

Cranfield University

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**The Application of MesoLite for Ammonium Removal
from Municipal Wastewaters**

School of Applied Science
Department of Sustainable Systems
Centre for Water Science

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from Municipal Wastewaters**

Supervisor: Professor Simon A. Parsons

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Doctor of Philosophy.

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ABSTRACT

Traditional methods of ammonium removal from municipal wastewaters rely on naturally occurring biological processes, where ammonium is converted into less harmful substances before being released into the environment. These processes are extremely effective at nitrogen removal but are less responsive to shock loads, in which case they can fall short of achieving the required effluent quality. In recent years research has been conducted into the possibility of using ion exchange technology as a complementary process for the removal of ammonium from wastewater streams. Much of the research has been concerned with the performance of naturally occurring materials, zeolites, with much of the work being undertaken at laboratory scale using synthetic solutions. This study investigates the performance of the modified media, MesoLite, using real and synthetic solutions, at both laboratory and pilot scale, in the presence of competing cations. Initial studies were performed under batch conditions to assess the effect of a number of parameters such as contact time, solution ammonium concentration and pH on the uptake of ammonium on to MesoLite. This was followed by an investigation into a number of design parameters under dynamic conditions, leading to a pilot scale examination of the potential of the process to be used for the application of removing ammonium from low concentration wastewater treatment works effluents. Subsequent experiments were performed pilot scale to investigate the benefit of using the ion exchange process for ammonium removal from high strength liquors arising from the sludge dewatering process. Results indicate that a range of parameters affects the performance of the media and optimum performance is observed at high ammonium concentrations with increased contact time at pH 6-7. Results also show that MesoLite was successful in removing ammonium from high concentration sludge liquors, giving a total capacity of 47-51 g $\text{NH}_4^+\text{-N kg}^{-1}$ and an operational capacity of 27-36 g $\text{NH}_4^+\text{-N kg}^{-1}$. The treatment of low concentration effluents return a total capacity of 19 g $\text{NH}_4^+\text{-N kg}^{-1}$ and an operational capacity of 9.5 g $\text{NH}_4^+\text{-N kg}^{-1}$. However, this reduced capacity is offset by the significant increase run time, from 1.5 to 22 days, and an increase in the amount of liquid treated from 140 bed volumes to in excess of 6000 bed volumes.

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ABBREVIATIONS AND NOTATIONS

Abbreviations

BOD – Biological oxygen Demand
BV – Bed volume based on void space
CEC – Cation exchange capacity
COD – Chemical oxygen demand
CSTR – Continually stirred tank reactor
EA – Environment Agency
EBCT – Empty bed contact time
HRT – Hydraulic retention time
IZA – International Zeolite Association
meq – milliequivalents
 NH_4^+ – Ammonium
 $\text{NH}_4^+\text{-N}$ – Ammonium nitrogen
PAC – Powdered activated carbon
PBU – Primary building unit
PE – Population equivalent
RAS – Return activated sludge
RQO – River quality objective
SAS – Surplus activated sludge
SBR – Sequencing batch reactor
SBU – Secondary building unit
SRT – Solids retention time
TSS – Total suspended solids
USEPA – United States Environmental Protection Agency
WwTW – Wastewater treatment works

Notations

b – Constant in the Langmuir Equation
 C_b – Breakthrough ammonium concentration
 C_e – Equilibrium ammonium concentration or effluent ammonium concentration

- C_0 – Initial or influent solution ammonium concentration
- k – Constant in the Freundlich Equation
- K – Constant in the Langmuir Equation
- n – Constant in the Freundlich Equation
- q – Mass of ammonium removed from solution
- $q_{\max}$ – Mass of ammonium removed from solution at exhaustion
- Q – Mass of ammonium exchanged per unit mass of media
- Q_e – Mass of ammonium exchanged per unit mass of media at equilibrium
- $Q_{\max}$ – Mass of ammonium exchanged per unit mass of media at exhaustion
- t_b – Time to reach breakthrough concentration
- $t_{(90)}$ – Time to reach 90 % equilibrium

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Project background

Incoming wastewaters to wastewater treatment works (WwTW's) comprise a number of constituents, which if left unmanaged, can have a detrimental effect on the natural environment. The principal aim of wastewater treatment is to effectively control the effluent concentrations of such pollutants, reducing them to levels deemed safe enough for discharge into receiving waters. One such constituent is ammoniacal nitrogen, which is present either as ammonia (NH_3) or more commonly ammonium (NH_4^+). The release of excess amounts of ammonium into surface waters can be extremely toxic to fish and other aquatic life and concentrations in the range 0.2 to 0.5 mg l^{-1} can be fatal (Weatherley and Miladinovic, 2004). In the developed world, increasingly strict discharge consent levels for ammoniacal nitrogen are being imposed (Karadag *et al.*, 2006) and it is not unreasonable to assume that in years to come, developing nations will follow suit. The council of the European Union (1980) has set a guide level of 0.05 mg l^{-1} and a maximum level of 0.5 mg l^{-1} and the American Committee on Water Quality (1995) recommends a limit of 0.02 mg l^{-1} (Weatherley and Miladinovic, 2004).

For any specific WwTW in the UK, the effluent discharge consent level is driven by the river quality objective (RQO). This is a standard imposed by the Environment Agency (EA), which sets a target ammonium concentration for each stretch of river under its control. Therefore, the ammonium discharge consent level for any particular WwTW will depend on the RQO and the amount of dilution the effluent receives when entering a particular stretch of river. This causes a two-fold issue in the Thames Water region. Firstly, water quality in the South East, is historically higher than that in the rest of the UK, leading to more stringent RQO's which in turn lead to lower discharge consent levels. Secondly, within the Thames Water region there are large urban areas (e.g. Swindon, Basingstoke, Aylesbury and Crawley) situated at the head of sensitive chalk streams. These are areas of high growth, which all discharge into very small watercourses, resulting in low effluent dilution. In these cases the effluent effectively has to meet the already stringent RQO before it can be discharged into the

river. Therefore, in these sensitive areas, the need for efficient ammonium removal from municipal wastewater streams is becoming increasingly critical.

The removal of ammonium from wastewaters can be achieved by a number of methods including biological nitrification/denitrification; air stripping; ion exchange and break point chlorination followed by treatment with activated carbon (Jorgensen *et al.*, 1976). The current preferred method adopted across much of the United Kingdom is nitrification/denitrification, where ammonium is biologically transformed by a series of processes to nitrite, nitrate and finally nitrogen gas (Hedstrom, 2001). However, biological processes although effective, lack the ability to react to shock ammonium loads and Thames Water is keen to investigate additional methods of ammonium removal in order to ensure that WwTW effluents are maintained below discharge consent levels. An option does exist within wastewater treatment to consider ammonium removal using ion exchange as a complementary process at problematic sites.

Two elements of the wastewater treatment process (Figure 1.1) are of particular interest when considering ion exchange as a practical solution. Firstly, high concentration liquors ($200\text{--}700\text{ mg NH}_4^+\text{-N l}^{-1}$) arising from the digested sludge dewatering process are recycled back to the inlet and constitute a significant proportion of the ammonium to be treated by the biological processes in the secondary treatment stage. Direct treatment of these liquors, to more manageable concentrations, could reduce the strain placed on mainstream treatment processes and help ensure that discharge consent levels are met (Mackinnon *et al.*, 2003). Secondly, at sites which have effluent ammonium concentrations approaching or even exceeding consent, it is possible to directly treat the effluent prior to release into surface waters (Beler Baykal and Guven, 1997).

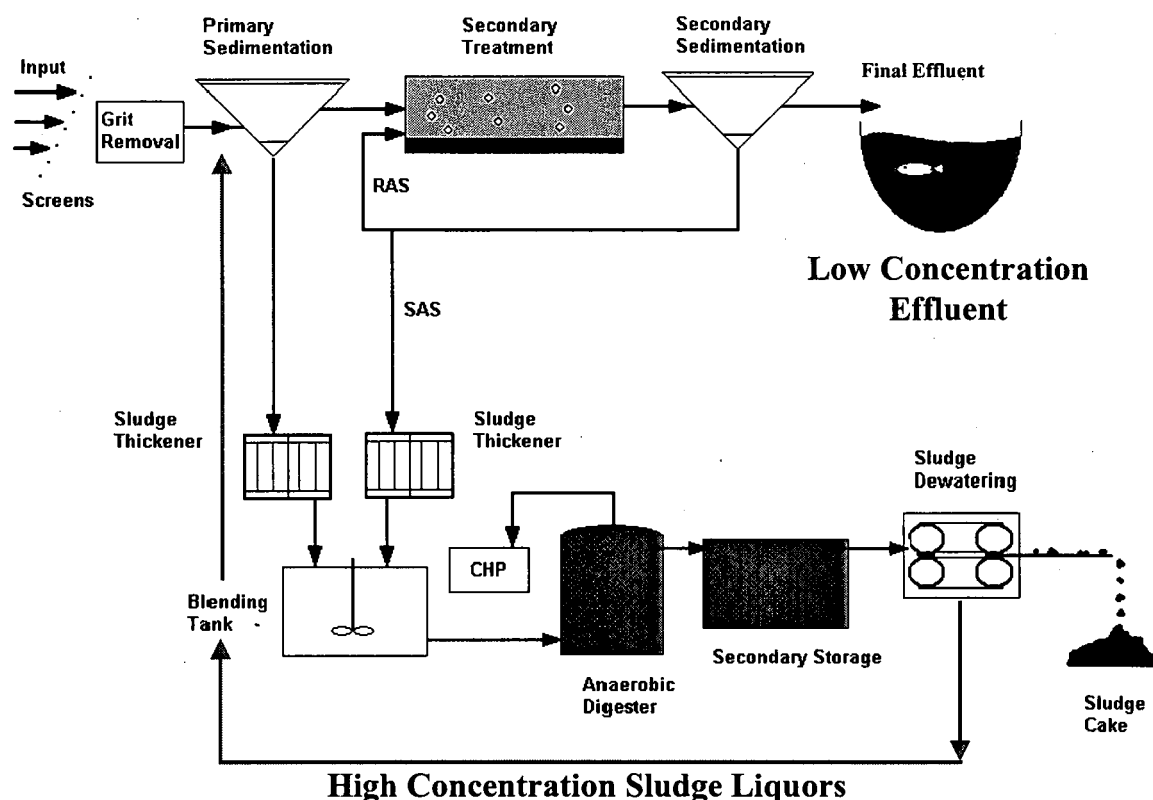


Figure 1.1 Simplified schematic diagram of a wastewater treatment process.

During the ion exchange process the ammonium ion is removed from wastewater by feeding the solution through a column or columns packed with exchange media (Bolto and Pawlowski, 1987), where the ammonium is transferred from the liquid on to the ion exchange media. Once the media is fully saturated with ammonium it can be replaced with fresh media but is more commonly regenerated by passing a brine solution through the column. The ammonium ions are displaced by cations (e.g. sodium) in the brine and the media can again be used for ammonium removal (Hedstrom, 2001).

Numerous studies have been undertaken to assess the potential of the naturally occurring mineral, zeolite, as an ion exchanger for the removal of the ammonium ion from problematic streams, with almost all research focusing on the use of clinoptilolite (Jorgensen *et al.*, 1976; Semmens and Porter, 1979; Hlavay *et al.*, 1982; Booker *et al.*, 1996; Baler-Baykal and Guven, 1997; Nguyen and Tanner, 1998; Weatherly and McVeigh, 2000; Hankins *et al.*, 2004; Farkas *et al.*, 2004; Du *et al.*, 2005; Sprynsky *et al.*, 2005). Results indicate that the removal of ammonium using

ion exchange has potential, with removal efficiencies in excess of 95 % being reported and media capacities in the range $0.94 \text{ g NH}_4^+\text{-N kg}^{-1}$ (Jorgensen *et al.*, 1976) to $21.52 \text{ g NH}_4^+\text{-N kg}^{-1}$ (Sprynskyy *et al.*, 2005). It is widely accepted that that clinoptilolite is the most suitable naturally occurring material for this process due to its high selectivity for the ammonium ion (Jung *et al.*, 2004). However, the majority of studies were undertaken at laboratory scale with only a small number being performed at pilot scale, and to date, full scale implementation remains unreported. Consequently, further research is required on the practical application of the ion exchange process for the treatment of streams arising from municipal wastewater treatment. Furthermore, due to the heterogeneous nature of naturally occurring materials, there is a difficulty in obtaining consistent results (De Silva, 1999) and modified or manufactured materials could provide a possible solution.

Recent studies performed on the modified media, MesoLite, (Mackinnon *et al.*, 2003) indicate that the media consistently returns an ammonium exchange capacity in the range $45\text{-}55 \text{ g NH}_4^+\text{-N kg}^{-1}$, which is significantly greater than that of naturally occurring materials. MesoLite media is produced by the chemical modification of clay and other aluminium-bearing minerals. The derivatives of these clays or aluminium-bearing materials are characterised by a predominance of tetrahedrally coordinated Al^{3+} , which has resulted from the chemical modification of octahedrally coordinated Al^{3+} in the parent mineral. This transformation of the atomic scale structure results in a higher number of exchange sites than would normally be available in the original clay structure (Mackinnon *et al.*, 2006).

The increased ammonium exchange capacity of MesoLite, compared to that of clinoptilolite, further increases the appeal of ion exchange and it is perceived that at some time in the future there will be an operational need for such a process within the Thames Water wastewater treatment network. However, although there is much published data on the performance of clinoptilolite, little scientific data is available for MesoLite. Consequently, further work is required to investigate the performance of the media and establish its effective capacity for the treatment of both low concentration effluents and high concentration sludge liquors. The focus of this thesis is to establish the effect of a range of parameters such as pH, contact time, influent

ammonium concentration and the required breakthrough concentration at both laboratory and pilot scale using synthetic and real solutions.

1.2 Project development

The work presented in this thesis was undertaken in conjunction with two research groups, well recognised for their contribution to research in the treatment of municipal wastewater: Thames Water Utilities Limited and Cranfield University. Investigations were concerned with the removal of ammonium from high concentration solutions arising from the dewatering of digested sludge. The project also examined the performance of the ion exchange process for the removal of ammonium from intermediate and low concentration solutions with particular attention being paid to the influence of operating conditions and design parameters on the effectiveness of the media as an ion exchanger under such conditions.

1.3 Aims and objectives

The purpose of this thesis is to broaden the understanding of the ion exchange process for the removal of ammonium from both high and low ammonium concentration municipal wastewaters using MesoLite media, with a view to optimising the process for a range of operating conditions. Consequently, a number of objectives were identified.

- To determine the capacity of the media and establish whether or not it is significantly greater than capacities reported for other materials previously studied.
- To investigate the performance of the media under both batch and dynamic conditions with a view to establishing whether or not batch experiments can be used to successfully predict the performance of the media.
- To develop a pilot scale reactor to evaluate the performance of the media both as an ion exchanger and suspended solids filter for the treatment of low concentration effluents in the presence of competing cations.

- To develop a pilot scale reactor to evaluate the performance of the ion exchange process for the treatment of high concentration recycle streams in the presence of competing cations.
- To investigate the effect of a number of operating parameters on the performance of the media including competing cations; breakthrough concentration; influent ammonium concentration; contact time and pH.

1.4 Thesis plan

This thesis is presented in paper format. All papers were written by the first author Andrew Thornton and edited by Professor Simon A. Parsons (academic supervisor) and Pete Pearce (industrial supervisor). All experimental work was conducted by the first author.

The work begins with a review of the literature on the removal technologies employed for the removal of ammonium from high strength recycle streams with a particular emphasis on the effectiveness of the ion exchange process (Chapter 2-submitted: Thornton, A., Pearce, P. and Parsons, S. A. *Methods for ammonium removal from wastewater sidestreams with a focus on ion exchange using zeolites: a review. Reviews in Environmental Science and Biotechnology*, 2007).

Chapters 3 to 6 cover the technical content of the thesis. Chapter 3 reports the results from laboratory investigations in to the effect of parameters such as contact time, solution concentration, pH and solution cations on the capacity of the media under batch conditions. (Chapter 3-published: Thornton, A., Pearce, P. and Parsons, S. A. *Ammonium removal from solution using ion exchange on to MesoLite: an equilibrium study. Journal of Hazardous Materials*, 2007).

Chapter 4 investigates the performance of the media under dynamic conditions with a view to assessing the effect of media bed depth, contact time, initial solution concentration and breakthrough concentration on both process efficiency and media capacity. The aim is to establish a process to assist in the design of future ion exchange processes for the treatment of municipal wastewaters. (Chapter 4-submitted:

Thornton, A., Pearce, P. and Parsons, S. A. *Ammonium Removal from Solution using ion Exchange on to MesoLite: A Dynamic. Microporous and Mesoporous materials*).

Chapter 5 examines the effectiveness of the media at pilot scale for the treatment of low concentration municipal wastewater effluent, with a particular view to assessing the impact of competing cations present in solution. The possibility of the media to act as a solids filter is also investigated. (Chapter 5-submitted: Thornton, A., Pearce, P. and Parsons, S. A. *Ammonium removal from wastewater treatment effluent by ion exchange on to MesoLite. Water Research*).

Chapter 6 evaluates the performance of the media for the removal of ammonium from high strength digested sludge liquors at pilot scale with a view to establishing both the total and operating capacity of the media. (Chapter 6-published: Thornton, A., Pearce, P. and Parsons, S. A. (2007) *Ammonium removal from digested sludge liquors using ion exchange. Water Research* **41** 433-439).

1.5 References

Belér Baykal, B. and Guven, D. A. (1997) Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater. *Water, Science and Technology* **35** (7), 47-54.

Bolto, B. A. and Pawlowski, L. (1987) Wastewater treatment by ion exchange, E and FN Spon, New York.

Booker, N. A., Cooney, E. L. and Priestly, A. J. (1996) Ammonia removal from sewage using natural Australian zeolite. *Water, Science and Technology* **34** (9), 17-24.

DeSilva, F. J. (1999) Essentials in ion exchange. Presented at the 25th Annual WQA Conference.

Du, Q., Shijun Liu, Q. D., Zhonghong, C. and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese Clinoptilolite. *Separation and Purification Technology* **44** 229-234.

Farkas, A., Rozic, M. and Barbaric-Mikocevic, Z. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* B117 25-33.

Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) Removal of NH_4^+ ion from NH_4Cl solution using clinoptilolite: A dynamic study using a continuous packed-bed column in upflow mode. *Separation Science and Technology* **36** (9), 1347-1364.

Hedstrom, A. (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of Environmental Engineering* **August 2001**, 673-681.

Hlavay, J., Vigh, G., Olaszi, V. and Inczedy, J. (1982) Investigation on natural Hungarian zeolite for ammonia removal. *Water Research* **16**, 417-420.

Jorgensen, S. E., Libor, O. Graber, K. L. and Barkacs, K. (1976) Ammonia removal

by use of clinoptilolite. *Water Research* **10**, 213-224.

Jung, J., Chung, Y., Shin, H. and Son, D. (2004) Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR Process. *Water Research* **38**, 347-354.

Karadag, D., Koc, Y., Turan, M. and Armagan, A. (2006) Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. *Journal of Hazardous Materials* B136 604-609.

Mackinnon, I. D. R., Millar, G. and Stoltz, W. (2006) Hydrothermal Synthesis of Zeolite N Aluminosilicates, *WIPO publication number*, W0/2006/096930.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient removal from wastewaters using high performance materials. *Water, Science and Technology* **47** (11), 101-107.

Nguyen, M. L. and Tanner C. C. (1998) Ammonium removal from wastewaters using natural New Zealand Zeolites. *New Zealand Journal of Agricultural Research* **41** 427-466.

Semmens, M. J. and Porter, P. S. (1979) Ammonium removal by ion exchange: Using biologically restored regenerant. *Journal WPCF* **51** (12), 2928-2940.

Sprynskyy, M, Lebedynets, M, Terzyk, A. P, Kowalczyk, P, Namiesnik, J. and Buszewski, B. (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Colloid and Interface Science* **284** 408-415.

Weatherly, L. R. and McVeigh, R. J. (2000) The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria In: *Proceedings of IEX 2000, Ion Exchange at The Millennium*, 16- 21 July, Cambridge, England. pp 133-141.

Weatherley, L. R. and Miladinovic, N. D. (2004) Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research* **38**, 4305-4312.

CHAPTER 2

**METHODS FOR AMMONIUM REMOVAL FROM WASTEWATER
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A REVIEW**

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2. METHODS FOR AMMONIUM REMOVAL FROM WASTEWATER SIDESTREAMS WITH A FOCUS ON ION EXCHANGE USING ZEOLITES: A REVIEW

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Key Words: ammonium, sidestreams, ion exchange, sludge liquors, zeolite, clinoptilolite.

Abstract

This review is concerned with the application of ion exchange processes for the removal of ammonium (NH_4^+) from liquors arising from the treatment of municipal wastewater, in particular highly concentrated streams (typically 200-700 mg $\text{NH}_4^+\text{-N l}^{-1}$) resulting from the sludge digestion and dewatering process. The role of the naturally occurring mineral zeolite (mainly clinoptilolite) as a material selective for the ammonium ion is discussed along with the merits of other systems (both chemical and biological) developed for the direct treatment of high strength ammonium liquors. General concepts of ion exchange; zeolite origin and structure; loading and regeneration characteristics and ammonium exchange capacities are included as well as factors which influence the uptake of ammonium during the loading phase. Conclusions from this review are that the majority of previous work was undertaken at laboratory scale with the use of synthetic liquors and these studies only go part of the way in assessing the feasibility of ion exchange treatment applied to wastewater at full scale. Full scale treatment employing this technique is relatively scarce but where implemented some degree of success has been achieved. However, the heterogeneous nature of naturally occurring deposits makes it difficult to consistently quantify the parameters within which such a process could operate.

2.1 Introduction

Domestic wastewaters comprise many organic and inorganic constituents, amongst these are organic nitrogen compounds derived from urine and faeces. During the transport to wastewater treatment works (WwTW's), much of the organic nitrogen is decomposed to form ammonium (Hedstrom, 2001). In countries such as the UK, consent levels for the amount of ammonium contained in the final effluent invariably dictates the need for a nitrogen treatment step to be included as part of the wastewater treatment process. It is not uncommon for consent levels to be as low as 1mg l^{-1} (Pearce *et al.*, 2000).

Nitrogen removal is generally achieved using a biological, nitrification-denitrification process, where ammonium is transformed firstly to nitrite, then to nitrate and finally nitrogen gas (Hedstrom, 2001).

As well as incoming wastewater, processes within WwTW's, such as sludge dewatering, may also contribute to the ammonium load applied to the nitrogen removal step. Belt presses, centrifuges and other dewatering measures all produce liquids, referred to as sidestreams, as process products (USEPA Report 1985). These are commonly fed back to the head of the works (Figure 2.1) and depending on their source, can markedly increase the ammonium loading on to the WwTW and in many cases these recycled liquors can constitute 8 – 25 % of the total nitrogen load going to the head of the works (Mackinnon *et al.*, 2003; Pearce *et al.*, 2000; Janus and van der Roest, 1997; Siegrist, 1996; Jeavons *et al.*, 1998). Due to urban expansion and the ever decreasing consent levels being imposed upon wastewater treatment works (Pearce *et al.*, 2000; Beler- Baykal *et al.*, 1994; Kamarowski and Yu, 1997), many plants may find themselves in the position where the design capacity for ammonium removal is being approached or even exceeded. Occasionally recycled liquors are only introduced to the head of the works at night, when incoming loads are at their lowest (Pearce *et al.*, 2000). It is not therefore unreasonable to assume that in the future some treatment processes may not be able to sustain a level of treatment required to meet the effluent consent values imposed.

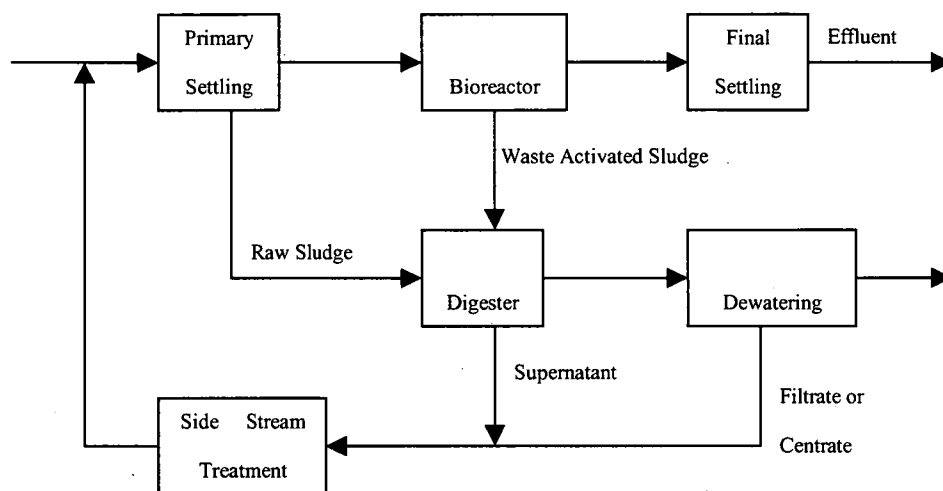


Figure 2.1 Process flow sheet for wastewater treatment (Mackinnon *et al.*, 2003)

2.2 Sidestreams and their characteristics

Sidestreams at WwTW's originate from either liquid treatment or the sludge handling process. Although the flow volumes of sidestreams are low in comparison to the overall flow (generally 5–10 %), USEPA Report (1985), they can contain significant quantities of organic and inorganic material. Janus and van der Roest, (1997) noted that sidestreams in Dutch WwTW's contributed up to 25 % of the total nitrogen load, yet the contribution to the total influent flow volume was only 2%. All sidestreams comprise the same constituents as the plant influent. However, the distribution of these constituents will be quite different and will not reflect that of those in the plant influent either proportionately or quantitatively (Evans *et al.*, 1987). Very little published data is available on the characteristics of sidestreams (USEPA Report, 1985). This arises from the fact plant operators are more inclined to monitor mainstreams as an indicator of plant performance than they are sidestreams. What quality data that is available is presented in Tables 2.1 and 2.2.

Table 2.1 Summary of sidestream characteristics

Liquor Type	Location	NH ₄ ⁺ -N (mg l ⁻¹)	Suspended Solids (mg l ⁻¹)	pH	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	PO ₄ -P (mg l ⁻¹)	Reference
Digester Effluent	Akeshov-Nockeby WwTW (Stockholm)	700	-	-	-	-	-	Hultgren and Hultman, 1984
Secondary Effluent	West Bari	7.4 - 20	-	-	-	-	-	Liberti <i>et al.</i> , 1986
Digester Effluent	Germany	950	1000	-	-	-	210	Fawcett <i>et al.</i> , 1995
Raw Sludge	Knostrop WwTW (Leeds)	250	300	-	-	-	-	Abeling and Seyfried, 1992
Digester Supernatant	-	800	-	7.5	-	-	360	Booker <i>et al.</i> , 1999
Sludge Liquor	Hiagari WwTW (Kitakyushu City)	423 - 623	38 - 136	7.7	-	9.4 - 14.3	66.5 - 121	Matsumiya <i>et al.</i> , 2000
Digester Effluent	Istanbul Landfill Sites	2170	-	8.11	180	-	-	Kabdasli <i>et al.</i> , 2000
Digester Supernatant	85,000 PE WwTW	165	-	7.4	274	50	13	Battistoni <i>et al.</i> , 2000
Digester Liquor	Germany	628	2900	-	-	-	-	Kolisch and Rolfs, 2000
Digester Centrate	Oxley Creek (Australia)	820	1100	-	-	-	-	Munch and Barr, 2000
Drying Bed	Woking WwTW	441	2025	-	-	-	-	Pearce <i>et al.</i> , 2000
Belt Press Liquors	Reading WwTW	400	200	-	-	-	-	Pearce <i>et al.</i> , 2000
Belt Press Liquors	Wargrave WwTW	651	242	-	-	-	-	Pearce <i>et al.</i> , 2000

Liquor Type	Location	NH ₄ ⁺ -N (mg l ⁻¹)	Suspended Solids (mg l ⁻¹)	pH	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	PO ₄ -P (mg l ⁻¹)	Reference
Settled Sludge Liquor	Barston WwTW	523	-	7.6	257	46	2	Parsons <i>et al.</i> , 2001
Settled Sludge Liquor	Coleshill WwTW	888	-	7.9	94	19	96	Parsons <i>et al.</i> , 2001
Settled Sludge Liquor	Mansfield WwTW	872	-	7.9	123	52	65	Parsons <i>et al.</i> , 2001
Settled Sludge Liquor	Milcote WwTW	426	-	7.5	165	34	9	Parsons <i>et al.</i> , 2001
Settled Sludge Liquor	Oswestry WwTW	658	-	7.2	185	31	80	Parsons <i>et al.</i> , 2001
Settled Sludge Liquor	Spernal WwTW	660	-	7.6	321	53	8	Parsons <i>et al.</i> , 2001
Settled Sludge Liquor	Wanlip WwTW	957	-	7.7	188	41	99	Parsons <i>et al.</i> , 2001
Digested Sludge Liquor	Slough WwTW	615	-	7.6	56	44	94.9	Parsons <i>et al.</i> , 2001
Digester Effluent	Turkey (Molasses Treatment)	1400	-	7.9	21.2	21.4	-	Celen and Turker, 2001
Digester liquor	Werdhoelizli WwTW (Zurich)	657	344	7.78	-	-	-	Fux <i>et al.</i> , 2002
Digester liquor	Au WwTW (St. Gallen)	619	384	7.37	-	-	-	Fux <i>et al.</i> , 2002
Digester Effluent	Pontevedra (Spain)	1060	150	8.3	-	-	-	Mosquera-Corral <i>et al.</i> , 2005

Table 2.2 Treatment processes and resulting sidestream characteristics (USEPA Report 1985).

Treatment Process	Type of Sidestream	BOD (mg l ⁻¹)	TSS (mg l ⁻¹)
Gravity Thickener	Supernatant	100-1200	200-2500
Dissolved Air Flotation	Supernatant	50-1200	100-2500
Anaerobic Digestion	Supernatant	100-2000	100-10000
Aerobic Digestion	Decant	100-2000	100-10000
Heat Treatment	Decant Liquor	1600-12000	100-10000
Wet Air Oxidation	Decant Liquor	3000-15000	100-10000
Purifax	Decant Liquor	1000-3000	100-3000
Sludge Lagoon	Supernatant	100-200	50-200
Sludge Drying Bed	Underdrainage	20-500	20-500
Vacuum Filter	Filtrate	100-1000	200-4000
Belt Filter Press	Filtrate	50-500	100-2000
Filter Press	Filtrate	50-250	50-1000

Most of the available data is concerned with liquors arising from sludge digestion at WwTW's. $\text{NH}_4^+\text{-N}$ concentrations are in the range 165 mg l⁻¹ (Battistoni *et al.*, 2000) to 957 mg l⁻¹ (Parsons *et al.*, 2001) with the majority being in excess of 400 mg l⁻¹ (Table 2.1). Higher concentrations are reported for digester liquors arising from the treatment of more specific wastes, for example, fish cannery effluent (Mosquera-Corral *et al.*, 2005) and molasses (Celen and Turker 2001) with concentrations of 1060 and 1400 mg l⁻¹ $\text{NH}_4^+\text{-N}$ respectively. These concentrations are considerably higher than those seen in both raw and settled sewage. Values reported by Parsons *et al.*, (2001) for Slough WwTW are 16.1mg l⁻¹ $\text{NH}_4^+\text{-N}$ for raw sewage and 23.9 mg l⁻¹ $\text{NH}_4^+\text{-N}$ for settled sewage. Suspended solids concentrations reported in Table 2.1 range from 36 mg l⁻¹ (Matsumiya *et al.*, 2000) to 2900 mg l⁻¹ (Kolisch and Rolfs, 2000). This is supported by figures reported in Table 2.2 where the majority of values are in the range 50-3000 mg l⁻¹, although some can be as high as 10,000 mg l⁻¹ (USEPA report 1985). Where reported, all sidestreams fall within the pH range 7.2-8.3.

Factors affecting sidestream characteristics include; the plant influent composition; the treatment processes utilised; equipment sizing; operating schedules and plant and process performance (Evans *et al.*, 1987). A change in any or a combination of these factors will influence the following characteristics; concentration and form of the constituents as well as their settling, thickening, dewatering, stabilization and oxidation properties (Evans *et al.*, 1987).

Generally it is not cost effective to use separate treatments for sidestreams i.e. high concentration-low flow and for this reason they are generally returned to the head of the works, although selected sidestreams are sometimes recycled into secondary treatment units (USEPA Report, 1985). However, problem sidestreams can contribute significant pollutant load on the plant due to a high concentration of one or a combination of the following factors, BOD, COD, NH_4^+ , organic nitrogen, P or suspended solids (Evans *et al.*, 1987). Here, separate biological or chemical treatment may prove essential (Pearce *et al.*, 2000; Jeavons *et al.*, 1998).

2.3 Minimising the effect of recycled high strength ammonium

Direct treatment of sidestream liquors is relatively uncommon (USEPA Report, 1985) and this review is concerned mainly with their treatment using natural zeolites as ammonium exchangers. In many cases the extra load incurred at the inlet can be mitigated against by modification of mainstream processes by methods including: equalisation of the supernatant flow with the overall loading profile of the WwTW (la Cour Jansen *et al.*, 1996), an increase in the volume of the anoxic zone coupled with an increased solids retention time (Siegrist, 1996) or the introduction of methanol as an additional carbon source for the denitrification process (Purtschert *et al.*, 1996; Siegrist, 1996).

La Cour Jansen *et al.*, (1996) investigated the possibility of minimising the impact of recycled sludge liquors by introducing a flow equalisation system at the Klagsham WwTW in Sweden. They considered a strategy where full flow equalising over 24 hours was performed by constructing a 120 m³ holding tank for the storage of liquors from the sludge dewatering process. These were then discharged in periods of low

loading in order to obtain a relatively constant ammonium loading ahead of the anoxic reactor. Equalisation of the flow over 24 hours resulted in a more constant effluent nitrate-N concentration of approximately 8 mg l^{-1} compared with $5\text{--}13 \text{ mg l}^{-1}$ prior to equalisation. The ammonium peaks of 2 mg l^{-1} were also minimised resulting in a constant low concentration of approximately $0.5 \text{ mg l}^{-1} \text{ NH}_4^+$.

Siegrist, (1996) concluded that, where the supernatant constituted 15 –20% of the total nitrogen load at the works inlet and the volume of the anoxic zone was 25% of the total activated sludge volume, then denitrification of the excess nitrogen could be accommodated by an extension of the anoxic volume by 20% and an increase in the solids retention time (SRT) from 11 to 15 days. This relies on the assumption that the existing infrastructure can accommodate these modifications.

An alternative to increasing the anoxic volume is the introduction of an additional carbon source to support denitrification, delivering a higher nitrogen removal efficiency for a given reactor volume. Purtschert *et al.*, (1996), indicated that denitrification was 55% with methanol addition and 35% without based on the total nitrogen in the influent and the adaptation period of the methanol degrader was only a few days. Approximately 3.5 kg of methanol was required per kg of $\text{NO}_3\text{-N}$ denitrified. Another alternative is denitrification in existing tertiary filters supported by the addition of methanol (Siegrist, 1996). This was performed in the gravity filter of the Werdhölzi plant in Switzerland where $10 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ liquor was denitrified with methanol addition at a surface loading rate of $6\text{--}10 \text{ m h}^{-1}$. As long as the influent nitrate load is used to control methanol addition practically no methanol is present in the filter effluent. However, extra methanol is required for oxygen reduction in the filter inlet water, resulting in a 25% increase in methanol usage (4.5 kg methanol per kg $\text{NO}_3\text{-N}$ denitrified).

2.4 Direct sidestream treatment

A number of alternative processes have been investigated for the suitability of reducing the ammonium concentration of recycled liquors to manageable concentrations. These include: recovery as magnesium ammonium phosphate (Celen and Turker, 2001; Kabdasli *et al.*, 2000; Siegrist, 1996; Siegrist *et al.*, 1992; Schulze-Rettmer, 1991; Booker *et al.*, 1999); air stripping (Siegrist, 1996; Kabdasli, 2000; la Cour Jansen *et al.*, 1993); various biological nitrification/denitrification processes (Siegrist, 1996; Siegrist *et al.*, 2000; Pickin and Saunders, 1994; Kolisch and Rolfs, 2000; Rostron *et al.*, 2001; la Cour Jansen *et al.*, 1993; Hultgren and Hultman, 1984; Abeling and Seyfried, 1992) including the Sharon process, the Anammox process or a combination of the two (Fux *et al.*, 2002; Fux *et al.*, 2003; Jetten *et al.*, 1997; van Dongen *et al.*, 2001; Mosquera-Corral *et al.*, 2005; Khin *et al.*, 2004; Schmidt *et al.*, 2003).

2.4.1 Recovery of ammonium as magnesium ammonium phosphate (struvite)

Many authors have discussed the merits of struvite precipitation for the recovery of phosphorus from industrial wastewaters (Battistoni *et al.*, 2000; Matsumiya *et al.*, 2000; Parsons *et al.*, 2001; Williams, 1999). Struvite recovery is very much dependent of the molar ratios of magnesium ammonium and phosphate where a 1:1:1 molar ratio is preferable (Kummel *et al.*, 2005). For this reason most liquors are more suitable for phosphorus recovery because in general there is an excess of ammonium present for the process and only the chemical addition of magnesium is required for optimum phosphorus recovery. Williams, (1999) concluded that no stream is ideal for the formation of struvite but it may be possible to combine two separate flows, one with high P and low N and the other with low P and high N (e.g. surplus activated sludge liquor and digested sludge centrate) to produce a more acceptable liquor. As single streams, digested sludge liquors typically have the highest potential to form struvite although this is usually limited by the magnesium concentration of the liquor (Parsons *et al.*, 2001). However, when considering struvite precipitation for ammonium recovery, the amount of phosphorus also becomes a limiting factor and for optimum recovery both magnesium and phosphorus chemical addition is required (Siegrist *et al.*, 1992; Schulze-Rettmer, 1990). Booker *et al.*, (1999) concluded that if only the

phosphorus available in the digester supernatant was used for struvite precipitation, then only 20% of the ammonium in the liquor would be removed, leaving the remainder to be recycled back to the head of the works. Furthermore, pH is a main driving force behind struvite formation with the formation potential increasing with increased pH (Parsons *et al.*, 2001), the optimum pH being between 8.5 and 9 (Celen and Turker, 2001). The pH can be somewhat increased by using magnesium oxide as the source of magnesium for the process but further increase may be gained by the separate addition of sodium hydroxide (Siegrist, 1996; Schultz-Rettmer, 1990; Kabdasli *et al.*, 2000).

Consequently, systems designed for ammonium recovery as struvite consist of three reactors operated in series (Siegrist *et al.*, 1992; Shultz-Rettmer, 1990), with phosphoric acid added to the first reactor as a source of phosphate, magnesium oxide to the second reactor as a source of magnesium and sodium hydroxide to the third reactor for optimising pH conditions for precipitation. A simplified schematic diagram of the process can be seen in Figure 2.2. Ahead of the first reactor remaining suspended solids in the digester liquors can be eliminated by flocculation with a highly cationic polyelectrolyte (Siegrist, 1996). Results from pilot scale studies indicate that the precipitation of 1 kg $\text{NH}_4^+\text{-N}$ produces 17.5 kg of struvite and requires the addition of 9.5 kg 75% H_3PO_4 , 4.0 kg MgO and 4.0 kg 30% NaOH (Siegrist *et al.*, 1992). These studies were conducted on liquors containing 600-1000 mg l^{-1} $\text{NH}_4^+\text{-N}$, with a hydraulic loading of 500 l h^{-1} with an ammonium removal efficiency of 85-90%.

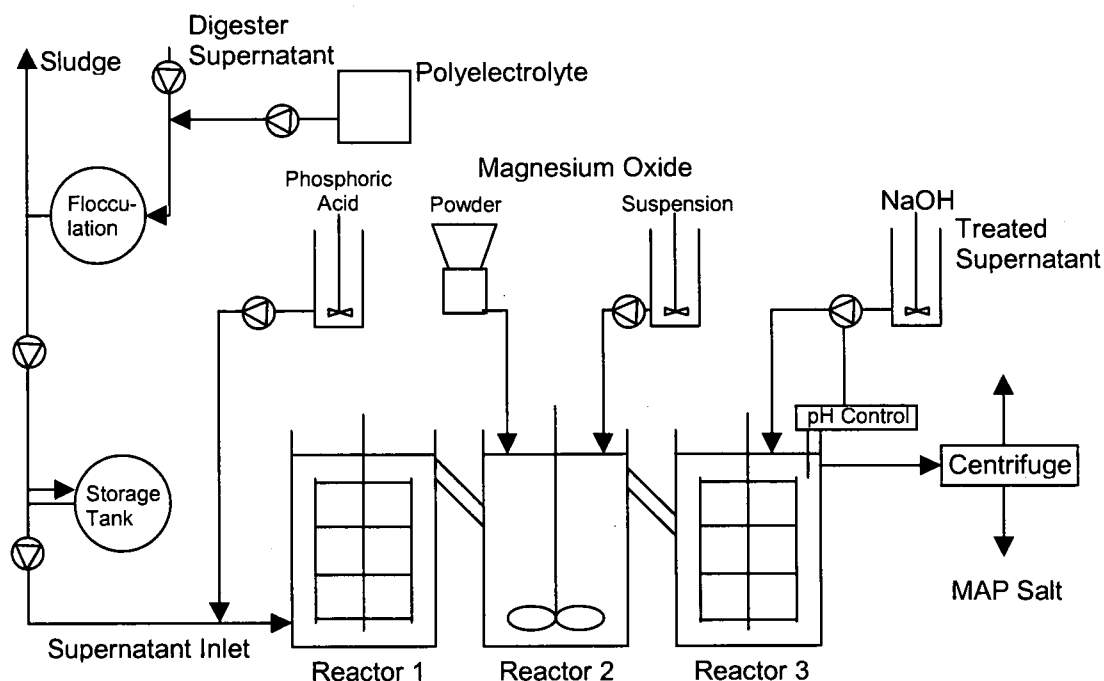


Figure 2.2 Process schematic for ammonium removal as struvite (Siegrist 1992)

Bench scale experiments conducted by Celen and Turker, (2001) and Kabdasli *et al.*, (2000) utilised a single batch reactor with mixing to recover ammonium from liquors of 1400 mg l^{-1} (digester effluent) and 2170 mg l^{-1} (landfill leachate) respectively. Again 85-90% recovery was achieved at a cost in the region of \$8.00 per kg of nitrogen recovered.

2.4.2 Recovery by air stripping

For air stripping to take place the liquors must first be pH adjusted to ensure that all ammoniacal nitrogen is in the free ammonia phase. The ammonium-ammonia equilibrium is largely pH dependant and at pH values of 10 and over almost all of the nitrogen is present in the form of ammonia (Hedstrom, 2001). This pH adjustment can be performed by the addition of sodium hydroxide (Siegrist, 1996) or lime (Kabdasli *et al.*, 2000). Free ammonia is then stripped by air or steam and then adsorbed by sulphuric acid. Pilot plant trials (Figure 2.3) in Switzerland (Siegrist, 1996) achieved 97% removal of nitrogen at influent flow rates of $150\text{-}300 \text{ l h}^{-1}$. A pre stripping sedimentation step was required to remove sludge flocs and precipitated calcium carbonate resulting from the pH adjustment. The removal of 1 kg nitrogen required

the addition of 24 kg of sodium hydroxide (30%) and 9.6 kg sulphuric acid, yielding 12 kg of 40% ammonium sulphate solution.

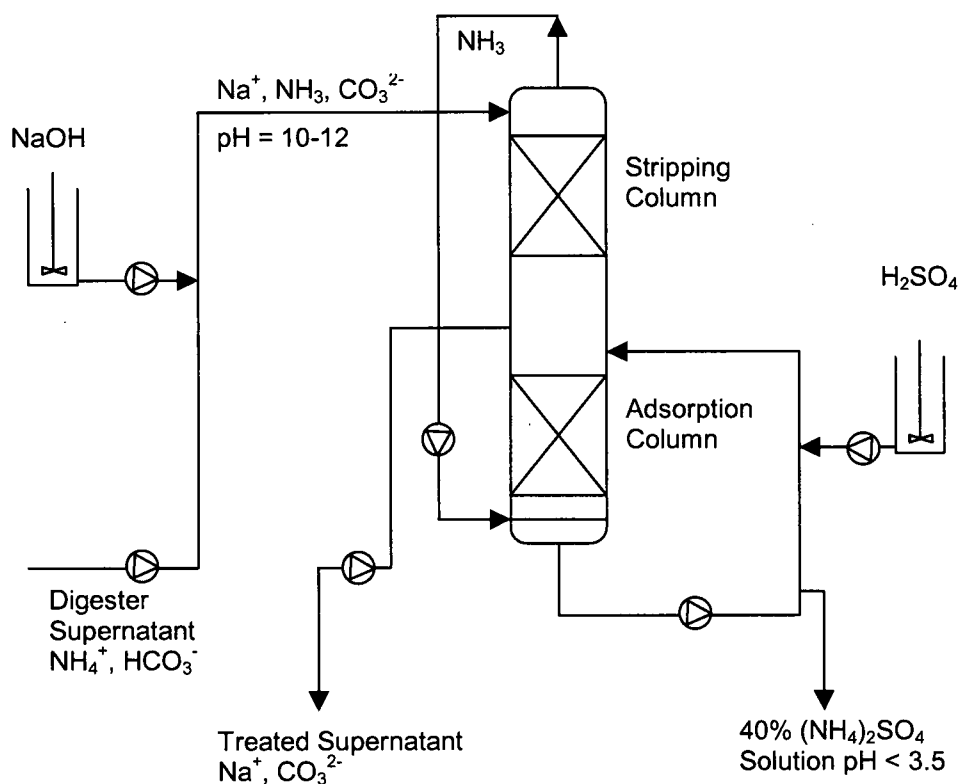


Figure 2.3 Diagram of an air stripping plant in Switzerland (Siegrist, 1996)

2.4.3 Biological solutions

Where existing mainstream biological processes are unable to be modified it is possible to directly apply biological nitrification/denitrification processes to high ammonium concentration sidestreams. Siegrist, (1996) investigated the intermittent nitrification/denitrification of digester supernatant of concentration 800 mg N l^{-1} . Due to the degradable organic content of the supernatant being low, a carbon source has to be added for the denitrification step. Trials at the Linköping plant in Sweden successfully treated digester supernatant using a sequencing batch reactor (SBR) for separate intermittent nitrification/denitrification. The feed rate to the reactor was $250\text{--}300 \text{ m}^3 \text{ d}^{-1}$, resulting in a reactor volume of 1400 m^3 and a solids retention time (SRT)

of 20 days. Hydrolysed starch was used as the additional carbon source and 75% of the total nitrogen was removed.

Fawcett *et al.*, (1997) performed pilot scale studies to investigate the treatment of raw sludge liquors with NH_4^+ -N concentration 250 mg l^{-1} using activated sludge, resulting in an ammonium nitrogen removal efficiency of 60%. Further to this research two full scale plants were constructed a WwTW in Leeds and Huddersfield in the United Kingdom.

Nitrification of high strength ammonium wastewaters with the aid of immobilisation media has been investigated as an option for reducing the ammonium concentration of return liquors (Rostron *et al.*, 2001). Five different immobilisation medias were investigated with the use of continuously stirred tank reactors (CSTR's) for the treatment of synthetic solutions with ammonium concentrations of $500 \text{ mg l}^{-1} \text{ NH}_4^+$ -N. Full nitrification was achieved at an hydraulic retention time (HRT) of two days. High rate nitrification of digested sludge liquors of concentration $500\text{-}1000 \text{ mg l}^{-1} \text{ NH}_4^+$ -N was also investigated by Pickin and Saunders, (1994). Bench and pilot scale studies concluded that loading rates of between 1000 and $2000 \text{ mg l}^{-1} \text{ NH}_4^+$ -N per m^3 of reactor volume per day were possible where an effluent standard of $40 \text{ mg l}^{-1} \text{ NH}_4^+$ -N was imposed.

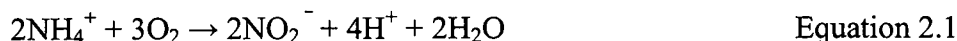
2.4.4 The combined Sharon/Anammox process.

Two factors to be considered in the nitrification/denitrification process are the oxygen consumption during nitrification and the total organic carbon to nitrogen ratio (C/N) in the denitrification process (Mosquera-Corral *et al.*, 2005). The partial nitrification of ammonium to nitrite reduces the oxygen consumption during nitrification greatly reducing the expense of aeration (Khin *et al.*, 2004). This in turn leads to a lowering of the amount of added carbon required for the denitrification process (Mosquera-Corral *et al.*, 2005). The Sharon process (Single reactor system for High Ammonium Removal Over Nitrite) developed at the Technical University Delft in the Netherlands (Hellinger, 1998) is designed to facilitate nitrification/denitrification process with nitrite (rather than nitrate) as an intermediate (van Kempen *et al.*, 2001). This process is suited to the treatment of high ammonium concentration liquors with low organic

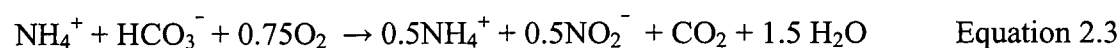
carbon content, such as digested sludge supernatants (Jetten *et al.*, 1997). In addition to this, the Anammox (anaerobic ammonium oxidation) process consists of the oxidation of ammonium to nitrogen gas using nitrite as the electron acceptor (Schmidt *et al.*, 2003) eliminating the need for the addition of organic matter. The idea of coupling these two processes for the treatment of sludge liquors has been successfully tested at laboratory scale (Jetten *et al.*, 1997) and more recently at full scale (van Dongen *et al.*, 2001). The principle of the combined process is that wastewater containing ammonium is only partially nitrified to nitrite using 50% of the ammonium in the influent. The effluent from this process is the used as the feed for the Anammox process where ammonium and nitrite are converted to nitrogen gas and water.

2.4.4.1 The Sharon process

Conventional nitrification takes place according to the following two equations (Brett *et al.*, 1997):



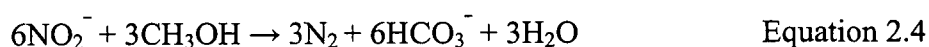
The Sharon process relies on the fact that full nitrification requires two different bacteria; ammonium oxidising bacteria (nitrosomas) responsible for nitrification (Equation 2.1) and nitrite oxidising bacteria (nitrobacter) responsible for nitrification (Equation 2.2) (Khin *et al.*, 2004; van Dongen *et al.*, 2001). At high temperatures nitrobacter has a distinctly slower growth rate than nitrosomas (Verstraete and Phillips, 1998). Due to a short retention time and the fact that the Sharon process has no sludge retention the nitrite oxidisers are washed out due to their slow growth rate. The faster growing ammonium oxidisers can survive at shorter residence times (Rogalla, 2005) and only nitrite is formed (Schmidt *et al.*, 2003). For the purpose of combining the Sharon and the Anammox process, only 50% of the ammonium needs to be converted to nitrite according to the following equation.



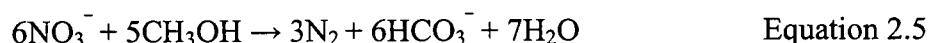
2.4.4.2 The Anammox process

Conventional anoxic denitrification is accomplished by converting nitrite and nitrate (resulting from the processes described by equations 1 and 2) into nitrogen gas and water (Khin *et al.*, 2004). To facilitate this process an additional carbon source is required, such as methanol (Siegrist, 1996; van Dongen *et al.*, 2001). The following simplified equations describe the process:

Denitrification of Nitrite



Denitrification of nitrate

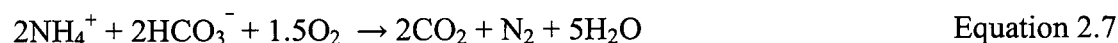


With the Anammox process ammonium can be converted to nitrogen gas without the addition of a carbon source. Under anaerobic conditions the bacteria utilise the available ammonium to convert nitrite into nitrogen gas (van Dongen *et al.*, 2001). This can be described by the simplified equation (Jetten *et al.*, 1997):



2.4.4.3 The combined process

The combination of the Sharon and Anammox processes for the treatment of sludge digester effluents has been successfully tested in the laboratory (Jetten *et al.*, 1997) and a full scale process has also been investigated (van Dongen *et al.*, 2001). From Equation 3 it can be seen that the effluent from the nitrification stage of the Sharon process serves as an ideal influent for the Anammox process. The net reaction equation for the overall combined process is:



Full scale studies performed by van Dongen *et al.*, (2001) operated the combined system (Figure 2.4) with a CSTR reactor for the Sharon process and an SBR for the Anammox stage.

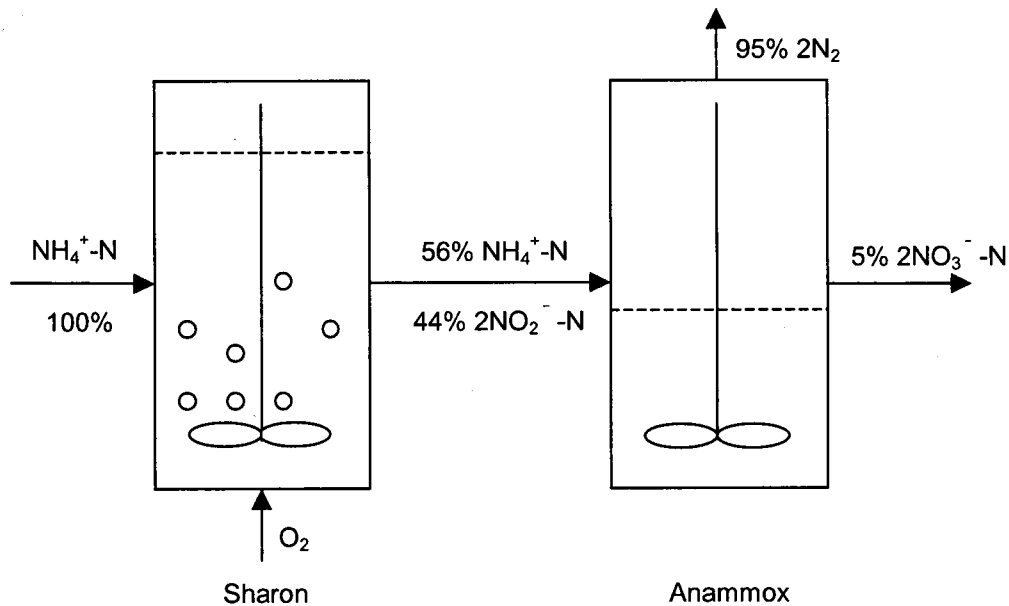


Figure 2.4 The combined Sharon/Anammox process (van Dongen *et al.*, 2001)

The combined process resulted in an ammonium removal efficiency of 83%. Only 1.7 kg of oxygen is required per kg of $\text{NH}_4^+\text{-N}$ removed and no COD addition is necessary which is low when compared to a conventional processes where 4.6 kg of oxygen and 4.5 kg COD would be required (Jetten *et al.*, 1997).

In addition to the systems outlined, it is also an option to remove ammonium from high strength liquors using ion exchange on to zeolite. The remainder of this review is concerned with zeolites and their application in the treatment of wastewater.

2.5 Zeolites

Zeolites are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium and barium (Breck, 1974). Their structure is based upon an infinite network of SiO_4 and AlO_4 tetrahedra, linked to each other by the sharing of all the oxygen atoms (Breck, 1974; Mumpton, 1984; and Flanigen, 1984). The term zeolite was first used by Swedish scientist Cronstedt in 1756 (Dyer, 1988) to describe naturally occurring siliceous minerals which became dehydrated when heated and the word zeolite is derived from the Greek word meaning boiling stones (De Silva, 1999). This is due to the fact that their structure contains channels and pores that are filled with a certain amount of water which can only evaporate when the sample is heated to about 250°C (Gottardi, 1985).

The presence of these channels or pores, which uniformly penetrate the entire volume of the solid, give the material a high internal surface area available for adsorption (Breck, 1974). The external surface of the particles only contributes a small amount of the total available surface area of the adsorbent (Breck, 1974) and an important property of zeolites as adsorbents is that some of the cations within the pores and channels may be exchangeable without any major change to the zeolite structure (Mumpton, 1984). Characteristics of naturally occurring zeolites depend on the origin, synthesis and variations in the naturally occurring processes during genesis and there currently in excess of 50 naturally occurring species accounted for (Kamarowski and Yu, 1997).

2.5.1 Formation, occurrence and classification of zeolites

For the most part zeolites are thought to derive from the in situ crystallisation in the cavities and fractures of volcanic and basaltic rocks during reaction with pervading pore waters. Until recently this was considered to be the typical mode of formation (Breck, 1974) of the majority of zeolites but recent discoveries (within the last 50 years) have found zeolites occurring in sedimentary rocks as alteration products of volcanic ash and other pyroclastic material (Breck, 1974). More recently, the use of x-ray diffraction has shown some zeolites form during the diagenesis of volcanic particles in alkaline environments (Breck, 1974). Alkaline environments ($\text{pH} > 8$)

greatly favour their formation due to the fact that silica is more soluble under these conditions (Hawkins, 1984). The mode of formation of a selection of zeolites along with the area of natural occurrence is outlined in Table 2.3.

Other factors influencing zeolite formation include, temperature, pressure, reaction time and the abundance of the zeolite forming minerals. As mentioned previously, zeolites are aluminosilicates of mainly group I and group II elements and therefore formation of zeolites tends to occur in areas where these elements are abundant in ionic solution (Hawkins, 1984). These conditions are best represented geologically in environments such as hydrothermal systems, saline lakes, deep-sea sediments and low-grade metamorphic rocks (Hawkins, 1984).

Table 2.3 Occurrence of zeolite minerals (modified after Breck 1974)

Name	Year Discovered	Typical Occurrence in Igneous Rocks	Examples of Occurrence in Sedimentary Rocks
Analcime	1784	Ireland, New Jersey	Extensive, Wyoming etc
Chabazite	1772	Nova Scotia, Ireland	Arizona, Nevada, Italy
Clinoptilolite	1890	Wyoming	Extensive USA, Australia, Europe, Asia
Erionite	1890	Oregon	Nevada, Oregon, Russia
Faujasite	1842	Germany	
Ferrierite	1918	British Columbia, Italy	Utah, Nevada
Herschelite	1825	Sicily	Arizona
Heulandite	1801	Iceland	New Zealand
Laumonite	1785	Nova Scotia, Faroe Islands	Extensive New Zealand, Russia
Mordenite	1864	Nova Scotia	Russia, Japan, Western US
Phillipsite	1824	Ireland, Sicily	Extensive, Western US, Africa, Deep sea floor

Distribution of zeolites around the world is widespread and although classified into groups and types each individual deposit will have its own individual characteristics. Various deposits have been used in ammonium removal experiments (Jorgensen *et al.*, 1979; Beler-Baykal, 1998; Lind *et al.*, 2000; Celik *et al.*, 2001; Demir *et al.*, 2002; Kovatcheva-Ninova *et al.*, 2002; Tzvetcov and Stoytcheva, 2003; Farkas *et al.*, 2005; Shijun Liu *et al.*, 2005; Sprnsky *et al.*, 2005) and it is important to note that two

separate deposits of different geographical location with the same classification will almost certainly possess differing characteristics. By far the most common zeolite used for ammonium removal is clinoptilolite (Hedstrom, 2001) and although occurring in many locations globally each deposit has its own characteristics. These properties will be affected by the distribution of the constituents within the deposit, which determine the chemical composition (Table 2.4). Tzvetcov and Stoytcheva, (2003) utilised four different clinoptilolites, three sourced from Bulgaria and one from Georgia, each having a different chemical composition but still remaining within the clinoptilolite classification “window.” This can also be compared with the Gordes clinoptilolite used by Celik *et al.*, (2001) and the Hungarian clinoptilolite used by Lind *et al.*, (2000). The Hungarian clinoptilolite has a silica content of 62.43%, whereas the silica content of the Gordes clinoptilolite and the Bulgarian clinoptilolites used by Tzvetcov and Stoytcheva, (2003) have silica content in the region of 70%, with those used by more recent authors (Farkas *et al.*, 2005; Shijun Liu *et al.*, 2005 and Sprynskyy *et al.*, 2005) falling in between these two values. The percentages of other constituents, from one deposit to another, are also variable most notably (considering that exchange performance is linked to Si/Al ratio) the Al_2O_3 percentage. This ranges from 9.08% in the K-BG Green clinoptilolite used by Tzvetcov and Stoycheva, (2003) to 14.41% in the Georgia-Dzedgvi clinoptilolite used by the same authors. This variation in deposits sourced from different areas can have an effect on the performance of the material as an ammonium adsorbent and in some cases results can appear conflicting (Booker *et al.*, 1996).

A further complication is added by the level of purity of the deposit. Due to the nature of genesis of zeolites, it is highly unlikely that naturally occurring deposits will be 100% pure mineral ore. Structural imperfections and the presence of clay may lead to internal channel blockage, rendering much of the material ineffective as an adsorbent. Therefore, it is impossible to predict with complete authority, the finite properties of a deposit based solely on its classification (De Silva, 1999).

However, the fact that a deposit is impure, does not necessarily exclude it from being used as an adsorbent and as mentioned previously, it is unlikely that a pure deposit exists. Jorgensen *et al.*, (1979) conducted experiments on ammonium solution using clinoptilolites ranging 50% - 90% in purity, whereas Curkovic *et al.*, (1997) used clinoptilolites of 40% - 50% purity (Hedstrom, 2001). Kamarowski and Yu, (1997) used zeolite with clinoptilolite content of 50%, which contained impurities including quartz and volcanic glass. In many cases some pre-treatment of zeolites is undertaken to give the material better performance properties but this is not necessarily done to remove impurities. It is more often than not used to introduce preferential cations (usually sodium) into the silicate framework prior to ammonium adsorption (Klieve and Semmens, 1979).

Table 2.4 Chemical composition of tested zeolite samples

Material	SiO ₂	SiO ₄	Si	CaO	K ₂ O	Al ₂ O ₃	MgO	TiO ₂	P ₂ O ₅	Fe ₂ O ₃	FeO	Na ₂ O	MnO	Reference
Tokaj Clinoptilolite	69.12	-	-	1.27	5.5	11.6	0.18	0.39	-	1.59	-	0.17	0.01	Jorgensen <i>et al.</i> , 1976
Beli Plast Clinoptilolite	65.9	-	-	2.3	4.93	12.97	-	-	-	-	-	2.12	-	Belér Baykal and Guven, 1996
Hungarian Clinoptilolite	62.43	-	-	3.17	2.74	10.95	0.79	-	-	-	0.12	0.13	-	Lind <i>et al.</i> , 2000
Swedish Wollastonite	63.2	-	-	3.12	2.62	4.2	-	-	0.01	1.12	-	0.12	0.26	Lind <i>et al.</i> , 2000
Encher Bentonite	52.7	-	-	4.3	1.1	15.9	3.5	-	-	4.5	-	0.9	-	Kovatcheva-Ninova <i>et al.</i> , 2000
Beli Plast clinoptilolite	66.16	-	-	2.8	2.9	11.41	0.06	0.15	-	0.8	-	0.22	-	Kovatcheva-Ninova <i>et al.</i> , 2000
Gordes Clinoptilolite	70	-	-	2.5	2.3	14	1.2	0.1	-	0.8	-	0.2	-	Celik <i>et al.</i> , 2001
1985 Bigadic Clinoptilolite	67.6	-	-	3.26	2.17	11.3	1.18	0.07	-	0.77	-	-	0.02	Demir <i>et al.</i> , 2002
1994 Bigadic Clinoptilolite	-	67.96	15.36	0.74	3.01	10.74	1.49	-	-	-	-	0.81	-	Demir <i>et al.</i> , 2002
1995 Bigadic Clinoptilolite	64.99	-	-	3.51	1.95	9.99	1.01	-	-	3.99	-	0.18	-	Demir <i>et al.</i> , 2002

Material	SiO ₂	SiO ₄	Si	CaO	K ₂ O	Al ₂ O ₃	MgO	TiO ₂	P ₂ O ₅	Fe ₂ O ₃	FeO	Na ₂ O	MnO	Reference
Georgia-Dzedgvi Clinoptilolite	68.04	-	-	6.87	1.8	14.41	2.2	-	-	3.93	-	2.08	-	Tzvetcov and Stoycheva, 2003
H-BG Green Clinoptilolite	70.3	-	-	0.56	2.86	9.14	0.19	-	-	0.55	-	0.46	-	Tzvetcov and Stoycheva, 2003
Ca-BG Green Clinoptilolite	71.1	-	-	4.2	2.98	9.2	0.18	-	-	0.68	-	0.65	-	Tzvetcov and Stoycheva, 2003
K-BG Green Clinoptilolite	70.9	-	-	1.16	5.25	9.08	0.2	-	-	0.86	-	0.55	-	Tzvetcov and Stoycheva, 2003
Croatian Clinoptilolite	64.93	-	-	2.0	1.3	13.39	1.08	-	-	2.07	-	2.4	-	Farkas <i>et al.</i> , 2005
Chinese Clinoptilolite	65.52	-	-	3.17	0.88	9.89	0.61	0.21	-	1.04	-	2.31	0.06	Shijun Liu <i>et al.</i> , 2005
Transcarpathian Clinoptilolite	66.7	-	-	2.1	2.96	12.3	1.07	-	-	1.05	-	2.06	-	Sprynskyy <i>et al.</i> , 2005

2.5.2 Structure and Properties of Zeolite

All zeolites contain primary building units (PBU's) and secondary building units (SBU's) (Breck, 1974). The simplest of these is the primary building unit, which consists of a tetrahedron of four oxygen ions surrounding a central ion of either Si^{4+} , or Al^{3+} as illustrated in Figure 2.5. The primary building units are linked together by oxygen atoms to form a framework structure where all of the oxygen ions are shared by two tetrahedra (Gottardi, 1985). Each AlO_4 tetrahedron in the framework results in a net negative charge which is balanced by a cation, usually a group I or a group II element (Tosheva, 1999), for example potassium (Figure 2.5). These cations can then be exchanged for other cations (Curkovic *et al.*, 1997). The secondary building units consist of single and double ring tetrahedra as shown in Figure 2.6 (Breck, 1974). The arrangement of these determines the nature of the framework and forms an important part of the zeolite classification system (Dyer, 1988).

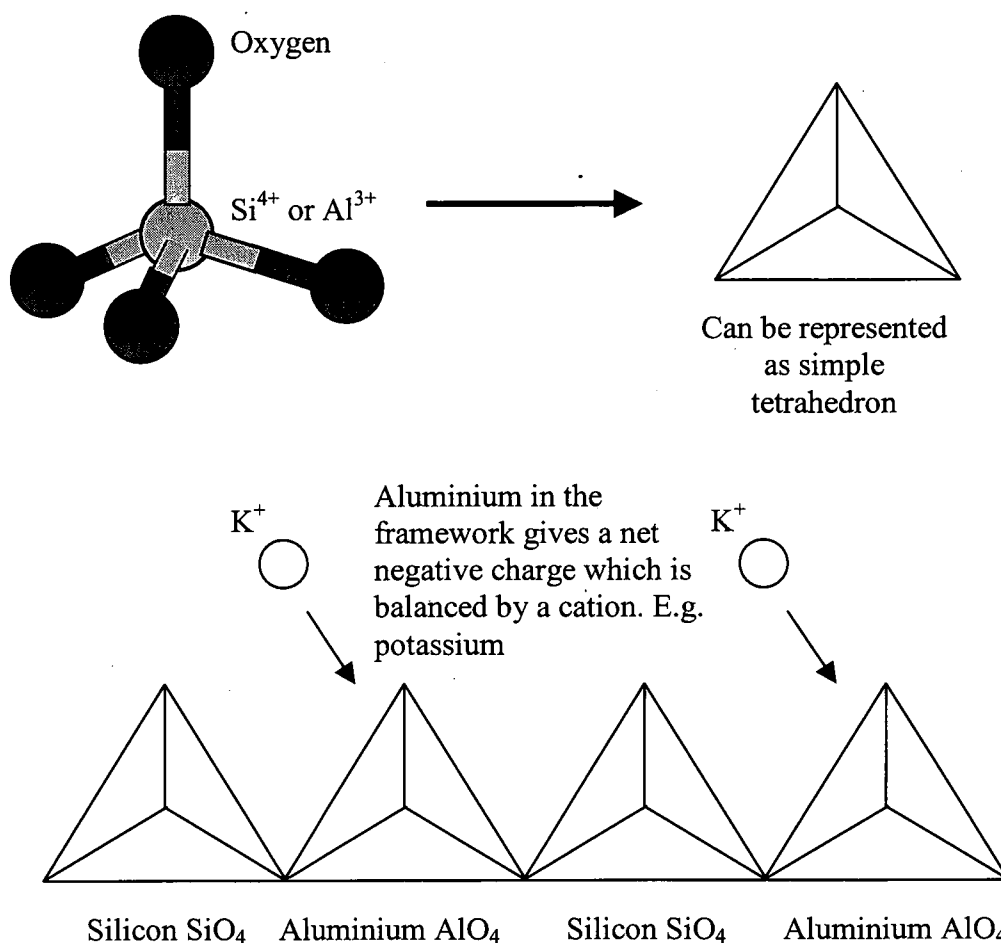


Figure 2.5 Primary building units of zeolites

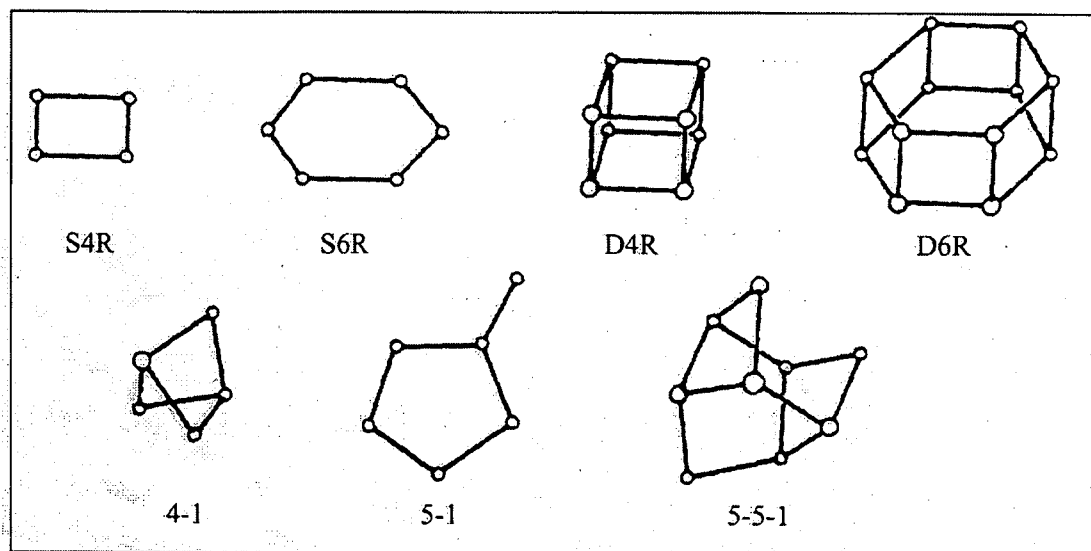


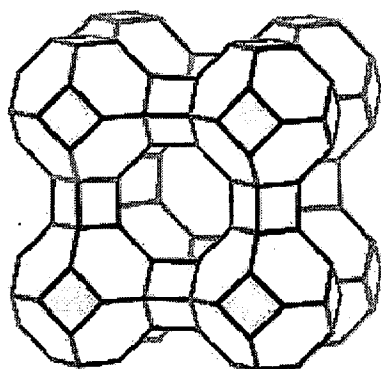
Figure 2.6 Zeolite secondary building units (Breck, 1974)

The Si/Al ratio of a zeolite can determine its fundamental property as an ion exchanger (Colella, 1995). As the ratio increases, the amount of cations available for exchange in the framework decreases (Tosheva, 1999). This results in pure silica (SiO_2) having no ion exchange properties at all. The Si/Al ratio therefore determines the cation exchange capacity (CEC) of any given zeolite (Colella, 1995). The CEC can be defined as the number of equivalents of fixed charges per amount of exchanger (Bolto and Pawlowski, 1987) and represents the amount of exchangeable cations (Semmens, 1984). The relationship between the Si/Al ratio and the CEC of some naturally occurring zeolites is presented in Table 2.5. At lower Si/Al ratios there is a greater amount of aluminium in the framework. This leads to an increased deficiency in positive charge and means that a greater amount of cations are required for electrical neutrality (Mumpton, 1984).

Table 2.5 Si/Al ratio versus CEC (Colella *et al.*, 1995)

Zeolite Name	Structure Type	CEC Meq g ⁻¹	Si/Al Ratio Ranges
Chabazite	CHA	3.84	1.43 - 4.18
Clinoptilolite	HEU	2.16	2.92 - 5.04
Erionite	ERI	3.12	3.05 - 3.99
Ferrierite	FER	2.33	3.79 - 6.14
Heulandite	HEU	2.91	2.85 - 4.31
Laumontite	LAU	4.25	1.95 - 2.25
Mordenite	MOR	2.29	4.19 - 5.79
Phillipsite	PHI	3.31	1.45 - 2.87
Faujasite	FAU	3.39	-

In addition, zeolite frameworks can be described as cage like structures (Figure 2.7) with micropores and channels (Tosheva, 1999). The type of framework formed will determine the pore size and in naturally occurring zeolites these pores fall within the size range of 3-15 Å (Celik *et al.*, 2001; Jung *et al.*, 2004; Salerno and Mendioroz, 2002). This allows zeolites to act as molecular sieves, which are selective for different cations on the basis of size. For this reason, clinoptilolite is highly selective for ammonium. The resulting ammonium removal process relies predominantly on these two factors, although the type of exchanging cation in the framework does also have an influence (Booker *et al.*, 1996). The ammonium ions are selectively adsorbed into the microstructure and ion exchange then takes place at the aluminium sites.

**Figure 2.7** Structure of zeolite A framework (Dyer, 1988)

The classification of zeolites is complicated and as with all classification systems there are possible anomalies (Dyer, 1988). It is the accepted convention that mineral species shall not be distinguished solely upon the framework Si/Al ratio, the exceptions to this being heulandite and clinoptilolite (Armbruster, 2001). Dyer, 1988 describes a classification based hierarchically on the following parameters; their SBU content; structure content (IUPAC nomenclature); name (the prefix zeolite means that the material is only known as a synthetic material) and typical unit cell content. This gives rise to many mineral types each with each one possessing unique properties (Table 2.6). This is by no means exhaustive and the International Zeolite Association (IZA) has a published handbook (Dyer, 1988) which presents a more detailed view of zeolite frameworks.

Table 2.6 Classification of zeolite by SBU content (Dyer, 1988)

Secondary Building Unit	Structure Type	Name	Typical Unit cell Content
S4R	ANA	Analcime	$\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96}10\text{H}_2\text{O}$
	ANA	Wairakite	$\text{Ca}_8\text{Al}_{16}\text{Si}_{32}\text{O}_{96}16\text{H}_2\text{O}$
	GIS	Gismondine	$\text{Ca}_4\text{Al}_8\text{Si}_8\text{O}_{32}16\text{H}_2\text{O}$
	GIS	Amicite	$\text{K}_4\text{Na}_4\text{Al}_8\text{Si}_8\text{O}_{32}10\text{H}_2\text{O}$
	GIS	Garronite	$\text{NaCa}_{2.5}\text{Al}_6\text{Si}_{10}\text{O}_{32}14\text{H}_2\text{O}$
	GIS	Gobbinsite	$\text{Na}_5\text{Al}_5\text{Si}_{11}\text{O}_{32}11\text{H}_2\text{O}$
	GIS	Zeolite NaP-1	$\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}12\text{H}_2\text{O}$
	LAU	Laumonite	$\text{Ca}_4\text{Al}_8\text{Si}_{16}\text{O}_{46}16\text{H}_2\text{O}$
	MER	Merlionite	$\text{K}_5\text{Ca}_2\text{Al}_9\text{Si}_{23}\text{O}_{64}24\text{H}_2\text{O}$
	PAU	Paulingite	$(\text{K}_2, \text{Na}_2, \text{Ca}, \text{Ba})_{76}\text{Al}_{152}\text{Si}_{520}\text{O}_{1344}700\text{H}_2\text{O}$
S6R	PHI	Phillipsite	$\text{K}_2\text{Ca}_{1.5}\text{NaAl}_6\text{Si}_{10}\text{O}_{32}12\text{H}_2\text{O}$
	PHI	Harmotome	$\text{Ba}_2\text{Ca}_{0.5}\text{Al}_5\text{Si}_{11}\text{O}_{32}12\text{H}_2\text{O}$
	YUG	Yugawaralite	$\text{Ca}_2\text{Al}_4\text{Si}_{12}\text{O}_{32}8\text{H}_2\text{O}$
	CAN	Cancrinite hydrate	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}8\text{H}_2\text{O}$
	ERI	Erionite	$\text{Na}_2\text{K}_2\text{Mg}_{0.5}\text{Ca}_2\text{Al}_9\text{Si}_{27}\text{O}_{72}27\text{H}_2\text{O}$
	LEV	Levynite	$\text{NaCa}_3\text{Al}_7\text{Si}_{11}\text{O}_{36}18\text{H}_2\text{O}$
	LTL	Zeolite L	$\text{K}_6\text{Na}_3\text{Al}_9\text{Si}_{27}\text{O}_{72}21\text{H}_2\text{O}$
	LOS	Zeolite Losod	$\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}19\text{H}_2\text{O}$
	MAZ	Mazzite	$\text{Mg}_2\text{K}_3\text{Ca}_{1.5}\text{Al}_{10}\text{Si}_{26}\text{O}_{72}28\text{H}_2\text{O}$
		(Zeolite Omega)	
8SR	OFF	Offretite	$\text{Kca}_2\text{Al}_5\text{Si}_{13}\text{O}_{36}15\text{H}_2\text{O}$
	SOD	Sodalite hydrate (HS)	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}8\text{H}_2\text{O}$
	Occurs in many structures but with other SBU's (Zeolite A, chabazite etc)		
D4R	LTA	Zeolite A	$\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}27\text{H}_2\text{O}$
D6R	CHA	Chabazite	$\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}13\text{H}_2\text{O}$
	CHA	Withendersonite	$\text{K}_2\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}10\text{H}_2\text{O}$
	FAU	Faujasite	$\text{Na}_{12}\text{Ca}_{12}\text{Mg}_{11}\text{Al}_{58}\text{Si}_{134}\text{O}_{384}235\text{H}_2\text{O}$
	FAU	Zeolite X	$\text{Na}_{88}\text{Al}_{88}\text{Si}_{104}\text{O}_{384}220\text{H}_2\text{O}$
	GME	Gmelinite	$\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}24\text{H}_2\text{O}$
	KFI	Zeolite-ZK5	$\text{Na}_{30}\text{Al}_{30}\text{Si}_{66}\text{O}_{192}98\text{H}_2\text{O}$
	RHO	Zeolite Rho	$(\text{Na}, \text{Cs})_{12}\text{Al}_{12}\text{Si}_{36}\text{O}_{96}46\text{H}_2\text{O}$
	EDI	Edingtonite	$\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20}8\text{H}_2\text{O}$
	NAT	Natrolite	$\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}16\text{H}_2\text{O}$
4-1	NAT	Tetranatrolite	$\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}16\text{H}_2\text{O}$
	NAT	Paranatrolite	$\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}24\text{H}_2\text{O}$
	NAT	Mesolite	$\text{Na}_{16}\text{Ca}_{16}\text{Al}_{48}\text{Si}_{72}\text{O}_{240}64\text{H}_2\text{O}$
	NAT	Scolecite	$\text{Ca}_8\text{Al}_{16}\text{Si}_{24}\text{O}_{80}24\text{H}_2\text{O}$
	THO	Thomsonite	$\text{Na}_4\text{Ca}_8\text{Al}_{20}\text{Si}_{20}\text{O}_{80}24\text{H}_2\text{O}$
	THO	Gonnardite	$\text{Na}_5\text{Ca}_2\text{Al}_9\text{Si}_{11}\text{O}_{40}14\text{H}_2\text{O}$
	BIK	Bikitaite	$\text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12}2\text{H}_2\text{O}$
5-1	DAC	Dachiardite	$\text{Na}_5\text{Al}_5\text{Si}_{19}\text{O}_{48}12\text{H}_2\text{O}$
	EPI	Epistilbite	$\text{Ca}_3\text{Al}_6\text{Si}_{18}\text{O}_{48}16\text{H}_2\text{O}$
	FER	Ferrierite	$\text{NaCa}_{0.5}\text{Mg}_2\text{Al}_6\text{Si}_{30}\text{O}_{72}20\text{H}_2\text{O}$
	MFI	Zeolite ZSM-5	$\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \sim 16\text{H}_2\text{O} (n \sim 3)$
	MOR	Mordenite	$\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{86}24\text{H}_2\text{O}$
	BRE	Brewsterite	$\text{Sr}_{12}\text{Al}_4\text{Si}_{12}\text{O}_{32}10\text{H}_2\text{O}$
	HEU	Heulandite	$\text{Ca}_4\text{Al}_8\text{Si}_{28}\text{O}_{72}4\text{H}_2\text{O}$
4-4-1	HEU	Clinoptilolite	$\text{Na}_6\text{Al}_6\text{Si}_{30}\text{O}_{72}24\text{H}_2\text{O}$
	STI	Stilbite	$\text{Na}_2\text{Ca}_4\text{Al}_{10}\text{Si}_{26}\text{O}_{72}34\text{H}_2\text{O}$
	STI	Stellerite	$\text{Ca}_4\text{Al}_8\text{Si}_{28}\text{O}_{72}28\text{H}_2\text{O}$
	STI	Barrerite	$\text{Na}_8\text{Al}_8\text{Si}_{28}\text{O}_{72}26\text{H}_2\text{O}$
	STI		

2.6 Applications of zeolites

The ability of zeolites to be selective for cations on the basis of size as well as charge gives them a multi functional role in industrial applications. The ion exchange properties of zeolites has resulted in their use as builders to enhance the cleaning efficiency of detergents primarily by removing calcium and magnesium ions from washing water to prevent their precipitation (Mondale *et al.*, 1995). This role was previously performed by polyphosphates up until the early 1970's when pressure was placed upon detergent manufacturers to find a replacement due to the growing awareness of the environmental damage they caused (Dyer, 1988). Another use has been the application of the ion exchange properties of zeolites in soil beneficiation (Dyer, 1988). The Japanese use in excess of 6000 tonnes of clinoptilolite and mordenite per annum to control soil pH, moisture content and manure odour. This has resulted in increased crop yields ranging from 15-63% depending on the crop (Table 2.7).

Table 2.7 Crop yield increases by zeolite addition (Dyer 1988)

Crop	Best yield index (control = 100)
Wheat	115
Eggplant	120
Apple	128
Rice	117
Carrot	163

The benefit of the addition of zeolites as an animal feed supplement, especially pigs, has been recognised for many years (Dyer, 1988). A 5-6% addition of clinoptilolite to their diet results in beneficial weight gain and reduced disease. The success seems to be derived from the ion exchange control of ammonium levels in the gut.

The sieving properties of zeolites are utilised in many processes (Breck, 1974) including the use for gas purification (Dyer, 1988), with perhaps the best known use being the removal of hydrogen sulphide from natural gas. Other uses include the removal of sulphur and nitrogen containing molecules and the trapping of mercury vapour, sulphuric dioxides and nitrogen sulphides.

One of the most common uses of zeolites is as drying agents. This relies on the property of previously dehydrated (activated) composites to efficiently scavenge for water. These composites can be sealed into a component keeping it water free for the whole of its working life (Dyer, 1988). Common applications of zeolites as drying agents include, the drying of halocarbon refrigerants in refrigeration circuits, the inclusion in vehicle braking and air conditions systems and in sealed double-glazing units containing gases where they scavenge out residual vapour from sealants used to fix the panes together.

The application of zeolites as ion exchanger's in wastewater treatment, other than that of ammonium removal, appears to be restricted to the removal of heavy metals (Ouki and Kavannagh, 1997). Most research is concerned with the use of clinoptilolite (Inglezakis and Grigoropoulou, 2004; Petrus and Warchol, 2003; Mier *et al.*, 2001; Erdem *et al.*, 2004) although Ouki and Kavannagh, (1997) investigated the merits of both clinoptilolite and chabazite and Mondale *et al.*, (1995) considered numerous zeolite species, both synthetic and naturally occurring.

Results indicate that efficient removal of heavy metals from wastewater is possible by exchange on to zeolites (Erdem *et al.*, 2004) and the efficiency is dependant on a number of factors. Metal removal typically increases with increasing pH (Mier *et al.*, 2001) and it was noted that zeolites themselves have the potential to alter the pH of the treated solution (Ouki and Kavannagh, 1997). The removal efficiency increases as flow rate (Inglezakis and Grigoropoulou, 2004), particle size (Mondale *et al.*, 1995) and concentration decrease (Petrus and Warchol, 2003). Ion exchange of heavy metals is only feasible when the exchanger has a high selectivity for the metals involved and the concentration of competing cations is low (Ouki and Kavannagh, 1997), suggesting that removal from liquors with a high ammonium concentration with clinoptilolite is unlikely due to the high selectivity for the ammonium ion (Dyer, 1988).

2.7 Application of zeolites in ammonium removal from wastewater

In 1850, two agricultural chemists, Thompson and Way (Paterson, 1970), noticed that when passing a liquid fertilizer containing ammonium through a soil sample, the ammonium was retained by the soil whilst the calcium was thrown off (DeSilva, 1999). They concluded that the aluminosilicates in the soil gave it ion exchange characteristics. In 1858 German scientist Eichorn proved that this ion exchange process was a reversible one. Lemberg confirmed this in 1876 (DeSilva, 1999). In 1905, German scientist Gans, applied zeolites to the use of water softening by exchanging magnesium and calcium ions for sodium ions (DeSilva, 1999). Since this early use, a greater understanding of the ion exchange process has been realized and there are now many practical applications of zeolite as the base for ion exchange processes (Varshney, 2002).

The ammonium removal process generally consists of ammonium rich solution being filtered through columns filled with the adsorbent media zeolite (Weatherly and Mcveigh, 2000; Liberti *et al.*, 1986; Koon and Kaufmann, 1975). Adsorption and ion exchange take place within the columns to remove the ammonium. The zeolite is then regenerated with a brine solution, where desorption of the ammonium occurs allowing the media to be used repeatedly. The drained brine can then be used as a fertilizer (Lahav and Green, 1998) or the regeneration can be followed by air stripping and the ammonia gas sorbed into sulphuric acid (Liberti *et al.*, 1982). Another option is a subsequent anion exchange step resulting in the precipitation of magnesium ammonium phosphate, which can be used as a slow release fertilizer (Liberti *et al.*, 1986). Although one column could suffice for the removal of ammonium, it is usual to use two or more because this allows regeneration to take place at the same time as removal without disturbing the system or risking nutrient discharge (Brett *et al.*, 1997).

2.7.1 Equilibrium studies

The performance of the media can, in part, be judged by equilibrium studies followed by the construction of ion exchange isotherms (Dyer, 1988) which pictorially display the relationship between the ion concentration in the fluid and solid phase (McCabe *et*

al., 1985). Isotherms that convex upward (Figure 2.8) are considered favourable because a relatively high loading can be obtained at a low solution concentration. The opposite can be said for isotherms that convex downwards.

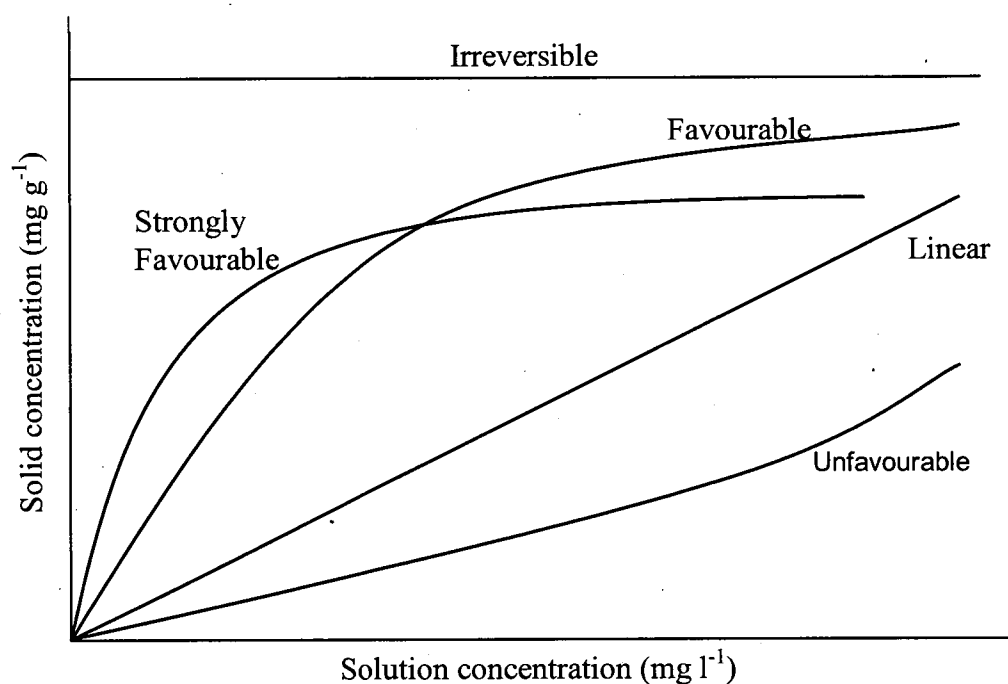
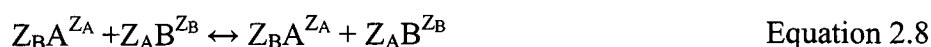


Figure 2.8 Example of experimental adsorption isotherms (adapted from McCabe *et al* 1985)

For the case of zeolites the ion exchange process between cation A^{Z_A} , initially in solution, and cation B^{Z_B} , initially in the zeolite framework, can be characterised as follows (Dyer, 1988):



Where Z_A and Z_B are the valences of the ions and the underlined characters relate to a cation inside the zeolite framework. Simple examples are shown in Equations 9 (for a uni-univalent exchange) and 10 (for a uni-divalent exchange).



Data for plotting isotherms is obtained by treating fixed volumes of liquid of known concentration with a series of known weights of media (Demir *et al.*, 2002). Before isotherms can be produced it is necessary to ensure ion exchange equilibrium has been reached (Dyer, 1988). Once the equilibrium time is determined the isotherm can be constructed. A representative sample of solution is chosen and a known volume is added to a series of flasks (a minimum of six is required and each flask contains the same volume of solution). Increasing weights of media are then added to the flasks and the flasks are then stirred at a constant temperature until equilibrium is reached (Wang *et al.*, 2005). It is advisable that the solution : solid volume ratio should not be less than 20 (Dyer, 1988). The media is then filtered out and the remaining solutions are again tested for residual concentration.

Various models exist for predicting the uptake of impurities by ion exchange media with two of the most notable being the Langmuir and Freundlich models (Weatherly and Milandovic, 2004). The Langmuir isotherm relates Q_e (mg of impurity removed per gram of exchange media) and C_e (the equilibrium ammonium concentration in solution) as shown in Equation 11.

$$Q_e = \frac{KbC_e}{1+KC_e} \quad \text{Equation 2.11}$$

Where K and b are constants. K corresponds to the surface concentration at monolayer coverage and represents the maximum value of Q_e that can be achieved as C is increased (Nguyen and Tanner, 1997).

For trials performed by Weatherly and Milandovic, (2004) (for ammonium uptake on to clinoptilolite) Q_e was calculated from the volume of solution, the mass of material exposed to solution and the equilibrium concentration in the solution. Rearranging the equation gives Equation 12, which is linear.

$$\frac{1}{Q_e} = \frac{1}{KbC_e} + \frac{1}{b} \quad \text{Equation 2.12}$$

The constants K and b were then determined by plotting $1/C_e$ versus $1/Q_e$.

The Freundlich model relates Q_e and C_e according to the following equation (Weatherly and Milandovic, 2004).

$$Q_e = kC_e^{1/n}$$

Equation 2.13

Where k and n are constants. The constant k is related to the capacity and $1/n$ represents the intensity of adsorption (Demir *et al.*, 2002).

This equation can also be represented as

$$\log Q_e = \log k + 1/n \log C_e$$

Equation 2.14

When $\log Q_e$ is plotted against $\log C_e$ the constants k and n can be calculated. Knowing all coefficients the Langmuir and Freundlich theoretical Q_e can be calculated for any given ion concentration in solution. A number of authors (Booker *et al.*, 1996; Demir *et al.*, 2002; Weatherley and Miladinovic, 2004 and Du *et al.*, 2005) have investigated the equilibrium performance of clinoptilolite for ammonium removal from aqueous solution and the giving rise to various k and n values (Table 2.8). Although the material used in each case was clinoptilolite, a wide range of performance can be observed, with Freundlich k values ranging from 0.32 (Booker *et al.*, 1996) to 2.27 (Weatherley and Miladinovic, 2004) and Langmuir k values ranging from 0.018 (Sarioglu, 2005) to 1.493 (Weatherley and Miladinovic, 2004).

Table 2.8 Isotherm constants for ammonium exchanged on clinoptilolite from various studies

Freundlich		Langmuir		Reference
K	1/n	K	Kb	
1.364	0.279	-	-	Du <i>et al.</i> , 2005
0.608	0.537	0.085	0.44	Demir <i>et al.</i> , 2002
0.806	0.727	0.069	0.77	Demir <i>et al.</i> , 2002
1.365-2.27	0.34-0.415	0.249-1.493	1.69-9.84	Weatherley and Miladinovic, 2004
0.3156	0.388	-	-	Booker <i>et al.</i> , 1996
-	-	0.018	0.046	Sarioglu, 2005

However, both isotherm models do have their limitations in accurately describing equilibrium ion exchange. Hankins *et al.*, (2004) argues that the Freundlich model imposes no intrinsic limit on the capacity of the zeolite although it is generally accepted that the capacity of any ion exchange material is limited to the number of exchange sites available and therefore, the single component Langmuir model is more applicable because a limit on adsorption is imposed. However, the authors further argue that the Langmuir model fails to account for the true nature of ion exchange as a binary, displacement adsorption process, which involves at least two species, whose relative proportions and hence concentrations alter.

Therefore, since ion exchange is a phenomenon involving chemical equilibria, the law of mass action may be applied, which is based on an equilibrium exchange process between two or more species (Equation 2.8) and also imposes a limit on maximum uptake (Hankins *et al.*, 2004). As a rule, the ion exchanger selects one species over another and thus results in a non-linear isotherm (Helfferic, 1995). At equilibrium the solution and solid phases should be analysed to determine the distribution of A^{Z_A} and B^{Z_B} between the phases (Dyer, 1988). An isotherm can then be plotted which records the equivalent fraction of the exchanging ion in solution (A_S) against that in the zeolite (A_Z) (Hankins *et al.*, 2004), where:

$$A_S = \frac{Z_A [A]}{Z_A [A] - Z_B [B]} \quad \text{Equation 2.15}$$

$$A_Z = \frac{Z_A [A]}{Z_A [A] - Z_B [B]} \quad \text{Equation 2.16}$$

The selectivity of a zeolite for an ion A can be expressed quantitatively as a separation factor (α) (Dyer, 1985) where:

$$\alpha = \frac{A_Z/A_S}{B_Z/B_S} \quad \text{Equation 2.17}$$

For the law of mass action in ion exchange equilibrium involving monovalent species (in this case ammonium and sodium), the following is true (Hankins *et al.*, 2004)



For which

$$K_{\text{eq}} = \frac{[\underline{\text{NH}_4^+}]/[\text{NH}_4^+]}{[\underline{\text{Na}^+}]/[\text{Na}^+]} \quad \text{Equation 2.19}$$

Where: K_{eq} = the equilibrium constant and is equal to the separation factor for mass action equilibrium.

Equilibrium studies can only go so far in assessing the potential of a material to be used as an ion exchanger for the removal of ammonium. The remainder of this review is concerned with the dynamic application of zeolites, where ammonium rich liquors are passed through a fixed bed of media situated in a column or series of columns in order to achieve a continuous contact between solution and exchanger.

2.7.2 The dynamic application of zeolites

During dynamic processes, the solution is continually fed (either upflow or downflow) through the media bed in order to remove the polluting ion; in this case ammonium. Here, the driving force (Wang *et al.*, 2006) behind the exchange process is continually renewed by the continual introduction of fresh solution and as a result a greater proportion of the media's capacity can be utilised. The media bed is exposed to a solution of concentration C_0 (Figure 2.9) and the media bed becomes systematically saturated with ammonium from the inlet, progressing towards the outlet, until at some point a pre-determined breakthrough concentration (C_b) is observed in the column effluent (Cooney, 1999).

As the solution moves through the bed, a series of equilibrations occurs between the ammonium ions and the ions in the solid phase on successive layers in the column (Paterson, 1970). The top layers are continually bathed with fresh ammonium solution to the point of saturation and further exchange takes place lower down the column.

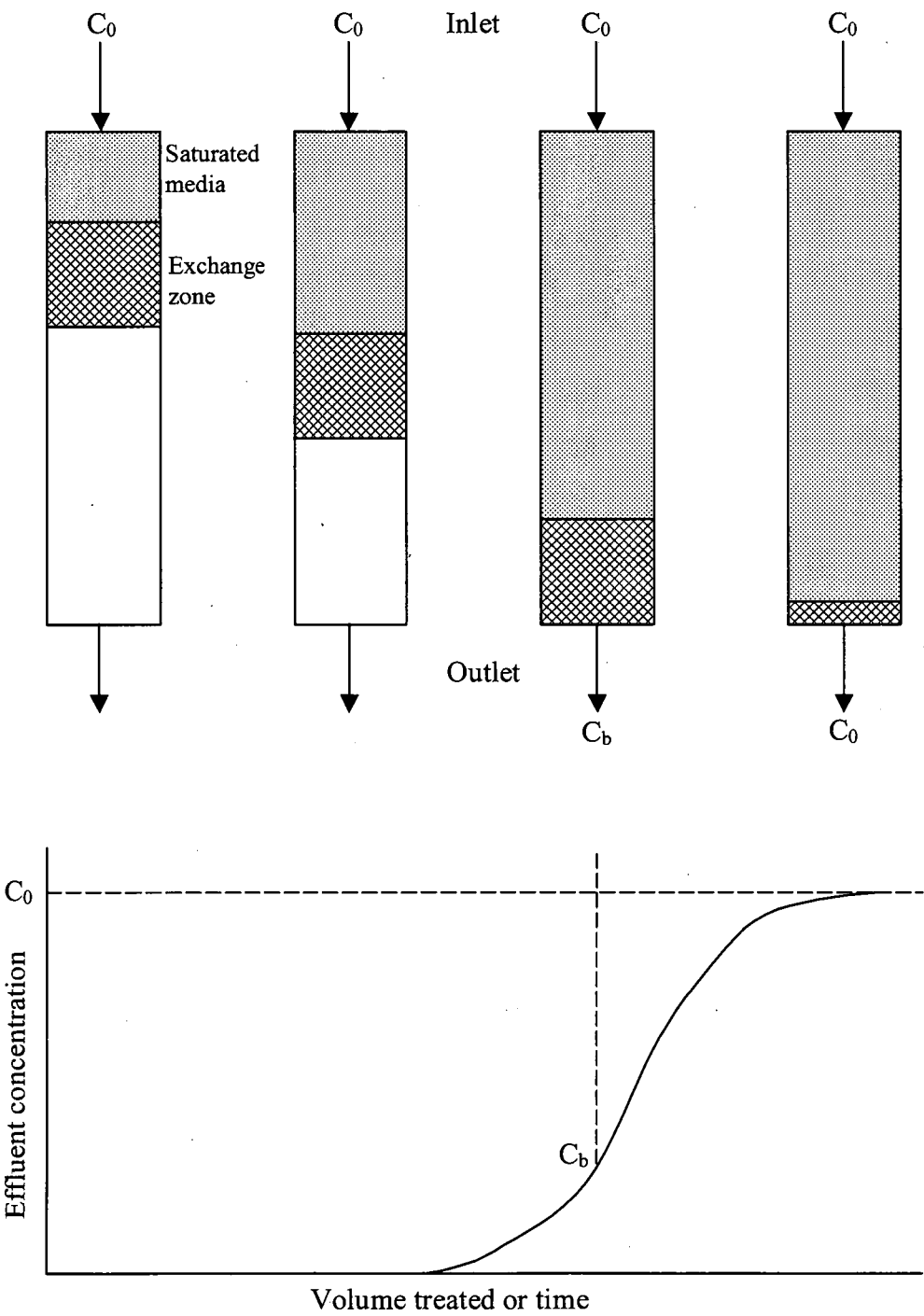


Figure 2.9 The progression of a mass transfer zone through a fixed bed (modified from Cooney, 1999)

The zone where exchange occurs is referred to as the mass transfer zone (Barros *et al.*, 2003) and the shorter its length, the longer the time to reach breakthrough (t_b) and as a result, more of the media's capacity is used. If the column were continually fed with solution until all zones were saturated, then the effluent concentration would equal that of the influent concentration (C_0). At this point, the whole bed (of length L) is in equilibrium and has reached its stoichiometric capacity (Barros *et al.*, 2003). The time to reach this stoichiometric capacity is referred to as the stoichiometric time equivalent (t_t) and this can be used to determine the length of unused bed (LUB). The length of unused bed is dependant on C_b and at breakthrough, can be determined from the following (Cooney, 1999):

$$\text{LUB} = \left[1 - \frac{t_b}{t_t} \right] L \quad \text{Equation 2.20}$$

This LUB represents the mass transfer zone (Barros *et al.*, 2003) and can be used as a design parameter, where the bed length can be designed to have the required capacity by making the column one LUB longer to account for unused capacity under actual conditions (Cooney, 1999)

2.7.3 Pre-treatment of zeolites

To enhance the performance of zeolites as ammonium adsorbents, they have been pre-treated with a solution containing preferred ions (i.e. calcium, magnesium and sodium) for the process (Klieve and Semmens, 1979; Jorgensen *et al.*, 1979; Hlvay *et al.*, 1982; Booker *et al.*, 1996; Beler Baykal *et al.*, 1996). The most suitable of these, when concerning ammonium removal, has been found to be sodium (Jorgensen *et al.*, 1979; Booker *et al.*, 1996) as the small sodium ion (hydrated diameter 15.8 Å) is free to migrate through the micropores and closely approach the exchange sites (Koon and Kaufmann, 1975). Due to the larger size of calcium cations (hydrated diameter 19.2 Å), they are unable to approach the exchange sites as closely as other ions and their mobility is further restricted by an affinity for the structural water contained in the zeolite framework (Koon and Kaufmann, 1975). Thus, zeolite treated with calcium has an even lower exchange capacity than untreated zeolite. It is a possibility that the

calcium ions become permanently sorbed into the media, consequently reducing its ion exchange capacity (Hlvay *et al.*, 1982). The most common pre-treatment is to load the zeolite with sodium hydroxide and then rinse with distilled water prior to use (Jorgensen *et al.*, 1979; Koon and Kaufmann, 1975), although if sodium hydroxide is the selected regenerant it has been shown that the performance of untreated zeolite, as an ammonium adsorbent, improves over the first few regeneration cycles (Jorgensen *et al.*, 1979; Demir *et al.*, 2002). Jorgensen *et al.*, (1978) concluded that pre-treatment of clinoptilolite with NaOH resulted in an increased operating capacity from 9.41 mg $\text{NH}_4^+\text{-N g}^{-1}$ to 10.64 mg $\text{NH}_4^+\text{-N g}^{-1}$.

2.7.4 Process characteristics and performance

The effective capacity of any adsorption media for ammonia is dependant upon a number of factors including, grain size (Hlvay *et al.*, 1982), the loading rate in BV h^{-1} (Shijun Liu *et al.*, 2005), solution concentration (Weatherley and McVeigh, 2000), pH (Koon and Kauffmann, 1975), running time, temperature and the scale of the operation (i.e. the amount of media used and the column dimensions). Performance data is presented in Table 2.9.

The grain size of the adsorbent used has a large impact on the performance of the process (Hedstrom, 2001). Various grain sizes of media have been used, ranging from less than 0.15mm (Beler Baykal, 1998 and Jung *et al.*, 2004) to 9mm (Mackinnon *et al.*, 2003), but there seems to be an optimum range for achieving the best results. The smaller the grain size the, the higher the ammonium exchange capacity (Aiyuk *et al.*, 2003). This concurs with Hlvay *et al.*, (1982) who conducted trials at a constant flow rate of 10 BV h^{-1} with both synthetic and municipal wastewater solutions for samples of clinoptilolite of varying grain size. Calculated capacities were 9.15, 5.91 and 1.37 mg $\text{NH}_4^+\text{-N g}^{-1}$ of clinoptilolite for grain sizes of 0.5-1.0, 0.2-1.6 and 1.6-4.0mm, respectively. However, there are practical issues associated with this, the smaller the grain size the greater the head loss will be in the column (Hlvay *et al.*, 1982). Therefore, grain size selection is a compromise between these two factors. The resulting optimum grain size tends to be between 1-2 mm (Jorgensen *et al.*, 1976; Aiyuk *et al.*, 2003) and Hlvay *et al.*, (1982) recommended a minimum grain size of 0.5 mm, stating that below this, the resulting head loss proved too restrictive. It is

important to note that Nguyen and Tanner, (1988) found that fine zeolites performed better than coarse ones in laboratory equilibrium experiments but concluded that removal efficiency in columns was unaffected by particle size.

Table 2.9 Performance data for various processes and media

Material	NH ₄ ⁺ -N Capacity (g kg ⁻¹)	Grain Size (mm)	Bed Volume (ml)	Flow Rate (BV h ⁻¹)	Influent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	Effluent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	pH	Reference
Clinoptilolite	4.8	0.3-0.84	-	15	18.8	Breakthrough of 1 mg l ⁻¹ reached at between 100-240 BV's	7.9-8.1	Koon and Kauffmann, 1975
Clinoptilolite –Tokaj region of Hungary	0.94 - 2.41	1.4 – 2.0 2.5 – 5.0 3.2 – 5.0	200	10 - 12	26 - 33	0.6 – 4.1	7.0	Jorgensen <i>et al.</i> , 1976
Clinoptilolite Buckhorn N.M. Double Eagle Mining Company	3.9	0.3 – 0.84	700	5.55-6.88	20	2 mg l ⁻¹ breakthrough reported after 16.5-20 hours	6.5-8.0	Semmens and Porter, 1979
Clinoptilolite -Tokaj region of Hungary	1.37-9.15	0.5 – 1.0	40-4000	5-7	12-45	4.5 at breakthrough	7.1-8.2	Hlvay <i>et al.</i> , 1982
Clinoptilolite – Beli Plast region of Bulgaria	2.0-3.6	2.0-2.3	96	6-20	15-17	-	-	Belar Bykal and Guven, 1997
Mordenite and Clinoptilolite	3.7-6.5	0.25-0.5 2.0-2.83	77-179	0.056-3.12	100	Breakthrough of 1- 1.2 mg l ⁻¹ reached after 40 BV's	7.5-7.7	Nguyen and Tanner, 1998

Material	NH ₄ ⁺ -N Capacity (g kg ⁻¹)	Grain Size (mm)	Bed Volume (ml)	Flow Rate (BV h ⁻¹)	Influent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	Effluent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	pH	Reference
Gordes Clinoptilolite and Sivrihisar Sepiolite (Turkey)	-	2.0-2.8	350	12	15	0.1 for 100 BV's	-	Celik <i>et al.</i> , 2001
MesoLite	45-55	3-9	107000	1-2.7	500-1000	5-15	7.1-10.2	Mackinnon <i>et al.</i> , 2003
Zeolite	6.0-7.4	<0.15	-	-	-	-	-	Jung <i>et al.</i> , 2004
Croatian Clinoptilolite	6.0-13.65	0.5-2.0	710	2+	130-850 (400 average)	Breakthrough reached at 14 and 32 BV's	7.3-7.77	Farkas <i>et al.</i> , 2005
Chinese Clinoptilolite – Jinyun in the Province of Zhejiang	5.89-7.74	0.45-0.9	-	6-24	25	Breakthrough set at 5 mg l ⁻¹	-	Shijun Liu <i>et al.</i> , 2005
Transcarpathian Clinoptilolite	3.56-21.52	0.125-2.0	14	8-40	100	Breakthrough set at 2 mg l ⁻¹	-	Sprynskyy <i>et al.</i> , 2005

Loading rates of the media have a direct bearing upon the hydraulic retention time and can affect the operating ammonium exchange capacity. Ammonium removal efficiency is shown to decrease with increased flow rates (Aiyuk *et al.*, 2003). Beler Baykal *et al.*, (1996) conducted experiments using clinoptilolite sourced from the Beli Plast region of Bulgaria over a range hydraulic retention times and concluded that the HRT should not be less than 3 minutes, or breakthrough would be reached too fast. However, this all depends upon the breakthrough concentration selected. Beler Baykal and Guven, (1997) performed trials at various flow rates resulting in contact times of between 3 and 10 minutes, giving varied results for the ammonium exchange capacity of clinoptilolite. The feed concentration of ammonium for these trials was 15 mg l^{-1} . They concluded that the optimum contact time was 5 minutes giving an overall capacity of $3.6\text{ mg NH}_4^+\text{-N g}^{-1}$ clinoptilolite. They then adopted this contact time for the concluding part of their study. Semmens and Porter, (1979) conducted trials using a synthetic feed of ammonium concentration 20 mg l^{-1} at flow rates in the range $5.55\text{--}6.88\text{ BV h}^{-1}$. The results of the study gave an average capacity for clinoptilolite of $3.9\text{ mg NH}_4^+\text{-N g}^{-1}$ clinoptilolite. This compares favourably with Booker *et al.*, (1996) with results giving an average capacity of $4.5\text{ mg NH}_4^+\text{-N g}^{-1}$ clinoptilolite. Experiments were performed using Australian zeolite in various homo-ionic forms with an influent concentration of $25\text{--}50\text{ mg l}^{-1}\text{ NH}_4^+\text{-N}$ and a breakthrough concentration of $1\text{ mg l}^{-1}\text{ NH}_4^+\text{-N}$. They reported that ammonium adsorption was a fast process and recommended that the HRT should be between 6 and 10 minutes, concluding that below 6 minutes breakthrough was reached considerably quicker but that 10 minutes was enough contact time for the adsorption process. Shijun Liu *et al.*, (2005) conducted experiments on synthetic ammonium solution at flow rates in the range $6\text{--}24\text{ BV h}^{-1}$ and concluded that maximum capacity ($7.74\text{ mg NH}_4^+\text{-N g}^{-1}$) was achieved at the lowest flow rate since the hydraulic retention time was the longest.

The solution concentration can have a considerable effect on the process performance where, for example, the effective capacity for clinoptilolite increases from 6.58 to $13.3\text{ mg NH}_4^+\text{-N g}^{-1}$ as solution concentration increases from 14 to $74\text{ mg NH}_4^+\text{-N l}^{-1}$ (Weatherly and McVeigh, 2000). Jorgensen *et al.*, (1979) concurs with this, concluding that greater concentrations in ammonium in the solution resulted in greater amounts of ammonium being exchanged. Hlvay *et al.*, (1882) found that a faster breakthrough occurred when increasing the influent concentration over a range of 17

to 45 mg $\text{NH}_4^+\text{-N l}^{-1}$. These experiments found, however, that the amount of ammonium exchanged remained roughly constant over this range. An explanation for this discrepancy may be the fact that Jorgensen *et al.*, (1979) used more concentrated solutions, allowing a greater percentage of the exchange sites to be used.

Koon and Kaufmann, (1975) conducted experiments over a range of pH values from 4-10 and found that the best conditions for ammonium exchange were at pH 6 (Hedstrom, 2001). They concluded that at high pH ammonium entered the gas phase as ammonia, whereas at low pH the ammonium had to compete with hydrogen ions at the exchange sites.

One advantage of the adsorption process, over biological processes, is that it appears to be independent of temperature. Koon and Kaufmann, (1975) conducted experiments in the range 10-20°C and concluded that temperatures within this range had no effect on the process performance.

At larger scales of operation ammonia removal efficiency decreases quite considerably. Hlavay *et al.*, 1982 observed that when scaling a system up 100 fold only 60% of the breakthrough capacity was achieved when compared to the smaller system. This was attributed to the fact that channelling occurs in larger columns of media, indicating that some of the media may not come into contact with the ammonium solution.

The maximum ammonium exchange capacity of zeolites, mainly clinoptilolite, ranges from 2.41 mg $\text{NH}_4^+\text{-N g}^{-1}$ (Jorgensen *et al.*, 1976) to 9.15 mg $\text{NH}_4^+\text{-N g}^{-1}$ (Hlavay *et al.*, 1982). The three notable exceptions to this are; the Croatian clinoptilolite used by Farkas *et al.*, 2005 (13.65 mg $\text{NH}_4^+\text{-N g}^{-1}$); the Transcarpathian clinoptilolite used by Sprynskyy *et al.*, 2005 (21.52 mg $\text{NH}_4^+\text{-N g}^{-1}$) and the modified bentonite, MesoLite, used by Mackinnon *et al.*, 2003 (55 mg $\text{NH}_4^+\text{-N g}^{-1}$). The variability of results is best outlined by the fact that both Jorgensen *et al.*, (1976) and Hlavay *et al.*, (1982) used clinoptilolite from the Tokaj deposit in Hungary yet reported different maximum capacities (2.41 and 9.15 mg $\text{NH}_4^+\text{-N g}^{-1}$ respectively). However, the former did operate at twice the flow rate.

2.8 Regeneration

Regeneration frequency depends on a number of parameters including, the amount of exchanger used, the influent concentration, the effluent concentration, the loading rate and the breakthrough concentration selected (Hedstrom, 2001). Regeneration is achieved by re-circulating a brine solution through the exhausted media (Booker *et al.*, 1996; Celik *et al.*, 2001; Witte and Keding, 1992; Koon and Kaufmann, 1975, Liberti *et al.*, 1981; Semmens and Porter, 1979; Hlvay *et al.*, 1982). The cations in the brine exchange with the ammonium and a high concentration ammonium solution is formed. Once the regeneration cycle is complete the media is then ready for use again in the exhaustion cycle. As mentioned previously the most suitable cation for ammonium removal is sodium (Booker *et al.*, 1996; Jorgensen *et al.*, 1979). A number of different of different brines have been used to achieve this exchange of sodium for ammonium (Table 2.10).

Many authors have used sodium chloride as the chosen brine (Witte and Keding, 1992; Koon and Kaufmann, 1975; Semmens and porter, 1979; Liberti *et al.*, 1981; Hlvay *et al.*, 1982; Shijun Liu *et al.*, 2005). Two factors affect the duration of regeneration required. These are namely the concentration of the solution and the operating pH. This assumes that the amount of regenerant used is fixed for any given process. Koon and Kaufmann, (1975) conducted experiments with pH conditions over a range of 11.5-12.5. At the lower pH, 20 BV of brine (0.34 M NaCl) was required for regeneration. At an increased pH level of 12.5 only 10 Bed volumes of regenerant was needed at a lower concentration of 0.21 M NaCl. Other regenerants have been used as an alternative to sodium chloride, most notably sodium hydroxide (Celik *et al.*, 2001) but the caustic nature of the brine can lead to attrition of the column media.

Table 2.10 Regeneration characteristics

Regenerant Brine	Flow Rate (BV h ⁻¹)	Duration (h)	pH	Reference
NaCl	15	0.7-1.3	11.5-12.5	Koon and Kauffmann, 1975
NaOH	-	0.5	-	Jorgensen <i>et al.</i> , 1976
NaCl/NaNO ₃	12-20	1.0	7.0-8.4	Semmens and Porter, 1979
NaCl	30	0.7	~7	Liberti <i>et al.</i> , 1981
NaCl	5-7.5	1.4-4.0	12.3	Hlvay <i>et al.</i> , 1982
NaCl	-	-	8.0	Belar Bykal and Guven, 1997
NaCl+NaOH	-	0.33-1.0	11.5	Celik <i>et al.</i> , 2001
Na ₂ CO ₃	0.5-1.5	4	-	Mackinnon <i>et al.</i> , 2003
NaCl	5-10	2.5-5.0	11-12	Shijun Liu <i>et al.</i> , 2005

Several authors (Semmens *et al.*, 1977; Semmens and Porter 1979; Green *et al.*, 1996; Lahav and Green, 1998; Chung *et al.*, 2002) have used biological regeneration as an alternative to the use of passing brine solution. Biological regeneration is a combination of chemical regeneration and the introduction of nitrifying bacteria. After the exhaustion of the columns nitrifying sludge is introduced in such a manner as to fluidise the bed (Semmens *et al.*, 1977). The system is dosed either with sodium nitrate (Semmens *et al.*, 1977) or sodium bicarbonate (Lahav and Green, 1996) and the media acts as a substrate for nitrifying bacteria. The addition of sodium compounds is to facilitate the exchange of sodium ions with the ammonium ions on the zeolite. The main driver for attempting biological regeneration was to reduce brine consumption. However, problems occur due to the re-adsorption of ammonium back onto the media and the regeneration rate is controlled by the nitrification rate as ammonium is displaced from the media column faster than the nitrifying bacteria were able to oxidise it (Semmens *et al.*, 1977).

2.9 Regenerant disposal

Mackinnon *et al.*, (2003) and Lahav and Green, (1996) both concluded that if the ammonium concentration of the used regenerant could be optimised it could be commercially viable as a fertiliser additive. Liberti *et al.*, (1986) developed a process including an anion exchange phase, resulting in the precipitation of magnesium ammonium phosphate, which can be used as a slow release fertilizer. Liberti, (1982) also performed sorption trials with sulphuric acid, with the resulting solution having a direct use as a fertiliser.

2.10 Alternative uses

The use of zeolite as a media for ammonium removal is not restricted to the treatment of municipal wastewater. Studies have been performed using zeolite as an ammonium adsorbent for landfill leachate (Townsend *et al.*, 2003) and the process has also been used to supplement biological treatment of pre-treated landfill leachate (Kargi and Pamukoglu, 2004). Townsend *et al.*, (2003) concluded that clinoptilolite was an effective treatment with an exchange capacity of $20 \text{ mg NH}_4^+\text{-N g}^{-1}$ clinoptilolite (Sprynskyy *et al.*, 2005 achieved a capacity of $21.52 \text{ mg NH}_4^+\text{-N g}^{-1}$ for wastewater treatment using clinoptilolite). It was also noted that the process appeared temperature independent in agreement with Koon and Kaufmann, (1975). However, although highly selective for ammonium, high concentrations of potassium did have an adverse effect, irreversibly reducing the exchange capacity of the media. Kargi and Pamukoglu, (2004) tested both powdered zeolite and powdered activated carbon (PAC) as treatment for landfill leachate. The zeolite removed 40% of the ammonium and the PAC 30% and although the zeolite outperformed the PAC for ammonium removal, the PAC outperformed the zeolite for COD removal. PAC was considered more suitable as a treatment for landfill leachate than zeolite, with the authors stating that zeolite had little advantage, as the ammonium could easily be removed by air stripping.

2.11 Summary

A range of techniques for the treatment of problematic sidestreams within the wastewater treatment process have been presented, with a view to minimising the impact of recycled high strength ammonium liquors. Sidestreams arise from a variety of sources but those resulting from the dewatering of digested sludge in particular, have the potential for the greatest detrimental effect. Modification of mainstream processes or the implementation of specific treatments, both biological and chemical, can be successful in mitigating against the problems created by inflated ammonium loadings. The emphasis of this review is on the use of ion exchange using zeolites as a potential solution. Clinoptilolite, in particular displays a high selectivity for ammonium and in selected cases a high capacity, up to $21.52 \text{ mg NH}_4^+ \text{-N g}^{-1}$, with MesoLite delivering $45\text{-}55 \text{ mg NH}_4^+ \text{-N g}^{-1}$. A number of parameters are reported to have an effect on the performance of the ion exchange process, including the influent ammonium concentration; the required ammonium concentration in the effluent; the loading rate and the pH. Optimum conditions appear to be a high influent concentration with a low loading rate at pH values between 6 and 8. Although considerable data is available on the regeneration process not much is offered in the method of disposal of the spent regenerant. Full scale implementation is scarce and the majority of studies were performed at laboratory scale in many cases on synthetic solutions, and as such, limited operational data is available. Therefore, further work is required to fully assess the potential of the ion exchange process for ammonium removal from municipal wastewater streams.

2.12 References

- Abeling, U. and Seyfried, C. F. (1992) Anaerobic-aerobic treatment of high-strength ammonium wastewater-nitrogen removal via nitrite. *Water, Science and Technology* **26** (5-6), 1007-1015.
- Aiyuk, s., Xu, H., van Haandel, A. and Verstraete, W. (2003) Removal of ammonium from pretreated domestic sewage using a natural ion exchanger. (LabMET), Ghent University.
- Armbruster, T. (2001) Clinoptilolite-heulandite: application and basic research. *Studies in Surface Science and Catalysis* **135**, 13-27.
- Barros, M. A. S. D., Zola, A. S., Arroyo, P. A., Sousa-Aguiar, E. F. and Tavares, C. R. G. (2003) Binary ion exchange of metal ions in Y and X zeolites. *Brazilian Journal of Chemical Engineering* **20** (4), 413-421.
- Battistoni, P., Pavan, P., Prisciandaro, M. and Cecchi, F. (2000) Struvite crystallisation: A feasible and reliable way to fix phosphorus in anaerobic supernatants. *Water Research* **34** (11), 3033-3041.
- Belér Baykal, B. (1998) Clinoptilolite and multipurpose filters for upgrading effluent ammonia quality under peak loadings. *Water, Science and Technology* **37** (9), 235-242.
- Belér Baykal, B., Oldenburg, M. and Sekoulov, I. (1994) Post equalisation of ammonia peaks. *Water Research* **28** (9), 2039-2042.
- Belér Baykal, B., Oldenburg, M. and Sekoulov, I. (1996) The use of ion exchange in ammonia removal under constant and variable loads. *Environmental Technology* **17**, 717-726.
- Belér Baykal, B. and Guven, D. A. (1997) Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater. *Water, Science and Technology* **35** (7), 47-54.

Bo-Bertil, L., Ban, Z. and Byden, S. (2000) The recovery of human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. *Bioresource Technology* **73** 169-174.

Bolto, B. A. and Pawlowski, L. (1987) Wastewater treatment by ion exchange, E and FN Spon, New York.

Booker, N. A., Cooney, E. L. and Priestly, A. J. (1996) Ammonia removal from sewage using natural Australian zeolite. *Water, Science and Technology* **34** (9), 17-24.

Booker, N. A., Cooney, E. L. and Fraser, I. H. (1999) Struvite formation in wastewater treatment plants: Opportunities for nutrient recovery. *Environmental Technology* **20** 777-782.

Breck, D. (1974) Zeolite and molecular sieves structure and chemistry, John Wiley & Sons, New York.

Brett, S., Guy, J., Morse, G. K and Lester, N. J. (1997) Phosphorus removal and recovery technologies, Selper Publications, London.

Celen, I. and Turker, M. (2001) Recovery of ammonia as struvite from anaerobic digester effluents. *Environmental Technology* **22** 1263-1272.

Celik, M. S., Ozdemir, B., Turan, M., Koyuncu, I., Atesok, G. and Sarikaya, H.Z. (2001) Removal of ammonia by natural clay minerals using fixed bed column reactors. *Water, Science and Technology: Water Supply* **1** (1), 81-88.

Chung, Y., Son, D. and You, M. (2004) Treatment of ammonium rich wastewater using natural zeolite as a medium in biofilter. Water Environment and Remediation Research Centre, Korea.

Colella, C., DE' Gennaro, M., Langella, A. and Pansini, M. (1995) In: Natural zeolites-cadmium removal from wastewaters using chabazite and phillipsite. Ming, D. W. and Mumpton, F. A (Eds), pp 377-384, Int. Comm. Natural Zeolites, Brockport, New York.

Cooney, D. O. (1999), Adsorption design for wastewater treatment, Lewis Publishing, New York.

Curkovic, L., Cerjan-Stefanovic, S. and Filpan, T. (1997) Metal ion exchange by natural and modified zeolites. *Water Research* **31** (6), 1739-1382.

Demir, A., Gunay, A. and Debik, E. (2002) Ammonium removal from aqueous solution by ion exchange using packed bed natural zeolite. *Water SA* **28** (3), 329-336.

DeSilva, F. J. (1999) Essentials in ion exchange. Presented at the 25th Annual WQA Conference.

Dyer, A. (1988) An introduction to zeolite molecular sieves, John Wiley and Sons Ltd, Chichester.

Erdem, E., Karapinar, N. and Donat, R. (2004) The removal of heavy metal cations by natural zeolites. *Colloid and Interface Science* **280**, 309-314.

Evans, F. L., Gilbert, W. G. and Walsh, T. K. (1987) Sidestreams in wastewater treatment plants *Journal WPCF* **59** (1), 54-59.

Farkas, A., Rozic, M. and Barbaric-Mikocevic, Z. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* B117 25-33.

Fawcett, N. S. J., Sidall, R. A. and Wheak, G. (1997) Side-stream treatment of raw-sludge liquors using activated sludge: Pilot investigations and full-scale design rationale. *J. CIWEM* **June 1997**, 209-216.

Flanigen, E. M. (1984) In: Zeo-agriculture, use of natural zeolites in agriculture and aquaculture- adsorption properties of molecular sieve zeolites. Pond, W.G. and Mumpton, F. A. (Eds), pp 55-68, Westview Press, Boulder, Colorado.

Fux, C., Boehler, M., Huber, P., Brunner, I. and Siegrist, H. (2002) Biological treatment of ammonium-rich wastewater by partial nitrification and subsequent ammonium oxidation (anammox) in a pilot plant. *Journal of Biotechnology* **99** 295-306.

Fux, C., Lange, K., Faessler, A., Huber, P., Grueniger, B. and Siegrist, H. (2003) Nitrogen removal from digester supernatant via nitrite – SBR or SHARON. *Water, Science and Technology* **48** (8), 9-18.

- Green, M., Mels, A., Lahav, And Tarre, S. (1996) Biological ion exchange process for ammonium removal from secondary effluent. *Water, Science and Technology* **34** (1-2), 449-458.
- Gottardi, G. (1978) In: Natural zeolites occurrence and properties – mineralogy and chemistry of zeolites. Use Sand, L.B. (Ed) pp 31-44, Pergamon Press, Oxford.
- Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) Removal of NH_4^+ ion from NH_4Cl solution using clinoptilolite: A dynamic study using a continuous packed-bed column in upflow mode. *Separation Science and Technology* **36** (9), 1347-1364.
- Hawkins, D. B. (1984) In: Zeo-agriculture, use of natural zeolites in agriculture and aquaculture- occurrence and availability of natural zeolites. Pond, W.G. and Mumpton, F.A. (Eds), pp 69-78, Westview Press, Boulder, Colorado.
- Hedstrom, A. (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of Environmental Engineering* **August 2001**, 673-681.
- Helfferich, F. (1962) Ion exchange, McGraw-Hill, New York.
- Hellings, C., Schellen, A. A. J. C., Mulder, J. W., van Loosdrecht, M. C. M. and Heijnen, J. (1988) The SHARON process: an innovative method for nitrogen removal from ammonium-rich waste water. *Water Science and Technology* **37** (9) 135–142.
- Hlavay, J., Vigh, G., Olaszi, V. and Inczedy, J. (1982) Investigation on natural Hungarian zeolite for ammonia removal. *Water Research* **16**, 417-420.
- Hultgren, J. and Hultman, B. (1984) Experimental and theoretical basis for expanding and upgrading the Akeshov-Nockeby plant. *Water, Science and Technology* **16**, 635-647.
- Inglezakis, V. J. and Grigoropoulou, H. (2004) Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors. *Journal of Hazardous Materials* **B112** 37-43.
- Janus, H. M. and van der Roest, H. F. (1997) Don't reject the idea of treating reject water. *Water, Science and Technology* **35** (10), 27-34.

Jeavons, J., Stokes, L., Upton, J. and Bingley, M. (1998) Successful sidestream nitrification of digested sludge liquors. *Water, Science and Technology* **38** (3), 111-118.

Jetten, M. S. M., Horn, S. J. and van Loosdrecht, M. C. M. (1997) Towards a more sustainable municipal wastewater treatment system. *Water, Science and Technology* **35** (9), 171-180.

Jorgensen, S. E., Libor, O., Graber, K. L. and Barkacs, K. (1976) ammonia removal by use of clinoptilolite. *Water Research* **10**, 213-224.

Jorgensen, S. E., Libor, O., Barkacs, K. and Kuna, L. (1979) Equilibrium and capacity data of clinoptilolite. *Water Research* **13**, 159-165.

Jung, J., Chung, Y., Shin, H. and Son, D. (2004) Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research* **38**, 347-354.

Kabdasli, I., Tunay, O., Ozturk, I., Yilmaz, S. and Arikan, O. (2000) Ammonia removal from young landfill leachate by magnesium ammonium phosphate precipitation and air stripping. *Water, Science and Technology* **41** (1), 237-240.

Kargi, F. and Pamukoglu, Y. N. (2004) Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation. *Bioresource Technology*.

Kamarowski, S. and Yu, Q. (1997) Ammonium ion removal from wastewater using Australian natural zeolite: Batch equilibrium and kinetics Studies. *Environmental Technology* **18** 1085-1097.

Khin, T. and Annachatre, A. P. (2004) Novel microbial nitrogen removal process. *Biotechnology Advances* **22** 519-532.

Klieve, J. R. and Semmens, M. J. (1979) An Evaluation of pretreated natural zeolites for ammonium removal. *Water Research* **14**, 161-168.

Kolisch, G. and Rolfs, T. (2000) Integrated sidestream treatment for enhanced enlargement of sewage plants. *Water, Science and Technology* **41** (9), 155-162.

Koon, H. J. and Kaufmann, W. J. (1975) Ammonia removal from municipal wastewaters by ion exchange. *Journal WPCF* **47** (3) 448-465.

la Cour Jansen, J., Nyberg, U., Aspegren, H. and Andersson, B. (1993) Handling of anaerobic supernatant combined with full nitrogen removal. *Water, Science and Technology* **27** (5-6), 391-403.

Lahav, O. and Green, M. (1998) Ammonium removal using ion exchange and biological regeneration. *Water Research* **32** (7), 2019-2028.

Liberti, L., Boari, G., Prtruzzelli, D. and Passino, R. (1981) Nutrient removal and recovery from wastewater by ion exchange. *Water Research* **15**, 337-342.

Liberti, L., Boari, G. and Passino, R. (1982) Advanced wastewater treatment by ion exchange. *Water Research* **15**, 337-342.

Liberti, L., Limoni, N., Lopez, A., Passino, R. and Boari, G. (1986) The 10m³ h⁻¹ RIM-NUT demonstration plant at West Bari for removing and recovering N and P from wastewater. *Effluent and Water Treatment Journal* **22** (7), 253-257.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient removal from wastewaters using high performance materials. *Water, Science and Technology* **47** (11), 101-107.

Matsumiya, Y., Yamasita, T. and Nawamura, Y. (2000) Phosphorus removal from sidestreams by crystallisation of magnesium-ammonium-phosphate using seawater. *J. CIWEM*, August 2000 291-296.

McCabe, W. L., Smith, J. C. and Harriott, P. (1985) Unit operations of chemical engineering. Carberry, J. J., Fair, R. J., Peters, M. s., Schowalter, W. P. and Wei, J. (Eds), McGraw-Hill, New York.

Mier, M. V., Callejas, R. L., Gehr, R., Jiminez Cisneros, B. E. and Alvarez, P. J. J. (2001) Heavy metal removal with Mexican clinoptilolite: multi component ion exchange. *Water Research* **35** (2), 373-378.

Mondale, K. D., Carland, R. M. and Aplan, F. F. (1995) The comparative ion exchange capacities of natural sedimentary and synthetic zeolites. *Minerals Engineering* **8** (4/5), 535-548.

Mosquera-Corral, A., Gonzalez, F., Campos, J. L. and Mendez, R. (2005) Partial Nitrification in a SHARON Reactor in The Presence of Salts and Organic Compounds. *Process Biochemistry* **40** 3109-3118.

Mumpton, F. A. (1984) In: Zeo-agriculture, use of natural zeolites in agriculture and aquaculture- natural zeolites. Pond, W.G. and Mumpton, F.A. (Eds), pp 33-43, Westview Press, Boulder, Colorado.

Munch, E. V. and Barr, K. (2001) Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Research* **35** (1), 151-159.

Nguyen, M. L. and Tanner C. C. (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural research* **41** 427-466.

Kovatcheva -Ninova, V., Nikolova, N. and Marinov, M. (2002) Investigation in the adsorption properties of natural adsorbents zeolite and bentonite towards copper Ions. *Annual of The University of Mining and Geology "St Ivan Rilski"* **45** (2), 93-97.

Ouki, S. K. and Kavannagh, M. (1997) Performance of natural zeolites for the treatment of mixed metal-contaminated effluents. *Waste Management & Research* **15**, 383-394.

Paterson, R. (1970) An introduction to ion exchange, Heyden and Son Ltd London.

Parsons, S. A., Wall, F., Doyle, J., Oldring, K. and Churchley, J. (2001) Assessing the potential for struvite recovery at sewage treatment works. *Environmental Technology* **22** 1279-1286.

Pearce, O., Clark, T. and Ndombasi, P (2000) Ammonia removal from sludge liquors. Thames Water Plc, Research and Technology report.

Petrus, R. and Warchol, J. (2003) Ion exchange equilibria between clinoptilolite and aqueous solutions of Na^+/Cu^+ , Na^+/Cd^+ and Na^+/Pb^+ . *Microporous and Mesoporous Materials* **61** 137-146.

Pickin, S. R. and Saunders, F. J. (1994) A novel high rate method for the nitrification of sludge liquors containing high levels of ammonia. *Water, Science and Technology* **29** (12), 139-147.

Purtschert, H., Siegrist, H. and Gujer, W. (1996) Enhanced denitrification with methanol at WWTP Zurich-Werdholzi. *Water, Science and Technology* **33** (12), 117-126.

Rogella, F. (2005) Battling the element. *Water and Waste Management* **December 2005**, 37-39.

Rostron, W. M., Stuckey, D. and Young, A. A. (2001) Nitrification of high strength ammonia wastewaters: comparative study of immobilisation media. *Water Research* **35** (5), 1169-1178.

Salerno, P. and Mendioroz, S. (2002) Preparation of Al-pillared montmorillonite from concentrated dispersions. *Applied Clay Science* **22** 115-123.

Sarioglu, M. (2005) Removal of ammonium from municipal wastewater using natural Turkish (dogantepe) zeolite. *Separation and Purification Technology* **41** (1) 1-11.

Schmidt, I., Sliekers, O., Schmid, M., Bock, E., Fuerst, J., Kuenen, J. G., Jetten, M. S. M. and Strous, M. (2003) New concepts of microbial treatment processes for the nitrogen removal in wastewater. *FEMS Microbiology Reviews* **27** 481-492.

Shijun Liu, Q. D., Zhonghong, C. and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese Clinoptilolite. *Separation and Purification Technology* **44** 229-234.

Schulze-Rettmer, R. (1991) The simultaneous chemical precipitation of ammonium phosphate in the form of magnesium-ammonium-phosphate. *Water, Science and Technology* **23**, 659-667.

- Siegrist, H., Gajcy, D., Sulzer, S., Roeleveld, P., Oschwald, R., Frischknecht, H., Pfund, D., Mörgeli, B. and Hungerbühler, E. (1992) Nitrogen elimination from digester supernatant with magnesium-ammonium-phosphate precipitation. *Chemical Water and Wastewater Treatment II* R. Klute, H. Hahn (Eds.). Springer Verlag, Berlin, 457-465.
- Siegrist, H. (1996) Nitrogen removal from digester supernatant – comparison of chemical and biological methods. *Water, Science and Technology* **34** (1-2), 399-406.
- Siegrist, H., Brack, T., Koch, G., Nussbaumer, A. and Gujer, W. (2000) Optimization of nutrient removal in the WWTP Zurich-Werholzi. *Water, Science and Technology* **41** (9), 63-71.
- Semmens, M. J. and Porter, P. S. (1979) Ammonium Removal by Ion Exchange: Using Biologically Restored Regenerant. *Journal WPCF* **51** (12), 2928-2940.
- Semmens, M. J., Wang, J. T. and Booth, A. C. (1977) Nitrogen removal by ion exchange: biological regeneration of clinoptilolite. *Journal WPCF* **49**, 2431-2444.
- Semmens, M. J. (1984) In: Zeo-agriculture, use of natural zeolites in agriculture and aquaculture- cation exchange properties of natural zeolites. Pond, W.G. and Mumpton, F.A. (Eds), pp 45-53, Westview Press, Boulder, Colorado.
- Sprynskyy, M., Lebedynets, M., Terzyk, A. P., Kowalczyk, P., Namiesnik, J. And Buszewski, B. (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Colloid and Interface Science* **284** 408-415.
- Tosheva, L. (1999) Zeolite macrostructures. Licentiate Thesis, Lulea University of Technology, Sweden.
- Townsend, A., Dickinson, K., Dobson, I., Batten, M., Liddle, B. and Coombs, C. (2003) Development of a novel ammonia filter for landfill leachate treatment. Wyvern Environmental Trust Final Report.

Tzvetcov, S. and Stoytcheva, M. (2003) The possibility of phosphates removal from waste waters and obtaining of mixed fertilizers with natural zeolites. *Annual of The University of Mining and Geology "St Ivan Rilski"* **46** (2), 123-125.

United States Environmental Protection Agency (1985) Sidestreams in advanced wastewater plants: Problems and remedies.

United States Environmental Protection Agency Technical Bulletin (1998) Zeolite a versatile air pollutant adsorber EPA 456/F-98-004.

van Dongen, L. G. J. M., Jetten, M. S. M. and van Loosdrecht, M. C. M. (2001) The combined Sharon/Anammox process: A sustainable method for N-removal from sludge water. STOWA report IWA Publishing, London.

van Kempen, R., ten Have, C. C. R., Meijer, S. C. F., Mulder, J. W., Duin, J. O. J., Uijterlinde, C. A. and van Loosdrecht, M. C. M. (2005) SHARON process evaluated for improved wastewater treatment plant nitrogen effluent quality. *Water Science & Technology* **52** (4) 55-62.

Varshney, K. G. (2002) Synthetic ion exchange materials and their analytical applications. Aligarh Muslim University, Aligarh.

Verstraete, W. and Phillips, S. (1998) Nitrification-denitrification processes and technologies in new contexts. *Environmental Pollution* **102** S1 717-726.

Wang, Y., Liu, S., Xu, Z., Han, T., Chaun, S. and Zhu, T. (2006) Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials* B136 735-740.

Weatherly, L.R. and McVeigh, R. J. (2000) The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria in: Proceedings of IEX 2000, Ion exchange at the millennium, 16- 21 July, Cambridge, England. pp 133-141.

Weatherley, L. R. and Miladinovic, N. D. (2004) Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research* **38**, 4305-4312.

Williams, S. (1999) Struvite precipitation in the sludge stream at slough wastewater treatment plant and opportunities for phosphorus recovery. *Environmental Technology* **20**, 743-747.

Witte, H. and Keding, M. (1992) Zeolite filters in wastewater treatment plants. In: Proceedings of the 5th Gothenburg Symposium Chemical and Wastewater Treatment II, 28-30 September, Nice, France. pp 467-484.

CHAPTER 3

**AMMONIUM REMOVAL FROM SOLUTION USING ION EXCHANGE ON
TO MESOLITE: AN EQUILIBRIUM STUDY**

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3. AMMONIUM REMOVAL FROM SOLUTION USING ION EXCHANGE ON TO MESOLITE: AN EQUILIBRIUM STUDY

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Abstract

This paper investigates the potential of MesoLite ion exchange media for ammonium (NH_4^+) removal from solution in the presence of competing cations. Batch tests were performed under a range of conditions to assess the effect of contact time, solution pH and solution concentration on the performance and capacity of the media for this application. The data obtained was fitted to the Langmuir and Freundlich isotherm models with the Langmuir model providing the better description of the process. Results indicate a maximum equilibrium capacity of $72 \text{ g NH}_4^+\text{-N kg}^{-1}$ is achievable, which is reduced to $49 \text{ g NH}_4^+\text{-N kg}^{-1}$ in the presence of competing cations. A detailed examination of the data shows that increasing solution concentration and increased contact time provide the best performance at an optimum pH of between 6-7.

3.1 Introduction

Ammoniacal nitrogen present in effluents arising from the treatment of municipal wastewater can promote eutrophication in receiving waters and increased toxicity to aquatic life (Nguyen and Tanner, 1998; Du *et al.*, 2005; Karadag *et al.*, 2006; Wen *et al.*, 2006). Hence, the removal of ammonium from wastewater is of great importance in the control of nitrogen pollution (Wen *et al.*, 2006). Traditional methods of ammonium removal focus mainly on biological removal (Jorgensen and Weatherley, 2003) with much research being undertaken in biological nitrification/denitrification processes (Siegrist *et al.*, 1996; Jetten *et al.*, 1997; Rostron *et al.*, 2001; van Kempen *et al.*, 2005; Mosquera-Corral *et al.*, 2005). These processes are extremely effective at nitrogen removal but are less responsive to shock loads in which case they can fall short of achieving the required effluent quality (Beler Baykal and Guven, 1997; Karadag *et al.*, 2006). This can be compounded by the ever decreasing nitrogen discharge consent levels (Weatherley and Miladinovic, 2004; Farkas *et al.*, 2005; Karadag *et al.*, 2006) imposed by regulatory bodies on wastewater treatment companies. In addition to this, rapid economic development and the improvement of the standard of living in developing nations will result in the production of much more treated wastewater (Wang *et al.*, 2006).

A possible solution to the resulting problems is the use of ion exchange for ammonium removal as a complimentary treatment option. Wastewater treatment plants could be upgraded for the direct treatment of high concentration problematic recycle streams or for the polishing of final effluent to meet the stringent consent levels imposed (Beler Baykal and Guven, 1997). In the last 30 years many authors (Mercer *et al.*, 1970; Koon and Kaufmann 1975; Jorgensen *et al.*, 1976; Klieve and Semmens, 1979; Hlavay *et al.*, 1982; Booker *et al.*, 1996; Kamarowski and Yu, 1997; Lahav and Green, 1998; Hankins *et al.*, 2004; Jung *et al.*, 2004; Sprynsky *et al.*, 2005) have investigated the use of the naturally occurring mineral, zeolite, as an ion exchanger for the removal of ammonium from municipal wastewater and other waste streams. Zeolites are hydrated aluminosilicates (Nguyen and Tanner, 1998) comprising silica and aluminium tetrahedra which are mutually bound by chemical covalent bonds with common oxygen atoms (Farkas *et al.*, 2005). This gives rise to a three dimensional framework which is generally very open, containing channels and cavities, which are filled with cations and water

molecules (Dyer, 1988). The cations are bound by weaker electrostatic bonds, increasing their mobility and the capability of being exchanged with cations present in solution (Farkas *et al.*, 2005). The exchange capacity of zeolites is governed by the extent of aluminium substitution for silicon in the framework. Each aluminium generates a net negative charge which needs to be balanced by a cation to achieve overall electroneutrality. Therefore, the higher the aluminium substitution, the greater the ion exchange potential (Nguyen and Tanner, 1998).

Organic resins are generally preferred to zeolites as ion exchangers due to their higher cation exchange capacity (CEC), higher reaction rates and chemical resistivity (Farkas *et al.*, 2005). However, zeolites are reported to possess a higher cation exchange selectivity (Mercer *et al.*, 1970; Colella *et al.*, 1995; Farkas *et al.*, 2005). A number of zeolites have been investigated for the potential to remove ammonium from solution and it is almost universally accepted that clinoptilolite is the most suitable for this application. Clinoptilolite has a silica rich framework and therefore a lower CEC but displays a high affinity for ammonium with capacities in the range 0.94-21.52 g $\text{NH}_4^+\text{-N kg}^{-1}$. However, initial work by Mackinnon *et al.*, (2003) indicates that MesoLite has an increased ammonium exchange capacity (45-55 g $\text{NH}_4^+\text{-N kg}^{-1}$) compared to that of naturally occurring materials used by previous authors. MesoLite ion exchange media is produced by the modification of clay and other aluminium bearing minerals, resulting in the formation of the synthetic zeolite, zeolite N (Mackinnon *et al.*, 2006). This results in an increase in the amount of exchange sites available giving the media a higher exchange capacity than would be seen in the parent mineral and an increased surface area. This study investigates the performance of MesoLite under equilibrium conditions to assess the potential of the media to be used as an ammonium ion exchanger.

3.2 Materials and Methods

MesoLite media supplied by Nanochem Pty Ltd, Australia was ground down to a grain size range of 0.1 – 0.6 mm and samples of 0.5 g were equilibrated with 100 ml of $\text{NH}_4^+\text{-N}$ solution (i.e. 5 g l^{-1}) of various concentration (0 – 2000 mg l^{-1} $\text{NH}_4^+\text{-N}$) at 20° C for 24 hours. The solutions were prepared by the addition of ammonium chloride powder (NH_4Cl), supplied by Fisher Scientific, Loughborough, UK to domestic tap water. The method of using tap water in solution preparation was

adopted to ensure the presence of competing cations (sodium, calcium potassium and magnesium) in solution (Table 3.1). A number of tests were also performed by adding NH₄Cl to distilled water. Kinetic experiments to study the effect of contact time on equilibrium capacity were performed under the same experimental conditions but samples were extracted at certain time intervals (5, 10, 15, 30, 45, 60, 120, 180 and 240 minutes) to assess the uptake characteristics of the material.

Table 3.1 Concentrations of competing cations in solution

Cation	Calcium	Magnesium	Sodium	Potassium
Concentration (mg l ⁻¹)	111 ± 6	3.1 ± 0.2	16.3 ± 0.8	3 ± 0.3

Equilibrium data for ammonium uptake on to MesoLite was compared to both the Freundlich and Langmuir isotherm models, which relate the amount of ammonium exchanged per gram of media, to the equilibrium ammonium concentration remaining in solution. The ammonium concentration remaining in solution was determined using a Lasa 100 spectrometer supplied by Hach Lange GMBH, Düsseldorf, Germany. Prior to testing, solution samples were filtered using a 45 µm microporous membrane filter to separate the solution and solid phases. The ammonium concentration in the solid phase was calculated using the following mass balance equation (Jorgensen *et al.*, 1976; Demir *et al.*, 2002; Farkas *et al.*, 2005; Karadag *et al.*, 2006).

$$Q_e = \frac{(C_0 - C_e)V}{M}$$

Equation 3.1

Where:

- Q_e is the amount of ammonium in the solid phase (mg/g)
- C₀ is the initial ammonium concentration in solution (mg/l)
- C_e is the ammonium remaining in solution at equilibrium (mg/l)
- V is the solution volume (l)
- M is the mass of MesoLite introduced (g)

3.3 Results and discussion

3.3.1 Isotherm models

The Langmuir model is represented by:

$$Q_e = \frac{KbC_e}{1+KC_e} \quad \text{Equation 3.2}$$

Where K is the maximum exchange capacity of 1 kg of exchanger ($\text{g NH}_4^+\text{-N kg}^{-1}$) and b is the Langmuir energy constant or binding index ($\text{m}^3 \text{g}^{-1}$) (Nguyen and Tanner, 1997). These constants can be determined by rearranging to Equation 3.3 and plotting $1/C_e$ versus $1/Q_e$. The resulting plot forms a straight line with an intercept of $1/b$ and a gradient of $1/kb$ (Demir *et al.*, 2002; Weatherley and Miladinovic, 2004).

$$\frac{1}{Q_e} = \frac{1}{KbC_e} + \frac{1}{b} \quad \text{Equation 3.3}$$

Experimental results give the Langmuir equation for MesoLite with respect to ammonium uptake as

$$Q_e = \frac{1.828C_e}{(1+0.0658C_e)} \quad \text{Equation 3.4}$$

The Freundlich model is represented by:

$$Q_e = kC_e^{1/n} \quad \text{Equation 3.5}$$

Where k and n are the Freundlich constants for any given exchanger in a given system. These constants can be determined by rearranging to equation 3.6 and plotting $\log C_e$

versus $\log Q_e$. The resulting plot is a straight line with an intercept of $\log k$ and a gradient of $1/n$ (Demir *et al.*, 2002; Weatherley and Miladinovic, 2004; Du *et al.*, 2005).

$$\log Q_e = \log k + 1/n \log C_e \quad \text{Equation 3.6}$$

From experimental results the Freundlich equation for MesoLite with respect to ammonium uptake is given by

$$Q_e = 2.196C_e^{0.534} \quad \text{Equation 3.7}$$

A comparison of experimental data with that of the models can be made by plotting liquid ammonium concentration (C_e) against solids concentration (Q_e) to produce isotherms (Figure 3.1). The Langmuir and Freundlich isotherms are generated using Equations 3.4 and 3.7 and experimental data for C_e to calculate theoretical Q_e values. For the case of MesoLite, the Langmuir model displays a much more consistent fit to experimental data than that of the Freundlich model, although at lower concentrations the fit is more consistent for both models. This concurs with previous authors (Demir *et al.*, 2002; Weatherley and Miladinovic, 2004; Wang *et al.*, 2006) and where a comparison is made all conclude that the Langmuir model best describes the process of ammonium uptake onto zeolites.

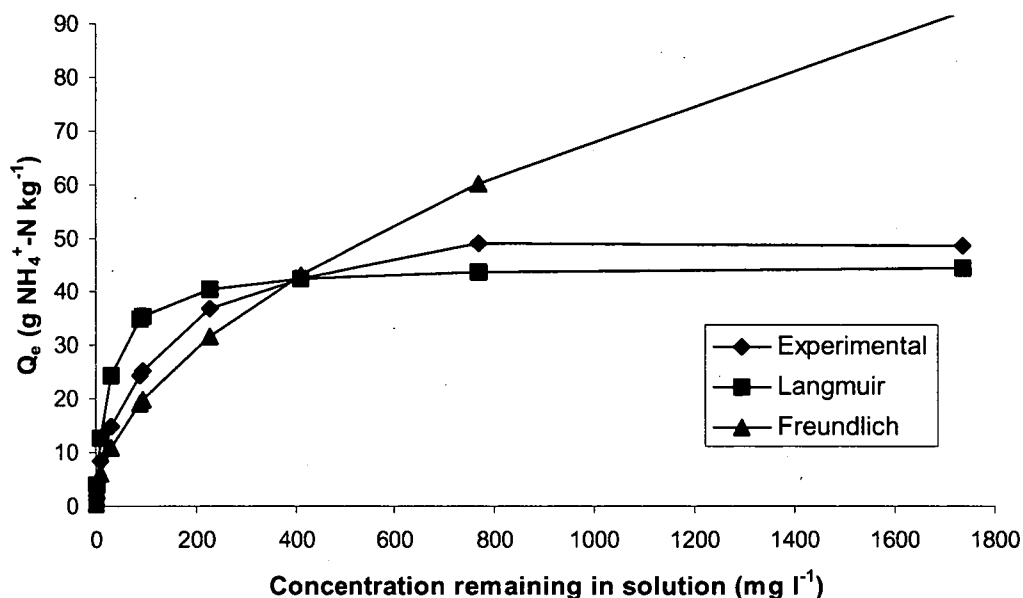


Figure 3.1 Ammonium equilibrium uptake on to MesoLite

It is important to note that both models have their limitations in accurately describing equilibrium exchange. Hankins *et al.*, (2004), argues that the Freundlich model imposes no intrinsic limit on the capacity of the zeolite although it is generally accepted that the capacity of any ion exchange material is limited to the number of exchange sites available and therefore, the single component Langmuir model is more applicable because a limit on adsorption is imposed. The authors further argue that the Langmuir model fails to account for the true nature of ion exchange as a binary, displacement adsorption process, which involves at least two species, whose relative proportions and hence concentrations alter. However, it is clear from Figure 3.1 that the Langmuir model, although not perfect, does provide a reasonable fit to the experimental data for ammonium uptake on to MesoLite. The comparison of isotherm coefficients to those stated by other authors for different materials is somewhat difficult as they are only true for specific experimental conditions (Inglezakis, 2005). Their values will be affected by the relative concentrations or absence of competing cations, pH, temperature and the media loading of the solution. Separate trials on MesoLite with a media loading of 1 g l⁻¹ (as opposed to 5 g l⁻¹) deliver the following Langmuir and Freundlich equations:

$$\text{Langmuir } Q_e = \frac{2.819C_e}{(1+0.0488C_e)} \quad \text{Equation 3.8}$$

$$\text{Freundlich } Q_e = 6.02 C_e^{0.3917} \quad \text{Equation 3.9}$$

The experimental conditions adopted by different authors is by no means consistent (Table 3.2). For example, Wang *et al.*, (2006), employed a clinoptilolite loading of 5 g per 100 ml (i.e. 50 g l⁻¹) and generated three different sets of equations for varying media grain size. Calculations using the derived equations at an equilibrium concentration of 100 mg NH₄⁺-N l⁻¹ result in maximum Q_e values of 2.33 g NH₄⁺-N kg⁻¹ (Langmuir) and 4.24 g NH₄⁺-N kg⁻¹ (Freundlich). Conversely, Weatherley and Miladinovic, (2004) used a significantly lower clinoptilolite loading of 10 g l⁻¹ over a similar range of concentrations. Calculations at the same equilibrium concentration, deliver Q_e values of 6.54 g NH₄⁺-N kg⁻¹ (Langmuir) and 10.66 g NH₄⁺-N kg⁻¹ (Freundlich). Calculations for MesoLite using Equations 3.4 and 3.7 result in 24 g NH₄⁺-N kg⁻¹ and 25.7 g NH₄⁺-N kg⁻¹ respectively, whereas, Equations 3.8, and 3.9 return values of 47.92 g NH₄⁺-N kg⁻¹ and 36.56 g NH₄⁺-N kg⁻¹. It is generally true to say that Q_e increases (up to a maximum) for any given concentration as the media loading decreases. However, isotherms are specific to the system they describe (Inglezakis, 2005) and to accurately compare two or more ion exchangers using these models requires the experiments to be performed under identical conditions.

Table 3.2 Experimental conditions and isotherm equations generated by a selection of authors

Material	Experimental Conditions	Langmuir Equation	Freundlich Equation	Q _e at C _e = 100 mg l ⁻¹ NH ₄ ⁺ -N		Author
				Langmuir	Freundlich	
Natural Chinese clinoptilolite	Media loading 50 g l ⁻¹ Temp 20° C, pH 6 Concentration range 23-115 mg l ⁻¹ NH ₄ ⁺ -N	Q _e = 0.387 C _e / (1+0.182C _e)	Q _e = 0.428 C _e ^{0.458}	2.02	3.53	Wang <i>et al.</i> , 2006
		Q _e = 0.442 C _e / (1+0.186C _e)	Q _e = 0.596 C _e ^{0.341}	2.26	2.87	
		Q _e = 0.412 C _e / (1+0.167C _e)	Q _e = 0.432 C _e ^{0.496}	2.33	4.24	
Natural Turkish clinoptilolite	Media loading 10 g l ⁻¹ Temp 25, 40 and 55° C Concentration range 25-150 mg l ⁻¹ NH ₄ ⁺ -N	Q _e = 0.236 C _e / (1+0.029C _e)	Q _e = 0.612 C _e ^{0.517}	6.05 (25°C)	6.62 (25°C)	Karadag <i>et al.</i> , 2006
		Q _e = 0.209 C _e / (1+0.034C _e)	Q _e = 0.437 C _e ^{0.550}	4.75 (40°C)	5.50 (40°C)	
		Q _e = 0.139 C _e / (1+0.027C _e)	Q _e = 0.405 C _e ^{0.498}	3.76 (50°C)	4.01 (50°C)	
Sulfonated polystyrene silica gel	Temp 25° C pH ≤ 7 Concentration range 0.4-140 mg l ⁻¹ NH ₄ ⁺ -N	Q _e = 1.88 C _e / (1+0.213C _e)	Q _e = 2.79 C _e ^{0.261}	8.43	9.28	Helminen and Paatero, 2006
Bigadic zeolite (Turkey)	Media loading 1 g l ⁻¹ Concentration range 10-80 mg l ⁻¹ NH ₄ ⁺ -N	Q _e = 0.440 C _e / (1+0.085C _e)	Q _e = 0.608 C _e ^{0.537}	4.6 (Raw)	7.21 (Raw)	Demir <i>et al.</i> , 2002
		Q _e = 0.770 C _e / (1+0.069C _e)	Q _e = 0.806 C _e ^{0.727}	9.7 (Conditioned)	22.9 (Conditioned)	

Material	Experimental Conditions	Langmuir Equation	Freundlich Equation	Q _e at C _e = 100 mg l ⁻¹ NH ₄ ⁺ -N		Author
				Langmuir	Freundlich	
New Zealand mordenite and clinoptilolite	Media loading 10 g l ⁻¹ pH < 7.5 Concentration range 0-200 mg l ⁻¹ NH ₄ ⁺ -N	Clinoptilolite Q _e = 9.835 C _e / (1+1.493C _e)	Clinoptilolite Q _e = 2.27 C _e ^{0.336}	6.54	10.66	Weatherley and Miladinovic, 2004
		Mordenite Q _e = 1.79 C _e / (1+0.139C _e)	Mordenite Q _e = 1.255 C _e ^{0.540}	12.01	15.09	
Natural Chinese clinoptilolite	Media loading 5 g l ⁻¹ pH < 6 Concentration range 2-94 mg l ⁻¹ NH ₄ ⁺ -N	-	Q _e = 1.364 C _e ^{0.279}	-	4.9	Du <i>et al.</i> , 2005
Chabazite	-	Q _e = 5.01 C _e / (1+1.690C _e)	-	2.94	-	Lahav and Green, 1998

3.3.2 The effect of pH

Ammoniacal nitrogen is present in aqueous solution in two forms: non-ionised ammonia (NH_3) or ionised ammonium (NH_4^+), according to the following equations (Weatherley and Miladinovic, 2004):



Ammonia-ammonium equilibrium in solution is largely pH dependant (Hedstrom, 2001) and it stands to reason that only the ionised form can be removed from solution by ion exchange. At pH 8 and below the substantial majority of ammoniacal nitrogen is present in the ionised form, therefore, it is reasonable to assume that these conditions would best favour the removal process. Above pH 8 the equilibrium shifts rapidly towards the non-ionised form and these conditions become increasingly less favourable.

Solutions were prepared at pH values in the range 2.8-10.1 to establish the optimum pH range for ammonium removal using MesoLite. Results show that a maximum capacity of $49 \text{ g NH}_4^+\text{-N kg}^{-1}$ is observed in the pH range 6-7 and confirms that at pH values of 8 and above the efficiency of the media decreases rapidly and at a pH of 10.1 the capacity is reduced to $29 \text{ g NH}_4^+\text{-N kg}^{-1}$ (Figure 3.2). This concurs with results reported by previous authors (Koon and Kaufmann, 1975; Hankins *et al.*, 2004; Du *et al.*, 2005) and can be explained by the fact that under alkaline pH conditions, the ammonium ion becomes neutralised by the hydroxyl ion rendering it uncharged (Hankins *et al.*, 2004) and therefore unavailable as an exchange ion.

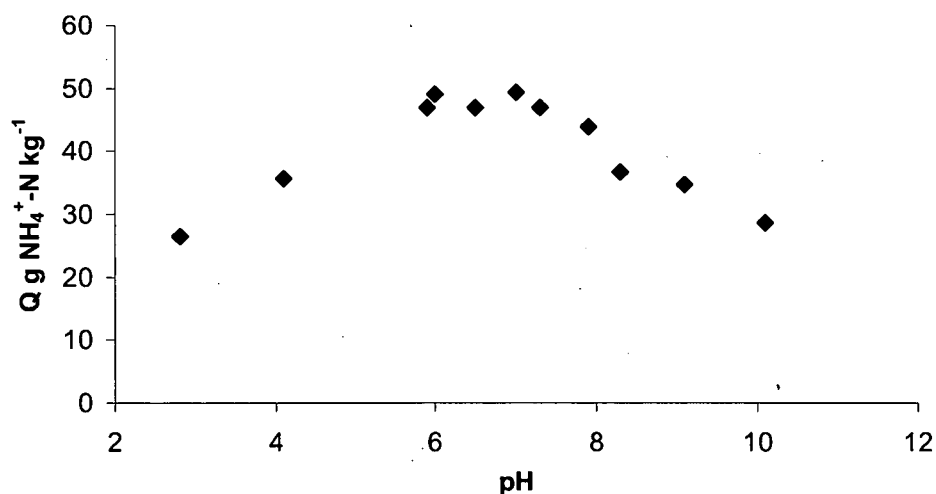


Figure 3.2 The effect of pH on ammonium exchange capacity

Below pH 6 a similar reduction in capacity can be observed with decreasing pH, and at pH 2.8 the capacity is reduced to $26.5 \text{ g NH}_4^+\text{-N kg}^{-1}$. This can be attributed to the fact that the increased number of hydrogen ions in solution at lower pH provides added competition for exchange sites (Koon and Kaufmann, 1975; Hedstrom, 2001; Hankins *et al.*, 2004).

3.3.3 The effect of initial ammonium concentration

Results indicate that the initial ammonium concentration has an influence on both the equilibrium capacity and the rate of uptake of $\text{NH}_4^+\text{-N}$. At higher initial concentrations the initial rate of uptake is far greater than at lower concentrations (Figure 3.3). This can be attributed to the fact that higher concentrations result in a higher solute gradient, providing the necessary driving force for ammonium ions to replace cations in the media framework for a given contact time (Du *et al.*, 2005; Wang *et al.*, 2006).

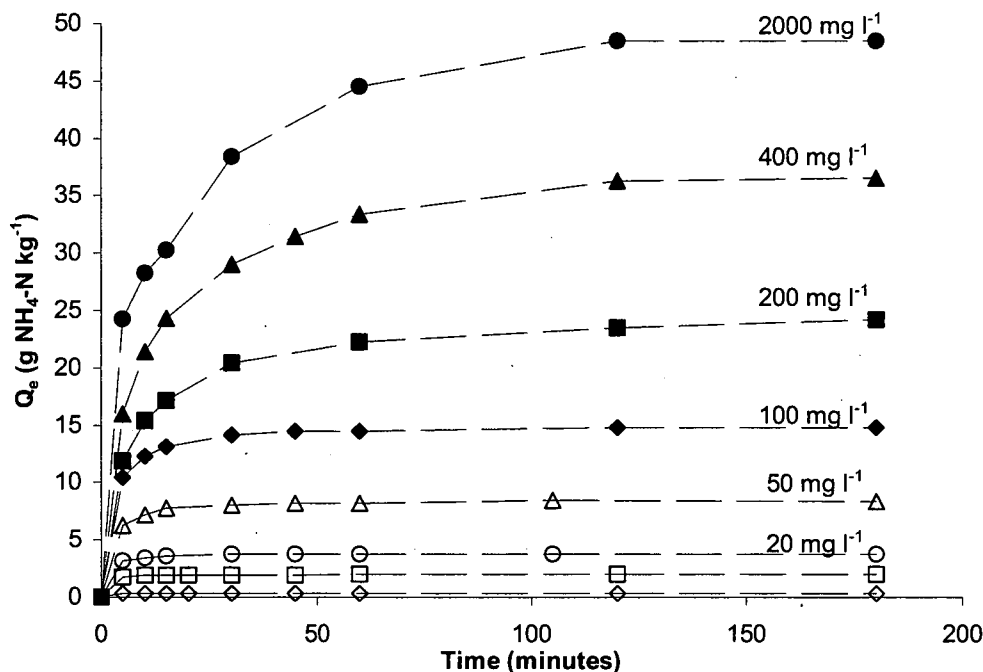


Figure 3.3 Effect of initial solution concentration on the rate of NH_4^+ uptake.

Increasing concentration also results in a higher equilibrium capacity being obtained for any given set of conditions. Initially, a sharp increase in capacity can be observed with increasing concentration. This reaches a maximum, in this case $49 \text{ g NH}_4^+\text{-N kg}^{-1}$, at an initial solution concentration of $1000 \text{ mg NH}_4^+\text{-N l}^{-1}$ (Figure 3.4). This maximum value is indicative of the fact that the ion exchange surface becomes increasingly saturated with the ammonium ion (Karadag *et al.*, 2006) and is reflected by the accompanying reduction in removal efficiency (Hankins *et al.*, 2004). The removal efficiency is the amount of $\text{NH}_4^+\text{-N}$ removed from solution, expressed as a percentage of the initial solution concentration (Equation 3.12). This maximum of $49 \text{ g NH}_4^+\text{-N kg}^{-1}$ is the maximum amount of ammonium, which can be exchanged on to the surface of the material under the experimental conditions. After this point further increases in solution concentration are ineffective in raising the media's capacity and even at a C_0 of almost $2000 \text{ mg NH}_4^+\text{-N l}^{-1}$, the capacity remains unchanged (Figure 3.4).

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e) \times 100}{C_0} \quad \text{Equation 3.12}$$

Experiments performed with distilled water at an initial concentration of $1000 \text{ mg NH}_4^+ \text{ N l}^{-1}$ show that a capacity of $72 \text{ g NH}_4^+ \text{ N kg}^{-1}$ is achievable. This is in agreement with Mackinnon *et al.*, (2003) who report an average CEC for MesoLite of $69 \text{ g NH}_4^+ \text{ N kg}^{-1}$. This indicates that the presence of competing cations in solution has a significant effect on the ammonium exchange capacity with only 70% of maximum removal being realised. Wang *et al.*, (2006) also reported a reduction in the capacity of clinoptilolite of 10-20% when competing cations were present in solution. Hankins *et al.*, (2004) further state that, in multi component systems, the presence of calcium ions in solution seems to have a deleterious effect on the exchange of NH_4^+ ions onto clinoptilolite.

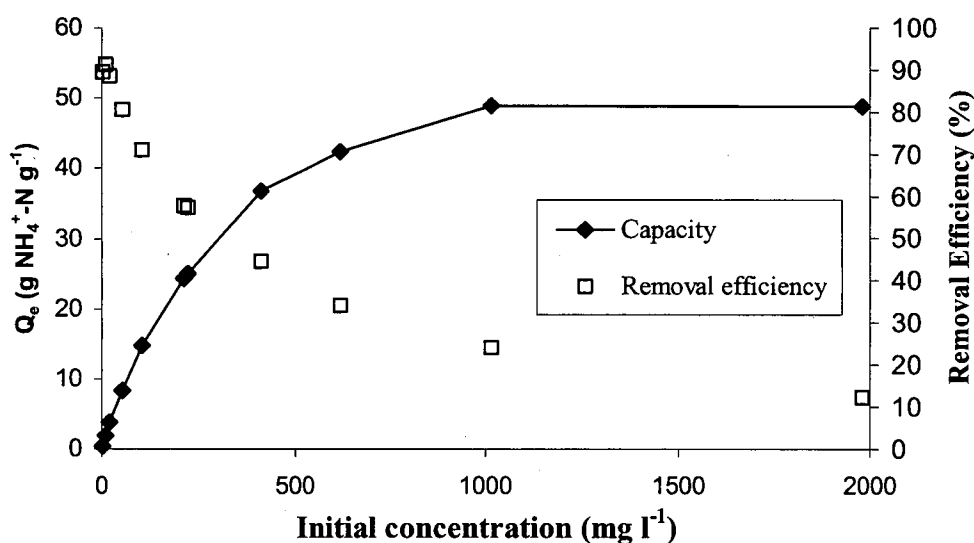


Figure 3.4 Effect of initial concentration on capacity and removal efficiency

3.3.4 The effect of contact time

Results from kinetic experiments indicate that the rate of uptake of ammonium by MesoLite is initially a fast process with over 90% of the equilibrium capacity reached within the first 60 minutes. After this time the rate of uptake slows dramatically and after 4 hours is negligible, indicating a state of equilibrium. This is consistent with results reported by previous authors, all of who observed the same behaviour. Hankins *et al.*, (2004) reported that 50% and 75% of uptake on to clinoptilolite was achieved in 15 and 60 minutes respectively. Wang *et al.*, (2006) also reports a high rate of uptake within the

first hour, which gradually decreases with increased contact time. Experiments by Booker *et al.*, (1996) and Du *et al.*, (2005) result in the majority of ammonium uptake being achieved in even shorter time periods of 10 and 15 minutes respectively. The reasons for these discrepancies may be specific to the materials used, the experimental conditions or a combination of the two. However, all authors are consistent in the fact that uptake is negligible after a period of four hours has elapsed. This is by no means an indication that the exchange process has ceased it is just an indication that the rate of adsorption is equal to the rate of desorption and there is therefore no net alteration of the concentration of ions in the solution and solid phases.

A more detailed examination of results for MesoLite indicates that the effects of contact time vary with the solution concentration. The exact point in time at which equilibrium is achieved is difficult to assess but the time to reach 90% of equilibrium can be easily calculated. At low concentrations the time to reach 90% equilibrium is significantly less than that at higher concentrations (Figure 3.5a). At an initial concentration of 2 mg l^{-1} 90% is reached in less than 3 minutes (Figure 3.5b) whereas at 1000 mg l^{-1} it takes 65 minutes to reach the same point (Figure 3.5g). Figures 3.5c to 3.5f show the relationship between contact time and equilibrium for a range of concentrations. Although the initial rate of uptake is less at lower concentrations (Section 3.3.3), most of the exchange process is completed in a shorter period of time. This can be attributed to the fact that at lower concentrations, the vast majority of exchange sites remain unused, even at equilibrium. At an initial concentration of 2 mg l^{-1} the loading on the media is $0.37 \text{ g NH}_4^+\text{-N kg}^{-1}$ whereas at a concentration of 1000 mg l^{-1} the loading on the media is a maximum $49 \text{ g NH}_4^+\text{-N kg}^{-1}$ (Figure 3.3). Therefore, because the initial rate of uptake is initially high at 1000 mg l^{-1} , the majority of the exchange sites are used up in the early stages (i.e. saturation is approached), leaving the remaining ammonium in solution to “scavenge” for less accessible exchange sites. The opposite is true at lower concentrations where exchange sites are abundant throughout the process.

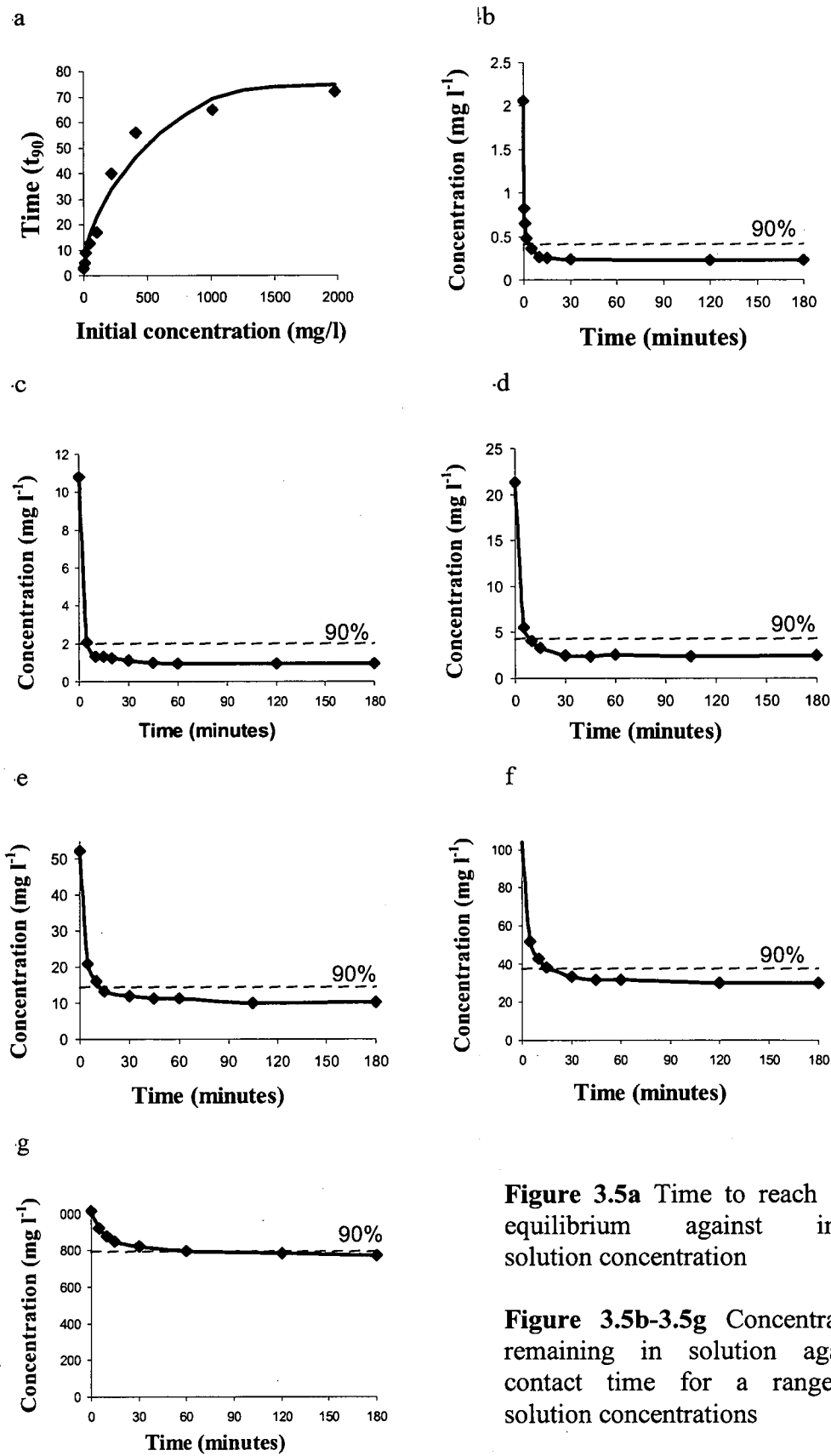


Figure 3.5a Time to reach 90% equilibrium against initial solution concentration

Figure 3.5b-3.5g Concentration remaining in solution against contact time for a range of solution concentrations

3.4 Conclusions

A range of batch tests were performed to assess the uptake of the ammonium ion by MesoLite media with the following conclusions:

- A comparison of the data with Langmuir and Freundlich isotherm models show a good correlation at low concentrations but over the whole range of experimental conditions the Langmuir model describes the process more accurately.
- The capacity of the material is affected by solution pH and optimum conditions for removal are between pH 6 and 7.
- The initial solution concentration has an effect on performance with both the rate of uptake and the capacity increasing with increased initial ammonium concentration.
- The capacity of the media is reduced when competing cations are present in solution and an approximate 30 % reduction in ammonium uptake is observed from 72 g $\text{NH}_4^+\text{-N kg}^{-1}$ to 49 g $\text{NH}_4^+\text{-N kg}^{-1}$. However, this is considerably higher than that of clinoptilolite, where reported capacities are in the range 0.94-21.52 g $\text{NH}_4^+\text{-N kg}^{-1}$.
- Ion exchange occurs at a high rate with the majority of the process being complete within the first hour and after 4 hours the rate of uptake becomes negligible for all solution concentrations studied.

3.5 References

Beler Baykal, B. and Guven, D. A. (1997) Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater. *Water, Science and Technology* **35** (7), 47-54.

Booker, N. A., Cooney, E. L. and Priestly, A. J. (1996) Ammonia removal from sewage using natural Australian zeolite. *Water, Science and Technology* **34** (9), 17-24.

Colella, C., DE' Gennaro, M., Langella, A. and Pansini, M. (1995) In: Natural zeolites-cadmium removal from wastewaters using chabazite and phillipsite. Ming, D.W. and Mumpton, F.A (Eds), pp 377-384, Int. Comm. Natural Zeolites, Brockport, New York.

Demir, A., Gunay, A. and Debik, E. (2002) Ammonium removal from aqueous solution by ion exchange using packed bed natural zeolite. *Water SA* **28** (3), 329-336.

Du, Q., Shijun Liu, Q. D., Zhonghong, C. and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese clinoptilolite. *Separation and Purification Technology* **44** 229-234.

Dyer, A. (1988) An introduction to zeolite molecular sieves, John Wiley and Sons Ltd, Chichester.

Farkas, A., Rozic, M. and Barbaric-Mikocevic, Z. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* B117 25-33.

Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) An equilibrium ion exchange study on the Removal of NH_4^+ Ion from Aqueous Effluent Using Clinoptilolite. *Separation Science and Technology* **39** (15), 3639-3663.

Hedstrom, A. (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of Environmental Engineering* (August 2001), 673-681.

Helminen, J. and Paatero, E. (2006) Ammonium removal from aqueous solution using sulfonated polystyrene grafted silica gel. *Separation Science and Technology* 41 1043-1059.

Hlavay, J., Vigh, G., Olaszi, V. and Inczedy, J. (1982) Investigation on natural Hungarian zeolite for ammonia removal. *Water Research* 16, 417-420.

Inglezakis, V. J. (2005) The concept of "capacity" in zeolite ion-exchange systems. *Journal of Colloid and Interface Science* 281 68-79.

Jetten, M. S. M., Horn, S.J. and van Loosdrecht, M. C. M. (1997) Towards a more sustainable municipal wastewater treatment system. *Water, Science and Technology* 35 (9), 171-180.

Jorgensen, S. E., Libor, O. Graber, K. L. and Barkacs, K. (1976) Ammonia removal by use of clinoptilolite. *Water Research* 10, 213-224.

Jorgensen, T. C. and Weatherley, L. R. (2003) Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. *Water Research* 37 1273-1278.

Jung, J., Chung, Y., Shin, H. and Son, D. (2004) Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research* 38 347-354.

Kamarowski, S. and Yu, Q. (1997) Ammonium ion removal from wastewater using Australian natural zeolite: Batch equilibrium and kinetics studies. *Environmental Technology* 18 1085-1097.

Karadag, D., Koc, Y., Turan, M. and Armagan, A. (2006) Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. *Journal of Hazardous Materials* B136 604-609.

Klieve, J. R. and Semmens, M. J. (1979) An Evaluation of pretreated natural zeolites for ammonium removal. *Water Research* 14, 161-168.

Koon, H. J. and Kaufmann, W. J. (1975) Ammonia removal from municipal wastewaters by ion exchange. *Journal WPCF* 47 (3) 448-465.

Lahav, O. and Green, M. (1998) Ammonium removal using ion exchange and biological regeneration. *Water Research* 32 (7), 2019-2028.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient removal from wastewaters using high performance materials. *Water, Science and Technology* 47 (11), 101-107.

Mackinnon, I.D.R., Millar, G. and Stoltz, W. (2006) Hydrothermal Synthesis of Zeolite N Aluminosilicates, *WIPO publication number, W0/2006/096930*.

Mercer, B. W., Ames, L. L., Touhill, C. J., Van Slike, W. J. and Dean, R. B. (1970) Ammonia removal from secondary effluents by selective ion exchange. *Journal WPCF* 42 448-465.

Mosquera-Corral, A., Gonzalez, F., Campos, J. L. and Mendez, R. (2005) Partial nitrification in a SHARON reactor in the presence of salts and organic compounds. *Process Biochemistry* 40 3109-3118.

Nguyen, M. L. and Tanner, C. C. (1998) Ammonium removal from wastewaters using natural New Zealand Zeolites. *New Zealand Journal of Agricultural research* 41 427-466.

Rostron, W. M., Stuckey, D. and Young, A. A. (2001) Nitrification of high strength Ammonia wastewaters: Comparative study of immobilisation media. *Water Research*

35 (5), 1169-1178.

Siegrist, H. (1996) Nitrogen removal from digester supernatant – Comparison of chemical and biological methods. *Water, Science and Technology* **34** (1-2), 399-406.

Sprynskyy, M, Lebedynets, M, Terzyk, A. P, Kowalczyk, P, Namiesnik, J. And Buszewski, B. (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Colloid and Interface Science* **284** 408-415.

van Kempen, R., ten Have, C. C. R., Meijer, S. C. F., Mulder, J. W., Duin, J. O. J., Uijterlinde, C. A. and van Loosdrecht, M. C. M. (2005) SHARON process evaluated for improved wastewater treatment plant nitrogen effluent quality. *Water Science & Technology* **52** (4) 55–62.

Wang, Y., Liu, S., Xu, Z., Han, T., Chaun, S. and Zhu, T. (2006) Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials* B136 735-740.

Weatherley, L. R. and Miladinovic, N. D. (2004) Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research* **38**, 4305-4312.

Wen, D., Ho, Y. S. and Tang, X. (2006) Comparative sorption kinetic studies of ammonium onto zeolite. *Journal of Hazardous Materials* B133 252-256.

CHAPTER 4

**AMMONIUM REMOVAL FROM SOLUTION USING ION EXCHANGE ON
TO MESOLITE: A DYNAMIC STUDY**

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4. AMMONIUM REMOVAL FROM SOLUTION USING ION EXCHANGE ON TO MESOLITE: A DYNAMIC STUDY

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Keywords: Ammonium; ion exchange; nutrient removal; wastewater; zeolite, breakthrough

Abstract

This study outlines the performance of the ion exchange media, MesoLite, for the removal of ammonium from solution under dynamic conditions in the presence of competing cations. MesoLite ion exchange media is produced by the chemical modification of clay and other aluminium bearing minerals, giving rise to an increased number of exchange sites (Mackinnon *et al.*, 2006). The principal aims are to investigate the effect of media bed depth and contact time on the breakthrough characteristics of the ion exchange process and the capacity of the media for a range of influent concentrations. The study also aims to provide an understanding of how the selection of a breakthrough concentration can influence the efficiency of the media for any given set of operating conditions. Results indicate that the capacity of the media is dependant on the influent $\text{NH}_4^+\text{-N}$ concentration with lower concentrations resulting in lower capacity. Results also indicate, that total media capacity (at exhaustion) is relatively unaffected for any given influent concentration over a range of bed depths. However, when a breakthrough concentration is selected, the effect of short media beds has a detrimental effect both on the service time of the process and the operational capacity of the media. Furthermore, the effect of breakthrough selection has a direct effect on the run time of the process and the efficient use of the media, with lower breakthrough concentrations resulting in shorter run times and reduced capacity.

4.1. Introduction

Conventional removal of $\text{NH}_4^+\text{-N}$ from municipal wastewaters is almost exclusively performed by taking advantage of naturally occurring processes, where ammonium is converted to less harmful substances by biological nitrification/denitrification (Karadag *et al.*, 2006). On the whole, these processes prove more than adequate in achieving the effluent ammonium concentrations (Beler Baykal and Guven, 1997) imposed by regulatory bodies and for the foreseeable future will continue to be the principal method of ammonium removal. However, over the last 30 years, selective ion exchange has been widely studied as an effective method for the removal of ammonium from municipal, industrial and agricultural wastewaters where conventional treatment methods experience difficulty in attaining the required targets. Research has largely been concerned with the use of the naturally occurring zeolite, clinoptilolite, as a removal media, due to its high selectivity for the ammonium ion in the presence of competing cations, such as calcium, magnesium, sodium and potassium (Jung *et al.*, 2004).

Ion exchange processing can be accomplished by either a batch method or continuous flow through a column or series of columns of ion exchange media. The batch method involves mixing the exchange media and solution in a batch tank until the system reaches equilibrium, at which point the media and solution are separated (Wachinsky and Etzel, 1997). Once equilibrium is reached there is no net removal of the pollutant from solution and therefore, batch removal rarely utilises the full capacity of the media. As a result, practical applications for ammonium removal seldom consider this system as an option.

In a continuous process, the media is suspended as a fixed bed in a column or series of columns and the solution to be treated is continually fed through the media bed (either upflow or downflow) to remove the polluting ion. Here, the driving force (Wang *et al.*, 2006) behind the exchange process is continually being renewed and as a result a greater proportion of the materials capacity can be utilised. Therefore, most investigations into practical applications of ammonium removal using ion exchange have been concerned with the fixed bed column process (Koon and Kaufmann, 1975; Semmens, and Porter, 1979; Beler Baykal *et al.*, 1996; Booker *et al.*, 1996a; Kamarowski and Yu, 1997; Lahav

and Green, 1998; Nguyen and Tanner, 1998; Celik *et al.*, 2001; Demir *et al.*, 2002; Hankins *et al.*, 2004; Du *et al.*, 2005; Sprynsky *et al.*, 2005; Farkas *et al.*, 2005).

During column operation the bed is exposed to solution (concentration C_0) and the media becomes systematically saturated with contaminant from the inlet, progressing towards the outlet, until at some point a pre-determined breakthrough concentration (C_b) is observed in the column effluent (Cooney, 1999) (Figure 4.1). At this point the process is stopped and the media is either, discarded and replaced with fresh media, or regenerated so that the removal process can be recommenced. In practice it is common to use two columns, alternating between the two, so that the removal process can operate uninterrupted by the regeneration process.

Studies on the recently developed ion exchange media, MesoLite, indicate that it has an ammonium exchange capacity in the range 45-55 g $\text{NH}_4^+\text{-N kg}^{-1}$ (Mackinnon *et al.*, 2003; Thornton *et al.*, 2007). This is significantly greater than that of clinoptilolite, where reported capacities are in the range 0.94 to 21.52 g $\text{NH}_4^+\text{-N kg}^{-1}$ with the majority of studies returning capacities in the range 0.95 to 13.65 g $\text{NH}_4^+\text{-N kg}^{-1}$. This study examines the performance of MesoLite for ammonium removal from solution under fixed bed conditions in the presence of competing cations. Investigations concentrate on the effect of media bed depth and hydraulic retention time (HRT) on the breakthrough characteristics and ammonium exchange capacity of the media.

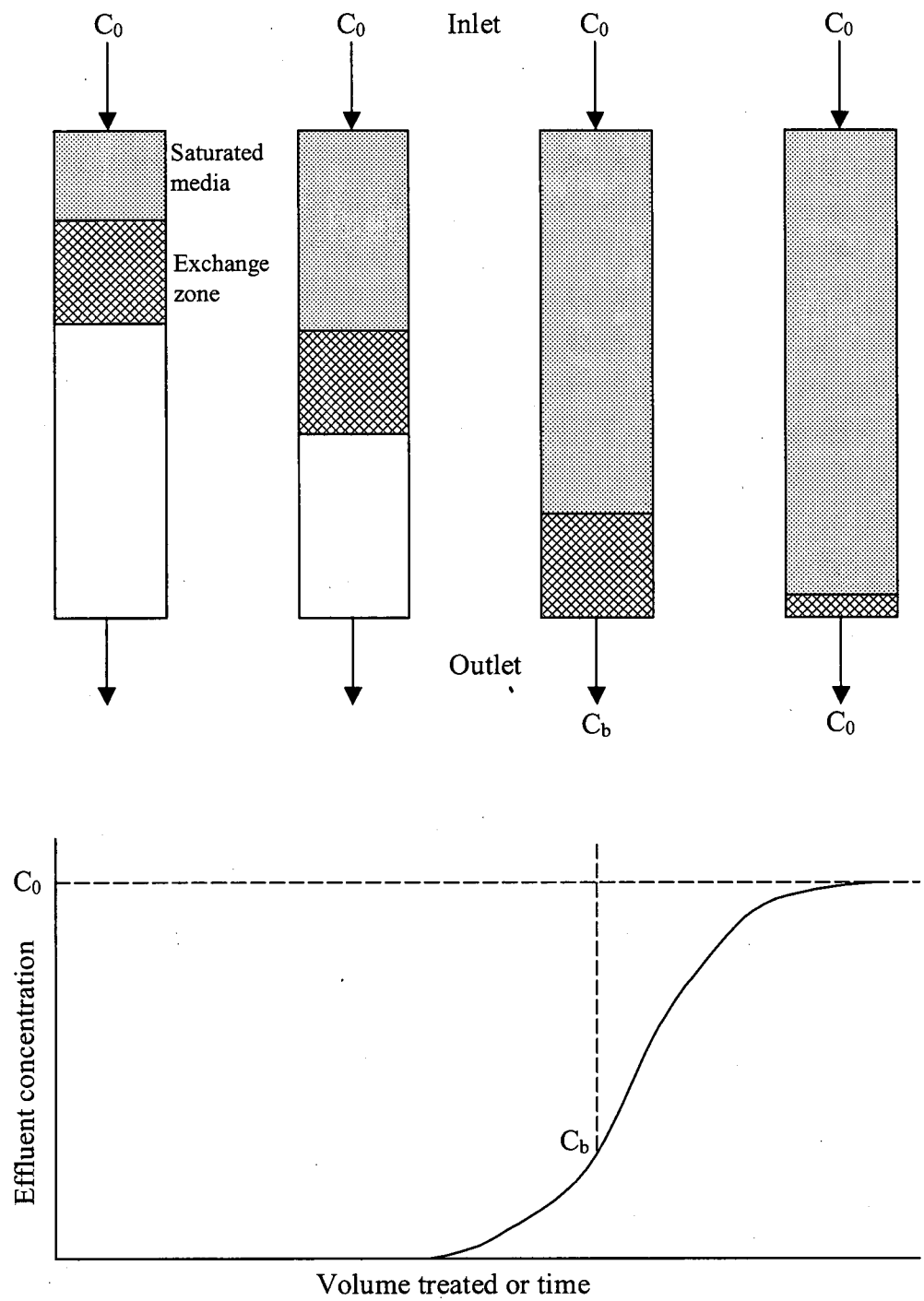


Figure 4.1 The progression of the exchange zone through a fixed bed (modified from Cooney, 1999)

4.2. Materials and Methods

Particle size analysis of the MesoLite, supplied by Nanochem Pty Ltd., Australia, was performed using sieve sizes, 0.6, 0.71, 1.0, 1.18, 1.4, 1.7, 2.0, 2.36, 2.5, 2.8, 3.35 and 5.0 mm. Results show that the media was within a narrow size range, with in excess of 99 % of the media falling between 1 and 2 mm in diameter.

Experiments were performed using a single vertical column of internal diameter 50 mm with an effective media bed depth of 500 mm. In order to obtain an understanding of the effect of bed depth on the performance of the media, the bed was split into ten vertical sections with each section being 50 mm in depth (Figure 4.2). Therefore, at sample point A, the depth of media that the influent has to pass through is 50 mm. At sample point B, the influent has to pass through two sections of media, resulting in a total bed depth of 100 mm. At each subsequent sample point, the total bed depth is increased by 50 mm, up to a maximum of 500 mm at sample point J.

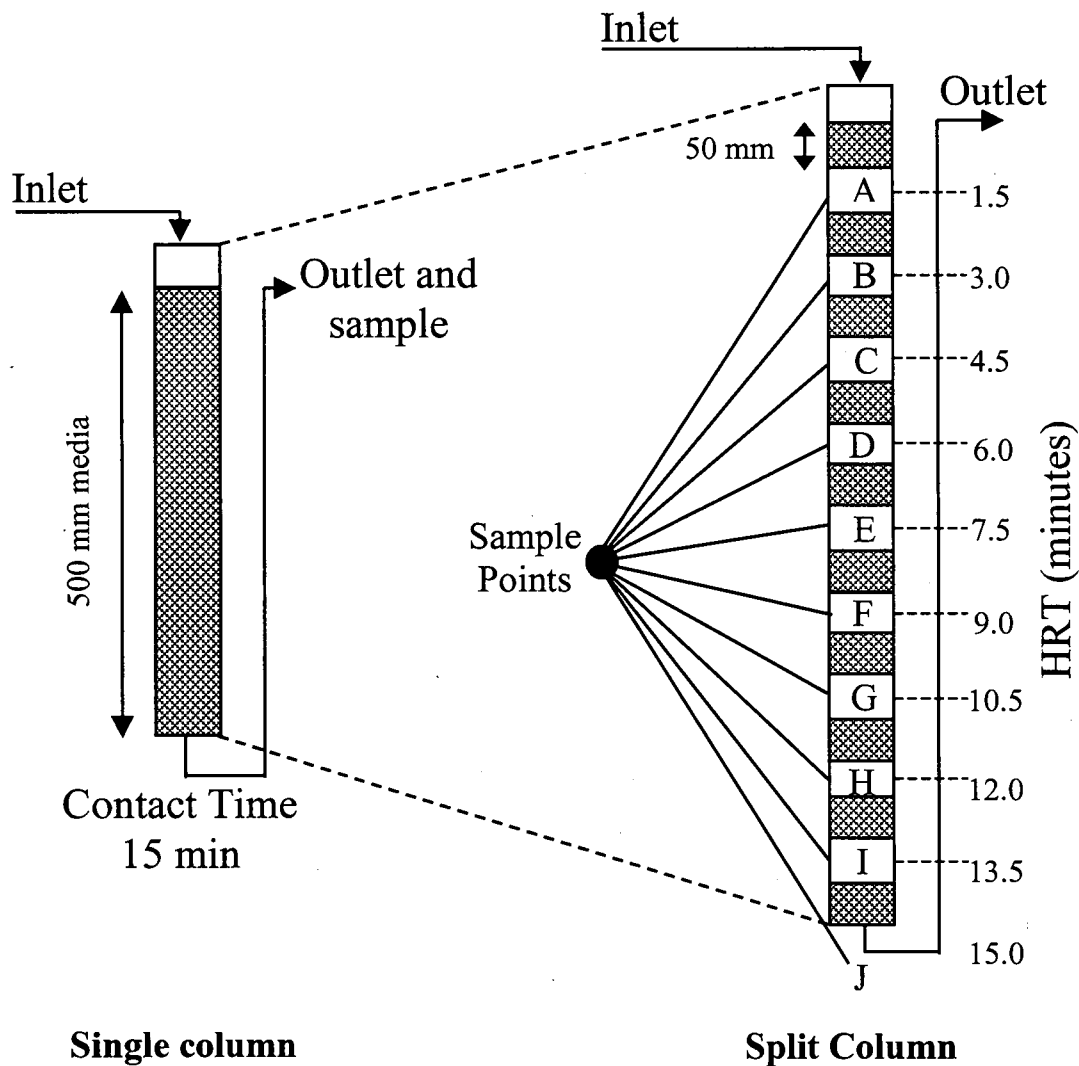


Figure 4.2 Development of the split bed column

This was achieved by assembling the column from separate smaller lengths of column, each one being 150 mm long, giving a total column height of 1.5 m. Each small section of column had a sealable flange at each end so that the shorter sections could be bolted together to make one single column of the required length. The column was built from the base upwards and as it was erected, the required amount of media was placed in each section. Each time a section of column was added, a piece of steel mesh (60 mm diameter) was placed between the two adjoining flanges to hold the next 50 mm section of media in place. Between each section of media a valve was inserted to act as a sample point so that the solution ammonium concentration could be measured at all stages of the process (Figure 4.3).

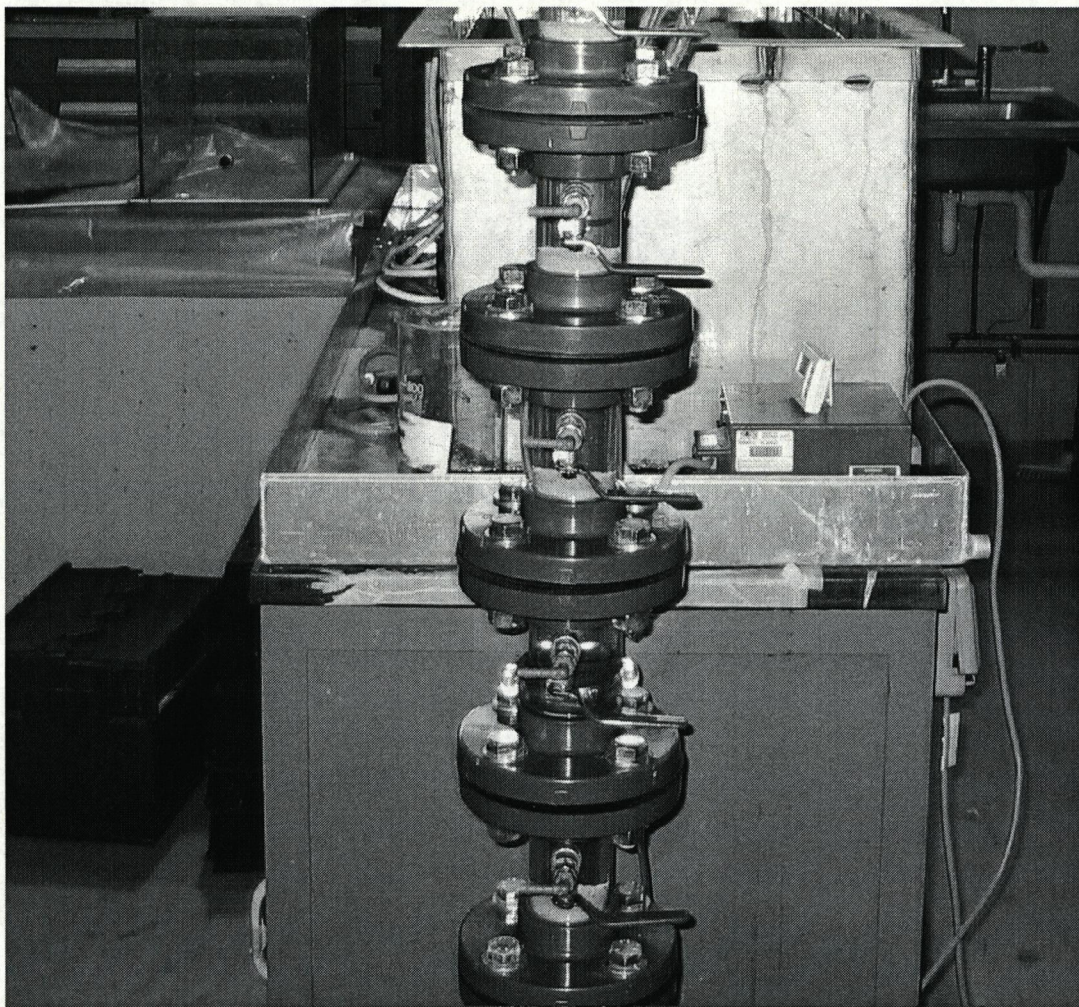


Figure 4.3 Ion exchange column with media bed split into sections.

The resulting sections each contained 83 g of media with an intergranular pore space of 30 ml which equates to a total weight of media of 830 g and a total bed volume (BV) of 300 ml. Ammonium solution was fed in a downflow direction through the column at a flow rate of 1.2 l h^{-1} (40 BV h^{-1} for each section), resulting in a HRT 1.5 minutes for each section of media. Therefore, at each sample point the total HRT was increased by 1.5 minutes up to a total of 15 minutes (i.e. 4 BV h^{-1}) at sample point J (Figure 4.2). For the purpose of this study the bed volume is defined, as the intergranular pore space available in the column with the media in place. This allows the actual contact time between the solution and the media to be calculated with ease, which in turn allows for a comparison with previously conducted equilibrium experiments, where contact time is absolute.

Solutions with ammonium concentrations of 5, 10 and 30 mg $\text{NH}_4^+\text{-N l}^{-1}$ were selected for treatment, as they represent typical concentrations of wastewater streams targeted by Thames Water where the ion exchange process could be beneficial. As discussed in Chapter 3, the rate of ammonium uptake is initially fast, with over 90 % of equilibrium being reached in the first 60 minutes. However, at a concentration of 30 mg $\text{NH}_4^+\text{-N l}^{-1}$ the time to reach this point is reduced to approximately 10 minutes and this is further reduced to less than 5 minutes at a concentration of 5 mg $\text{NH}_4^+\text{-N l}^{-1}$ (Figure 3.4 a). Therefore, a total HRT of 15 minutes was deemed to be more than adequate for the purpose of these experiments.

Initially, samples were taken at each sample point on a daily basis and analysed for ammonium concentration. Analysis was performed using a Lasa 100 spectrometer supplied by Hach Lange GMBH, Düsseldorf, Germany. The spectrometer was calibrated by Hach Lange on a regular basis and tested against a standard solution at the start of each day on which testing occurred. Selected samples were also duplicated and sent to Thames Water laboratory for analysis. After the first 10 days, the sampling frequency was reduced to every 2 to 3 days. The feed solution was prepared by the addition of ammonium chloride powder (NH_4Cl), supplied by Fisher Scientific, Loughborough, UK to domestic tap water. The method of using tap water in solution preparation was adopted to ensure the presence of competing cations in solution (Table 4.1).

Table 4.1 Concentrations of competing cations in solution

Cation	Calcium	Magnesium	Sodium	Potassium
Concentration (mg l^{-1})	88 ± 2.7	3.1 ± 0.06	13.65 ± 0.01	3.13 ± 0.08

4.3 Results and discussion

Initial studies were performed with an average influent concentration of $30.70 \text{ mg NH}_4^+ \text{-N l}^{-1}$ under the conditions outlined in Section 2. $\text{NH}_4^+ \text{-N}$ analysis at each sample point was used to produce a series of breakthrough curves (Figure 4.4) to assess the effect of bed depth on the breakthrough performance of the media, which is totally dependant on the breakthrough concentration adopted. At a breakthrough concentration of $15.35 \text{ mg NH}_4^+ \text{-N l}^{-1}$ (i.e. $C_b = 0.5 \times C_0$), a relationship between the bed depth and time to reach breakthrough (t_b) can be observed (Figure 4.5). This linear relationship indicates that t_b and hence service time is proportional to the media bed depth, ranging from 2.25 days at a bed depth of 50 mm up to 45.5 days for a bed depth of 500 mm. This relationship is also observed for lower breakthrough concentrations but with significantly reduced service times. At a breakthrough concentration of $5 \text{ mg NH}_4^+ \text{-N l}^{-1}$, resulting service times range from 0.5 days at a media depth of 50 mm, up to 29.5 days at a bed depth of 500 mm. This indicates that at a bed depth of 50 mm, breakthrough is almost instantaneous. This is further illustrated when a breakthrough concentration of $2.5 \text{ mg NH}_4^+ \text{-N l}^{-1}$ is adopted. At a bed depth of 50 mm, breakthrough is reached before the first sample is taken (Figure 4.4) and service times range from 1.3 days at a bed depth of 100 mm up to 25 days at a bed depth of 500 mm. Therefore, for any given bed depth, reducing the breakthrough concentration reduces the service time of the process with the combination of a short bed depth and low breakthrough concentration resulting in the most significant reduction.

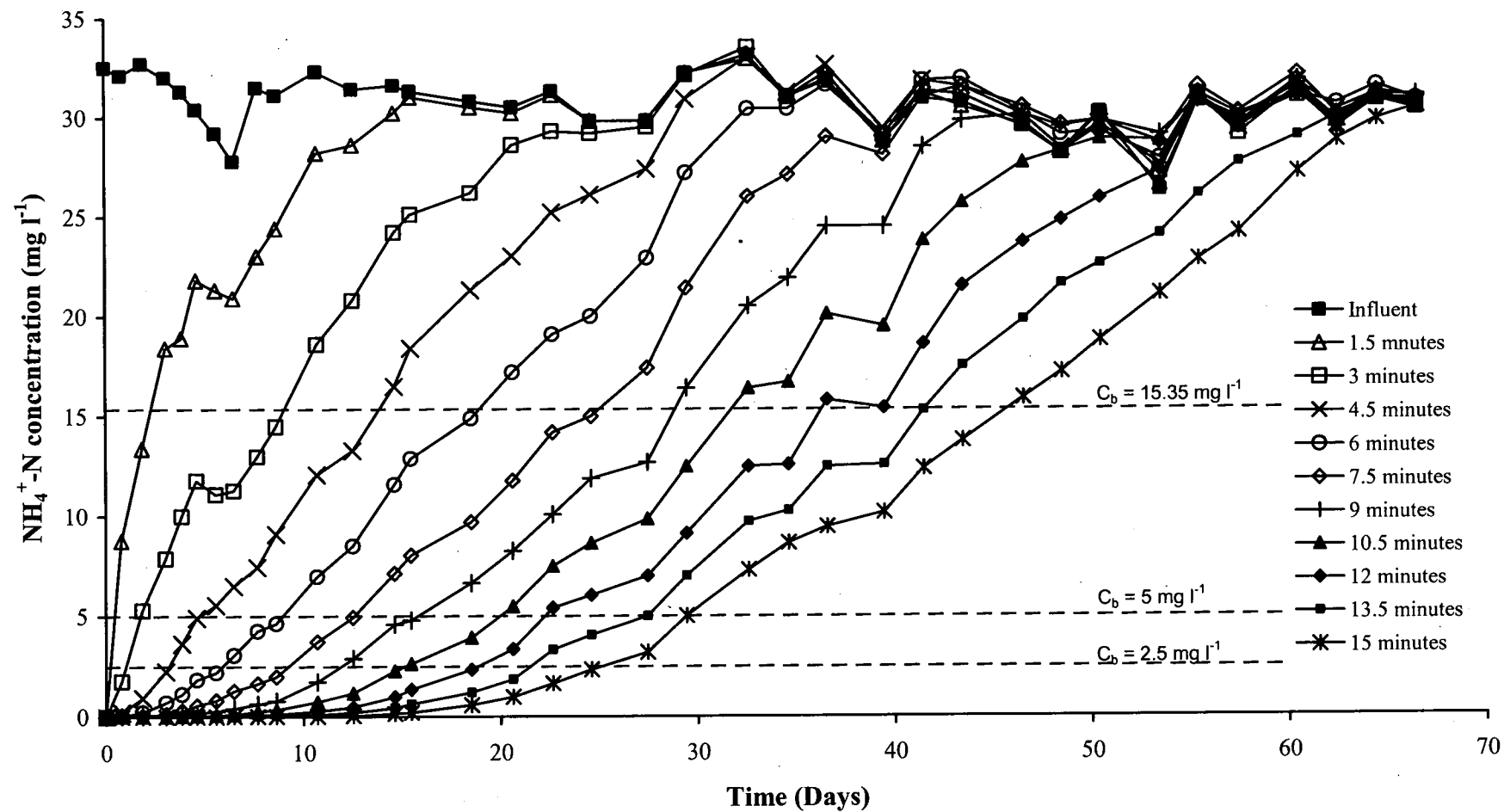


Figure 4.4 Breakthrough curves for trials conducted at $30.7 \text{ mg NH}_4^+-\text{N l}^{-1}$

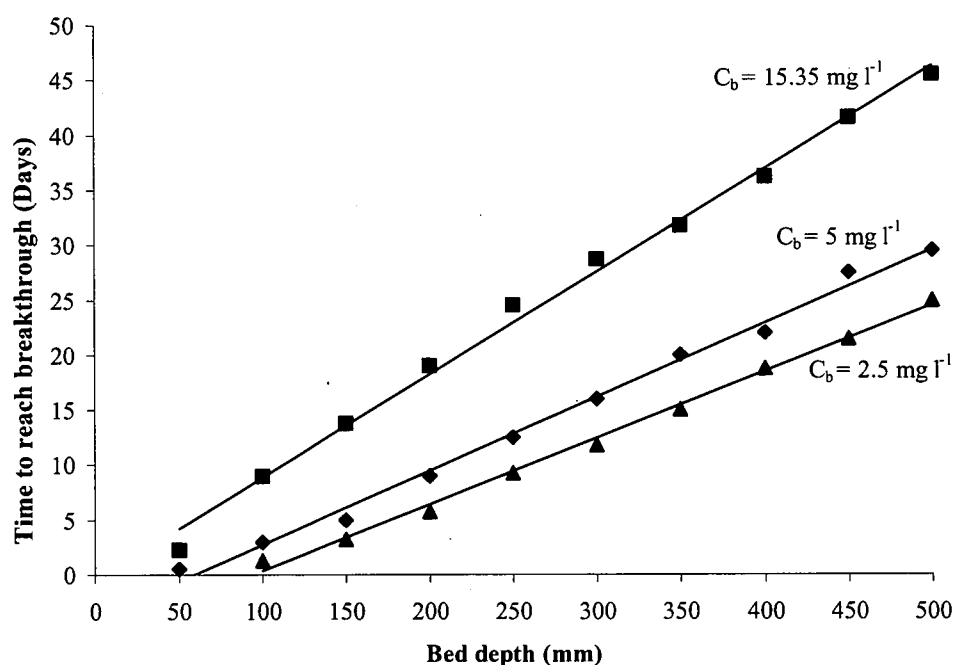


Figure 4.5 Bed depth vs time to reach breakthrough at $C_0 = 30.7 \text{ mg NH}_4^+ \text{-N l}^{-1}$

The effect of bed depth for any given set of operating conditions can be determined by analysing the media dosage required to treat a set amount of solution (i.e. kg m^{-3}) to the required breakthrough concentration and is a measure of how efficiently the media is used (Table 4.2). A relationship between bed depth (and hence contact time) and the amount of media required to treat a fixed amount of solution can be established (Figure 4.6). At short bed depths, the media dosage is irrelevant, as the required breakthrough concentration cannot be delivered or is only achievable for an impractically short amount of time. As the bed depth increases, the more efficient the process becomes and as contact time increases, less media is required per unit of treated solution. This reaches a minimum, where the required dosage levels out and further increases in bed depth have no impact on media dosage and would only serve to increase the service time.

However, results clearly indicate that short bed depths result in an inefficient use of the media. At a bed depth of 500 mm, 0.95 kg of media is required to treat 1 m³ of solution to a breakthrough concentration of 5 mg NH₄⁺-N l⁻¹, whereas at a much shorter bed depth of 100 mm, this is greatly increased to 3.46 kg m⁻³. This is further impacted upon by the breakthrough concentration, with lower breakthrough concentrations leading to a less efficient use of the media. At a reduced breakthrough concentration of 2.5 mg NH₄⁺-N l⁻¹, a bed depth of 500 mm results in an increased dosage 1.15 kg m⁻³, which is further increased to 5.53 kg m⁻³ at a bed depth of 100 mm.

Table 4.2 Media dosages required for varying bed depths at breakthrough

Sample Point	HRT (min)	Media Mass (g)	C _b = 2.5 mg NH ₄ ⁺ -N l ⁻¹		C _b = 5 mg NH ₄ ⁺ -N l ⁻¹	
			Volume Treated (m ³)	Media Dosage (kg m ⁻³)	Volume Treated (m ³)	Media Dosage (kg m ⁻³)
A	1.5	83	-	-	0.0045	18.44
B	3	166	0.03	5.53	0.048	3.46
C	4.5	249	0.093	2.68	0.135	1.84
D	6	332	0.168	1.98	0.255	1.30
E	7.5	415	0.258	1.61	0.363	1.14
F	9	498	0.339	1.47	0.447	1.11
G	10.5	581	0.438	1.33	0.54	1.08
H	12	664	0.546	1.22	0.63	1.05
I	13.5	747	0.624	1.20	0.789	0.95
J	15	830	0.714	1.16	0.856	0.98

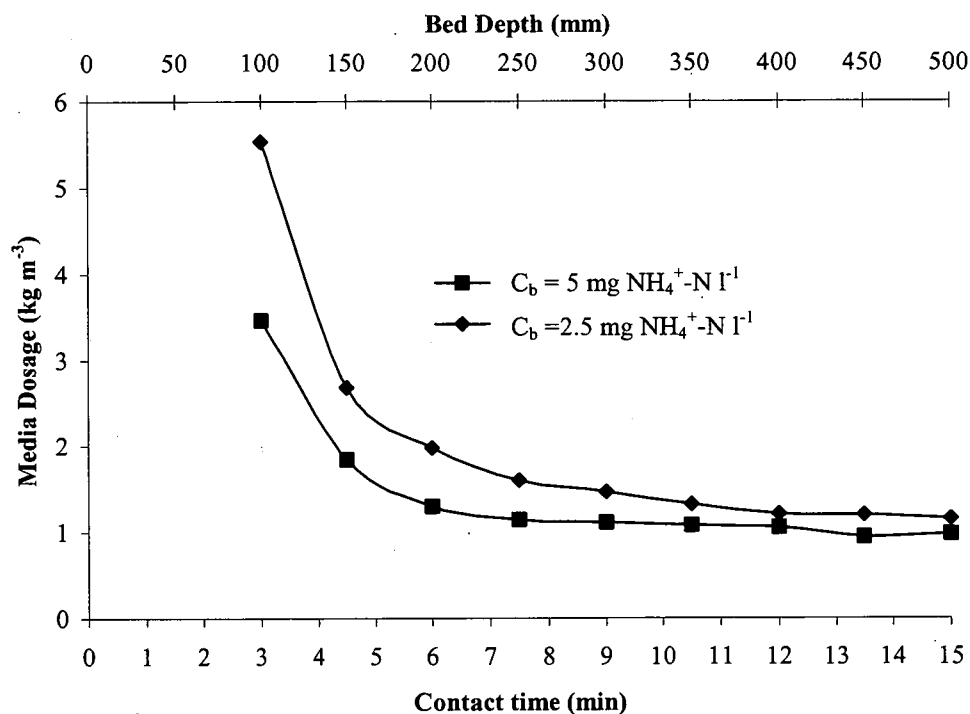


Figure 4.6 Contact time vs media dosage at an average influent concentration of $30 \text{ mg NH}_4^+-\text{N l}^{-1}$

Further studies were performed under identical operating conditions but this time with average influent concentrations of $5.26 \text{ mg NH}_4^+-\text{N l}^{-1}$ and $9.75 \text{ mg NH}_4^+-\text{N l}^{-1}$ respectively. The resulting breakthrough curves show that, as expected, service time is significantly increased when the influent concentration is reduced to these lower values (Figure 4.7 and 4.8). A summary of the results is presented in Table 4.3.

As with the trials performed at $30.7 \text{ mg NH}_4^+-\text{N l}^{-1}$, similar conclusions with regards to the effect of media bed depth and breakthrough concentration on both service time and media dosage can be made. With an influent concentration of $5.26 \text{ mg NH}_4^+-\text{N l}^{-1}$ and a breakthrough concentration of $1 \text{ mg NH}_4^+-\text{N l}^{-1}$, bed depths ranging from 100-400 mm deliver service times ranging from 9-78 days. This range is reduced to 4-65 days when the breakthrough concentration is decreased to $0.5 \text{ mg NH}_4^+-\text{N l}^{-1}$. A corresponding rise in the minimum media dosage from $0.3\text{-}0.36 \text{ kg m}^{-3}$ can also be observed. Similarly, with an influent concentration of $5.75 \text{ mg NH}_4^+-\text{N l}^{-1}$ and a breakthrough concentration of $2 \text{ mg NH}_4^+-\text{N l}^{-1}$, bed depths ranging from 100-250 mm deliver service times ranging

from 9-40 days. This range is reduced to 6-38 days when the breakthrough concentration is reduced to $1 \text{ mg NH}_4^+-\text{N l}^{-1}$, with a corresponding rise in the minimum media dosage from $0.36\text{-}0.47 \text{ kg m}^{-3}$.

Table 4.3 Results for trials performed at 5.26 and $9.75 \text{ mg NH}_4^+-\text{N l}^{-1}$.

Average Influent Concentration ($\text{mg NH}_4^+-\text{N l}^{-1}$)	Breakthrough Concentration ($\text{mg NH}_4^+-\text{N l}^{-1}$)	Bed Depth (mm)	Service Time (Days)	Required Media Dosage (kg m^{-3})
5.26	1	100	9	0.66
		250	41	0.34
		400	78	0.30
	0.5	100	4	1.30
		250	30	0.48
		400	65	0.36
9.75	2	100	9	0.64
		200	31.5	0.38
		250	40	0.36
	1	100	6	0.98
		200	30.5	0.55
		250	38	0.47

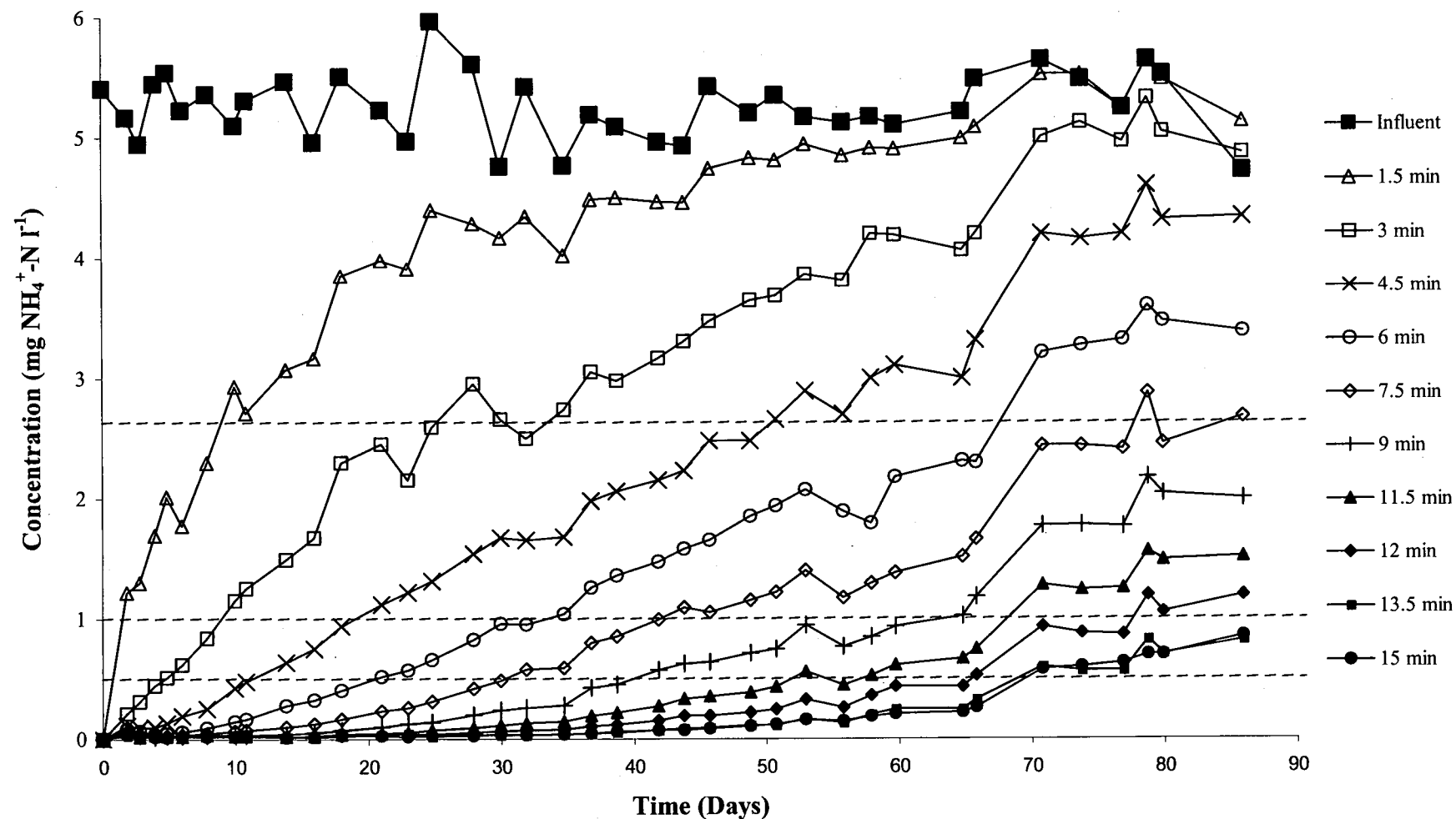


Figure 4.7 Breakthrough curves for trials conducted at $5.26 \text{ mg NH}_4^+ \text{-N l}^{-1}$

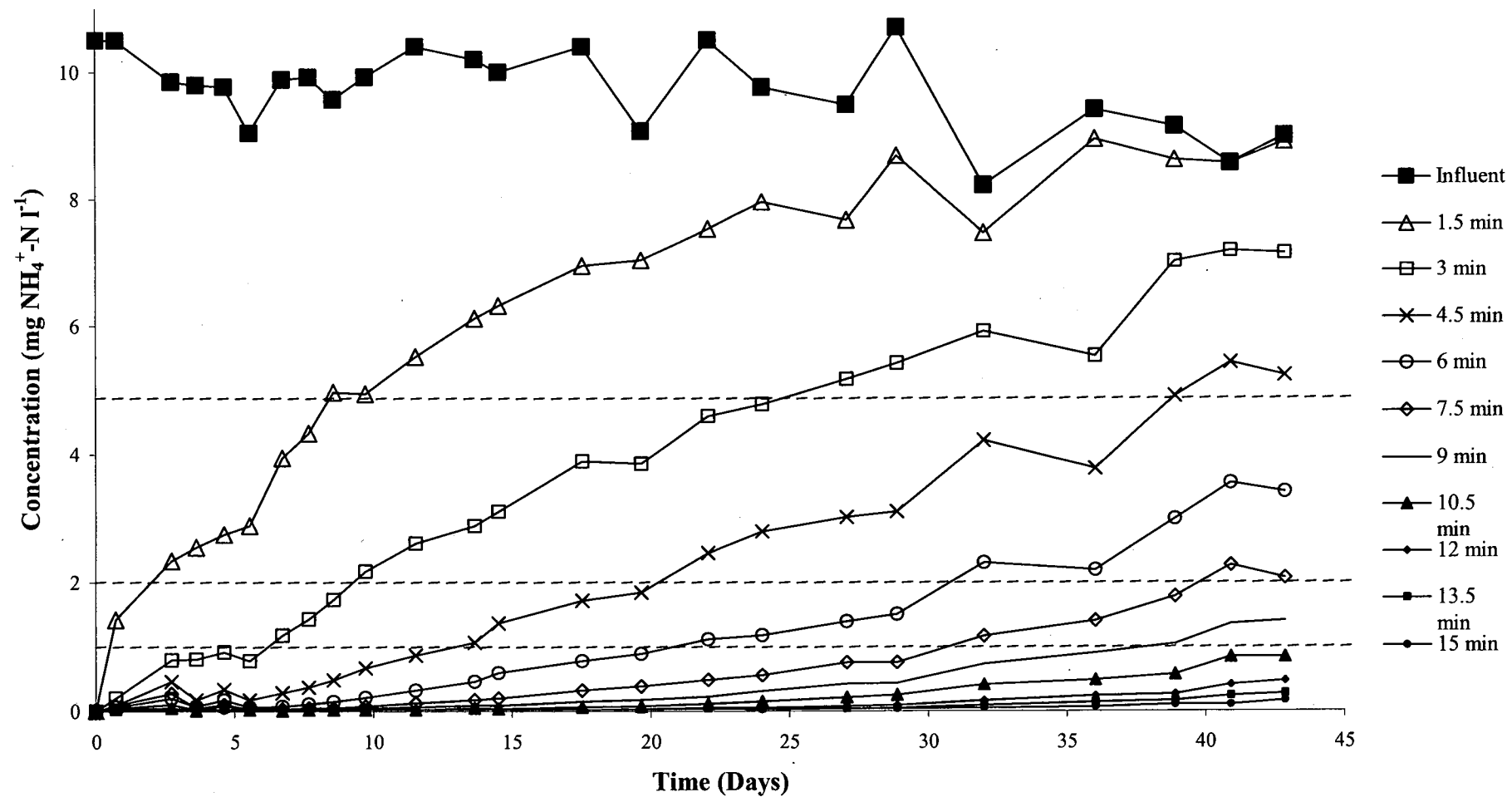


Figure 4.8 Breakthrough curves for trials conducted at $9.75 \text{ mg NH}_4^+ \text{-N l}^{-1}$

When considering the capacity of the media, there are two ways in which the process can be assessed. Firstly, the total capacity can be assessed by running the media to exhaustion (i.e. the effluent $\text{NH}_4^+\text{-N}$ concentration equals the influent $\text{NH}_4^+\text{-N}$ concentration). In all cases, the depth of media in the column has no significant effect on the total capacity of the media. This can be best illustrated using the initial trial conducted at an influent concentration of $30.7 \text{ mg NH}_4^+\text{-N l}^{-1}$, where all column sections were run to exhaustion. Calculations at each sample point consistently return a total capacity for MesoLite in the range $47\text{--}49 \text{ g NH}_4^+\text{-N kg}^{-1}$, indicating that at saturation the capacity remains unaffected.

Secondly, the operational capacity of the media can be assessed by determining the amount of $\text{NH}_4^+\text{-N}$ exchanged at a selected breakthrough concentration. Once a breakthrough is selected, the bed depth has a marked effect on the operational capacity (Figure 4.9). At a breakthrough concentration of $5 \text{ mg NH}_4^+\text{-N l}^{-1}$, a bed depth of 150 mm results in a capacity of $16 \text{ g NH}_4^+\text{-N kg}^{-1}$, whereas a bed depth of 500 mm returns a capacity of $31 \text{ g NH}_4^+\text{-N kg}^{-1}$. Similar results were reported by Milan *et al.*, (1997) who performed experiments on Cuban zeolite with a breakthrough concentration of $2 \text{ mg NH}_4^+\text{-N l}^{-1}$. The author reports a significant increase in both removal efficiency and service time as bed depth increases from 60 mm to 270 mm.

Therefore, selecting a breakthrough concentration results in a large proportion of the medias capacity being unused and this is further impacted on as the bed depth decreases. Furthermore, the breakthrough concentration itself also has a bearing on the amount of capacity utilised (Figure 4.9). At a reduced breakthrough concentration of $2.5 \text{ mg NH}_4^+\text{-N l}^{-1}$ it can be observed that for any given bed depth the capacity of the media is consistently reduced, ranging from $11 \text{ g NH}_4^+\text{-N kg}^{-1}$ at a bed depth of 150 mm to $26.25 \text{ g NH}_4^+\text{-N kg}^{-1}$ at a bed depth of 500 mm.

The effect of the establishment of a breakthrough concentration on operating capacity has been reported for a number of other trials. Thornton *et al.*, (2007a) reported a total capacity for MesoLite of 47-51 g $\text{NH}_4^+\text{-N kg}^{-1}$ for the treatment of liquors of concentration 500-700 mg $\text{NH}_4^+\text{-N l}^{-1}$. This was significantly reduced to 27-32 g $\text{NH}_4^+\text{-N kg}^{-1}$ when a breakthrough concentration of 50 mg $\text{NH}_4^+\text{-N l}^{-1}$ was established. Later trials (Chapter 6) on low concentration effluents (4-5 mg $\text{NH}_4^+\text{-N l}^{-1}$) resulted in a total capacity of 19 g $\text{NH}_4^+\text{-N kg}^{-1}$ being reduced to 9.5 g $\text{NH}_4^+\text{-N kg}^{-1}$ at a breakthrough concentration of 1 mg $\text{NH}_4^+\text{-N l}^{-1}$. Farkas *et al.*, 2005, conducted experiments using Croatian clinoptilolite on liquors with an average concentration of 400 mg $\text{NH}_4^+\text{-N l}^{-1}$ and the results indicated a total capacity of 6.9 g $\text{NH}_4^+\text{-N kg}^{-1}$ but an operational capacity at breakthrough of 3.98 g $\text{NH}_4^+\text{-N kg}^{-1}$.

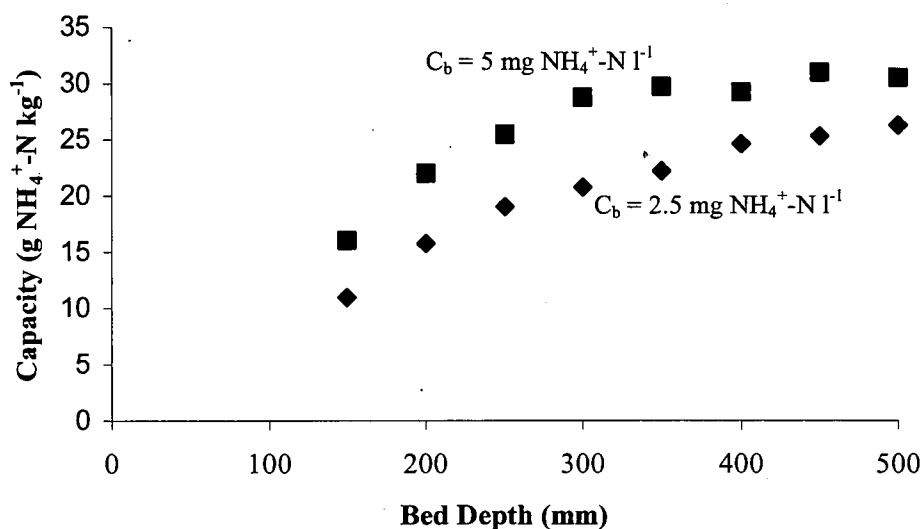


Figure 4.9 Bed depth vs capacity for trials conducted at 30.7 mg $\text{NH}_4^+\text{-N l}^{-1}$

The effect of the bed depth and breakthrough set point can also be observed in subsequent trials. At an influent concentration of 9.75 mg $\text{NH}_4^+\text{-N l}^{-1}$ and a breakthrough concentration of 2 mg $\text{NH}_4^+\text{-N l}^{-1}$, operating capacity ranges from 6 g $\text{NH}_4^+\text{-N kg}^{-1}$ at a bed depth of 50 mm to 25 g $\text{NH}_4^+\text{-N kg}^{-1}$ at 300 mm. The establishment of a breakthrough of 1 mg $\text{NH}_4^+\text{-N l}^{-1}$ further reduces the operating capacity, which ranges from 2-20.5 g $\text{NH}_4^+\text{-N kg}^{-1}$ for equivalent bed depths (Figure 4.10).

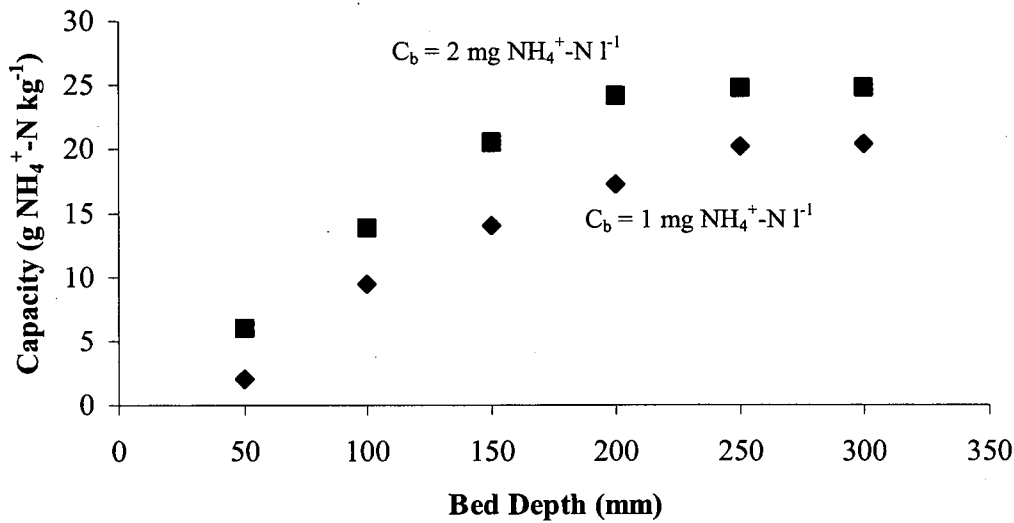


Figure 4.10 Bed depth vs capacity for trials conducted at 9.75 mg NH₄⁺-N l⁻¹

At a lower influent concentration of 5.26 mg NH₄⁺-N l⁻¹ and a breakthrough of 1 mg NH₄⁺-N l⁻¹, operating capacity ranges from 7.4-16.9 g NH₄⁺-N kg⁻¹ for bed depths of 100 and 400 mm respectively. Reducing the breakthrough concentration to 0.5 mg NH₄⁺-N l⁻¹ results in a lower range of 4.1-13.8 g NH₄⁺-N kg⁻¹ (Figure 4.11).

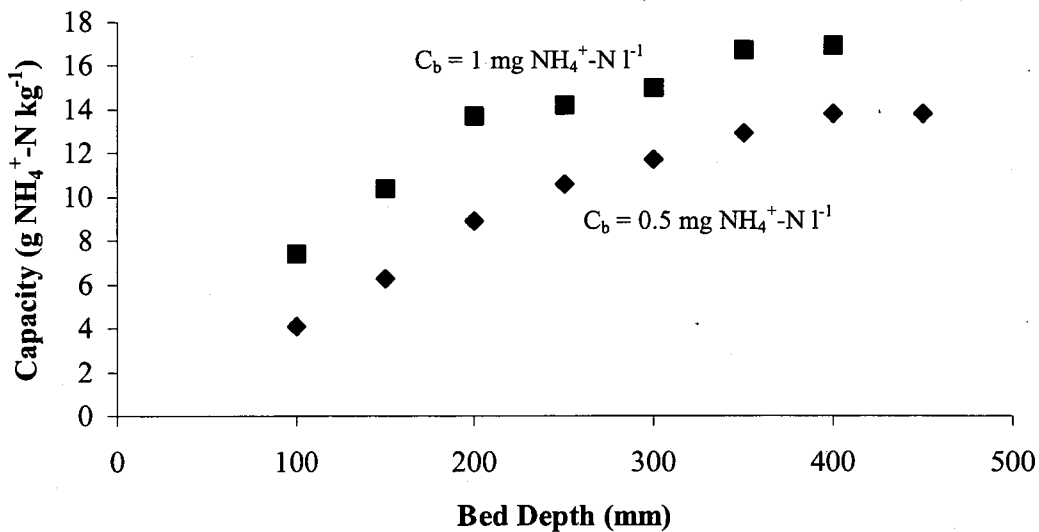


Figure 4.11 Bed depth vs capacity for trials conducted at 5.26 mg NH₄⁺-N l⁻¹

A major factor impacting on the efficient use of the media is the length of the mass transfer zone (Figure 4.1), which can be investigated by determining the length of unused bed (LUB) at breakthrough. The LUB represents the length of the mass transfer zone (Barros *et al.*, 2003) and can be calculated from:

$$\text{LUB} = \left[1 - \frac{t_b}{t_t} \right] L \quad \text{Equation 4.1}$$

Where:

- LUB is the length of unused bed
- t_b is the time to reach breakthrough
- t_t is the time to reach stoichiometric capacity
- L is the total length of media bed

Consider the trial conducted at $30.7 \text{ mg NH}_4^+ - \text{N l}^{-1}$, with a breakthrough concentration set at $5 \text{ mg NH}_4^+ - \text{N l}^{-1}$ (Figure 4.4) with a total bed length (L) of 500mm. In this case t_b equals 29 days and t_t equals 66 days and the LUB, calculated from Equation 4.1, equals 280 mm. If the breakthrough concentration is increased to that of half the influent concentration (i.e. $15.25 \text{ mg NH}_4^+ - \text{N l}^{-1}$), the LUB decreases to 143 mm. At a total bed length (L) of 250 mm, t_t is reduced to 39 days and at a breakthrough concentration of $5 \text{ mg NH}_4^+ - \text{N l}^{-1}$, $t_b = 13$ days (Figure 4.4). Equation 4.1 returns an LUB of 167 mm. Figure 4.12 illustrates the relationship between L and LUB for differing breakthrough concentrations and indicates that the LUB (expressed as a percentage of L) decreases as both C_b and L increase. Thus longer bed lengths and increased breakthrough concentrations result in a more efficient use of the media. The LUB can be used as a design parameter, where the bed length can be designed to have the required capacity by making the column one LUB longer to account for unused capacity under any given conditions (Cooney, 1999).

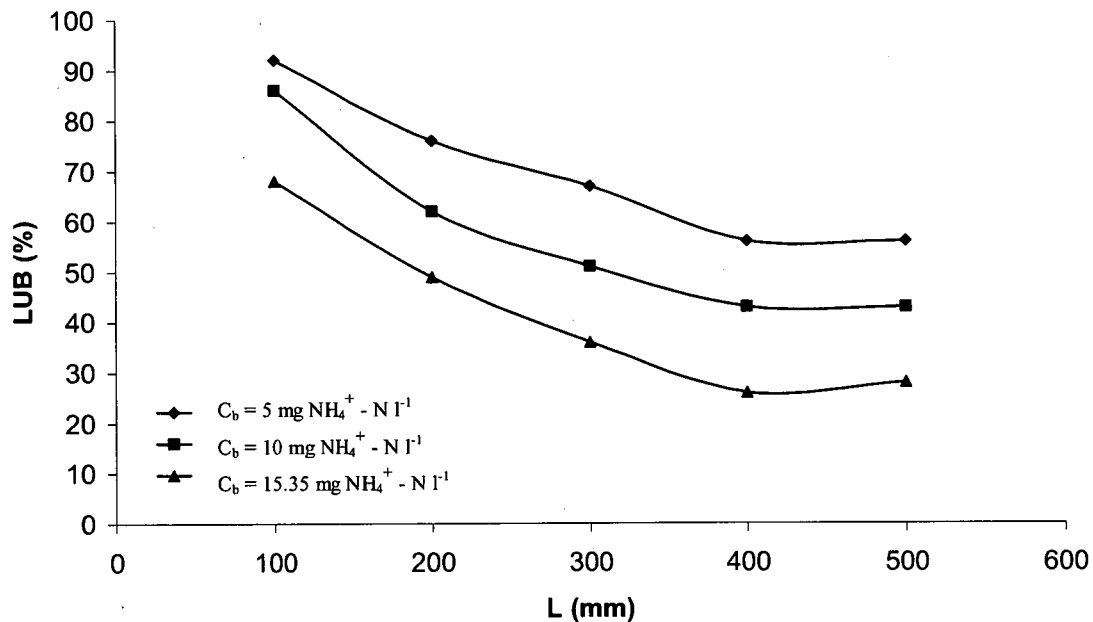


Figure 4.12 LUB as a percentage of total bed length for breakthrough concentrations of 5, 10 and 15.35 $\text{mg NH}_4^+ - \text{N l}^{-1}$

However, results indicate that the length of the mass transfer zone is rather elongated and a possible reason for this is the relatively high loading rate. This is supported by the gentle gradient of the breakthrough curves (Figure 4.4). If mass transfer were instantaneous, then the breakthrough curve would be a vertical line at time $t_b = t_i$ (Cussler, 1997) and the LUB would be zero. This would result in an ideal solution concentration profile across the bed as shown in Figure 4.13 where at any given time the all parts of the bed to the left of the mass transfer front will have reached stoichiometric capacity and all those to the right would still be available for exchange.

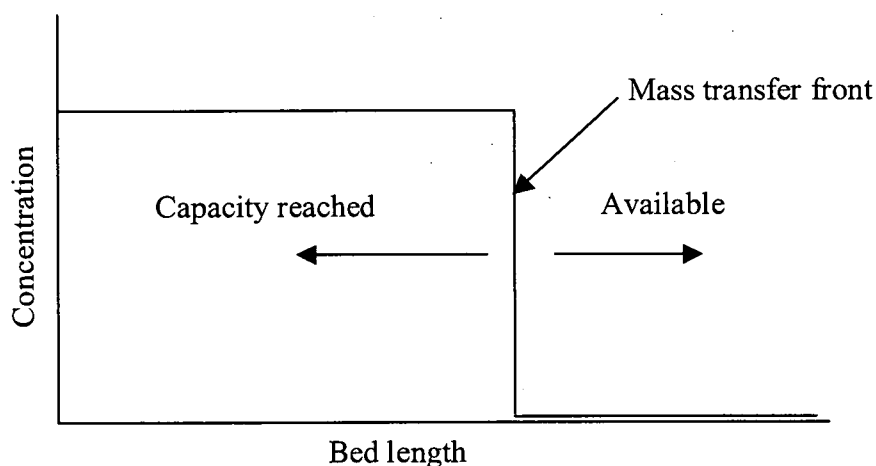


Figure 4.13 An idealised concentration profile (Adapted from Cussler, 1997)

Results show that this is not the case and that the concentration profile across the bed at any given time (Figure 4.14) is not a step function but a gradual slope, which is indicative of an elongated mass transfer zone, rather than a mass transfer front.

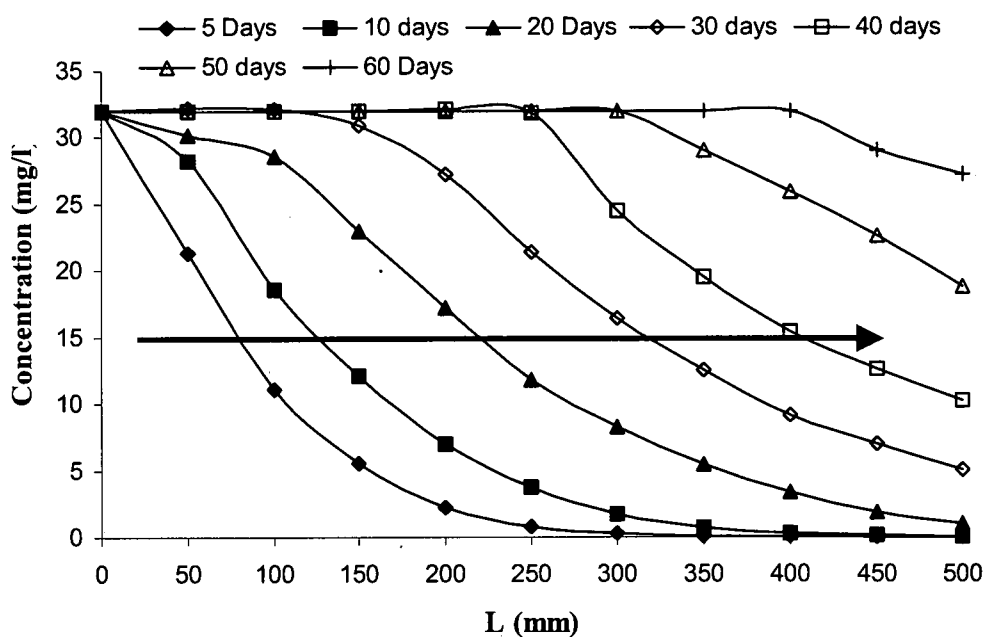


Figure 4.14 Solution concentration profiles for trials at $30 \text{ mg NH}_4^+ - \text{N l}^{-1}$

The arrow indicates the direction of movement of the mass transfer zone through the column with time and the gradient of the curves is linked to the length of the mass transfer zone or LUB. The shallower the gradient is, the longer the mass transfer zone. For any given set of conditions (i.e. influent concentration and breakthrough set point), it is possible to increase the gradient of the curves by reducing the flow rate, thus resulting in a shorter length of unused bed.

Further investigations of Figures 4.9, 4.10 and 4.11 also reveal a relationship between the influent concentration and media capacity. For any given bed depth, the proportion of the media capacity utilised for ammonium exchange is significantly reduced with decreasing influent concentration. For example, at a bed depth of 300 mm and upper breakthrough concentration, influent concentrations of 30.7, 9.75 and 5.26 mg $\text{NH}_4^+\text{-N l}^{-1}$ return respective capacities of 29, 25 and 15 g $\text{NH}_4^+\text{-N kg}^{-1}$. This relationship can also be observed at exhaustion, with these influent concentrations resulting in total capacities of 48, 42 and 28 g $\text{NH}_4^+\text{-N kg}^{-1}$. This phenomenon is a result of the effect of competing cations in solution. Previous studies on MesoLite (Thornton *et al.*, 2007b) indicate that the detrimental effect of solution cations on the media's total and operating capacity becomes more significant at lower ammonium concentrations, with reductions in capacity of up to 70% being reported. Studies on naturally occurring materials deliver similar results. Booker *et al.*, (1996 b) reported that the presence of competing cations in solution has the effect of reducing the capacity of natural Australian clinoptilolite by approximately 60 %. Similarly, Farkas *et al.*, (2005) noted that the presence of potassium ions in solution resulted in a 32 % reduction in the capacity of Transcarpathian clinoptilolite.

4.4. Conclusions

- Results clearly indicate that for any fixed set of operating conditions, reductions in media bed depth lead to corresponding reductions in service time, with almost instantaneous breakthrough being observed for short bed depths.
- The required media dosage is significantly reduced as bed depth increases until a minimum dosage is established.
- Although media bed depth has no significant effect on the overall capacity of the material, once a breakthrough is established, reductions in bed depth lead to further reductions in the operating capacity of the media. With an influent concentration of $30.7 \text{ mg NH}_4^+-\text{N l}^{-1}$ and breakthrough set at $5 \text{ mg NH}_4^+-\text{N l}^{-1}$ the media's capacity is reduced from $31 \text{ g NH}_4^+-\text{N kg}^{-1}$ at a bed depth of 500 mm to $16 \text{ g NH}_4^+-\text{N kg}^{-1}$ at a bed depth of 150 mm.
- The breakthrough set point also has an effect on how efficiently the media is used and relatively low breakthrough concentrations resulting an inefficient use of the media. In all cases, halving the breakthrough concentration results in a 20 % increase in the required media dosage.
- The capacity of the media is also dependant on the influent concentration, with decreasing concentration resulting in a significantly reduced capacity. At an influent concentration of $30.7 \text{ mg NH}_4^+-\text{N l}^{-1}$, the total capacity for the material is $49 \text{ g NH}_4^+-\text{N kg}^{-1}$. This is reduced to $28 \text{ g NH}_4^+-\text{N kg}^{-1}$ when an influent concentration of $5.26 \text{ mg NH}_4^+-\text{N l}^{-1}$ is used. However, even at reduced capacity, MesoLite media still compares favourably with naturally occurring materials used in previous studies, which return capacities in the range $0.95\text{-}21.52 \text{ g NH}_4^+-\text{N kg}^{-1}$.

4.5 References

- Barros, M. A. S. D., Zola, A. S., Arroyo, P. A., Sousa-Aguiar, E. F. and Tavares, C. R. G. (2003) Binary ion exchange of metal ions in Y and X zeolites. *Brazilian Journal of Chemical Engineering* **20** (4), 413-421.
- Belér Baykal, B., Oldenburg, M. and Sekoulov, I. (1996) The use of ion exchange in ammonia removal under constant and variable Loads. *Environmental Technology* **17**, 717-726.
- Belér Baykal, B. and Guven, D. A. (1997) Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater. *Water, Science and Technology* **35** (7), 47-54.
- Booker, N. A., Cooney, E. L. and Priestly, A. J. (1996 a) Ammonia removal from sewage using natural Australian zeolite. *Water, Science and Technology* **34** (9), 17-24.
- Booker, N. A., Cooney, E. L. and Priestly, A. J. (1996 b) Innovative Physico-Chemical Wastewater Treatment Research Down-Under. Proceedings of the 7th Gothenburg symposium, Springer, New York.
- Celik, M. S., Ozdemir, B., Turan, M., Koyuncu, I., Atesok, G. and Sarikaya, H. Z. (2001) Removal of ammonia by natural clay minerals using fixed bed column reactors. *Water, Science and Technology: Water Supply* **1** (1), 81-88.
- Cooney, D. O. (1999), Adsorption design for wastewater treatment, Lewis Publishing, New York.
- Cussler, E. L. (1997) Diffusion: Mass transfer in fluid systems, Cambridge University Press.
- Demir, A., Gunay, A. and Debik, E. (2002) Ammonium removal from aqueous solution by Ion Exchange using Packed Bed Natural Zeolite. *Water SA* **28** (3), 329-

336.

Du, Q., Shijun Liu, Q. D., Zhonghong, C. and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese Clinoptilolite. *Separation and Purification Technology* **44** 229-234.

Farkas, A., Rozic, M. and Barbaric-Mikocevic, Z. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* **B117** 25-33.

Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) Removal of NH_4^+ ion from NH_4Cl solution using clinoptilolite: A dynamic study using a continuous packed-bed column in upflow mode. *Separation Science and Technology* **36** (9), 1347-1364.

Jung, J., Chung, Y., Shin, H. and Son, D. (2004) Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research* **38** 347-354.

Kamarowski, S. and Yu, Q. (1997) Ammonium ion removal from wastewater using Australian natural Zeolite: Batch equilibrium and kinetics studies. *Environmental Technology* **18** 1085-1097.

Karadag, D., Koc, Y., Turan, M. and Armagan, A. (2006) Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. *Journal of Hazardous Materials* **B136** 604-609.

Klieve, J. R. and Semmens, M. J. (1979) An evaluation of pretreated natural zeolites for ammonium removal. *Water Research* **14**, 161-168.

Koon, H. J. and Kaufmann, W. J. (1975) Ammonia removal from municipal wastewaters by ion exchange. *Journal WPCF* **47** (3) 448-465.

Lahav, O. and Green, M. (1998) Ammonium removal using ion exchange and biological regeneration. *Water Research* **32** (7), 2019-2028.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient removal from wastewaters using high performance materials. *Water, Science and Technology* **47** (11), 101-107.

Mackinnon, I. D. R., Millar, G. and Stoltz, W. (2006) Hydrothermal Synthesis of Zeolite N Aluminosilicates, *WIPO publication number, W0/2006/096930*.

Milan, Z., Sanchez, E., Weiland, P., de Las Pozas, C., Borja, R., Mayari, R., and Roviroso, N. (1997) Ammonia removal from anaerobically treated piggery manure by ion exchange in columns packed with homoionic zeolite. *Chemical Engineering Journal* **66** 65-71.

Nguyen M. L. and Tanner C. C. (1998) Ammonium removal from wastewaters using natural New Zealand Zeolites. *New Zealand Journal of Agricultural Research* **41** 427-466.

Semmens, M. J. and Porter, P. S. (1979) Ammonium removal by ion exchange: Using biologically restored regenerant. *Journal WPCF* **51** (12), 2928-2940.

Sprynskyy, M, Lebedynets, M, Terzyk, A. P, Kowalczyk, P, Namiesnik, J. And Buszewski, B. (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Colloid and Interface Science* **284** 408-415.

Thornton, A., Pearce, P. and Parsons, S. A. (2007a) Ammonium removal from digested sludge liquors using ion exchange. *Water Research* **41** 433-439.

Thornton, A., Pearce, P. and Parsons, S. A. (2007b) Ammonium removal from wastewater treatment effluent by ion exchange on to MesoLite. Submitted to *Water Research*, 2007.

Wachinsky, A. M. and Etzel, J. E. (1997), Environmental ion exchange, principles

and design, Lewis Publishing, New York.

Wang, Y., Liu, S., Xu, Z., Han, T., Chaun, S. and Zhu, T. (2006) Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials* B136 735-740.

CHAPTER 5

**AMMONIUM REMOVAL FROM WASTEWATER TREATMENT WORKS
EFFLUENT BY ION EXCHANGE ON TO MESOLITE**

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5. AMMONIUM REMOVAL FROM WASTEWATER TREATMENT WORKS EFFLUENT BY ION EXCHANGE ON TO MESOLITE

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Keywords: Ammonium; ion exchange; nutrient removal; effluent; competing cations; zeolite

Abstract

This paper investigates the performance of the ion exchange media MesoLite for the removal of the ammonium ion from low concentration wastewater treatment work effluents in the presence of competing cations. Previous work using this media concentrates on its effective use in the treatment of high ammonium concentration recycle streams within the wastewater treatment process where the effect of cations on the removal performance is minimal. In this study, results indicate that the capacity of the material is significantly affected by the presence of calcium ion, with only 30 % of the media's capacity being utilised. However, results also show that the media can be used to successfully remove ammonium from effluents arising from the municipal wastewater treatment works and that the process adopted is capable of maintaining a 1 mg NH₄⁺-N l⁻¹ breakthrough concentration for a period of 22 days.

5.1 Introduction

The adverse effects of ammonium (NH_4^+) present in effluents resulting from the treatment of municipal and industrial wastewaters are well documented (Du *et al.*, 2005; Karadag *et al.*, 2006 and Wang *et al.*, 2006) and the control of its release into the surrounding environment is critical. Excess amounts introduced into receiving waters can result in depleted dissolved oxygen concentration (Wen *et al.*, 2005) and increased toxicity to fish and other aquatic life. Conventional methods of ammonium removal from municipal wastewaters are performed using biological processes (Jorgensen and Weatherley, 2003) which in most cases prove sufficiently efficient in reducing the effluent concentration to a safe level. However, some sites find themselves under increasing strain and as a result complementary methods of ammonium reduction have to be considered as a possible solution to maintaining an effective removal performance. A number of methods have been concerned with the treatment of high strength internal recycle streams within the wastewater treatment works (WwTW) in order to alleviate the strain placed on the mainstream biological processes. These include; air stripping (Siegrist, 1996); struvite precipitation (Celen and Turker, 2001 and Kabdasli *et al.*, 2000) ion exchange and more recently the combined Sharon/Anammox process (Fux *et al.*, 2003; Schmidt *et al.*, 2003 and van Dongen *et al.*, 2001) which have all achieved some degree of success.

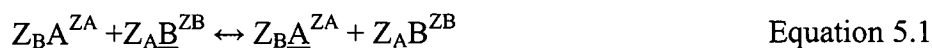
Over the last 30 years much experimental work has been performed to investigate the merits of ion exchange on to zeolite (mainly clinoptilolite) as an effective treatment for the removal of the ammonium ion from both high concentration and low concentration wastewater streams (Table 5.1). Ion exchangers are insoluble solids which carry exchangeable cations or anions within their framework (Helfferich, 1962) which can then be exchanged for the polluting ion in solution leading to a significant reduction in its concentration.

Table 5.1 Operating conditions and material characteristics for materials used in various trials

Material	NH ₄ ⁺ -N Capacity (g kg ⁻¹)	Grain Size (mm)	Bed Volume (ml)	Flow Rate (BV h ⁻¹)	Influent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	Effluent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	pH	Reference
Clinoptilolite	4.8	0.3-0.84	-	15	18.8	Breakthrough of 1 mg l ⁻¹ reached at between 100-240 BV's	7.9-8.1	Koon and Kauffmann, 1975
Clinoptilolite –Tokaj region of Hungary	0.94 - 2.41	1.4 – 2.0 2.5 – 5.0 3.2 – 5.0	200	10 - 12	26 - 33	0.6 – 4.1	7.0	Jorgensen <i>et al.</i> , 1976
Clinoptilolite Buckhorn N.M. Double Eagle Mining Company	3.9	0.3 – 0.84	700	5.55-6.88	20	2 mg l ⁻¹ breakthrough reported after 16.5-20 hours	6.5-8.0	Semmens and Porter, 1979
Clinoptilolite -Tokaj region of Hungary	1.37-9.15	0.5 – 1.0	40-4000	5-7	12-45	4.5 at breakthrough	7.1-8.2	Hlavay <i>et al.</i> , 1982
Clinoptilolite – Beli Plast region of Bulgaria	2.0-3.6	2.0-2.3	96	6-20	15-17	-	-	Belér Baykal and Guven, 1997
Mordenite and Clinoptilolite	3.7-6.5	0.25-0.5 2.0-2.83	77-179	0.056-3.12	100-400	Breakthrough of 1- 1.2 mg l ⁻¹ reached after 40 BV's	7.5-7.7	Nguyen and Tanner, 1998

Material	NH ₄ ⁺ -N Capacity (g kg ⁻¹)	Grain Size (mm)	Bed Volume (ml)	Flow Rate (BV h ⁻¹)	Influent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	Effluent NH ₄ ⁺ -N Concentration (mg l ⁻¹)	pH	Reference
Gordes Clinoptilolite and Sivrihisar Sepiolite (Turkey)	-	2.0-2.8	350	12	15	0.1 for 100 BV's	-	Celik <i>et al.</i> , 2001
MesoLite	45-55	3-9	107000	1-2.7	500-1000	5-15	7.1-10.2	Mackinnon <i>et al.</i> , 2003
Zeolite	6.0-7.4	<0.15	-	-	-	-	-	Jung <i>et al.</i> , 2004
Croatian Clinoptilolite	6.0-13.65	0.5-2.0	710	2+	130-850 (400 average)	Breakthrough reached at 14 and 32 BV's	7.3-7.77	Farkas <i>et al.</i> , 2005
Chinese Clinoptilolite – Jinyun in the Province of Zhejiang	5.89-7.74	0.45-0.9	-	6-24	25	Breakthrough set at 5 mg l ⁻¹	-	Du <i>et al.</i> , 2005
Transcarpathian Clinoptilolite	3.56-21.52	0.125-2.0	14	8-40	100	Breakthrough set at 2 mg l ⁻¹	-	Sprynskyy <i>et al.</i> , 2005
MesoLite	47-51	1.4-2.5	100,000	4-5	500-700	Breakthrough set at 50 mg l ⁻¹	7.8-8.1	Thornton <i>et al.</i> , 2007

In the case of zeolite, the ion exchange process is cationic between cation A^{Z_A} , initially in solution, and cation B^{Z_B} , initially in the zeolite framework and can be characterised as follows (Dyer, 1988):



Where Z_A and Z_B are the valences of the ions and the underlined characters relate to a cation inside the zeolite framework. The most common exchange ion used in the removal of NH_4^+ is sodium (Na^+) resulting in the following relationship:



Studies to date indicate that the modified media MesoLite has an increased exchange capacity ($45\text{--}55 \text{ g NH}_4^+\text{-N kg}^{-1}$) when compared to other naturally occurring materials (Table 5.1). The media is produced by the modification of clay and other aluminium bearing minerals, resulting in an increase in the amount of exchange sites available. This gives the media a higher exchange capacity than would be seen in the parent mineral and an increased surface area (Mackinnon *et al.*, 2006). Previous work undertaken to investigate the performance of MesoLite (Mackinnon *et al.*, 2003, and Thornton *et al.*, 2007) has been concerned with ammonium removal from internal recycle streams ($>500 \text{ mg l}^{-1} \text{NH}_4^+\text{-N}$) where NH_4^+ is the most predominant ion and therefore the effect of other solution cations on the ammonium exchange capacity is minimal. This study investigates the performance of the media for the treatment of low concentration effluents ($1\text{--}5 \text{ mg l}^{-1} \text{NH}_4^+\text{-N}$) where the ammonium ion forms only a small proportion of the total cation concentration.

5.2 Materials and Methods

Studies were undertaken using final effluent from Reading WwTW, part of the Thames Water network of wastewater treatment facilities. Ammonium removal was performed using a single column (Figure 5.1) of internal diameter 0.075 m filled with 2 kg of media (supplied by Nanochem Pty Ltd, Australia) resulting in a bed height of 0.55 m and intergranular pore space of 0.725 litres.

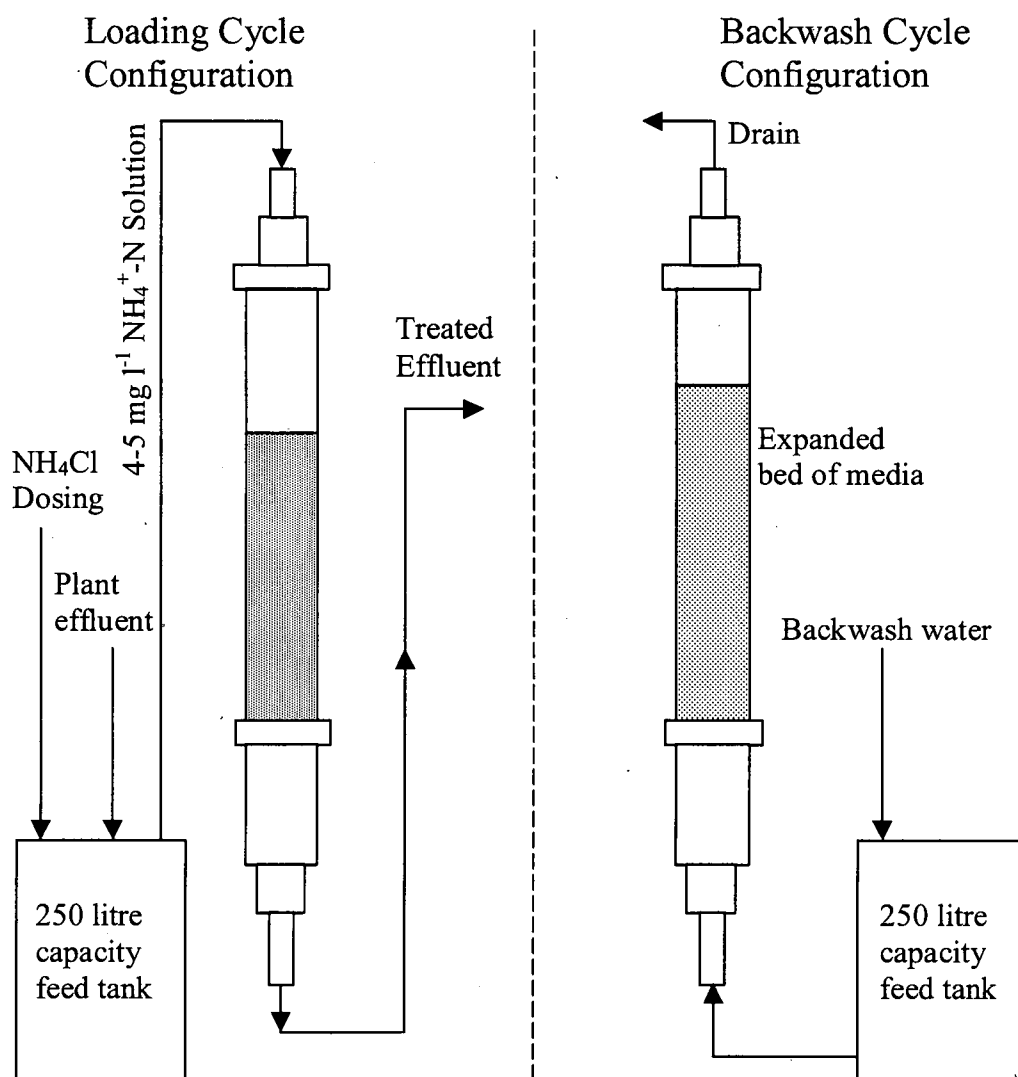


Figure 5.1 Process schematic of the pilot plant at Reading WwTW

The feed was taken from a 250 litre capacity tank which was continually replenished with site effluent and dosed with ammonium chloride powder (supplied by Fisher Scientific, Loughborough, UK) to deliver the required ammonium concentration. The column influent and effluent were then sampled every 2-3 days and analysed for ammonium concentration. Analysis was performed using a Lasa 100 spectrometer supplied by Hach Lange GMBH, Düsseldorf, Germany. In addition to this, the column was periodically backwashed to remove any excess solids accumulating on the media (Figure 5.1). The backwash cycle was performed by feeding domestic tap water in an upflow direction, at a flowrate resulting in a 10 % bed expansion, for a period of 6 minutes. The degree of bed expansion was determined by measuring the height of the media bed prior to backwashing. By using a variable speed pump the flow was slowly increased until the bed height was 10 % greater than the initial bed height. After the backwash cycle normal loading with effluent was resumed.

Before assessing the media for ammonium removal it was necessary to investigate whether or not the media would withstand a significant amount of backwashing. Two backwash trials were conducted on 2 kg samples of fresh media. In each case the media bed was continuously exposed to backwashing for a period of 100 hours with the only difference being the degree of bed expansion. Trial 1 was conducted at a bed expansion of 10 % whilst Trial 2 was performed with a 20 % bed expansion. Prior to backwashing, the media was washed and then dried at room temperature. It was then weighed at regular intervals until a constant weight was recorded and the media considered dry. A particle size analysis was undertaken on a 300 g sample using sieve sizes 0.6, 0.71, 1.0, 1.18, 1.4, 1.7, 2.0, 2.36, 2.5, 2.8, 3.35 and 5.0 mm. The media was then placed into the column and backwashed at the required bed expansion. After 100 hours of backwashing, the media was removed from the column, dried, weighed and a particle size analysis was repeated.

5.3 Results and Discussion

5.3.1 Backwash and attrition studies

Results from the backwashing trials indicate that a small amount of media is lost during the backwashing cycle with 2.38 and 2.44 % of weight loss observed in trials 1 and 2 respectively. Backwashing the media for a period of 100 hours represents almost three years of media life under normal operating conditions (Ives, 1975) for conventional filter media. This is based on the assumption that filters are washed every day and that a washing cycle lasts for about 6 minutes. Furthermore, a particle size analysis of the media before and after backwashing also gives an indication of the amount of attrition the media has been exposed to. Investigation of the weight loss alone gives no indication of the condition of the media remaining in the column and if the media is significantly reduced in size it can result in resistance to flow in the column, leading to unacceptable head loss across the media. Cumulative frequency distribution for all samples (Figure 5.2) shows no detectable difference in the particle size range between the media before and after backwashing. This indicates that although a small proportion of the media would be lost over a three-year operating period, the filtration properties of the remaining media would be relatively unaffected.

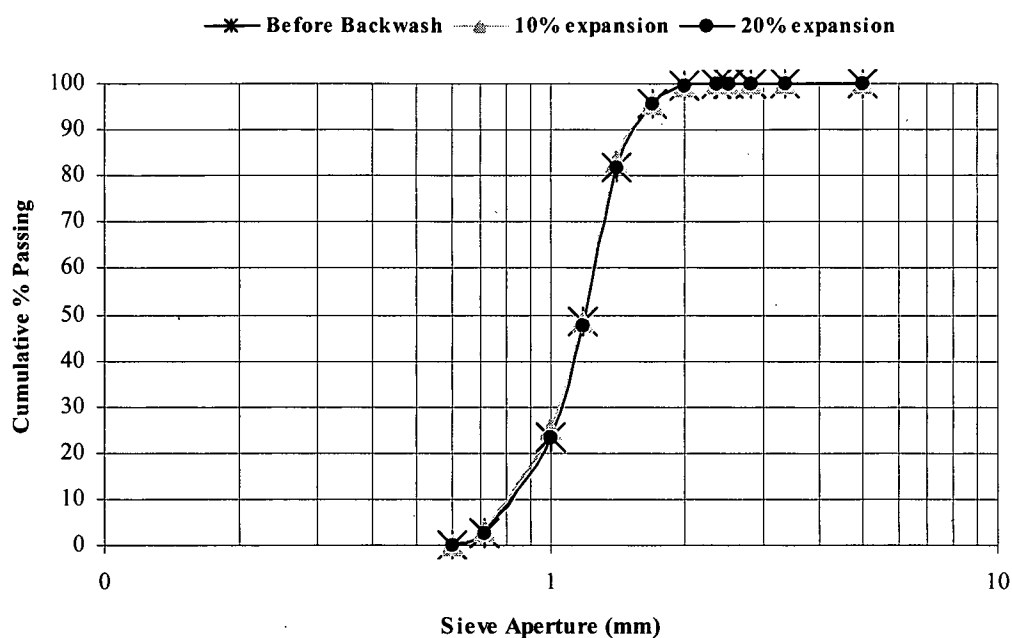


Figure 5.2 Cumulative frequency distribution curves for particle size analysis

5.3.2 Ammonium removal studies

The column was exhausted in a downflow direction at a flow rate of 8.65 l h^{-1} , which equates to 12 bed volumes (BV) per hour and a resulting hydraulic retention time (HRT) of 5 minutes. This is equivalent to three times the loading rate used in Chapter 4, where at a bed depth 500 mm, the flow rate was at a reduced rate of 4 BV h^{-1} , resulting in an extended HRT of 15 minutes. However, as the media was also intended to act as a solids filter, this faster flow rate was considered to be more representative of how the process would be operated in practice. In reality, the effluent solids concentration was not high enough to block the column ($< 2 \text{ mg l}^{-1}$) with any regularity as the plant effluent was already filtered prior to being used in this study and as a result the media was only backwashed on two occasions.

The media was initially loaded at an influent concentration of $4\text{--}5\text{ mg l}^{-1}\text{ NH}_4^+\text{-N}$, and for the first 14 days was successful in removing $> 95\%$ of ammonium from solution (Figure 5.3). At a selected breakthrough concentration of $1\text{ mg NH}_4^+\text{-N l}^{-1}$, the total running time for continuous operation was approximately 22 days. Similar influent concentrations used in Chapter 4 resulted in the same breakthrough concentration being reached in a much longer time period of approximately 90 days (Figure 4.7). This discrepancy can, in part, be explained by the increased loading rate. The loading rate adopted for this study is three times that used in Chapter 4 and as a consequence, the time to reach breakthrough should be approximately one third of that observed previously (Cooney 1999), resulting a predicted run time of 30 days. However, the resulting service time at breakthrough (22 days) is still approximately 25 % less than would have been predicted and reasons for this will be discussed later.

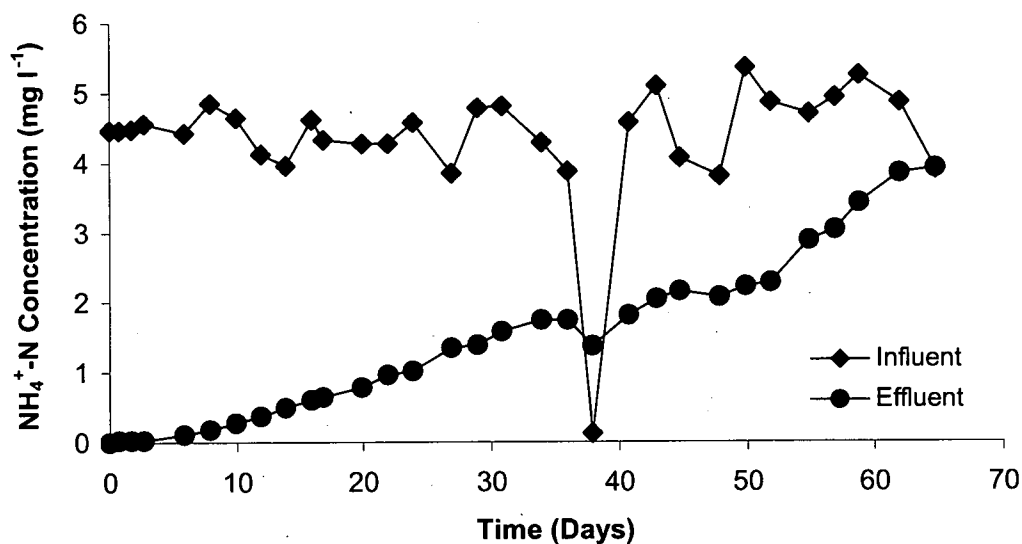


Figure 5.3 Breakthrough curve for effluent treatment at Reading WwTW

A service time of 22 days is still considerably longer than the run times encountered in other studies on MesoLite, which operated at run times of between 8-25 hours (MacKinnon *et al.*, 2003) and 27-35 hours (Chapter 6). Although these trials were operated at lower loading rates (3 BV h^{-1} and $4\text{-}5 \text{ BV h}^{-1}$ respectively), the extremely high concentration of the treated solutions ($500\text{-}1000 \text{ mg l}^{-1} \text{ NH}_4^+\text{-N}$) resulted in an accelerated loading of the media. In previous studies performed on naturally occurring materials, mainly clinoptilolite, influent concentrations rarely exceeded $100 \text{ mg NH}_4^+\text{-N l}^{-1}$, with the exception of Nguyen and Tanner, 1998; Hankins *et al.*, 2004 and Farkas *et al.*, 2005 (Table 5.1). The other trials (Koon and Kauffmann, 1975; Jorgensen *et al.*, 1979; Semmens and porter, 1979; Hlavay *et al.*, 1982; Beler Baykal and Guven, 1997; Celik *et al.*, 2001; Du *et al.*, 2005 and Sprynskyy *et al.*, 2005) were operated at much lower influent ammonium concentrations of $12\text{-}45 \text{ mg NH}_4^+\text{-N l}^{-1}$, with calculated run times in the range of 3 hours (Semmens and Porter, 1979) to 16 hours (Koon and Kauffman, 1975). These run times are extremely short compared to those seen in this study, but are dependant on many factors, including initial ammonium concentration; flow rate; media capacity; the scale of operation and most importantly the breakthrough concentration selected. However, it is worth noting that Beler Baykal and Guven, (1997) successfully removed ammonium peaks of up to 20 mg l^{-1} from domestic wastewater effluent by ion exchange on to clinoptilolite, for a continual period of over 10 days.

Although run time is an important factor (i.e. it is advantageous to keep the effluent below breakthrough for as long as possible), the capacity of the media is a much better indicator of performance. In this study, the media reached exhaustion after a period of 65 days resulting in a total ammonium exchange capacity of $19 \text{ g NH}_4^+\text{-N kg}^{-1}$, with a total of 38 g of $\text{NH}_4^+\text{-N}$ being removed from solution. At a breakthrough concentration of $1 \text{ mg NH}_4^+\text{-N l}^{-1}$ this is significantly reduced, with only $19 \text{ g NH}_4^+\text{-N}$ being removed from solution, resulting in an operational capacity of $9.5 \text{ g NH}_4^+\text{-N kg}^{-1}$. This capacity is considerably lower than results reported when treating high concentration liquors, where a total capacity of $47\text{-}51 \text{ g NH}_4^+\text{-N kg}^{-1}$ and an operational capacity of $27\text{-}32 \text{ g NH}_4^+\text{-N kg}^{-1}$ were reported (Thornton *et al.*, 2007). However, a capacity of $19 \text{ g NH}_4^+\text{-N kg}^{-1}$ is still relatively high when compared to the capacity of clinoptilolite reported in the majority of previous studies (Table 5.1). A closer investigation of the operating conditions clearly shows that the performance of the media at lower concentrations is significantly reduced by the presence of other cations in solution.

Analysis of cation concentrations in the column influent and effluent (Figure 5.4) shows that there is no net change in the solution concentration of either sodium or magnesium and therefore, the effect of these on the ammonium exchange capacity can be considered negligible. Conversely, there is a significant increase in the potassium effluent concentration compared to the influent potassium concentration. This is due to the fact that the media is supplied in the potassium form and therefore potassium is the exchange ion in the process (Equation 5.3).



This is a uni-univalent exchange process (Dyer, 1988), and as ion exchange is a stoichiometric process (Helfferich, 1962), each potassium ion released from the media should result in an ammonium ion being removed from the solution. If this was the case, the number of milliequivalents (meq) of ammonium removed should be equal to the number of meq of potassium entering the solution, at any stage of the process. However, there is a significant shortfall between the amount of ammonium removed and the amount of potassium released. For example at exhaustion, 5230 meq of potassium had entered solution whereas only 2580 meq of ammonium were removed. As electroneutrality of the exchange material must be preserved at all times (Paterson, 1970), each potassium ion removed from the media must be replaced by another cation. Closer inspection of the calcium concentrations in both the column influent and effluent (Figure 5.4) indicates that some calcium is indeed removed from solution, but initially this appears not to be significant enough to account for the shortfall in ammonium exchange. However, two factors have to be taken into consideration. Firstly the initial concentration of calcium in solution is significantly higher (89-116 mg l⁻¹) than that of ammonium (4-5 mg l⁻¹) and what seems to be a small change in concentration between the influent and effluent (Figure 5.4) is a product of scale, and is

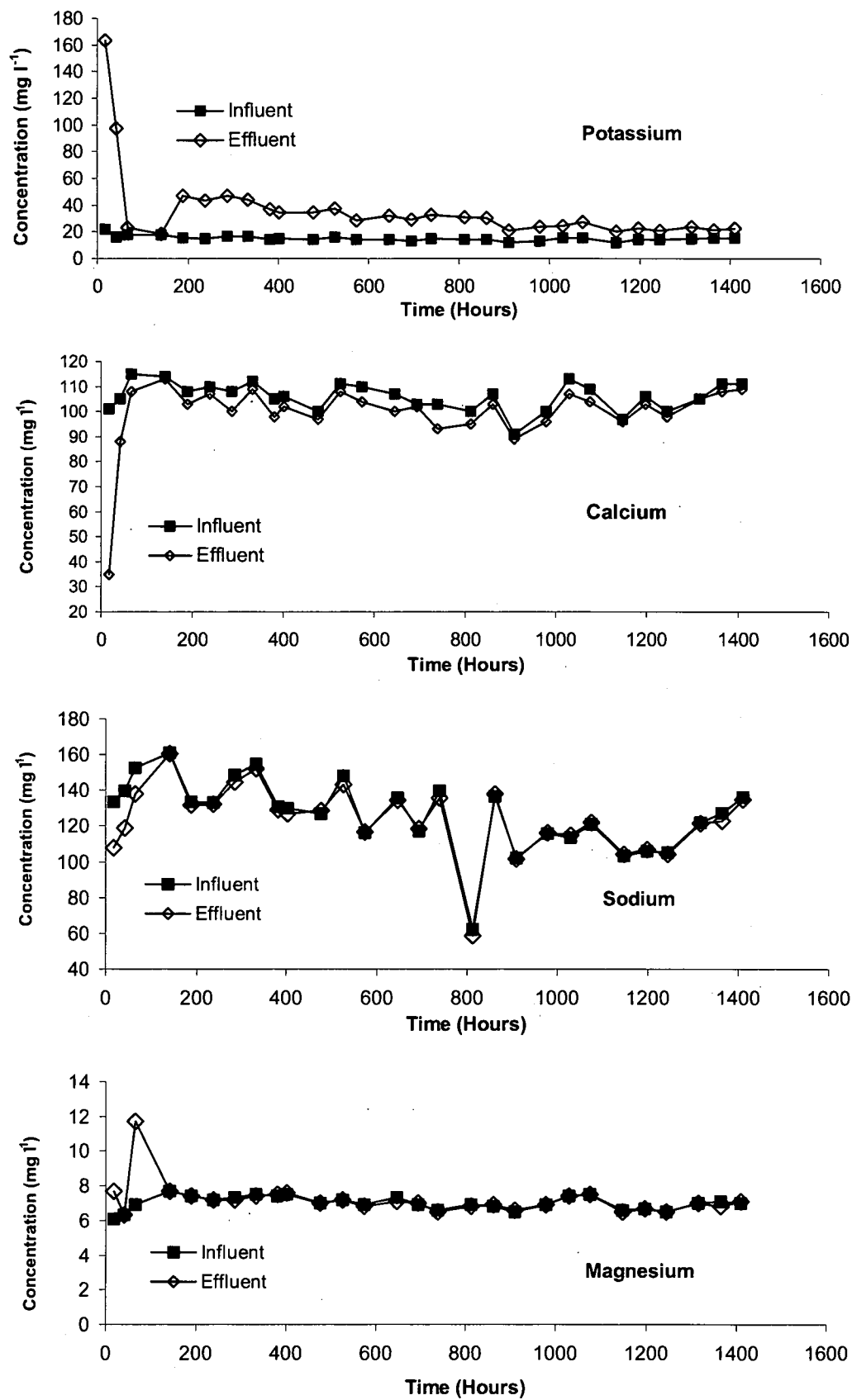


Figure 5.4 Influent and effluent cation concentrations

more significant than would at first appear to be the case. Secondly, the exchange of calcium for potassium is a uni-divalent exchange process (Equation 5.4).



Therefore, for every calcium ion removed from solution, two potassium ions are removed from the media, which makes the quantity of calcium exchanged even more significant and this is enough to account for the discrepancy between the quantities of exchanged ammonium and potassium (Figure 5.5). At exhaustion, 2870 meq of calcium were removed from solution. This, when added to the ammonium removed, balances approximately with the total potassium entering solution. This relationship can be observed throughout the loading cycle.

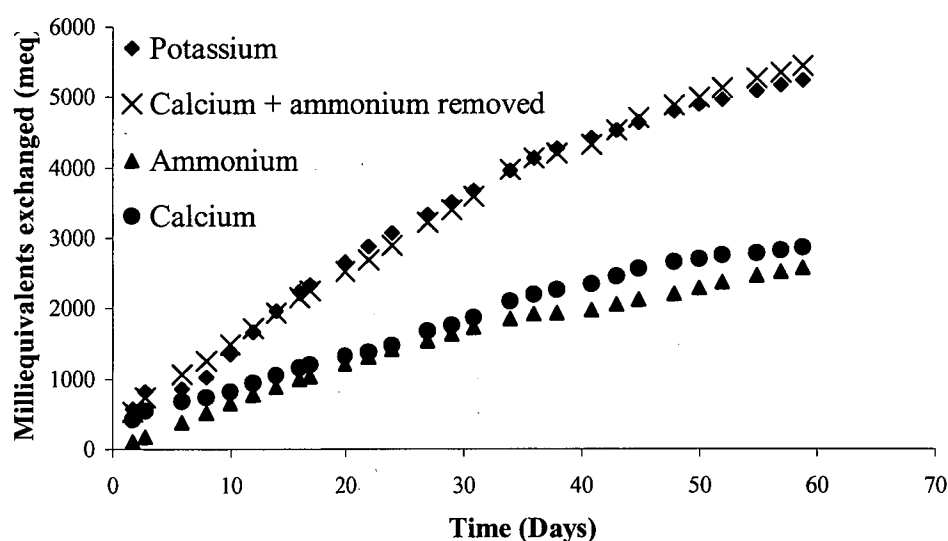


Figure 5.5 Cumulative exchange of ammonium, calcium and potassium.

The detrimental effect of competing cations has also been observed in previous studies. Weatherley and Miladinovic (2004) performed batch tests on the sodium form of clinoptilolite, concluding that calcium had the greatest detrimental effect on the uptake of ammonium (observing a 14 % reduction), followed by potassium, with magnesium having the least effect. In contrast, McVeigh (1999) conducted trials on commercial clinoptilolite and reported that potassium resulted in a greater reduction in capacity (22 %) followed by calcium then magnesium. Little is understood of the reasons why zeolite minerals are selective for different ions. It is known that ionic size and charge are important parameters and that the following rules apply (McVeigh, 1999):

- At low concentrations and room temperature and pressure, the exchange increases with the increasing valence of the ion
- With ion valence remaining the same, exchange increases with increasing atomic number and
- At high concentrations the exchange potential of different valences diminishes and the ion of lower valence can possess a higher selectivity.

This could be a further explanation as to why MesoLite shows improved performance at higher ammonium concentrations where ion valence is less important in the selectivity process.

As stated previously, the service time reported for this part of the study was 25 % less than that which would have been predicted from observations made in Chapter 4. However, it is possible that the effect of competing cations may go some way in accounting for this discrepancy. It has already been established that the calcium ion has the most detrimental effect on the uptake of ammonium on to MesoLite. Here, the assumption is made that the greater the calcium concentration in solution, the greater the detrimental effect will be on the ammonium uptake by the media for any given ammonium concentration. A closer investigation shows that there is, on average, 20 % more calcium present in the final effluent used in this study (106 mg l^{-1}) than there was in the solutions used in the previous chapter (88 mg l^{-1}). Therefore, it is possible that the increased uptake of calcium resulted in a reduced service time of the process.

Prior to the operation of the pilot plant, small scale experiments were performed to outline the design parameters for the larger scale process. At an influent concentration of $2 \text{ mg NH}_4^+-\text{N l}^{-1}$, the effluent was maintained below $0.5 \text{ mg NH}_4^+-\text{N l}^{-1}$ for an initial period of 30 days (Figure 5.6). After 33 days the effluent concentration started to fall significantly and further investigations identified an inflated amount of nitrate in the column effluent. This is a possible indication that nitrifying bacteria were present and that some of the ammonium was being converted to nitrate. After a period of 40 days the column was continually dosed with nitrification inhibitor, allylthiourea (ATU) and as a result the column effluent ammonium concentration proceeded to increase. When nitrification inhibition was stopped the same pattern was observed again and as a result constant addition of ATU was carried out. The loading cycle was then continued to exhaustion, which was achieved after 200 days. However, the capacity of the material for these conditions could not be established as it was unclear how much ammonium had been exchanged and how much had been nitrified.

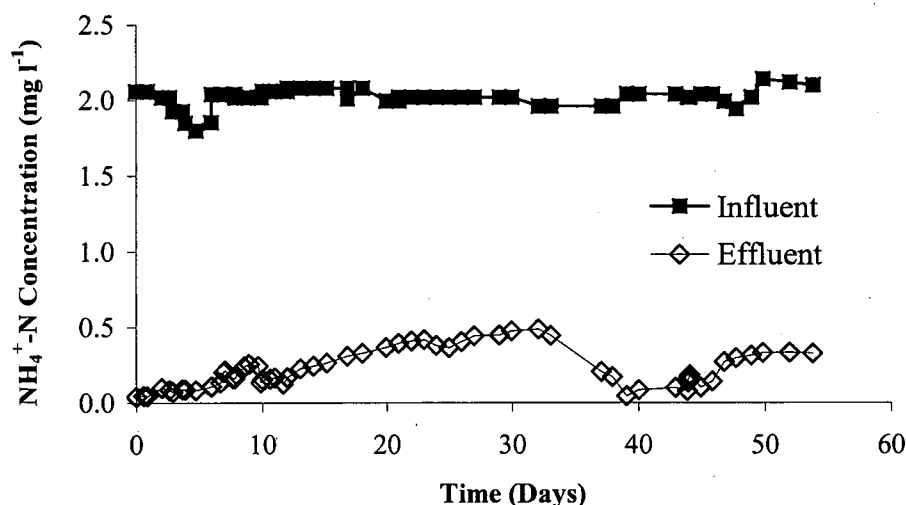


Figure 5.6 The effect of nitrification on plant performance

For this reason influent and effluent nitrate concentrations were continually monitored throughout the exhaustion cycle at pilot scale (Figure 5.7). Results show that there is no significant difference between the influent and effluent nitrate concentrations and as a result it can be concluded that all ammonium removed from solution was as a result of the ion exchange process.

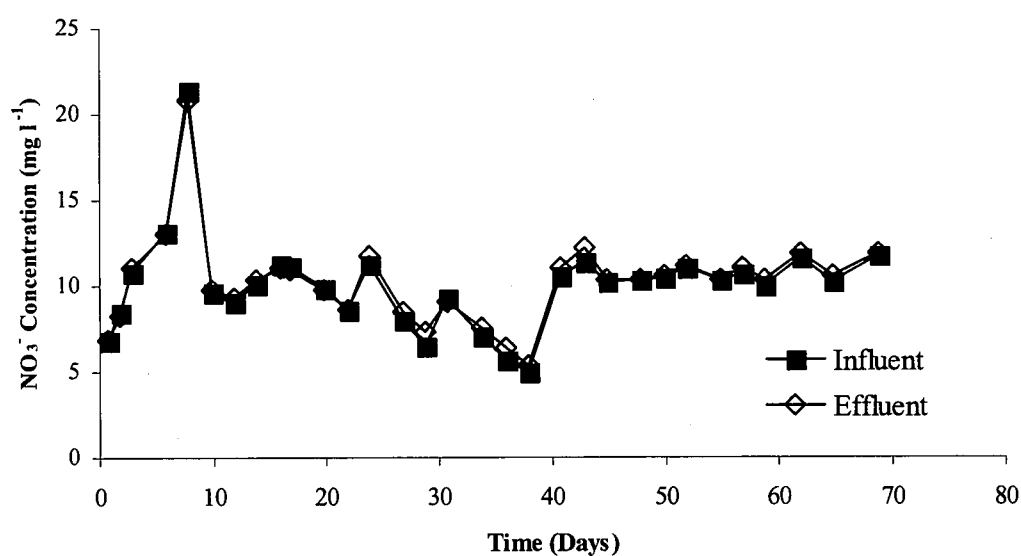


Figure 5.7 Influent and effluent nitrate concentrations for the plant at Reading WwTW

5.4 Conclusions

- Studies at Reading WwTW indicate that MesoLite media can withstand a significant degree of backwashing and that little degradation is observed over the projected lifetime of the material.
- Results also show that the media can be used as an effective treatment for low concentration effluents but has a significantly lower capacity under the conditions reported.
- This reduction in capacity can be attributed that to the fact that for the treatment of low ammonium concentration solutions, the impact of competing cations (in this case calcium) is much greater than at higher ammonium concentrations where little or no effect is observed.
- The performance of the material in this study still compares favourably with that of other ion exchange media (Table 5.1) and the reduction in capacity is offset by significant increases in both the amount of liquid treated and the run time of the process. With an influent concentration of 4-5 mg $\text{NH}_4^+\text{-N l}^{-1}$ and a breakthrough concentration of 1 mg $\text{NH}_4^+\text{-N l}^{-1}$ it was possible to treat 6,300 bed volumes of effluent for a total of 22 days.

5.5 References

- Belér Baykal, B. and Guven, D. A. (1997) Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater. *Water, Science and Technology* **35** (7), 47-54.
- Celen, I. and Turker, M. (2001) Recovery of ammonia as struvite from anaerobic digester effluents. *Environmental Technology* **22** 1263-1272.
- Celik, M. S., Ozdemir, B., Turan, M., Koyuncu, I., Atesok, G. and Sarikaya, H.Z. (2001) Removal of ammonia by natural clay minerals using fixed bed column reactors. *Water, Science and Technology: Water Supply* **1** (1), 81-88.
- Du, Q., Shijun Liu, Q. D., Zhonghong, C. and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese Clinoptilolite. *Separation and Purification Technology* **44** 229-234.
- Dyer, A. (1988) An introduction to zeolite molecular sieves, John Wiley and Sons Ltd, Chichester.
- Farkas, A., Rozic, M. and Barbaric-Mikocevic, Z. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* B117 25-33.
- Fux, C., Lange, K., Faessier, A., Huber, P., Grueniger, B. and Siegrist, H. (2003) Nitrogen removal from digester supernatant via nitrite – SBR or SHARON. *Water, Science and Technology* **48** (8), 9-18.
- Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) Removal of NH_4^+ ion from NH_4Cl solution using clinoptilolite: A dynamic study using a continuous packed-bed column in upflow mode. *Separation Science and Technology* **36** (9), 1347-1364.
- Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) An equilibrium ion exchange study on the removal of NH_4^+ ion from aqueous effluent using clinoptilolite.

Separation Science and Technology **39** (15), 3639-3663.

Helfferich, F. (1962) Ion exchange, McGraw-Hill, New York.

Hlavay, J., Vigh, G., Olaszi, V. and Inczedy, J. (1982) Investigation on natural Hungarian zeolite for ammonia removal. *Water Research* **16**, 417-420.

Ives, K. J. (1975) Specifications for granular filter media. *Effluent and Water Treatment Journal* **15**, 298-305.

Jorgensen, S. E., Libor, O. Graber, K. L. and Barkacs, K. (1976) Ammonia removal by use of clinoptilolite. *Water Research* **10**, 213-224.

Jung, J., Chung, Y., Shin, H. and Son, D. (2004) Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research* **38**, 347-354.

Kabdasli, I., Tunay, O., Ozturk, I., Yilmaz, S. and Arikan, O. (2000) Ammonia removal from young landfill leachate by magnesium ammonium phosphate precipitation and air stripping. *Water, Science and Technology* **41** (1), 237-240.

Karadag, D., Koc, Y., Turan, M. and Armagan, A. (2006) Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. *Journal of Hazardous Materials* **B136** 604-609.

Koon, H. J. and Kaufmann, W. J. (1975) Ammonia removal from municipal wastewaters by ion exchange. *Journal WPCF* **47** (3) 448-465.

Mackinnon, I. D. R., Millar, G. and Stoltz, W. (2006) Hydrothermal Synthesis of Zeolite N Aluminosilicates, *WIPO publication number*, W0/2006/096930.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient removal from wastewaters using high performance materials. *Water, Science and Technology* **47** (11), 101-107.

McVeigh, R.J., 1999. The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria. Ph.D. Research dissertation, Department of Chemical and Process Engineering, The Queen's University of Belfast.

Nguyen M. L. and Tanner C. C. (1998) Ammonium removal from wastewaters using natural New Zealand Zeolites. *New Zealand Journal of Agricultural research* **41** 427-466.

Cooney, D. O. (1999), Adsorption design for wastewater treatment, Lewis Publishing; New York.

Paterson, R. (1970) An introduction to ion exchange, Heyden and Son Ltd London.

Schmidt, I., Sliekers, O., Schmid, M., Bock, E., Fuerst, J., Kuenen, J. G., Jetten, M. S. M. and Strous, M. (2003) New concepts of microbial treatment processes for the nitrogen removal in wastewater. *FEMS Microbiology Reviews* **27** 481-492.

Semmens, M. J. and Porter, P. S. (1979) Ammonium removal by ion exchange: Using biologically restored regenerant. *Journal WPCF* **51** (12), 2928-2940.

Siegrist, H. (1996) Nitrogen removal from digester supernatant – Comparison of chemical and biological methods. *Water, Science and Technology* **34** (1-2), 399-406.

Sprynskyy, M, Lebedynets, M, Terzyk, A. P, Kowalczyk, P, Namiesnik, J. And Buszewski, B. (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Colloid and Interface Science* **284** 408-415.

Thornton, A., Pearce, P. and Parsons, S. A. (2007) Ammonium removal from digested sludge liquors using ion exchange. *Water Research* **41** 433-439.

van Dongen, L. G. J.M., Jetten, M. S. M. and van Loosdrecht, M. C. M. (2001) The combined Sharon/Anammox process: A sustainable method for N-removal from sludge water. STOWA report IWA Publishing, London.

Weatherley, L. R. and Miladinovic, N. D. (2004) Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research* **38**, 4305-4312

Wen, D., Ho, Y. S. and Tang, X. (2006) Comparative sorption kinetic studies of ammonium onto zeolite. *Journal of Hazardous Materials* B133 252-256.

Wang, Y., Liu, S., Xu, Z., Han, T., Chaun, S. and Zhu, T. (2006) Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials* B136 735-740.

CHAPTER 6

**AMMONIUM REMOVAL FROM DIGESTED SLUDGE LIQUORS USING
ION EXCHANGE**

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6. AMMONIUM REMOVAL FROM DIGESTED SLUDGE LIQUORS USING ION EXCHANGE

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Abstract

Liquors arising from the dewatering of digested sludge typically contain ammonium levels in the range 200 – 700 mg l⁻¹ NH₄⁺-N. These liquors are frequently recycled to the head of the wastewater treatment works (WwTW) untreated and can constitute in excess of 25 % of the total nitrogen load entering the works at inlet. This paper investigates the use of a clay based material, MesoLite, as an ion exchange media for ammonium removal from recycle streams. Pilot scale studies performed at Didcot WwTW, part of the Thames Water wastewater treatment network, indicate MesoLite is highly selective for the ammonium ion. Results show that in excess of 95% of ammonium was removed from belt press liquors with an initial ammonium nitrogen concentration in excess of 600 mg l⁻¹, with an overall ion exchange capacity in excess of 51g NH₄⁺-N kg⁻¹ media and a resulting operating capacity in the range 27 – 36 g NH₄⁺-N kg⁻¹.

Keywords Ammonium; ion exchange; nutrient removal; regeneration; sludge liquors

6.1 Introduction

Domestic wastewaters comprise, amongst other constituents, organic nitrogen compounds derived from urine and faeces (Hedstrom 2001), which during transport to WwTW's, can be decomposed to form ammonium. In many developed countries, consent levels for the amount of ammonium contained in the final effluent invariably dictates the need for a nitrogen treatment step to be included as part of the wastewater treatment process. It is not uncommon for consent levels for $\text{NH}_4^+ - \text{N}$ to be as low as 1 mg l^{-1} (Pearce *et al.*, 2000). Nitrogen removal is commonly achieved using a biological, nitrification-denitrification process, where ammonium is transformed firstly to nitrite and then to nitrate and finally to nitrogen gas (Hedstrom, 2001).

In addition to incoming wastewaters, recycle streams within the WwTW may also contribute to the nitrogen load applied to the biological nitrogen removal process. Liquors arising from dewatering of digested sludge by belt presses, centrifuges or alternative dewatering measures are referred to as sidestreams. These are recycled back to the head of the works and depending on their source, can markedly increase the ammonium loading on the WwTW (Siegrist, 1996; Pearce *et al.*, 2000; Mackinnon *et al.*, 2003). Although forming only a small proportion of the overall volumetric flow, the high concentration of recycled liquors (typically $200 - 700 \text{ mg l}^{-1} \text{ NH}_4^+ - \text{N}$) results in a disproportionate impact. Janus and van der Roest (1997) noted that sidestreams in Dutch WwTW's contributed up to 25% of the total nitrogen load, yet the contribution to the total influent flow was only 2%.

Due to urban expansion, ever-decreasing discharge consent levels and centralisation of selected sites as sludge handling centres (Beler-Baykal *et al.*, 1994; Kamarowski and Yu, 1997; Pearce *et al.*, 2000), many treatment plants find themselves in the position where the design capacity for ammonium removal is being approached or even exceeded. It is not unreasonable to assume that in the future some treatment processes may not be able to sustain the level of treatment required to meet the effluent discharge consent values imposed. In some cases an option may be to modify the operation of, or enlarge, the mainstream processes already on site and this may be the most cost effective option. However, some works may not have this option available and on sites where sidestreams comprise a significant proportion of the total

ammonium loading on the mainstream processes, a possible option is to directly treat the sidestream liquors.

An available method of treatment is ion exchange on to materials selective to the ammonium ion. In recent years, many authors (Jorgensen *et al.*, 1976; Semmens and Porter, 1979; Hlavay *et al.*, 1982; Liberti *et al.*, 1986; Booker *et al.*, 1996; Baler-Baykal and Guven, 1997; Nguyen and Tanner, 1998; Weatherly and McVeigh, 2000; Mackinnon *et al.*, 2003; Farkas *et al.*, 2004; Du *et al.*, 2005; Sprynskyy *et al.*, 2005) have investigated the ion exchange potential of various materials with respect to ammonium removal, including treatment of sludge dewatering liquors. Most of the research undertaken has studied the effectiveness of naturally occurring materials, mainly zeolites. To date the most suitable zeolite for this process has been clinoptilolite, a selective aluminosilicate of volcanic provenance, which shows an ammonium exchange capacity in the range 0.94 – 21.52 g NH₄⁺-N kg⁻¹ (Table 6.1). Initial studies by Mackinnon *et al.* (2003) indicate that MesoLite has a greater ammonium exchange capacity than naturally occurring materials used in previous studies (Table 6.1).

Table 6.1 Summary of ammonium exchange capacities for materials used in various studies

Author	Adsorbent	Capacity (g NH ₄ ⁺ -N kg ⁻¹)	Scale of Work
Sprynskyy <i>et al.</i> , 2005	Clinoptilolite	13.56 - 21.52	Lab
Du <i>et al.</i> , 2005	Clinoptilolite	5.81 - 7.74	Lab
Farkas <i>et al.</i> , 2005	Croatian Clinoptilolite	6.0 - 13.65	Lab
Jung <i>et al.</i> , 2004	Zeolite	6.0 - 7.4	Lab
Mackinnon <i>et al.</i> , 2003	MesoLite	45 - 55	Pilot
Nguyen and Tanner, 1998	Mordenite/Clinoptilolite	3.7 - 6.5	Lab
Weatherly and McVeigh, 2000	Clinoptilolite	6.58 - 13.3	Lab
Beler-Baykal and Guven, 1997	Bulgarian Clinoptilolite	2.0 - 3.6	Lab
Booker <i>et al.</i> , 1996	Australian zeolite	4.5	Lab
Hlavay <i>et al.</i> , 1982	Clinoptilolite	1.37 - 9.15	Lab
Semmens and Porter, 1979	Clinoptilolite	3.9	Pilot
Jorgensen <i>et al.</i> , 1976	Clinoptilolite	0.94 - 2.41	Lab

MesoLite ion exchange media is produced by the chemical modification of clay minerals and other aluminium bearing minerals. The resulting material is characterised by a predominance of tetrahedrally coordinated Al^{3+} , which has resulted from the chemical modification of octahedrally coordinated Al^{3+} in the parent mineral (Mackinnon *et al.*, 1997a,b). This modification results in the availability of more exchange sites than would be in the parent mineral, giving the material a high ion exchange capacity.

This paper outlines a study undertaken to evaluate the potential of MesoLite as an ion exchange media for the treatment of high ammonium concentration sludge dewatering liquors. Experimental work has been undertaken on a pilot plant installed at Didcot WwTW, part of the Thames Water network of wastewater treatment facilities. The works treats an average flow of $9000 \text{ m}^3 \text{ d}^{-1}$ and treats a population equivalent of 31000. Sludge dewatering is undertaken using a single belt press fed by two anaerobic digesters.

6.2 Materials and Methods

Particle size analysis of the MesoLite, supplied by Nanochem Pty Ltd., Australia, was performed using sieve sizes, 0.6, 1.18, 1.4, 1.7, 2.0, 2.36, 2.5, 2.8, 3.35 and 5.0 mm. Results show that the media falls within a narrow size range, with in excess of 99 % of the media falling between 1.4 and 2.5 mm in diameter.

A proportion of the liquors arising from the dewatering process were collected for treatment. Due to the discontinuous operation of the belt press, it was necessary to store the amount of liquor required to operate the pilot plant. Prior to storage, liquors were pre-treated using a ceramic media filter to remove any excess solids. This prevented excess fouling of the ion exchange media, keeping head loss to a minimum and eradicating the need for backwashing of the ion exchange media.

The stored filtered sludge liquor was pumped at a selected flow rate through two columns containing MesoLite Media. Each column was 1.8 m high with an operating bed height of approximately 1.2 m and internal diameter of 0.6 m resulting in an operating bed volume of 0.35 m^3 with 100 litres intergranular pore space. This

equates to each column containing 290 kg of MesoLite media. The columns were exhausted in a downflow direction and the final effluent drained to the head of the works. A series of valves was incorporated to allow the column order to be reversed and also enable upflow feed for regeneration purposes. The plant was also designed to allow single column operation. A schematic of the pilot plant process operated at Didcot WwTW is presented in Figure 6.1.

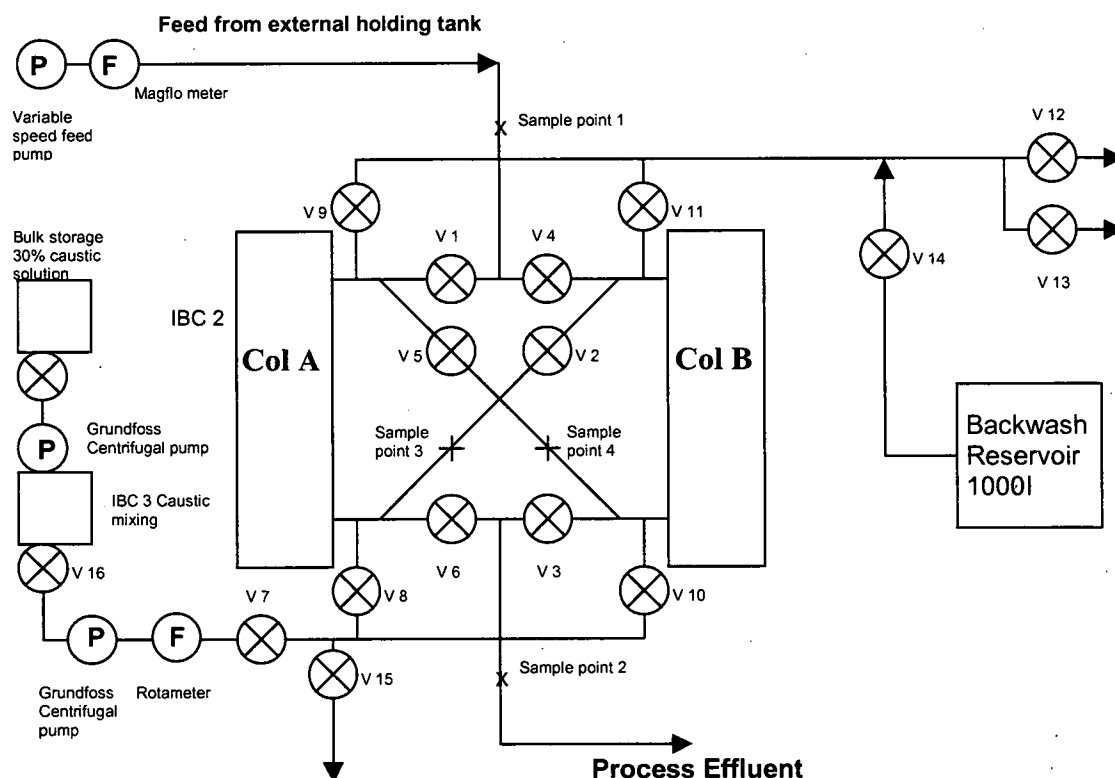


Figure 6.1 Schematic process diagram of the pilot plant installed at Didcot WwTW

The columns were exhausted in series, with column A as the primary column, at a flow rate 500 l h^{-1} , which corresponds to 5 bed volumes per hour (BV h^{-1}) per column, giving a hydraulic retention time (HRT) of 12 minutes in each column. At the end of the cycle, the primary column was regenerated. The columns were again exhausted in series, with column B as the primary column. At the end of each exhaustion cycle, regeneration occurred and the series flow reversed, resulting in each column being used as the primary column on alternate exhaustions.

250 ml samples of influent, primary column effluent and final process effluent were collected every two hours and analysed for ammonium concentration. Analysis was performed using a Lasa 100 spectrometer supplied by Hach Lange GMBH, Dusseldorf, Germany. From loading 6 onwards, sampling frequency was increased to thirty minute intervals. This was made possible by the installation of online, AM200 ammonium analysers supplied by Data Link Instruments, Grenoble, France.

Regeneration was performed by re-circulating 600 l of 5 % NaOH solution through the exhausted media at 5BV h^{-1} for a total of four hours. The regenerated column was then rinsed with 600 l of final effluent. The rinse water was subsequently collected and treated with high strength caustic solution to be used as the regenerant for the next regeneration cycle.

6.3 Results and discussion

Influent liquor characteristics are summarised in Table 6.2 along with those of liquors used by authors in previous studies. Ammonium concentrations at Didcot WwTW were considerably higher than those reported in earlier work, with the exception of Farkas *et al.*, 2005, MacKinnon *et al.*, 2003 and Nguyen and Tanner, 1998. Where reported, pH values are within the range of 6.0 – 8.2, with those at Didcot WwTW being no exception. Didcot WwTW liquors contain relatively low concentrations of competing cations (calcium, magnesium, sodium and potassium) with ammonium being present as the most predominant ion in solution. The opposite is true of most other studies and where reported, the concentration of competing cations in solution is greater than the ammonium concentration.

Table 6.2 Characteristics of liquors used in various trials.

$\text{NH}_4^+\text{-N}$ (mg l^{-1})	pH	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Reference
520-690	7.8-8.1	160-180	15-20	60-80	100-110	Liquors at Didcot WwTW
640	7.77	128	196	1085	801	Farkas <i>et al.</i> , 2005 (waste dump leakage)
100	-	-	-	-	-	Sprynskyy <i>et al.</i> , 2005 (synthetic solution)
25	-	-	-	-	-	Du <i>et al.</i> , 2005 (synthetic solution)
160	7-8	170	-	3232	160	Hankins <i>et al.</i> , 2004 (synthetic solution)
500-800	-	-	-	-	-	Mackinnon <i>et al.</i> , 2003 (sludge centrate)
400	7.87	46	30	73	278	Nguyen and Tanner, 1998 (piggery waste)
180	7.41	38	11	33	215	Nguyen and Tanner, 1998 (dairy waste)
29	7.8	20	9	25	107	Nguyen and Tanner, 1998 (domestic waste)
14	7.5	29	7	57	21	Nguyen and Tanner, 1998 (synthetic solution)
40	-	60	30	220	20	Lahav and Green, 1998 (synthetic solution)
20	-	-	-	-	-	Belar Baykal and Guven, 1997 (domestic wastewater)
30-51	-	-	-	-	-	Booker <i>et al.</i> , 1996 (synthetic and real)
12-45	7.1	82.32	43.9	41.3	29.8	Hlavay <i>et al.</i> , 1982 (synthetic wastewater)
10-18	8.2	105.6	41.7	39.8	30.8	Hlavay <i>et al.</i> , 1982 (municipal wastewater)
10.88	7.45	34	8	58	12	Klieve and Semmens, 1979 (synthetic solution)
20	-	14	12	62	4	Semmens and Porter, 1979 (synthetic solution)
75	-	-	-	-	-	Jorgensen <i>et al.</i> , 1976 (synthetic solution)
16.4-19.4	6.0-8.0	26-140	3-53	13-175	1-35.4	Koon and Kauffman, 1975 (synthetic and real)

A total of 11 loading cycles were performed at Didcot WwTW and breakthrough curves for each loading cycle were generated, with $\text{NH}_4^+\text{-N}$ concentration plotted against effluent throughput, expressed in terms of BV h^{-1} . The total amount of ammonium exchanged by a column for any given volume of liquid passed is represented by the area enclosed between the breakthrough curve and the influent plot from $V = 0$ to $V = V_{\text{final}}$ (Figure 6.2).

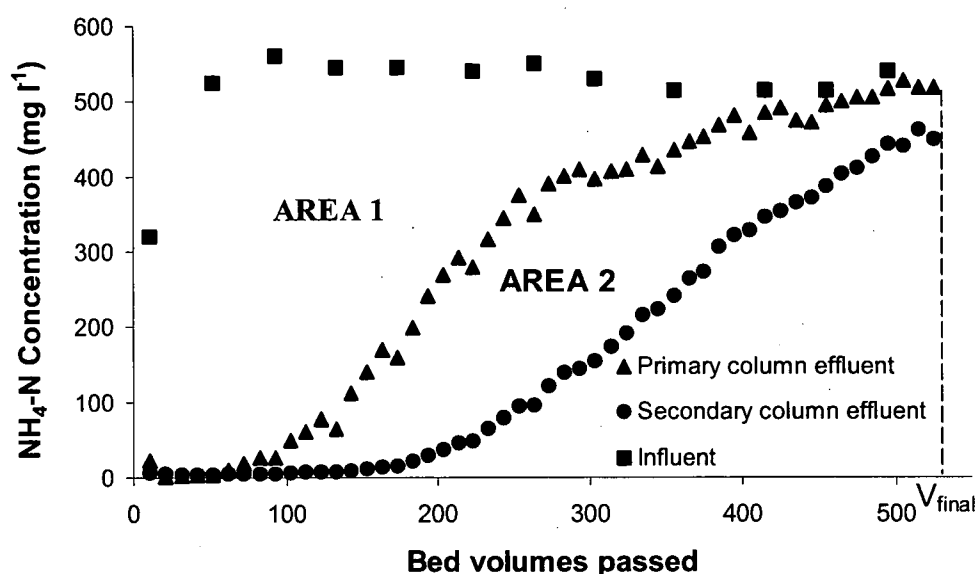


Figure 6.2 Primary and secondary breakthrough curves for loading 4

For example, in loading cycle 4, the amount of ammonium removed by the primary column at exhaustion is represented by area 1, equating to $11.41 \text{ kg NH}_4^+ - \text{N}$. Furthermore, the primary column effluent also serves as the influent to the secondary column and as such the amount of ammonium exchanged by the secondary column in loading cycle 4 is represented by area 2, equating to $6 \text{ kg NH}_4^+ - \text{N}$. This calculation can be represented by Equation 6.1:

$$q = \int_0^{V_{\text{final}}} (C_0 - C) dV \quad \text{Equation 6.1}$$

Where q = the amount of $\text{NH}_4^+\text{-N}$ exchanged, C_0 = the influent $\text{NH}_4^+\text{-N}$ concentration and C = the effluent $\text{NH}_4^+\text{-N}$ concentration.

An approximation of Equation 6.1 can be used to calculate the ammonium removed from solution between any two sampling intervals as follows:

$$q = (C_0 - C_2)(V_2 - V_1) \quad \text{Equation 6.2}$$

Where V_1 and V_2 = the respective volumes of liquid treated at the time the samples are taken and C_2 = the effluent concentration. Therefore, the amount of $\text{NH}_4^+\text{-N}$ removed after n samples is given by:

$$q = (C_0 - C_1)(V_1 - V_0) + (C_0 - C_2)(V_2 - V_1) \dots + (C_0 - C_n)(V_n - V_{(n-1)}) \quad \text{Equation 6.3}$$

This can be used to keep a cumulative record of the amount of $\text{NH}_4^+\text{-N}$ removed throughout any loading cycle (Figure 6.3) along with the amount of $\text{NH}_4^+\text{-N}$ removed per kg of media (Q). When the primary column effluent concentration is equal to the influent concentration (i.e. $C_n = C_0$) then the media is fully exhausted and $q = q_{\text{max}}$, the maximum amount of $\text{NH}_4^+\text{-N}$ which can be removed under the specific loading conditions and Q_{max} = the materials capacity, in this case 47 g $\text{NH}_4^+\text{-N kg}^{-1}$ media.

The first four loading cycles were conducted to establish the operational parameters for the pilot plant. In loadings 2 and 4 the media in the primary column was run to exhaustion (i.e. the medias full capacity was used) and in subsequent loadings (5 – 11) a final effluent breakthrough concentration of 50 mg l⁻¹ $\text{NH}_4^+\text{-N}$ was established. When run to exhaustion the media displayed a total capacity of 47 – 51 g $\text{NH}_4^+\text{-N kg}^{-1}$ with later loading cycles delivering an operational capacity in the range 27 – 32 g $\text{NH}_4^+\text{-N kg}^{-1}$ (Table 6.3).

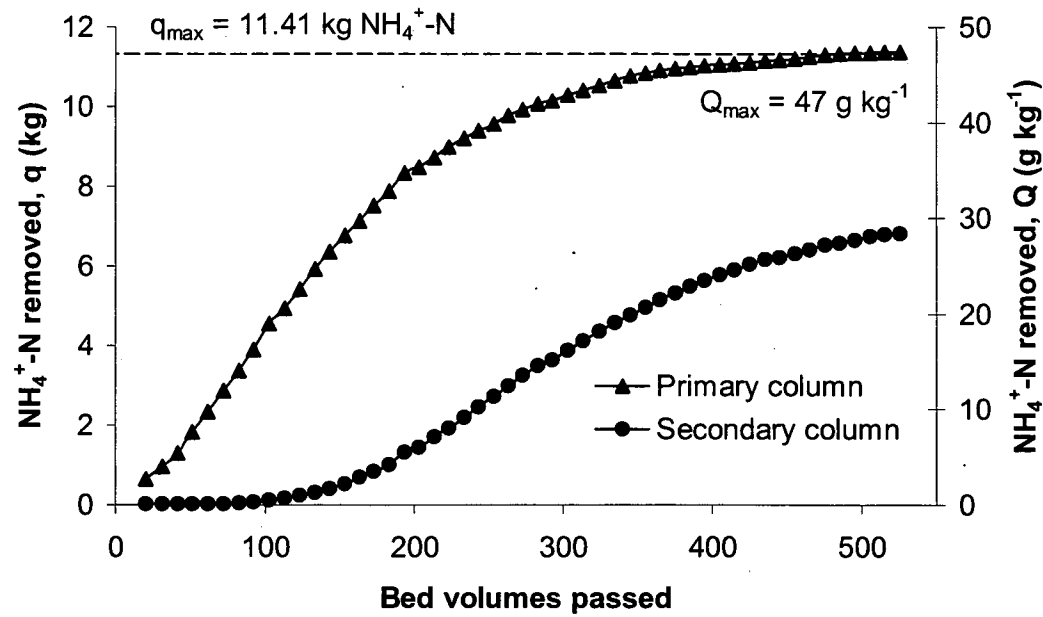


Figure 6.3 Cumulative ammonium exchange for loading 4

Table 6.3 Loading conditions for pilot trials performed

Run	Feed concentration (mg l ⁻¹ NH ₄ ⁺ -N)	Flow rate (l h ⁻¹)	Run time (h)	Volume treated (l)	Ammonium removed (kg)	Capacity (g NH ₄ ⁺ -N kg ⁻¹)
1	440 – 580	520	15	7800	3.71	N/A
2	500 – 605	515	77	40000	12.73	51
3	570 – 620	520	56	29000	6.17	25
4	525 – 540	510	98.5	51000	11.41	47
Effluent breakthrough selected at 50 mg l ⁻¹ NH ₄ ⁺ -N						
5	625 – 650	405	46.5	18300	9.75	39
6	625 – 680	405	27.5	10800	7.1 (2.9,4.2)	29
7	630 – 680	400	27	10050	6.8 (3.9,2.9)	27
8	625 – 650	390	35	14000	8.4 (2.5,5.9)	29
9	660 – 685	390	34.5	13750	8.1 (5.2,5.9)	32
10	630 – 715	395	35.5	14000	10.7 (4.0,6.7)	36
11	640 – 715	405	29	11900	6.7 (2.4,4.3)	27

This reduced operational capacity has been reported for a number of other zeolite trials. Farkas *et al.*, 2005 conducted experiments on Croatian clinoptilolite and the results indicated a total capacity of 6.9 g NH₄⁺-N kg⁻¹ but an operational capacity at breakthrough of 3.98 g NH₄⁺-N kg⁻¹. Semmens and Porter (1979) reported

clinoptilolite capacities at pilot scale when the effluent concentration reached a breakthrough value equal to 10% of the influent concentration, returning an operational capacity of $3.9 \text{ g NH}_4^+\text{-N kg}^{-1}$. Here, loadings 5 and 10 did deliver apparently higher operational capacities of 39 and $37 \text{ g NH}_4^+\text{-N kg}^{-1}$ respectively but these inflated figures can be attributed to distinct factors. Loading 5 was conducted with the primary column containing freshly regenerated media, i.e. it had not been reduced in capacity by being used previously as a secondary column and therefore the cycle time was considerably longer. In loading 10 the breakthrough value was exceeded (i.e. the final effluent concentration reached 100 mg l^{-1}) resulting in extra removal by the primary column.

When a breakthrough concentration was in place, the pilot plant delivered consistent results with a high degree of repeatability (Figure 6.4). With influent concentrations consistently above $600 \text{ mg l}^{-1} \text{ NH}_4^+\text{-N}$ final effluent concentration was maintained below breakthrough concentration for an average of 33.5 hours. Regeneration occurred each time breakthrough was reached but had no detrimental effect on the ammonium removal performance of the media.

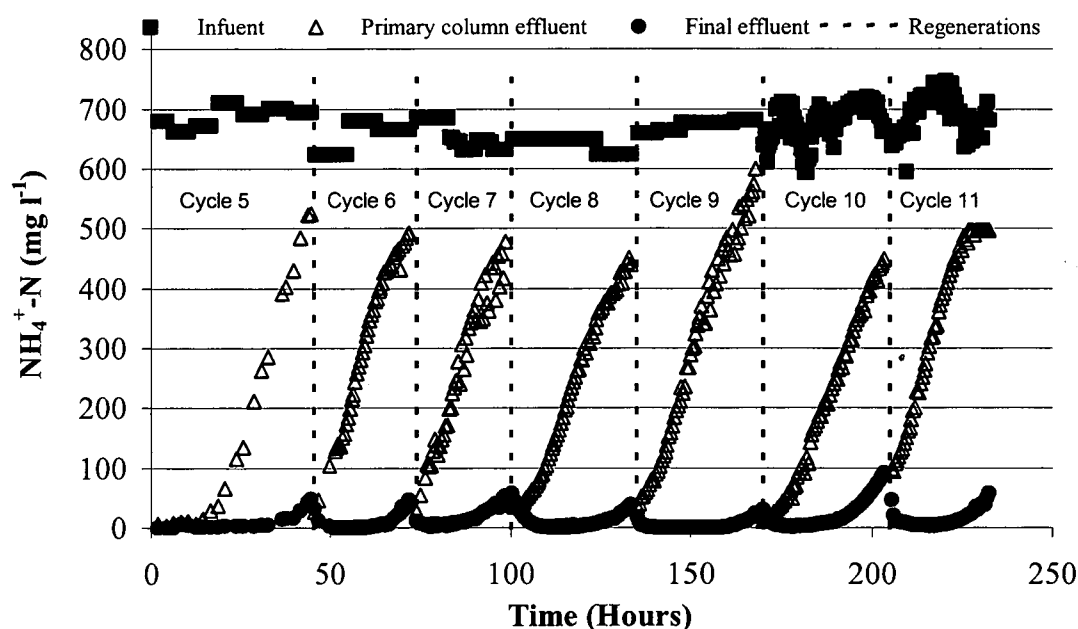


Figure 6.4 Breakthrough curves for all experiments performed at Didcot WwTW

As the secondary column was not regenerated between loadings, a notable proportion of the media capacity was utilised in keeping the final effluent concentration below breakthrough. In loading 8 (Figure 6.5) the primary column removed a total of 8.36 kg $\text{NH}_4^+\text{-N}$ resulting in a capacity of $28.81 \text{ g NH}_4^+\text{-N kg}^{-1}$. A breakdown of the data indicates that 2.45 kg $\text{NH}_4^+\text{-N}$ was removed by the primary column during loading 7 (when acting as the secondary column) with a further 5.91 kg $\text{NH}_4^+\text{-N}$ removed in loading 8. Figures in parentheses in Table 6.3 show this breakdown of the results for loadings 6 to 11.

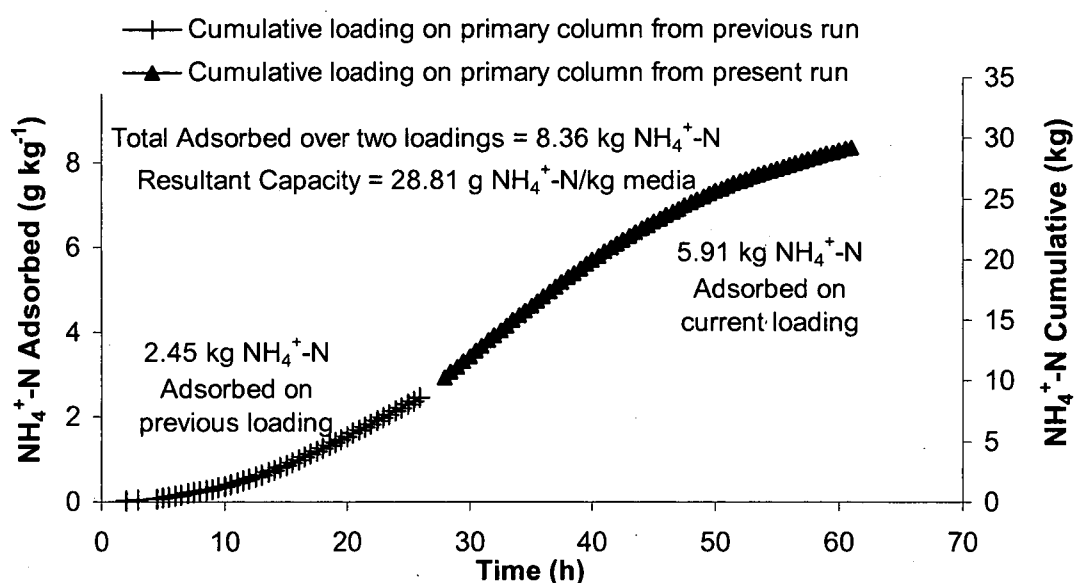


Figure 6.5 Cumulative ammonium uptake on primary column over two loading cycles

Although the operational capacity of MesoLite is considerably lower (approximately 60 % of the total capacity) for this particular mode of operation, results still compare favourably with work performed on other ion exchange materials (Table 6.1). Clinoptilolite is by far the most frequently used material for ammonium removal and capacities reported are largely in the range $0.94 - 13.65 \text{ g NH}_4^+\text{-N kg}^{-1}$ with the bulk of the results being at the lower end of this range. However, a notable exception is the Transcarpathian clinoptilolite used by Sprynskyy *et al.* (2005) which has a capacity of $13.56 - 21.52 \text{ g NH}_4^+\text{-N kg}^{-1}$ at a breakthrough value set at $2 \text{ mg l}^{-1} \text{ NH}_4^+\text{-N}$.

Experiments on powdered MesoLite gave an average cation exchange capacity (CEC) of $490 \text{ meq } 100\text{g}^{-1}$ (Mackinnon *et al.*, 2003) which equates to $69 \text{ g NH}_4^+\text{-N kg}^{-1}$. However, it is unlikely that the maximum CEC can ever be realised in practical applications for various reasons, including, short circuiting within the column, competition from other cations in solution and the fact that too much ammonium leaches out when trying to saturate the media (Hedstrom 2001). Results from Didcot WwTW deliver an exchange capacity ($47 - 51 \text{ g NH}_4^+\text{-N kg}^{-1}$), which is considerably lower (68 – 74 %) even when a total saturation of the primary column is performed. This was observed by Nguyen and Tanner (1998) who performed both batch and column studies on New Zealand clinoptilolite and Mordenite. Results showed that in practical applications it was difficult to obtain an operating exchange capacity that exceeded 50 % of the CEC. This is supported by Townsend and Loizidou (1984) who achieved an ammonium exchange capacity for clinoptilolite equal to 76 % of the CEC.

The throughput rate at employed at Didcot WwTW ($4 - 5 \text{ BV h}^{-1}$) resulted in HRT's between 12 and 15 minutes and this was considered the optimum range for the application of the media. Bench scale trials were conducted on the same liquors at higher flow rates of 8 and 12 BV h^{-1} . Although the capacity was relatively unaffected, a final effluent breakthrough concentration of $50 \text{ mg l}^{-1} \text{ NH}_4^+\text{-N}$ was observed after 12 and 5 hours respectively. Hlavay *et al.* (1982) and Booker *et al.* (1996) both noted the detrimental effect of very high loading rates and concluded that for given operating conditions there would be an optimum loading rate.

6.4 Conclusions

Studies at Didcot WwTW give a total loading capacity of $47 - 51 \text{ g NH}_4^+\text{-N kg}^{-1}$ for MesoLite media. This is consistent with values given by Mackinnon *et al.* (2003) who reported a capacity in the range $45 - 55 \text{ g NH}_4^+\text{-N kg}^{-1}$. When a breakthrough value is selected, this total capacity cannot be fully utilised and the resulting practical operational capacity is in the range $27 - 32 \text{ g NH}_4^+\text{-N kg}^{-1}$. However, this still compares favourably with other ion exchange media (Table 6.1). With a breakthrough value set at $50 \text{ mg l}^{-1} \text{ NH}_4^+\text{-N}$, it was possible to treat 100 – 140 bed volumes of high

strength liquor before regeneration was required and removal efficiencies in excess of 95 % were observed.

6.5 References

- Belér Baykal, B., Oldenburg, M. and Sekoulov, I. (1994) Post Equalisation of Ammonia Peaks. *Water Research* **28** (9), 2039-2042.
- Belér Baykal, B. and Guven, D. A. (1997) Performance of Clinoptilolite alone and in Combination with Sand Filters for the Removal of Ammonia peaks from Domestic Wastewater. *Water, Science and Technology* **35** (7), 47-54.
- Booker, N. A., Cooney, E. L. and Priestly, A. J. (1996) Ammonia Removal from Sewage using Natural Australian Zeolite. *Water, Science and Technology* **34** (9), 17-24.
- Du, Q., Shijun Liu, Q. D., Zhonghong, C. and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese Clinoptilolite. *Separation and Purification Technology* **44** 229-234.
- Farkas, A., Rozic, M. and Barbaric-Mikocevic, Z. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* B117 25-33.
- Hankins, N. P., Pliankarom, S. and Hilal, N. (2004) Removal of NH_4^+ Ion from NH_4Cl Solution Using Clinoptilolite: A Dynamic Study Using a Continuous Packed-Bed Column in Upflow Mode. *Separation Science and Technology* **36** (9), 1347-1364.
- Hedstrom, A. (2001) Ion Exchange of Ammonium in Zeolites: A Literature Review. *Journal of Environmental Engineering* (August 2001), 673-681.
- Hlavay, J., Vigh, G., Olaszi, V. and Inczedy, J. (1982) Investigation on Natural Hungarian Zeolite for Ammonia Removal. *Water Research* **16**, 417-420.
- Janus, H. M. and van der Roest, H. F. (1997) don't Reject the Idea of Treating Reject Water. *Water Science and Technology* **35** (10), 27-34.

Jorgensen, S. E., Libor, O. Graber, K. L. and Barkacs, K. (1976) Ammonia Removal by Use of Clinoptilolite. *Water Research* **10**, 213-224.

Jung, J., Chung, Y., Shin, H. and Son, D. (2004) Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research* **38** 347-354.

Kamarowski, S. and Yu, Q. (1997) Ammonium Ion Removal From wastewater using Australian Natural Zeolite: Batch Equilibrium and Kinetics Studies. *Environmental Technology* **18** 1085-1097.

Klieve, J. R. and Semmens, M. J. (1979) An Evaluation of Pretreated Natural Zeolites for Ammonium Removal. *Water Research* **14**, 161-168.

Koon, H. J. and Kaufmann, W. J. (1975) Ammonia Removal from Municipal wastewaters by Ion Exchange. *Journal WPCF* **47** (3) 448-465.

Lahav, O. and Green, M. (1998) Ammonium Removal using Ion Exchange and Biological Regeneration. *Water Research* **32** (7), 2019-2028.

Mackinnon, I. D. R., Singh, B. and Page, D. (1997a). Alumino-silicate derivatives, *Australian Patent Number 686895*.

Mackinnon, I. D. R., Singh, B. and Page, D. (1997b). Processes to form alumino-silicate derivatives, *Australian Patent Number 685326*.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient Removal from Wastewaters using High Performance materials. *Water, Science and Technology* **47** (11), 101-107.

Nguyen M. L. and Tanner C. C. (1998) Ammonium removal from wastewaters using natural New Zealand Zeolites. *New Zealand Journal of Agricultural Research* **41** 427-466.

Pearce, O., Clark, T. and Ndombasi, P (2000) Ammonia Removal from Sludge Liquors. Thames Water Plc, Research and Technology report.

Semmens, M. J. and Porter, P. S. (1979) Ammonium Removal by Ion Exchange: Using Biologically Restored Regenerant. *Journal WPCF* **51** (12), 2928-2940.

Siegrist, H. (1996) Nitrogen Removal from Digester Supernatant – Comparison of Chemical and Biological Methods. *Water, Science and Technology* **34** (1-2), 399-406.

Semmens, M.J. and Porter, P.S. (1979) Ammonium Removal by Ion Exchange: Using Biologically Restored Regenerant. *Journal WPCF* **51** (12), 2928-2940.

Sprynskyy, M, Lebedynets, M, Terzyk, A. P, Kowalczyk, P, Namiesnik, J. And Buszewski, B. (2005) Ammonium Sorption from Aqueous Solutions by the Natural Zeolite Transcarpathian Clinoptilolite Studied Under Dynamic Conditions. *Colloid and Interface Science* **284** 408-415.

Weatherly, L. R. and McVeigh, R. J. (2000) The Enhancement of Ammonium Ion Removal onto Columns of Clinoptilolite in the Presence of Nitrifying Bacteria In: Proceedings of IEX 2000, Ion Exchange at The Millennium, 16- 21 July, Cambridge, England pp 133-141.

CHAPTER 7

IMPLICATIONS FOR WATER UTILITIES

7. IMPLICATIONS FOR WATER UTILITIES

7.1 Introduction

A review of the literature (Chapter 2) has outlined the extensive research undertaken on the ion exchange process as a possible method of controlling the concentration of ammonium present in effluents discharged from WwTW's. The majority of previous studies have investigated the effectiveness of clinoptilolite as an ammonium ion exchange media with varying degrees of success, and to date, the implementation of full scale practical applications is rare if indeed it is practised at all. A possible contributing factor to the lack of development of full scale operations is the heterogeneous nature of clinoptilolite. The properties of the material vary greatly from deposit to deposit and even material sourced from the same region will exhibit a varied degree of purity. Therefore, the unpredictable nature of the material makes process design parameters difficult to evaluate with any degree of consistency, especially with regards to capacity, which where reported, ranges from 0.94-21.52 g $\text{NH}_4^+\text{-N kg}^{-1}$. The homogenous nature of MesoLite, on the other hand, allows the process to be approached with some degree of confidence and predictability, and this coupled with the increased capacity (when compared to clinoptilolite) of 45-55 g $\text{NH}_4^+\text{-N kg}^{-1}$ significantly increases the viability of ion exchange as a treatment option.

The results from this investigation have broadened the understanding of the utilisation of MesoLite media for this application over a wide range of operating conditions. Much of the work was undertaken at pilot scale, where a greater understanding of the practical implications can be achieved when compared to work carried out in the laboratory. Furthermore, approximately 50 % of the study (Chapters 5 and 6) was concerned with the treatment of actual waste streams arising from the wastewater treatment process as opposed to synthetic solutions largely investigated in literature. Overall, the findings from this study have established that MesoLite can provide effective removal of ammonium from both high and low concentration wastewater streams.

7.2 A comparison of batch and dynamic data

Results from batch equilibrium experiments (Chapter 3) indicate that the capacity of the media is dependant on the initial ammonium concentration in solution and that capacity increases as solution strength increases, up to a maximum of $49 \text{ g NH}_4^+\text{-N kg}^{-1}$ under the experimental conditions studied. This value correlates well with the total capacities observed for dynamic studies of $48 \text{ g NH}_4^+\text{-N kg}^{-1}$ (Chapter 4) and $47\text{--}51 \text{ g NH}_4^+\text{-N kg}^{-1}$ (Chapter 6) and indicates that batch tests are a suitable method of predicting the total capacity of the media which can be achieved under dynamic conditions when operating conditions are favourable. However, a closer inspection of the results indicates that batch tests are of little use in predicting the capacity of the media under dynamic conditions for lower strength solutions (Figure 7.1).

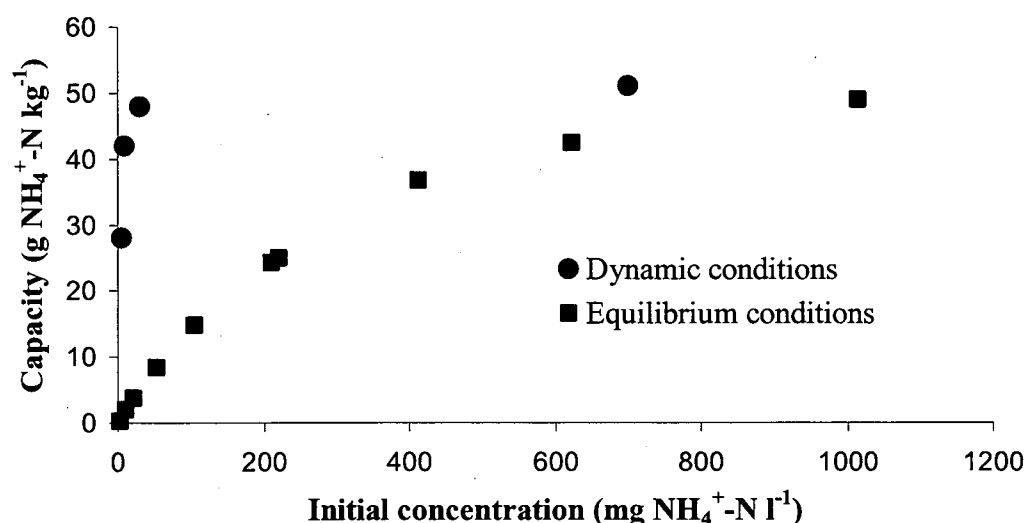


Figure 7.1 MesoLite capacity against solution concentration under equilibrium and dynamic conditions

Under dynamic conditions, a much higher capacity is achievable for any given solution concentration. As solution ammonium concentration increases the discrepancy between the two sets of data diminishes but it is only at high solution concentrations ($> 1000 \text{ mg NH}_4^+\text{-N l}^{-1}$) that equilibrium studies deliver the same capacity as dynamic studies. This can be explained by the fact that under batch

conditions, once equilibrium is reached, there is no change in the net concentration of ions in the solution and solid phases. Although there may be many available exchange sites, the driving force is removed and therefore, the lower the solution concentration; the lower the amount of exchanged ammonium. As the mass of media used is constant for each batch test, a lower amount of exchanged ammonium results in a lower ammonium loading on the media.

Hence, at low concentrations the equilibrium capacity is not a true reflection of the total capacity of the media. However, under dynamic conditions, the column is continually replenished with ammonium solution and the driving force behind the ion exchange process is continually renewed until exhaustion is reached, resulting in a much greater ammonium loading on the media. Results from Chapter 4 show, that at exhaustion, an average influent concentration as low as $30.7 \text{ mg NH}_4^+-\text{N l}^{-1}$ results in a total capacity of $48 \text{ g NH}_4^+-\text{N kg}^{-1}$ (i.e. the total capacity of the media). A similar initial concentration under batch conditions would result in an equilibrium capacity of approximately $5 \text{ g NH}_4^+-\text{N kg}^{-1}$ (Figure 7.1). Therefore, equilibrium studies cannot be used alone to determine the performance of the ion exchange process under batch conditions and as a result it is necessary to conduct dynamic experiments to fully understand how the process will operate in practice.

7.3 Stream selection

On site mainstream biological processes are designed to manage a range of pollutants in municipal wastewater. As a result, direct replacement of the mainstream ammonium removal process is not a practical solution as this would result in the need to develop a range of separate processes, each one specifically designed for the treatment of an individual pollutant. Therefore, ammonium removal by ion exchange is to be considered as a complementary process to be used in conjunction with those processes already in operation on any particular WwTW. The two options considered in this study are the treatment of low concentration effluents (Chapters 4 and 5) and high strength recycle streams arising from the dewatering of digested sludge (Chapter 6).

The benefits of treating effluent result from the fact that, in comparison to sludge liquors, the ammonium concentration is significantly lower (typically $< 5 \text{ mg NH}_4^+ \text{-N l}^{-1}$). Therefore, the amount of ammonium to be removed from solution is dramatically decreased. This greatly increases the run time of the process and has the benefit of significantly reducing the regeneration frequency when compared to the treatment of high strength liquors. Studies at Reading WwTW show that with an influent concentration of $5 \text{ mg NH}_4^+ \text{-N l}^{-1}$, it was possible to maintain a breakthrough concentration of $1 \text{ mg NH}_4^+ \text{-N l}^{-1}$ for a total of 22 days. In addition to this, continual treatment of the effluent will generally not be necessary and the process need only be operated at times when effluent ammonium concentration approaches the imposed discharge consent. Research into failing sites indicates that the process would only be required for approximately 4-6 hours in any 24 hour period. This would significantly increase the service time of the process resulting in service times in excess of 100 days, leading to a significant reduction in the amount of regenerant brine required. As a result, the regeneration process may not be required at all and it may be more efficient to dispose of the exhausted media, replacing it with fresh media. The benefits here are two fold. Firstly, the requirement to purchase regenerant and store it on site is removed and secondly, there is no associated regenerant disposal costs.

In addition to this, the presence of nitrifying bacteria in the column could prove beneficial to the process and further reduce the need for regeneration. In Chapter 5 the fact that nitrification was occurring was seen as a problem as it impacted on the process in such a way that the capacity of media could not be determined under the operating conditions studied. However, a number of authors (Semmens and Porter, 1976; Semmens *et al*, 1977; Green *et al.*, 1996; Lahav and Green, 1998) have previously considered the possibility of biological regeneration of naturally occurring zeolites, where the media acts as a carrier for the biofilm (Lahav and Green, 1998). Hence, it is a distinct possibility that the presence of nitrifying bacteria could significantly improve the process leading to a further increase in service time and reduction in regeneration. Observations in Chapter 5 show that the occurrence of nitrification has the effect of significantly reducing the effluent ammonium concentration (Figure 5.6). It could be argued, however, that once a biofilm in place, the media becomes redundant as an ion exchanger for the purpose of ammonium removal as the bacteria themselves will do the work. However, the whole concept of

treating effluents is to remove peaks and although biological treatments are very effective under constant loads, they are less capable under variable conditions (Beler Baykal, 1998). In contrast, the ion exchange process is particularly effective at removing peaks. Trials using MesoLite for the investigation of a possible potable water treatment solution show that it performs well under variable load and that peak concentrations in the influent have very little effect on the effluent concentration (Figure 7.2).

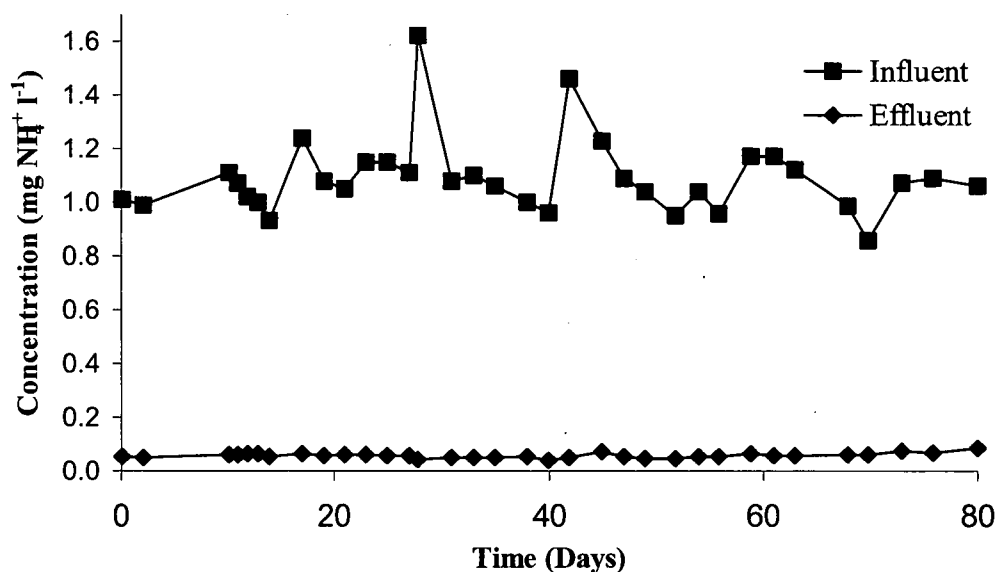


Figure 7.2 Removal of ammonium peaks by ion exchange on to MesoLite

Trials at Reading WwTW also show that it is possible to use the media as a solids filter and as result the need for a pre treatment step is eradicated. However, this does require that a backwashing facility is incorporated into the column design. An understanding of backwashing was not fully established at Reading WwTW as the solution treated by the pilot plant was a filtered effluent and as such the solids concentration was extremely low (generally < 2 mg l⁻¹). For this reason it was only necessary to backwash the media on two occasions but this had no effect on the ion exchange properties of the media. However, if the media is used to retrofit existing solids filters on site a backwashing facility would already be in place.

The benefits of treating sludge liquors are two fold. Firstly, a significant reduction in the ammonium concentration of liquors recycled to the inlet significantly reduces their impact on the mainstream processes, providing a far more manageable stream. This can provide an increase in the efficiency of secondary treatment and greater ease in meeting discharge consent levels. Secondly, a number of sites throughout the United Kingdom don't dewater sludge, as the mainstream processes don't have the capacity to treat the liquors that would arise from the process. Consequently, liquid sludge has to be transported off site for disposal or treatment elsewhere. The transport of liquid sludge is extremely expensive and a reduction in the transport costs in excess of 80 % can be achieved if the sludge is dewatered and only the cake has to be transported. Although the implementation of a sludge dewatering process and subsequent ion exchange step requires considerable capital outlay, this could well be offset by the significant reduction in transport costs.

Results from pilot scale work undertaken at Didcot WwTW (Chapter 6) show that it is possible to significantly reduce the ammonium concentration of high strength liquors which would otherwise be recycled to the works inlet untreated. The benefits of this would be site specific but research indicates that treating these liquors could result in a reduction of up to 25 % of the nitrogen load to be treated by the mainstream biological processes (Mackinnon *et al.*, 2003; Janus and van der Roest, 1997; Siegrist, 1996; Jeavons *et al.*, 1998). However, the high strength of the liquors (500-700 mg $\text{NH}_4^+\text{-N l}^{-1}$) treated at Didcot WwTW resulted in a significant reduction in the run time of the process compared with effluent treatment, with breakthrough being reached in approximately 1.5 days when the plant was in operational mode. Therefore, a much greater regeneration frequency is required when treating high strength liquors and hence the process becomes intermittent, leading to the requirement of more than one exchange column if the process is required to be continuous. There will also be an associated increase in operating cost due to the significant increase in the amount of regenerant brine required. This, in turn, results in the production of a much greater volume of regenerant to be disposed of, again, increasing the cost of the process. Furthermore, the suspended solids concentration of the press liquors at Didcot WwTW (80-120 mg l^{-1}) resulted in the requirement of a pre treatment step, in the form of a sand filter, to remove the solids prior to the ion exchange process. The implementation of a pre filtration step will increase the cost of

the process but will simplify the design of the exchange columns, as the need for backwashing is eradicated.

Results indicate that there are benefits arising from both the treatment of digested sludge liquors and final effluents and the decision of which stream to treat will be dependant on a number of parameters and as a result, any decision will be site specific. The relative merits of effluent and sludge liquor treatment by ion exchange are summarised in Table 7.1.

Table 7.1 Comparison of the effluent and sludge liquor treatment process

Final effluent treatment	Digested sludge liquor treatment
Extended run time	Short run time
Low or zero use of regenerant	High use of regenerant
Low or zero production of high strength ammonium solution	Need to dispose of larger quantity of high strength ammonium solution
No pre-treatment required can act as a solids filter as well as ion exchanger	Pre-treatment required to remove solids from liquors
Backwashing of media essential	No backwashing required
Possible multi site application	Site specific installation and design
Possibility of biological regeneration	Biological regeneration not possible
	Large savings on sludge disposal costs

7.4 Design implications

For the purpose of this study, the bed volume is defined as the intergranular pore space, which allows the HRT to be calculated with ease (i.e. the $HRT = \text{flow rate (l h}^{-1}\text{)} \div \text{the bed volume (l)}$). However, for design purposes engineers often prefer to work with empty bed volume or hydraulic loading (Cooney, 1999). Using empty bed volume results in an empty bed contact time (EBCT), which is a measure

of how much time the solution spends in the column on the basis that the column contains no media. The EBCT is calculated by dividing the column volume by the flow rate and will remain constant for any given set of operating conditions irrespective of the nature of the media (i.e. particle size shape or distribution). The hydraulic loading is simply the flow rate divided by the cross sectional area of the media and resulting units are therefore vertical flow velocity (e.g. m h^{-1}) again based on the column containing no media and is also independent of bed depth. This is of particular interest if the media is to be used to retrofit existing filters on site as, for filtration purposes, operating conditions are almost always quoted in terms of hydraulic loading. The operating parameters for each part of this study, in terms of HRT, EBCT and hydraulic loading are outlined in Table 7.2.

Table 7.2 Comparison of HRT, EBCT and hydraulic loading for dynamic studies

	HRT	EBCT	Hydraulic loading (m h^{-1})
Chapter 4	1.5 minutes per section 15 minutes overall	5 minute per section 50 minutes overall	0.62
Chapter 5	5 minutes	16.67 minutes	1.96
Chapter 6	15 minutes	50 minutes	1.77

As outlined in Chapter 4, the time to reach breakthrough is an important factor in assessing the performance of the ion exchange process and for any given set of column dimensions, is inversely proportional to the influent flow rate (i.e. if the flow rate is doubled then the service time will be halved). This is also true when considering the influent concentration. If the influent concentration is doubled, then the time to reach breakthrough will also be halved (Cooney, 1999). This allows for a comparison to be drawn on how the media would perform on one WwTW, compared to another, if it was proposed to retrofit existing filters with MesoLite for WwTW effluent treatment. In this case, the media bed depth available would be fixed and therefore there would not be an option to increase the scale of the process without a significant cost attached. However, approximate service time could be predicted from

existing processes by taking account of the differences in both flow rate (i.e. hydraulic loading) and ammonium concentration. For example in Chapter 4, Figures 4.7 and 4.8 show breakthrough curves over a range of bed depths for influent concentrations of 5.26 and 9.75 mg $\text{NH}_4^+\text{-N l}^{-1}$ respectively at a hydraulic loading of 0.62 m h^{-1} . At a fixed media bed depth (e.g. 300 mm) the time to reach breakthrough is approximately proportional to the flow rates (i.e. 37 and 65 days respectively). Therefore, the experience obtained from the operation of one installation could be used to effectively predict whether or not another installation would be viable.

It is also important to note that it would not always be necessary to treat all of the effluent to confidently ensure that any site would meet the required consent level. The aim of directly treating the effluent is to bring the overall ammonium concentration below the imposed consent level and not to remove all of the ammonium present. Therefore, partial treatment of the flow may prove more than adequate in achieving the target concentration. This could be achieved by treating a proportion of the effluent and blending it with the untreated effluent before discharge. The proportion of the effluent to be treated will be site specific and is dependant on the maximum effluent ammonium concentration and the discharge consent level imposed. For example, a site with a discharge consent of 5 mg $\text{NH}_4^+\text{-N l}^{-1}$, an average effluent concentration of 3 mg $\text{NH}_4^+\text{-N l}^{-1}$ but a peak effluent concentration of 6 mg $\text{NH}_4^+\text{-N l}^{-1}$ would require treatment under peak conditions. Treatment of 50 % of the flow with an ion exchange process of 80 % removal efficiency would result in a recombined effluent concentration of 3.6 mg $\text{NH}_4^+\text{-N l}^{-1}$. Partial treatment of sludge liquors is not an option, as the purpose of this application is to remove the majority of ammonium from solution.

This study by no means answers all of the questions and further work is required if practical applications are to be operated to an acceptable degree of success. It is obvious that initial projects would require further research and in depth financial assessment. However, once a number of practical installations are in use, the experience gained from operating these installations would prove invaluable in assessing the potential of future projects.

7.5 References

Belér Baykal, B. and Guven, D. A. (1997) Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater. *Water, Science and Technology* **35** (7), 47-54.

Cooney, D. O. (1999), Adsorption design for wastewater treatment, Lewis Publishing, New York.

Green, M., Mels, A., Lahav, O. and Tarre, S. (1996) Biological ion exchange process for ammonium removal from secondary effluent. *Water, Science and Technology* **34** (1-2), 449-458.

Janus, H. M. and van der Roest, H. F. (1997) Don't reject the idea of treating reject water. *Water, Science and Technology* **35** (10), 27-34.

Jeavons, J., Stokes, L., Upton, J. and Bingley, M. (1998) Successful sidestream nitrification of digested sludge liquors. *Water, Science and Technology* **38** (3), 111-118.

Lahav, O. and Green, M. (1998) Ammonium removal using ion exchange and biological regeneration. *Water Research* **32** (7), 2019-2028.

Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S. and Pinel, T. (2003) Nutrient removal from wastewaters using high performance materials. *Water, Science and Technology* **47** (11), 101-107.

Semmens, M. J. and Porter, P. S. (1979) Ammonium removal by ion exchange: Using biologically restored regenerant. *Journal WPCF* **51** (12), 2928-2940.

Semmens, M. J., Wang, J. T. and Booth, A. C. (1977) Nitrogen removal by ion exchange: biological regeneration of clinoptilolite. *Journal WPCF* **49**, 2431-2444.

Siegrist, H. (1996) Nitrogen removal from digester supernatant – Comparison of chemical and biological methods. *Water, Science and Technology* **34** (1-2), 399-406.

CHAPTER 8

CONCLUSIONS AND FURTHER WORK

8. CONCLUSIONS AND FURTHER WORK

8.1 Conclusions

During this study, a series of experiments have investigated the novel material MesoLite and tested it at laboratory and pilot scale. Laboratory scale studies have concentrated on the equilibrium characteristics of MesoLite, whilst pilot scale studies have been concerned with the practical application of the media for the removal of the ammonium ion from a number of wastewater streams. Conclusions arising from the study are as follows:

- MesoLite media has a significantly higher capacity than that of naturally occurring materials used in previous studies, even in the presence of competing cations. Under dynamic conditions a total capacity of 47-51 g $\text{NH}_4^+\text{-N kg}^{-1}$ was returned, which compares favourably with the maximum 49 g $\text{NH}_4^+\text{-N kg}^{-1}$ reported under batch conditions. In contrast, the capacity of the naturally occurring materials is significantly lower, ranging from 0.94-21.52 g $\text{NH}_4^+\text{-N kg}^{-1}$, with the majority being at the lower end of this range.
- Although batch studies can be used to predict the total capacity of the media, they cannot be used in isolation to predict the performance of the material under dynamic conditions over a range of operating conditions. Therefore, it is essential to undertake dynamic studies to fully evaluate the potential of the media to remove ammonium from a range of wastewater streams.
- The ion exchange process can be used to successfully reduce the ammonium concentration of final effluents arising from the treatment of municipal wastewater. This can be achieved by the treatment of either high concentration recycled digested sludge liquors or direct treatment of the final effluent itself. However, the performance of the process is significantly affected by a range of parameters including competing cations; breakthrough concentration; influent ammonium concentration; contact time and pH.

- The presence of competing cations has a detrimental effect on the ammonium uptake of the media. The reported CEC of the media is $72 \text{ g NH}_4^+ \text{-N kg}^{-1}$ and even under optimum operating conditions it is only possible to utilise 70 % of the media's capacity for ammonium uptake when other cations are present in solution. Investigations show that the calcium ion has the most significant effect on reducing the media's capacity.
- The establishment of a breakthrough concentration further reduces the operating capacity of the media for practical applications. Ion exchange processes are seldom run to exhaustion and therefore, a significant proportion of the media's capacity remains unused. Under optimum conditions the maximum operating capacity observed in this study was equal to 60 % of the total capacity at exhaustion or 43 % of the total CEC.
- The performance of the media is dependant on the solution ammonium concentration. At high concentrations the rate of ammonium uptake is faster due to an increased solute gradient providing the driving force behind the exchange process. Furthermore, the detrimental effect of competing cations on the performance of the media is more significant at lower concentrations, with 60 % reductions in both total and operating capacity being observed when treating low concentration effluents.
- Contact time between solution and media is an important factor. Although equilibrium studies indicate that the majority of ammonium uptake is completed within the first hour, dynamic studies show that both the efficiency of the process and the capacity of the media are increasingly reduced as contact time reduces from 15 minutes to 1.5 minutes. Again this phenomenon is more pronounced at low influent concentrations.
- The capacity of the material is affected by solution pH and optimum conditions for removal are between pH 6 and 7.

- Results indicate that MesoLite media has the integrity to withstand a significant degree of backwashing and could therefore perform a dual role both as an ion exchanger and a filter media.

8.2 Further work

The results from this study have shown that ion exchange using MesoLite media can be used as a complementary method of ammonium removal from wastewater streams resulting in an overall reduction in the ammonium concentration of final effluents. However, the optimisation of this process requires further research, concentrating on the following issues:

- One of the most important concerns regarding the implementation of the ion exchange process is the disposal of the regenerant. In this study, the regenerant used was sodium hydroxide resulting in a highly concentrated ammonium hydroxide solution. Studies need to be performed with a number of regenerant brines to establish which is the most suitable with both regards to process efficiency and how easily the resulting solution can be disposed of. Literature indicates that a number of disposal possibilities exist including use as an additive in the production of agricultural fertilisers; air stripping; composting and direct disposal as a waste product.
- In this study, regeneration was only performed during the pilot scale treatment of sludge liquors, where a total of 11 regenerations were performed and the condition of the media remained largely unaltered by the end of the study. Investigations need to be performed into the continual loading and regeneration of the media. It is assumed that, over time, degradation of the media will be observed, largely due to the regeneration process, eventually rendering it unusable. The rate of degradation will effect the operational lifetime of the media and hence, influence the cost of the process.
- Once the media has degraded to the point where it is unusable, media disposal becomes an issue. Investigations into the possible disposal routes for the media

need to be undertaken where one possible solution may be the direct application of fully loaded media to land as a slow release fertiliser.

- In the case of effluent treatment there is a distinct possibility of developing a plant that serves more than one site. This “one size fits all” scenario would consist of a mobile unit on standby, which could be transported to sites experiencing problems, at short notice. The development of such a process relies on extensive research being undertaken on a range of effluents from suitably selected sites, to establish whether or not a single system would be effective for a range of scenarios.
- The presence of nitrifying bacteria could be considered as beneficial during the treatment of WwTW final effluent. However, further investigations are required to assess the impact of the nitrification process on the long term performance of the media.

APPENDIX

APPENDIX A

SUPPLEMENTARY MATERIAL FOR CHAPTER 4

Split column 30 mg/l					
Run Time (Hours)	Influent Concentration (mg/l)	Effluent (A) Concentration (mg/l)	Effluent (B) Concentration (mg/l)	Effluent (C) Concentration (mg/l)	Effluent (D) Concentration (mg/l)
0.00	32.500	0.000	0.000	0.000	0.000
19.00	32.100	8.760	1.770	0.215	0.040
44.50	32.700	13.400	5.290	0.939	0.228
73.00	32.000	18.400	7.880	2.260	0.720
92.50	31.300	18.900	10.000	3.640	1.130
110.50	30.400	21.800	11.800	4.920	1.840
134.00	29.200	21.300	11.100	5.560	2.210
155.50	27.800	20.900	11.300	6.510	3.070
184.50	31.500	23.000	13.000	7.450	4.270
207.00	31.100	24.400	14.500	9.110	4.650
257.00	32.300	28.200	18.600	12.100	6.990
300.50	31.400	28.600	20.800	13.300	8.510
351.00	31.600	30.200	24.200	16.500	11.600
371.00	31.300	31.000	25.100	18.400	12.900
444.50	30.800	30.500	26.200	21.300	14.900
495.00	30.500	30.200	28.600	23.000	17.200
543.50	31.300	31.100	29.300	25.200	19.100
590.50	29.800	29.800	29.200	26.100	20.000
659.00	29.800	29.800	29.500	27.400	22.900
706.50	32.200	32.200	32.100	30.900	27.200
782.00	33.100	32.900	33.500	33.000	30.400
831.00	31.000	31.000	31.000	31.200	30.400
878.00	31.900	32.200	31.800	32.600	31.600
947.50	28.800	28.800	29.100	29.400	29.000
995.50	30.900	31.200	31.300	31.800	31.800
1043.00	30.700	30.500	31.100	31.500	31.900
1117.00	29.500	29.600	29.700	30.100	30.200
1164.00	28.200	28.200	28.200	28.400	29.100
1211.00	30.200	29.500	30.100	29.600	29.300
1284.00	26.300	26.600	27.200	27.600	27.900
1331.00	30.800	30.800	31.000	31.000	31.100
1380.00	29.400	29.700	29.100	29.400	30.100
1452.00	31.200	31.000	31.400	31.700	31.100
1500.00	29.700	29.900	29.800	30.300	30.600
1548.00	30.800	31.200	30.800	31.100	31.500
1596.00	30.300	30.900	30.500	30.500	30.800

Split column 30 mg/l					
Effluent (E) Concentration (mg/l)	Effluent (F) Concentration (mg/l)	Effluent (G) Concentration (mg/l)	Effluent (H) Concentration (mg/l)	Effluent (I) Concentration (mg/l)	Effluent (J) Concentration (mg/l)
0.000	0.000	0.000	0.000	0.000	0.000
0.024	0.021	0.020	0.017	0.019	0.015
0.061	0.027	0.021	0.020	0.018	0.015
0.136	0.048	0.019	0.021	0.023	0.018
0.301	0.100	0.043	0.021	0.021	0.020
0.570	0.179	0.059	0.027	0.012	0.013
0.808	0.277	0.097	0.038	0.020	0.018
1.280	0.419	0.125	0.074	0.028	0.026
1.650	0.628	0.257	0.099	0.041	0.024
2.000	0.789	0.364	0.121	0.051	0.024
3.740	1.740	0.744	0.274	0.112	0.032
4.950	2.900	1.170	0.488	0.203	0.056
7.140	4.590	2.270	0.983	0.437	0.156
8.050	4.790	2.630	1.350	0.626	0.210
9.710	6.650	3.930	2.340	1.200	0.580
11.800	8.270	5.480	3.360	1.860	0.976
14.200	10.100	7.510	5.420	3.330	1.650
15.000	11.900	8.650	6.050	4.060	2.340
17.400	12.700	9.870	7.010	5.000	3.200
21.400	16.400	12.500	9.140	7.010	5.020
26.000	20.500	16.400	12.500	9.740	7.320
27.100	21.900	16.700	12.600	10.300	8.670
29.000	24.500	20.100	15.800	12.500	9.480
28.100	24.500	19.500	15.400	12.600	10.200
31.000	28.500	23.800	18.600	15.300	12.400
31.500	29.800	25.700	21.500	17.500	13.800
30.500	30.100	27.700	23.700	19.800	15.900
29.600	29.500	28.300	24.800	21.600	17.200
29.800	29.800	28.900	25.900	22.600	18.800
28.700	29.100	28.800	27.300	24.100	21.100
31.500	30.800	31.000	30.800	26.100	22.800
30.200	29.600	29.600	29.900	27.700	24.200
32.100	31.800	31.200	31.500	29.000	27.200
30.100	29.400	29.400	29.800	30.000	28.800
30.900	31.000	30.800	31.200	30.900	29.800
30.800	31.000	30.700	30.400	30.500	30.400

Split column 10 mg/l					
Run Time (Hours)	Influent Concentration (mg/l)	Effluent (A) Concentration (mg/l)	Effluent (B) Concentration (mg/l)	Effluent (C) Concentration (mg/l)	Effluent (D) Concentration (mg/l)
0.00	10.500	0.000	0.000	0.000	0.000
17.50	10.500	1.420	0.194	0.084	0.068
65.50	9.850	2.340	0.802	0.464	0.206
87.00	9.800	2.550	0.807	0.173	0.072
111.00	9.780	2.750	0.927	0.342	0.175
133.00	9.050	2.890	0.789	0.179	0.067
161.50	9.890	3.950	1.190	0.283	0.079
184.00	9.930	4.340	1.440	0.374	0.114
205.50	9.580	4.970	1.740	0.484	0.145
233.00	9.920	4.950	2.180	0.670	0.217
276.50	10.400	5.530	2.610	0.876	0.324
327.50	10.200	6.130	2.890	1.070	0.459
348.00	10.000	6.320	3.110	1.380	0.601
421.00	10.400	6.950	3.900	1.730	0.793
471.50	9.070	7.040	3.860	1.850	0.895
530.00	10.500	7.540	4.600	2.460	1.120
576.50	9.760	7.960	4.790	2.800	1.190
649.50	9.490	7.680	5.170	3.030	1.400
693.00	10.700	8.690	5.430	3.110	1.510
768.50	8.220	7.480	5.930	4.220	2.310
864.50	9.410	8.950	5.540	3.790	2.200
934.00	9.150	8.620	7.020	4.910	3.000
982.00	8.580	8.580	7.200	5.440	3.560
1029.00	9.000	8.910	7.160	5.240	3.420

Split column 10 mg/l					
Effluent (E) Concentration (mg/l)	Effluent (F) Concentration (mg/l)	Effluent (G) Concentration (mg/l)	Effluent (H) Concentration (mg/l)	Effluent (I) Concentration (mg/l)	Effluent (J) Concentration (mg/l)
0.000	0.000	0.000	0.000	0.000	0.000
0.092	0.053	0.043	0.015	0.017	0.012
0.280	0.097	0.056	0.018	0.012	0.018
0.052	0.023	0.018	0.015	0.016	0.021
0.098	0.083	0.086	0.043	0.019	0.016
0.032	0.027	0.026	0.022	0.026	0.012
0.035	0.022	0.016	0.017	0.015	0.019
0.046	0.031	0.030	0.025	0.021	0.017
0.055	0.029	0.025	0.019	0.016	0.013
0.076	0.045	0.029	0.032	0.037	0.023
0.121	0.059	0.030	0.022	0.026	0.020
0.176	0.082	0.044	0.031	0.023	0.021
0.206	0.089	0.036	0.027	0.022	0.021
0.325	0.146	0.064	0.031	0.027	0.023
0.387	0.177	0.079	0.033	0.026	0.034
0.491	0.223	0.115	0.053	0.036	0.040
0.564	0.310	0.155	0.056	0.040	0.026
0.763	0.430	0.209	0.072	0.038	0.036
0.766	0.441	0.246	0.086	0.048	0.039
1.180	0.737	0.412	0.157	0.085	0.054
1.410	0.914	0.490	0.238	0.140	0.058
1.790	1.050	0.577	0.258	0.164	0.100
2.280	1.360	0.848	0.407	0.236	0.100
2.070	1.410	0.851	0.478	0.279	0.158

Split column 5 mg/l					
Run Time (Hours)	Influent Concentration (mg/l)	Effluent (A) Concentration (mg/l)	Effluent (B) Concentration (mg/l)	Effluent (C) Concentration (mg/l)	Effluent (D) Concentration (mg/l)
0.00	5.410	0.000	0.000	0.000	0.000
43.00	5.170	1.220	0.215	0.110	0.085
66.50	4.950	1.300	0.311	0.091	0.067
94.00	5.450	1.690	0.444	0.102	0.039
115.50	5.540	2.010	0.512	0.135	0.048
143.50	5.230	1.770	0.620	0.195	0.061
187.50	5.360	2.300	0.838	0.256	0.092
238.00	5.100	2.930	1.150	0.426	0.145
258.50	5.310	2.710	1.250	0.478	0.166
331.50	5.470	3.070	1.490	0.641	0.277
382.00	4.960	3.160	1.670	0.754	0.326
430.50	5.510	3.850	2.300	0.941	0.408
503.50	5.230	3.980	2.450	1.120	0.522
550.50	4.970	3.910	2.150	1.220	0.571
594.00	5.970	4.400	2.590	1.310	0.661
669.50	5.610	4.290	2.950	1.540	0.829
718.50	4.760	4.170	2.660	1.670	0.959
765.50	5.420	4.350	2.500	1.650	0.952
834.00	4.770	4.020	2.740	1.680	1.040
882.00	5.190	4.490	3.050	1.980	1.260
929.50	5.090	4.500	2.980	2.060	1.360
1003.50	4.960	4.470	3.160	2.150	1.470
1050.00	4.930	4.460	3.300	2.230	1.580
1097.00	5.420	4.740	3.470	2.480	1.650
1170.00	5.200	4.830	3.640	2.480	1.850
1217.00	5.350	4.810	3.680	2.660	1.940
1270.00	5.170	4.940	3.860	2.890	2.070
1338.00	5.120	4.850	3.810	2.700	1.890
1389.00	5.170	4.910	4.200	3.000	1.790
1432.50	5.100	4.900	4.190	3.100	2.180
1554.00	5.210	4.990	4.060	3.000	2.310
1578.00	5.480	5.080	4.200	3.310	2.300
1698.00	5.640	5.520	5.000	4.200	3.210
1769.00	5.480	5.520	5.120	4.160	3.270
1844.00	5.240	5.240	4.960	4.200	3.316
1889.50	5.640	5.640	5.320	4.600	3.596
1917.00	5.520	5.480	5.040	4.320	3.468
2062.00	4.720	5.130	4.870	4.340	3.380

Split column 5 mg/l					
Effluent (E) Concentration (mg/l)	Effluent (F) Concentration (mg/l)	Effluent (G) Concentration (mg/l)	Effluent (H) Concentration (mg/l)	Effluent (I) Concentration (mg/l)	Effluent (J) Concentration (mg/l)
0.000	0.000	0.000	0.000	0.000	0.000
0.100	0.067	0.062	0.041	0.034	0.041
0.046	0.030	0.021	0.017	0.023	0.020
0.020	0.018	0.032	0.021	0.018	0.017
0.028	0.025	0.024	0.015	0.013	0.015
0.031	0.025	0.022	0.027	0.026	0.020
0.048	0.033	0.030	0.031	0.026	0.021
0.067	0.043	0.027	0.027	0.027	0.023
0.074	0.032	0.027	0.019	0.019	0.025
0.102	0.038	0.023	0.019	0.021	0.016
0.125	0.050	0.026	0.024	0.016	0.020
0.168	0.074	0.038	0.028	0.028	0.042
0.236	0.103	0.046	0.042	0.036	0.025
0.262	0.126	0.055	0.037	0.045	0.022
0.314	0.143	0.073	0.041	0.021	0.025
0.422	0.203	0.095	0.051	0.037	0.027
0.486	0.243	0.115	0.064	0.033	0.037
0.578	0.263	0.135	0.076	0.031	0.030
0.595	0.283	0.144	0.083	0.042	0.039
0.799	0.424	0.191	0.107	0.047	0.047
0.852	0.451	0.220	0.119	0.054	0.063
0.991	0.573	0.275	0.155	0.072	0.070
1.090	0.626	0.334	0.194	0.088	0.071
1.050	0.642	0.350	0.191	0.094	0.086
1.150	0.715	0.385	0.222	0.110	0.104
1.220	0.748	0.436	0.245	0.114	0.122
1.400	0.947	0.560	0.328	0.164	0.159
1.170	0.767	0.443	0.263	0.133	0.149
1.290	0.844	0.523	0.357	0.197	0.189
1.380	0.934	0.611	0.433	0.244	0.208
1.510	1.020	0.664	0.436	0.248	0.219
1.660	1.180	0.747	0.525	0.329	0.258
2.440	1.770	1.280	0.930	0.598	0.580
2.440	1.780	1.240	0.882	0.566	0.600
2.409	1.764	1.250	0.868	0.568	0.632
2.880	2.180	1.560	1.190	0.826	0.696
2.460	2.040	1.486	1.050	0.707	0.699
2.680	2.000	1.510	1.190	0.816	0.850

APPENDIX B

SUPPLEMENTARY MATERIAL FOR CHAPTER 5



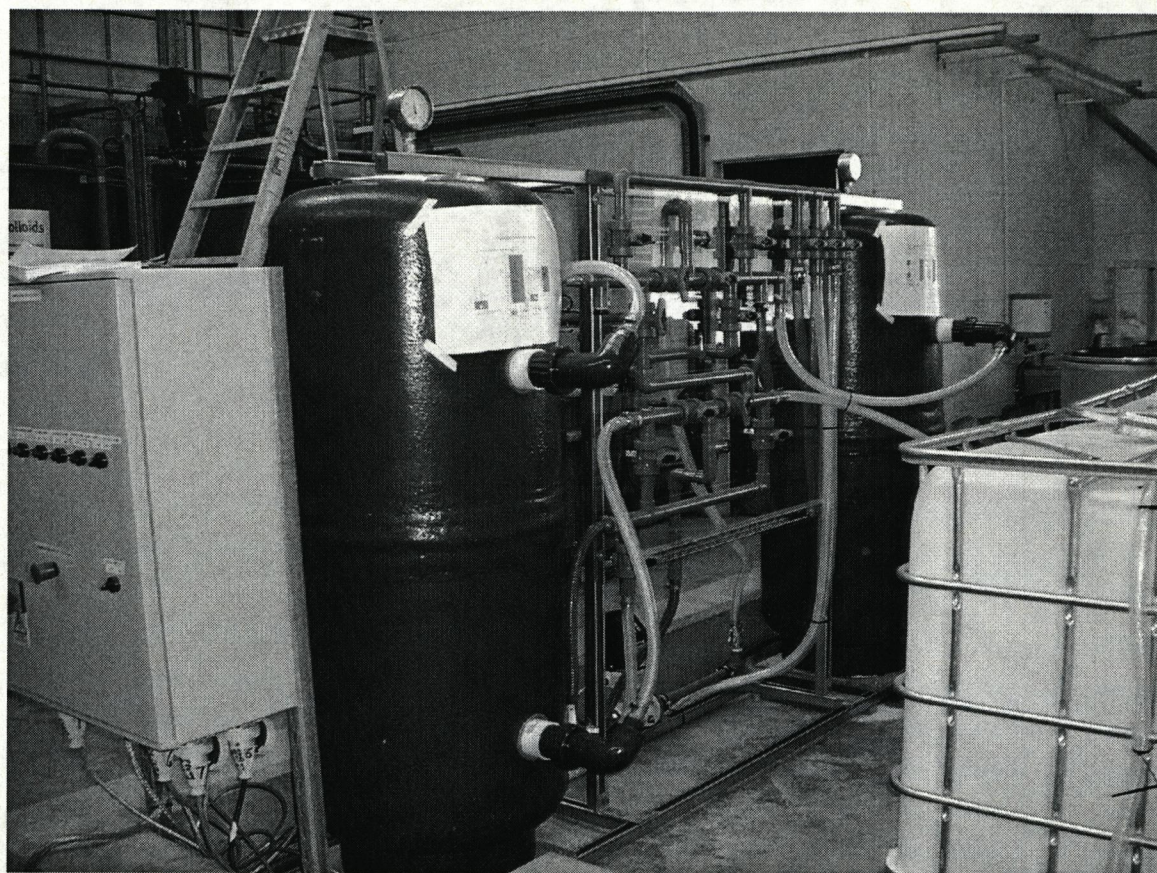
Pilot plant at Reading WwTW

Effluent Treatment						
Run Time (Hours)	Influent ammonium Concentration (mg/l)	Effluent ammonium Concentration (mg/l)	Potassium influent conc (mg/l)	Potassium effluent conc (mg/l)	Calcium influent conc (mg/l)	Calcium effluent conc (mg/l)
0.00	4.460	0.000				
18.00	4.460	0.023	21.9	163.6	101	35
41.50	4.480	0.026	16.2	97.3	105	88
66.00	4.560	0.033	17.6	22.9	115	108
140.50	4.420	0.112	18.1	18.2	114	113
189.00	4.850	0.176	15.4	46.7	108	103
238.00	4.640	0.275	15	43.4	110	107
286.00	4.120	0.369	16.4	46.8	108	100
333.00	3.960	0.491	16.6	44.1	112	109
382.00	4.620	0.607	14.4	37.1	105	98
402.50	4.330	0.651	14.7	34.3	106	102
477.50	4.270	0.778	14.1	34.2	100	97
526.00	4.270	0.962	16.1	37.5	111	108
574.00	4.570	1.010	14.5	28.8	110	104
646.00	3.840	1.350	14.5	32.3	107	100
694.00	4.780	1.380	13.1	29.1	103	102
739.00	4.810	1.580	15.1	32.6	103	93
813.00	4.280	1.750	14.2	31.1	100	95
862.00	3.870	1.750	14.3	30.3	107	103
910.00	0.122	1.370	11.6	20.8	91	89
979.00	4.570	1.810	13.2	23.9	100	96
1030.00	5.100	2.050	15.2	24.5	113	107
1075.00	4.070	2.160	15.5	27.3	109	104
1147.50	3.810	2.080	11.9	20.2	97	96
1198.00	5.350	2.220	14.4	22.4	106	103
1245.00	4.860	2.280	14.4	20.7	100	98
1316.00	4.700	2.890	14.8	23.9	105	105
1365.00	4.930	3.030	15.2	21.3	111	108
1410.00	5.240	3.420	15.7	22.3	111	109

Effluent Treatment					
Sodium influent conc (mg/l)	Sodium effluent conc (mg/l)	Magnesium influent conc (mg/l)	Magnesium effluent conc (mg/l)	Influent nitrate conc (mg/l)	Effluent nitrate conc (mg/l)
				-	-
133.6	107.9	6.1	7.7	6.87	6.82
139.6	118.8	6.3	6.3	8.47	8.28
152.5	138	6.9	11.7	10.8	11
160.8	160.6	7.7	7.7	13.1	13
133.7	131.9	7.4	7.4	21.4	20.8
133	132.1	7.2	7.2	9.66	9.81
148.5	144.5	7.3	7.2	9.09	9.26
154.9	152.2	7.5	7.4	10.1	10.3
131	129	7.4	7.5	11.3	11.1
130	127	7.5	7.6	11.2	10.9
126.9	128.6	7	7	9.9	9.8
147.9	143.2	7.2	7.2	8.64	8.59
116.4	116.5	6.9	6.8	11.3	11.8
135.8	134.5	7.3	7.1	8.03	8.46
117.1	118.5	6.9	7	6.51	7.37
139.8	135.8	6.6	6.5	9.36	9.11
62.3	58.8	6.9	6.8	7.09	7.59
136.4	138	6.8	6.9	5.64	6.43
102	101.4	6.5	6.6	5.01	5.3
115.8	116.4	6.9	6.9	10.6	11
113.6	114.7	7.4	7.4	11.4	12.2
121	121.8	7.5	7.5	10.2	10.4
103.3	104.1	6.6	6.5	10.3	10.4
106	107	6.7	6.7	10.5	10.6
105.1	104.4	6.5	6.5	11	11.2
122	121.4	7	7	10.3	10.4
127.3	122.7	7.1	6.8	10.7	11
136.3	134.8	7	7.1	10	10.4

APPENDIX C

SUPPLEMENTARY MATERIAL FOR CHAPTER 6



Pilot plant at Didcot WwTW

LOADING 1						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH ₄]-N mg/L	[NH ₄]-N mg/L	[NH ₄]-N mg/L
L1-1	0.0	520.00	1300.00		2.34	440.00
L1-2	3.0	520.00	1560.00	12.5		
L1-3	5.0	520.00	2600.00	16.5	0.19	
L1-4	7.0	520.00	3640.00	20.5	0.34	
L1-5	9.0	520.00	4680.00	18.5	0.002u	527.00
L1-6	11.0	520.00	5720.00	26.4	0.004u	
L1-7	13.0	520.00	6760.00	36.0	0.004u	580.00
L1-8	15.0	520.00	7800.00	48.4	0.006u	553.50

LOADING 2						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH ₄]-N mg/L	[NH ₄]-N mg/L	[NH ₄]-N mg/L
L2-1	2.00	500.00	1000.00	1.82	0.006	605.00
L2-2	4.00	500.00	2000.00	3.22	0.005	
L2-3	6.00	520.00	3040.00	5.41	0.001	567.00
L2-4	8.00	520.00	4080.00	8.95	0.005	
L2-5	10.00	505.00	5090.00	11.80	0.006	531.00
L2-6	12.00	505.00	6100.00	17.80	0.005	
L2-7	14.00	505.00	7110.00	26.00	0.007	
L2-8	16.00	505.00	8120.00	35.90	0.007	
L2-9	18.00	520.00	9160.00	36.40	0.006	517.00
L2-10	20.00	520.00	10200.00	49.40	0.007	
L2-11	22.00	520.00	11240.00	62.80	0.006	
L2-12	24.00	510.00	12260.00	66.10	0.008	506.00
L2-13	26.00	510.00	13280.00	82.20	0.007	
L2-14	28.00	510.00	14300.00	95.90	0.006	
L2-15	30.00	510.00	15320.00	111.00	0.007	
L2-16	32.00	510.00	16340.00	127.80	0.003	
L2-17	34.00	510.00	17360.00	153.00	0.015	494.00
L2-18	36.00	510.00	18380.00	192.40	0.023	
L2-19	38.00	510.00	19400.00	229.20	0.026	
L2-20	40.00	525.00	20450.00	218.30	0.017	599.00
L2-21	42.00	525.00	21500.00	258.00	0.013	
L2-22	46.00	530.00	23620.00	313.20	0.015	625.80
L2-23	48.00	530.00	24680.00	334.50	0.014	
L2-24	50.00	520.00	25720.00	331.50	0.012	623.70
L2-25	52.00	520.00	26760.00	351.00	0.017	
L2-26	54.00	520.00	27800.00	381.00	0.013	
L2-27	56.00	520.00	28840.00	355.80	0.009	531.30
L2-28	58.00	520.00	29880.00	379.80	0.014	
L2-29	60.00	520.00	30920.00	406.20	0.013	
L2-30	62.00	520.00	31960.00	397.20	0.008	
L2-31	64.00	510.00	32980.00	388.20	0.010	526.80
L2-32	66.00	510.00	34000.00	374.40	0.006	
L2-33	68.00	510.00	35020.00	433.20	0.002	
L2-34	70.00	510.00	36040.00	437.40	0.004	
L2-35	72.00	500.00	37540.00	436.20	0.004	527.40
L2-36	75.00	530.00	38600.00	375.60	0.009	404.40
L2-37	77.00	530.00	39660.00	387.60	0.016	

LOADING 3						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L3-1	2.00	530.00	1060.00	304.80	0.008u	618.00
L3-2	4.00	530.00	2120.00	349.80	0.008u	
L3-3	6.00	530.00	3180.00	349.20	0.007u	
L3-4	8.00	530.00	4240.00	340.20	0.010u	
L3-5	10.00	515.00	5270.00	283.20	0.012u	586.00
L3-6	12.00	515.00	6300.00	291.60	0.008u	
L3-7	14.00	515.00	7330.00	320.40	0.008u	
L3-8	16.00	515.00	8360.00	358.20	0.009u	
L3-9	18.00	520.00	9400.00	356.40	0.007u	612.00
L3-10	20.00	520.00	10440.00	345.00	0.008u	
L3-11	22.00	520.00	11480.00	346.20	0.010u	
L3-12	24.00	520.00	12520.00	375.60	0.009u	
L3-13	26.00	505.00	13530.00	364.80	0.011u	585.60
L3-14	28.00	505.00	14540.00	372.60	0.008u	
L3-15	30.00	505.00	15550.00	395.40	0.012u	
L3-16	32.00	505.00	16560.00	390.00	0.012u	
L3-17	34.00	505.00	17570.00	417.00	0.012u	
L3-18	36.00	525.00	18620.00	387.60	0.012u	606.00
L3-19	38.00	525.00	19670.00	401.40	0.008u	
L3-20	40.00	525.00	20720.00	411.00	0.008u	
L3-21	42.00	520.00	21760.00	406.20	0.013u	584.00
L3-22	44.00	520.00	22800.00	420.00	0.02	
L3-23	46.00	520.00	23840.00	436.20	0.02	
L3-24	48.00	520.00	24880.00	448.80	0.013u	
L3-25	50.00	530.00	25940.00	437.40	0.007u	570.00
L3-26	52.00	530.00	27000.00	440.40	0.007u	
L3-27	54.00	530.00	28060.00	445.80	0.013u	
L3-28	55.50	530.00	28855.00	466.20	0.004u	

LOADING 4						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L4-1	0.00	521.00	1042.00	23.50	6.52	320.00
L4-2	2.00	521.00	2084.00	1.72	4.53	
L4-3	4.00	521.00	3126.00	2.23	4.28	
L4-4	6.00	521.00	4168.00	4.26	4.43	
L4-5	8.00	506.00	5180.00	3.66	3.96	525.00
L4-6	10.00	506.00	6192.00	10.60	4.94	
L4-7	12.00	506.00	7204.00	18.90	5.40	
L4-8	14.00	506.00	8216.00	27.20	4.93	
L4-9	16.00	510.00	9491.00	26.60	5.31	560.00
L4-10	18.50	510.00	10256.00	49.60	6.40	
L4-11	20.00	510.00	11276.00	61.50	7.76	
L4-12	22.00	510.00	12296.00	78.00	7.88	
L4-13	24.00	505.00	13306.00	65.10	7.34	545.00
L4-14	26.00	505.00	14316.00	112.20	9.39	
L4-15	28.00	505.00	15326.00	140.80	11.90	
L4-16	30.00	505.00	16336.00	169.20	14.50	
L4-17	32.00	503.00	17342.00	159.50	15.70	545.00
L4-18	34.00	503.00	18851.00	199.10	21.90	
L4-19	37.00	503.00	19354.00	240.90	29.50	
L4-20	38.00	503.00	20360.00	269.50	37.30	
L4-21	40.00	503.00	21366.00	292.60	45.80	
L4-22	42.00	500.00	22366.00	279.40	48.40	540.00
L4-23	44.00	500.00	23366.00	316.80	64.80	
L4-24	46.00	500.00	24366.00	344.30	78.90	
L4-25	48.00	500.00	25366.00	375.10	94.80	
L4-26	50.00	493.00	26352.00	349.80	96.00	550.00
L4-27	52.00	493.00	27338.00	390.50	121.40	
L4-28	54.00	493.00	27831.00	401.10	139.50	
L4-29	55.00	493.00	28817.00	409.50	144.10	
L4-30	57.00	520.00	29857.00	396.90	154.00	530.00
L4-31	59.00	520.00	30897.00	407.40	173.80	
L4-32	61.00	520.00	31937.00	409.50	191.40	
L4-33	63.00	520.00	32457.00	428.40	215.60	
L4-34	64.00	520.00	33497.00	413.70	223.30	
L4-35	66.00	495.00	34487.00	434.70	240.90	515.00
L4-36	68.00	495.00	35477.00	447.30	264.00	
L4-37	70.00	495.00	36467.00	453.60	272.80	
L4-38	72.00	495.00	37457.00	468.30	305.80	
L4-39	74.00	495.00	38447.00	480.90	321.20	
L4-40	76.00	495.00	39437.00	457.80	327.80	
L4-41	78.00	503.00	40443.00	485.10	345.40	515.00
L4-42	80.00	503.00	41449.00	491.40	353.10	
L4-43	82.00	503.00	42455.00	474.60	365.40	
L4-44	84.00	503.00	43461.00	472.50	371.70	
L4-45	86.00	500.00	44461.00	495.60	386.40	540.00
L4-46	88.00	500.00	45561.00	499.80	403.20	
L4-47	90.20	500.00	46211.00	506.10	411.60	
L4-48	91.50	500.00	47211.00	506.10	426.30	
L4-49	93.50	504.00	48219.00	516.60	443.10	540.00
L4-50	95.50	504.00	49227.00	527.10	441.00	
L4-51	97.50	504.00	49731.00	518.70	462.00	
L4-52	98.50	504.00	50739.00	518.70	449.40	

LOADING 5						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L5-1	2.00	395.00	790.00	13.20	0.00	680.40
L5-2	4.00	395.00	1678.75	6.32	0.00	
L5-3	6.25	395.00	2468.75	2.95	0.00	
L5-4	8.25	407.50	3283.75	7.45	0.00	662.50
L5-5	10.25	407.50	4098.75	10.40	6.38	
L5-6	12.25	407.50	4913.75	10.70	4.14	
L5-7	14.25	414.00	5741.75	7.03	2.16	672.00
L5-8	16.25	414.00	6631.85	14.90	1.88	
L5-9	18.40	414.00	7459.85	28.90	1.94	
L5-10	20.40	398.00	8255.85	36.50	1.98	710.00
L5-11	22.40	398.00	9449.85	65.80	2.45	
L5-12	25.40	398.00	10245.85	115.20	3.23	
L5-13	27.40	404.00	11457.85	135.30	2.66	692.00
L5-14	30.40	404.00	12265.85	212.10	3.86	
L5-15	32.40	404.00	13073.85	262.50	4.86	
L5-16	34.40	404.00	14689.85	285.60	5.40	701.00
L5-17	38.40	404.00	15093.85	390.60	14.20	
L5-18	39.40	404.00	15901.85	403.20	16.70	
L5-19	41.40	400.00	16701.85	430.50	15.60	695.10
L5-20	43.40	400.00	17501.85	485.10	28.10	
L5-21	45.40	400.00	17901.85	523.50	42.60	
L5-22	46.40	400.00	18301.85	525.00	48.80	

LOADING 6						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L6-1	1.00	400.00	400.00	26.90	31.50	623.70
L6-2	2.00	400.00	1700.00	45.87	12.40	623.70
L6-3	5.25	400.00	2300.00	104.06	3.41	623.70
L6-4	6.75	400.00	2400.00	129.00	0.10	623.70
L6-5	7.00	400.00	2500.00	132.40	0.30	623.70
L6-6	7.25	400.00	2600.00	134.91	0.10	623.70
L6-7	7.50	400.00	2700.00	137.00	0.00	623.70
L6-8	7.75	400.00	3000.00	139.74	0.00	623.70
L6-9	8.50	400.00	3200.00	135.53	0.00	623.70
L6-10	9.00	400.00	3400.00	151.06	0.00	623.70
L6-11	9.50	400.00	3600.00	156.37	0.00	623.70
L6-12	10.00	400.00	3800.00	173.78	0.03	623.70
L6-13	10.50	400.00	4000.00	185.21	0.14	680.00
L6-14	11.00	400.00	4200.00	198.49	0.59	680.00
L6-15	11.50	400.00	4400.00	214.36	0.68	680.00
L6-16	12.00	400.00	4600.00	223.40	0.27	680.00
L6-17	12.50	400.00	4800.00	243.49	0.44	680.00
L6-18	13.00	400.00	5000.00	258.95	1.24	680.00
L6-19	13.50	400.00	5200.00	270.00	0.97	680.00
L6-20	14.00	400.00	5400.00	280.90	0.62	680.00
L6-21	14.50	400.00	5600.00	293.52	0.92	680.00
L6-22	15.00	400.00	5800.00	304.77	0.28	680.00
L6-23	15.50	400.00	6000.00	320.13	1.60	680.00
L6-24	16.00	400.00	6200.00	331.79	0.85	680.00
L6-25	16.50	400.00	6400.00	347.08	1.32	680.00
L6-26	17.00	400.00	6600.00	355.86	2.13	680.00
L6-27	17.50	400.00	6800.00	364.20	2.69	680.00
L6-28	18.00	400.00	7000.00	378.67	2.89	680.00
L6-29	18.50	400.00	7200.00	383.17	3.20	665.00
L6-30	19.00	400.00	7400.00	396.53	4.04	665.00
L6-31	19.50	400.00	7600.00	401.65	5.03	665.00
L6-32	20.00	400.00	7800.00	409.22	6.09	665.00
L6-33	20.50	400.00	8000.00	426.75	6.64	665.00
L6-34	21.00	400.00	8200.00	427.44	4.51	665.00
L6-35	21.50	400.00	8400.00	432.67	6.58	665.00
L6-36	22.00	400.00	8600.00	440.48	7.04	665.00
L6-37	22.50	400.00	8800.00	436.81	11.09	665.00
L6-38	23.00	400.00	9000.00	451.87	14.50	665.00
L6-30	23.50	400.00	9200.00	456.57	16.57	665.00
L6-40	24.00	400.00	9400.00	460.49	19.33	665.00
L6-41	24.50	400.00	9600.00	464.58	22.32	665.00
L6-42	25.00	400.00	9800.00	431.99	23.66	665.00
L6-43	25.50	400.00	10000.00	471.01	36.02	665.00
L6-44	26.00	400.00	10200.00	476.51	30.61	665.00
L6-45	26.50	400.00	10400.00	483.54	33.94	665.00
L6-46	27.00	400.00	10600.00	490.60	41.72	665.00

LOADING 7						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L6-1	2.00	400.00	400.00	27.00	12.00	684.60
L6-2	3.00	400.00	1000.00	54.00	8.00	684.60
L6-3	4.50	400.00	1200.00	84.10	4.10	684.60
L6-4	5.00	400.00	1400.00	105.50	4.60	684.60
L6-5	5.50	416.31	1608.16	102.25	4.21	684.60
L6-6	6.00	419.92	1818.12	103.83	1.36	684.60
L6-7	6.50	418.48	2027.36	127.92	5.80	684.60
L6-8	7.00	421.72	2238.22	148.07	5.14	684.60
L6-9	7.50	401.60	2439.02	137.61	5.67	684.60
L6-10	8.00	402.58	2640.31	121.71	2.74	684.60
L6-11	8.50	400.71	2840.66	136.49	4.46	684.60
L6-12	9.00	405.22	3043.27	147.27	5.32	684.60
L6-13	9.50	401.89	3244.22	155.99	5.43	684.60
L6-14	10.00	401.93	3445.18	170.20	5.89	684.60
L6-15	10.50	404.63	3647.50	172.18	3.94	684.60
L6-16	11.00	405.14	3850.07	198.96	6.52	653.00
L6-17	11.50	403.51	4051.82	201.01	5.12	653.00
L6-18	12.00	405.36	4254.50	225.06	7.35	651.00
L6-19	12.50	406.35	4457.68	234.74	7.44	645.00
L6-20	13.00	407.57	4661.46	245.79	6.55	645.00
L6-21	13.50	408.12	4865.52	277.34	8.16	647.00
L6-22	14.00	409.56	5070.30	240.38	9.31	645.00
L6-23	14.50	409.02	5274.81	305.78	9.99	632.00
L6-24	15.00	407.35	5478.49	264.31	10.74	632.00
L6-25	15.50	406.41	5681.69	317.20	10.29	634.00
L6-26	16.00	406.29	5884.84	289.07	11.99	634.00
L6-27	16.50	404.92	6087.30	333.64	13.09	634.00
L6-28	17.00	403.41	6289.00	344.00	14.53	634.00
L6-29	17.50	403.67	6490.84	352.89	14.21	632.00
L6-30	18.00	405.32	6693.50	363.57	15.78	632.00
L6-31	18.50	403.39	6895.19	346.09	13.78	648.00
L6-32	19.00	400.83	7095.61	381.23	18.54	648.00
L6-33	19.50	401.88	7296.55	345.06	21.50	648.00
L6-34	20.00	397.05	7495.07	408.63	21.97	648.00
L6-35	20.50	396.82	7693.48	350.38	24.99	648.00
L6-36	21.00	396.82	7891.89	422.54	26.22	648.00
L6-37	21.50	395.62	8089.70	375.45	29.39	648.00
L6-38	22.00	394.57	8286.99	362.82	31.10	644.00
L6-30	22.50	395.01	8484.49	434.31	32.40	644.00
L6-40	23.00	396.05	8682.52	443.18	34.88	632.00
L6-41	23.50	394.92	8879.98	434.56	37.42	632.00
L6-42	24.00	397.90	9078.93	379.88	39.39	632.00
L6-43	24.50	395.20	9276.53	453.31	39.45	632.00
L6-44	25.00	396.31	9474.68	402.55	34.41	632.00
L6-45	25.50	395.14	9672.25	459.24	40.30	632.00
L6-46	26.00	395.30	9869.90	417.32	49.21	632.00
L6-47	26.50	394.67	1067.24	477.42	53.42	632.00

LOADING 8						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L8-1	2.00	405.03	810.06	39.11	57.37	648.90
L8-2	2.50	407.46	1013.79	35.79	47.25	648.90
L8-3	3.00	404.07	1215.83	34.99	38.69	648.90
L8-4	3.50	409.72	1420.69	34.93	32.66	648.90
L8-5	4.00	395.58	1618.48	37.55	28.27	648.90
L8-6	4.50	400.44	1818.70	37.77	23.66	648.90
L8-7	5.00	403.16	2020.28	42.12	21.90	648.90
L8-8	5.50	396.73	2218.64	44.56	17.65	648.90
L8-9	6.00	403.52	2420.40	49.62	15.42	648.90
L8-10	6.50	401.83	2621.32	53.04	11.66	648.90
L8-11	7.00	400.07	2821.35	57.39	9.50	648.90
L8-12	7.50	407.40	3025.05	61.96	7.32	648.90
L8-13	8.00	404.66	3227.38	64.10	6.33	648.90
L8-14	8.50	405.60	3430.18	71.10	5.03	648.90
L8-15	9.00	405.54	3632.95	76.05	3.93	648.90
L8-16	9.50	403.03	3834.47	80.27	3.11	648.90
L8-17	10.00	400.82	4034.88	87.08	2.52	648.90
L8-18	10.50	401.18	4235.47	90.56	2.31	648.90
L8-19	11.00	401.81	4436.37	99.36	1.71	648.90
L8-20	11.50	400.28	4636.51	104.83	1.12	648.90
L8-21	12.00	402.48	4837.75	116.10	1.52	648.90
L8-22	12.50	403.73	5039.62	123.31	0.60	648.90
L8-23	13.00	401.16	5240.20	132.53	1.68	648.90
L8-24	13.50	403.29	5441.84	139.92	1.44	648.90
L8-25	14.00	402.14	5642.91	147.80	0.73	648.90
L8-26	14.50	401.11	5843.47	155.33	0.55	648.90
L8-27	15.00	400.98	6043.96	163.35	2.78	648.90
L8-28	15.50	399.66	6243.79	174.87	0.72	648.90
L8-29	16.00	399.53	6443.55	184.82	0.60	648.90
L8-30	16.50	398.86	6642.98	197.57	0.05	648.90
L8-31	17.00	398.82	6842.39	201.48	3.39	648.90
L8-32	17.50	398.13	7041.46	213.95	0.44	648.90
L8-33	18.00	400.54	7241.73	224.23	1.05	648.90
L8-34	18.50	402.38	7442.92	233.41	1.18	648.90
L8-35	19.00	398.78	7642.31	243.09	4.62	648.90
L8-36	19.50	399.03	7841.82	251.51	1.44	648.90
L8-37	20.00	396.00	8039.82	262.82	0.98	648.90
L8-38	20.50	396.64	8238.14	263.99	1.26	648.90
L8-39	21.00	394.27	8435.28	281.82	3.81	648.90
L8-40	21.50	392.99	8631.77	281.33	3.65	648.90
L8-41	22.00	394.04	8828.79	299.43	3.50	648.90
L8-42	22.50	394.56	9026.07	291.12	4.96	648.90
L8-43	23.00	394.77	9223.46	313.02	4.15	648.90
L8-44	23.50	396.90	9421.91	308.58	5.15	648.90
L8-45	24.00	397.75	9620.78	325.83	5.24	648.90
L8-46	24.50	395.79	9818.68	319.34	6.03	648.90
L8-47	25.00	398.47	10017.91	332.97	6.77	648.90

LOADING 8						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L8-48	25.50	397.10	10216.46	348.14	6.72	623.70
L8-49	26.00	400.22	10416.57	359.32	8.31	623.70
L8-50	26.50	397.12	10615.13	363.22	9.24	623.70
L8-51	27.00	398.61	10814.44	367.48	10.42	623.70
L8-52	27.50	401.26	11015.07	375.03	10.18	623.70
L8-53	28.00	400.87	11215.50	377.73	12.32	623.70
L8-54	28.50	400.82	11415.91	374.58	11.64	623.70
L8-55	29.00	399.15	11615.49	386.94	13.20	623.70
L8-56	29.50	399.97	11815.47	391.48	15.02	623.70
L8-57	30.00	402.01	12016.48	391.58	15.77	623.70
L8-58	30.50	399.02	12215.99	393.89	14.10	623.70
L8-59	31.00	401.61	12416.79	398.52	17.14	623.70
L8-60	31.50	403.32	12618.45	408.02	19.35	623.70
L8-61	32.00	405.05	12820.98	426.31	23.57	623.70
L8-62	32.50	401.01	13021.48	409.75	25.62	623.70
L8-63	33.00	398.95	13220.96	428.59	26.94	623.70
L8-64	33.50	399.31	13420.61	427.42	29.38	623.70
L8-65	34.00	398.85	13620.04	441.92	31.52	623.70
L8-66	34.50	393.15	13816.61	450.10	35.43	623.70
L8-67	35.00	400.00	14016.61	439.37	37.86	623.70

LOADING 9						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L9-1	2.00	405.63	811.26	35.86	17.67	659.30
L9-2	2.50	402.43	1012.48	39.30	8.84	659.30
L9-3	3.00	399.48	1212.22	51.38	5.26	659.30
L9-4	3.50	402.91	1413.67	53.56	4.01	659.30
L9-5	4.00	401.16	1614.25	59.25	3.10	659.30
L9-6	4.50	407.67	1818.09	64.91	2.20	659.30
L9-7	5.00	402.39	2019.28	71.98	2.15	659.30
L9-8	5.50	402.54	2220.55	78.80	1.35	659.30
L9-9	6.00	400.96	2421.03	79.44	1.43	659.30
L9-10	6.50	403.33	2622.70	78.76	0.87	659.30
L9-11	7.00	406.73	2826.06	89.13	0.26	659.30
L9-12	7.50	397.17	3024.65	93.86	0.69	663.60
L9-13	8.00	405.24	3227.27	102.38	0.00	663.60
L9-14	8.50	403.61	3429.07	111.64	0.16	663.60
L9-15	9.00	407.60	3632.87	120.93	0.18	663.60
L9-16	9.50	404.99	3835.37	127.02	0.00	663.60
L9-17	10.00	401.73	4036.23	137.25	0.16	663.60
L9-18	10.50	405.18	4238.82	151.73	0.00	663.60
L9-19	11.00	398.66	4438.15	158.40	0.18	663.60
L9-20	11.50	401.36	4638.83	169.81	0.00	663.60
L9-21	12.00	397.65	4837.66	184.59	0.00	663.60
L9-22	12.50	401.97	5038.64	195.03	0.21	663.60
L9-23	13.00	401.29	5239.29	204.47	0.15	663.60
L9-24	13.50	398.09	5438.33	211.34	0.00	663.60
L9-25	14.00	396.11	5636.39	234.28	0.00	676.20
L9-26	14.50	392.79	5832.78	224.38	0.00	676.20
L9-27	15.00	393.10	6029.33	235.19	0.00	676.20
L9-28	15.50	394.37	6226.52	267.08	0.00	676.20
L9-29	16.00	393.61	6423.32	267.31	0.00	676.20
L9-30	16.50	390.05	6618.35	288.46	0.00	676.20
L9-31	17.00	390.24	6813.47	300.01	0.08	676.20
L9-32	17.50	391.10	7009.02	303.67	0.00	676.20
L9-33	18.00	389.70	7203.87	324.49	0.25	676.20
L9-34	18.50	387.71	7397.72	337.62	0.00	676.20
L9-35	19.00	387.20	7591.32	351.62	0.00	676.20
L9-36	19.50	383.62	7783.13	370.65	0.00	676.20
L9-37	20.00	384.58	7975.42	342.26	0.00	676.20
L9-38	20.50	384.27	8167.56	342.10	0.00	676.20
L9-39	21.00	379.41	8357.26	386.40	0.00	676.20
L9-40	21.50	378.32	8546.42	410.01	0.00	676.20
L9-41	22.00	377.50	8735.17	363.39	0.00	676.20
L9-42	22.50	377.78	8924.06	429.99	0.00	676.20
L9-43	23.00	375.60	9111.86	394.24	0.00	676.20
L9-44	23.50	374.81	9299.27	407.63	0.00	676.20
L9-45	24.00	373.48	9486.01	448.90	0.21	676.20

LOADING 9						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L9-46	24.50	382.65	9677.33	420.45	0.43	676.20
L9-47	25.00	392.41	9873.54	464.96	0.17	676.20
L9-48	25.50	394.56	10070.82	441.21	1.10	676.20
L9-49	26.00	395.03	10268.33	473.33	1.43	676.20
L9-50	26.50	394.50	10465.58	484.53	1.44	676.20
L9-51	27.00	398.97	10665.07	464.23	2.21	676.20
L9-52	27.50	399.18	10864.66	454.98	2.92	676.20
L9-53	28.00	403.67	11066.49	496.40	4.12	676.20
L9-54	28.50	399.60	11266.29	456.65	4.07	682.00
L9-55	29.00	401.97	11467.28	476.99	5.19	682.00
L9-56	29.50	403.47	11669.01	484.04	6.75	682.00
L9-57	30.00	404.85	11871.44	536.00	7.59	682.00
L9-58	30.50	403.77	12073.32	500.00	8.89	682.00
L9-59	31.00	403.67	12275.16	540.00	9.33	682.00
L9-60	31.50	402.46	12476.39	516.00	10.96	682.00
L9-61	32.00	403.87	12678.32	549.00	11.79	682.00
L9-62	32.50	403.67	12880.16	521.00	14.33	682.00
L9-63	33.00	403.51	13081.91	557.00	16.13	682.00
L9-64	33.50	403.11	13283.47	562.00	17.63	682.00
L9-65	34.00	407.33	13487.13	574.00	19.69	682.00
L9-66	34.50	408.53	13691.40	600.00	23.45	682.00

LOADING 10						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH ₄]-N mg/L	[NH ₄]-N mg/L	[NH ₄]-N mg/L
L10-1	2.00	401.33	802.66	10.88	30.68	639.57
L10-2	2.50	399.37	1002.35	12.38	20.51	665.27
L10-3	3.00	400.72	1202.71	14.71	14.63	611.70
L10-4	3.50	401.63	1403.52	17.29	11.67	637.06
L10-5	4.00	396.69	1601.87	19.64	9.98	643.07
L10-6	4.50	398.42	1801.08	18.31	8.49	652.41
L10-7	5.00	396.28	1999.22	25.18	7.50	664.99
L10-8	5.50	399.18	2198.81	26.90	5.50	698.57
L10-9	6.00	398.31	2397.96	32.60	4.51	705.82
L10-10	6.50	397.45	2596.69	35.58	4.88	671.37
L10-11	7.00	396.90	2795.14	39.00	4.05	711.38
L10-12	7.50	395.49	2992.88	43.28	3.82	704.76
L10-13	8.00	394.80	3190.28	44.63	3.10	685.75
L10-14	8.50	395.57	3388.07	51.62	3.96	662.30
L10-15	9.00	392.17	3584.15	57.16	2.98	712.14
L10-16	9.50	391.49	3779.90	63.14	3.60	651.24
L10-17	10.00	386.88	3973.34	50.35	2.22	708.57
L10-18	10.50	381.25	4163.96	67.07	2.36	685.18
L10-19	11.00	380.88	4354.40	70.99	2.53	674.19
L10-20	11.50	385.47	4547.14	84.80	2.64	648.91
L10-21	12.00	385.48	4739.88	93.50	2.63	663.24
L10-22	12.50	385.50	4932.63	99.52	2.76	633.21
L10-23	13.00	396.26	5130.76	106.54	2.78	609.20
L10-24	13.50	393.96	5327.74	91.65	3.50	593.64
L10-25	14.00	391.62	5523.55	117.84	3.35	593.58
L10-26	14.50	389.97	5718.53	108.01	3.41	616.15
L10-27	15.00	398.40	5917.73	143.33	4.00	622.14
L1028	15.50	395.46	6115.46	155.70	4.43	653.32
L10-29	16.00	393.25	6312.09	165.09	5.27	678.46
L10-30	16.50	396.88	6510.53	169.56	5.03	685.56
L10-31	17.00	396.18	6708.62	178.22	5.62	691.72
L10-32	17.50	395.35	6906.29	187.58	6.33	706.86
L10-33	18.00	395.03	7103.81	186.54	6.43	681.74
L10-34	18.50	396.33	7301.97	199.48	7.50	698.62
L10-35	19.00	396.49	7500.22	208.46	8.02	678.59
L10-36	19.50	394.54	7697.49	212.57	7.29	665.09
L1037	20.00	394.63	7894.80	207.26	7.58	686.02
L10-38	20.50	393.04	8091.32	221.90	8.94	657.45
L10-30	21.00	391.14	8286.89	232.53	9.98	674.39
L10-40	21.50	388.46	8481.12	240.66	9.95	635.09
L10-41	22.00	391.04	8676.64	247.87	9.13	665.44
L10-42	22.50	389.65	8871.47	247.89	11.71	692.29
L10-43	23.00	392.09	9067.51	264.57	14.15	682.13
L10-44	23.50	393.49	9264.26	276.01	15.02	699.54
L10-45	24.00	400.52	9464.52	267.07	15.20	698.30

LOADING 10						
sample No	sampling	flow rate	treated water	Col A	Col B	Influent
	hrs	L/h	L	[NH ₄]-N mg/L	[NH ₄]-N mg/L	[NH ₄]-N mg/L
L10-46	24.50	398.59	9663.81	290.94	17.29	685.21
L10-47	25.00	393.26	9860.44	286.74	19.32	700.11
L10-48	25.50	396.34	10058.61	304.70	20.58	709.63
L10-49	26.00	396.58	10256.90	314.96	23.57	702.55
L10-50	26.50	392.80	10453.30	313.81	26.40	711.42
L10-51	27.00	393.88	10650.24	328.14	27.69	704.95
L10-52	27.50	395.26	10847.87	339.33	30.51	717.27
L10-53	28.00	394.17	11044.96	347.48	33.53	709.09
L10-54	28.50	392.21	11241.06	354.55	35.80	713.30
L10-55	29.00	391.00	11436.56	356.94	39.29	711.43
L10-56	29.50	385.82	11629.47	373.52	42.30	704.62
L10-57	30.00	385.91	11822.43	363.19	45.80	694.36
L10-58	30.50	385.33	12015.09	388.45	48.78	719.41
L10-59	31.00	388.20	12209.19	394.87	51.75	709.31
L10-60	31.50	387.54	12402.96	395.87	55.51	715.60
L10-61	32.00	395.88	12600.90	409.90	59.85	718.16
L10-62	32.50	387.89	12794.85	418.60	64.55	714.60
L10-63	33.00	388.63	12989.16	424.11	67.87	697.37
L10-64	33.50	378.44	13178.38	414.41	73.04	710.06
L10-65	34.00	378.59	13367.68	433.74	77.51	688.00
L10-66	34.50	374.73	13555.04	437.21	83.01	680.32
L10-67	35.00	371.44	13740.76	443.43	86.23	662.29
L10-68	35.50	375.31	13928.42	449.63	92.07	671.81

LOADING 11						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH ₄]-N mg/L	[NH ₄]-N mg/L	[NH ₄]-N mg/L
L5-1	2.00	405.53	811.06	97.40	46.20	637.64
L5-2	2.50	411.61	1016.87	95.08	20.09	647.78
L5-3	3.00	430.21	1231.97	107.77	12.92	642.96
L5-4	3.50	399.56	1431.75	112.43	11.07	662.89
L5-5	4.00	404.33	1633.92	119.04	11.11	654.93
L5-6	4.50	410.27	1839.05	127.47	9.99	661.87
L5-7	5.00	389.89	2034.00	130.90	9.49	657.28
L5-8	5.50	388.49	2228.24	141.33	8.90	668.53
L5-9	6.00	403.70	2430.09	150.39	8.27	595.38
L5-10	6.50	404.89	2632.54	161.42	7.57	673.19
L5-11	7.00	405.52	2835.30	166.44	7.12	699.02
L5-12	7.50	410.73	3040.66	181.67	6.23	689.57
L5-13	8.00	411.14	3246.23	195.43	5.59	659.14
L5-14	8.50	414.42	3453.44	201.08	5.43	715.00
L5-15	9.00	410.01	3658.45	227.12	4.12	697.69
L5-16	9.50	416.14	3866.52	226.27	4.90	694.42
L5-17	10.00	412.21	4072.62	241.02	4.31	722.08
L5-18	10.50	418.08	4281.66	252.03	4.13	723.80
L5-19	11.00	417.33	4490.33	263.12	4.35	724.10
L5-20	11.50	415.22	4697.94	274.62	4.56	719.17

LOADING 11						
sample No	sampling	flow rate	treated water	Col B	Col A	Influent
	hrs	L/h	L	[NH4]-N mg/L	[NH4]-N mg/L	[NH4]-N mg/L
L5-21	12.00	419.86	4907.87	291.36	4.11	714.28
L5-22	12.50	421.06	5118.40	303.49	3.61	710.88
L5-23	13.00	420.39	5328.59	316.96	4.38	719.49
L5-24	13.50	420.16	5538.67	319.38	3.81	743.70
L5-25	14.00	421.01	5749.18	334.41	2.84	741.12
L5-26	14.50	418.94	5958.65	337.63	4.15	733.89
L5-27	15.00	421.80	6169.55	360.33	4.57	736.65
L528	15.50	419.85	6379.47	372.42	5.04	735.40
L5-29	16.00	420.05	6589.50	383.47	5.84	727.22
L5-30	16.50	414.01	6796.50	391.53	6.21	702.88
L5-31	17.00	418.65	7005.83	401.28	7.10	747.51
L5-32	17.50	417.29	7214.47	410.48	7.05	726.55
L5-33	18.00	415.13	7422.04	422.46	7.88	682.73
L5-34	18.50	419.38	7631.73	432.07	8.60	742.47
L5-35	19.00	419.03	7841.24	440.75	9.21	714.73
L5-36	19.50	414.89	8048.69	448.11	10.15	722.96
L537	20.00	413.43	8255.40	443.12	11.36	710.78
L5-38	20.50	413.73	8462.27	453.20	12.77	689.12
L5-30	21.00	408.63	8666.58	471.72	12.52	696.46
L5-40	21.50	408.57	8870.87	463.68	14.37	683.61
L5-41	22.00	407.12	9074.43	487.64	16.03	636.96
L5-42	22.50	411.22	9280.04	481.38	16.85	661.69
L5-43	23.00	410.97	9485.52	476.80	20.13	640.03
L5-44	23.50	407.51	9689.28	496.55	21.37	688.07
L5-45	24.00	408.90	9893.73	496.47	23.20	661.26
L5-46	24.50	408.18	10097.82	496.47	24.68	646.80
L5-47	25.00	409.90	10302.77	489.70	29.31	669.19
L5-48	25.50	404.81	10505.17	496.60	35.36	666.11
L5-49	26.00	404.96	10707.65	496.47	30.69	682.60
L5-50	26.50	399.85	10907.58	496.57	35.12	680.84
L5-51	27.00	395.63	11105.39	496.51	40.04	650.73
L5-52	27.50	408.20	11309.49	496.46	37.74	682.08
L5-53	28.00	395.77	11507.38	496.50	39.12	690.84
L5-54	28.50	394.90	11704.83	496.62	48.98	712.38
L5-55	29.00	391.94	11900.80	496.63	57.17	681.94