoLite under pH 12 and (D) Na-MesoLite under pH 12.

6.3.2 Comparison of brine reuse and fresh brine use (pH 7) for Na-MesoLite and K-MesoLite at an EBCT of 15 minutes.

The influent ammonia concentration was more stable during the second set of experiments with average ammonium concentrations of 6.4 ± 2, 15 ± 2, 12 ± 1, 14 ± 1, 6, 7.5 ± 2 and 9 ± 1 mg L^{-1} for cycle 1 to 7. As with the previous experiment, the run time decreased with each cycle congruent with the accumulation of ammonium in the brine. For instance, the cycle times for Na-MesoLite were 8.4, 4 and 1.2 days for the first three cycles and 4.5 and 1.2 hours for the next two cycles (Figure 6-3). In comparison, cycle times for K-MesoLite were 8.1 and 3 days for the first two cycles and 6.5, 6.5 and 3 hours for the final three cycles indicating as before that the Na-MesoLite delivered a longer total run time across the five cycles. Corresponding regeneration efficiencies were 26 %, 19 %, 0 % and 4 % for NaCl and 90 %, 57 %, 51 % and 0 % for KCl resulting in final ammonium concentrations in the brines of 147 and 436 mg L^{-1} for NaCl and KCl respectively. The overall observed capacity across the five cycles were 9.3 and 4.5 mg g^{-1} [0.51 and 0.25 meq g^{-1}] for Na-MesoLite and K-MesoLite respectively. The lower observed capacity for K-MesoLite at higher EBCT reflected that the cycle times decreased more rapidly indicating the significance of the inappropriate reusing of the brine may have on the overall efficacy of the system.

Switching to fresh brine extended the cycle time of the 6th and 7th cycles to 5.2 and 4 days for Na-MesoLite and 4 and 5.4 days for K-MesoLite confirming the impact was due to the accumulating ammonium ions in the regeneration liquid. This supports previous findings that with appropriate regeneration management, the operation of the zeolites can be maintained. For instance, in a previous trial with Clinoptilolite treating a low strength ammonium concentration, the columns operated for a total of 500 cycles without the media requiring any form of significant restoration beyond standard regeneration (Liberti *et al.,* 1981). Capacity recovery across a number of trials has been close to 100 % at both neutral and pH 12 using NaCl with a regeneration volume of 20 BV for every cycle and brine concentrations between 0.21 and 0.6 M (Hedström, 2001).

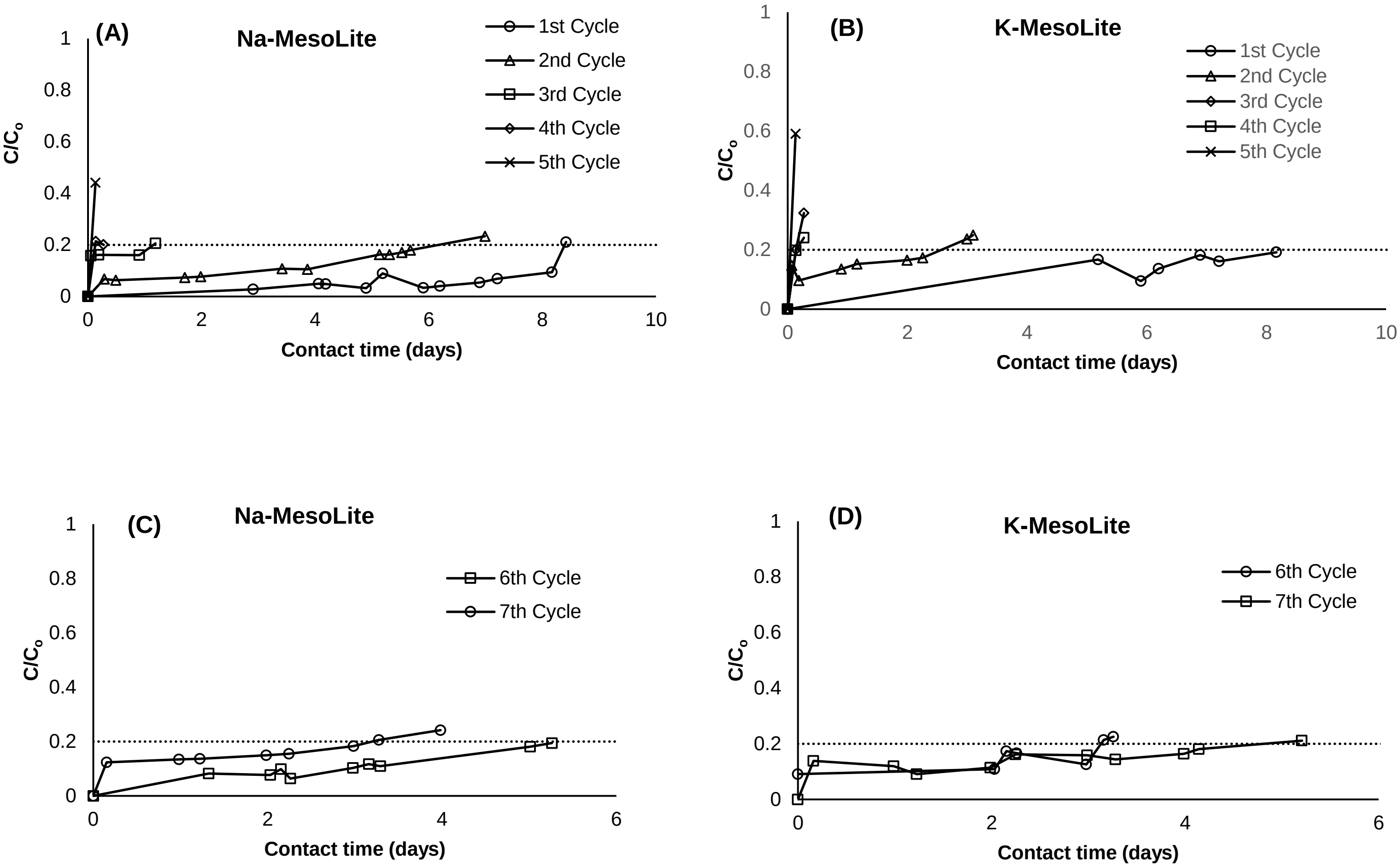

Figure 6-3 Dynamic studies using 15 min EBCT (6.6 mL min^{-1}) and 5 consecutive cycles (adsorption and regeneration). (A) Cycles using Na-MesoLite at pH 7. (B) Cycles using K-MesoLite at pH 7. (C) Impact of clean regenerant on Na-MesoLite. (D) Impact of clean regenerant on K-MesoLite.

6.3.3 Impact of solids loading on ammonium uptake

The average suspended solids in the feed wastewater decreased from 45 ± 20 mg L^{-1} to 29 ± 19 mg L^{-1} after the sedimentation stage and to 14 ± 15 mg L^{-1} after the rotary filter (Figure 6-4). The MesoLite column further reduced the solids to 9 ± 6 mg L^{-1} representing an average accumulation into the media bed of 5 mg L^{-1}. This compares to effluent solids of 2 mg L^{-1} from a previous trial where MesoLite was used to treat filtered sludge liquors where the initial solids concentration was between 80 and 120 mg L^{-1} (Thornton et al, 2007b). To understand the potential impact of solids loading in terms of capacity reduction, a series of experiments were performed using three different solid concentrations (Figure 6- 5). Breakthrough (80 % removal), occurred after 7 days in the control using tap water corresponding to an operational capacity of 16 mg g^{-1} [0.8 meq g^{-1}]. The run times decreased to 5 and 2.5 days for trials conducted on wastewater from before and after sedimentation where the concentrations of suspended solids were 29 and 45 mg L^{-1} respectively resulting in maximum solids loadings of 53 and 633 mg h^{-1} (Figure 6-5). The corresponding capacity was 10 and 4 mg g^{-1} [0.5 and 0.2 meq g^{-1}] representing a reduction of 37 and 75 %.

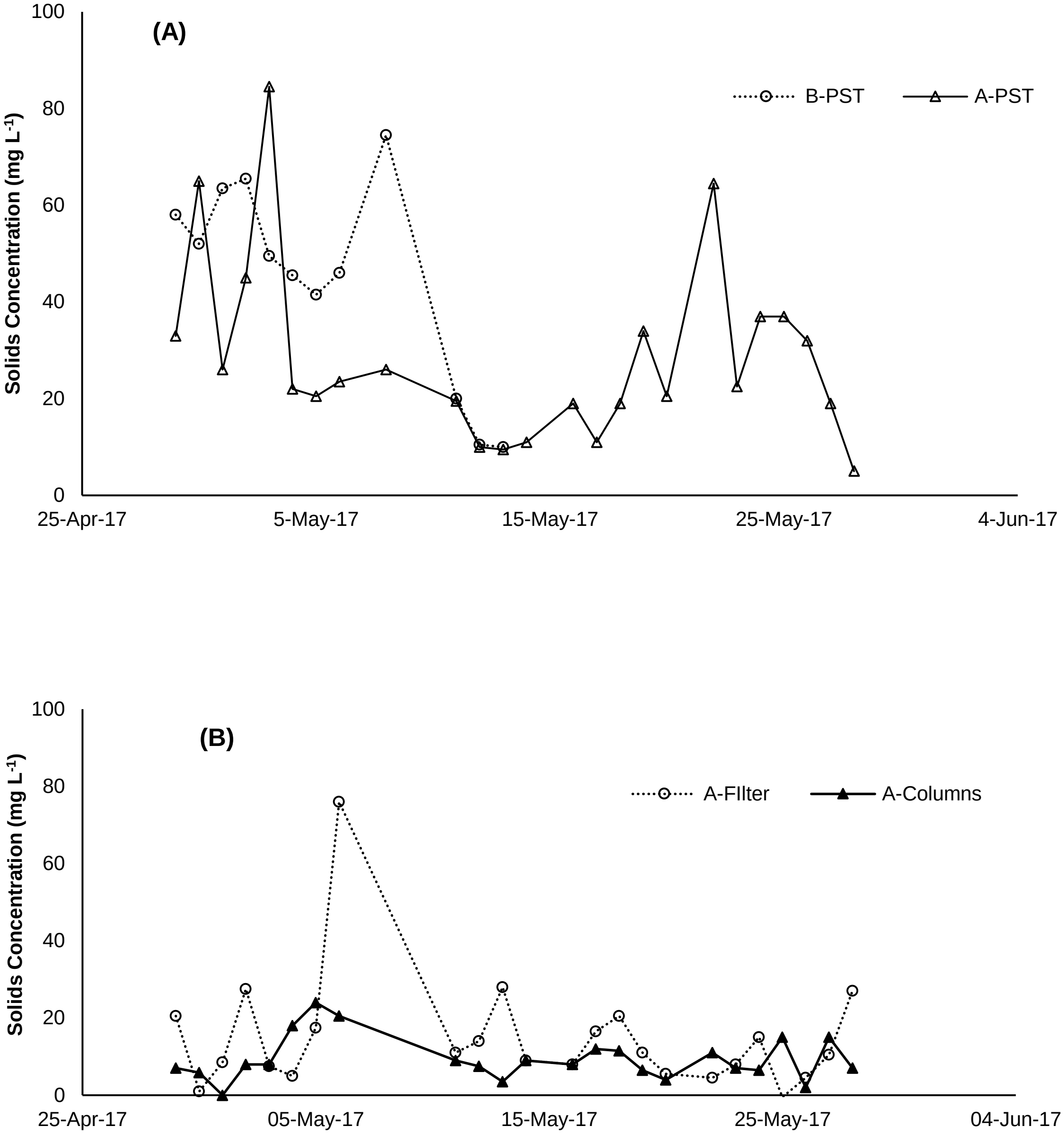

Figure 6-4 Daily solids concentration (A) before and after the primary settlement tank (PST) and (B) after rotatory filter and after the ion exchange columns.

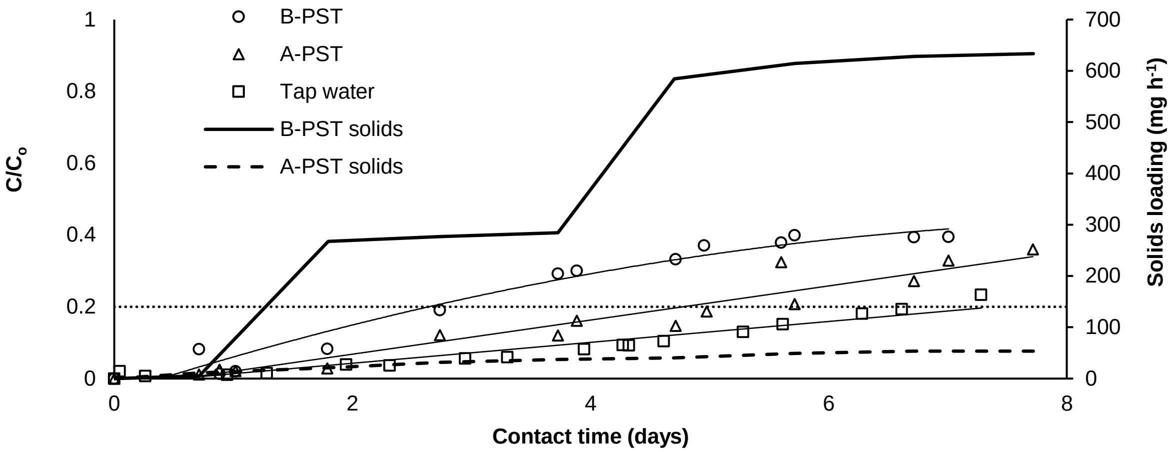

Figure 6-5 One cycle dynamic adsorption performed at 8 min EBCT using Na-MesoLite. The average initial NH_4-N concentration for B-PST, A-PST and A-Filter was measured to be 7, 11 and 10 mg L^{-1} respectively.

6.3.4 Comparison between synthetic and real wastewater

Characterisation of the constituents in the wastewater revealed that the major ions were sodium and calcium with concentrations of 3.68 and 2.85 meq L^{-1}. The other components were potassium at 0.47 meq L^{-1}, magnesium at 0.75 meq L^{-1} and ammonium at a concentration of 0.27 meq L^{-1}. Accordingly, ammonium represented only 3.5 % of the total available equivalence. Comparison of the current data (8 minutes EBCT) to an equivalent trial treating a mono component synthetic solution revealed a reduction in the operating capacity from 21.3 mg g^{-1} to 6.9 mg g^{-1}, equating to a decrease of 75 % (Table 6-2). The impact in the cycle time was a reduction of 86 % from 3531 BV to 876 BV showing the combined impact of the suspended solids and competing ions. Previous full scale application of Clinoptilolite used a cycle time of 80 BV indicating that the current operation is suitable for use with real wastewater (Liberti *et al.,* 1981).

Table 6-2 Comparison of dynamic experiments using Na-MesoLite in multi and mono-component influents.

	Real wastewater Effluent	Synthetic mono-component NH_4^+ solution
EBCT (min)	8	8
Time to reach $C/C_0 = 0.2$ (days)	4.8	19.6
Cycle time (BV)	875	3531
Initial NH_4^+ concentration (mg L^{-1})	6	5
Solids concentration (mg L^{-1})	5	0
Operating capacity (meq g^{-1})	0.4	1.18
Operating capacity (mg g^{-1})	6.90	21.31

6.4 Conclusions

Zeolite pretreated with KCl showed a lower operational capacity relative to zeolite pretreated with NaCl during real wastewater trials, 6.90 and 6.68 mg g^{-1} for Na-MesoLite and K-MesoLite respectively during the first cycle. The efficacy of brine reuse was limited at pH 7 due to accumulation of ionic ammonium in the regeneration liquor with values of the regeneration efficiency of 57 %, 8 %, 4 % and 16 % for potassium and 20 %, 2 %, 4 % and 8 % for sodium. Reuse of brine was possible at pH 12 for five cycles with run times of 3, 3, 1.8, 1.2 and 0.3 days for Na-MesoLite compared to 3, 3, 1.7, 1.1 and 0.97 days for K- MesoLite. It is recommended to limit brine reuse to three cycles to maintain effective run times. The presence of solids was found to adversely affect the zeolite's ability to adsorb NH_4-N, reducing capacity and thus running times. For instance, breakthrough occurred after 7 days when tap water was used, compared to 5 and 2.5 days for trials that used wastewater before and after sedimentation which had concentrations of suspended solids of 29 and 45 mg L^{-1}. Finally, the presence of competing species and solids produced a decrease of operation capacity of 75 % when compared to the dynamic experiments performed in synthetic mono component solution.

6.5 Acknowledgements

The authors acknowledge the financial support of the project sponsors Thames Water, Severn Trent, Anglian Water, Yorkshire Water and Scottish Water.

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7 AMMONIA REMOVAL USING MESOLITE – AN ECONOMIC ANALYSIS.

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Abstract

The total cost of using ion exchange processes as a polishment treatment is the biggest challenge for this process to be considered as an alternative to the current biological treatments. The business cases for this paper were established based on a 2,000 popular equivalent (PE) wastewater treatment works (WWTW) without nutrient recovery option and a 20,000 PE WWTW with recovery option. In both cases the treatment at 1 min empty bed contact time (EBCT) was considered to be the cheapest capital cost, of £60/PE and £13PE^{-1}. In each of the cases the ion exchange contactors resulted to contribute in a higher percentage to the total cost. Regarding operational expenses, reusing the brine turned out to be essential to lower the total annual cost. For the 2,000 PE plant the total annual cost decreased by 25 % at 15 min EBCT when the regenerant was reused for 3 consecutive cycles. For the 20,000 PE plant reuse of brines reduced the total operational expenses by 50 %. Adding a recovery option decreased the total operation cost by an additional 15 % to 65 % relative to the option where a clean regenerant was used each time. Unlike the 2,000 PE, the cheapest operation cost option for the 20,000 PE was found to be when the flow is treated at 1 min EBCT. This study also showed that it is preferable to use a zeolite that has high capacity rather than high durability. For example, when capacity increased 4 times, the annual operational cost was reduced from £1.7 M to £0.8 M. However, when the zeolites life is increased 10 times the annual operational cost only reduced by 10 %.

Key Words: Ammonium, ion exchange, CAPEX, OPEX, COST

7.1 Introduction

Removing ammoniacal nitrogen (NH_4-N) from wastewater is critical to avoid detrimental effects on our freshwater ecosystems such as accelerated eutrophication (Canfield *et al.,* 2010). Biological nitrification processes are a robust and resilient way to achieve this and can be easily incorporated into the secondary treatment step of wastewater treatment by extending sludge age / reducing the food to micro-organism ratio to ensure the biological community contains sufficient nitrifying organisms. However, situations can arise that reduce the efficacy of the approach such as low temperatures, limited alkalinity, highly variable ammonia loads (daily and seasonally), industrial inputs adding nitrification inhibitors and in the case of total nitrogen removal, a low BOD/N ratio (Hedström, 2001). In addition, discharge standards for ammonia are becoming more restrictive with many sites requiring to meet a lower than 1 mg L^{-1} standard, including small wastewater works that incorporate passive technologies such as trickling filter which are more difficult to adapt to meet such standards. Accordingly, polishing technologies have to be incorporated such as nitrifying submerged aerated filters (N-SAF) an aerated constructed wetlands although very low discharge standards remain a challenge (Butterworth *et al.,* 2016). Consequently, there is increasing research interest in non-biologically based technologies that may make it possible to efficiently remove NH_4-N from wastewater. One example gaining increasing interest is the use of ion exchange. The technology is conventionally used for water softening and removal of nitrates and other ions in drinking water and industrial water production. Ion exchange (IEX) processes are less commonly used in wastewater treatment plants (Hedström, 2001; Wang and Peng 2010). Although a number of studies have considered applications related to removing ammonium from sludge liquors to reduce aeration demands on the main biological process (Mackinnon *et al*., 2003; Thornton *et al.,* 2007b.). Others have investigated the use of zeolites for main flow ammonium removal through a combination of batch and column studies on both synthetic and real wastewaters (Booker *et al.,* 1996; Deng *et al.,* 2014; Liberti *et al.,* 1981). The ability of zeolites to remove ammonium is well proven (Wang and Peng, 2010) and whilst load capacity is reduced by the competing ions in wastewater, robust and resilient removal of ammonia has been demonstrated at large scale (Liberti *et al.,*1981; Mackinnon *et al.,* 2003). The process operates as a relatively short cycle batch process followed by regeneration of the media by contacting it with a high strength brine solution, typically NaCl. The use of the brine and its management have previously been highlighted as the key barriers to further implementation and wide use of the technology as it has been estimated to contribute up to 80 % of the total operating cost (Deng *et al.* 2014; Liberti *et al.,* 1981; Miladinovic and Weatherley 2008).

Recent work has highlighted the use of MesoLite as an alternative to Clinoptilolite for ammonium polishing applications leading to extended run times (Chapter 4) that potentially change the overall assessment, especially for works that need tertiary upgrading to meet future compliance. Further, regenerant reuse (Chapter 5) and recent advances in brine clean-up indicate that there may be a more promising economic case for using ion exchange. Accordingly, the current work examines the business case for application of MesoLite contactors for tertiary ammonium polishing at two scales of operation: a small works (2000 PE) and a medium size works (20,000 PE). For both cases, the whole life cost is estimated and compared to the benchmark case of N-SAF to establish the operating condition that generate a favourable business case for use of zeolites.

7.2 Business case scenarios

The economic evaluation is based on the use of a fixed bed ion exchange process for polishing of NH_4-N from wastewater for two different sizes of wastewater treatment works (WWTW). The first study is based on a size of 2,000 PE (Figure 7-1) to represent a small works where there is a desire for limited additional infrastructure and hence it is assumed brine clean-up would occur remotely. Two scenarios were compared single use of the brine and reuse of the brine three times before replacement. In the second case, a 20,000 PE works, it is assumed that the brine clean-up will be located on the site (Figure 7-2). The initial concentration of NH_4-N assumed in the study was 5 mg L^{-1}, a representative value for most existing sewage works that require an upgrade. The target breakthrough concentration was set at 1 mg L^{-1} to reflect potential conservative limits for discharge (Directive 1991; European parliament 2000). To limit the impact of suspended solids on the performance of the process, a drum filter (100 mm pore size) was included in both flowsheets. It is assumed that backwash flows would be returned to the head of the works and the costs associated with this flow were not included in the estimation.

In both cases the cost estimate was based on the major plant items including: (1) tanks, (2) drum filter, (3) pumps and (4) ion exchange contactors (2000 PE plant) with additional inclusion for regeneration clean-up of (5) chemical and buffer tanks, (6) mixing tank, (7) filter and (8) membrane for the larger plant. The operational cost considered were (1) energy of the active equipment, (2) use of chemicals, (3) zeolite refill and (4) labour.

The costs were estimated for the five empty bed contact times that were studied throughout this thesis (1, 2.5, 4, 8 and 15 min) and the whole life cost compared to the bench make case of an N-SAF.

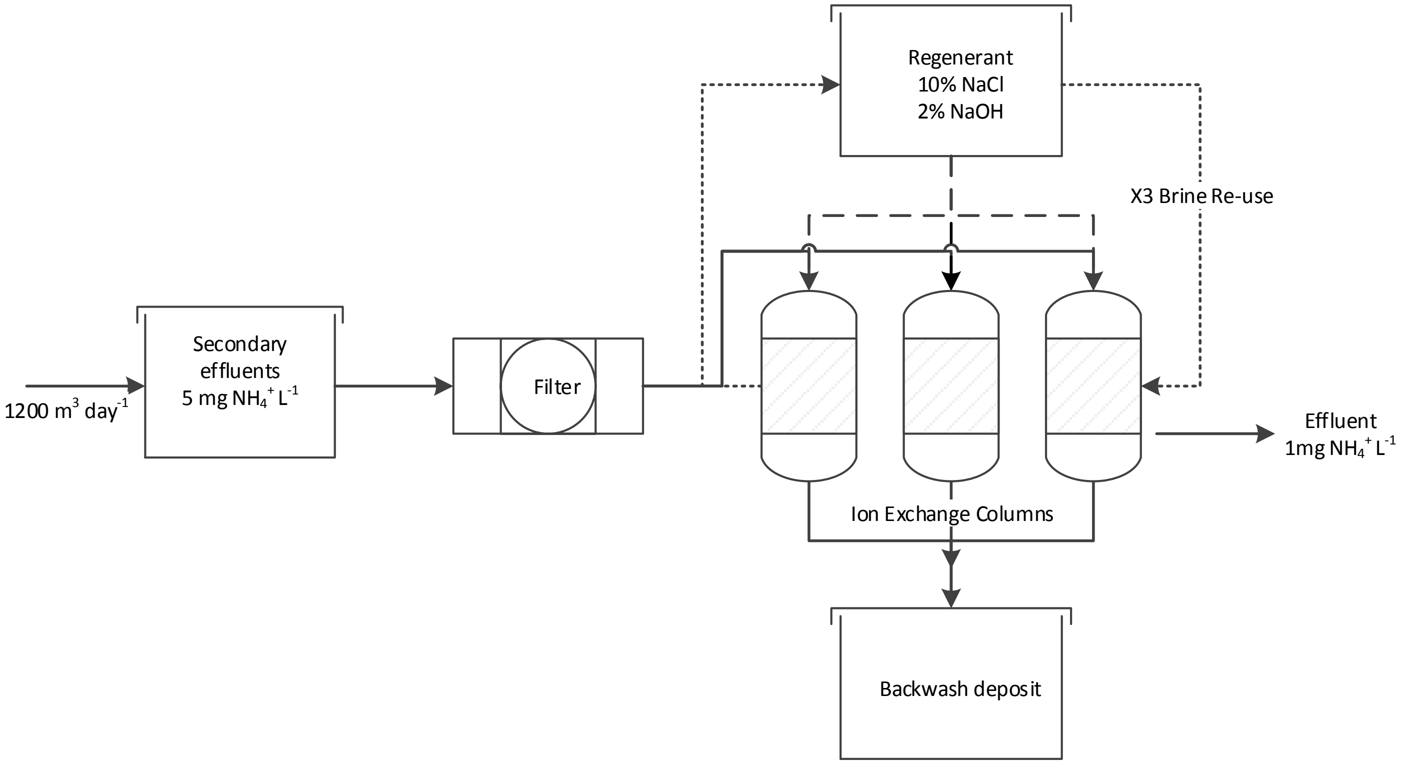

Figure 7-1 Simplified flow sheet for a plan that treats effluent from 2,000 PE. The process does not include the recovery of nitrogen from the regeneration brines.

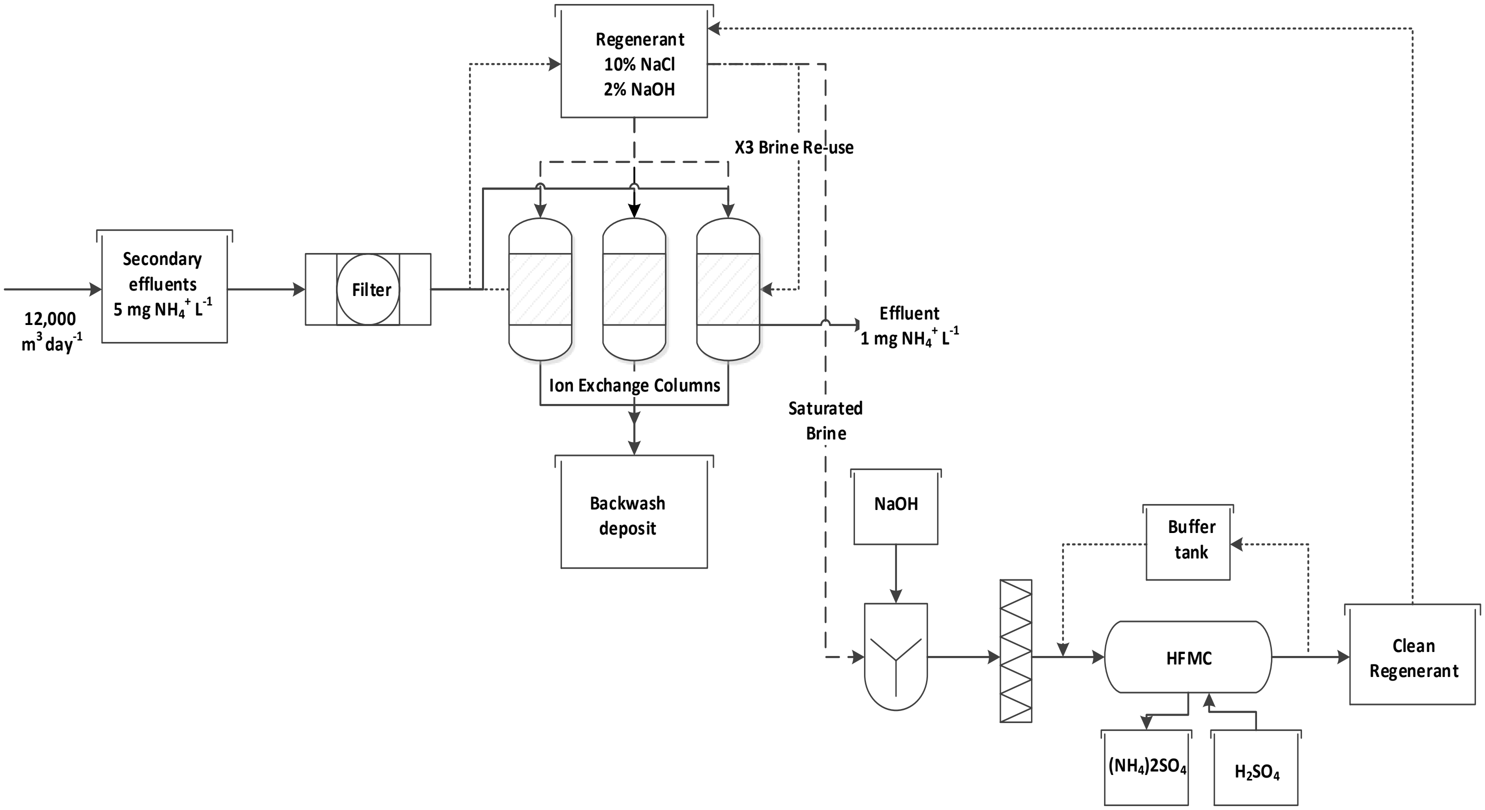

Figure 7-2 Simplified flow sheet for a plant that treats effluent from 20,000 PE. The process consider the recovery of nitrogen from the regeneration brines.

7.3 Design Parameters

The design for the fixed bed contactor and the regeneration and recovery process were all calculated based on the data derived throughout this study supplemented using literature and manufacturer information (Loh *et al.,* 2002; Towler and Sinnot, 2013). Calculations of power requirements for electricity and active equipment assumed 50 % efficiency. The design in both business cases were based on full flow treatment (FFT), which is assumed to be three times the dry weather flow set at 200 L head^{-1} day^{-1}.

7.3.1 Fixed bed ion exchange contactor

The design of the ion exchange contactors was based on parallel contactor operation with the limiting conditions to an individual contactor defined as a maximum diameter of 3 m, a maximum bed depth of 1 m and a maximum head loss of 2 bar in line with standard ion exchange design (Table 7-1) (Towler and Sinnot. 2013). The capacity for MesoLite was calculated based on experiments from this thesis (Chapter 4 and 6) and adjusted to reflect experience from pilot trials used during investigations of MesoLite for sludge liquor treatment (Thornton *et al*. 2007b). Consequently, a conservative cycle time of 1,000 BV was assumed with a media life of 50 cycles. This reflects full scale operational experience with Clinoptilolite were no decay in media properties were observed during the first 50 cycles (Liberti *et al.,* 1981). The drum filter was sized based on a fixed hydraulic loading rate of 3 m^3 m^{-2} min^{-1} at FFT (Metcalf and Eddy 2003) and the area adjusted to the nearest size available from a commercial supplier of drum filter with an aperture of 100 µm (Andritz Separation 2017).

The number of pumps required for each EBCT and vessel were based on the recommended flow rate range of between 0.25 and 103 m^3 h^{-1} per pump (Towler and Sinnot 2013). To calculate the power required for each pump the Equation 7-1 was used and converted to a power requirement assuming a motor efficiency of 75 % (Equation 7- 2) (Towler and Sinnot 2013):

$$g\Delta z + \frac{\Delta P}{\rho} - \frac{\Delta P_f}{\rho} - W = 0$$

Equation 7.1

$$Power = (W\ x\ m)\ \frac{100}{\eta}$$

Equation 7.2

Where; *W* is the work done by the fluid (J kg^{-1}), *ΔZ* is the difference in elevations (m), *ρ* is the liquid density (kg m^{-3}), *ΔP* is the difference of pressure between the tank and the column (N m^{-2}), ΔP_f is the pressure drop inside the column (N m^{-2}), *ΔZ* is the difference in hydrostatic head (m), m is the mass flow rate (Kg s^{-1}) and ŋ is the pump efficiency (%).

Table 7-1 Key parameters for the design of the ion exchange contactors.

		EBCT (min)					
Design Parameter	**Units**	**1**	**2.5**	**4**	**8**	**15**	**Notes and References**
2,000 PE							
FFT	$m^3 d^{-1}$			1,200			
Media	m^3	0.83	2.08	3.33	6.66	12.5	Calculated
Media Life	Cycles			50			(Liberti *et al.,* 1981)
Media Capacity	Bv to reach 1 mg N L^{-1}			1,000			(Thornton *et al.*, 2007b)
N° of contactors		1	6	2	3	13	Active contactors, calculation
Diameter	m	2	1	2	2	3	Optimal diameter (0.5 to 3 m Towler and Sinnot, 2013
Bed Depth	m	0.45	0.79	0.53	0.70	0.99	Calculated
Pressure Drop	Bar	1.80	2.0	1.8	1.6	0.10	Calculated
Drum filter area	m^2			0.28			Assuming hydraulic loading rate of $m^3 m^{-2} min^{-1}$. (Loh *et al.,* 2002; Metcalf and Eddy 2003)
20,000 PE							
FFT	$m^3 d^{-1}$			12,000			
Media	m^3	8.3	20.83	33.33	66.6	125	Calculated
Media Life	Cycles			50			(Liberti *et al.,* 1981)
Media Capacity	BV to reach 1 mg N L^{-1}			1,000			(Thornton *et al.*, 2007b)
N° of contactors		3	7	9	12	65	Active contactors, Assumption
Diameter	m	3	3	3	3	2	Optimal diameter (0.5 to 3 m) Towler and Sinnot, 2013
Bed Depth	m	0.70	0.75	0.94	0.78	0.94	Calculated
Pressure Drop	Bar	1.76	1.81	1.76	1.98	0.98	Calculated
Drum filter area	m^2			2.8			Assuming hydraulic loading rate of $m^3 m^{-2} min^{-1}$. (Loh *et al.,* 2002; Metcalf and Eddy 2003)

7.3.2 Regeneration of the media

Experimental results indicated that regeneration efficiency increased at high pH (Chapter 6). Therefore, the regeneration solution was based on a combined 10 % NaCl and 2 % NaOH (Deng *et al.* 2014). For each EBCT, the number of days between regenerations was calculated along with the number and size of the brine tanks.

Table 7-2 Parameters to regenerate the synthetic MesoLite

		EBCT (min)					
Design Parameter	**Units**	**1**	**2.5**	**4**	**8**	**15**	**Notes and References**
General							
NaCl Concentration	%			10			Deng Q. et al, 2014
NaOH Concentration	%			2			Deng Q. et al, 2014
EBCT	min			60			Experimental work
Regenerant required	BV			5			Thornton et al., 2007b
Nº of Cycles	year^{-1}	542	260	171	89	49	Calculated
2,000 PE							
Brine Tank	m^3	5	15	15	20	50	Calculated
Nº of tanks		1	1	2	2	2	Calculated
20,000 PE							
Brine Tank	m^3	25	25	50	50	100	Calculated
Nº of tanks		2	4	6	7	6	Calculated

7.3.3 Brine clean-up using a hollow fibre membrane

The impact of local brine clean-up was evaluated for the 20,000 PE WWTW. It was decided to use a hollow fibre membrane since it is commercially available and technical information is available (Table 7-3). The concentration of nitrogen in the brines was calculated assuming 90 % removal efficiency during 3 consecutive cycles. The flow rate of the membrane was adjusted between 0.9 and 6.8 m^3 h^{-1} (Liqui-Cel, 2017) to obtain a clean-up time compatible with the regeneration time required of each EBCT. Equation 7-3 was used to estimate the number of cycles required (N_R) to clean-up. Equations 7-4 to 7-9 were used to determine the number of recirculations required.

$$N_R = C_N x \left(\frac{N_1}{N_o}\right)$$

Equation 7.3

Where C_N is the regenerant concentration after x recirculations, N_1/N_o is the ratio between NH_3 out in a single pass and the initial concentration.

$$N = \frac{-4.6\ x\ u_e\ x\ l_{eff}}{-K_o x\ a}$$

Equation 7.4

Where N is the number of modules in series, u_e is the effective regenerant liquid velocity (m s^{-1}), l_{eff} is the effective membrane length (m), and a is the specific surface area (m^{-1}).

$$\mu_e = \frac{\ln(\mathcal{E})\ x \ln(2x d_m - d_c)\ x\ (d_m - d_t - d_c) x \left({}^{Q_L}/_{\pi}\ x\ {}^{l_{eff}}/_{2}\right)}{(4x\left(\mathcal{E}^{1/2} - 1\right) x\ (2x(d_t + d_c)}$$

Equation 7.5

Where $\mathcal{E}$ is the porosity of the membrane, d_m *is* the inner shell diameter (m), d_c is he cell diameter (m), d_t is the approximate centre feed tube diameter (m), Q_L is the regenerant flow rate set at maximum (m^3 s^{-1}).

$$K_o = H + K_m$$ **Equation 7.6**

$$K_l = \frac{ShxD}{d_h}$$ **Equation 7.7**

$$Sh = 2.15xRe^{0.42} * Sc^{0.33}$$ **Equation 7.8**

$$K_m = \frac{D_N x\ \varepsilon\ x\ H}{L\ x\ T}$$ **Equation 7.9**

K_L is the liquid mass transfer (m s^{-1}), *Sh* is Sherwood number, *D* is the NH_3 diffusivity in water (m^2 s^{-1}), *Re* is the Reynolds number and *Sc* the Schmidt number, K_m is the mass transfer coefficient of the membrane (m s^{-1}), $D_{N'}$ diffusivity of NH_3 (m^2 s^{-1}), *H* is the henry's constant, *T* is the pore tortuosity

The time to reach 99% (t) of removal was calculated as;

$$t = \frac{N\ x\ V}{Q_R}$$ **Equation 7.10**

V is the volume of the regenerant and Q_R is the regenerant flow rate. Find constant values in appendix C.

Table 7-3 Recovery unit. Hollow Fibre design parameters.

		EBCT (min)					
Design Parameter	**Units**	**1**	**2.5**	**4**	**8**	**15**	**Notes and References**
Brines from 3-Reuse cycles - 20,000 PE plant							
Nitrogen concentration	mg L^{-1}	3000					Calculated
Membrane		Liqui-Cel extra flow 4x28 (SS=20 m^2)					Calculated
Surface Area	m^2	20					Liqui-cel ®
Flow Rate	m^3 h^{-1}	4	5	5	5	5	Calculated
Pressure drop	Bar	0.26	0.41	0.41	0.41	0.41	Calculated
Volume of Brine	m^3	42	104	167	333	625	Calculated
Number of recirculations		4	5	5	5	5	Calculated
Time to clean-up	Days	2	4	7	14	28	Calculated
NaOH	Ton / Clean-up	0.0625					Calculated
H_2SO_4	Ton / Clean-up	1.180					Calculated
$(NH_4)_2SO_4$ formed	Ton / Clean-up	0.61					Calculated
Regenerant tanks	m^3	25	20	25	50	50	Calculated
Nº of tanks		2	3	2	3	3	Calculated
Buffer Tanks	m^3	5	15	15	15	15	Calculated
Nº of tanks		1	1	1	1	1	Calculated

The 4x28 Liqui-cel ® Extra flow was selected for use based on the balance of cost and operating time as it is possible to clean the brine (2 to 28 days) during the time the columns would be adsorbing (Table 7-3; Liqui-Cel 2017). The required amount of chemicals was calculated through a mass balance, while the amount of NaOH was calculated based on the assumption that the pH in the brines after regeneration was lowered to pH 7 and it would need to be elevated to pH 11. According to Ulbricht *et al.* (2013) the ratio of H_2SO_4 required to keep the pH <1.5 through the membrane would be 4.5:1 of the NH_3 concentration, which in return will form $(NH_4)_2SO_4$ at a ratio of 1:5.

7.3.4 Nitrifying Submerged Aeration Filter

Nitrifying submerged Aeration Filter (N-SAF) are constructed above ground and the external walls can be constructed of concrete, steel or stainless steel. Sizing was based on a hydraulic retention time of 1.5 h at FFT (Table 7-4; Butterworth *et al.,* 2016) with aeration supplied through a blower with an estimated energy demand of 58 W PE^{-1} day^{-1} (Butterworth *et al.,* 2016). Backwashing was undertaken every day for 30 min to avoid clogging.

Table 7-3 Main design parameters of a N-SAF process

		Value		
Design Parameter	**Units**	**2,000 PE**	**20,000 PE**	**Reference**
Flow	m^3 day^{-1}	1200	12,000	
Volume of the reactor	m^{-3}	75	750	Calculated
Design footprint	m^2 PE^{-1}	0.015	0.015	(Jenkins, 2017)
Total footprint	m^{-2}	30	300	Calculated
Energy demand: Feed pump	kW	2.8	28	(Towler and Sinnot, 2013)
Energy demand: Air blower	kW	4.83	48.3	(Butterworth et al., 2016)
Energy demand: Backwash	kW	2.8	28	(Towler and Sinnot, 2013)

7.4 Economic Evaluation

The total capital expenses (CAPEX) and operational expenses (OPEX) were calculated in British Pounds. Present worth adjustments for each parameter was performed using the chemical engineering plant cost index (CEPCI) for each year (1996-1998 CEPCI values; 2009-2012 CEPCI values; 2015-2017 CEPCI values). The change of currency was performed using the different consumer price index (CPI) for 2018 for each country (Data International Financial Statics). The cost has been based on the main equipment

(Table 7-5). To improve accuracy of the attained results, each of the cost components were calculated individually based on the specific design parameters. The capital cost for the N-SAF process was supplied by Severn Trent UK, which includes civils, mechanical and electrics. To compare, the whole plant costs for the ion exchange plant was adjusted by applying a Lang factor of 4.7 to the sum of the costs of the major plant item (Towler and Sinnot 2013).

Table 7-4 Summary for the cost estimates and energy consumption.

Design Parameter	Cost	Unit	Energy	Unit	Notes	Reference
Drum Filter	22,622 to 34,837	£ m^{-2}	0.085	£ kWh^{-1}	For Filters between 2.8 and 5 m^2	Loh *et al*. 2002
Contactors	12,794 to 27,417	£ m^{-1}			For contactors between 1 – 3 m diameter	Sinnott 2005
Tanks	6,360 to 10,227	£ m^{-3}			For tanks between 5 – 100 m^3	Towler and Sinnott, 2013
Pumps	515 to 1,500 for flows from 28 to 7 L s^{-1}	£ s L^{-1}	0.085	£ kWh^{-1}	75% efficiency	Towler and Sinnott, 2013
Mixer			950-1,900	£ kWh^{-1}	From 1.06 to 4.5 kWh motor	Towler and Sinnott, 2013
Membrane	657	£ m^{-2}			For a 4x28 hollow fibre membrane	Liqui-Cell
MesoLite	1.64	£ L^{-1}			Assumed for synthetic zeolite A	Alibaba, zeolite A
NaCl	62.53	£ ton^{-1}				Deng, *et al*. 2014
NaOH	469	£ ton^{-1}				Deng, *et al*. 2014
H_2SO_4	70	£ ton^{-1}				Alibaba 2018
Electricity			0.0	£ kWh^{-1}		Verrecht *et al*. 2010

7.4.1 Whole life estimates

The whole life cost consists of the capital cost and the operational cost for the life span of the plant (Anglian Water, 2010). As advised by the water companies, the life time of the installation was assumed to be 40 years and the discount rate was assumed to be 7% (equation 7.11) (Anglian Water, 2010).

$$Whole\ life\ cost\ (£) = CAPEX + \ (OPEX\ X\ 14)$$ **Equation 7.11**

7.5 Results and Discussion

7.5.1 Capital costs

The capital cost of the ion exchange systems for 2,000 PE was estimated to be £ 75 K, £ 143 K, £ 118 K, £ 145 K and £ 477 K for 1, 2.5, 4, 8 and 15 min EBCT (Figure 7-3). For the capital cost of the 20,000 PE plant, the cost was divided between two options: (i) not including a recovery plant and (ii) including a recovery plant. In the first case the capital cost was estimated at £ 309 K, £ 454 K, £ 551 K, £ 697 K and £ 1.8 M for 1, 2.5, 4, 8 and 15 minutes EBCT (Figure 7- 3). Inclusion of a recovery plant added an addition £ 78 to £ 100 K to the capital cost, representing between and 5 and 25 % of the base cost. In comparison, the capital cost of the N-SAF was estimated at £ 525 K and £ 1,950 K for the 2,000 PE and the 20,000 PE size plants respectively. Consequently, the capital cost of the ion exchange systems was below that of the N-SAF at all the tested EBCTs and substantially lower once a EBCTs of 8 minutes or less was used. For instance, at an EBCT of 8 minutes, the capital cost of the ion exchange plant was 36 % of that of the N-SAF.

Analysis of the cost components reveals that the drum filter and the ion exchange vessels are the major plant items (Figure 7-4). In the case of the small site, the IEX tanks contributed 28, 53, 36, 44 and 80 % of the total capital for EBCTs of 1, 2.5, 4, 8 and 15 minutes (Figure 7-4 (A)). The screen contributed between 7 and 46 % of the total capital costs showing that management of solids is a major consideration in using ion exchange plants. Previous studies have used depth filters (Liberti *et al.,* 1981), ceramic filters (Thornton *et al.,* 2007b) or larger media (7-15 mm) to manage the solids load. A wide range of media sizes have been used from 0.1 to 5 mm and in some cases without pretreatment such that the bed required regular backwashing (Liberti *et al.,* 1981). In the current study, the media was 1-1.7 mm and so is similar to media commonly used in depth filtration processes (Metcalf and Eddy, 2003). Typical hydraulic loading rates for a tertiary depth filter are between 5 and 15 m^3 m^{-2} h^{-1} such that with a bed depth of 1 m, the EBCT would be around 4 to 12 minutes and hence in the required range. Operated at EBCTs of 1 and 2.5 minutes represents hydraulic loading rates of 60 and 24 m^3 m^{-2} h^{-1} which are outside the range of normal gravity depth filters with pressure filters able to operate at higher hydraulic loading rates of up to 40 m^3 m^{-2} h^{-1} (Ncube *et al.,* 2016). Thus, in principle, if the influent solid concentration is not too high (e.g. < 40 mg L^{-1}) then no pre-treatment would be required if an EBCT over 4 minutes was used and the bed was backwashed on a daily basis reducing the cost of the technology and potentially enabling it to be retrofitted into existing depth filters. A key issue is the mechanical robustness of the media and whether it can remain viable with daily high shear backwashing. Liberti *et al.,* (1981) treated a municipal wastewater with an effluent solid concentration of between 10 and 20 mg L^{-1} and was able to operate a Clinoptilolite bed for 500 cycles of 80 BV with no reported deterioration in the media indicating that this may be a viable approach.

The contribution made by the vessel and filter was reduced for the larger plant at a combined level of 66, 69, 66, 65 and 81 % of the total for EBCTs of 1, 2.5, 4, 8 and 15 minutes respectively (Figure 7-4). The costs of the media become more significant to the overall capital cost of the larger plants where it contributes 4.4, 7.5, 9.9, 15.7 and 11 % of the total for EBCTs of 1, 2.4, 4, 8 and 15 minutes (Figure 7-4 (B)). If a recovery unit is included the total capital cost increased by 20, 16, 12, 11 and 4 % for 1, 2.4, 4, 8 and 15 minutes EBCT (Figure 7- 4 (C)). However, IEX vessels still constitute the main cost factor for EBCT from 2.5 to 15 min, while the filter is the main cost component for 1 minute EBCT. The regeneration system contributes between 7.2 and 22.1 % for the total capital cost, progressively becoming a smaller component of the total capital cost as the EBCT increases. The large vessel costs reflect the boundary conditions where the bed depth was limited to 1 m and the maximum diameter was set at 3 m such that with the longer EBCTs, a large number of vessels are required (Table 7-1). This is traditional for ion exchange systems that are based on relatively short cycle times (e.g. 80 BV) whereas in the current case the cycle time was set at 1000 BV. Consequently, alternative delivery approaches can be considered which should significantly reduce the capital cost of the contactors further and this should be an area for future investigation.

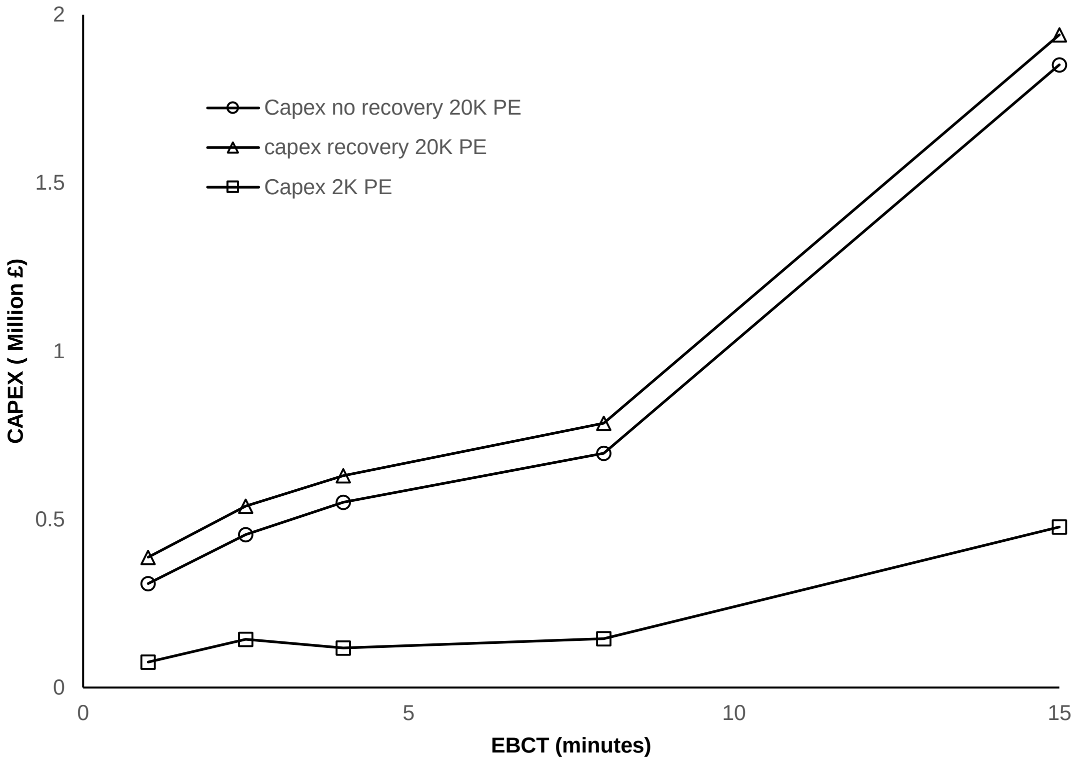

Figure 7-3 CAPEX for 2,000 PE and for 20,000 PE including the cost for recovery plant.

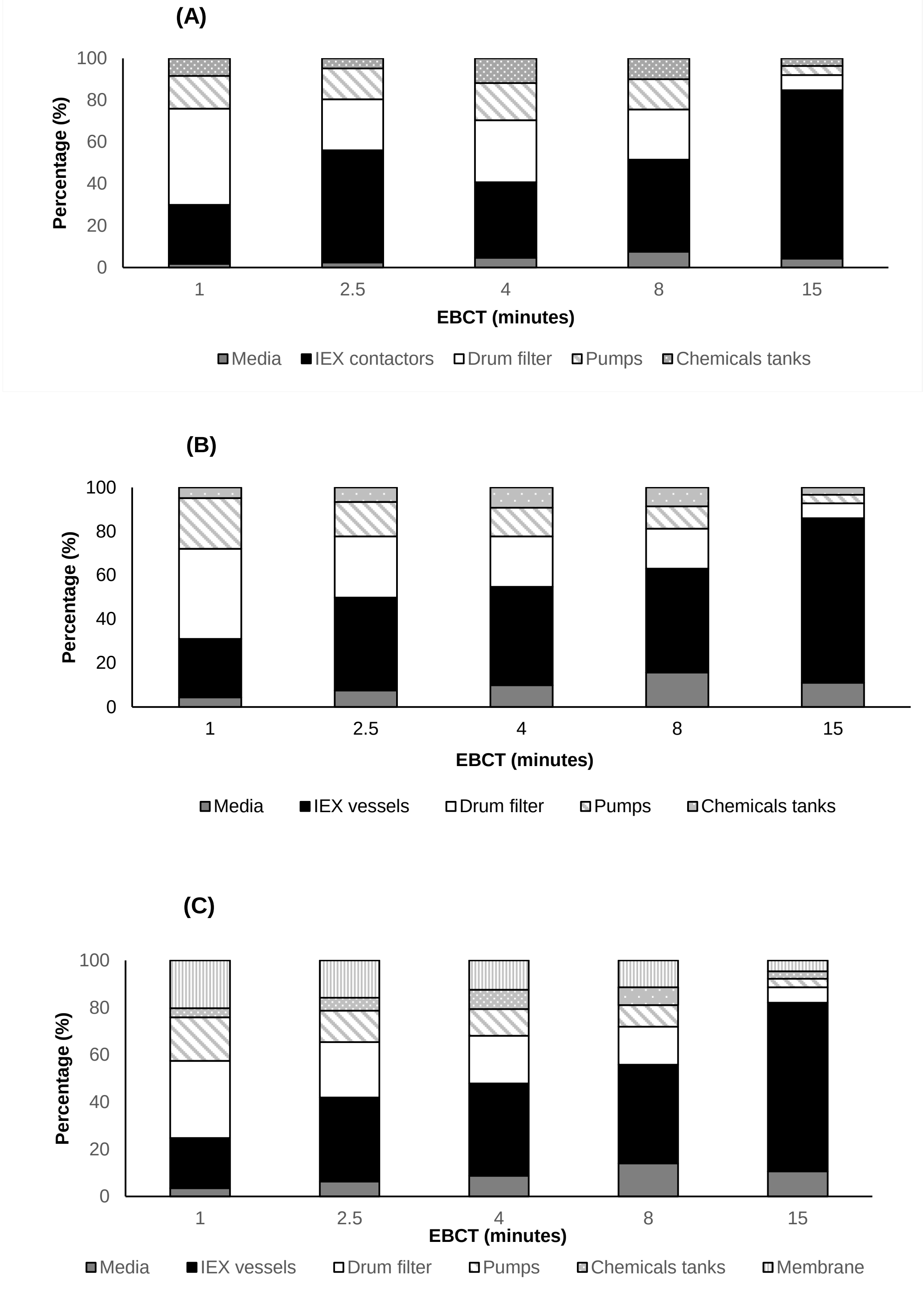

Figure 7-4 Breakdown of the capital cost for the major plant items for (A) the 2,000 PE plant, (B) the 20,000 PE plant and (C) the 20,000 PE with onsite regeneration and clean-up.

7.5.2 Operating costs

During the experimental work (Chapter 6) it was observed that if the pH was maintained at 12 it was possible to re-use the brines for up to 3 cycles. To evaluate the impact that re-use has on operational cost, both options (i) brine re-used during 3 cycles and (ii) use of new brine for each cycle and (iii) for the larger plant a brine recovery unit were considered.

In the case of the 2,000 PE WWTW when the brine is not re-used, the annual operational cost remains fairly stable as a function of EBCT at between £ 64 K and £ 66 K (Figure 7- 5 (A)). This reduces to between £ 42 K and £ 32 K when the brine is reused three times before being sent for clean-up. The decrease in operating costs with EBCT reflects the reduction in the number of cycles from 542 to 49 as the EBCT increased from 1 minutes to 15 minutes. In the case of 20,000 PE, the operating costs stayed fairly stable as a function of EBCT with levels between £ 133 K and £ 165 K for the case with brine recovery, £ 263 K and £ 283 K when the brine was used three times and £ 510 K and £ 620 K when the brine is used once (Figure 7-5 (B)). Thus, the inclusion of brine recovery reduced the annual operating costs by between £ 377 K and £ 455 K which represents annual savings of 74 % compared to single use application of the brine.

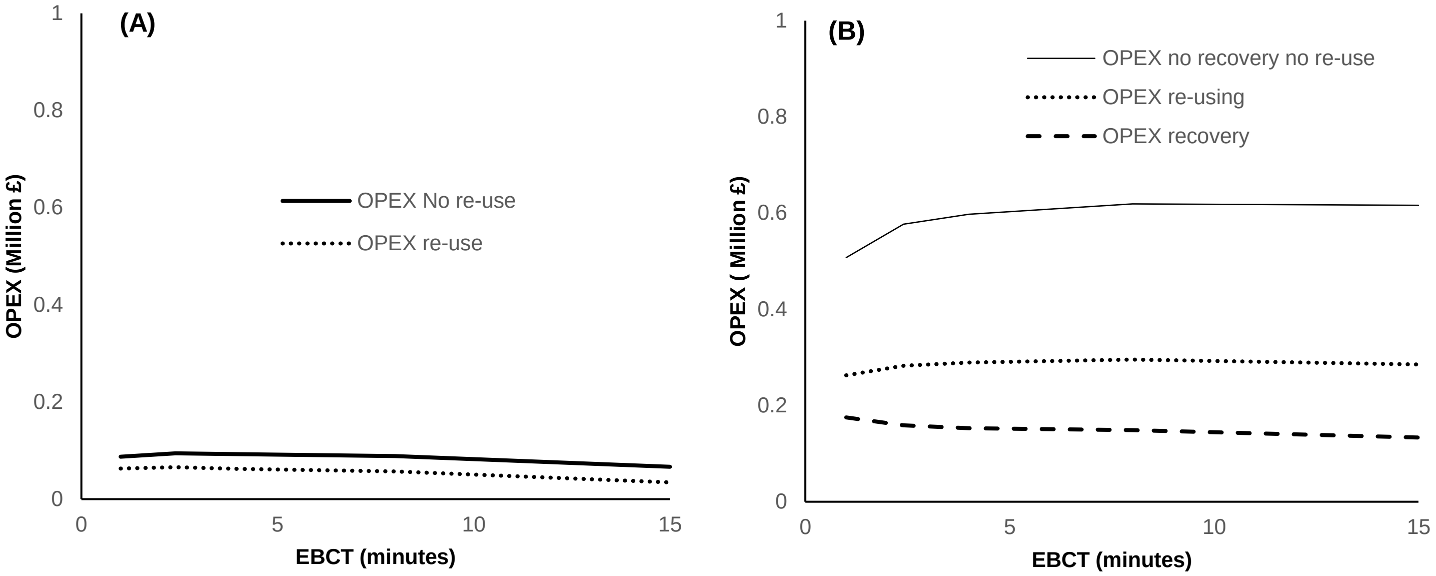

Figure 7-5 OPEX calculation for (A) 2,000 PE and (B) 20,000 PE.

Analysis of the breakdown of the operating cost components for the 2,000 PE plant, revealed that cost of the chemicals was the most significant component and ranged between 54 % at an EBCT of 1 minute to 75 % at an EBCT of 15 minutes (Figure 7-6). Reuse of the brine reduced the relative contribution of the chemical cost to between 28 and 50 % of the total annual operating costs (Figure 7-6 (B)). Previous studies have suggested that regeneration of Clinoptilolite can account for up to 80 % of the total operating cost of ion exchange based removal of ammonium (Deng *et al*., 2014; Miladinovic and Weatherley, 2008; Verrecht *et al.,* 2010). The lower levels here reflect the better capacity of MesoLite over Clinoptilolite (Chapter 3, 4) enabling longer operating cycles of up to 1000 BV. The other major costs components were the media replacement and labour with the media replacements accounting for approximately 16 % of the total operating costs.

In comparison, for the larger plant with single use brine, chemicals contributed between 72 and 80 % and media replacement between 16.7 and 20.5 % of the total operational cost (Figure 7-7). Reuse of the brine reduced the contribution associated with chemicals to between 46 and 58 % (Figure 7-7 (B)). Incorporation of the recovery unit reduces this component further to between 7.5 and 16 %, represented as the operating cost of the membrane plant (Figure 7- 7 (C)). In these cases, the operating cost of the plant become dominated by the replacement cost of the media which represents between 59 and 77 % of the total. Accordingly, reducing the media replacement rate or the unit cost of the media are important items for future consideration in minimising the total cost of the use of ion exchange. In comparison, the operating costs of the N-SAF was £ 19 K and £ 184 K for the 2,000 and 20,000 PE respectively indicating a higher capital but lower operating cost compared to the ion exchange plant (Appendix B).

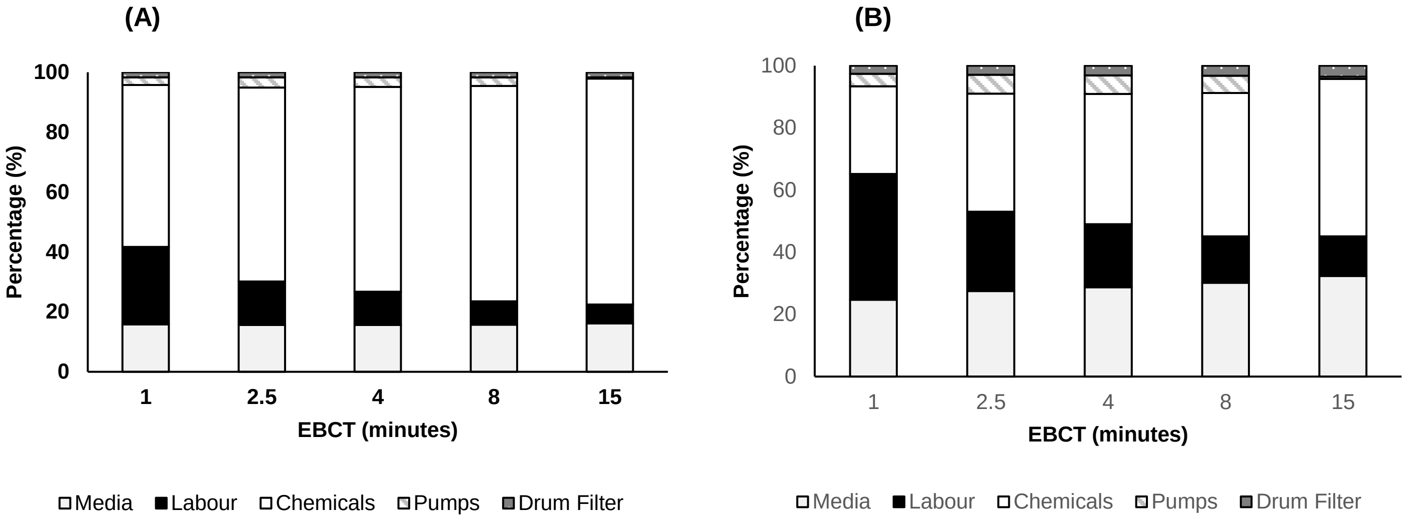

Figure 7-6 OPEX for 2,000 PE WWTW (A) without regenerant re-use (B) with re-use of regenerant during 3 cycles.

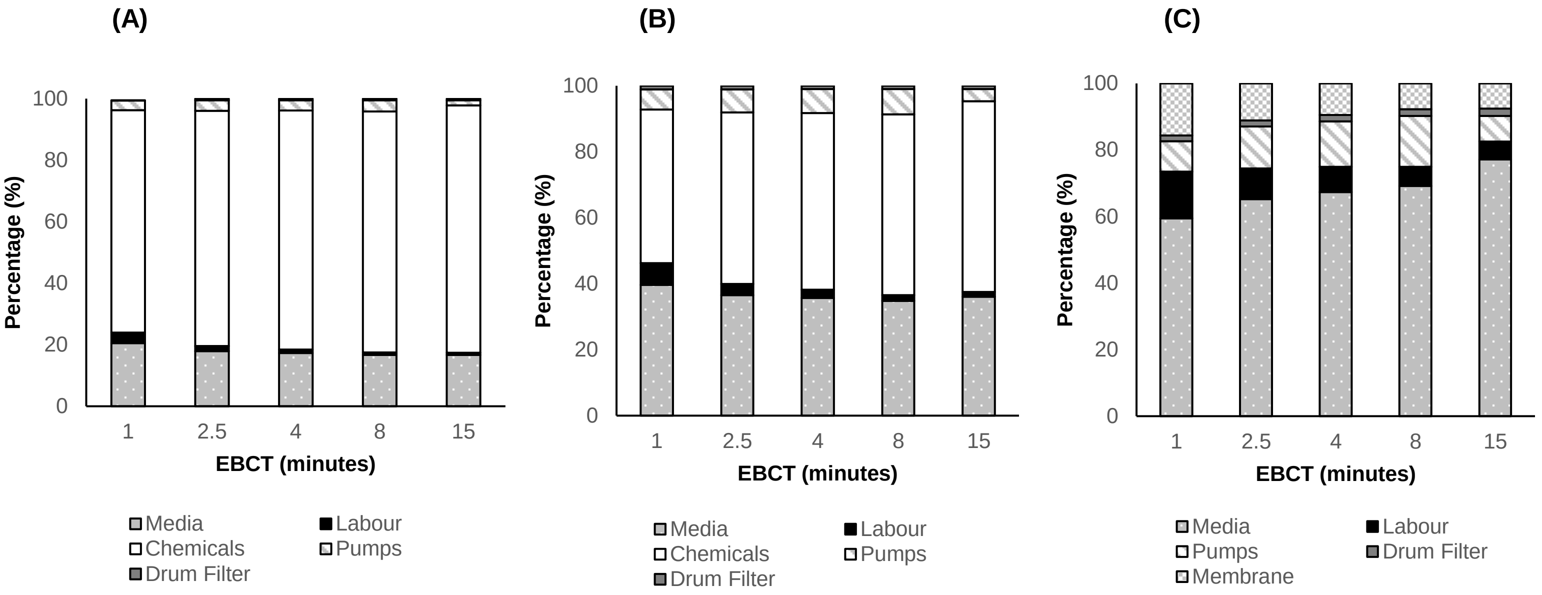

Figure 7-7 OPEX for 20,000 PE (A) without brine re-use (B) with brine re-use x3 cycles (C) with recovery of the nitrogen present in a brine re-used for 3 consecutive cycles.

7.5.3 Whole Life Cycle

In the case of 2,000 PE works, the whole life cost, was estimated at £ 649 K, £ 653 K, £ 605 k, £ 608 K, £ 908 K when the brine was re-used against £ 971 K, £ 1.04 M, £ 1.01 M, £ 1.03 M and £ 1.34 M for 1, 2.5, 4, 8 and 15 min EBCT with one single use of brine (Figure 7-8). In comparison, the WLC of the N-SAF plant was £ 661 K. Although incorporation of a Lang factor reduces precision on the overall cost (Lemmens 2016; Sinnott 2005), the analysis shows that the IEX process is economically feasible when the brine is re-used for all the EBCTs but 15 min (Figure 7-8). The capital cost represents between 11 and 52 % of the WLC as the EBCT increases from 1 to 15 minutes. The overall picture is that the WLC is driven by the operating costs which is minimised at the lowest EBCT. Further, the large overall proportion of the WLC from operating components offers potential for cost optimisation and minimisation that provide confidence that the use of ion exchange systems for small sewage works is economically plausible and worthy of further investigation. One potential area is the use of mobile regeneration of the brine such that the overall chemical costs can be reduced similar to the larger plant without the need for the extra infrastructure. This concept was investigated in a similar assessment but for phosphorus removal identified that the use of a single mobile brine recovery plant, servicing a number of small works reduced the total cost significantly (Muhammad, 2018).

In the case of the 20,000 PE works, the WLC when the brine is used once is £ 7.2 M, £ 8.2 M, £ 8.6 M, £ 9 M and £ 10 M for EBCTs of 1, 2.5, 4, 8 and 15 minutes. When the brine is re-used during 3 consecutive cycles the WLC cost is reduced to £ 3.9 M, £ 3.8 M, £ 4.5 M, £ 4.7 M and £ 5.7 M (Figure 7-8). When additional recovery of the regenerant is added the WLC reduces considerable to £ 2.6 M, £ 2.7 M, £ 2.7 M, £ 2.8 M and £ 3.7 M. This compares to a solution based on N-SAF at £ 4.4 M such that the ion exchange system offers a higher WLC for each of the EBCTs when brine is used only for a single time. However, reuse of the brine makes the WLC comparable to N-SAF for 1 and 2.5 min EBCTs whereas brine recovery reduces the WLC significantly such that the ion exchange system offers a lower WLC than the N-SAF at all EBCTs. The WLC of the ion exchange system under these conditions is between 60 and 85 % of that of the N-SAF. The significant impact reflects the contribution the operating cost has on the ion exchange system. For instance, in the case of the single brine use, the operating cost represented between 69 and 92 % of the total cost. This compares to previous data from a large scale systems (38,000 m^3 day^{-1}) to treat municipal secondary effluents where the NaCl make up costs represented 50 % of the total investment (Liberti *et al.,* 1981).

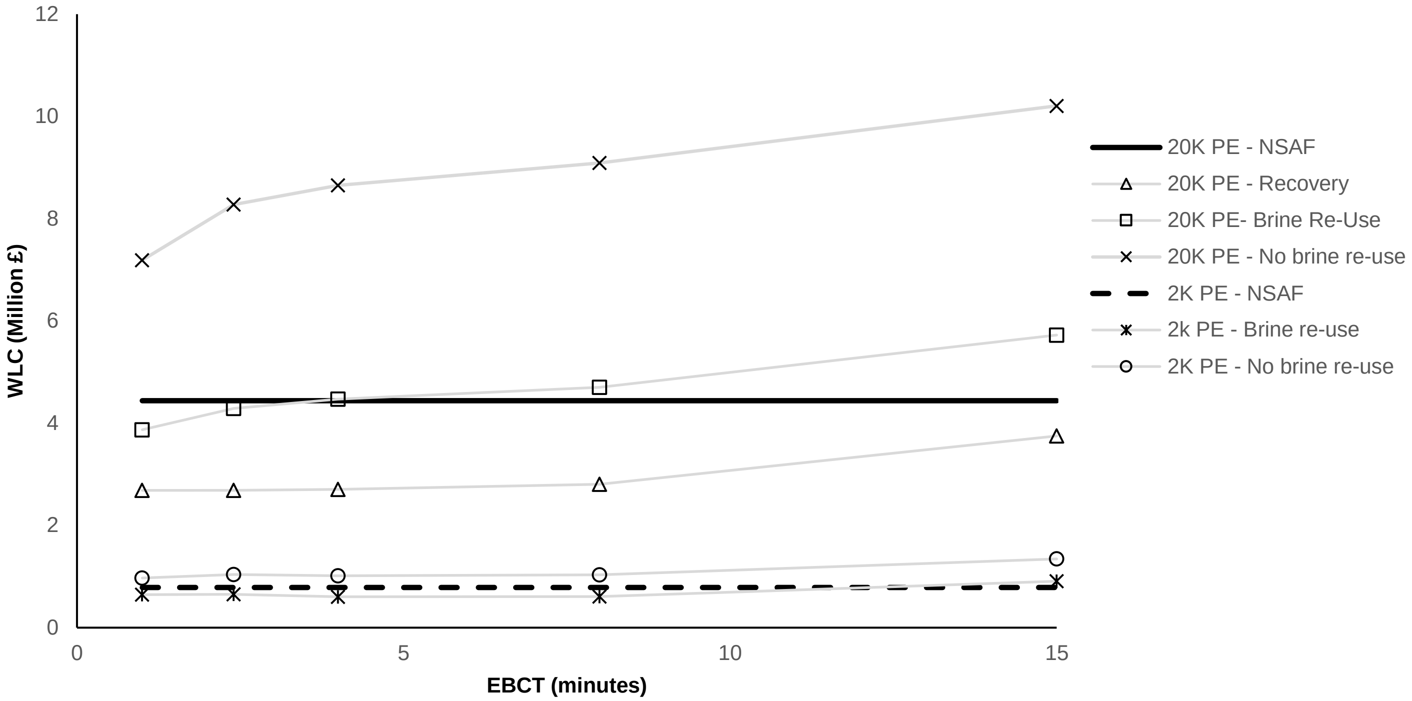

Figure 7-8 Whole Life Cycle for 2,000 PE and 20,000 PE.

7.5.4 Sensitivity Study

A trade-off exists between capacity and life of the zeolite such that to increase a synthetic zeolite's life, capacity needs to be sacrificed since the binding materials make mass transfer more difficult (Fakin *et al.,* 2016). To understand the impact of this, a sensitivity analysis was undertaken for the 20,000 PE site to ascertain the relationship between different media life cycles, capacity and WLC. At a fixed media life of 50 cycles, the WLC decreased from £ 1.7 M to £ 0.8 M as the cycle length increased from 1,000 to 4,000 BVs (Figure 7-9). Further, if cycle time is kept at 1000 BV and the zeolite's life is increased to 500, the WLC reduces by approximately 10 %. In comparison, at a media life of 50 cycles, a 30 % reduction in WLC is achieved by doubling the cycle time to 2,000 BV. Overall, this indicates that the key to WLC reduction is derived around increasing the capacity of the media to deliver longer cycle times rather than increases the media life.

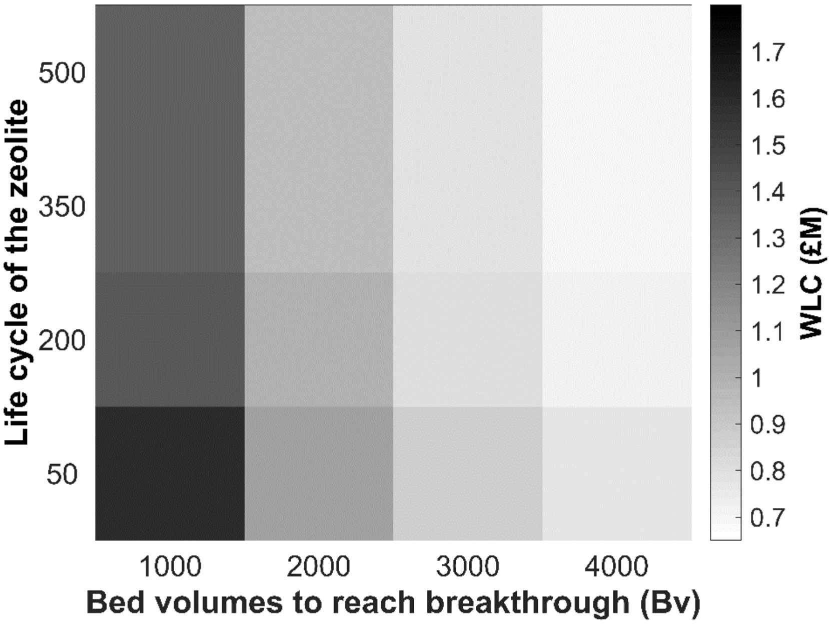

Figure 7-9 Sensitivity analysis for 20,000 PE WWTW where whole life cost is depicted as a function of capacity (bed volumes to reach breakthrough) and zeolite's life is linked to whole life cost.

7.6 Conclusions

The total capital expenditure for a 2,000 PE WWTW was estimated as £ 75 K, £ 143 K, £ 118 K, £ 145 K and £ 477 K for 1, 2.5, 4, 8 and 15 minutes EBCT. Ion exchange vessels account for the largest part of the investment at around 50 % of the total cost for each of the EBCT. For the 20,000 PE WWTW with no recovery option the total capital cost was estimated to be £ 309 K, £ 454 K, £ 551 K, £ 696 K and £ 1.8 M for EBCT of 1, 2.5, 4, 8 and 15 minutes. The IEX vessels were the largest cost factor. When a recovery process was included, the total capital cost increased to £ 387 K, £ 539 K, £ 629 K, £ 785 K and £ 1.9 M for 1 to 15 minutes EBCT. In the case of the 2,000 PE WWTW the annual operational cost was between £ 64 K and £ 66 K when the brine was not reused. When brine was reused, this cost decreased to between £ 32 K and £ 42 K. For the 20,000 PE plant, the operating cost, without brine reuse or recovery was between £ 507 K and £ 626 K. Brine reuse reduced operating cost by 50 % whereas brine recovery lead to a

73 % reduction in the operating cost compared to single use brine regeneration. Overall the WLC comparison to the benchmark technology (N-SAF) indicated that the ion exchange process can be an economically plausible alternative. Sensitivity analysis showed cost minimisation is most effectively achieved through extending the cycle time between regenerations.

7.7 Acknowledgements

The authors acknowledge the financial support of the project sponsors Thames Water, Severn Trent, Anglian Water, Yorkshire Water and Scottish Water.

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8 DISCUSSON – Implications of the work

The current thesis has been concerned with the removal of ammonium from wastewater using zeolites as an ion exchange media. In particular, the application of tertiary ammonium polishing is considered where the effluent ammonium needs to be reduced from around 5 mg L^{-1} to potentially less than 1 mg L^{-1} (Directive, 1991; European parliament, 2000). The application reflects a situation emerging on a number of small and medium sewage works where the main biological process is a trickling filter or a rotating biological contactor. Such relatively passive technologies are harder to adapt to changing consents, especially as incoming flow and load tends to increase with age due to population growth. The systems become particularly strained during the colder months when the activity levels of the micro-organisms decreases (Butterworth *et al.,* 2016). In the case of activated sludge processes, the sludge age can be increased to reduce the food microorganism ratio (F:M) to maintain the correct overall conditions for effective nitrification. Alternatively, the process can be adapted by inclusion of biofilm carriers converting the process into the *integrated fixed film activated sludge* process (IFAS) (Kim et al., 2010). This is not possible with trickling filters where additional capacity must be included either as more repeat units or tertiary nitrification processes such as nitrifying submerged aerated filters (N-SAF) and aerated horizontal flow wetlands (Butterworth *et al.,* 2016). These generally work well but can find it difficult to attain ammonium concentrations lower than 1 mg L^{-1} which adds a disproportionate energy and economic cost to the overall works in order to meet compliance levels.

Accordingly, the use of zeolites is considered to provide an alternative approach to polishing the residual ammonium. The process offers robustness and resilience against shock loads and the impacts of low temperatures and can so potentially offer an interesting option for comparison with traditional solutions such as N-SAFs. Literature on zeolites has confirmed their efficacy for the application and indeed there have been full scale applications of the technology (Chapter 2). Critically, reports from such systems highlight concerns over solids management, the cost of regeneration chemicals and spent brine management as the key challenges for wide spread application. However, the previous work was based around Clinoptilolite and mainly considered higher feed concentrations than is the focus of the current thesis. In addition, MesoLite has been shown to offer higher capacity and selectivity for ammonium but has only been tested for high concentration sludge liquor applications. Accordingly, the thesis provides fresh insight into the case of tertiary polishing with MesoLite, examining the operating constraints and establishes the economic plausibility for its use.

Whilst outside the scope of the current discussion, the use of zeolites extends beyond such applications to include the treatment of sludge liquor return lines, full load treatment of ammonium and incorporation into new flow sheets based on anaerobic membrane bioreactors (Jefferson *et al*., 2018). Importantly, biological nutrient removal is challenging in such new flow sheets and reduces the overall value generation prospect, such that ion exchange systems are likely to be an important feature of future flowsheets aligned to the ideas of processing wastewater in resource factories rather reducing pollution risk in a sewage works. In such cases the recovery of ammonium becomes more important as it offsets new production required by the Haber-Bosch process and generates new products in the form of fertilisers (Canfield *et al,* 2010) or feed stocks for microbial protein production (Matassa *et al.,* 2015).

The work outlined in the thesis has considered the impact of zeolite selection and identification of the most appropriate conditions for operation and regeneration leading to the following key observations:

1. The selection of MesoLite increases both capacity and selectivity for the application considered compared to Clinoptilolite. Operational batch capacities (feed concentration of around 16 mg L^{-1}) of 0.78 and 0.58 meq g^{-1} were observed when treating synthetic and real wastewater respectively. These compare to the best alternative Clinoptilolite with capacities of 0.49 and 0.28 meq g^{-1}. The improved capacity is associated with Si:Al ratio of the material (1:1) which is much lower than available with alternative natural zeolites (> 4:1) (Chapter 3). Comparison of the zeolites in continuous column experiments confirmed the

improved capacity for MesoLite at 47 mg g^{-1} compared with 22 and 25 mg g^{-1} for Clinoptilolite and Mordenite (Chapter 4).

2. The impact of increasing empty bed contact time between 1.2 minutes and 15 minutes was to extend the cycle time between 5 days and 40 days respectively. This equates to cycle times of 6490 and 3950 BVs and shows that the system can be run for extended times between regeneration cycles (Chapter 4). This outcome compares favourably with data from other studies with Clinoptilolite where cycle times of around 80 BV were used (Liberti *et al.,* 1981).

3. Changes in the feed concentrations impact the cycle time and achievable capacity such that the cycle time, for an EBCT of 1.2 minutes, decreased from 2662 BV when treating 5 mg L^{-1} to 255 BV when treating 30 mg L^{-1}. Modelling of the system using the Thomas second order rate model indicated that concentration would impact operation up to a maximum feed concentration of 42 mg L^{-1} and hence changing feed strength will impact operation for the application of tertiary polishing (Chapter 4).

4. Effective regeneration was observed with both NaCl and KCl where the uptake capacity of MesoLite remained stable for five cycles. Comparison of the two regeneration liquids revealed improved performance with KCl over NaCl such that a much lower molarity of KCl (0.1 M) achieved the same regeneration efficiency as 1.0 M NaCl. At molarities of 1.0 M, KCl was able to deliver a 10 to 26 % improvement in regeneration efficiency over NaCl. Raising the pH between 9 and 12 had no significant impact on the regeneration efficiency of either brine but at pH 12 the media was able to be regenerated without the presence of brine (Chapter 5).

5. Translation of the column trials to real wastewater revealed no improvement in regeneration with KCl in contrast to the synthetic trials. Direct reuse of the brine was only really possible when the pH was raised to 12 under which conditions the

brine was able to be reused five times. In addition, the impact on solids accumulation within the media bed was a reduction in operational capacity of between 37 and 75 % when treating influent solids levels of 29 and 45 mg L^{-1} compared to a solid free synthetic solution (Chapter 6).

6. Comparison between synthetic and real wastewater at an EBCT of 8 minutes revealed an operational capacity reduction from 21.3 mg g^{-1} to 6.9 mg g^{-1} equating to a cycle time of 19.6 and 4.8 respectively (Chapter 6).

Based on the findings outlined above the following ion exchange system is recommended for use as a tertiary polishing process (Figure 8-1; Table 8-1). The elevated operational capacity and selectivity observed for MesoLite in both synthetic and real wastewater during batch and continuous trials means that it is the preferred zeolite to use. The process could also work with Clinoptilolite but is expected to be more effective when MesoLite is used. Design and operating selection then depend on economic aspects in comparison to an N-SAF. Critically, the brine needs to be reused for multiple cycles and ideally locally cleaned-up and reused for prolonged periods as it is the dominate component of the whole life cost (Chapter 7). Under such conditions, the process appears economically plausible across the full range of investigated EBCTs. In the current case, the clean-up was proposed using commercially available membrane technology (Liqui-Cel, 2017) that converts the recovered nitrogen into precipitated ammonium sulphate solid. Other options are available such as stripping off the ammonium and condensing for processing elsewhere. This can be achieved in a simplified version of the membrane plant, as well as alternative systems, offering the potential to convert it into a mobile systems that could service multiple sites and hence bring the economic benefits for brine clean up to the smaller scale systems. Overall, the work outlined in the thesis has demonstrated that the use of MesoLite in a zeolite filter is both technically feasible and economically plausible as a tertiary ammonium polishing process.

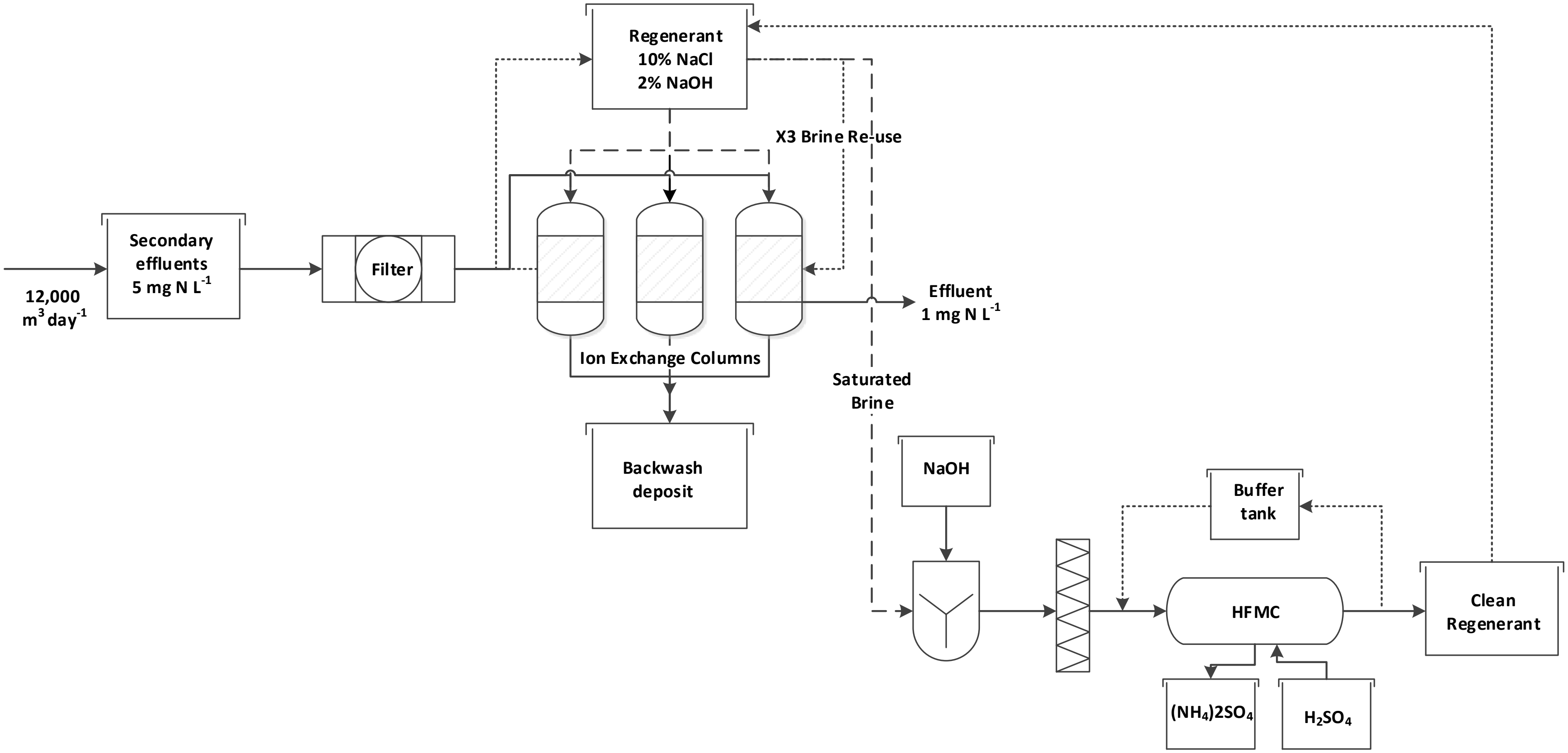

Figure 8-1 Schematic of the proposed zeolite contactor process for use as a tertiary ammonium polishing process (Chapter 7).

Table 8-1 : Summary of key design and operating parameters for the proposed zeolite contactor.

Parameter	Value	Chapter
Zeolite	MesoLite	3, 4 ,5 and 6
Pretreatment	Filtration	6
EBCT (minutes)	< 8	4, 6
Operating cycles (BV)	> 880	6
Operating cycle (days)	> 5	6
Expected Capacity (mg g^{-1})	> 7	6
Brine	NaCl	3, 6
Brine strength	1.0 M, pH 12	3, 6
Brine volume per cycle (BV)	10	6
Brine reuse	3 cycles	6
Brine clean-up	yes	6, 7

8.1 References

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9 CONCLUSIONS

The overall conclusions are presented in line with the main aim and objectives of this Ph.D. thesis.

Objective 1: Establish the impact of zeolite selection on the efficacy of a zeolite for ammonium removal.

The saturation capacity of MesoLite was 4.6 meq g^{-1} compared to 1.5 meq g^{-1} for the natural zeolites. These are associated with the zeolites pre saturated into their sodium form. The difference was attributed to the Si:Al ratio which controls the number of exchange sites within the zeolite lattice. The natural zeolites all have a Si:Al ratio between 4:1 and 5:1 compared to 1:1 for MesoLite. The capacity was substantially reduced when the zeolites were pre-saturated into the calcium form leading to a reduction of 68 % for MesoLite and between 91 and 88 % for the natural zeolites. The experimental data fit to a Freundlich isotherm model with the capacity coefficient for MesoLite being $K_f = 7.3$.

Objective 2: To understand the impact that Empty Bed Contact Time (EBCT), feed ammonia concentration, and the presence of competing ions and suspended solids on the capacity and selectivity of zeolites.

Continuous column experiments reinforced the batch studies showing the elevated operational capacity with MesoLite compared to the natural Zeolites. Increasing the EBCT increased the operating cycle between 5 days and 40 days for MesoLite compared to between 2 and 22 days for Clinoptilolite and between 3 and 27 days for Mordenite. In addition, increasing feed concentration decreased cycle time such that for an EBCT of 1.2 minutes operating cycle lasted 255 BV when fed with a 30 mg L^{-1} solution compared to 3672 BV when fed with a 5 mg L^{-1} solution. Analysis of the data with the Thomas second order rate model revealed that concentration will impact the operating cycle up to a maximum concentration of 42 mg L^{-1} when the Bv=100 mL. Therefore, it will be important during the use of the media for tertiary ammonium polishment.

Objective 3: Establish the requirements to ensure effective media regeneration.

Regeneration during synthetic trials was seen to be effective with both NaCl and KCl with a higher regeneration efficiency with KCl. This translated to being able to regenerate to the same level with a 0.2 M KCl solution compared to a 1 M NaCl solution. Translation into treatment of real wastewater no longer showed an improvement with KCl. However, operating the regeneration cycle at elevated pH (12) enabled reuse of the brine up to five times with either brine.

Objective 4: To understand the key parameters that influence the overall economic viability of using zeolites for ammonia removal from wastewater.

The use of MesoLite as an ion exchange media for tertiary ammonium polishing appears economically plausible in comparison to using a nitrifying submerged aerated filter as long as the brine is effectively managed. This means reusing the brine as much as possible and preferentially including a local brine clean up system. Sensitivity analysis revealed that the key area for future development is the operational cycle time which can be achieved by changing in operation or increasing the operational capacity of the media.

9.1 Recommendations for future work

- Performing batch equilibrium experiments in binary for different competing ions to establish the selectivity order for MesoLite (e.g. (Na^+ and NH_4^+), (Ca^{2+} and NH_4) and afterwards applying a multicomponent system. Ideally, the experimental data should be compared to the law of mass action model with Langmuir or Freundlich models.
- To study the effect that competing ions have on MesoLite in a dynamic system, tests should be performed using binary and multicomponent synthetic solutions at 1 min EBCT, specifically to understand why Ca^{2+} detrimentally affects the capacity of the zeolite.

- To be able to scale up the columns it would be recommended to perform different dynamic experiments using different bed depth and consequently applying the bed service time model which can be used in design.
- Regeneration in real effluents using KCl at high pH offered the possibility to re-use the brine during 5 consecutive cycles. Further regeneration cycles at lower KCl concentration at pH 12 would be interesting, since the high selectivity towards K^+ can lower the chemical cost.
- To have a better understanding on why the regeneration efficiency of the zeolite is drastically reduced when NH_4^+ is present in the brine it is recommended to perform batch regeneration experiments at different Na:NH_4^+ ratios in the brine, while keeping ionic strength constant to establish the critical ammonium concentration in the brine that inhibits regeneration.

APPENDICES

Appendix A – Batch equilibrium constant

A.1 Freundlich and Langmuir constants

Table A-1 Freundlich and Langmuir constant values obtained on natural and synthetic zeolites on mono-component and real wastewater effluents.

	Zeolites + NaCl adsorbing synthetic NH_4^+						Zeolites + NaCl and adsorbing NH_4^+ real wastewater					
	Freundlich Model			Langmuir Model			Freundlich Model			Langmuir Model		
Zeolites	K_F (mg g^{1})	1/n	R^2	q_{max} (mg g^{-1})	b (l mg $^{-1}$)	R^2	K_F (mg g^{1})	1/n	R^2	q_{max} (mg g^{-1})	b (l mg $^{-1}$)	R^2
MesoLite	7.18	1.16	0.98	-46.73	-0.13	0.52	2.70	0.81	0.99	27.8	0.10	0.96
US-Clinoptilolite	4.16	0.67	0.99	0.42	1.44	0.88	1.18	0.51	0.98	6.50	0.14	0.99
sMordenite	4.20	0.66	0.99	0.41	1.47	0.83	1.27	0.68	0.99	6.78	0.18	0.99
UK-Clinoptilolite	2.77	0.77	0.98	19.80	0.16	0.97	1.06	0.36	0.89	7.43	0.11	0.96
Ca-Chabazite	4.30	0.64	0.95	0.39	1.58	0.62	1.56	0.38	0.97	4.83	0.11	0.98
Na-Chabazite	2.03	1.08	0.92	-24.21	-0.073	0.90	1.26	0.54	0.78	7.72	0.12	0.83
Thermally modified US- Clinoptilolite	2.81	0.61	0.99	0.41	1.44	0.88	1.18	0.51	0.98	6.72	0.2	0.98

Appendix B – Cost analysis

B.1 CAPEX and OPEX for a N-SAF plant

Table B-1-1 CAPEX for 2,000 and 20,000 PE for NSAF plant

CAPEX			
	2,000 PE	**20,000PE**	**Reference**
N-SAF Plant	425,000	1,760,000	Severn Trent, 2018
Pumping station	100,000	190,000	Severn Trent, 2018
TOTAL	**525,000**	**1,950,00**	

Table B-1-2 OPEX for 2,000 and 20,000 PE for N-SAF plant

NSAF OPEX				
Units	**kW/year**	**£/unit**	**£/year**	**Reference**
2,000 PE				
Feed pumps	168,991	0.085	14,364	(Towler and Sinnot, 2013)
Blowers	42,340	0.085	3,599	(Butterworth et al, 2016)
Backwash Pumps	3,521	0.085	299	(Towler and Sinnot, 2013)
Manual Labour	**Frequency**	**Time (hours)**	**£/unit**	**£/year**
Flushing of valves	Weekly	0.5	26.5	691
Blower maintenance	Monthly	1	26.5	318
		TOTAL	**19,271**	

NSAF OPEX				
Units	**kW/year**	**£/unit**	**£/year**	**Reference**
20,000 PE				
Feed pumps	1,689,090	0.085	143,642	(Towler and Sinnot, 2013)
Blowers	423,400	0.085	35,989	(Butterworth et al, 2016)
Backwash Pumps	35,206	0.085	2,993	(Towler and Sinnot, 2013)
Manual Labour	**Frequency**	**Time (hours)**	**£/unit**	**£/year**
Flushing of valves	Weekly	0.5	26.5	691
Blower maintenance	Monthly	1	26.5	318
		TOTAL	**183,632**	

B.2 - Whole life cycle calculation for N-SAF Process

Table B-2 Whole Life Cycle for 2,000PE for N-SAF

2,000 PE			20,000 PE		
YEAR	**CAPEX**	**OPEX**	**YEAR**	**CAPEX**	**OPEX**
0	525,000	19,271	0	1,950,00	183,633
1		17,922	1		170,778
2		16,668	2		158,824
3		15,501	3		147,706
4		14,416	4		137,367
5		13,407	5		127,751
6		12,468	6		118,809
7		11,596	7		110,492
8		10,784	8		102,758
9		10,029	9		95,565
10		9,327	10		88,875
11		8,674	11		82,654
12		8,067	12		76,868
13		7,502	13		71,487
14		6,977	14		66,483
15		6,489	15		61,829
16		6,034	16		57,501
17		5,612	17		53,476
18		5,219	18		49,733
19		4,854	19		46,252
20		4,514	20		43,014
21		4,198	21		40,003
22		3,904	22		37,203
23		3,631	23		34,599
24		3,377	24		32,177
25		3,140	25		29,924
26		2,921	26		27,830
27		2,716	27		25,882
28		2,526	28		24,070
29		2,349	29		22,385
30		2,185	30		20,818

2,000 PE			20,000 PE		
YEAR	**CAPEX**	**OPEX**	**YEAR**	**CAPEX**	**OPEX**
31		2,032	31		19,361
32		1,890	32		18,005
33		1,757	33		16,745
34		1,634	34		15,573
35		1,520	35		14,483
36		1,414	36		13,469
37		1,315	37		12,526
38		1,223	38		11,649
39		1,137	39		10,834
40		1,057	40		10,076
CAPEX		**£ 525,000**	**CAPEX**		**£ 1,950,000**
OPEX		**£ 261,256**	**OPEX**		**£ 2,489,464**
WLC		**£ 786,256**	**WLC**		**£ 4,439,464**
Capex + (14*OPEX)		**£ 794,798**	**Capex + (14*OPEX)**		**£ 4,520,858**

B.3 Hollow fibre design constant parameters

Table B-3 Hollow fibre design parameters constant values

Parameter	**Value used**
l_{eff} (the effective membrane length (m))	0.620
ν (kinematic viscosity of water(298K))	8.93×10^{-7}
μ (dynamic viscosity of water (298K))	1.76×10^{-9}
D (the NH_3 diffusivity in water ($m^2 s^{-1}$))	1.76×10^{-9}
$D_{N'}$ (diffusivity of NH_3 ($m^2 s^{-1}$))	4.00×10^{-6}
H (the henry's constant)	6.5×10^{-4}
$\mathcal{E}$ (porosity of the membrane)	0.4
T (the pore tortuosity)	2.5
d_m (inner shell diameter (m))	0.1161
d_t (approx. centre feed tube diameter(m))	0.0254
d_f (outer fibre diameter (m))	3×10^{-4}
Q_L (regenerant flow rate set at maximum ($m^3 s^{-1}$))	1.39×10^{-3}