AMMONIA REMOVAL FROM WATER BY ION EXCHANGE USING SOUTH AFRICAN AND ZAMBIAN ZEOLITE SAMPLES

Submitted in fulfilment of the requirements for the degree of
MASTER OF SCIENCE
of Rhodes University

by

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January 2000

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To the loving memory of my late mother and father

ACKNOWLEDGEMENTS

I would like to acknowledge my supervisor Dr Horst Kaiser for the guidance and active participation during this research. His encouragement and patience were a great help to me.

I would like to acknowledge Mr Pratley and J.J. Maree of the Pratley Manufacturing and Engineering company for supplying me with the clinoptilolite used in this study. Special thanks go to H. Tsikos for help with sample preparation and X-ray diffraction and Prof. R.E. Jacob N. Hammond and J.R. Hepple of the Geology department of Rhodes University for the assistance given in analysing the zeolite samples. I also wish to thank R.H.M. Cross and S.C. Pinchuck of the Electron Microscopy Unit of Rhodes University for assistance with the Scanning Electron Microscope. Special thanks go to Mr Liyungu of the Ministry of Mines and Dr G.K. Nkonde of the School of Mines and Survey, University of Zambia for the supply of the Zambian zeolite that was used in this research.

I also thank Prof. Tom Hecht, The Liberty Life Education Foundation and the Andrew Mellon Scholarship committee for the financial assistance given for this research work. I acknowledge the valuable support and encouragement of my colleagues Irene Muriuki and Sylvia Tshivunge, and graduate students in the Ichthyology department. Special thanks to Tom Shipton for assisting with the Micro-Kjeldhal analysis, Emmanuel Kaunda for constructive criticisms and Dr Irene Naigaga for proof reading some of my earlier manuscripts. I also thank my sisters and brothers for their love, encouragement and support.

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ABSTRACT

One problem of intensive fish culture systems is the progressive build-up of toxic wastes such as ammonia. The possibility of improving aquaculture water quality using two kinds of zeolite is discussed. Zeolites are alumino-silicates whose framework allows them to exchange cations. Ion exchange has been demonstrated to be competitive with other methods of ammonia removal due to the high selectivity for ammonia exhibited by zeolite materials. In this study an unknown Zambian zeolite (identified as laumontite by X-ray diffraction techniques) and Pratley clinoptilolite (a South African zeolite) were tested under laboratory conditions and in a fresh water recirculating system. Ammonia cation exchange capacities (CEC) and suitable application rates for efficient water treatment were determined using the batch and column ion exchange procedures. Estimated ammonia uptake, the most important criterion used to assess performance of zeolite filters was strongly influenced by zeolite type, particle size, pre-treatment, regeneration and ion exchange method used.

Statistical analysis showed significant differences in average ammonia CEC values between clinoptilolite (14.94 mg g^{-1}) and laumontite (2.77 mg g^{-1}), with the former displaying a higher $Na^+ \rightarrow NH_4^+$ exchange rate especially in the early reaction stages. This difference accords with the higher purity of clinoptilolite, 47% as opposed to 4.7% for laumontite, which makes it a better zeolite for ammonium removal. CEC increased linearly as particle size of the clinoptilolite was reduced resulting in a linear regression model (y = 18.29 – 3.704 x; r^2 = 74 %). Pre-treatment of clinoptilolite using 1N NaCl significantly improved the ammonia CEC of clinoptilolite. Overall performance of both the batch and column methods achieved after regeneration (18.3 mg g^{-1}) was 25% higher than the estimated CEC values (13.0 mg g^{-1}) for the unregenerated samples of clinoptilolite. Comparison of CEC estimates using Pratley clinoptilolite, showed that average batch CEC estimates were significantly lower than the column method estimates. The average ammonia CEC values estimated in a fresh water recirculating system (5.80 mg g^{-1} and 4.12 mg g^{-1} for the 0.7-1.0 and 1.0-1.4 mm particle sizes, respectively) were significantly lower than the column and

batch estimates for the same particle sizes ($P < 0.05$). Some nitrite (NO_2) and nitrate (NO_3) build up was experienced probably due to the growth of autotrophs in the filters. Mass balance of nitrogen (N) for the three treatments of the fish trial (0.7-1.0 mm, 1.0-1.4 mm and the control treatment that had no zeolite in the filter) indicated that less that 10% of the N was retained for growth. It was found that 60 % of the NH_4-N present associated with the soluble N was available for absorption by the zeolite filter or biological nitrification and that a total of approximately 22 % of NH_4-N available was absorbed by clinoptilolite. The results indicate that the rate of nitrification can be deductively estimated by allowing a zeolite filter to become a biological filter. It is concluded that water treatment by ion exchange using natural zeolites, provides a reliable and efficient method for ammonia removal and appears to be a viable supplementary water treatment method for fresh water systems.

CHAPTER 1

Introduction

1.1 General Introduction

The last three decades have seen a tremendous growth in the science of aquaculture in Southern Africa and throughout the world (Haylor and Muir, 1998). Today, the social, economic and environmental constraints increasingly challenge governments, investors and policy makers as living standards and environmental conditions continue to decline (Haylor and Muir, 1998). The importance of aquaculture production for not only improving the availability of protein but also enhancing economies is increasingly becoming apparent. An important trend in aquaculture has been towards greater intensification of production with efforts to obtain higher fish yields through increasing stocking densities (Liao and Mayo, 1974; Landau, 1992). However, in many parts of the world intensive fish production is handicapped by either climatic conditions or reliable suitable water availability (Poxton and Allouse, 1982). In Southern Africa, water is a major limiting factor such that economically feasible technologies of water reconditioning and re-use techniques are becoming very important. Water re-use and reconditioning technology results in the production of larger quantities of fish from a given water source and it also addresses increasingly stricter environmental concerns (Liao and Lin, 1981). Other considerations that might favor production of fish in re-use facilities are more efficient space utilization and higher labour efficiency (Semmens and Porter, 1979).

One operational problem of intensive recirculating systems is the progressive build-up of toxic metabolic wastes that affect water quality and result in functional and structural disorders in the fish (Mumaw *et al*., 1981). These biochemical changes occur over extended periods of time and include an increase in nitrogenous end products, organic

substances and phosphates. Alkalinity and pH values usually decrease under such conditions (Poxton and Allouse, 1982). There are five primary sources of nitrogenous compounds in the aquatic environment: ammonia, and amino acids excreted by the living organism, organic debris from dead organisms, uneaten food, faeces, and nitrogen gas from the air (Wheaton *et al.,* 1991; López-Ruiz and Goméz-Garrudo, 1994; Goddard, 1996).

Ammonia comprises between 70 to 90 % of these nitrogenous catabolites (Goddard 1996) and is one of the major problems of intensive systems. The significance of ammonia in fish culture is due to the acute toxicity of free ammonia (NH_3) to fish. As ammonia concentrations in water increase, excretory processes are impaired, and ammonia levels build up in the animal tissues and circulatory system. Ammonia can also irreversibly bind to haemoglobin in the red blood cells. This results in an elevation of blood pH and adverse effects on enzyme-catalysed reactions and the stability of cell membranes (Goddard 1996). Short-term exposure can cause gill damage and reduced ability for oxygen intake, while long-term exposure can result in poor growth, loss of appetite, increased susceptibility to disease or to other stress conditions and in extreme cases death (Russo and Thurston, 1991; Mumpton, 1994; Goddard, 1996). This problem is potentially serious in hatcheries where water is reused or where ammonia accumulates as water flows through a series of raceways (Marking and Bills, 1982). A value of 0.005 mg L^{-1} ammonia (NH_3) has been suggested as the maximum allowable level (Russo and Thurston, 1991). In oxygen-poor environments even lower NH_3 levels can lead to hyperplasia of gill tissue and substantial reduction in growth rates (Mumpton, 1983). Furthermore, other toxic nitrogen compounds e.g., nitrite (NO_2) and the less toxic nitrate (NO_3) are formed from the oxidation of ammonia.

Ammonia with its toxic biological effects is harmful in varying degrees to most aquatic species (Tomasso and Brune, 1991). In fish cultivation, we deal with both long and short periods of exposure. The physiological condition of the fish or its stage of development as well as the water quality (pH, dissolved oxygen, temperature, and presence of other

chemicals) influence toxicity of ammonia (Poxton and Allouse, 1982). The toxic effect of ammonia also depends on the proportion and distribution of its ionic forms, i.e., un-ionised (NH_3) and ionised (NH_4^+), shown by the equilibrium equation (Russo and Thurston, 1991);

$$NH_3 + nH_2O = NH_3 . nH_2O = NH_4^+ + OH^- + (n-1)H_2O \; ; \; n > 3$$

The toxicity of ammonia is related to un-ionised NH_3, which is a highly soluble gas that can readily pass through the gill membranes. The relative concentrations of NH_3 and NH_4^+ in the culture water are a function of pH, temperature and ionic strength of the solution (Warrer-Hansen, 1993). As the pH increases, the concentration of NH_3 increases exponentially while NH_4^+ decreases. Temperature increase will favor the NH_3 form while an increase in the ionic strength of the solution at low concentrations favors the NH_4^+ form. Total ammonia is the sum of NH_3 and NH_4^+, and it is total ammonia that is most commonly measured and the concentration of NH_3 is then calculated using the equation provided by Russo and Thurston (1991). Maintaining low ammonia levels is therefore one of the major objectives in the culture of fish in closed aquatic systems. There are various techniques for reducing ammonia concentrations in culture water. The most common procedures are water exchange, aeration/air stripping, biological filtration by nitrification, water plants/algae ponds, and ion exchange (Jorgensen *et al.,* 1976; Liao and Lin, 1981; Dryden and Weatherley, 1987a, 1987b; Chiayvareesajja and Boyd, 1993).

This study will look at ion exchange treatment of aquaculture water using natural zeolite. Ion exchange has been successfully used to purify waste waters from aquatic systems and sewage waters (Koon and Kaufman, 1975; Jorgensen *et al.,* 1976). The process of ion exchange is electrochemical and occurs between two or more phases, usually a solution and a solid that is insoluble in the solution (Colella, 1996). These phases exchange two or more similarly charged ions (cations or anions), more or less strongly bound to each phase (Liao and Lin, 1981; Wheaton, 1982). Ion transfer from one phase to another occurs in order to maintain electroneutrality and is regulated by the ion concentration in both phases

and selectivity which is the measure for the preference of one ion compared with another (Colella, 1996). The quantity of ions exchangeable by the solid exchanger, depending on its chemical and structural features, is called the ion exchange capacity and is usually expressed in milliequivalents per gram (meq g^{-1}). Substitution is stoichiometric and provided that suitable experimental conditions exist, it can be exhaustive covering the entire ion exchange capacity, unless partial or total exclusion occurs, due to inaccessibility of specific exchange sites (Colella, 1996). Ion exchange is generally a reversible reaction though it can be irreversible (Dyer, 1988).

Natural zeolites showing cation exchange properties have been recognised in sedimentary deposits of volcanic origin for more than a century (Sheppard, 1983; Pansini, 1996). The unique physical and chemical properties of zeolites, their capability of undergoing cation exchange and reversible dehydration, and their open framework structures liable to act as molecular sieves, render zeolite as a sedimentary deposit of commercial value. Due to these factors and combined with their geographically widespread abundance, zeolite minerals have generated world-wide interest for use in a broad range of applications such as nuclear and municipal waste, water treatment, stack-gas clean-up, natural gas purification, petroleum production, and in agriculture and aquaculture (Mumpton, 1983; Palaban, 1994).

Naturally, zeolites occur in the cavities or vesicles of volcanic rocks as a result of very low-grade metamorphism. They are mostly formed by reaction of pore waters with volcanic glass, and also by alteration of pre-existing feldspars, feldpathoids, poorly crystalline clays and biogenic silica (Palaban, 1994). These minerals are 3-dimensional, micro-porous crystalline solids with well defined structures composed of aluminium (Al_3^-), silicon (Si_4^+) and oxygen (O_2) in their regular framework (Dyer, 1988). The Si_4^+ and Al_3^- atoms are tetrahedrally connected with each other through shared O_2 atoms forming an infinitely extending tetrahedral network (Figure 1.1). Void spaces or cavities between the tetrahedral rings can host cations, water and other molecules (Gottardi and Galli, 1985).

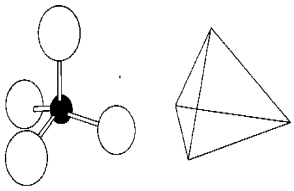

Figure 1.1. Representations of $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ tetrahedra (Dyer, 1988)

The most commonly represented framework-linked ions according to Bergero *et al.*, (1994), are potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and iron (Fe^{2+}), more rarely lithium (Li^+), strontium (Sr^{2+}) and barium (Ba^{2+}). The general formula of natural zeolites is:

$$(Li, Na, K)_a\ (Mg, Ca, Sr, Ba)_d\ [Al_{(a+2d)}\ Si_{n-(a+2d)}O_{2n}] \cdot mH_2O \quad ; \quad \text{usually } m \leq n$$

where the part in square brackets represents the framework or structural atoms and the parts outside the square brackets are the extra framework atoms or exchangeable cations plus water molecules (Gottardi and Galli, 1985). No zeolites are known that contain more Al_3^- atoms than Si_4^+, thus the Si:Al ratio is always equal to or greater than 2:1 (Mumpton, 1983). Cation exchange is a function of the degree of Al substitution for Si^{4+} in the framework structure: the greater the substitution the greater the deficiency of the positive charge and the greater the number of alkali and alkaline earth cations required for electrical neutrality (Mumpton, 1983).

The structure and affinity of zeolites for ammonia is the basis for their use as ion exchangers (Wheaton, 1982; Dryden and Weatherley, 1987a, 1987b). In zeolites, ion exchange arises from the presence of extra framework cations, located in the regular array

of channels and cages (Sherry, 1975; Dyer, 1988; Colella, 1996). The extent of ion sieving exhibited by a zeolite depends primarily on the size of the openings into the ion cages and on the energy with which the structural water is bound to the zeolitic framework (Koon and Kaufman, 1975). The cavities/channels are significant in ion exchange reactions and allow zeolites to exchange cations with a capacity ranging from 2.16 meq g^{-1} to 4.73 meq g^{-1} (Wheaton, 1982; Bergero *et al.*, 1994). When zeolites remove NH_4^+ ions from solution, the concentration of NH_3 is likewise reduced by the shift of $NH_3 \rightarrow NH_4^+$ in accordance with the NH_4^+/NH_3 equilibrium at the given water temperature, pH and salinity (Mumaw *et al*., 1981; Amend *et al*., 1982). Ammonium ion exchange takes place according to the equilibrium equation

$$\boldsymbol{Z}\,Na^+ + NH_4^+ \leftrightarrow \boldsymbol{Z}\,NH_4^+ + Na^+$$

where $\boldsymbol{Z}$ stands for the zeolite and Na^+ can be any of the extra framework cations (Dryden, 1985). There is a limit to the amount of NH_4^+ ions the zeolite will accept. When this stage is reached the zeolite may either be replaced or regenerated. Zeolites can be regenerated using a solution with a concentration of Na^+ ions greater than that of the NH_4^+ ions being replaced from the zeolite (Wheaton, 1982).

Ion exchange offers several advantages, including a high degree of ammonia ion removal independent of temperature, influent ammonia levels and the ability of the filter to function at maximum effectiveness almost immediately (McLaren and Farquhar, 1973; Liao and Lin, 1981; Dryden and Weatherley, 1987a). This process is stable and predictable with respect to product quality. It appears to be a viable supplement to biological nitrification and water exchange (where water is limiting), and provides more efficiency for ammonia removal for fresh water systems. On the other hand it is also a useful backup to biofiltration, due to its tolerance to changes in temperature and chemical conditions, and in some cases low costs (Johnson and Sieburth, 1974). Zeolites can also be used to create oxygen enriched air by selective absorption of nitrogen, N_2 (Mumpton, 1983).

1.2 Literature Review

Ammonia-selective ion exchange using synthetic and natural zeolites has been used successfully to remove ammonia from aquaculture waters in the laboratory (Johnson and Sieburth, 1974; Teo *et al.,* 1989; Bergero *et al.,* 1994; Ferreiro *et al.,* 1995) and on a pilot scale in the culture of different fish species (Bruin *et al.,* 1981; Liao and Lin, 1981; Mumaw *et al.,* 1981; Slone *et al.,* 1981; Horsh and Holway, 1983). However, most studies that demonstrated the ammonia removal efficiency of zeolites have been conducted using clinoptilolite while, very few studies have looked at the performance of other natural zeolites. This is because clinoptilolite is one of the most abundant natural zeolites that displays a high affinity for the ammonium ion. Few other zeolites have been considered for ammonia equilibrium studies. The major ones being chabazite, ferrierite, mordenite and phillipsite which have also shown good selectivities. The selectivity coefficient (K_a) at 25 °C for $Na^+ \rightarrow NH_4^+$ (Na^+ meq/ NH_4^+meq) exchange in chabazite was found to be 5.32. The same selectivity value for mordenite at 25 °C, ferrierite at 24 °C and phillipsite at 20 °C proved to be 2.58, 6.43 and 13.26, respectively (Colella, 1996). The selectivity coefficient, K_a is similar to an equilibrium constant for the reaction, except that the former is typically written in terms of concentrations (mg or meq) rather than activities/valences (Semmens, 1983).

However, variations in the measured capacities of samples of clinoptilolite as well as other zeolites have been reported by many investigators. For example, samples of clinoptilolite obtained from various areas of the Western United States had ammonia adsorption capacities ranging from 3.42 - 9.12 mg ammonia g^{-1} clinoptilolite (Murphy *et al*., 1994). Dryden and Weatherley (1987a) obtained high results of 2.066 and 2.159 meq g^{-1} for clinoptilolite A and B (distinguished by different colourations), respectively, which are among the highest results obtained for Hector clinoptilolite. Klieve and Semmens (1980) observed that clinoptilolite had higher ammonia exchange capacities than erionite and

mordenite while phillipsite with a capacity of 2.64 meq g^{-1} was clearly superior to clinoptilolite (0.844 - 0.857 meq g^{-1}). Unfortunately, phillipsite is structurally weak and breaks down to fines, limiting its application for water treatment.

It is thus clear that the adsorption efficiency for ammonia exhibited by natural zeolites is very variable. This is due to the various chemical and physical factors that affect the adsorption efficiency of zeolites in waste water treatment. Among these are water hardness, salinity, pH, temperature, and organic matter content. The zeolite type (source), different granule sizes, pre-treatment and flow rate through the exchange bed also affect ammonia adsorption efficiency (Pansini, 1996). All the above mentioned factors will be discussed in relation to their significance for the ion exchange process.

1.2.1 Zeolite Type

There are both natural and synthetic zeolites in the zeolite mineral group and selectivity for specific cations varies considerably between zeolite types and deposits (Klieve and Semmens, 1980). Properties like Si/Al ratio, partial density, theoretical CEC, cation selectivity, void volume, molecular pore size and shape of the cages in the structure, channel geometry, and crystal shape vary according to the zeolite in question (Flanigen, 1983). Table A1 (Appendix A) shows zeolites listed as economically important and their different properties. Compositionally, zeolites can be grouped according to their Si:(Al + Fe) structural cation ratios and their K, Na and Ca (exchangeable cations) ratios (Hawkins, 1983). Clinoptilolite and mordenite are silica rich zeolites, with large Si:(Al + Fe) ratios; heulandite, chabazite, phillipsite, and erionite are intermediate silica zeolites; and analcime and laumontite are silica poor zeolites. The exchangeable cations of analcime are predominantly Na, those of clinoptilolite are Na and K (although Ca-clinoptilolites are known), and those of laumontite are almost invariably Ca (Dyer, 1988). Physical and chemical properties also vary for zeolites of the same type that come from different sources. Differences between zeolites of the same type are determined by the environmental conditions under which the zeolite was formed and are primarily a result of

the manner of cementation of the zeolite rock and the amount and kinds of impurities (Hawkins, 1983).

Each zeolite has a rigid crystalline framework that generates a particular electric field. Therefore, various cations react differently with various zeolite frameworks and their resulting electric fields (Pansini, 1996). Zeolites separate molecules based on size, shape, polarity and degree of saturation. Three mechanisms influence zeolite selectivity, these are sieve action, hydration of the cation species and anionic site separation (McLaren and Farquhar, 1973). Sieve action is based on the uniform pore size distribution in zeolites that limits absorption. These intra-crystalline cavities make up from 20 to 50 % of the total crystal volume of most zeolites. For example, void spaces of erionite and chabazite are close to 30% while those of most other natural zeolites such as clinoptilolite, mordenite and ferrierite are near 20% (Flanigen, 1983). The diameters of the cavities or pores range from the very small pore in analcime (2.8 Å) to near 7 Å in mordenite (Flanigen, 1983). The size of the cavities is based on the number of members in the ring (4, 5, 6, 8 or 12). The ring size determines the ion that the mineral can extract from a solution; a molecule smaller than the pore can enter the crystal structure and be adsorbed, but larger molecules are excluded from the structure and not adsorbed. Thus, the size of molecules passing through the cavities is restricted (Figure B1: Appendix B). In some of the denser zeolites the pores are too small to allow molecular sorption while others may have a lower density and pore volume with small pore openings (Dyer, 1988).

The effect of hydration is due to the loosely bound water available for hydration and results in an increase of the effective radius of the zeolite. McLaren and Farquhar (1973) state that a high energy of hydration of cations increases the attraction of cations for water such that the cation approaches the anionic exchange sites less closely within the zeolite. This is in agreement with the results of Dryden and Weatherley (1987a, 1987b) in which the ammonium ion was selected ahead of divalent metallic ions such as calcium and magnesium. The hydration spheres of high field strength cations prevent their close approach to the seat charge in the framework; therefore cations with low field strengths

are more tightly held and selectively exchanged by the zeolites than other ions (Mumpton, 1983). Zeolite selectivity for a given cation depends on its anionic field strength (or framework charge density) which in turn is related to the silica/aluminium ratio (Colella, 1996). When the ratio is large as with clinoptilolite and the separation distance is small, divalent cations are capable of satisfying two anionic sites (Flanigen, 1983; McLaren and Farquhar, 1973). This discussion shows that each zeolite species has its own set of physical and chemical properties and even the same zeolite may differ considerably in its properties when obtained from different geological environments or locations (Mumpton, 1983).

1.2.2 Pre-treatment

The capacity of zeolites is greatly influenced by chemical and physical treatments that are usually done to condition or activate the zeolite (Klieve and Semmens, 1980). Pre-treatment methods include, treatment with acid or mineral acid to remove carbonates and clay impurities which may block pores and add weight to the zeolite; treatment with alkali, like sodium hydroxide and common salt; and thermal treatment. Investigations into various pre-treatment methods have shown both positive and negative effects of pre-treatment on the ammonia exchange capacities of zeolites. For example, pre-treatment with mineral acid has shown a consequent reduction in capacity, while in the case of alkali pre-treatment increases have been observed (Klieve and Semmens, 1980; Dryden and Weatherley, 1987a). Using Hector clinoptilolite, Murphy *et al*. (1994) showed that samples treated with 72 g L^{-1} hydrochloric acid (HCl) for 2 hours and then caustic brine solution (0.5 g NaOH L^{-1} and 30g NaCl L^{-1}) for 2 hours resulted in the greatest increase in effective cation exchange capacity (CEC). This pre-treatment increased the effective CEC by over 20 % when compared with other treatments that used either acid or alkali leading to increases of about 5 %. Jorgensen *et al*. (1979) found that treatment of clinoptilolite with sodium hydroxide improved selectivity and capacity. The ion exchange capacity of the treated rocks was higher than that of the untreated (0.76 meq g^{-1} vs. 0.65 meq g^{-1}). These methods are also known as conditioning of the zeolite, and the same methods are used in the regeneration of zeolites.

1.2.3 Organic matter

Organic matter has been shown to affect the ion exchange process. Presence of organic matter in natural or industrial waste waters reduces the exchange capacities of the exchange medium by causing physical blockage of the exchange bed and coating the ion exchange substrate (Watten and English, 1985). This build-up of biofilm or other organic matter on the surface of the exchanger particles interferes with both ion diffusion and liquid dispersion in the exchange bed during use. Johnson and Sieburth (1974) reported a 74 % reduction in CEC after the treatment of culture water containing 30 mg L^{-1} of dissolved and particulate organic carbon/matter as compared with a control of equal ammonia nitrogen concentration in distilled water. Watten and English (1985) recorded that organic matter had a highly significant effect on the operating exchange capacity of the treatment solutions. In their pilot studies, Liao and Lin (1981) clearly demonstrated that solids removal prior to the ion exchange column was necessary to maintain high exchange efficiencies for ion exchange. Briggs and Funge-Smith (1996) observed that the lower levels of agitation and higher levels of dissolved organic material present in ponds decreased the absorption efficiency of the zeolite, by limiting the number of sites available for inorganic species. Therefore, most of the studies on ion exchange systems have been done in recirculating systems where water is passed through the exchanger due to lower organic matter levels when compared to other aquaculture systems such as in pond aquaculture. The relatively high organic matter content found in the effluent of culture systems must therefore be greatly reduced or completely reduced before ion exchange treatment can take place (Wheaton, 1982).

1.2.4 Particle Size

Particle size affects adsorption efficiency through its influence on the basic physical properties of the zeolite such as the extent and rapidity of ion exchange. Of greater importance is the porosity and permeability of the individual fragments of the zeolitic material. These factors affect the access of fluids to the zeolite exchange sites. Various researchers have observed that large granules are less efficient than smaller granules in the removal of ammonia due to the reduced surface area for pore diffusion because the

diffusion path is shorter (Johnson and Sieburth, 1974; Jorgensen *et al*., 1976; Chiayvareesajja and Boyd, 1993). Small particle sizes allow more and easier access to the exchange sites by cations. Marking and Bills (1982), observed a lower removal rate 5.37 mg g^{-1} for large granules (8x18 mesh), as opposed to 8 mg g^{-1} for smaller granules. However, smaller granules tend to clog the exchange bed much more frequently resulting in a slow filtration rate and thus may be impractical in filtering water used in fish culture (Semmens, 1983).

1.2.5 Ionic strength of the solution

Ionic strength of the solution and water hardness can have an impact on the exchange capacities of zeolites. Typical farm effluents will contain sodium, potassium, calcium and magnesium ions which may enter into exchange reactions with the zeolite (Semmens, 1983). These will compete with ammonium ions for exchange sites and ammonium ions will exchange on only a part of the available sites within the zeolite. It has been observed that the concentration of NH_4^+ ions and the concentration of competing cations such as K^+, Na^+, Ca^{2+} and Mg^{2+} influence the capacity of zeolites for ammonia (Semmens *et al*., 1978). As a result of two studies, McLaren and Farquhar (1973) found that exchange capacity doubled by increasing the ammonium ion levels from 14 - 18 mg L^{-1} and 0 - 5 mg L^{-1}, respectively. Jorgensen *et al.* (1976) showed that tap water gave a lower capacity (about half) than distilled water, due to the presence of other ions with polyvalent charges such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). The selectivity sequence of clinoptilolite for cation pairs including ammonium and the most common alkali and alkaline earth cations found in natural waters according to Dryden and Weatherley (1987a, 1978b) and Colella (1996) is as follows;

$$K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$$

The same pattern, apart from the possible inversion of potassium with ammonium, is exhibited by several natural zeolites, such as chabazite, mordenite and phillipsite which accounts for the preferred exchange by zeolites with lower field strengths for cations

having a low range density (Colella, 1996). This sequence is consistent with the fact that zeolites are ion selective with a preference for ions with high ionic radius and low hydration energy. Thus, cation specificity may be viewed as a result of interactions between cations and water, and cations and anionic sites (Ames, 1965). The equilibrium of each cation pair in a multi component system is independent of the other ion pairs and the selectivity coefficients vary as a function of the cation concentration ratios (McLaren and Farquhar, 1973).

1.2.6 Salinity

Most studies in which both natural and synthetic zeolites have been used as ion exchangers for absorbing ammonia have only revealed positive effects in freshwater (Marking and Bills, 1982; Briggs and Funge-Smith, 1996; Konstantinov and Pelinpenko, 1983). Salinity in water results from dissolved ions and half of these dissolved ions are cations that can be exchanged for ions on zeolite (Chiayvareesajja and Boyd, 1993). Thus, as the salinity of the water increases, there are more cations competing with ammonia for a fixed number of exchange sites on the zeolite. The ion exchange capacity of zeolites in sea water is reduced due to inter-ionic competition for active sites on the exchange medium and a high dissolved organic matter content (Wheaton, 1982). Johnson and Sieburth (1974) reported that a salinity of only 5 % reduced the NH_4^+ removal efficiency of both synthetic and natural zeolite (clinoptilolite) ten-fold over that of freshwater and that higher salinity levels reduced efficiency still further. Chiayvareesajja and Boyd (1993) added zeolite at 2 g L^{-1} to solutions of different salinities with pH 7.7 to 8.1 and a total ammonia nitrogen (TAN) concentration of 2 mg L^{-1}. The results they obtained for different salinities of 0, 4, 8, 16, and 32 ppt showed TAN removal values of 1.76, 0.24, 0.20, 0.16 and 0.08 mg L^{-1}, respectively. Brackish water also drastically reduced the effectiveness of zeolite for ammonia removal relative to fresh water ($P < 0.05$). However, López-Ruiz and Goméz-Garrudo (1994) have reported that zeolite ion exchange in sea water can be done. In experiments with water containing sodium chloride (NaCl) at 3.5 % and 1 g L^{-1} of 38 % protein fish food revealed that zeolite was effective in adsorbing NH_4^+ at high application rates (25 g zeolite $litre^{-1}$). It was observed that at higher quantities of zeolite, an effective

reduction of ammonium occurs , but if the zeolite is present in small doses, it seems to potentiate ammonium formation due to the displacement of NH_4^+ by Na^+.

1.2.7 Flow rate

The flow rate of water entering an ion exchanger is of critical importance. A high flow rate results in poor ion exchange kinetics since the exchange of ions between the water and the exchanger site cannot take place at extreme velocities or short contact times, and physical fracturing of the resin beads may occur (Semmens, 1983). Too low a flow rate results in poor water distribution across the exchange bed which in turn leads to shortened treatment runs. The explanation for this is that water will follow the path of least resistance through the exchange bed, which at low flow rates is a narrow column of exchanger from the top of the bed to the bottom. This "channelling" effect rapidly exhausts the ion exchange capacity of the exchanger in this column and results in premature passage of untreated water from the exchange bed (Semmens, 1983). This is a very inefficient condition because of the large volume of exchanger that is not used during the service cycle.

1.3 Conclusion and objectives

The aim of this research is to establish the optimum absorption efficiencies and suitable application rates in water treatment systems of natural zeolite samples from Zambia and South Africa to determine their potential in aquaculture and waste water treatment. Due to different chemical and physical characteristics of zeolites from the same or different deposits and between zeolite types, it is necessary to characterize each zeolite species by determining its ammonia removal efficiency. This study aims to have fundamental relevance in identifying and establishing the potential of the two zeolite resources in water treatment and to establish methods for the comparison of any other unknown zeolite

samples. So far no work has been published on either of these two samples. The specific objectives of this study therefore are:

1. To compare the efficiency of ammonia removal by different natural zeolite types and quantify the effect and the optimum particle sizes on ammonia absorption capacity.
2. To observe the effect of regeneration on the ammonia exchange capacities of used zeolite.
3. To compare possible differences in ammonia absorption capacity values estimated by the two methods of establishing the cation exchange capacity (CEC).

All these objectives are aimed at establishing the basis and information necessary for the optimum application of zeolite ion exchange for aquaculture water treatment. Therefore this research will conclude with an evaluation of the ammonia absorption efficiencies of these two zeolite samples in an aquaculture system. This research will have practical relevance through the development of a basis for designing zeolite exchange systems and establishing treatment costs. The ultimate goal will be to contribute to a database that establishes parameters for water treatment technology.

CHAPTER 2

Evaluation of the cation exchange capacities for ammonia removal of South African and Zambian natural zeolite samples

2.1 Introduction

The cation exchange capacity (CEC) is defined as a measure of exchangeable ions present per unit weight or volume of the zeolite and represents the number of cations available for exchange (Semmens, 1983). In zeolites CEC is a result of the fixed negatively charged sites occurring throughout the crystalline structure. To maintain electrical neutrality, the negative charges are neutralised by the presence of an equivalent number of exchangeable cations that are only loosely bound in the crystal structure and are free to exchange with the cations in solution (Semmens, 1983). Therefore, the cation exchange process occurs when counter ions from the solution replace the exchangeable ions within the crystal structure of the rock. CEC is affected by the chemistry of the zeolite, the abundance of the zeolite mineral in the rock, the kind and amount of impurities in the rock and the zeolite type (Sheppard, 1983). The cation exchange capacity is therefore an important characteristic of a particular zeolite species.

The CEC of the zeolite needs to be established to allow estimation of the zeolite requirements for a particular system and determine the optimum design of ion exchange systems. There is a need to define zeolite samples that exhibit optimum exchange to reduce operating costs and make zeolite systems more competitive with biological processes of ammonia removal (Murphy *et al.,* 1994). The most commonly tested natural zeolite is clinoptilolite. It has displayed a high selectivity for ammonium ions compared with its selectivity for Ca, Mg and Na ions (the major competing ions in solution) and as such, the zeolite maintains a good working capacity in the presence of these other ions (Semmens *et al.,* 1978). However, clinoptilolite has shown both high and variable

ammonia adsorbing capabilities between different deposits (Klieve and Semmens, 1980; Murphy *et al.,* 1994). All clinoptilolites or clinoptilolite-rich materials do not have the same capacity and/or selectivity for ammonia ions. This statement is also generally true for all other natural zeolites. Therefore, the cation exchange properties as well as the adsorption properties are of great importance in the application of zeolite materials in aquaculture and must be firmly established before trials with metabolic end products from fish can be conducted.

This work is intended to establish the absorption efficiencies and suitable application rates of natural zeolite samples from the Zambian Kafue area and South African Pratley vulture creek clinoptilolite. The objective was to evaluate and compare a Zambian sample with samples of South African origin. As particle size influences the basic properties of the zeolite mineral such as the extent and rapidity of cation exchange, five different particle size ranges were studied to establish their ammonia exchange capacity and to quantify the effect of particle size on the CEC. Ammonia refers to total NH_4^+ and NH_3 ions as measured by the nesslerization unless stated otherwise (APHA, 1989).

2.2 Materials

Two zeolitic materials were available for this experiment. One was an unidentified sample from Zambia, Lusaka province from the Kafue area (10 km south of Kafue town on the Chirundu road). The second was a South African sample provided by the Pratley Manufacturing and Engineering Company limited, already identified as clinoptilolite with the trade name “Pratley vulture creek clino”. The South African zeolite occurs at Nxwala Estate in northern KwaZulu-Natal (32° 17’; 28 43’) and forms part of the Mkuze Nature reserve (Wipplinger and Horn, 1998). Table 2.1 below shows the typical chemical and physical properties of the Pratley vulture creek clino provided by the suppliers.

Table 2.1: Chemical and physical properties of Pratley Vulture Creek Clino by the suppliers specification

Formula	$Na_5K_5[AlO_2]_7[SiO_2]_{30}$
Pore size	3.4 x 3.5 Å and 3.4 x 7.2 Å
Porosity	15 %
Specific gravity	2.2 g ml^{-1}
Density	1.92 g ml^{-1}
Packing density	0.94 g ml^{-1}
Appearance	2 - 4 mm buff-coloured chips
Solubility in water at 20 °C	slight

2.3 Methods

2.3.1 Structure identification and characterization of the zeolite samples

The unknown Zambian zeolite sample was identified and characterized using X-ray diffraction (XRD) and scanning electron microscopy methods, using a JEOL JSM 840 scanning electron microscope of the Electron Microscopy Unit (EMU) of Rhodes University. Electron micrographs at different magnifications were taken to characterize the crystalline structure of the zeolites.

Mineralogical identification by X-ray diffraction was done on powder patterns that were obtained using a Philips standard water-cooled diffractometer from the chemistry department of Rhodes University. Prior to X-ray diffraction analysis, samples were ground using a swing mill and the powdered samples were packed onto standard

aluminium slide holders. Cu $K\alpha_1$ radiation was used with the variable instrumental settings (30.6-40.0 kV voltage, 20-30 mA current) and a scan rate of 1° 20 and a time constant of 1 minute. X-ray irradiation of the zeolite powder produced a scattering

pattern (from the regular arrays of atoms (or ions) within the structure) of a diagnostic fingerprint of 2 *q* (or *d*) spacings (Dyer, 1988). The mineral was then identified by comparison with the values of d-spacings given in the Powder diffraction data file published by the International Center for Diffraction Data (JCPDS, 1974; database of standard mineral patterns).

The Pratley clinoptilolite was analysed for major and trace elements using X-ray fluorescence (XRF) analysis with a Philips PW 1480 X-ray spectrophotometer of the geology department of Rhodes University. Two samples, based on the two different colours of particles that were homogeneously distributed were selected from this mineral. These particles were white and green in colour (designated as W and G, respectively). The samples were crushed and ground in two stages starting with the swing mill followed by a pestle and mortar. All major elements except sodium (Na) were determined on fused duplicate lithium tetraborate glass discs prepared after the method of Norrish and Hutton (1969), and trace elements and Na were determined on pressed pellets.

An index of comparison for the minor and major element composition of Pratley clinoptilolite was used to find out if the two different coloured particles in the samples were similar (Kruger, 1995). The ratios between concentrations for each element were calculated for all elements i.e., white/green (W:G). In order to quantify how closely the estimated mineral composition of the two samples matched each other, simple linear regression analyses were performed and the coefficients of determination (r^2) calculated.

2.3.2 Estimation of the cation exchange capacity (CEC)

The zeolite samples were crushed and sieved to the desired particle sizes. To minimise the retention of grains of a particular size with grains in a larger size range, sieving was repeated several times. The range of sizes for the Pratley clinoptilolite was 0.5 - 1, 1 - 2, 0.295 - 0.595, 0.7 - 1 and 1 - 1.4 mm which are denoted as 18 x 35, 10 x 18, 30 x 50, 18 x 25 and 14 x 18 US standard mesh sizes, respectively. Particle size for the Kafue sample was 0.5 – 1 mm (18 x 35 mesh size). Various sizes were studied to establish the CEC and to compare the effect of particle size on the exchange capacity. After sieving, the zeolite was washed with distilled water to remove any fine material and dried in an oven at 105 °C overnight.

The NH_4^+ exchange capacity was studied using ion exchange columns. 50-ml-burettes were filled with 20 g of the sample supported on a glass wool plug. No air bubble was allowed inside the column. The zeolite was converted to the sodium form by flushing the column with an excess of 1 N sodium chloride (NaCl) solution (Sheppard, 1983). This was done to replace all counter ions by the sodium ion. More than 5 litres of the NaCl solution was passed through each column. The column was then flushed with distilled water to remove all the excess NaCl solution and chloride ions. A solution of ammonium chloride (NH_4Cl) in distilled water with a starting concentration of 10 mg L^{-1} NH_4^+-N was passed through the column. The feed solution was supplied to the column from an elevated reservoir by gravity feeding (Figure 2.1).

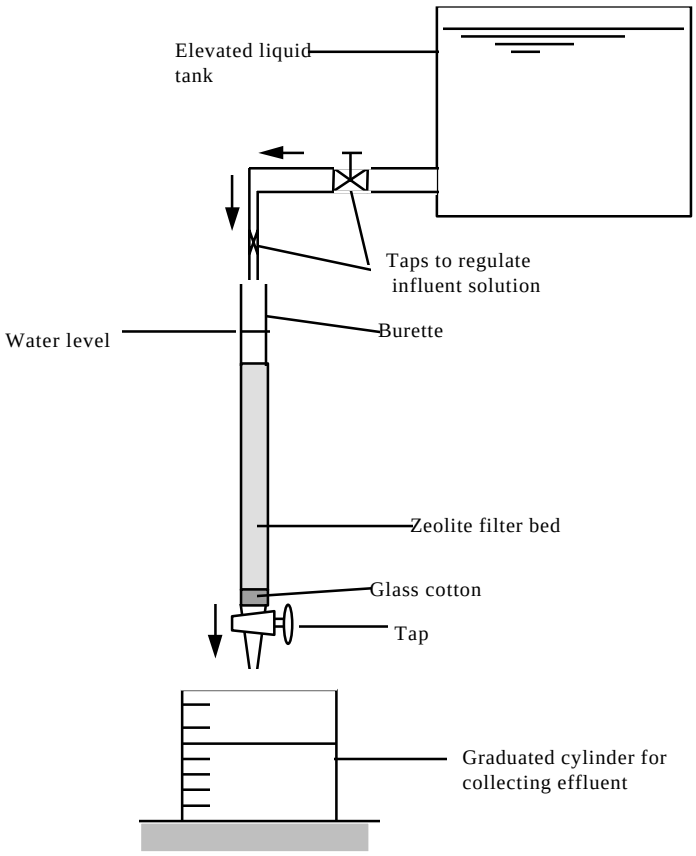

Figure 2.1: Ion exchange column apparatus used for ammonia CEC estimation. The arrows show the direction of flow of the ammonium chloride solution

Samples of the feed solution were collected each time an effluent sample was collected to check if there was any change in the feed concentration. Ammonia was analysed photometrically by nesslerization in accordance with "Standard Methods" (APHA, 1989). When effluent ammonia concentration was the same as that of the feed (within analytical error), the zeolite was flushed with distilled water. Temperature and pH (Hanna HI 9023 Micrometer pH meter) of the solution were measured every second day throughout the experiment. Nitrate and nitrite concentrations were measured every second day applying the methods given in Merck (1974) to check for possible bacterial activity.

2.4 Results

The standard X-ray diffraction pattern for the powdered sample of the Kafue identified the major zeolite in the rock as laumontite (Fig. C1: Appendix C), a calcium based zeolite whose general formula according to Gottardi and Galli (1985) is $Ca_4[Al_8Si_{16}O_{48}].16H_2O$. The X-ray diffraction pattern of pure laumontite (Borg and Smith, 1969) and the physical and chemical properties of this zeolite are given in Figure C2 (Appendix C) and Appendix D, respectively. Laumontite has one fourfold calcium-site on a mirror plane, the co-ordination polyhedron of this cation is nearly a trigonal prism with two vertices occupied by water molecules and four by framework oxygen molecules, which are part of the aluminium tetrahedron.

Figures 2.2 to 2.3 are the scanning electron micrographs (SEM) from a JEOL JSM 840 scanning electron microscope for the Kafue and Pratley samples, respectively. SEM observations also indicated that the Kafue sample was laumontite, a white-coloured zeolite. The structural morphology of the clinoptilolite can be seen in the micrographs of the Pratley clino (figure 2.2). The clinoptilolite crystal size distribution ranged from 10 - 30 μm.

Table 2.2 and 2.3 show the results of the XRF analysis for the major and minor elements of the clinoptilolite sample. The water content of the zeolite was 5.8 ± 0.031 % when the samples were heated to 100 °C for 24 hours. The most abundant major elements for both samples apart from the structural elements (Al, Si, Fe and O) were potassium, sodium, calcium and magnesium. There was a high content of heavy and rare earth metals such as strontium (Sr), zirconium (Zr), lanthanum (La), rubidium (Rb) and cerium (Ce) in both samples. Comparison of the mineral composition for both the major and minor elements between the white and green clinoptilolite particles revealed a high degree of similarity (Figure 2.4). The correlation coefficients (r^2) were 97.3 % and 99.9 % for the minor and major elements, respectively, where the minor elements lanthanum, cobalt and vanadium were slightly higher in the white-coloured clinoptilolite particles.

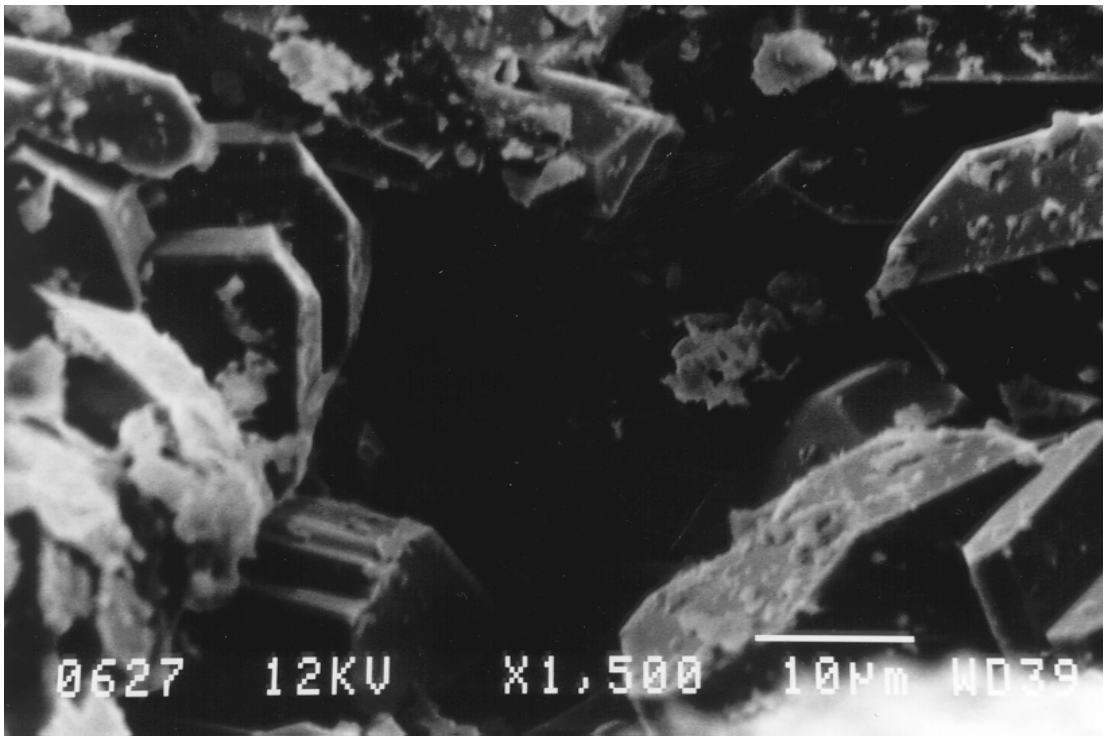

Figure 2.2: Scanning electron micrograph of Pratley clinoptilolite (x1500) showing the normal tabular and pseudo-orthorhombic or trapezoidal crystalline morphology

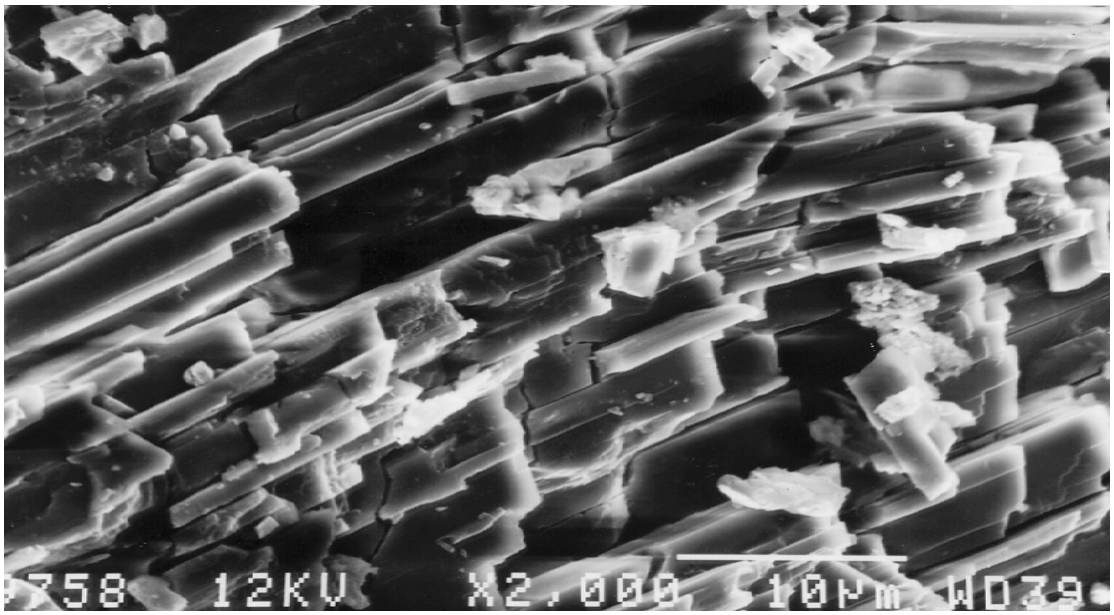

Figure 2.3: The scanning electron micrograph of the sedimentary Zambian laumontite (x2000) showing the small prismatic and columnar crystalline morphology

Table 2.2: X-ray fluorescence results of the minor elements for Pratley vulture creek Clinoptilolite showing compositions of the elements (μg/L) and the ratio of each element (white to green) based on the estimated concentrations in the mineral. Means ± standard deviations are based on analysis of 3 replicates for each of the two samples (white and green)

Name of Element	White (μg/L)	Green (μg/L)	L.L.D [a] (μg/L)	Ratio W:G
Zinc	30 ± 0.60	39.8 ± 0.60	1.50	0.75
Copper	6 ± 0.60	7.8 ± 0.60	1.80	0.77
Nickel	n.d.	n.d.	1.80	
Niobium	37 ± 0.38	41.6 ± 0.38	1.22	0.89
Zirconium	151 ± 0.35	170.1 ± 0.36	1.13	0.89
Yttrium	27 ± 0.35	30.7 ± 0.36	1.13	0.88
Strontium	615 ± 0.93	561.9 ± 0.90	1.13	1.09
Rubidium	102 ± 0.54	101.7 ± 0.54	1.16	1.00
Cerium	73 ± 1.24	67.7 ± 1.23	3.19	1.08
Neodymium	26 ± 0.62	24.8 ± 0.62	1.67	1.05
Lanthanum	128 ± 0.82	41.0 ± 0.61	1.40	3.12
Cobalt	n.d.	n.d.	1.60	
Chromium	2 ± 0.20	1.0 ± 0.20	0.90	2.00
Vanadium	3 ± 0.30	1.4 ± 0.30	1.40	2.14
r^2 (%)				97.3

[a] L.L.D = Lower limit of detection; n.d. = not detectable

Table 2.3: X-ray fluorescence results of the major elements for Pratley vulture creek clinoptilolite and the ratio between the white (W) and green (G) particles based on the estimated element compositions. Coefficient of determination = r^2

Oxide (weight %)	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**FeO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**MnO**	**Cr_2O_3**	**NiO**	**[a]LOI**	**[b]H_2O**	**Total**	**r^2 (%)**
Corrected analysis Fe_2O_3 (white)	68.07	11.02	1.20	n.d.	0.78	1.06	2.06	3.04	0.13	0.02	0.02	n.d.	n.d.	6.80	5.73	99.94	
Corrected analysis Fe_2O_3 (green)	65.93	12.43	1.29	n.d.	0.86	1.06	1.88	3.60	0.15	0.02	0.03	n.d.	n.d.	7.02	5.79	100.05	
Mean	67.00	11.73	1.25		0.82	1.06	1.97	3.32	0.14	0.02	0.03			6.91	5.76	99.99	
Ratio W:G	1.03	0.89	0.93		0.91	1.00	1.09	0.84	0.87	1.11	0.67						99.92

[a] LOI stands for the Loss On Ignition (CO_2, H_2S and other gases) at 1000 °C

[b] H_2O is lost water after raising temperature to 100 °C for 4 hours

n.d. = not detected

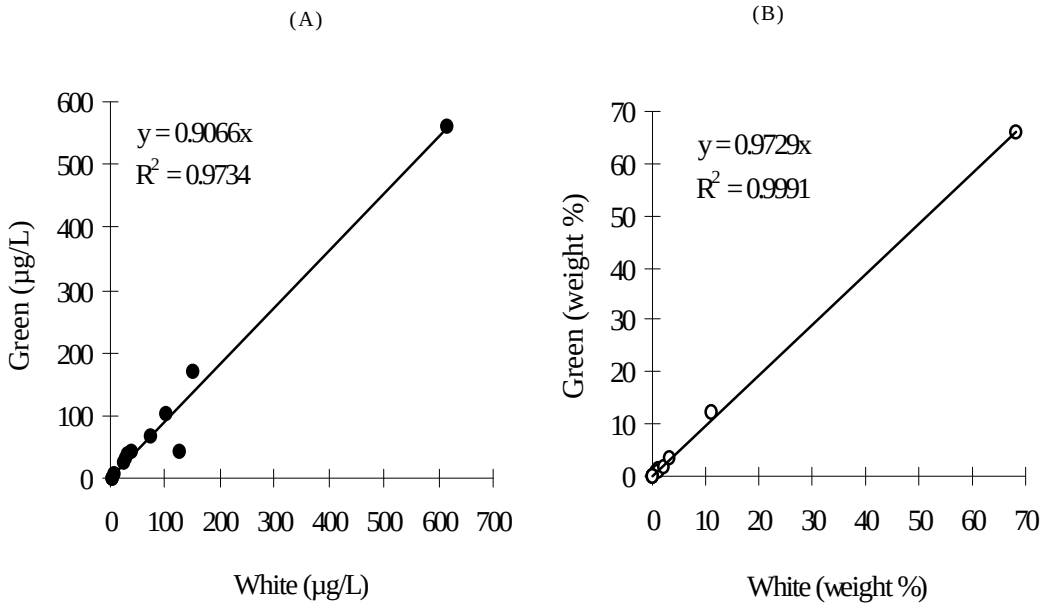

Figure 2.4: The simple linear regression analyses showing the comparison of the estimated mineral composition of the two samples and the coefficients of determination (r^2). Graphs A and B are the regression lines of the minor and major elements, respectively.

The results from the NH_4^+ exchange capacity studies indicate a substantial difference in the calculated capacities between the clinoptilolite samples and the laumontite zeolite (Table 2.4). Pratley clino had a higher average ammonia CEC of 14.94 mg g^{-1} (1.07 meq g^{-1}) for all particle sizes when compared to 2.77 mg g^{-1} (0.20 meq g^{-1}) for the Kafue sample. The CEC range for Pratley clino was from 12.07 to 16.86 mg g^{-1}. The results of the Kafue sample are of a single treatment as insufficient material was available for replication. Unfortunately, the laumontite was extremely friable or structurally weak and broke down easily to produce fines.

Table 2.4: Ammonia exchange capacities of a clinoptilolite sample of South African origin for five different particle size ranges and one laumontite sample from the Kafue area of Zambia

Sample mass (g)	**Particle Size range (mm)**	**CEC in mg NH_4^+ g^{-1} of zeolite**	**CEC in meq NH_4^+ g^{-1} of zeolite**	**Model** y = mg NH_4^+ absorbed g^{-1} x = mg NH_4^+ at outflow
		Clinoptilolite		
30	1.0 - 2.0	12.07	0.86	$y = 0.524+e^{-13.56+(1.150)x}$; r = 0.97
20	1.0 - 1.4	13.65	0.97	$y = 0.524+e^{-13.56+(1.150)x}$; r = 0.97
20	1.0 - 1.4	14.94	1.07	$y = -0.171+e^{-11.03+(0.893)x}$; r = 0.99
20	0.7 - 1.0	16.07	1.15	$y = -0.143+e^{-15.65+(1.168)x}$; r = 0.99
20	0.7 - 1.0	15.37	1.11	$y = -0.162+e^{-14.95+(1.075)x}$; r = 0.98
30	0.5 - 1.0	14.08	1.00	$y = -0.009+e^{-21.62+(1.700)x}$; r = 0.99
20	0.3 - 0.6	16.45	1.17	$y = -0.016+e^{-43.76+(2.793)x}$; r = 0.99
20	0.3 - 0.6	16.86	1.20	$y = -0.032+e^{-51.32+(3.180)x}$; r = 0.99
		Laumontite		
30	0.5 - 1.0	2.77	0.20	$y = 0.454+e^{-3.222+(1.898)x}$; r = 0.97

The curves in figure 2.5 show the relationship between the ammonia concentration in the effluent and the accumulated amount of ammonia absorbed by the zeolite. Breakthrough in this experiment was defined as the milli-equivalents (meq) of ammonia nitrogen (NH_4-N) removed per gram of zeolite at that point in time when the influent ammonia concentration was equal to the effluent ammonia concentration (Colella *et al.,* 1983; Murphy *et al*., 1994). The ammonia breakthrough of both samples was exponential and ammonia values increased rapidly once ammonia began to leak through the ion exchange column. Each curve was fitted with a model (table 2.4) to explain the relationship between effluent and accumulated amount of ammonia absorbed by the zeolite.

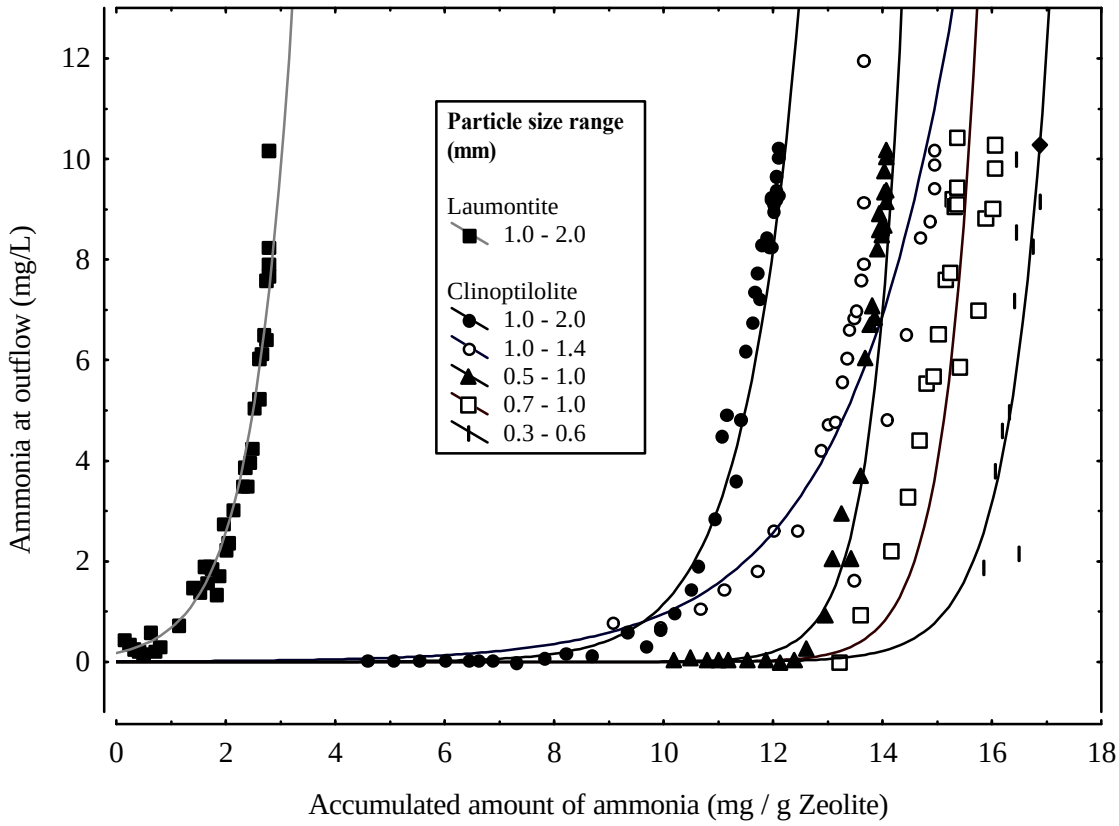

Figure 2.5: Ammonium levels (NH_4^+ mg L^{-1}) at the outflow of the exchange columns for different particle size ranges (Pratley clino) and types (laumontite versus clinoptilolite) as a function of the accumulated amount of ammonium g^{-1} of zeolite.

The exponential increase in effluent ammonia concentration was evident in all particle sizes with particularly high increases in the smallest particle size range (Figure 2.5). The effect of particle size on the CEC values was modeled using least square regression analysis (Fig. 2.6). CEC increased linearly as the particle size of the zeolite was reduced and showed the following trend, $y = 18.29 - 3.704\,x$ ($r^2 = 74\%$, $p<0.006$)

where: y = CEC in mg NH_4^+/g of zeolite and

x = particle size of the zeolite in mm

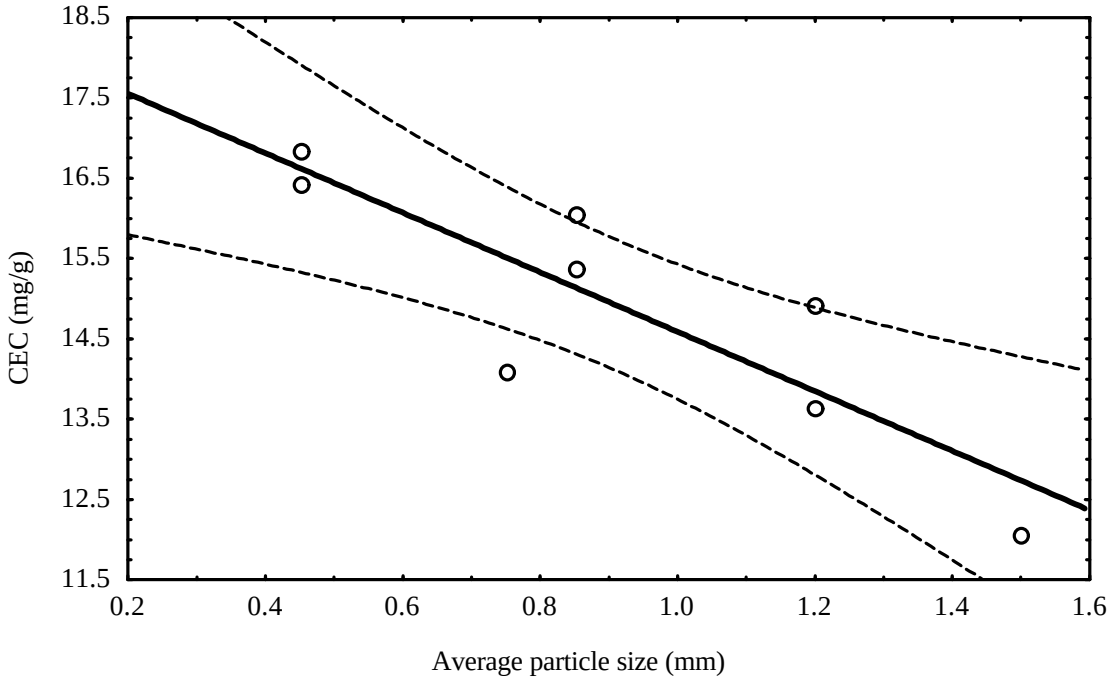

Figure 2.6: The linear regression model (Y =18.29-3.704x; r^2=74%) ± 95% confidence intervals of calculated cation exchange capacities (CEC) for Pratley clinoptilolite for five different particle size ranges.

There were no nitrate or nitrite ions detected in the effluent solution. However, there was a noticeable decline in pH from around 8 to 6 during the course of the experiment. The temperature of the solution was within the range of 15 – 25 °C.

2.5 Discussion

The unknown Zambian sample was identified and characterized as laumontite which is among the eight zeolites listed as being sufficiently abundant in sedimentary deposits as an industrial commodity (Pansini, 1996). This zeolite also has a high theoretical CEC (4.25 meq g^{-1}) that can be exploited in ion exchange processes. Unfortunately, there is no published information of the geological distribution of zeolites in Zambia. This data will therefore make a contribution to the database on Zambian zeolites and may provide an incentive for future investigations. Additional data are necessary for the mineral content and chemical composition, homogeneity of the sample and a proper geological description of this deposit. It will be important to know the size and grade of the deposits, their mineralogy, transportation and processing costs and environmental considerations. These factors are important because they affect the economics of the possible applications and thus will be useful in estimating the economic potential of this deposit.

XRF analysis for the major and minor elements of Pratley clino showed a typical general element composition of sedimentary clinoptilolite and fits the general formula provided by the suppliers. K^+ and Na^+ are the predominant exchangeable cations followed by Ca^{2+} and Mg^{2+}, other major elements are in small amounts and therefore are not likely to be significant in ion exchange. Since K^+, Na^+, Ca^{2+} and Mg^{2+} are present in high amounts in typical fish farm water, this zeolite would not have a toxic effect on the aquatic organisms when used in aquaculture water treatment. The XRF analyses results are within the range of values for minor and major elements of clinoptilolite given by Gottardi and Galli (1985). Heavy and rare earth metals such as zirconium (Zr), strontium (Sr), rubidium (Rb), lanthanum (La) and cerium (Ce) were high in this sample. However, rare earth metals are highly immobile and thus would not take part in the ion exchange process and pollute the treated water. Although the analysis lists many minor elements, most of these are bound in insoluble silicate minerals and are therefore not available to the system during the ion exchange process (Sheppard, 1983). In general, only those elements or cations in the cation exchange positions in the zeolite mineral will be available.

The high degree of similarity revealed by the W:G ratios and the estimated coefficient of determination (r^2) values demonstrates that the white and green particles can be regarded as the same mineral, since they were closely correlated in their element composition for both major and minor elements. Difference in coloration could be due to iron oxides (Gottardi and Galli, 1985).

The average ammonia exchange capacities for clinoptilolite and laumontite were estimated as 1.07 and 0.20 meq g^{-1}, respectively. These values are lower than the theoretical equilibrium exchange capacities, which are calculated on the basis of the unit-cell formula (Colella, 1996). However, the observed capacities for the clinoptilolite sample are within the range (0.8 - 2.5 meq g^{-1}) of values given by other authors for this zeolite (Koon and Kaufman, 1975; Klieve and Semmens, 1980; Ciambelli *et al*., 1983). Differences in CEC can be explained by factors such as the purity of the rock ore, the type and degree to which it is pre-activated, the cation composition of the zeolite and the composition of the water being treated. As stated in the literature review (chapter 1), different deposits of the same zeolite behave differently in their cation exchange characteristics.

The NH_4^+ capacity of the Pratley clinoptilolite could be lower than the theoretical value for this zeolite due to the purity of the rock ore that was estimated as 47 %. The Kafue sample had a lower capacity for ammonia exchange than the Pratley clino probably because laumontite has a high amount of calcium in its regular framework while clinoptilolite is sodium based. Calcium ions have a larger size (19.2 Å) and a higher affinity for the water held in the zeolite framework as opposed to sodium ions that have a smaller hydrated diameter (15.8 Å) and are therefore freer to migrate through the zeolite channels where they are exchanged (Koon and Kaufman, 1975).

The low CEC values for the laumontite also indicate that the zeolite content of the sample is very low. According to Hawkins (1983) all mined zeolites contain amounts of quartz,

feldspar, clay minerals, cristobolite/tridymite, calcite, gypsum and unreacted volcanic glass, which are natural constituents of the zeolitic bed itself or contaminants (few mined zeolites contain 100% of a single zeolite). To estimate the zeolite content of this sample, measured values were compared with those of pure laumontite. From these results, the Kafue sample contained approximately 4.7 % zeolite, calculated on the basis of its ion exchange capacity (0.20 meq g^{-1}) when compared to that of pure laumontite (4.25 meq g^{-1}). This could limit the application of this zeolite in water treatment. However, this zeolite can still be used if larger amounts are used in the filters. Otherwise, suitable methods of purifying or beneficiating this rock ore to improve its effective ammonia CEC should be considered.

It was observed that ammonia breakthrough of both samples was exponential (ultimately sigmoid) and that the ammonia concentration in the effluent increases rapidly once the ammonia begins to leak through the ion exchange column. This has also been reported by Slone *et al*. (1981). Smaller particles also attain breakthrough or are saturated much faster than large particle sizes once ammonia starts to leak through the column. This is indicated by the models for the breakthrough curves where the highest slopes are exhibited by the smallest particle sizes. Large particles were less efficient than smaller particle sizes in removing ammonia from the water. This is in accordance with results obtained by other workers who have also observed that the CEC increases as the particle size is reduced (Marking and Bills, 1982). This is because pore diffusion which affects the rate of equilibrium increases with reduction in particle size and therefore speeds up the exchange process. However, although smaller sizes were more efficient, these tend to clog more easily than larger particle sizes and may therefore be impractical for filtering water used in fish culture (Dryden and Weatherley, 1987a). Water flow rate is also generally impeded if particles are too small. For these reasons, the most suitable and recommended size from this study was the 0.5 – 1 mm particle size range (18 x 35 mesh). Absence of nitrite and nitrite ions indicated that no autotrophic bacteria were present within the column such that absorbed ammonia must have been taken up by the zeolite samples.

2.5.1 Conclusion

The use of zeolites and in particular Pratley vulture creek clino in intensive aquaculture systems seems promising due to the efficient NH_4^+-N removal. The present work does indicate advantages in using the Pratley vulture creek clino in the field of aquaculture. Studies should be done on pilot fish farms to evaluate the absorption efficiency in the presence of fish. The Pratley clinoptilolite was more efficient in ammonia absorption than laumontite and would therefore be more desirable for use in water treatment. For the Kafue sample, there is need to find suitable ways of purifying the zeolite to improve its absorption efficiency. Increasing the strength of this zeolite through the use of a binder (to make pellets) may further result in better performance. The capacity of zeolites for ammonia is influenced by the concentration of ammonia ions and competing ions such as calcium, magnesium, sodium and potassium in solution. The reported exchange capacities would not be valid for any combination of competing ions. Thus, these estimates provide a basis which needs further testing in aquaculture systems. They are thus an estimate of maximum capacities that may be expected when these samples are used in any aquaculture system (Dryden and Weatherley, 1987a, 1987b). However, data is needed on solutions containing competing ions. Therefore, another objective of this study will be to look at ways of using Pratley clino in fish rearing systems, so that the effect of competing ions on NH_4^+-N exchange capacity can be established.

CHAPTER 3

Equilibrium and capacity data of Pratley clinoptilolite

3.1 Introduction

The most commonly applied method of estimating the cation exchange capacity is the column method that has been described in the previous chapter. However, another method used for the removal of specific cations from solution is available. This method is known as the batch procedure and involves mixing the zeolite with the solution to be treated and then separating the zeolite and the solution by sedimentation and/or filtration. There does not appear to be a difference in separation procedure between a column and batch procedure. In both procedures, the substance of interest becomes attached to the ion exchanger on its cation exchange sites. However, the column method is preferred because of its efficient use of the zeolite (Pharmacia Fine Chemicals, 1980). This is because the column method provides continuous contact between the solution and the zeolite, thereby enabling the exchange reaction to go to completion as the solution passes slowly through the exchange bed. The zeolite is thus more effectively used in column processes because it approaches an equilibrium state with the influent solution. In addition, if zeolite is being used in aquaculture systems it is likely to be packed into the filter with water flowing around it, rather than in a batch process. However, it may be more expensive due to the cost of exchange columns when compared with the relatively inexpensive tanks and equipment used to mix and separate the zeolite in batch processes (Semmens, 1983).

In mixed or batch systems, however, the zeolite approaches an equilibrium state with the whole solution. Although batch procedures are less efficient and preferred than column methods, they have certain advantages especially in large-scale processes (Sheppard, 1983). Information from a batch procedure may be useful in estimating zeolite requirements if the concentrations of ions in the water are not too variable (Semmens,

1983). Although waste waters contain a complement of cations such as calcium, magnesium and sodium, if one is concerned with the removal of a specific ion such as ammonia, it may be possible to develop an isotherm for the ammonium ions using a batch method (Ames, 1965; Semmens *et al.,* 1978). An ion exchange isotherm has been defined by Dyer (1988) as a pictorial representation of the equilibrium concentrations of the equivalent fractions of the respective ions in both solution and zeolite phases. It conveniently characterizes the stoichiometric reactions occurring during ion exchange. However, when large changes take place in the ionic composition of the water, ion exchange using the batch procedure may be erroneous (Semmens, 1983). Therefore, there is need to carry out tests to establish the optimum conditions of the batch method and compare its efficiency to the column exchange method.

This experiment will therefore look at the efficiency of the batch method in estimating the ammonia cation exchange capacity of Pratley vulture creek clino and compare the estimated CEC values with those of the column method given in the previous chapter. It is necessary to see the efficiency of the batch method in CEC evaluation. Batch studies were conducted to measure ammonia ion exchange capacities directly and to determine whether the data collected in batch studies could be employed to predict column performance.

3.2 Materials and Methods

Pratley vulture creek clino was the only sample available for this study. To determine the ammonia exchange capacity using the batch method, static tests were performed using a shaker. The zeolite was sieved to 0.7 - 1 mm and 1 - 1.4 mm (18x25 and 12x18 US mesh sizes, respectively) and all samples were washed with distilled water to remove any fine material. These samples were then dried for 24 hrs at 105 °C. Pre-treatment to convert the clinoptilolite to the sodium form was done by placing a gram of each sample into a

container to which 250 ml of 1N NaCl solution was added. The containers were sealed and the mixture was shaken for 2 hours. The treated zeolite was rinsed with distilled water to remove all the excess sodium chloride as well as the chloride ions. Each particle size test was replicated six times, with new material used for each test.

Ammonia exchange capacity was measured by putting a gram of the pre-treated zeolite into a 500-ml container to which 250 ml of 10 mg L^{-1} ammonium chloride (NH_4Cl) solution was added. The six replicates of the two particle sizes that had been pre-treated were used for the estimation of the ammonia CEC. The containers were shaken for 2 hours after which a sample of the water from each container was analyzed for its ammonia content. The clinoptilolite was then filtered and contacted with an additional 250 ml of the NH_4Cl solution. This procedure was repeated until there was no difference between initial and final ammonia concentrations after shaking, implying that the zeolite exchange sites were saturated with ammonium ions. Control samples with no added clinoptilolite and 10 mg L^{-1} NH_4Cl solution were shaken as in the experimental containers. The ammonia exchange capacity was calculated using the following formula;

$$NH_4 \text{ CEC (mg g}^{-1}) = \Sigma C_Z \quad (3.1)$$

where C_Z is the difference between the initial and final concentration of NH_4^+ ions in solution before and after shaking after adjusting for any ammonia losses in the control. Summation of all C_Z values per replicate is equal to CEC since 1 gram of clinoptilolite was used. This data was used to plot ion exchange isotherms where the y-axis values were cumulative C_Z (mg g^{-1}) after each shaking and x-axis values were the cumulative amount of NH_4^+ ions remaining in solution (C_S) after each shaking and zeolite absorption.

To quantify the effect of pre-treatment on the ammonia absorption efficiency of clinoptilolite a test was conducted using zeolite that was only washed with distilled water and immediately contacted with the 10 mg L^{-1} ammonium chloride solution. The same particle sizes (1.0 - 1.4 and 0.7 - 1.0 mm) as in the previous experiment were used to

estimate ammonia CEC of untreated clinoptilolite (Table 3.1). There were two replicates for each particle size. The ammonia exchange capacity for untreated clinoptilolite was also calculated as described above (Equation 3.1).

Table 3.1: Experimental design and data used for the Kruskal-Wallis non-parametric test for the pre-treated and untreated clinoptilolite (total $N = 16$)

Factor or Treatment	Levels (Particle size mm)	Replicate observations
1N NaCl treated clinoptilolite	0.7 - 1.0	6
	1.0 - 1.4	6
Untreated clinoptilolite	0.7 - 1.0	2
	1.0 - 1.4	2

Kruskal-Wallis non-parametric test was used to determine statistically significant differences between means of estimated ammonia CEC values for the pre-treated and natural clinoptilolite samples and between the two particle sizes ranges. Analysis of covariance (ANCOVA) was used to determine whether significant differences were present in slopes of ion exchange isotherms of the pre-treated and natural clinoptilolite and between particle sizes (Zar, 1974). Logarithms of the amount of NH_4^+ ions in solution (C_S) and absorbed on the zeolite (C_Z) were used to get linear equations to be used in the ANCOVA procedure.

3.3 Results

Average ammonia CEC values for the pre-treated clinoptilolite were 12.63 ± 0.34 mg g^{-1} and 11.39 ± 0.56 mg g^{-1} for the 0.7 - 1.0 and 1.0 - 1.4 mm particle sizes, respectively (Table 3.2). Ammonia CEC was lower for the untreated clinoptilolite for both particle sizes (0.7 - 1.0 and 1.0 - 1.4 mm), 10.14 ± 0.11 mg g^{-1} for the former and 8.58 ± 0.23 mg g^{-1} for the latter. Analysis of variance (Kruskal-Wallis non-parametric test) results suggested that there were significant differences ($P < 0.05$) in average ammonia CEC values between the pre-treated and untreated clinoptilolite samples. However, there were no significant differences ($P > 0.05$) in ammonia CEC between the two different particle sizes tested for both the pre-treated and natural clinoptilolite samples using non-parametric Kruskal-Wallis test.

The results of the ion exchange reactions obtained for the pre-treated and untreated clinoptilolite were plotted into ion exchange isotherms (figures 3.1 and 3.2). Isotherms show the comparison between actual data points and model predictions for NH_4 absorption by the zeolite. Results of the ANCOVA procedure showed that there were no significant differences ($0.22 > P > 0.05$) between slopes of the models for the pre-treated and natural clinoptilolite ($F_{0.05(1)3,82} = 1.48$). There were significant differences ($P < 0.05$) among slopes of the two different particle sizes with the 0.7 – 1.0 mm particle size having a higher slope than the 1.0 – 1.4 mm particle size range. From the graphs, it is also apparent that each particle size yielded a separate curve. The results were replotted into Langmuir isotherms to show the linear relationship (figures 3.3 and 3.4).

Table 3.2: The calculated cation exchange capacities of Pratley clinoptilolite under different pre-treatment conditions and the isotherm model equations

Treatment	**Particle size range (mm)**	**CEC in mg NH_4^+ g^{-1} of zeolite**	**CEC in meq NH_4^+ g^{-1} of zeolite**	**Model** **y = mg NH_4^+ absorbed g^{-1} zeolite** **x = mg NH_4^+ absorbed in solution**
Pre-treated	0.7 - 1.0	12.97	0.93	y = 2.20 Ln(x) - 5.95 ; r = 0.98
		12.93	0.92	
		12.25	0.88	
		12.21	0.87	
		12.59	0.90	
		12.82	0.92	
	0 ± SD*	12.63 ± 0.34		
	1.0 - 1.4	11.93	0.85	y = 2.51 Ln(x) - 6.64 ; r = 0.98
		12.15	0.87	
		10.73	0.77	
		10.87	0.78	
		11.34	0.81	
		11.34	0.81	
	0 ± SD	11.39 ± 0.56		
Untreated	0.7 - 1.0	10.22	0.73	y = 2.71 Ln(x) - 2.35 ; r = 0.97
		10.07	0.72	
	0 ± SD	10.14 ± 0.11		
	1.0 - 1.4	8.75	0.62	y = 2.41 Ln(x) - 1.48 ; r = 0.97
		8.42	0.60	
	0 ± SD	8.58 ± 0.23		

Note: * 0 is the average of all replicates and SD is the standard deviation

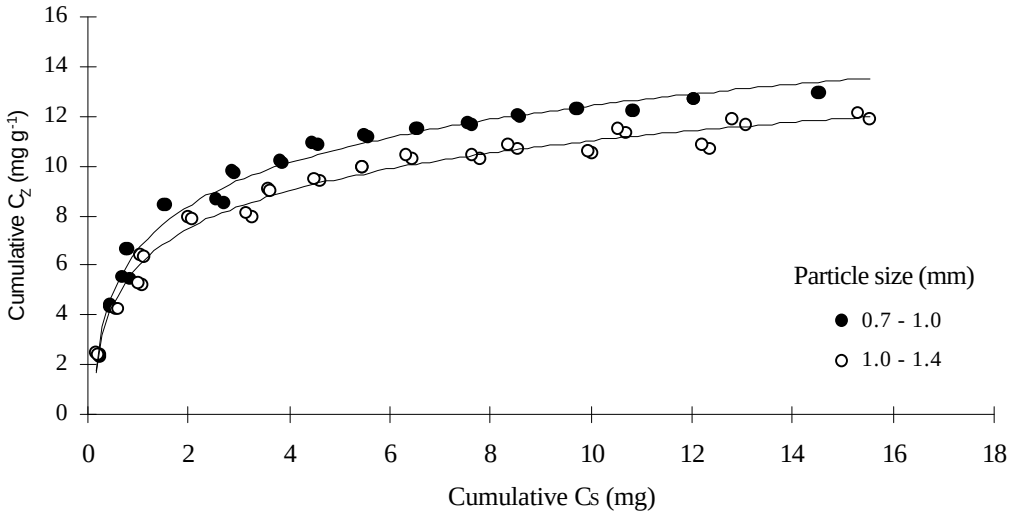

Figure 3.1: The $Na^+ \leftrightarrow NH_4^+$ ion exchange isotherms for ammonia exchange capacity using 10 mg L^{-1} NH_4Cl solution and pre-treated clinoptilolite (● $r^2 = 0.98$; o $r^2 = 0.98$).

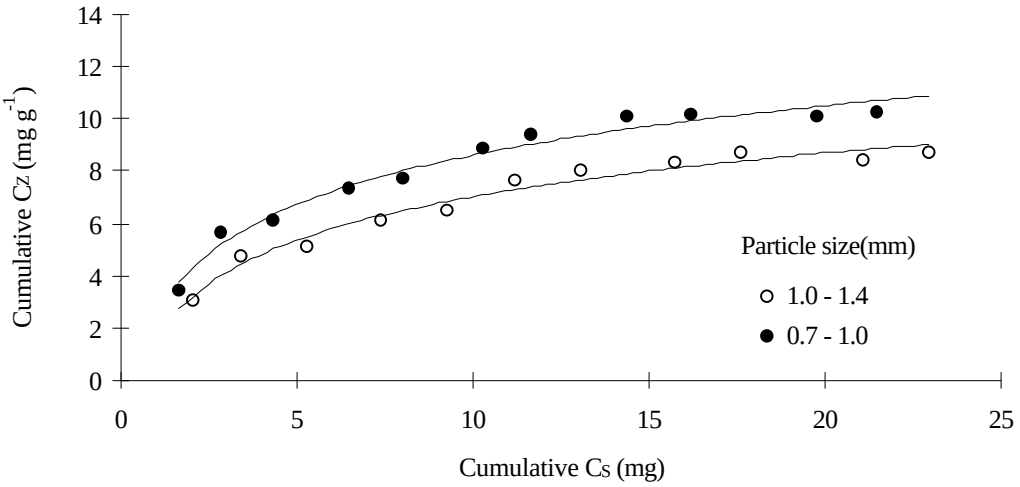

Figure 3.2: The $Na^+ \leftrightarrow NH_4^+$ ion exchange isotherms for ammonia exchange capacity using 10 mg L^{-1} NH_4Cl solution and untreated clinoptilolite (● $r^2 = 0.97$; o $r^2 = 0.97$)

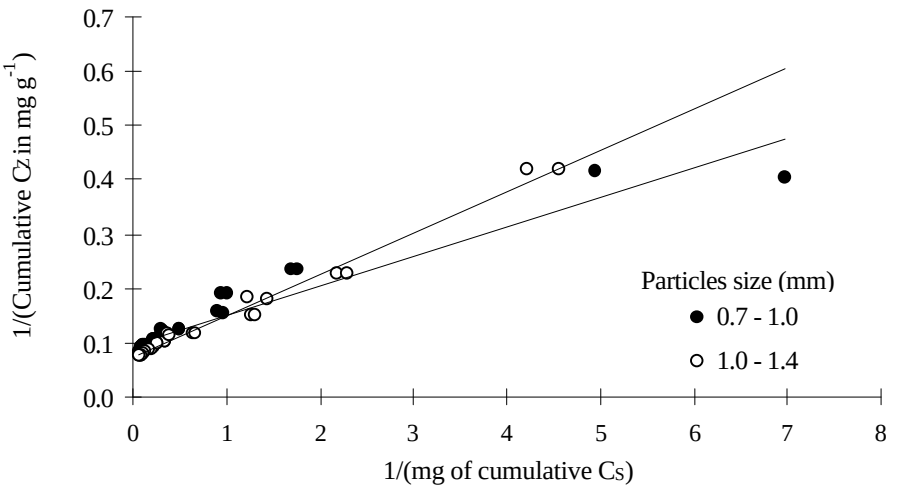

Figure 3.3: Batch equilibrium data for the two particle sizes of pre-treated clinoptilolite replotted into linear Langmuir isotherms (● $y = 0.076x + 0.074$, $r^2 = 0.99$; o $y = 0.054x + 0.097$, $r^2 = 0.92$)

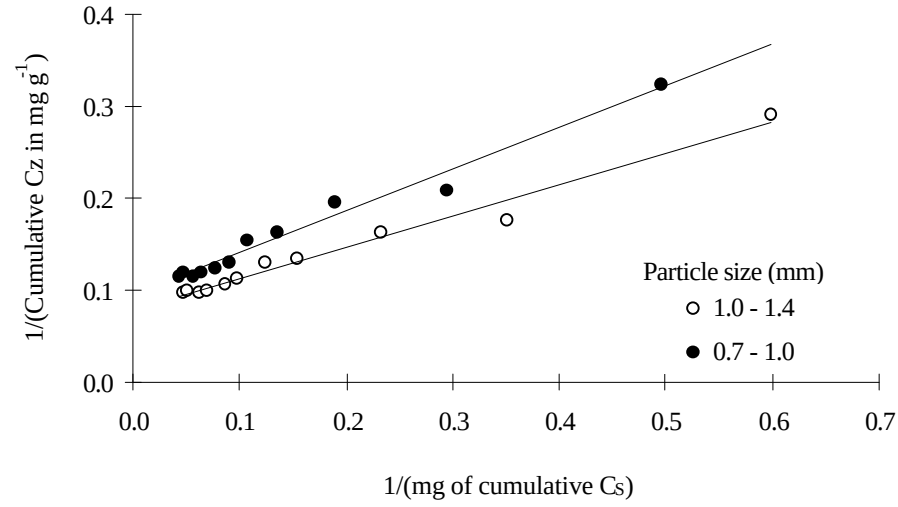

Figure 3.4: Batch equilibrium data for the two particle sizes of untreated clinoptilolite replotted into the linear Langmuir isotherms (● $y = 0.457x + 0.094$, $r^2 = 0.98$; o $y = 0.340x + 0.080$, $r^2 = 0.98$)

3.4 Discussion

3.4.1 Batch method

The average ammonia ion exchange capacity of the treated rocks was significantly higher than that of the untreated clinoptilolite suggesting that pre-treatment increased the ammonia exchange capacity of the zeolite. The shapes of the curves show that, especially in the early reaction stages, the $Na^+ \rightarrow NH_4^+$ exchange rate is higher for Na^+ exchanged zeolite than for untreated zeolite. This could be due to the presence of other exchangeable cations on the exchange sites of the natural or untreated clinoptilolite. From the XRF analyses results shown in the second chapter, the exchange sites of this clinoptilolite are composed of univalent potassium ions and divalent calcium and magnesium ions. Although clinoptilolite selectivity results in the preference Na^+ K^+ > Ca^{2+} Mg^{2+}, steric factors that affect both selectivity and diffusion of ions through the zeolites restrict the mobility of Ca^{2+} and Mg^{2+} ions more than that of Na^+ and K^+ ions, because calcium and magnesium have a stronger affinity for the structural water in the clinoptilolite framework (Koon and Kaufman, 1975). This results in superior exchange kinetics for sodium relative to calcium and magnesium, regardless of whether these ions are being displaced from the zeolite or entering it. Thus, Ca^{2+} and Mg^{2+} have lower diffusivity than either Na^+ or K^+, therefore correspondingly slower exchange kinetics (Semmens and Porter, 1979). Pre-treatment with a high salt solution assists in the removal of these divalent ions and makes more exchange sites available. It also removes carbonates and clay impurities that may block pores and interfere with both ion diffusion and liquid dispersion, thus limiting the number of available exchange sites on the zeolite structure (Klieve and Semmens, 1980). The results of this study agree with those obtained by Jorgensen *et al*. (1976), who found capacities of 0.76 meq g^{-1} and 0.65 meq g^{-1} for treated against untreated rocks, respectively. Murphy *et al.* (1994) found that pre-treatment increased the effective exchange capacity of clinoptilolite by over 5 % when compared with samples lacking any pre-treatment. In summary therefore, the capacity of natural zeolites can be improved by pre-treatment.

3.4.2 Comparison of batch and column method

Ion exchange isotherms are convenient and were used in this study because differences in ion preference during ion exchange reactions by exchangers can be explained by the shape of the isotherm. Variation in isotherm shape reflects the differences in the character of the solid surface, the size and shape of the pores, the porosity and surface area of the solid, and the energy of interaction between the adsorbed molecule and solid surface. A comparison of the shapes of the isotherm models between those obtained from the column method (data from chapter 2) and the batch method provides an insight into the kinetics of these different processes. To make such a comparison, the data from chapter 2 were plotted as ion exchange isotherms with predicted models (Table 3.3 and Figure 3.5). Since the service cycles of the ion exchange columns were operated to exhaustion in the column method, the measured capacities yielded values that could be plotted on an isotherm versus their corresponding influent ammonia concentrations. Analysis of both data sets using Kruskal-Wallis non-parametric test was done to compare the difference between the means of ammonia CEC values estimated by the batch and column methods. ANCOVA was also used to determine whether significant differences were present in slopes of isotherms. Logarithms of the amount of NH_4^+ ions in solution (C_S) and absorbed on the zeolite (C_Z) were used to get linear equations to be used in the ANCOVA procedure.

Table 3.3: Ammonium exchange capacity data and predicted ion exchange isotherm models of the ion exchange column method data from Chapter 2 for Pratley clinoptilolite and Zambian laumontite

Particle Size range (mm)	CEC in mg NH_4^+ g^{-1} of zeolite	CEC in meq NH_4^+ g^{-1} of zeolite	Isotherm Model y = mg NH_4^+ absorbed g^{-1} x = mg NH_4^+ in effluent
	Clinoptilolite		
1.0 - 2.0	12.07	0.86	$y = 0.5975 \ln(x) + 11.356$; $r^2 = 0.99$
1.0 - 1.4	14.30	1.02	$y = 1.5605 \ln(x) + 12.399$; $r^2 = 0.79$
0.7 - 1.0	15.72	1.12	$y = 0.5856 \ln(x) + 14.887$; $r^2 = 0.72$
0.5 - 1.0	14.08	1.00	$y = 0.6781 \ln(x) + 13.824$; $r^2 = 0.80$
0.3 - 0.6	16.66	1.19	$y = 0.4433 \ln(x) + 16.611$; $r^2 = 0.76$
	Laumontite		
0.5 - 1.0	2.77	0.20	$y = 0.3717 \ln(x) + 2.7409$; $r^2 = 0.93$

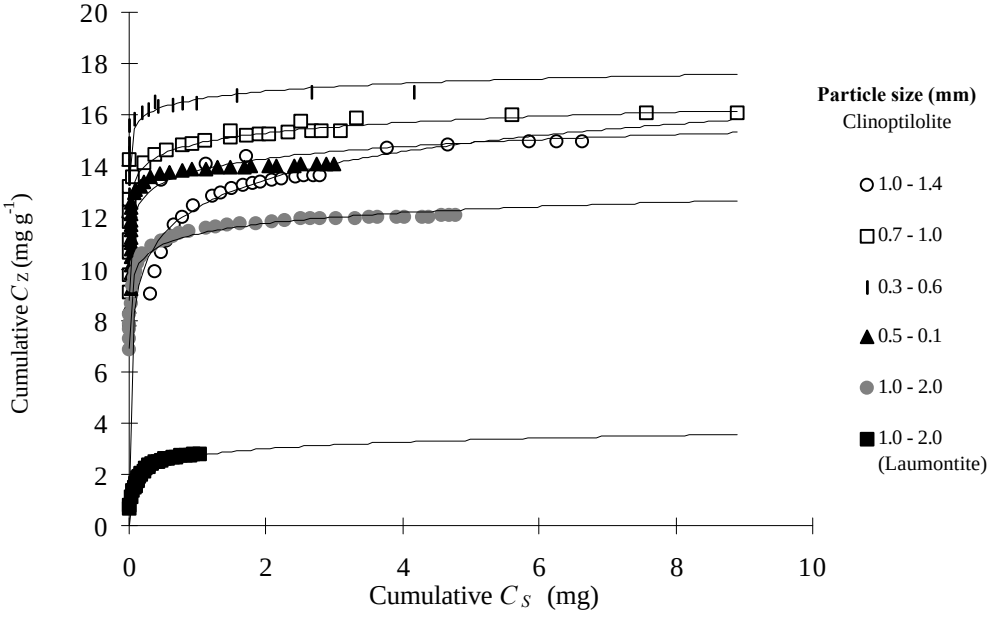

Figure 3.5: Isotherms developed from column breakthrough curves from the data of figure 2.5 (chapter 2) replotted to show the equilibrium relationship

The results suggested that there were significant differences in average ammonia CEC values between the batch and column ion exchange methods ($P < 0.05$). The column method estimated higher NH_4^+ ion CEC values of 15.72 mg g^{-1} and 14.30 mg g^{-1} when compared to those obtained for the batch method (12.63 mg g^{-1} and 11.39 mg g^{-1}) for the 0.7 - 1.0 mm and 1.0 - 1.4 mm particle size ranges, respectively. Estimated CEC values of the column method were 20 % higher for both particle sizes. There were significant differences ($P < 0.05$) in NH_4^+ ion exchange capacity between the different particle sizes tested for both ion exchange methods.

Results of ANCOVA showed that there were significant differences ($6 \times 10^{-12} < P < 0.05$) between slopes of the plots of the two methods ($F_{0.05(1)1,56} = 75.32$). Slopes of the linear equations for the different particle sizes were also significantly different ($P < 0.05$) for both the batch and column method. The slopes for the column method were higher than the slopes of the batch method results. The isotherm shapes derived (figures 3.1, 3.2 and 3.5) show that the mechanism of absorption by Pratley clinoptilolite and Zambian laumontite is one of volume filling of the micropores. All the isotherms followed the shape of curve 1 (figure 3.6) which is commonly known as the type I isotherm. A type I isotherm reflects a very strong interaction of water with the zeolite surface (Flanigen, 1983).

The results of this study are in agreement with Dryden and Weatherley's (1987b) suggestion that ammonia exchange on to sodium-based clinoptilolite could be a two stage process with the bulk of the exchange occurring in a fairly rapid first stage followed by a very slow approach to completion. The ion exchange isotherms for the batch and column methods, reflect that the NH_4^+ ion is selectively taken up by the clinoptilolite. The slopes of the models were not significantly different ($P < 0.05$) for the particle sizes for pre-treated and untreated clinoptilolite, indicating that the shapes of the ion exchange isotherms in both cases followed the same trend implying that the mechanism of absorption is the same.

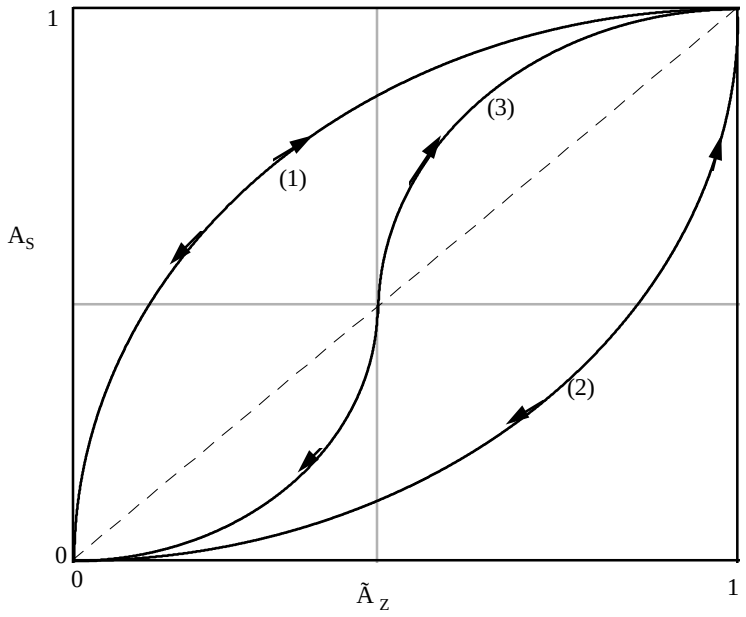

Figure 3.6: Idealised ion exchange isotherms (Dyer, 1988; Colella, 1996), where A_s is the ion concentration in solution and $\tilde{A}_z$ is the concentration on the zeolite. If the solid phase has equal preference for two cations A and B then the isotherm would be a straight line (dotted line on the figure). Isotherm (1) illustrates the case where A is selectively taken up by the zeolite, unlike isotherm (2) where A remains in solution whilst ion B is preferred by the zeolite. (3) Occurs in heterovalent ion exchange where the zeolite exhibits increasing preference or selectivity for the cation of higher charge. Arrows indicate the reversibility of the exchange reaction

The results of the pre-treated and untreated clinoptilolite (batch method) were replotted in linear form of a Langmuir isotherm which also incorporates the equilibrium relationship between the solid and the liquid phase ammonia concentrations (Barrow, 1966; McLaren and Farquhar, 1973). The good correlation (92 - 98 %) achieved by the Langmuir isotherm between the solid and liquid phases also indicates that the NH_4^+ ion is selectively

taken up by clinoptilolite and confirms indirectly that the slopes for the equations of the different particle sizes were not significantly different.

Differences in absorption efficiency between the two methods can be related to the different rates of attaining equilibrium. In practice equilibrium may be reached if perfect mixing is achieved and an adequate contact time is provided. The column method could have been more efficient because there was more contact time (about 36 hours) between the zeolite and the ammonium chloride solution. Cation exchange is not an instantaneous process; it takes time for ions to diffuse into and out of the zeolite (Semmens, 1983). If the contact time is inadequate for complete exchange, a larger quantity of zeolite must be employed. It is therefore suggested that the column method is more efficient in NH_4^+ CEC estimation.

The isotherms derived from the ion exchange column data, show that the Zambian zeolite laumontite is selective for the NH_4^+ ion following a type I isotherm shape and reflects a very strong interaction of ammonia ions with the zeolites surface. This agrees with the suggestions of the previous chapter to explore the possibilities of using this zeolite in water treatment. Operating characteristics of clinoptilolite filters determined in these experiments should be useful in designing water re-use systems with aquacultural applications.

CHAPTER 4

Evaluation of the cation exchange capacities of Pratley clinoptilolite after regeneration

4.1 Introduction

Regeneration is the process by which the ammonia ions adsorbed on the zeolite exchange sites during the water treatment phase are removed before the zeolite can be re-used. The regeneration methods commonly used in zeolite adsorption processes for the desorption of the adsorbed molecules include washing with tap water (pH 7.8-8.4), air drying, thermal and pressure processes, use of sodium-based solutions and biological regeneration. The most effective method is the use of caustic regenerant solutions (Klieve and Semmens, 1980). Washing with caustic solutions can only work if the regenerant solution has a concentration of counter ions (generally sodium ions) greater than that of the ammonia ions being replaced (Wheaton, 1982). The salt should contain a high concentration of the counter-ion of the ion exchanger to facilitate equilibrium, and it should remove any ion bound by ionic forces. As soon as the zeolite containing a large amount of ammonia ions is placed in a salt solution, ion exchange takes place according to equation 4.1, showing NH_4^+ displacement from the zeolite (*Z*) by the Na^+ ions in solution.

$$Z.NH_4^+ + Na^+ \leftrightarrow Z.Na^+ + NH_4^+ \qquad (4.1.)$$

Regeneration studies of fresh water columns showed that the ammonia binding capacity of zeolites can be easily restored (Johnson and Sieburth, 1974; Wheaton, 1982; Dryden and Weatherley, 1987a, 1987b). Regeneration of the zeolite is considered complete when the NH_4^+ concentration in the regenerant effluent reaches zero or a low value of about 0.1 mg L^{-1} (Semmens *et al.,* 1977). Marking and Bills (1982) observed that a brine solution of pH 11-12 was sufficient in removing the ammonia ions adsorbed on clinoptilolite. Other

authors have used caustic solutions such as sodium hypochlorite to restore the ammonia exchange capacity of the zeolites (Klieve and Semmens, 1980). However, some work has demonstrated that the clinoptilolite framework is altered when caustic solutions were used. This was shown by loss in weight of the zeolite per regeneration cycle (Koon and Kaufman, 1975).

Heat has been used in regenerating zeolites used in ammonia ion exchange. Results from tests by Murphy *et al*. (1994) on thermally regenerated clinoptilolite indicated that samples regenerated at 500 °C had an effective exchange capacity similar to that of the virgin clinoptilolite. Thermal regeneration was more effective at 500 °C and 600 °C where 80% and 90% of ammonia was desorbed, respectively than at 300 °C and 400 °C (25% and 65%, respectively). These differences could be due to the oxidation of larger quantities of ammonia to nitrogen at higher temperatures (Murphy *et al*., 1994).

However, though all these methods of regeneration are available, the choice of the most suitable method for a particular system is not a trivial problem. This is because regeneration is one of the major costs of running an ion exchange system and if done effectively can reduce running costs substantially and optimise the ion exchange process. It constitutes a significant fraction of the total cost of the ion exchange process and has been estimated to represent about 50 to 60 % of the total ion exchange treatment costs (Semmens and Porter, 1979). Optimum regeneration would make the ion exchange process an attractive method for removing toxic ammonia from water when compared to other water treatment methods. Therefore, the use of brine in regeneration where ion exchange filtration is desired is more practical due to its easy availability and lower cost as opposed to other regenerant solutions or methods. Furthermore, chemical regeneration using salt solutions gives better breakthrough capacities when compared with other methods (Koon and Kaufman, 1975; Klieve and Semmens, 1980; Murphy *et al.,* 1994). Sea water has also been successfully used and would be highly beneficial in places situated near the coast (Wheaton, 1982).

Using brine solutions is also practical because the ammonia collected by the solution can be easily removed from the salt or regenerant solution (Semmens *et al.,* 1977). This can be accomplished by either aerating the salt solution or removing the ammonia as a gas or biologically oxidising (using nitrifying bacteria) the NH_4^+ to nitrate. The economics of an ion exchange process therefore clearly depend on the optimum use of regenerant chemicals. The ease and efficiency of the regeneration of the exhausted exchange material will determine an ion exchange system's practicality.

The objective of this section of the study was therefore to identify the influence of exhaustion and regeneration cycles on the ammonia removal performance of Pratley clinoptilolite in column and batch processes. The effective regeneration of the zeolite following maximum uptake of the ammonia ion was examined in relation to the conditions during exhaustion. Exhaustion refers to the experiments (chapter 2 and 3) when the clinoptilolite samples were initially contacted with 10 mg L^{-1} NH_4Cl solution up to breakthrough or saturation to determine their total ammonia exchange capacities. The main objective of this laboratory study was to identify operational difficulties and offer some design characteristics that would be desirable on a larger scale study.

4.2 Materials and Methods

The exhausted Pratley clinoptilolite samples used in the ammonia CEC estimation using the ion exchange column and batch procedures (Chapters 2 and 3) were used as material for this study. This trial was done in two parts. The first part was the regeneration process to remove the adsorbed ions from the zeolite and the second part were experiments to observe the efficiency of the regenerated zeolite in NH_4^+ ion exchange. The two methods of estimating ion exchange that were evaluated and compared in the previous chapter were used to collect the CEC data. For the column method, approximately 20 g of previously exhausted clinoptilolite was contacted with 4 litres of distilled water to remove all the ammonia ions in solution. The clinoptilolite was then drained and dried at 105 °C for 24 hrs.

The particle size ranges of Pratley clinoptilolite available for this study were 0.295 - 0.595, 0.7 - 1 and 1 - 1.4 mm which are denoted as 30x50, 18x25 and 14x18 US standard mesh sizes, respectively. A regenerant solution was prepared by dissolving sodium chloride in distilled water made up to a concentration of 1N NaCl (Dryden and Weatherley, 1987a, 1987b). Exchange columns consisted of 50-ml-burettes filled with 20 g of each sample. Each sample was supported on a glass wool plug inside the column. The columns were then contacted with the 1N NaCl solution until there were no ammonia ions in the effluent solution. It normally took about 5 litres of the NaCl solution to accomplish this. Each particle size was replicated twice with new material used for each test. After treatment with the regenerant solution, the clinoptilolite columns were immediately washed with distilled water to remove all the excess chloride ions. About four litres of distilled water was used during this phase. The effective ammonia exchange capacity of the regenerated clinoptilolite was subsequently determined by passing a solution of 10 mg L^{-1} NH_4Cl through the column according to the procedure described in chapter 2.

In the batch procedure, regeneration was achieved by shaking 1 g of the previously exhausted clinoptilolite with 250 ml of 1N standard sodium chloride solution for 2 hours. A standard of two hours recharge time was chosen based on the results of Mumaw *et al.* (1981) and Semmens *et al.* (1977) for chemical regeneration of clinoptilolite filters. After recharge, the samples were rinsed with distilled water to remove all excess regenerant solution. The clinoptilolite was then filtered and contacted for 2 hours with 250 ml of the 10 mg L^{-1} NH_4Cl solution. A sample of the solution from each container was analysed for ammonia. This procedure was repeated until there was no difference between the initial and final ammonia concentration after shaking, implying that the zeolite exchange sites were saturated with ammonia ions. The saturated samples were washed with distilled water. Two particle sizes (0.7 - 1.0 and 1.0 - 1.4 mm) were used in this experiment and each test was replicated twice with new material for each test. The equilibrium data were determined indirectly by analysing the ammonia taken up by the clinoptilolite and analysing the change in ammonia concentration in the solution. Ammonia CEC was estimated according to Equation 3.1 (Chapter 3) and batch isotherms were plotted. Ammonia was analysed by nesslerization (APHA, 1989).

Non parametric Kruskal Wallis test was used to test for significance in estimated ammonia CEC values between samples regenerated using the batch and column methods at different particle sizes. Analysis of covariance (ANCOVA) was used to determine whether significant differences were present in slopes of isotherm models derived for column and batch regenerated samples, as well as for the different particle size ranges. In order to get linear equations for ANCOVA, the x and y values (cumulative C_S and C_Z, respectively) of the isotherm models were log-transformed. ANCOVA was also used to determine whether significant differences were present in slopes of isotherm models derived for regenerated and unregenerated samples, and the different particle size ranges.

4.3 Results

4.3.1 Column method

Average ammonia capacities for regenerated clinoptilolite from the ion exchange column method were 17.44 ± 0.1 mg g^{-1}, 17.50 ± 3.0 mg g^{-1} and 17.32 ± 1.5 mg g^{-1} for the 0.3 - 0.6, 0.7 - 1.0 and 1.0 - 1.4 mm particle size ranges, respectively (table 4.1). The results of the ion exchange reactions obtained for each particle size were plotted into breakthrough graphs using least square regression analysis and are presented in figure 4.1. There was an average correlation of 98 ± 0.084 % for the three least square models. The isotherm curves for the three particle sizes are presented in figure 4.2, with the fitted predicted models. The equations for the predicted isothermal models are presented in table 4.2. There were significant differences ($P < 0.05$) between slopes for all particle sizes.

Table 4.1 : NH_4^+ exchange capacities of Pratley clinoptilolite for three different particle sizes after regenerating the zeolite with 1 N sodium chloride solution using ion exchange columns

Particle size range (mm)	**CEC in mg NH_4^+ g^{-1} of zeolite**	**CEC in meq NH_4^+ g^{-1} of zeolite**	**Model y = mg NH_4^+ absorbed g^{-1} x = mg NH_4^+ at outflow**
1.0 - 1.4	18.39	1.31	$y = 0.524+e^{-13.56+(1.150)x}$; $r^2 = 0.97$
1.0 - 1.4	16.26	1.16	$y = -0.171+e^{-11.03+(0.893)x}$; $r^2 = 0.99$
0 ± SD *	17.32 ± 1.5		
0.7 - 1.0	19.62	1.37	$y = -0.143+e^{-15.65+(1.168)x}$; $r^2 = 0.99$
0.7 - 1.0	15.39	1.10	$y = -0.162+e^{-14.95+(1.075)x}$; $r^2 = 0.98$
0 ± SD	17.50 ± 3.0		
0.3 - 0.6	17.36	1.24	$y = -0.016+e^{-43.76+(2.793)x}$; $r^2 = 0.99$
0.3 - 0.6	17.51	1.25	$y = -0.032+e^{-51.32+(3.180)x}$; $r^2 = 0.99$
0 ± SD	17.44 ± 0.1		

Note: * 0 is the mean of the replicates and SD is the standard deviation

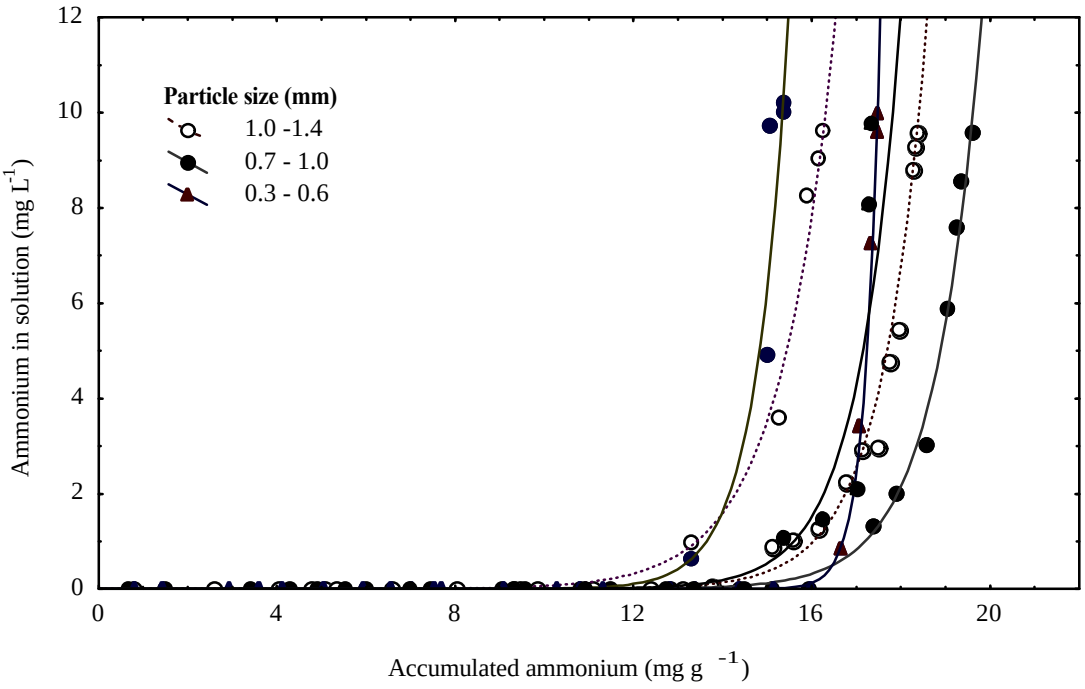

Figure 4.1: Breakthrough curves for regenerated Pratley clinoptilolite for three different particle sizes and their replicates with the estimated models from the ion exchange column data

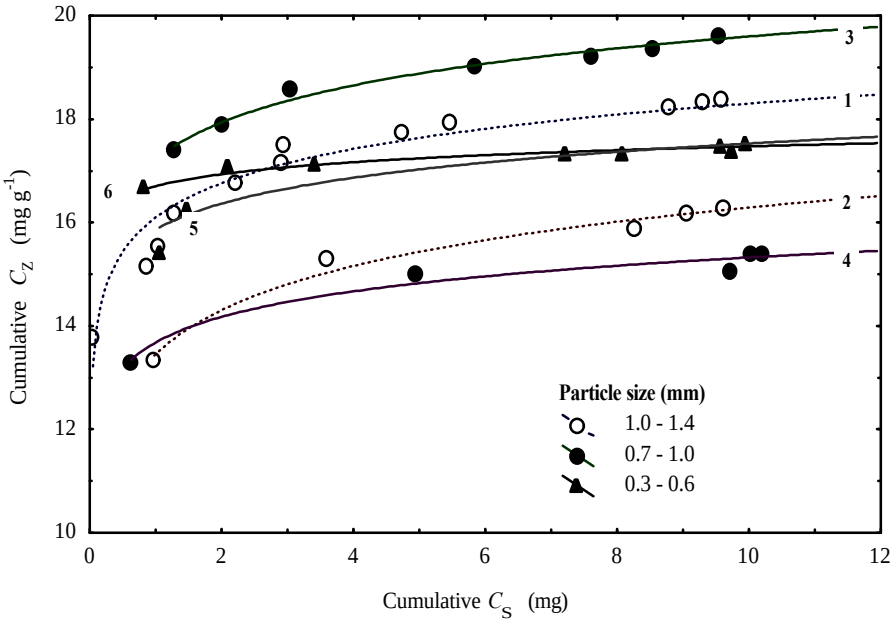

Figure 4.2: The batch ion exchange isotherms for regenerated Pratley clinoptilolite for three particle size ranges using ion exchange column data, see table 4.2 for a description of the numbers of each curve.

Table 4.2: Predicted models for the ion exchange isotherms of the column method data for figure 4.2

Curve number	Particle size range (mm)	CEC in mg NH_4^+ g^{-1} of zeolite	Isotherm model y = mg NH_4^+ absorbed g^{-1} x = mg NH_4^+ in solution
1	1.0 - 1.4	18.39	$y = 0.960 \ln(x) - 16.09$; $r^2 = 0.93$
2	1.0 - 1.4	16.26	$y = 1.235 \ln(x) - 13.45$; $r^2 = 0.98$
3	0.7 - 1.0	19.62	$y = 1.035 \ln(x) - 17.22$; $r^2 = 0.98$
4	0.7 - 1.0	15.39	$y = 0.715 \ln(x) - 13.68$; $r^2 = 0.97$
5	0.3 - 0.6	17.36	$y = 0.334 \ln(x) - 16.70$; $r^2 = 0.99$
6	0.3 - 0.6	17.51	$y = 0.724 \ln(x) - 15.86$; $r^2 = 0.75$

ln = natural logarithm

4.3.2 Batch method

Mean equilibrium ammonia capacities estimated using the batch method were 20.32 ± 0.3 mg g^{-1} (1.45 meq g^{-1}) and 17.68 ± 0.03 mg g^{-1} (1.26 meq g^{-1}) for the 0.7 - 1.0 and 1.0 - 1.4 mm particle sizes, respectively (table 4.3). These ammonia CEC values were calculated on the basis of the changes of ammonia ions in the solutions. The isotherm curves for the two particle sizes after batch regeneration are presented in figure 4.3 and the fitted predicted models are listed in table 4.3. Each particle size yielded a separate curve, which is reflected by the different resultant ammonia capacities. The slope of the curve for the 0.7 - 1.0 mm particle size range was significantly different ($P < 0.05$) from the 1.0 - 1.4 mm particle size, suggesting that the ion exchange rate is affected by particle size.

Table 4.3: Ammonium exchange capacities of Pratley clinoptilolite using the batch procedure for two different particle size ranges after regenerating with 1 N sodium chloride solution

Particle Size range (mm)	**CEC in mg NH_4^+ g^{-1} of zeolite**	**CEC in meq NH_4^+ g^{-1} of zeolite**	**Isotherm model y = mg NH_4^+ absorbed g^{-1} x = mg NH_4^+ in solution**
1.0 - 1.4	17.65	1.26	$y = 3.868 \ln(x) - 9.711$; $r^2 = 0.81$
1.0 - 1.4	17.70	1.26	
0 ± SD	17.68 ± 0.03		
0.7 - 1.0	20.11	1.44	$y = 3.284 \ln(x) - 15.032$; $r^2 = 0.85$
0.7 - 1.0	20.54	1.47	
0 ± SD	20.32 ± 0.3		

Note: * 0 is the mean of the replicates and SD is the standard deviation

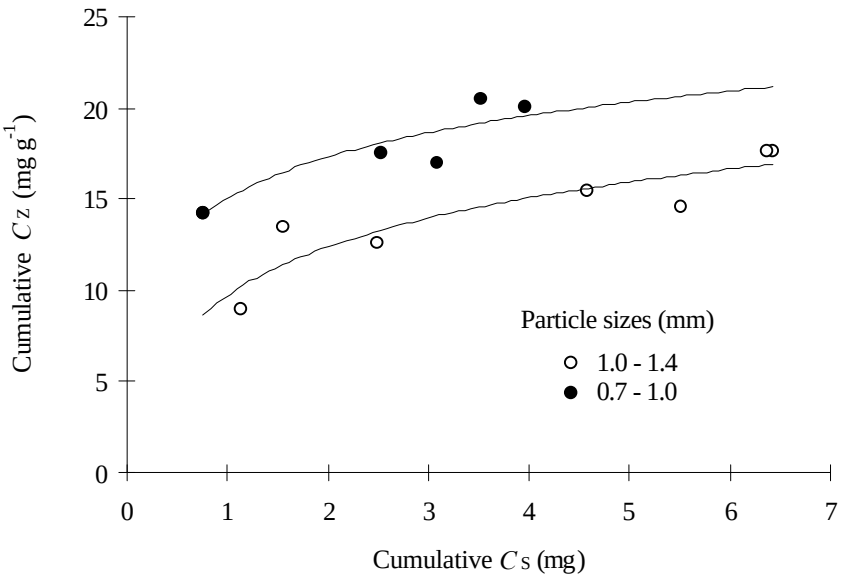

Figure 4.3: The ion exchange isotherm for regenerated Pratley clinoptilolite for two particle size ranges using the batch procedure

4.3.3 Comparison of column and batch regeneration data

Non-parametric analysis of variance (Kruskal-Wallis test) showed that there were no significant differences ($P > 0.05$) between average ammonia CEC values for samples regenerated using the batch or column method. However, there were significant differences ($P < 0.05$) in ammonia CEC between the different particle sizes tested for both regeneration methods. The smaller particle sizes had higher ammonia CEC values. There was a significant difference ($P < 0.05$) between the slopes of the linear equations for the two ion exchange methods ($F_{0.05(1),3,34} = 3.57$). The slopes of the batch method were higher than the slopes of the column method.

4.4 Discussion

4.4.1 Column and batch regeneration data

Average ammonia capacities estimated in the ion exchange column method were not significantly different to those achieved by the batch procedure after regeneration (17.42 ± 1.50 mg g^{-1} versus 19.0 ± 1.54 mg g^{-1}). The plots of the ion exchange isotherms of the column and batch method indicate a good correlation between predicted models and actual data points. This trend followed the type 1 isotherm shape (see figure 3.5, in chapter 3). Factors such as regeneration rates and time, volume of regenerant and weight of zeolite all might have influenced the observed performance and contributed to the observed scatter in the data points. However, it is clear from figure 4.2 and 4.3 (r-values) that the models derived represent a highly significant fit. The similar and regular behavioural trend of the isothermal data for NH_4^+ ion concentration in solution and on the zeolite suggests that a relatively simple model can describe NH_4^+ sorption mechanism by clinoptilolite.

Column performance differed between the different particle sizes. That is, the time that is required for leakage of ammonia in the column and to attain breakthrough was variable. Generally, higher leakage and earlier breakthroughs were obtained for the larger particle sizes. It was also noticeable that the smallest particle size range did not have a correspondingly high increase in ammonia CEC after regeneration when compared to the other two particle sizes. During the ion exchange process, there are two mechanisms of ion exchange at work, these are pore diffusion and film diffusion (Semmens, 1983). Pore diffusion works by ionic bonding while film diffusion is generally covalent bonding. For small particle sizes, there is more pore diffusion at work due to a larger surface area, therefore it is much more difficult to displace ions once they are adsorbed due to the strong ionic forces. Smaller particle sizes are also much more liable to clogging, further limiting the number of available sites to the regenerant solution (Hawkins, 1983). Future research is necessary to effectively quantify these factors and there influence on the regeneration process.

4.4.2 Comparison of regenerated and unregenerated clinoptilolite

In order to estimate the effect of regeneration on ammonia absorption capacity, the differences between the means of ammonia CEC values determined for the regenerated and unregenerated (chapter 2 and 3) samples at different particle size ranges were tested for significance. Estimated CEC values of regenerated and unregenerated samples were significantly different ($P < 0.05$) from each other (non-parametric Kruskal-Wallis test). The results indicated that regeneration improves the performance of the Pratley clinoptilolite filter bed. There was a noticeable increase in the ammonia exchange capacities after regeneration for both the batch and column methods as indicated by the NH_4^+ breakthrough curves and ion exchange isotherms. Results of ANCOVA showed that there were significant differences ($P < 0.05$) between slopes of the plots for the regenerated and unregenerated Pratley clinoptilolite. The slopes of the linear equations for the two ion exchange methods with regards to regenerated and unregenerated samples were also significantly different (regenerated samples had higher slopes). For all particle sizes tested, both leakage and breakthrough times improved after regeneration with 1N sodium chloride solution for both ion exchange methods.

The data in table 4.1 were used to calculate the percentage in increase in ammonia absorption capacity as a function of regeneration inorder to improve the potential of the ion exchange water treatment method by reusing exhausted zeolites. The overall level of performance achieved after regeneration (18.3 mg g^{-1}) was 25 % higher than the estimated capacity values (13.0 mg g^{-1}) of the unregenerated Pratley clinoptilolite samples for both the batch and column methods (Chapter 2 and 3). This increase in capacity has also been observed by various other authors (Dryden and Weatherley, 1987a; Koon and Kaufman, 1975; Jorgensen *et al.,* 1976). Jorgensen *et al.* (1976) also noticed that capacity increased with the number of regenerations. Capacity almost doubled as the number of regenerations increased from 0-5. Jorgensen *et al.* (1976) concluded that the regenerant (sodium hydroxide) activates the clinoptilolite.

Average ammonia capacities estimated in the ion exchange column method were not significantly different to those achieved by the batch procedure after regeneration. This was because the increase in ammonia capacity after batch regeneration (58 %) was significantly higher than that of the samples regenerated using exchange columns (16 %). Thus, although the ammonia CEC estimates of unregenerated samples were significantly lower for the batch method, their higher increase in CEC after regeneration resulted in their CEC values being almost equal to the column method CEC estimates. The observed variations in resultant CEC values after regeneration are attributable to the variations in methods that relate to contact time, volume of regenerant and amount of exchanger used during regeneration.

The overall average ammonia capacity of Pratley clinoptilolite found through these experiments as percentage of the theoretical clinoptilolite was 58 %. Though the estimated CEC increased after regeneration, it was still not possible to achieve more than 65 % of theoretical capacity which corresponds to the highest capacity (20.54 mg g^{-1} or 1.47 meq g^{-1}) obtained by the batch method for the 0.7 - 1.0 mm particle size range. The difference between the theoretical and practical capacity can be due to the layer not used entirely or purity of the rock ore as stated in the previous chapter. As the ammonia ion exchange rate is determined by diffusion processes, the volume of the material not used includes the internal volume of the clinoptilolite particles that are not saturated. It should be tested in future studies if the layer not used could be due to flow rate for the column method and contact time in the batch procedure. For this reason and due to the observed differences in column performance following regeneration, it would appear that completely mixed filter beds would be more desirable in water treatment systems.

The results indicate that regeneration of Pratley clinoptilolite using salt solutions is stable and effective. This is in agreement with results given by other authors (Koon and Kaufman, 1975; Semmens *et al.,* 1977; Murphy *et al.,* 1994) suggesting that regeneration

improves ion exchange capacities of clinoptilolite. The results also suggest that the efficiency of regeneration methods can be better evaluated by comparing increase in resultant CEC values after the process of regeneration. Further studies should be conducted to verify the effect of regeneration, using zeolites exhausted with solutions containing ammonium ions in the presence of other competing cations. This is because apart from the type of regenerant used, the type of major cation that is absorbed on the zeolite also affects the rate of regeneration.

CHAPTER 5

Evaluation of the ammonia exchange capacity of clinoptilolite in a recirculating fresh water fish culture system

5.1 Introduction

Ammonia is the most toxic end product of protein metabolism in teleosts (Porter *et al.,* 1987). It represents about 75 - 90 % of the end products of protein metabolism (Dosdat *et al.,* 1995). Other organic and inorganic metabolites released into the water include phosphorous, sulphur and organic solids. These affect fish indirectly through long term degradation of water quality. The toxicity of ammonia (NH_4^+/NH_3) is influenced by a number of water quality parameters most importantly pH and temperature, alkalinity and dissolved oxygen concentration (Goddard, 1996). These parameters as well as fish loading density and water exchange rate will also affect the rate of the ion exchange process and hence the efficiency of water treatment. Culture solutions contain cations such as potassium, calcium and magnesium, which may enter into exchange reactions with the zeolite (Dryden and Weatherley, 1987b). This probably results in the ammonia ions exchanging only onto some of the available sites within the zeolite while other sites will be occupied by the competing ions (Dryden and Weatherley, 1987a). Presence of organic matter as well as activity of nitrifying bacteria in an aquaculture system may also have a significant effect on the operating exchange capacity of zeolites (Piper and Smith, 1983). Thus, the working or effective cation exchange capacity of the zeolite might only be a fraction of the values obtained by laboratory column and batch ion exchange experiments in which the above mentioned factors are excluded.

The task of designing low-cost, efficient zeolite ion exchange systems for removal of ammonia in intensive fish culture systems is therefore not a trivial problem due to the complex interrelationships between water quality and feeding in intensive fish farming systems. Daily variations in metabolic rates and their influences on water quality affect

system performance and should therefore be considered, when designing water treatment systems or estimating ammonia exchange capacities. Since maintaining good water quality is essential for rapid fish growth and cost-effective production, it is important to understand the interrelationships among the various water quality criteria and zeolite performance in a fish culture system to achieve the highest performance of an ion exchange filter.

Therefore, the aim of this experiment was to describe the ammonia removal efficiency of zeolites in the presence of various water quality criteria that may influence ion exchange reactions under fish culture conditions. The trial was conducted to compare the ammonia absorption efficiencies of different zeolite particle sizes treating the water in a fresh water recirculating system. This was aimed at producing more reliable ammonia exchange capacity estimates that can be related to different water quality conditions. The capacity of Pratley clinoptilolite for ammonia removal in batch and ion exchange methods will be compared to its application in a fish culture system. In addition, growth and survival of fish in the presence of the absorbent will be quantified and compared to a control group in a culture system without the absorbent.

5.2 Materials and Methods

Three hundred juvenile guppies (*Poecilia reticulata*) with an average mass of 0.1 g of a common genetic base were obtained from a recirculating system at the fish farm of the department of Ichthyology and Fisheries Science of Rhodes University (Olivier, 1995). After weighing, the fish were randomly assigned to 9 conical fish tanks with volumes of approximately 3 litres at a density of 10 fish per litre. Total system volume including the water in the filter was approximately 6.5 litres per unit. The experimental units were part of an indoor recirculating system (Figure 5.1). Fish were fed a commercial flake food diet from Amatikulu fish farm limited, KwaZulu Natal with 38% protein, at approximately 5%

body mass/day (Goddard, 1996). The daily ration was divided equally into the morning (8:00 to 8:30) and the evening (17:00 to 17:30) feeding.

Figure 5.1: The indoor recirculatory system showing arrangement of 11 experimental units

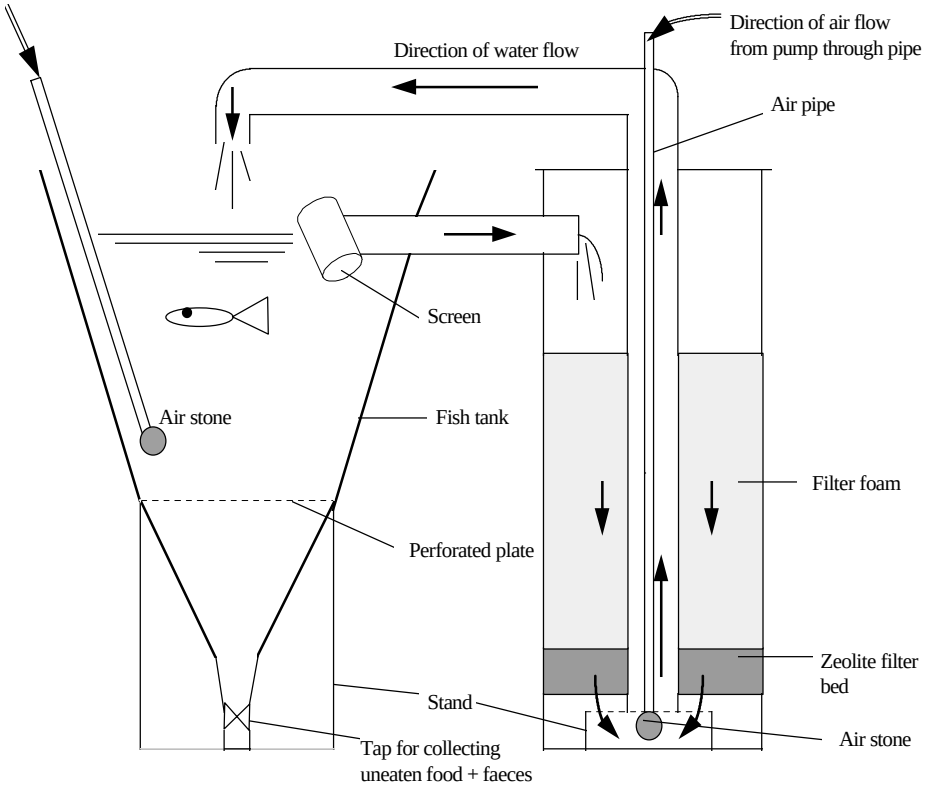

Figure 5.2: The experimental recirculating system airlift pump design. The arrow ➞ indicates the flow of water through the system, while ⇨ indicates the direction of air.

Water was recirculated by an airlift pump system (Hirayama, 1974). Each tank had its individual filtration system and all tanks were aerated continuously with a single aquarium air stone (Figure 5.2). Water temperature was regulated by room temperature by means of a heater that maintained the air temperature above 20 °C. Flow rate through the system was set to achieve approximately 5 exchanges per hour (0.5 L min^{-1}). Pratley clinoptilolite was spread uniformly in the filter column below the filter floss on a perforated plate and applied at 25 g per tank. This was done to reduce the possible blocking of exchange sites by organic wastes from metabolised and uneaten food. Two zeolite particle sizes, at three replicates each were used; 1.0 - 1.4 and 0.7 - 1.0 mm, which are 14x18 and 18x25 US

standard mesh sizes, respectively. These sizes were chosen as they had been used successfully in previous experiments. Three control units with no zeolite were run at the same time. The fish were kept on a 12L:12D photoperiod.

Dissolved oxygen and temperature (Oxyguard Handy II), pH (H1 90232 Hanna portable pH meter Kit), and ammonia values were monitored daily while nitrate and nitrite levels were tested once a week. Average daily pH values of each treatment were transformed into hydronium (H_30^+) ion concentrations, pH = -log [H_30^+]. The hydronium ion concentrations were then averaged and log values of the averages were calculated to get average pH values. Samples of the water from each of the 12 tanks were analysed for ammonia by nesslerization (APHA, 1989). Analysis for nitrite (NO_2^-) and nitrate (NO_3^-) was done photometrically using the HACH DR/2000 Direct Reading Spectrophotometer. At each sampling, 100 ml of water was taken from each tank. An average of 0.5 litres (7% of the total system volume) was added per day to make up for the losses due to evaporation or any possible leaking and the 100 ml used for analyses. Faeces and wasted feed were collected from the tanks by means of a tap at the bottom of the tank by siphoning with a tube. The collected organic matter was oven dried at 70 °C to constant dry weight overnight and stored in a freezer until analysed. The samples were analysed for total nitrogen content by means of the Micro-Kjeldahl method (APHA, 1989). This method involved heating 100 mg of the sample in concentrated sulphuric acid (AR grade) with a selenium catalyst and digesting until the carbon and the hydrogen were oxidised and the protein nitrogen was reduced and transformed into ammonium sulphate. Concentrated sodium hydroxide was added and the digest was heated to drive off the liberated ammonia into a known volume of standard hydrochloric acid. The unreacted acid was determined and the results transformed by calculating the figures into protein percentage in the sample. Each sample was replicated twice and differences between replicates were less than 5%.

Mortalities were recorded daily and the experiment was carried out for a duration of 26 days.

Upon termination of the experiment, the tanks were drained and the number surviving fish in each tank were weighed to determine the final fish biomass per tank. All solid wastes were collected and analysed for nitrogen content as described previously. Ten fish were then randomly sampled from each tank and their individual fresh weight and constant dry weight (70 °C) after 24 hrs were obtained. The loss on drying was expressed as the percentage moisture content. Dried fish samples were analysed for nitrogen content using the Micro-Kjeldahl method (APHA, 1989) as described above. A hundred (100) mg of the dried and ground fish was used in the analysis and each sample was replicated twice. The same analysis was carried out at the start of the experiment on 30 randomly selected fish. Nitrogen compounds were the only metabolites that were considered in this experiment (Table 5.1).

In order to assess the success of the ion exchange system with regards to fish production, the following fish production performance measures were estimated. Mortality was calculated by the difference between the initial number of fish stocked and the remainder at the end of the experimental period, expressed as a percentage of the initial stocking density (Hopkins, 1992). Measures of weight gain, combined with the measures of the amount of food fed to produce the resultant weight gain were used to determine the food conversion ratios (FCR) according to the formula: FCR = Food fed (wet weight)/weight gain (Goddard, 1996).

Table 5.1: Definitions of terms used for nitrogen sources and output in the nitrogen budget

Nitrogen form	Term
Nitrogen input from feed	N_I
Daily nitrogen input from feed (Sum of $N_{DI} = N_I$)	N_{DI}
Nitrogen in zeolite	N_Z
Nitrogen lost to conversion and oxidation to NO_2^- and NO_3^- (nitrification)	N_N
Nitrogen retention (fish growth)	N_R
Solids (Faeces and food nitrogenous wastes)	N_W
Dissolvable nitrogen ($N_U + N_Z + N_N$)	N_S
Nitrogen in solution after zeolite absorption and nitrification ($N_S - N_N - N_Z$)	N_U
Nitrogen not in solution ($N_Z + N_N + N_R + N_W$)	N_A
Total nitrogen ($N_U + N_Z + N_N + N_R + N_W$ or $N_S + N_R + N_W$)	N_{total}

Note: - $N_{total} \leq N_I$; $N_I = N_A + N_U$

N_S = The cumulative soluble nitrogen discharged into the system as a result of fish metabolism and deaminated uneaten food

N_U, N_Z and N_N are all cumulative values of their daily nitrogen concentrations

A nitrogen budget was established using the available data according to the format given by Suresh and Kwei Lin (1992).

1. Nitrogen intake: amount of nitrogen consumed by the fish via feed (total nitrogen supplied by feed).
2. Nitrogen retention: the amount of nitrogen gained by the fish in the carcass during the experiment (endogenous).
3. Nitrogen waste (exogenous):
   (a) Solids: amount of nitrogen excreted by fish via faeces and in uneaten food
   (b) Solubles:
   - nitrogen in the rearing water or
   - nitrogen intake - (nitrogen retention + nitrogen waste as solids)

Ammonia CEC values were estimated using the data available for the nitrogen budget. The concentrations of ammonia absorbed by zeolite were calculated on the basis of the available nitrogen (78% of ammonium is nitrogen). All values were corrected for the ammonia lost as a result of the 100 ml used for daily water quality analyses. There were three possible ways or cases used in estimating the nitrogen absorbed by the zeolite and the ammonia cation exchange capacity.

CASE I

Amount of nitrogen absorbed by the zeolite for the two particle sizes were estimated by subtracting the amount of nitrogen ions remaining in solution from the total nitrogen input from the feed ($N_I - N_U$). This resultant value (N_A) was assumed to be made up of nitrogen retained for growth, nitrogen in solid wastes and nitrogen available for zeolite absorption and/or nitrification ($N_R + N_W + N_Z + N_N$). The difference in the N_A values between the treatments with clinoptilolite in their filters and the control treatment was assumed to be the amount of N absorbed by the clinoptilolite.

CASE II

The ammonia absorbed by the zeolite was estimated by subtracting the estimated total daily nitrogen retention, soluble nitrogen unabsorbed and nitrogen in solid wastes from the daily nitrogen intake (N_{DI}) and summing up these daily differences. This was done for the days up to the day (14^{th}) when the ammonia concentration in solution reached a peak followed by a steady decline in concentration. Thus the total ammonia absorbed is expressed as;

$$N_Z = N_I - (N_U + N_R + N_W + N_N)$$

It was assumed that absorption after peak ammonia concentration could be attributed to both zeolite absorption and nitrification and that absorption by zeolite could not be distinguished from oxidation through nitrification. N_I in this instance was the N input from food up to the 14^{th} day and not for the whole experimental period of 26 days. This method would have the advantage that it takes nitrification into account and thus allows us to deductively to estimate the onset of biological activity. In addition it provides an alternative to the isotherm model which can use accumulative loads of nitrogen and results in the kinetics of ammonia uptake.

CASE III

The amount of ammonia absorbed by the zeolite was estimated as in case II, except that all the experimental days were considered, values of total N_I, N_R, N_W, N_U and N_N were used in the calculation of the CEC estimates.

One way analysis of variance (ANOVA) followed by a Tukey's multiple range test was used to test for differences between means of the three treatments.

5.3 Results

The average daily ammonia concentration in solution over the 26-day-period differed dramatically between the tanks from the control treatment and those that had clinoptilolite in their filters (figure 5.3). The total accumulated ammonia in solution in the control tanks (with no zeolite) amounted to 228.87 mg compared to 125.34 mg and 102.54 mg for the tanks with the 1.0 - 1.4 mm and 0.7 - 1.0 mm particle sizes, respectively. Pratley clinoptilolite significantly reduced the concentrations of ammonia in the water for the two treatments with zeolite relative to the control ($P < 0.05$).

The highest concentrations or peaks for the reduced nitrogenous compounds in the three treatments were observed between the 10-14th day (Figure 5.3). Ammonia (NH_4^+) and nitrite (NO_2^-) ions increased until day 11, levelled and then dropped for all treatments. The plots also indicate the conversion of NH_4^+ to NO_2^- and then finally the oxidation of NO_2^- to nitrate (NO_3^-). The oxidation of NH_4^+ to NO_2^- ensued rapidly after the 6th day. The oxidation of NO_2^- to NO_3^- began 12 days after NO_2^- was detected in the water. NO_2^- rose to a peak of 13.7 mg L^{-1} after which it had a steady decline until it reached a value of 9.4 mg L^{-1} at the end of the experiment. The NO_2^- concentrations in the tanks with clinoptilolite in their filters were significantly lower than the control concentrations ($P < 0.05$). There were no significant differences in the NO_3^- concentrations among the three treatments throughout the course of the experiment ($P > 0.05$).

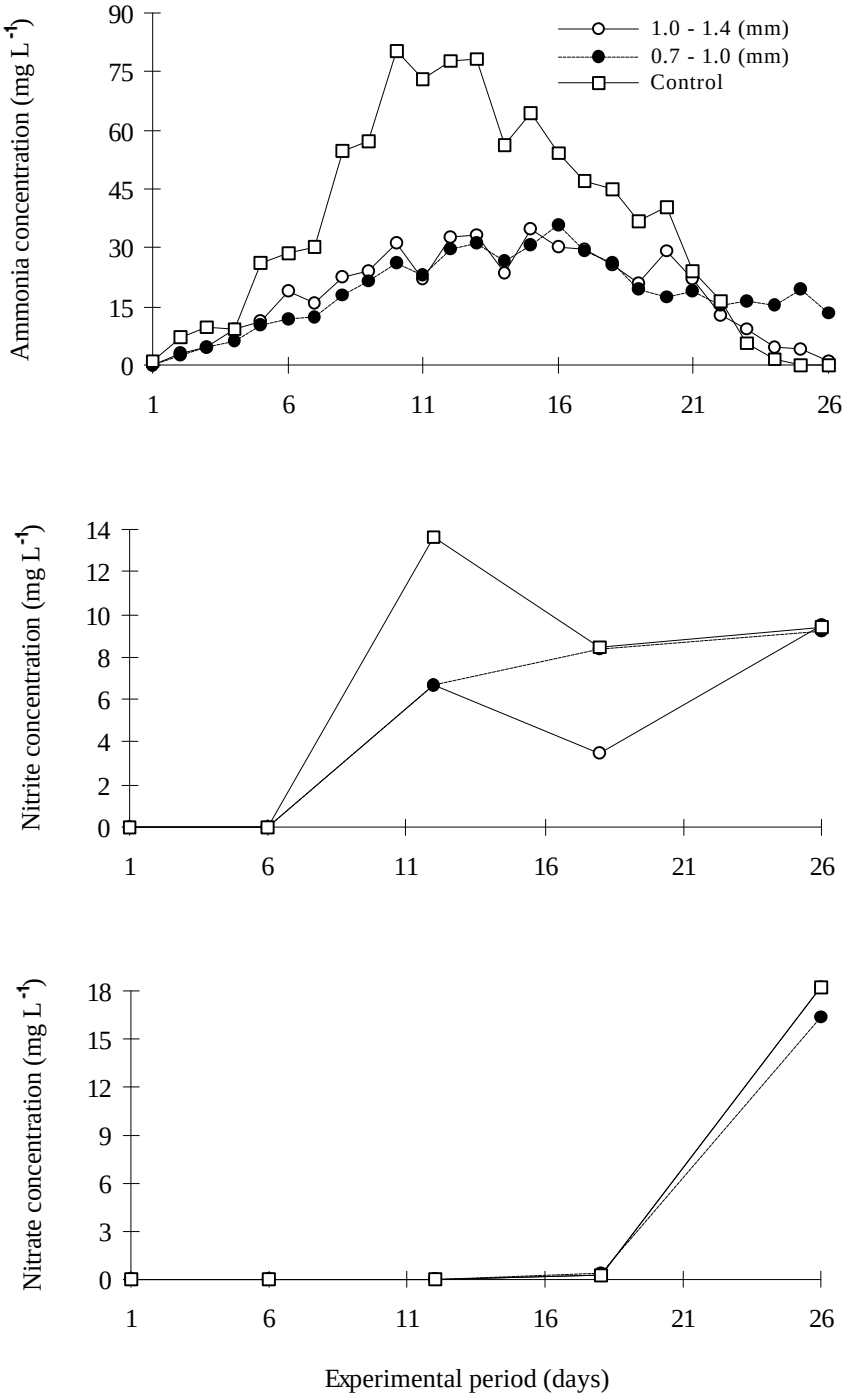

Figure 5.3: Measured average concentrations of ammonia, nitrite and nitrate concentrations in the culture tanks for the three different treatments over the 26-day experimental period. Each data point represents an average concentration of three tanks or replicates.

The pH throughout the 26 experimental days ranged from 6.2 - 8.3, while the temperature ranged from 18.2 to 27.2 °C. Dissolved oxygen concentration in the tanks ranged from 7.5 to 9.5 mg L^{-1} (Table 5.2). Daily average variations in pH, oxygen and temperature of three replicates per three treatments are presented in figure 5.4.

Table 5.2: Water quality parameters of culture water for the three treatments (± standard deviations).

TREATMENT	Replicates	pH	Dissolved oxygen (mg L^{-1})	Temperature (°C)
(Particle size mm)	**(tanks)**	**mean**	**mean ± s**	**mean ± s**
1.0 - 1.4	1	7.70	8.4 ± 0.38	22.9 ± 1.55
	2	7.34	8.3 ± 0.37	22.9 ± 1.66
	3	7.27	8.5 ± 0.43	22.0 ± 1.65
0.7 - 1.0	1	8.14	8.5 ± 0.37	21.8 ± 1.66
	2	7.02	8.6 ± 0.38	21.9 ± 1.72
	3	6.93	8.6 ± 0.41	21.9 ± 1.72
Control	1	7.04	8.4 ± 0.49	22.1 ± 1.60
	2	7.18	8.4 ± 0.43	22.3 ± 1.66
	3	7.15	8.4 ± 0.37	22.8 ± 1.72

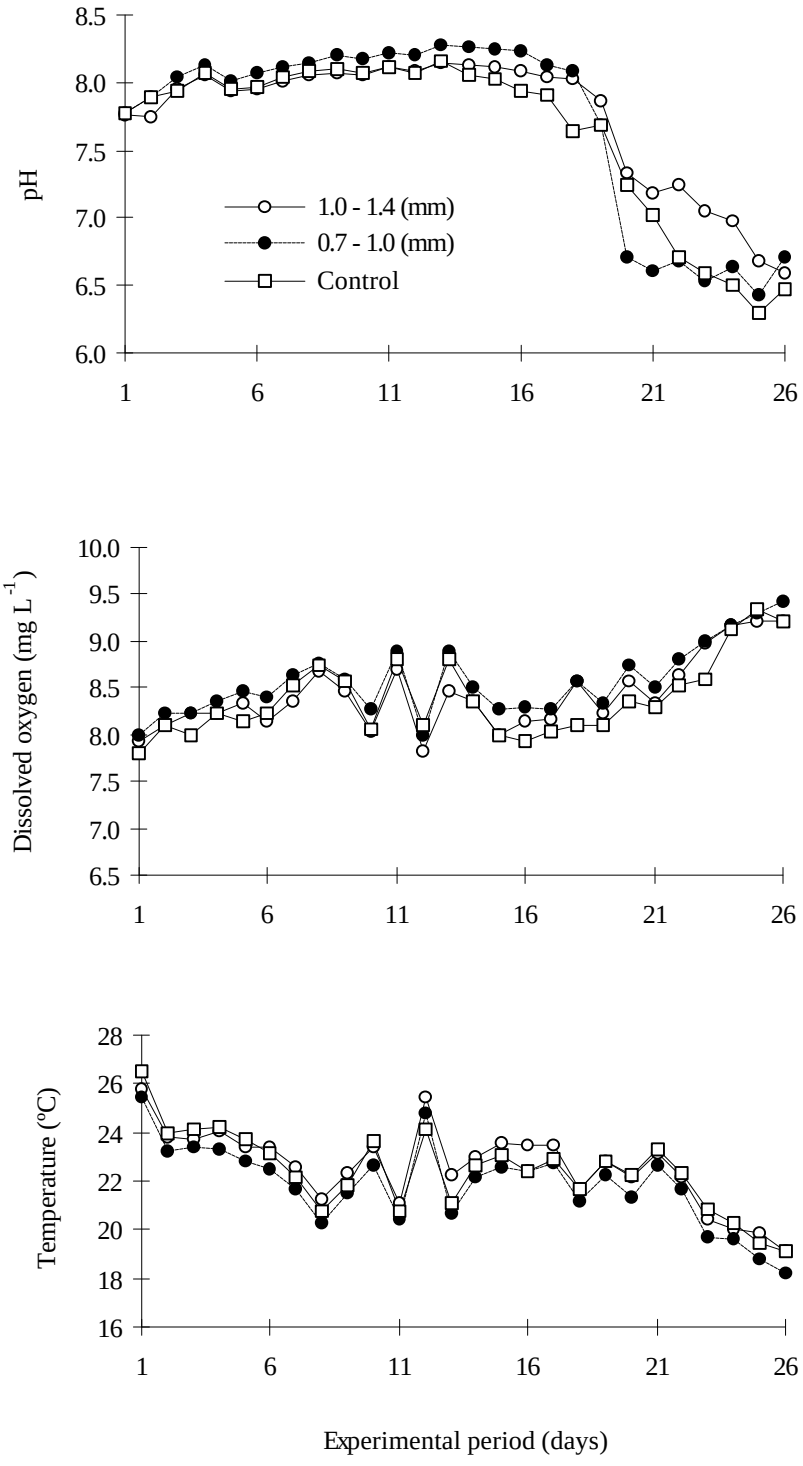

Figure 5.4: Average daily variations in pH, dissolved oxygen concentrations and temperature for three different treatments throughout the experimental period

The mean feed conversion ratio was 3.5, 3.7 and 3.5 for the 1.0 - 1.4 mm, 0,7 -1.0 mm and control treatments, respectively. The mean estimated FCR value for all the tanks was 3.5 ± 0.45, and FCR values ranged from 2.97 to 4.1 over all treatments (Table 5.3). The mortality rates of the treatment groups were similar and low with a mean value of 4 % (range 0 - 10 %). Cumulative mortality was less than 10 % and did not differ significantly between treatment tanks ($p > 0.05$).

Table 5.3: Production characteristics of the guppy (*Poecilia reticulata*) for three different treatments in relation to daily feed intake and mass gain (wet mass).

TREATMENT (Particle size mm)	Replicates (tanks)	Final fish #	Daily food fed as DM* (g)	Total food fed as DM (g)	Initial fish mass (g)	Final fish mass (g)	Mass gain (g)	FCR
1.0 - 1.4	1	27	0.30	7.50	6.00	8.41	2.41	3.11
	2	28	0.30	7.44	5.95	8.29	2.34	3.18
	3	30	0.29	7.31	5.85	7.71	1.86	3.93
0.7 - 1.0	1	29	0.29	7.31	5.85	7.62	1.77	4.13
	2	28	0.31	7.65	6.12	8.32	2.20	3.48
	3	29	0.30	7.52	6.02	8.14	2.12	3.55
Control	1	30	0.31	7.76	6.21	8.09	1.88	4.13
	2	29	0.30	7.54	6.03	8.27	2.24	3.36
	3	28	0.32	7.89	6.31	9.06	2.75	2.87

Note: * DM = dry matter and # = number

There was no significant difference in body composition including moisture (73 - 75 %) and crude protein (49.5 - 54.0 % DM) between fish of all treatments and the 30 randomly selected fish at the start of the experiment (Table 5.4). Average crude protein content was estimated as 51.6 ± 1.7 % (13.4 % on wet mass basis). Faecal protein content on a dry matter basis ranged from 48 % to 53 % with an average of 49.7 % (table 5.5). Similarly, there was no significant difference ($P > 0.05$) among treatments in faecal protein content.

Table 5.4: Results of the Micro-Kjeldahl analysis and moisture content of the guppy (*Poecilia reticulata*) for three different treatments.

TREATMENT (Particle size mm)	**Replicates**	**Wet mass (10 fish)**	**Dry mass (10 fish)**	**% moisture content**	**% protein in sample (DM)**	**Weight gained as DM (g)**	**N in gained weight (mg)***
1.0 - 1.4	1	2.82	0.75	73.4	52.84	0.63	53.57
	2	2.67	0.69	74.2	53.23	0.62	52.39
	3	2.64	0.72	72.7	50.80	0.49	39.75
0.7 - 1.0	1	2.80	0.71	74.6	53.95	0.47	40.17
	2	2.36	0.62	73.7	52.35	0.58	48.45
	3	2.71	0.72	73.4	49.49	0.56	44.13
Control	1	2.50	0.66	73.6	49.88	0.49	39.44
	2	2.50	0.67	73.2	52.65	0.59	49.61
	3	3.37	0.86	73.5	49.63	0.72	57.42
Initial 30 fish	1	6.55	1.72	73.7	52.27		

Note: * Conversion factor for nitrogen content was 6.25

Table 5.5: Results of the Micro-Kjeldahl analysis for the protein and nitrogen content of the collected faeces from the three different treatments

TREATMENT (Particle size mm)	Replicates	Total weight collected (gram)	% protein in sample	Protein in faeces (gram)	Nitrogen in faeces (mg)
1.0 - 1.4	1	1.94	48.89	0.95	151.74
	2	1.86	50.57	0.94	150.50
	3	1.73	49.46	0.86	136.91
0.7 - 1.0	1	2.02	48.53	0.98	156.86
	2	1.63	48.37	0.79	126.15
	3	2.03	49.70	1.01	161.42
Control	1	1.83	52.79	0.97	154.56
	2	1.66	51.15	0.85	135.86
	3	1.53	47.95	0.73	117.38

Note: * Conversion factor for nitrogen content was 6.25

Table 5.6 shows how the nitrogen offered to the fish from the feed was utilised under the different treatments and cases I, II and III. Less then 11 % of the nitrogen fed was converted into body protein. The rest was excreted as solid and soluble waste. There was no significance difference in the various constituents of the nitrogen budget between treatments ($p > 0.05$) and among the three cases. Average N percentage composition for all treatments was 10 %, 30%, and 60 % for N_R, N_W, and N_S, respectively (Table 5.7). However, there was a very small difference between the total nitrogen input from feed (N_I) and the total nitrogen (N_{total}) that was calculated as a sum of the endogenous and exogenous nitrogen sources ($N_S + N_R + N_W$). Average N_{total} was +1 %, -1 % and +0.8% less or greater than N_I for the 0.7 - 1.0 mm, 1.0 - 1.4 mm and control treatments, respectively for the all Cases. The mass balance estimation calculated using Case I for the treatment with the 0.7 - 1.0 mm particle size range is presented in figure 5.5.

Table 5.6: Total nitrogen budget (mg) in the culture water of *P. Reticulata* using the 38 % crude protein diet and estimated ammonia CEC values for the two particle sizes, for the three different cases. The results are averages of the three replicates. There were no significant differences among treatments

CASE	Treatment or particle size (mm)	N_I	N_{DI}	N_R	N_W	N_U	N_N	N_Z	N_S	N_{total}	Estimated NH_4^+ CEC (mg g^{-1})	Estimated NH_4^+ CEC (meq g^{-1})
I	1.0 - 1.4	468.97	18.04	48.57	146.38	125.34		77.31	202.65	468.95	3.96	0.28
	0.7 - 1.0	468.97	18.04	44.25	148.14	102.54		102.66	205.20	468.95	5.26	0.38
	Control	490.05	18.85	48.83	141.05	228.87	71.35		290.93	490.10		
II	1.0 - 1.4	255.78	18.04	26.15	1.12	125.34		97.30		249.90	4.99	0.36
	0.7 - 1.0	255.78	18.04	23.83	1.03	102.54		129.32		256.71	6.63	0.47
	Control		18.85									
III	1.0 - 1.4	468.97	18.04	48.57	146.38	125.34		66.33		466.15	3.40	0.24
	0.7 - 1.0	468.97	18.04	44.25	148.14	102.54		107.27		472.39	5.50	0.39
	Control	490.05	18.85	48.83	141.05	228.87	79.53			498.27		

* N_U = sum of daily nitrogen accumulation in solution after zeolite absorption, nitrification and/or volatilisation.

From the nitrogen budget data, the mean ammonia CEC values for Case I, II and III were estimated as 5.80 mg g^{-1} and 4.12 mg g^{-1} for the 0.7 – 1.0 and 1.0 – 1.4 mm particle sizes, respectively. There were no significant differences ($p > 0.05$) in the CEC estimates for all three cases (Table 5.6). There were also no significant differences between estimated CEC values of the two particle sizes ($p > 0.05$).

Table 5.7: Total nitrogen budget (%) in the culture water of *P.Reticulata* for the three treatments using the 38% protein diet for the different three cases (values are percentages of the total nitrogen in the food consumed)

CASE	Treatment (mm)	N_U	N_R	N_W	N_Z	N_N	$N_Z + N_N$	N_{total}
I	1.0 - 1.4	26.7	10.4	31.2	16.5	15.2	31.7	100.0
	0.7 - 1.0	21.9	9.4	31.6	21.9	15.2	37.1	100.0
	Control	47.7	10.0	28.8			14.6	100.0
II	1.0 - 1.4	49.0	10.2	0.4	38.0			97.7
	0.7 - 1.0	40.1	9.3	0.4	50.6			100.4
	Control							
III	1.0 - 1.4	26.7	10.4	31.2	14.1	17.0	31.1	99.4
	0.7 - 1.0	21.9	9.4	31.6	22.9	16.9	39.8	102.7
	Control	47.7	10.0	28.8			16.2	101.7

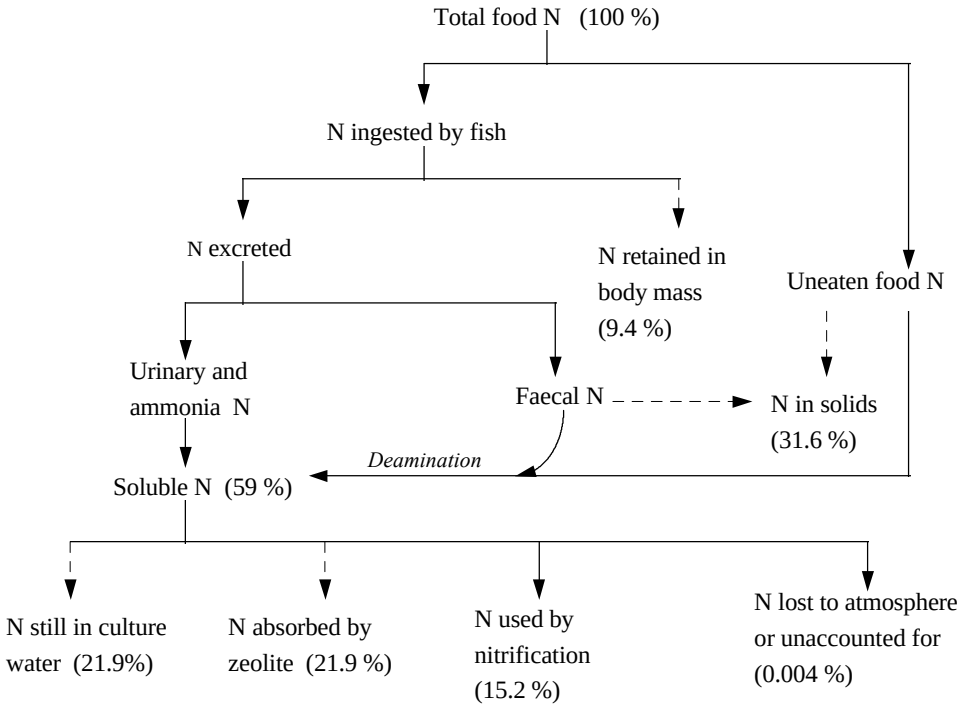

Figure 5.5: A mass balance estimation of nitrogen (N) for the treatment with the 0.7 - 1.0 mm clinoptilolite particle size (Case I). Dashed lines indicate the nitrogen types that were measured

5.4 Discussion

The ammonia concentrations in the treated groups with clinoptilolite in their filters were significantly lower than the control concentrations. This is most likely due to the effect of clinoptilolite which effectively reduced ammonia levels in solution. The estimated average NH_4^+ CEC values for cases I, II and III (5.80 mg g^{-1} and 4.12 mg g^{-1} for the 0.7 - 1.0 and 1.0 - 1.4 mm particle sizes, respectively) were significantly lower than the column and batch estimates for the same particle sizes ($P < 0.05$). The average NH_4^+ CEC values estimated by the batch and column methods were (14.18 mg g^{-1} and 12.84 mg g^{-1} for the

0.7 - 1.0 and 1.0 - 1.4 mm particle sizes, respectively) were more than 100% higher than these estimates. This difference was probably caused by some ion exchange sites being blocked as a result of organic material originating from fish feed and faeces coating the zeolite particles. Piper and Smith (1983) also observed a reduction in CEC from 2.25 g NH_4^+ kg^{-1} of clinoptilolite to 1.21 g NH_4^+ kg^{-1} when this zeolite was used in a recirculating system as opposed to column tests. The difference could also be a result of the higher ionic strength of the culture water when compared to the distilled water used in the column and batch experiments. When zeolites are in contact with solutions containing NH_4^+ ions, ion exchange and adsorption take place simultaneously, however the ratio of ion exchange and adsorption is a function of the ionic concentration in the solutions (Jorgensen *et al.,* 1976). At low ionic strength (distilled water) competition for charged groups on the ion exchanger is at a minimum and substances are bound strongly. Increasing ionic strength increases the competition and reduces the interaction between the ion exchanger and the ammonium ions to be removed (McLaren and Farquhar, 1973).

Ammonia concentration was the only critical parameter that was not maintained within optimal limits comparable to those trials without fish during this fish trial. By day 6 for all tanks, ammonia concentrations had increased to above 10 mg L^{-1}. A mean value of 7 % of the volume of water in each system was added daily to compensate for loss by evaporation. This small volume did not represent removal and dilution adequate to prevent accumulation of large concentrations of ammonia. The alarming levels of unionised ammonia encountered did not seem to be a limiting factor to fish production. No observable stress was manifested in fish behaviour, feeding activity or feed conversion at the stocking density (10 fish L^{-1}) and water exchange rate (5 exchanges per hour) used in this study. This is in agreement with results obtained by Kaiser *et al.,* (1998) who tested diurnal water quality fluctuations of guppies at 3 and 20 fish L^{-1} at different water flow rates (0.25, 2 and 6 turnovers per hour). These authors observed no differences in mortality between the stocking densities. The water quality conditions of their study with the same species (*P. reticulata*) were similar to the conditions encountered this study. It therefore appears to be feasible to keep guppies up to 10 or 20 fish L^{-1} and at these flow

rates for short periods. There is a complex interaction between pH, oxygen and ammonia toxicity. According to Russo and Thurston (1991) the toxicity of ammonia increases when dissolved oxygen concentrations decrease. As ammonia discharges are frequently associated with reduced oxygen concentrations, the effect of dissolved oxygen on ammonia toxicity can be very important. Furthermore, ammonia is less toxic to fish at temperatures near the higher end of their normal environmental range than near the lower end (Russo and Thurston, 1991).

The pH through out the experiment was within the acceptable range of 5-9 to which most fish species as well as the guppy are tolerant (Teo and Chen, 1993; Piper and Smith, 1983; Randall, 1991). This pH was also suitable for effective zeolite ammonia removal. Optimum pH for ammonia exchange exists between pH 4 and 8 with little variation in ammonia exchange capacities between these values (Koon and Kaufman, 1975). These authors observed that column performance outside this range resulted in a rapid decrease of ammonia exchange capacity and increased ammonia leakage before the onset of breakthrough. This is because acidic and alkaline conditions inhibit Na^+/NH_4^+ exchange (Koon and Kaufman, 1975). The noticeable general decline in pH (acidification) in all treatments over time (figure 5.4) is a common feature of closed recirculation systems and is associated with nitrate accumulation in the water and the decrease of alkali due to some magnesium precipitation and the production of H^+ ions by nitrifying bacteria (Wheaton *et al.,* 1991; Hirayama *et al.*, 1988).

Most sources of nitrogen entering the system, nitrogen losses and nitrogen sinks were quantified to determine the mass balance of this nutrient and account for the major sources of influx in a zeolite filtration system. Input data included amount of feed and its nitrogen content while nitrogen sinks and losses were effluent solution concentration, nitrogen in faeces and nitrogen deposited in fish tissue. The cumulative amount of nitrogen in the solution (N_S) was about 60 % of the total nitrogen input. This was assumed to be composed of nitrogen sources of urea, liquid fraction of faeces, fish mucous and metabolite wastes voided through the gills (mostly NH_4^+). This fraction was considered to

be in solution and available for removal by zeolite ion exchange. About 22 % and 15 % of this ammonia source was absorbed by the zeolite for the 0.7 - 1.0 and 1.0 - 1.4 mm particle sizes (case I and II), respectively. It is important to note that although the amount of ammonia in an aquaculture system can be contributed by the source water and by microbial breakdown of waste feed, most of it comes from fish metabolism (Piper and Smith, 1983). The level of ingested nitrogen was the most important factor in determining the nitrogen budget. The amount of protein in the feed affects ammonia levels or nitrogen that is excreted as a result of protein breakdown and amino acid metabolism of feed.

The endogenous nitrogen excretion or weight gain representing body proteins and nucleic acid metabolism were determined by the Kjeldahl method. This nitrogen was assumed to include natural materials such as proteins, peptides, nucleic acids and urea. The estimated mean for N_G for all three treatments was 10 %. This implies that about 90 % of the nitrogen consumed by the fish was wasted in the form of solids and solubles. The Kjeldahl method determines nitrogen in the tri-negative state. It fails to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime and semi-carbazone (APHA, 1989). It was therefore assumed that these unquantified nitrogen forms, were also part of the ammonia in the system that could not be accounted for in the budget. It was assumed that some nitrogen would be lost to the atmosphere through volatilisation of ammonia during periods of high pH, aided by the heavy aeration (Hopkins *et al.,* 1993).

Some of the urea, faeces and slime accumulating in the tanks are assumed to have been reduced by biofiltration to produce ammonia, which was added to what was produced by fish respiration. These substances are high in organic matter and could have supported the growth of heterotrophic bacteria. A significant amount of ammonia can be produced from solids when they are biologically decomposed (Slone *et al.,* 1981). Liao and Mayo (1974) found that about 70 % of the ammonia present in solution is associated with organic solids. Therefore, to eliminate this secondary source of ammonia production continuous removal of organic solids or faeces from the culture tanks is recommended. Later this

ammonia produced from the decomposition of solids was oxidised to nitrites and then nitrates as the bacteria became more established. This can be clearly observed from the graphs in figure 5.3 showing the changes in concentration of ammonia, nitrite and nitrate ions over time. These curves are similar to the typical curves of NH_4^+, NO_2^- and NO_3^- ions when setting up a biofilter (Fig. E1: Appendix E). Ammonia is oxidised to nitrite and then nitrate by nitrifying bacteria as follows (Semmens and Porter, 1979; Wheaton *et al.,* 1991):

$$NH_4^+ + 1½O_2 \rightarrow NO_2^- + 2\,H^+ + H_2O$$

$$½O_2 + NO_2^- \rightarrow NO_3^-$$

In the absence of nitrifying bacteria, exchange would have taken place according to the ion exchange equation ($Z.Na^+ + NH_4^+ \rightarrow Z.NH_4^+ + Na^+$) until chemical equilibrium was reached. However, when bacteria are present as was assumed in this experiment, the liberated ammonia (from solid wastes) was oxidised and contributed to the increase in ammonia in solution. The nitrification process consumes the ammonium ions and may also encourage more ammonium ions to leave the clinoptilolite. Thus, it was possible to account for ammonia absorption by the zeolite in three different ways. By assuming that there was negligible biological uptake of ammonia before the peak and drop in ammonia concentration in the solution (case II), ion exchange was assumed to have reached equilibrium, and ammonia CEC values were estimated. Cases I and III took account of the biological filtration and ammonia CEC values were estimated by comparison with the control treatments without zeolite in their filters. However, ammonia CEC estimates of all 3 cases were not significantly different from each other. It is suggested that little or no zeolite uptake took place once the ammonia concentration in the tanks began to drop and biological filtration became established. That is most of the ammonia uptake was biological because the zeolite had become established as a biological filter. This is because accounting for all the days of the experimental period (Case I and III) produced results similar to analysis of ammonia uptake up to day 14 (case II). According to Piper and Smith (1983), the zeolite filter bed can become established as a biofilter. It has also been

observed by various authors that bacteria nitrify more effectively in the pH range of 7.4 - 8.4 which was the general pH encountered in this study (Semmens and Porter, 1979).

In conclusion, bacteria were able to establish themselves on the clinoptilolite and perhaps also use it as their food source while filtering NH_4^+ out of the water. This was because no attempt was made to sterilise the clinoptilolite filter and to reduce the rate of bacteria colonisation. Any ion exchange unit can develop into a biofilter if bacteria become established in it (Piper and Smith, 1983). Stabilising a new biofilter typically takes 20 - 35 days (Wheaton *et al*., 1991). Since clinoptilolite has a lesser affinity for Ca^{2+} and Mg^{2+} ions it could have become a source of these ions for utilisation by the bacteria. According to Horsh and Holway (1983), Ca^{2+} and Mg^{2+} are very necessary in the nitrification process, with increasing efficiency as the total hardness level increases. Therefore in an attempt to use zeolites in aquaculture systems these factors must be considered in ammonia CEC estimation. The estimated CEC values are lower than the column and batch estimates due to presence of biological filtration which prevented the complete exhaustion of the clinoptilolite to take place. These results furthermore suggest that the clinoptilolite filter bed can function efficiently as a biological filter but that it can reduce ammonia peaks in the early phases of the establishment of a system as became evident from the comparison of ammonia values from the control treatment. The ability of clinoptilolite to act as a substrate as well as a food source during biological filtration makes this zeolite a superior filter medium (Horsh and Holway, 1983).

CHAPTER 6

Final Discussion

The principal objective of this study was to optimise the application of the zeolite ion exchanger to the removal of ammonia from fresh water and to relate the results of this process to the design of fresh water recirculatory systems. The challenge is to build and operate an economically viable system. In order for such a system to be practical, the exchange capacity of the natural zeolite must be such that its use can be justified over the use of other water purification methods (Semmens and Porter, 1979). The laboratory results obtained for Pratley clinoptilolite and the Zambian laumontite using the batch and column methods show that these natural zeolites can effectively reduce toxic ammonia levels from water. The ion exchange isotherms obtained clearly showed the preference for ammonia exhibited by the two zeolites. The estimated CEC values were within the range of values obtained by various authors for clinoptilolite. Though a lot of work has been done on clinoptilolite, it is clear that different deposits of this mineral behave differently. Each zeolite deposit must therefore, be evaluated separately and all the parameters involved determined. Work done by Murphy *et al*., (1994) showed differences of up to 170 % between different deposits. There is a definite potential in using the Zambian laumontite in water treatment, the estimated ammonia CEC value was relatively high in relation to the low purity of the rock. Therefore further exploration of this deposit would be very beneficial. It was observed that pre-treatment improves the ammonia CEC of clinoptilolite, most likely due to the increase in the number of sites available for ion exchange. Thus, pre-treatment can be recommended in order to achieve optimal zeolite ammonia removal.

The second major factor determining an ion exchange systems practicability is the ease and effectiveness involved in the regeneration of the exhausted exchange material. As stated

by Semmens *et al.* (1977) approximately 50 to 60 percent of the ion exchange process total costs are caused by chemical regeneration of the zeolite. Improving the regeneration process would greatly reduce the cost of the overall ion exchange process perhaps to the extent that, economically, it may be the most attractive water treatment process. Estimated CEC values for Pratley clinoptilolite increased after regeneration giving a better ammonia removal performance. This was achieved by the use of a NaCl solution that can be easily replaced by sea water, thereby reducing the cost of the ion exchange process in areas near the sea. Exhausted zeolites can be used as nitrogen fertilisers in agriculture and the ammonia exchanged NaCl solution can be purified to obtain $MgNH_4PO_4$, and NH_4NO_3 once again utilisable as a high premium quality slow release solid fertiliser (Marking and Bills, 1982; Bergero *et al.,* 1994). This investigation concentrated on defining various operational parameters necessary to remove ammonia efficiently through ion exchange by using zeolite (Koon and Kaufman, 1975). By studying different aspects of column and batch processes, it was possible to evaluate more clearly the applicability of the ion exchange process to operating conditions and to predict more accurately column performances.

One of the other primary purposes of this study was to derive design criteria for combining water treatment with zeolite and fish culture. The tests were designed to evaluate ammonia removal efficiencies of different particle sizes under fresh water recirculation operating conditions. It was observed that the interrelationships between water quality and feeding in recirculatory culture systems are complex. Water temperature, pH and oxygen not only influence feeding activity, metabolism and growth but the ion exchange process as well. These are all of fundamental importance in the application of zeolite ion exchange water treatment processes whose effects were studied. It was observed that high populations of fish could be kept in a closed recirculatory system in healthy conditions in a limited volume of water. This is in agreement with results obtained by Kaiser *et al*., (1998) who concluded that it may be feasible to keep guppies at stocking densities of up to 20 fish L^{-1} and at fast flow rates for short (6 turnovers h^{-1}). It appears that there are no environmental problems associated with ion exchange water

treatment, in particular there were no harmful effects on fish, with regards to growth and feeding activity.

To determine the optimum use of natural zeolites in water treatment or any other practical application, it is necessary to recognise not only the full potential of these materials but also their limitations. For example the ability of zeolites to absorb ammonia from water is adversely affected by the presence of competing ions, such as Na^+ and Ca^{2+}. As the concentration of Na^+ and Ca^{2+} increases, less capacity is available for ammonia and the zeolite is less effective in ammonia removal, as was demonstrated by the lower CEC estimations of the fish trial when compared to the batch and column method estimates (Semmens, 1983). However, increasing the application rate of zeolite in the filter can easily solve this problem.

The major conclusions of the investigation are summarised below.

(1) The Pratley clinoptilolite proved to be better than the Zambian laumontite in ammonia absorption capacity. Unfortunately, laumontite is structurally weak and breaks down easily into fine particles. However there is still room for improvement and considering this zeolite in water treatment due to its preference for the ammonia as shown by equilibrium ion exchange isotherms. Both zeolites take up ammonia quickly; however the trends of the curves show that especially in the early reaction stages, the $Na^+ \rightarrow NH_4^+$ exchange rate is definitely higher for clinoptilolite than for laumontite. The results of these tests can be used to estimate the ammonia exchange capacity of water containing cation concentrations not unusually different from concentrations used in these tests.

(2) The pre-treatment of clinoptilolite with 1N NaCl significantly improved the ammonia exchange capacity of clinoptilolite. Pre-treatment affects the kinetics of the ion exchange process. In summary therefore, the capacity of natural zeolites is influenced significantly by the pre-treatment the zeolite has received. Therefore, pre-treatment is necessary inorder to achieve higher removal efficiencies in water treatment

(3) Particle size affects the efficiency of the ion exchange process. The capacity for the smaller particle size ranges was higher than that of the larger sizes for both the pre-treated and untreated samples, and the batch and column method estimates. This is due to the greater surface area for pore diffusion such that uptake of ammonia is higher by a small particle size.

(4) The ammonia ion exchange capacity increases with regeneration. It appears that sodium chloride activates the zeolite. However, column performance following regeneration with 1N NaCl solution was not as good as batch performance. The observed difference in performance was believed to be a result of incomplete regeneration of the ion exchange column. It was suggested that ion exchange columns must be especially checked during regeneration to ensure that this is finished to completion or to prevent any channelling.

(5) The contact time available for ion exchange to occur also influences the ammonia absorption performance of zeolites. This is because ion exchange is not an instantaneous process, but requires time for ions to diffuse from the pore sites through the structure to the contacting solution. For this reason exchange was better for the column method (more contact time) than the batch method and for smaller particle sizes where the diffusion path is shorter (Semmens *et al.,* 1978; Semmens, 1983).

(6) The presence of other ions or chemical characteristics of the water appears to reduce the exchange capacity. Ammonia removal from the recirculating system was considerably lower than for the column and batch laboratory processes where distilled water was used. This was suggested to be due to the competition between the other ions with ammonia for the zeolite exchange sites. However the results of the fish trial suggest that the use of clinoptilolite has practical applications in a fresh water recirculation facility since it reduces ammonia peaks in the early phases of establishment of a biofilter. Some nitrite and nitrate build up was experienced due to the growth of autotrophs in the filters. In the future it could be desirable to prevent bacterial growth by periodically flushing

filters with hypochlorite (Mumaw *et al.,* 1981) (For this, the filter unit containing the zeolite must be removable from the rest of the system). An alternative would be to allow the clinoptilolite filter bed to run for sufficient time to become established as a biological filter by encouraging bacterial growth. It is clear that loading capacities of zeolite filters are dependent on the densities of the cultured animals, feeding as well as metabolic rates. Nevertheless, it may be said that at least as far as this trial and under higher zeolite application rates in a fresh water recirculatory system, fish may be reared safely during the start-up phase of a biofilter.

(7) The sources of nitrogen entering the fresh water recirculatory system, nitrogen losses and sinks were quantified to determine the mass balance of this nutrient. From the nitrogen budget, it was found that 60 % of the ammonia present associated with the soluble nitrogen was available for absorption by the zeolite filter or biological nitrification and that a total of approximately 22 % of ammonia was absorbed by the zeolite. It was concluded that nitrogen budget experiments such as the fish trial in chapter 5 for the particular species to be cultured under the given conditions, makes it possible to determine the amount, nature and effect of the dissolved nitrogen load both within the aquaculture facility and on the zeolite ion exchange process. This is necessary to institute appropriate action to prevent or at least mitigate the effects of ammonia toxicity. It is suggested the use of zeolite can be used to predict the amount of biological filtration. Biological filtration can be measured deductively by comparison of the absorption rates between filters with zeolite and filters without, as was demonstrated by the three methods (case I, II and III) used in the CEC estimation in chapter 5.

All these data depict a very favourable situation for actual or potential applications in industrial, agricultural and aquacultural waste water purification. The results suggest that the ion exchange system provides a reliable efficiency for ammonia removal and appears to be a viable treatment process for fresh water systems. The operating characteristics that were determined in these experiments should provide directions in designing other water

re-use systems with aquacultural applications. The zeolite ion exchange system appears to be an effective and viable alternative to biological oxidation processes of water treatment which are highly susceptible to minor changes in temperature and chemistry of recirculatory systems. In the event of failure of the biological filters one could quickly switch to the exchange column and repair the defective conditions. Secondly, diseased fish could be treated with antibiotics without harm to the nitrifying flora by temporary use of the ion exchange column (Johnson and Sieburth, 1974). Water treatment by ion exchange can furthermore be maintained over a wider range of temperatures and concentrations. Ion exchange has also shown useful application for water treatment during fish transportation in the presence of antibiotics (Bower and Turner, 1982; Dryden and Weatherley, 1987a). However, it clearly appears that a lot is still to be done. The laboratory and pilot fish study processes already developed seem to require further improvements. Therefore the following studies and recommendations will be important in obtaining optimal design and operational data that could be used to develop recirculatory culture systems.

1. Investigate the application of an ion exchange bed in marine water in both pilot scale and preliminary laboratory operations for ammonia removal. The use of clinoptilolite in a marine system could also be restricted to emergency use as a backup system to biological nitrification.
2. More data is needed on solutions containing competing ions in laboratory trials to properly quantify their effect on ammonia absorption by clinoptilolite. It will be important to note the concentrations at which the competing ions significantly affect or impair ammonia absorption.
3. To investigate the possibility of improving the technique of regenerating zeolites and ensure complete regeneration. The possible use of sea water as a regenerant solution should be attempted.
4. To fully establish the total costs of establishing an ion exchange fresh water treatment system. Factors such as transportation, cost of disposal of regenerant solutions, ion

exchange vessels and piping, through put and pumping costs, engineering, labour and contingencies should be evaluated with regards to these two zeolite samples.

In conclusion, aquaculture is a growing industry and a very good alternative to fisheries, an industry that has seen a noticeable drop in production over the last decade. World demand for aquatic products has however continued to increase (Haylor and Muir, 1998). Intensified aquaculture production that is cost effective and good water quality is therefore in demand and depends upon the water treatment processes being used.

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APPENDIX A

Table A1: Representative formulae and selected physical properties of important zeolites[a]

Zeolite	Representative unit-cell formula	Void volume (%)	Channel dimensions (Å)	Thermal stability (relative)	Cation Exchange Capacity[b] (meq/100g)
Analcime	Na_2 ($Al_{16}Si_{32}$ O_{96}) . $16H_2O$	18	2.6	High	4.54
Chabazite	(Na_2 ,Ca)$_6$ ($Al_{12}Si_{24}$ O_{72}) . $40H_2O$	47	3.7 x 4.2	High	3.84
Clinoptilolite	(Na_3 K_3) (Al_6Si_{30} O_{72}) . $24H_2O$	34	3.9 x 5.4	High	2.16
Erionite	(Na,$Ca_{0.5}$K) (Al_9Si_{27} O_{72}) . $27H_2O$	35	3.6 x 5.2	High	3.12
Faujasite	Na_{58} ($Al_{58}Si_{132}$ O_{384}) . $240H_2O$	47	7.4	High	3.39
Ferrierite	(Na_2 Mg_2) (Al_6Si_{30} O_{72}) . $18H_2O$	28	4.3 x 5.5 3.4 x 4.8	High	2.33
Heulandite	Ca_4 (Al_8Si_{28} O_{72}) . $24H_2O$	39	4.0 x 5.5 4.4 x 7.2	Low	2.91
Laumontite	Ca_4 (Al_8Si_{16} O_{48}) . $16H_2O$	34	4.6 x 6.3	Low	4.25
Mordenite	Na_8 (Al_8Si_{40} O_{96}) . $24H_2O$	28	2.9 x 5.7 6.7 x 7.0	High	2.29
Phillipsite	(Na ,K)$_5$ (Al_5Si_{11} O_{32}) . $20H_2O$	31	4.2 x 4.4 2.8 x 4.8 3.3	Medium	3.31
Synthetic	**Zeolites**				
Linde A	Na_{12} ($Al_{12}Si_{12}$ O_{48}) . $27H_2O$	27	4.2	High	5.48
Linde X	Na_{86} ($Al_{86}Si_{106}$ O_{384}) . $264H_2O$	50	7.4	High	4.73

[a] Data after Mumpton (1983) and Colella (1996)

[b] Calculated from unit-cell formula

APPENDIX B

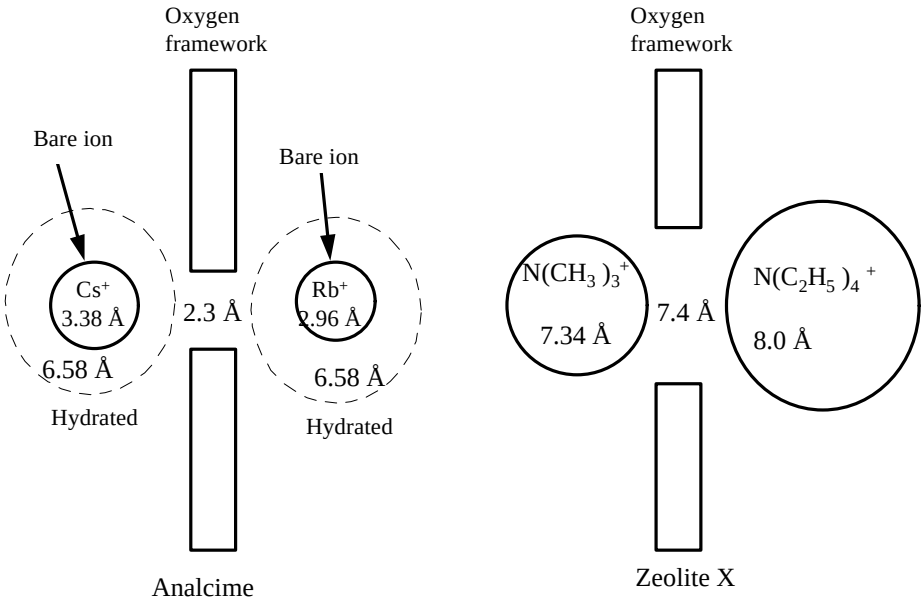


Figure B1: Schematic representation of ion sieving based on pore size. Cesium (Cs) and Rubidium (Rb) are excluded by analcime (left) as both hydrated and non-hydrated species. The trimethylammonium ion, left (B) exchanges into zeolite X, but the branch chained tetrathylammonium ion does not (Dyer, 1988)

APPENDIX C

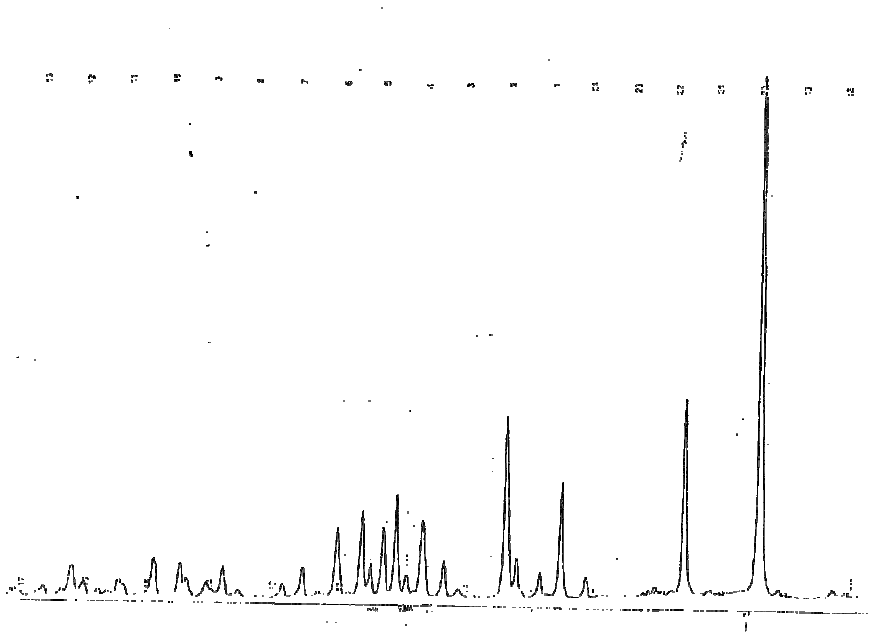


Figure C1: X-ray diffraction pattern of the Zambian laumontite

APPENDIX C

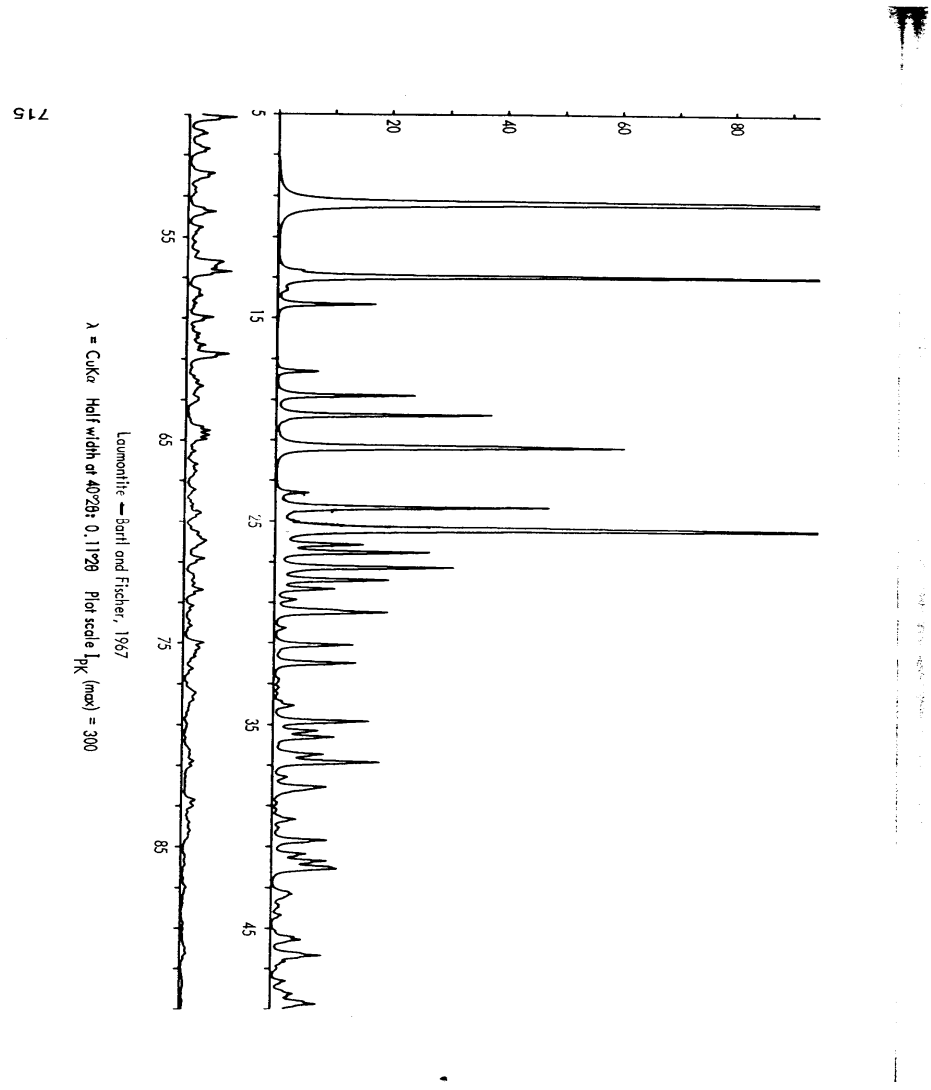


Figure C2: X-ray diffraction pattern of laumontite (Borg and Smith, 1969)

APPENDIX D

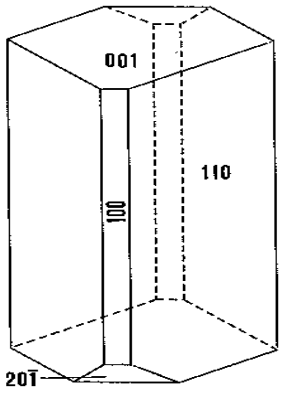
Physical and chemical properties of laumontite, $Ca_4[Al_8Si_{16}O_{48}]. 16H_2O$

Cystal system: Monoclinic

Cell dimensions: a = 14.90, b = 13.17, c = 7.55; β = 111°30'

Habit: as small prismic crystals often with oblique terminations, also massive, or as columnar and radiating aggregates.

Cleavage: Prismatic, pinacoidal; {010}, {110} perfect



Hardness: 3 -3½

Fracture: Uneven

Colour and transparency: White sometimes reddish, transparent to translucent

Distinguishing features: Looses part of its water on exposure to air and becomes powdery, friable and chalky and is then known as leonhardite

Occurrence: Laumontite occurs with other zeolites in veins an amygdales in igneous rocks. It is produced as a result of very low grade metamorphism of some sedimentary rocks and tuffs. Laumontite is named after G Laumont, who discovered the mineral

Other properties: laumontite is strongly pyroelectric (its crystals have no centre of symmetry)

APPENDIX E

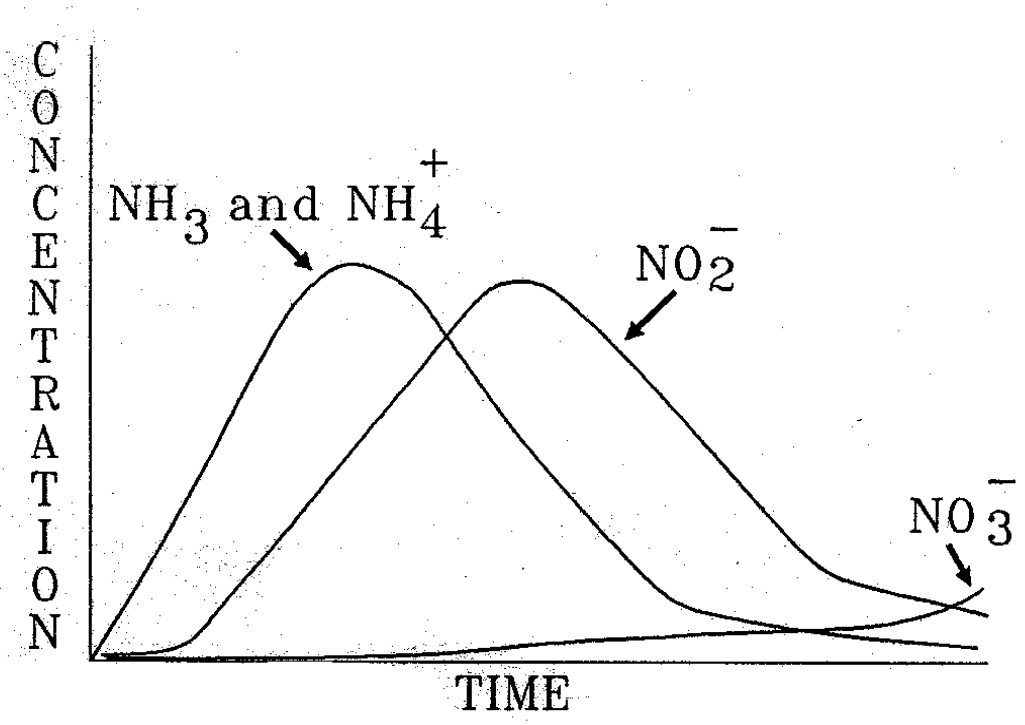


Figure E1: Typical break-in curves for a biofilter, showing typical ammonia, nitrite and nitrate curves (Wheaton *et al.,* 1991)