A STUDY ON THE UTILIZATION OF ZEOLITE FOR AMMONIA REMOVAL FROM COMPOSTING LEACHATE

by

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Abstract

This thesis studied the feasibility of using zeolite to remove ammonia in the treatment of composting leachates. Composting is considered to be one of the best treatment methods for biological solid wastes. However, the leachate resulting from the composting process has the potential to impact seriously on the environment if it is not handled properly. This is due to the presence in composting leachates of high levels of nutrient contaminants, especially nitrogen. The main purpose of this study was to investigate the potential use of applications of the Canadian zeolite, clinoptilolite, in the removal of ammonia from composting leachate. Zeolite is considered to have potential use in efficient and cost effective treatment of composting leachate because of its affinity for ammonia and its capacity as a selective ion exchanger.

Adsorption capacities, the effect of adsorption on initial solution concentrations, contact time and zeolite particle sizes were the parameters analyzed during batch studies. Adsorption capacities of zeolite ranged from 14.35-17.81 mg N/g. The Langmuir isotherm was found to describe the equilibrium better than the Freundlich model for this study. Particle diffusion was identified as the rate-controlling mechanism at the beginning of contact between zeolite and the wastewater.

A batch-scale system using coarse zeolite packed columns was operated to investigate the continuous removal of ammonia from composting leachate. The effects of hydraulic retention time, operating adsorption capacities and regeneration efficiency were measured. A hydraulic retention time of 6 hours was found to be optimal for ammonia removal, which yielded an operating capacity of 1.31 mg N/g zeolite. Over 98% of the ammonia in the wastewater influent was consistently removed by the zeolite columns over approximately 5 bed volumes (BV) of leachate pass through. A 0.6M NaCl regenerating solution at a flow rate of 1 BV/ hr was preferred for the regeneration process. More than 95% of adsorbed ammonium ions were recovered in the effluent.

In both the batch and column experiments, the presence of very high concentrations of potassium in the composting leachate meant that potassium acted as a competitive ion. This meant a reduction in the overall performance of the zeolite both in terms of ammonia removal and in terms of column regeneration efficiency.

This study concluded that using zeolite as an ion exchanger has potential for increasing the efficiency of ammonia removal from composting leachates.

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Chapter 1: Introduction

This thesis studies the feasibility of using zeolite to remove ammonia in the treatment of composting leachate from a pilot-scale composting plant for vegetable greenhouse solid waste.

The greenhouse vegetable industry in the Lower Mainland of British Columbia, Canada, is a rapidly expanding agricultural sector. One area of concern for this growing industry is the tremendous amount of solid waste such as leaves, stems etc. produced during the growing season and crop residue which remain at the end of the growing season is completed. Composting is considered to be one of the best treatment methods for this type of biological solid waste. However, the production of leachate from the composting process has the potential to impact seriously on the environment if it is not handled properly, as such leachate often contains a high level of nutrient contaminants, especially nitrogen. Most composting plants either discharge the leachate untreated or allow the leachate to be carried away via rain water. This raises serious concerns that the nutrients in the effluents might induce eutrophication in reservoirs and lakes and alter the structure and dynamics of the aquatic ecosystems. Stringent regulations are therefore being introduced all over the world to limit nitrogen concentrations in effluents. For example, a permit obtained from the Ministry of Environment, Lands and Parks authorized Envirowaste to discharge a maximum 155 m^3/d of treated runoff with a maximum concentration of 5 mg/l for BOD, Ammonia-N, Nitrate-N and TKN (Chase, 1997).

As it is highly soluble, most of the nitrogen in treated secondary effluent occurs in the ammonium form. Various treatment methods have been used employing chemical, physical and biological systems to limit or control the amount and form of nutrients discharged by the treatment systems. Initially, the processes most used were biological nitrification for nitrogen removal, and chemical precipitation for phosphorus removal. A thorough biological treatment would require a relatively long retention time, resulting in a very expensive system.

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A review of the published literature revealed that the use of zeolite might have potential in the efficient and cost effective treatment of composting leachate. Zeolite has a high affinity for ammonia and works as a selective ion exchanger. Thus ammonia could be removed from the wastewater by means of an ion exchange process. The ion exchange process is a physical process which can potentially offer a high rate alternative to the conventional biological processes, requiring relatively small land areas. The advantages of this process are that it facilitates either the recovery of ammonia or its conversion into nitrogen gas by oxidation; that it has good rates of ammonia removal under low temperatures, and that the treatment facilities can be compact in size, requiring a relatively small land area and they are easy to maintain.

Work done all over the word to develop the ammonia adsorption process has used zeolite from many different deposits. For the removal of ammonium ions from wastewater, clinoptilolite, a naturally occurring zeolite, has been found to be one of the best natural exchange resins. In addition to having a greater affinity for ammonium ions than other exchange media, it is relatively inexpensive when compared to synthetic media. Clinoptilolite is the most common zeolite produced and has a greater affinity for ammonium ions, as well as for other ions present in the wastewater, than other zeolites (Jørgensen et al., 1976). Its characteristics in cation-exchange capacity and cation selectivity have led to its frequent use in wastewater treatment, mostly for waters with high levels of ammonium.

There are a total 48 known zeolites in all the groups (Hogg, 1997). Each zeolite species has its own unique crystal structure and hence its own set of physical and chemical properties. Even within the same species, each zeolite has it's own set of properties. A review of published literature revealed past research and development of ammonium adsorption processes using zeolites, especially clinoptilolite, from overseas deposits. However, there is a significant variation in the adsorption characteristics and structural rigidity of zeolites from different sources. The potential of Canadian natural zeolite for application to ammonia removal treatment is not yet known.

1.1 Objectives

The main purpose of this study is to investigate the potential of Canadian zeolite, clinoptilolite, for application to ammonia removal from composting leachate. The specific objectives of this study were as follows:

a) To determine the capacity of zeolite to adsorb ammonium ions;

b) To examine the effect of particle size, ion concentration and contact time on the adsorptivity of zeolite;

c) To evaluate the rate of uptake of ammonium ions by the zeolite;

d) To determine the effects of loading flow rate on the ammonia removal efficiency under operation in a column;

e) To investigate the factors affecting the regeneration process and to determine whether the zeolite can be fully regenerated;

f) To distinguish the effect of competing cations present in the composting leachate.

Chapter 2: Literature Review

2.1 Control of nutrients

Given our current increase in population and the reduction in water reservoirs, the reuse of wastewater after adequate treatment is nowadays considered important. Treated wastewater can be used in many ways -- in agricultural land irrigation, in irrigation of recreational areas, grass, gardens, and golf courses, in pulp and paper production, in maintenance of natural environments, and in the recharging of underground water supplies. It is important, however, that sufficient attention be paid to human activity of any scale which could impact on the ecology of reservoirs, lakes and oceans. Eutrophication is one of the ways in which such human activity impacts on the environment. It is currently a problem of growing concern.

Eutrophication results from the enrichment of a body of water with fertilizing elements which, in the presence of sunlight, stimulate the growth of algae and other aquatic plants. Extensive growth of these plants can have many undesirable effects. They tend to clog streams and to form floating mats which decrease water clarity. They form breeding grounds for flies and insects and the decomposition of algae can lead to unpleasant odors. In addition, they can have various adverse effects on impounded water used for water supplies. Many elements are essential for the growth of algae; however, in natural waters compounds of nitrogen and phosphorus are frequently in limited supply, which tends to control the extent of growth that occurs.

Various treatment methods have been used employing chemical, physical and biological systems to limit or control the amount and form of nutrients discharged by the treatment systems. Initially the processes most commonly used were biological nitrification for nitrogen removal, and chemical precipitation for phosphorus removal. In recent years, a number of biological treatment processes have been developed for the removal of nitrogen and phosphorus alone or in combination (Linsley & Franzini, 1972, Tchobanoglous & Burton, 1991).

2.2 Control and removal of nitrogen

Most nitrogen present in wastewaters occurs in the form of organic nitrogen and ammonia. Untreated wastewater usually contains little or no nitrite or nitrate. A portion of the organic particulate matter is removed during primary sedimentation. During biological treatment, most of the remaining particulate organic nitrogen is transformed to ammonium and other inorganic forms. Most of the nitrogen in treated secondary effluent is in the ammonium form because it is highly water soluble.

Stringent regulations have been introduced all over the world to limit nitrogen concentrations in effluents. The U.S. EPA interim drinking-water standards limit it to 45 mg/l as NO_3^-. It may vary in concentration from 0-20 mg/L as N in wastewater effluents. A typical range is from 15-20 mg/l as N (Tchobanoglous & Burton, 1991). A permit obtained from the Ministry of Environment, Lands and Parks authorized Envirowaste to discharge a maximum 155 m^3/d of treated runoff with a maximum concentration of 5 mg/l for BOD, Ammonia-N, Nitrate-N and TKN (Chase, 1997).

The available techniques for ammonia removal include the following (Singh & Prasad, 1997):

i)   recovering ammonia by concentrating it (ion exchange, reverse osmosis, or chemical precipitation);

ii)   stripping it as ammonia gas (air or steam stripping);

iii)   destroying it by converting it into nitrogen (breakpoint chlorination or biological nitrification-denitrification) .

Traditionally, biological systems have provided an economical solution, with the retrofitting of biological phosphorus and ammonia removal facilities to existing organic treatment systems. However, due to the slowness of the biological conversion of nutrients, these systems often require large land areas and thus have high capital costs. Wilson *et al.* (1981) selected the city of Penticton, B. C. as the test site for a full-scale demonstration of nitrogen removal. Three biological nitrogen-removal processes were

selected for detailed evaluation of biological nitrification/denitrification processes operated at the low temperatures typical of winter operation in northern U.S. and Canada. The processes included two-sludge post-denitrification and both one-sludge pre- plus post-denitrification. The process designs were based on achieving 5 mg/l NO_3-N and 1 mg/l NH_4-N in the treated effluent throughout the year. Pre-denitrification was found to be the most cost-effective process for Penticton. Based on present worth and annual cost, it was found that one-sludge pre-denitrification was the most cost effective of the three nitrogen alternatives. They also discussed alternative methods other than biological nitrification and denitrification. However, land disposal, ammonia stripping, and ion exchange proved to be more expensive than the biological methods of nitrogen removal.

Selective ion exchange is a physical process which can remove ammonia by using ion exchangers. It can offer a high rate alternative to the conventional biological processes, and requires relatively small land areas, thus lowering capital costs. It is also a well-known technique for purification of wastewater. For nitrogen control, the ion typically removed from the waste stream is ammonium, NH_4^+. Ion exchange may be done with ion-exchange resins, synthetic polymeric materials, natural zeolites, or synthetic zeolites. By using these ion exchangers, a selective ion-exchange process could be developed as an effective and cost-effective ammonia-removal process. The advantage of this process is that it facilitates either recovery of ammonia or conversion of it into nitrogen gas by oxidation. This ion-exchange process has the following added advantages (Singh & Prasad, 1997): (1) good performance of ammonia removal under low temperature and (2) compact size and easy maintenance of the full-scale plant.

For the removal of ammonium ions from wastewater, clinoptilolite, a naturally occurring zeolite, is one of the best natural exchange resins. In addition to having a greater affinity for ammonium ions than other exchange media, it is relatively inexpensive when compared to synthetic media. Ion exchange has so far had limited application because of the extensive pretreatment required, because of concerns about the life of the ion exchange media, and because of the complex regeneration system required.

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However, by using these ion exchangers, it was feasible that a selective ion-exchange process could be developed as a very useful ammonia-removal process

2.3 Ion exchange

Ion exchange is one of the sorption reactions. It is also called "Exchange adsorption": It is defined as a process where an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of like charge into solution in a chemically equivalent amount. The process occurs with no structural changes in the resin. The ions in solution rapidly diffuse into the molecular net work of the resin, where exchange occurs. The exchanged ions proceed by the same path into solution. At some point during the ion exchange process an ion exchange equilibrium is established. The general reaction for the exchange of ions A and B on a cation exchange resin can be represented as follows:

$$n\text{R}^-\text{A}^+ + \text{B}^{n+} \leftrightarrow \text{R}_n^-\text{B}^{n+} + n\text{A}^+$$
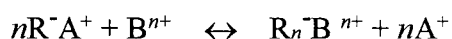
where R^- is an anionic group attached to the ion exchange resin, and A^+ and B^{n+} are ions in solution (Weber, 1972). Choosing a resin with a high affinity for the ion to be exchanged has the following advantages: (a) sharp breakthrough curve (b) shorter ion exchange column and (c) greater flow rate applied to ion exchange column.

One common application of ion exchange is in water treatment for the purpose of softening hard waters. This is accomplished through removal of the "hardness" ion (Mg^{2+} & Ca^{2+}) from the water. Ion exchange may be done with ion-exchanger resins, synthetic polymeric materials, natural zeolites, or synthetic zeolites. Although both natural and synthetic ion exchange resins are available, clinoptilolite, a naturally occurring zeolite, is one of the best exchange resins for the removal of ammonium ions from wastewater. In addition to having a greater affinity for ammonium ions than other exchange media, it is relatively inexpensive when compared to synthetic media.

Column operation is preferred for most applications of ion exchange in water and wastewater treatment systems. The mode is a packed fixed bed. For good operation, the flow direction is usually top to bottom to avoid channeling and uneven distribution. As the influent begins to pass through the column, the exchanger will be exhausted very soon at the upstream portion of the zone due to the higher concentration of exchanging ions. The middle portion of the zone will still contain a relatively large quantity of unspent exchanger and also a relatively high concentration of exchanging ions remaining in the solution phase. The exchange reaction is most rapid in this portion of the column. Near the downstream edge of the reaction zone, the solution contains a low concentration of ions to be removed.

As the polluted feed water continues to flow into the column, the exhausted zone will become larger and larger and the active exchange zone will move downward. More and more exchanging ions tend to escape into the effluent. When the forward edge of the exchange zone reaches the bottom of the column, exchanging ions appear in the effluent. That is the breakpoint. Additional removal of ions will occur beyond this point. However, when the concentration of ammonium in the effluent becomes unacceptably high, the exchanger must be regenerated or replaced. This is called the break-through curve, and is an important indicator for column operation (Helfferich, 1962, Weber, 1972).

2.4 Introduction of zeolites

The name "zeolite" was coined by Cronstedt in 1756 from the Greek words for 'to boil' and 'stone' in order to describe the behavior of the newly discovered mineral stilibite, which loses water rapidly on heating and thus seems to boil. Zeolites have been extensively studied since then, leading to the synthesis of novel structures and to a great number of applications as ion exchangers, molecular sieves, catalysts and so on.

2.4.1 Occurrence of natural zeolites

Most deposits of sedimentary zeolites have been formed by the reaction of volcanic ash (glass) and pervasive ground, lake, or seawater. Although these systems often require large land areas, a variety of other aluminosilicate materials have also served as reactants. In fact, given sufficient time, almost any silica-rich reactant in an appropriate chemical environment will produce crystalline zeolites. Since Ca, Na, and K are needed in their structure, zeolites tend to form in environments where these elements are abundant (Hawkins, 1983). Mining a zeolite deposit is relatively simple compared to mining most other minerals. Zeolite-bearing formations are generally at or close to the surface and only require the removal of small amounts of overburden to expose the ore. The mined ore is usually crushed and screened to size at the mine site and shipped directly to the consumer in bags or in bulk.

2.4.2 Structure of natural zeolites

Zeolites include a group of hydrous aluminum-silicates, which have close similarities in chemical composition, geological association and mode of occurrence. They can be described chemically as aluminum silicates. Seven groups of zeolite species are included within the same framework. These groups are analcime, chabazite, gismondine, heulandite, natrolite, harmontome and stilbite. In each zeolite group, the cations are exchangeable within a particular framework and this results in a variety of compositions. The order and disorder of silicon and aluminum ions in the framework produce different symmetry and crystal systems which characterize the subdivisions of the groups. There are a total of 48 known zeolites in all the groups (Hogg, 1997). As each zeolite species has its own unique crystal structure it also has its own set of physical and chemical properties. Even each zeolite within the same species has it's own set of properties.

Tetrahedra are the primary building units of the zeolite framework, which is a three-dimensional structure of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ linked together by the sharing of all oxygen atoms. The linkage of the tetrahedra leads to the formation of rings and cages

which consist of chain- or layer-like units. These comprise the second building units or SBUs. These units form the three dimensional structure of the zeolite material (Figure 1-1). Variations in the composition of this structure result in the different forms of zeolite. Zeolite contains channels filled with water and exchangeable cations. The cations can be freely removed or exchanged with cations in solution without affecting the structure. One simple way to classify the types of zeolites is based on the SBU's. In this classification system, all known zeolite frameworks are classified according to the way in which the 16 possible SBU's are linked (Feng, 1991).
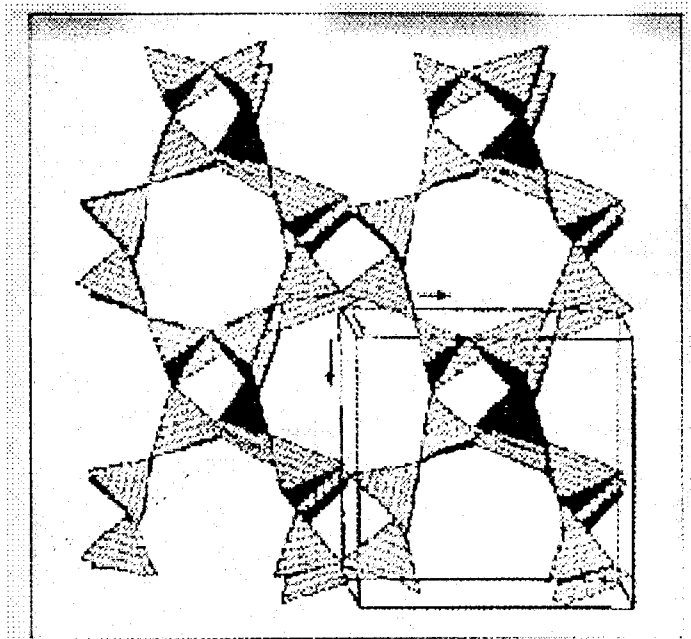
Figure 1-1. The primary building units combine to form the secondary building unit which the zeolites structure is comprised of (http://trigger.ch.umist.ac.uk:8081/zeolites/)

2.4.3 Adsorption properties of natural zeolites

The large cavities and entry channels of zeolites are generally filled with water molecules that form hydration spheres around the exchangeable cations. If the water is removed, molecules having effective cross-sectional diameters small enough to fit through the entry channels are readily adsorbed on the inner surfaces of the dehydrated central cavities. Molecules too large to fit through the entry channels are excluded and

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pass around the outside of the zeolite particle, giving rise to the well-known "molecular sieving" property of most crystalline zeolites. The surface area available for adsorption ranges up to several hundred square meters per gram (Mumpton, 1983). The extent of ion sieving depends on (1) the size of openings into the ion cages contained in the 3-D lattice structure (2) the energy or strength of bonding between the water and zeolite framework.

There are two main adsorption processes which occur when using zeolites for wastewater treatment. The first process is physical adsorption. The second process is chemical adsorption through ion exchange. Physical adsorption occurs when dissolved contaminants in the water adhere and become immobilized onto the surface of the zeolite particle without disrupting the atomic structure of the zeolite. The ion-exchange capacity is basically a function of the degree of substitution of aluminium for silicon in the framework structure. In zeolite structures, the negative charge is created by the substitution of Al^{3+} for Si^{4+} in the tetrahedra, giving rise to a deficiency of positive charge in the framework. This negative charge is balanced by mono- and divalent cations (typically Na^+, K^+, Mg^+, Sr^{2+} and Ba^{2+}) which are located in the channels. The greater the substitution, the greater the charge deficiency, and the greater the number of cations required for electrical neutrality. The general oxide formula of a zeolite is given as:

$$M_{x/n} (AlO_2)_x (SiO_2)_y \cdot mH_2O$$
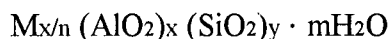
where M represents any exchangeable cation of valence n, and mH_2O represents the water molecules of hydration. The silicon to aluminum ratio, y/x, is invariably found to be equal to or greater than one and can approach infinity for completely 'aluminum free' frameworks.

The ion-exchange capacity of zeolites also depends on the nature of the cation species (size, charge etc.), the concentration of the cation species in solution, the presence of competitive ions and the structural characteristics of the zeolite (Kithoure & Paul, 1996). Of all these zeolite types, the clinoptilolite is the most common zeolite produced and has a greater affinity for ammonium ion and for other ions present in the wastewater than other zeolites (Jørgensen et al., 1976). The small amount of aluminum in clinoptilolite

results in a relatively low ion-exchange capacity (about 2.3 meq/g). (Metropoulos *et al.*, 1993) However, its cation selectivity has been reported as:

$$Cs^+ > Rb^+ > K^+ > NH4^+ > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$$
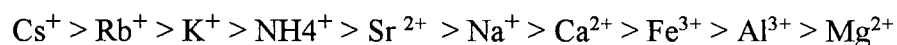
From the selectivity series, it can be seen that clinoptilolite shows a high preference for ammonium ions. Except for potassium, the cations which are more amenable to selection by clinoptilolite are not commonly found in municipal sewage streams. The channel diameters within the clinoptilolite structure range from 2.5-5.0 angstroms with an average diameter of 3.5 angstroms. Clinoptilolite's unusual selectivity for $NH4^+$ ions is caused by structurally related ion sieve properties found to differing degrees in many zeolites. Clinoptiloite's cation-exchange capacity and cation selectivity have led to its frequent use in wastewater treatment, mostly for waters with high levels of ammonium. Of the high-rate ammonia removal processes available, selective ion exchange using natural zeolite offers a number of distinct advantages (Cooney *et al.* 1999a):

i)   The natural zeolite, clinoptilolite, is highly selective for ammonium ions, compared with most other cations typically present in sewage;

ii)   The efficiency of ion exchange by the zeolite is relatively independent of temperature;

iii)   Ammonia removal by ion exchange is not coupled with increases in dissolved suspended solids.

2.4.4 Applications of zeolites

A review of the published literature revealed considerable prior research and development of ammonia adsorption processes using zeolites, especially clinoptilolite. Based on zeolites' attractive ion-exchange, adsorption, and hydration properties, numerous studies have been carried out. The applications of zeolite include the following:

a) Use of natural zeolite in agriculture

An important consideration in plant production is the efficiency of fertilizer use. The pronounced selectivity of clinoptilolite for large cations, such as ammonium and potassium, has been exploited for the preparation of chemical fertilizers that offer a slower release of these elements to the soil and thus a more efficient uptake by plants. Studies have generally been conducted on both the zeolite as received and on zeolites that have been pretreated with nutrient elements, such as potassium, ammonium, and various trace metals. In either case, the zeolite appears to act as a reservoir, holding such elements in its structure for slow release to the soil solution and thence to the plants, thereby increasing the overall efficiency of such additives and reducing the total cost of fertilization.

The greatest success appears to have been achieved with root crops, such as radishes, carrots, and sugar beets, where nitrogen is a vital nutrient. Lewis *et al.* (1983) found that the use of clinoptilolite increased fertilizer efficiencies. The ammonium-treated clinoptilolite also behaved like a slow-release N fertilizer. A 10- to 20-fold increase in the residual NH_4-N was found to occur in sandy soil upon the addition of zeolite. The natural zeolite also increased the fresh weight of radish-root by 59% vs. the control in a sandy-textured soil. In field experiments, Pirela *et al.* (1983) found that the addition of 8 metric ton/ha of clinoptilolite significantly decreased corn yield, possibly due to the increased availability of NH_4^+ or to the high level of Na^+ released to the soil by the clinoptilolite. Like their synthetic counterparts, the high adsorption capacities in the dehydrated state and the high ion-exchange capacities of many natural zeolites have also contributed to their ability to act as effective carriers of herbicides, fungicides, and insecticides.

b) Zeolite applications in aquaculture

Intensive culture of aquatic organisms is becoming more and more necessary as the production limits of natural bodies of water are reached. Intensive aquaculture is, however, complicated by the accumulation of toxic substances, primarily metabolic nitrogen. The toxic nitrogen compounds are mainly due to the release of ammonia by

fish. Ammonia is almost the only nitrogenous product of amino acid catabolism. Ammonia can therefore be a growth-limiting factor in aquacultural systems and is toxic at various concentrations to many species of fish.

As reported in several papers, the ion-exchange removal of ammonia from fish hatchery water supplies has been accomplished using natural zeolites (Chiayvareesajja & Boyd, 1993, and Marking & Bills, 1982). By adsorbing ammonia salts, Konstantinov & Pelipenko (1983) suggested that clinoptilolite inhibits the formation of nitrates and nitrites as the products of catabolism of ionized ammonia, thereby greatly reducing pollution by toxic products of nitrogen metabolism. Bergero *et al.* (1994) found that zeolites could be used to remove ammonia from recirculating systems of aquacultural water effectively at both 2.5mg/l and 10 mg/l concentration for over 3 weeks. The use of zeolites in intensive aquaculture systems seems promising, not only for their efficiency in NH_4^+ removal, but also in terms of cost.

c) Animal feed supplements, animal hygiene and odor control

The addition of zeolites to the normal diets of poultry, swine, and ruminants has resulted in increased body weights and feed efficiencies. This is possibly due to their capacity to slow down the passage of nutrients in the digestive system with a resultant improvement in caloric efficiency. The feces of animals were found to be firmer, better formed, and less odoriferous (Vrzgula & Bartko, 1983). These findings are of environmental importance, since odors from intensive livestock buildings cause large numbers of complaints and ammonia emissions from them are believed to represent a serious environmental risk (Amon *et al.*, 1997).

The potential of zeolites to reduce odor and ammonia emissions has been shown to be due to their excellent sorption properties. The ammonia and ammonium adsorption properties of zeolites have been reported by Bernal & Lopez-Real (1993), who suggest that aerial ammonia is adsorbed at a rate of 6 –14 g/Kg of zeolite. Karakhanyan *et al.* (1990) found that the addition of 23% natural zeolite to wastewater sediment make it possible to completely eliminate the unpleasant odors associated with the drying of the

sediment. It also assured disinfection and the removal of water from the sediment. During the composting of sewage sludge, Witter & Lopez-Real (1988) found that a cover of zeolite (clinoptilolite) placed on top of the compost pile proved very effective in adsorbing the volatilized ammonia; the ammonia adsorption increased the Kjeldahl nitrogen content of the zeolite up to 2.5%.

(d) Use of natural zeolite as soil amendments

Land disposal represents one method of effectively treating wastewater generated from agricultural and industrial activities. Unfortunately, not all soils are suitable receptors of wastewater due to their physical and chemical properties. Recently, there has been considerable interest in developing management practices that enhance the ability of soils to retain contaminants such as N, P and heavy metals (Sakadevan & Bavor, 1998). A soil amendment such as zeolite is capable of improving the sorption properties of coarse-textured soils and thereby increases their ability to remove contaminants. Based on their high ion-exchange capacity and water retentivity, natural zeolites have been used extensively as amendments for sandy, clay-poor soils.

As soil amendments, zeolites appear to increase the soil's ability to retain moisture longer after irrigation. They also improve the cation-exchange capacity of sandy and volcanic soils. Zeolite was found to significantly increase the soil's ability to remove NH_4^+ from solution when added at a rate of 10% to a sandy soil (Phillips, 1998). Furthermore, it is argued that gypsum/zeolite in combination should be considered as a means of improving the ability of soils to retain NH_4^+ and P. This would apply to such cases as coastal sands which receive sewage effluent, to natural and constructed wetlands used for effluent treatment, or to golf course greens fertilized with large amounts of nitrogen and phosphorus fertilizers.

e) Removal of heavy metals and radioactive ions from industrial and municipal effluents

The intensive development of industry without efficient emission controls to protect the ambient environment can cause the accumulation of high amounts of heavy metals in soils. As a consequence, harmful elements enter the food chain. Some of the treatment

processes for contaminated soils produce metal-laden extracts which also require treatment before reuse or disposal. Ion exchange is generally quite effective for removing metals from aqueous streams, and the ion-exchange properties of zeolites allow them to be exploited to trap undesirable metals to reduce the transfer of heavy metals, such as Cu, Cd, Pb, and Zn, from ground water or soils into food chain.

A number of researchers have done experiments to determine the different selectivity sequences of natural zeolites for a range of various heavy metals. They have agreed that Clinoptilolite shows a strong affinity for lead and cadium (Ćurković et al., 1997). Gworek (1992) found that the addition of zeolite pellets to soils contaminated with cadmium significantly reduced the cadmium concentrations in the roots and shoots of a range of crop plants. Olin & Bricka (1998) screened twelve sorbents in initial batch testing, and found zeolite demonstrated the highest capacity for Pb, Cr, and Cd. Cost analysis also indicates that for small volumes of waste, zeolite is likely to be more cost effective than commercial ion exchange media.

2.4.5 Review of the usage of zeolites for wastewater treatments

The importance of nutrient removal from wastewater is becoming more recognized. Traditionally, biological systems have provided an economical solution and biological phosphorus and ammonia removal facilities have been retrofitted to exist organic treatment systems. However, these systems generally require large spaces and long retention times due to the slowness of biological conversion of nutrients. This results in high capital costs. The value of developing methods of simple and efficient nutrient removal by means of small-scale on-site wastewater treatment systems is increasingly apparent. Such systems can provide at-source pollution control measures in areas where a centralized large-scale wastewater treatment system is not cost-effective.

Given the ion selectivity characteristics of clinoptilolite, it should be well suited for use in ammonia removal from aqueous solutions or effluents. A review of the published literature revealed considerable prior research and development of ammonia ion-

exchange processes using zeolite. Overseas studies, which used zeolites from many different deposits, have established that zeolite, especially clinoptilolite, has the potential to removal NH4+ from municipal, industrial, and aquaculture wastewaters. Most research examined the ammonia-clinoptilolite ion exchange system and proposed ways to use clinoptilolite for the treatment of effluents primarily at the laboratory and pilot plant scale. The use of clinoptilolite for the removal of ammonia in a full scale municipal wastewater treatment plant has also been reported by Liberti *et al.* (1986). A physico-chemical process named "RIM-NUT" was used to remove ammonia and phosphates from wastewater. Recovery of a slow release fertilizer by means of selective ion exchange and chemical precipitation was also part of the process. The results obtained during 6 months of operation of a 10 m³/h demonstration plant for the tertiary treatment of domestic effluent ensured ≥ 90% removal of both nutrients.

2.4.5.1 Ammonium adsorption capacity studies of zeolites

Initial studies have been done all over the world which have sought to establish the basic characteristics of zeolite from different deposits, since the capacity and diffusion characteristics are specific to each place of origin and consistency of performance between different deposits cannot be assumed. Natural zeolites, from deposits in the United States, Hungary, Greece, Croatia, and Australia, have been shown to achieve high ammonium removal efficiencies at relatively low cost. Generally, laboratory investigations sought to study the equilibrium and kinetic characteristics of ammonium exchange in the zeolite. A synthetic ammonium solution was favored when determining the capacity of zeolite in order to exclude the interference of other ions. Based on the aluminum content and the molecular weight of the zeolite sample as determined by chemical analysis, the theoretical capacity of the zeolite sample was determined by assuming each aluminum atom created an exchange site. It was assumed that all of the cation exchangeable sites on zeolites are taken up with NH4+, and that therefore the values reflect the NH4+ removal capacity of zeolites. Ammonium-adsorption capacities of clinoptilolite were reported from 5.7 to 31.86 mg N/g, 1.5-2.853 meq/g, or around 8

mmol/100g. (Haralambous $et\ al.$, 1992, Jørgensen $et\ al.$, 1976, Metropoulos $et\ al.$, 1993, Nguyen & Tanner, 1998, and Singh & Prasad, 1997).

A sample of clinoptilolite from the Ash Meadows deposit in California was studied by Semmens & Martin (1988). The theoretical capacity was 2.1 meq/g and the measured capacity was approximately 95% of the theoretical capacity of the zeolite sample. They found that approximately 10% of the sodium, 50% of the calcium and all of the magnesium did not appear to be exchangeable. It was thought that these ions were associated with impurities in the zeolite matrix. Another clinoptilolite sample from New Mexico was found to have the capacity of 1.64 meq/g by using 100mg NH_4^+-N/l solution. Cooney $et\ al.$ (1999a) studied a natural zeolite mined north of Sydney, Australia, and found that the saturation capacity of the zeolite was experimentally determined as 1.5 meq/g. Neither solution equilibrium pH nor initial ammonium concentration were found to influence the selectivity of the zeolite for ammonium. Two New Zealand zeolites from different sources were studied by Nguyen & Tanner (1998). They found both zeolites were equally effective (87-98%) at NH_4^+ removal. The maximum NH_4^+ removal capacity of the zeolites was 5.7-8.3 mg N/g, lower than those predicted from the theoretical exchange capacity values (accounting for only 39% of that predicted for clinoptilolite). A study from the UK examined four different sources of clinoptilolite zeolites and one sepiolite. The maximum adsorption of NH_4^+-N was found between 8.149-15.169 mg N/g for the clinoptilolite zeolites and 1.47 mg N/g for sepiolite (Bernal & Lopez-Real, 1993).

Generally, the results revealed that: (1) clinoptilolite showed a higher selectivity for ammonia compared to other type of zeolites; (2) the measured NH_4^+ removal capacity of the studied zeolites was not adequately reflected by their theoretical capacity; (3) the ion exchange of zeolite for ammonium ions was a very fast process (most of the ammonium uptake was taken in the first 5 minutes to 1 hour).

2.4.5.2 Column performance studies of zeolite

Extensive studies by different authors on the ammonium exchange potential with a view to wastewater treatment applications have been undertaken and published. A continuous packed column process has been widely used to investigate the performance of zeolite in a pilot-scale process for wastewater treatment. The design and operation of the zeolite pilot-scale processes enabled the evaluation of continuous, high-rate, ammonium removal from wastewater. The physical characteristics of the column, and subsequent loading and regeneration cycles were able to reveal a number of important conclusions for the optimum performance of the column. A number of wastewaters have been used in the studies: synthetic, dairy, piggery, and sewage effluents, landfill leachates and aquaculture wastewater. The performance of the zeolite columns has been examined under various conditions such as single column and columns in series, with and without effluent recycling, flow rate and bed height (Bergero *et al.*, 1994, Cooney *et al.*, 1999, Hlavay *et al.*, 1982, Nguyen & Tanner, 1998, and Papadopoulos *et al.*, 1996).

The results for ammonium removal efficiency have revealed that under certain conditions clinoptilolite is very effective in removing ammonium ions from wastewater effluents. For low ammonia concentration effluents ranging from 25-50 mg N/l, the zeolite column process was able to reduce the effluent down to levels below 1 mg N/l when sufficient contact time was allowed. The adsorption capacity of the zeolite for this range of influent ammonium concentrations was about 4.5 mg N/g (Booker *et al.*, 1996). When the initial ammonium concentration of the sample was as high as 2772-3257 mg N/l, a value of 84% ammonia removal by three clinoptilolite columns in series with effluent recycling was reached (Papadopoulos *et al.*, 1996). Partial COD removal (16%) was also accomplished during the ion exchange procedure.

Hlavay *et al.* (1982) used natural Hungarian zeolite for ammonia removal from synthetic and municipal wastewater. It was found that the ammonia breakthrough capacity was about 2.4 mg NH_3-N /g zeolite, less than a half of the value obtained with synthetic wastewater. They therefore suggested that only secondary wastewater should be

treated by this method because the suspended material and the organic compounds present in the raw wastewater can block the ion exchange sites of the clinoptilolite. However, the presence of suspended solids in the influent generated increased head loss through the bed, and periodic backwashing of the system was needed. It was therefore suggested that in order to minimize disturbance to the zeolite bed during backwash, a dual media filtration at the SS filter was necessary.

2.4.5.3 Factors that affect the ammonia removal ability of zeolite

The capacity of zeolites to remove NH_4^+ from wastewaters is dependent on many factors such as the type and particle size of zeolite used, contact time, temperature, pH, size of the exchanging ions, ion concentration, the presence of other ions, etc. Results from several research studies have indicated some major factors that affect the performance of zeolite exchange capacity as follows:

(a) Contact time

A specific time of contact is essential if the optimal removal capacity is to be reached. The length of contact time between the water and the ion-exchanger is therefore a very important parameter in the design of ion-exchange facilities. In many cases, it is the main reason for poor performance and shortened operating cycles. A lower loading flow rate increases the ammonium exchange capacity. With an increase in the contact time the ammonium adsorption rate by zeolite also increases. Too short a contact time results in lower ammonium removal rates, indicating that the contact time between the zeolite and NH_4^+ ions is insufficient for NH_4^+ adsorption and diffusion into the internal structure of the zeolite. The importance of the wastewater loading flow rate on NH_4^+ removal efficiency has been reported for overseas zeolites. By changing the flow rate from 10 to 5 BV/h the ammonia breakthrough capacity increased as much as 35% (Hlavay *et al.* 1982). Nguyen & Tanner (1998) found the NH_4^+ breakthrough capacity of zeolites increased by 29-57 % with a decrease in flow rate from 15.9 mm/min to 0.47 mm/min. At a slow (0.47 mm/min) flow rate with 17.8 hours of contact time, zeolite columns with a BV of 245.4 cm^3 effectively removed 100g N/ m^3 to ≤ 1.2 g N/m^3 after 40BVs.

(b) Ion concentrations

With an increase in the concentration of ammonium in solution, the adsorption rate of ammonium by zeolite increases. Investigations revealed that a column's ammonium removal performance was dependent upon both the initial ammonium concentration and the feed flow rate (Cooney et al., 1999b). The higher the ammonia concentration in solution the more NH_3 was adsorbed by zeolite (Singh & Prasad, 1997). It was found that adsorption capacities were observed to be 15 and 31.08 mg NH_4^+/g, with an initial ammonium concentration of 200 and 1000 mg NH_4^+-N /l, respectively. Jørgensen et al. (1976) put the zeolite from the equilibrium solutions into distilled water and measured the adsorbed NH_4^+ ions in the water. They found that, independent of the concentration of the NH_3 solution, NH_4^+ ions equal to the ion exchange capacity of the zeolite always remained. Only the NH_4^+ ions adsorbed on the surface of the zeolite went into the distilled water. The amount of these NH_4^+ ions is a function of the NH_3 concentration; it increases with an increasing NH_3 concentration in the solutions. They also suggested that clinoptilolite works by a combination of ion exchange and adsorption. With a small concentration of the counter ion in the solution, only ion exchange takes place. With a higher concentration, adsorption takes place – the higher the concentration, the greater the adsorption. When zeolite is 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 initial concentration in the solutions. Dimova et al. (1999) found that at a fixed water velocity, increasing the initial NH_4^+ concentration increases the ion-exchange velocity. After reaching a certain length of contact time, the ion-exchange velocity becomes practically zero.

(c) Particle size

The particle size also influences the ammonium uptake capacity of zeolite. The smaller the particle size, the higher the ion-exchange capacity for the zeolite; that is, the surface area for the uptake is bigger with small particles. With a particle size of 2.5-5.0 mm the static capacity is 0.47 meq/g, and with 1.4-2.0 mm even 0.62 meq/g (Jørgensen et al., 1976). Marking & Bills (1982) found large granules were less efficient than smaller ones. The removal rate was 5.37 mg/g for 8 x 18 mesh granules, as compared with about

8 mg/g for 30 x 50 mesh granules. However, the smaller granules tended to restrict flow and to clog more readily than large granules. These effects can be reduced by vigorous shaking and a prolonged contact time (17 hours). It has also been suggested that the effect of zeolite particle size on NH_4^+ removal performance depends on the contact time, and that this is governed by the wastewater loading flow rate through the zeolite beds (Nguyen & Tanner, 1998). The interaction between wastewater flow rate and zeolite particle size highlights the need to conduct flow-through studies to assess the NH_4^+ removal rate of zeolites.

(d) Presence of competitive ions

The experimental results of the exchange capacities are usually much lower than the theoretical exchange capacity of zeolite obtained from its analysis. The reason may be that most of the theoretical exchange capacities for zeolite have been obtained from its chemical structures and X-ray diffraction patterns, or by using a synthetic ammonium solution (such as NH_4Cl). In wastewater treatment applications, other cations such as Na^+, Ca^+, and Mg^{2+} etc. which are present in significant concentrations in the wastewater may be approaching the ion-exchange site of the zeolite, inhibiting further adsorption of ammonia in the zeolite column (Singh & Prasad, 1997). By using three columns in series, these authors found that the third column had a greater efficiency than the previous columns. Ammonium adsorption in the third column was quite efficient. This may be attributed to a decrease in the concentration of other competitive cations due to their adsorbtion by the first and second columns.

Nguyen & Tanner (1998) found that the capacity of zeolites to adsorb NH_4^+ was significantly related to the surface charge density of the zeolites. The presence of Na^+ in treated NH_4Cl solutions under batch adsorption resulted in a 15% reduction in ammonium removal. Cooney et al. (1999) found that the presence of magnesium and calcium ions reduced the amount of ammonium ions in the solid phase (zeolite) by approximately 25%. The presence of potassium caused a significant decrease in the zeolite's ammonium adsorption, as anticipated by the very high selectivity coefficient for potassium. Jørgensen et al. (1976) also found that the presence of Ca^{2+} in tap water and

wastewater resulted in a considerably lower ammonium removal capacity than the use of distilled water. However, the influence of competing cations depends on the concentrations of each cation present.

(e) Pretreatment of zeolite

Many investigators have reported variations in the measured capacities of zeolites. The practical exchange capacity is frequently less than the theoretical capacity. This means that in actual practice, part of the exchange capacity cannot be used. The impurities which are inevitably present may be a major reason for this, especially if this material is deposited in the zeolite channels. It has been suggested that pretreatment of zeolite samples can improve the ammonium removal performance. Semmens & Martin (1988) suggested that by exposing the zeolite to large volumes of a concentrated NaCl solution, much of the potassium could be displaced. Since the potassium ions are very selectively held by the zeolite, the removal of these ions should result in an effective increase in the removal capacity. Similar results have been reported by other researchers (Booker et al., 1996, Ćurković et al., 1997, and Metropoulos et al., 1993).

Researchers investigating different pretreatments for zeolite have shown that increased removal capacity could be achieved by converting the ion exchange site to the sodium form. Zeolite samples were kept in contact with a highly concentrated NaCl solution (1-2 M) for 24h to 8 days under 20 °C to 70 °C, in order to convert them to a near homoionic state in Na-form. Klieve & Semens (1980) found that heat pretreatment (600 °C for 1h) improved zeolite's ammonium selectivity significantly in the presence of competing cations. Ammonium removal capacity was increased by approximately 17% for heat treated zeolite samples. However, it must be stressed that the pretreatment of the mineral would have to be minimized, since the cost of purification would render the material less competitive for use in wastewater treatment.

2.4.5.4 Applications of zeolite in conjunction with other treatment processes

Some applications of zeolites are accomplished in conjunction with other treatment systems. The effect of zeolite on the performance of the activated sludge process was evaluated by Carrondo et al., (1980). Primary settled wastewater was fed to the units at different hydraulic retention times (2.4 and 4 h HRT) in aerators with zeolite concentrations at the inlet of 15 and 30 mg/l. The experimental program was carried out at a sludge age of 6 days. The results showed the settling capacity of the activated sludge was improved in the presence of zeolite, and there was no increase in the effluent SS. It also seemed to improve the dewatering capacity of the activated sludge, which could result in better filtering. Average COD removal of 80% was obtained and no effects resulting from the presence of the zeolite could be detected. There was also a marginal increase in the MLVSS in the aerator.

Ratanatamskul et al. (1995) used an on-site small-scale combined system of a membrane separation bioreactor (MSB) and a zeolite-iron (Z-Fe) column in series to investigate both ammonia and phosphorus removal. The effluent from the MSB was treated by the Z-Fe column. The zeolite was used to remove the residual ammonia owing to its high selectivity as well as its ability to entrap some of the leached iron particles. The results indicted that average nitrogen removal by the MSB was between 50-83%. Residual ammonia nitrogen in the effluent from the MSB was further polished by the Z-Fe column to an initially non-detectable concentration (1.2 mg/l). The average phosphorus removal by this system was 70%. With variation in the iron bed height from 15-45 cm, the phosphorus removal rate increased rapidly. A phosphorus removal efficiency of 92 % for almost 20 days could be reached by providing aeration to the bottom part of the iron bed in the long column.

The utilization of sand beds in water and wastewater filtration is commonly practiced. In a filtration operation, wastewater passes through a filtering bed on which the greater parts of solid particles in suspension are retained by the filtering media. These particles progressively create a film that increases the capacity for retention of small particles.

During filtration, hydraulic loading capacity and the organic matter removal efficiency change with time due to the retention of pollutant particles. The losses of hydraulic loading capacity depend on the size of the filtering media, the rate of filtration and the media porosity. The use of natural zeolite instead of sand has been used to improve the operation of these systems.

A comparative study of sand and natural zeolite as filtering media for the effluents from an anaerobic digestion process in a fixed bed reactor (AFBR) used to treat sewage water from tourist areas was carried out by Reyes *et al.* (1997). Their aim was to obtain final effluents of sufficient quality for land irrigation or disposal in these tourist zones. Zeolite and sand beds operated with similar removal capacity for suspended solids and pathogenic microorganisms. However, the bed operating with zeolite had lower pressure losses and consequently a longer operating time. In addition, zeolite was able to remove a considerable amount of ammonia nitrogen under these operating conditions. A maximum removal of 95% was obtained in the first hour of filtration. This efficiency decreased progressively, and a minimum value was achieved of 50% at 8 h of operation. The final concentration of total coliforms obtained after the filtration with zeolite can be considered adequate for water reuse in land irrigation. Milan *et al.* (1997) also used a column packed with zeolite to treat the effluent from an AFBR treating piggery manure. For 20 BV of waste treated with an initial ammonia nitrogen concentration of 600 mg/l, a value of 91% removal efficiency was obtained using a Na-Zeo column. These authors suggested that the best operational conditions were obtained with surface hydraulic loadings of up to 9m³/m²d and bed heights of 9 and 18 cm, and diameter ratios of 2 and 4, respectively. The pressure drops would be lower and lead to a reduction in the operating costs.

Due to the increasing efficiency requirements for nutrient removal from wastewater, filtration units primarily designed for the removal of suspended solids have been upgraded to include biological processes. Commonly this type of filtration is termed biofiltration. The kind of filtration determines the priority of the processes. Upflow filters are mainly designed for biological activity and downflow filters are primarily constructed for the removal of suspended solids. Widely varying inflow conditions, oscillating flow

rates or concentrations can disturb such a biofiltration unit. Peak loading of ammonia can cause strongly oscillating effluent concentrations. Filtration units have only a low capacity for equalizing fluctuating inflow conditions and often the influent pattern can be found in the effluent, due to a low retention time. To avoid effluent peaks, large volume equalization basins are usually necessary. As an alternative to these, post-equalization in the filtration unit may be applied using filters with biological capacity and with selective ion-exchangers.

In research on the biological-ion exchange process, use was made of the ion exchange material zeolite as the carrier for the nitrifying biomass, enabling the two mode process to be carried out in a single reactor (Green *et al.,* 1996). In the first mode (ion exchange), secondary effluent was passed through an ion exchange column where ammonium was concentrated in the zeolite. During the second mode (bioregeneration), the adsorbed ammonium was released gradually and converted to nitrate by the active biomass residing on the zeolite. Nitrification was carried out batchwise and in a small volume reactor where optimal conditions could be easily maintained. The addition of chemicals for the desorption of ammonium was minimal due to regenerant reuse during several cycles of nitrification. This concept allowed for nitrogen removal in minimal volumes. As a result, operational costs and production of large volumes of brine were minimized.

The idea for the utilization of a combined filter filled with zeolite and biologically activated material with a nitrifying biofilm was proposed by a team of German scientists and examined for the treatment of wastewaters (Oldenburg and Sekoulov, 1995). Zeolite was used as ion-exchanger for equalization of ammonia peak loadings in aerated biological activated filters by mixing it with a filter medium to form a nitrifying filtration unit. The results showed that the addition of zeolite can equalize variations in ammonia; during the phase of high inflow ammonia concentrations the zeolite collected ammonia and worked to dampen its effluent concentration. When the influent concentration decreased, ammonia was desorbed from the zeolite and was nitrified by the bacteria growing on the filter medium. These authors suggested that existing filter units could be upgraded in this way and the stability of the operating process of biofilters improved

significantly. Green *et al.* (1996) investigated the possible interference by the attached biofilm with the ion-exchange (diffusion limitations), and found no significant effect on the ion exchange column efficiency.

Clintoli *et al.*(1995) found that the combination of ion-exchange by zeolite and anaerobic digestion in Upflow Anaerobic Sludge Blanket Activated (UASB) or Up flow Anaerobic Sludge Blanket-Anaerobic Filter (UASB-AF) reactors was a solution capable of reducing the pollution potential of piggery wastewaters. A reduction of ammonium concentration from 1500 mg/l to 400-500 mg/l and an organics removal of up to 80% at a 2 day HRT were achieved. A reduction of toxicity of wastewater to anaerobic microbial populations and improvement of the UASB and UASB-AF reactor yields in the reduction of organics and gas production was achieved. It was proposed that the zeolitized rocks, after maturation and drying, could be mixed with the solid fraction of the slurry and used as a biological manure. The authors claimed this system could compete with other technologies not only in terms of efficiency and low costs, but also for the possible reuse of final products.

Another new biotechnology involving the immobilization of nitrifying bacteria has been developed to improve the effect of nitrification. A concentrated, enriched culture of nitrifiers is entrapped in a special biomass carrier and immobilized by sodium alginate to form spherical pellets. Zeolite was also immobilized in the pellets to enhance the transfer of ammonium into the pellets as the nitrifiers' substrate. The results showed that both the effects of ammonium exchange and nitrification were enhanced by higher initial ammonia concentrations (50-100 mg N/l). This might be attributed to the higher ammonium concentrations in the system enhancing the ion exchange by the zeolite entrapped inside the pellets. This new ammonia removal biotechnology appeared well suited to the treatment of wastewaters containing high ammonia concentrations (Yang, 1997). The advantages of using immobilization biotechnology to treat wastewaters include long retention time of biomass in the systems, manipulation of growth rate independent of washout, obvious phase separation of cell mass due to enhanced settlability of the biopellets, high cell concentration within the reactor, use of vertical

reactors which reduces land requirements, and possible protection from inhibitory compounds.

2.4.5.5 Reuse of exchanged zeolite

Zeolites are useful not only for their efficiency in ammonium removal, but also in terms of cost. It is possible to use zeolite as a natural material, replacing exhausted zeolite with new zeolite, or to re-use the same material with periodic NaCl-operated regeneration. Neither of these methods results in any environmental problems.

(a) Chemical regeneration

Zeolites are known for their ability to remove ammonium from wastewater due to their preferential selectivity for this ion. Usually the cycle of zeolite use is first in a packed bed column followed by chemical regeneration (usually by highly concentrated NaCl). After washout of the exchanged ions from the zeolites, another loading cycle can be undertaken. This step is where the primary costs of treatment arise ($\cong 80\%$ of the total cost). In studies, concentrations of NaCl from 0.35M-1.0M were used (Bergero *et al.*, 1994, Cooney *et al.*, 1999, Hlavay *et al.*, 1982, Liberti *et al.*, 1981, Singh and Prasad, 1997). All the exchange sites in the exchanger were converted back to sodium form and ready for the next run without any loss in ammonium uptake capacity. No appreciable deterioration in the performance of the zeolite was seen after repeated cycles of loading and regeneration of the pilot column. This indicates that any costs associated with recharging the process with new zeolite are minor. Haralambous *et al.* (1992) suggested that the loading of the zeolite with ammonium and the addition of a regeneration step would improve its ion exchange capacity. It seemed that the zeolite can be self-purified in a process where ammonium is the ion that has to be removed.

Jørgensen *et al.* (1976) noted that the capacity of a sample of clinoptilolite increased with the number of regenerations undertaken. Their regeneration process consisted of treatment with 4% NaOH for 30 min, followed by a rinse with 1 l of deionized water for 40 min. After repeating this procedure four times, the measured capacity was found to be

constant. They concluded that the sodium hydroxide " activates" the clinoptilolite. It should therefore be noted that no pre-treatment is required. The solution is purely physical-chemical and due to the use of the same elution liquid, which can also be regenerated, the running costs are rather moderate, considering the water quality.

Liberti *et al.,* (1981, 1986 and 1995) suggested that the regeneration eluates can be purified to obtain a premium-quality slow-release solid fertilizer, $MgNH_4PO_4$. This investigation led to a patented process with the name RIM-NUT (removal of nutrients) that allows ammonium and /or phosphate ions to be removed selectively from wastewater by a natural zeolite and/or a strong anionic exchanger. This process was developed with the following characteristics: two ion exchange resins, cationic and anionic, in series, treated a municipal secondary effluent, removing residual suspended solids by filtration, bioresistant organics by adsorption and ammonium and phosphate ions by selective ion exchange. Resin regeneration was performed with a 0.6M neutral NaCl solution. The regeneration eluates were properly mixed and added Mg salt and P salts, under controlled pH conditions, to obtain a stoichiometric ratio $Mg : NH_4 : PO_4 = 1 : 1 : 1$. with $MgNH_4PO_4$ as precipitate according to the following reaction:

$$NH^{4+} + Mg^{2+} + PO_4^{3-} \rightarrow MgNH_4PO_4 + H^+$$
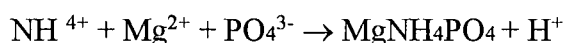
After the separation of the precipitate, the eluates were recycled for further regeneration. A fully automatic pilot plant was built to remove both ammonium and phosphate ions from secondary municipal effluents. The combined use of clinoptilolite and a strong base anion resin, regenerated in a "closed-loop" fashion with 0.6 M neutral NaCl, ensured $\geq$ 90% removal of both nutrients (N & P). Overall, this process has the advantages of using a very simple ion exchange-regeneration procedure and of recovering a high-value fertilizer by-product.

(b) Biological regeneration

Instead of chemical regeneration, many researchers have studied biological regeneration (hybrid biological-ion exchange system) of the zeolite saturated with

ammonium. The concept here is that when ammonium-saturated clinoptilolite is exposed to nitrifying bacteria in a salt solution, ammonium is displaced into solution by ion exchange. The liberated ammonium is available for oxidation to nitrate by the nitrifying bacteria (Semmens & Porter, 1979). The exhausted zeolite in this study was regenerated by using a neutral brine containing 0.3-0.4 M NaNO$_3$. The spent regenerant then flowed to a feed reservoir from which it was fed to a nitrification unit. Because of the presence of nitrifying bacteria in the biofilms between and within the zeolite particles, the nitrification rate in these biofilms could be enhanced easily by aeration and recirculation of a regeneration solution through the zeolite beds to promote NH$_4^+$ desorption from the adsorption sites on the zeolites.

In contrast to the above study of combined biological-ion exchange multireactor systems, Green $et\,al.$ (1996) and Lahav & Green (1998), introduced a process which used the ion exchange material, zeolite, as the carrier for the nitrifying biomass. Here the entire process is carried out in a single reactor. The reactor was operated in two sequential modes and can be described by the following reactions:

I.   Ion exchange into the zeolite

$$R\text{-}Na^+ + NH_4^+ \leftrightarrow R\text{-}NH_4^+ + Na^+$$
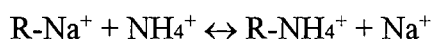
II.   Natural desorption of zeolite and biological regeneration

$$R\text{-}NH_4^+ + Na^+ \leftrightarrow R\text{-}Na^+ + NH_4^+ \text{ - desorption}$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \text{ - nitrification}$$
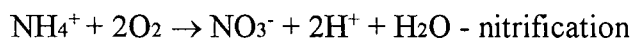
They found that this process has the following advantages: a) Optimal conditions for nitrification during the second mode can easily be maintained due to the batchlike conditions and the gradual release of adsorbed ammonium from the zeolite. b) The addition of chemicals for the desorption of ammonium is minimal due to regenerant reuse during several cycles of nitrification. As a result, operational costs and production of large volumes of brine are minimized. The analysis of the ion-exchange and the biological nitrification kinetics shows that the biological nitrification is the slower reaction and would be the limiting process in a combined facility.

Dimove *et al.* (1999) investigated the influence of water velocity and water hardness on desorption. It was found that lower velocity negatively affects the process of NH_4^+ desorption. The reason might be that the increased contact time caused saturation of the water around the zeolite grains with NH_4^+, thereby reducing the concentration gradient between the water film and the grain surface. They suggested that high water velocities (over 10 m/h) are advisable because the effect of regeneration remains the same but the time is greatly reduced. The Mg^{2+} ions didn't influence the desorption and only Ca^{2+} took part in it. Water hardness in the examined range (0.9-5 mg-eq/l) did not affect the NH_4^+ desorption process.

Jung *et al.* (1999) focused on the role of biofilm on the zeolite surface. Using an optical microscope and scanning electron microscope, they found that the biofilm was fully developed on the zeolite surface. This bio-flocculated zeolite could contribute to ammonium removal during the denitrification period and nitrifers could easily regenerate it during the nitrification period. Due to the bio-flocculated zeolite, a higher buffer capacity against shock loading of ammonium-rich wastewater beneficial to nitrogen removal could be obtained.

(c) Fertilizer

Exhausted zeolites can directly be used as slow-release nitrogen fertilizers in agriculture (Cintoli *et al.*, 1995). After maturation and drying, they can be mixed with the solid fraction of the slurry and then used as a biological manure. Zeolites have beneficial effects on the soil: (1) they are antacid; (2) exchange with ammonium helps to redissolve fixed phosphate or directly dissolve phosphorites and apatites; (3) they can hold up to 20-30% of their weight in nitrates thus slowing down the leaching of nitrates and drastically reducing the potential pollution of groundwater.

The granulometric distribution of zeolite can correct both clay and sandy soil; an increase in sprouting per unit of area is also aided by the greater rock porosity. Zeolites have recently been introduced as an inorganic soil amendment for golf course

management (Hogg, 1997). As a soil amendment, four basic characteristics of zeolite affect it's performance. These characteristics are as follows. (1) The fundamentals of soil cation exchange capacity (CEC) is the relative ability of the soil to store one particular group of nutrients, i.e. the cations. Zeolites increase the CEC of soil or the relative ability of the soil to store soil cations of Ca^{+2}, Mg^{+2}, K^+, NH_4^+ and Na^+. (2) Cation trapping capacity refers to the ability of the zeolite to trap and retain ammonium for later use. (3) Water retentiveness is a measure of the zeolite's ability to hold available water for use by plants. (4) Electrical conductivity is a measure of the presence of soluble salts.

Chapter 3: Materials and Methods

3.1 Zeolite

The natural zeolite (clinoptilolite) used in this research was supplied by Canmark International Resources Inc., Vancouver, B.C.. Large blocks of the material were crushed and sieved into the following three particle size ranges which are all commercially available (Figure 3-1): pebble size (>10 mesh size; or >2mm), coarse sand-granular (between 10-35 mesh size; or 2mm-500μm) and powder (< 35 mesh size; or <500μm). Their ability to remove ammonium was evaluated by both batch and flow-through column experiments.

(powder size)   (coarse size)   (pebble size)
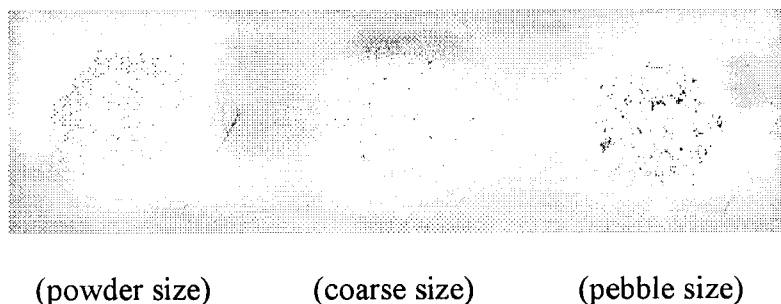
Figure 3-1. Different particle size of zeolites used in the studies

3.2 Wastewater

Wastewater samples used in this experiment were of composting leachate collected from a pilot-scale plant for vegetable greenhouse solid waste composting at Hazelmere Greenhouse Ltd, Surrey, B.C.. All the leachate samples were transported to the laboratory and stored in a cold room at 4°C. The wastewater was allowed to reach ambient room temperature (20 ± 2 °C) before being used for all the tests. It was already known that the leachate had very high concentrations of ammonia (typically > 200 mg/l ammonia-N). The characteristics of the leachate were analyzed and are presented in Table1. These include BOD, COD, all forms nitrogen: Nitrate (NO_3-N), ammonia-nitrogen (NH_4-N) and

total Kjeldahl nitrogen (TKN), phosphate (PO4-P), all the solid content measurements (TS, TSS & TVS) and pH. These were determined according to the Standard Methods (APHA, 1995). The characteristics of the composting leachate are shown in Table 3-1.

Table 3-1. Characteristics of the wastewater

Parameter		Unit (mg/l, except for pH)
pH		8.75
Solid contents	TS	13.52
	TSS	0.07
	TVS	8.66
BOD		103
COD		978
Nitrogen	Nitrate NO_3-N	1.2
	Ammonia NH_3-N	213.3
	TKN	346.5
Orthro-P		2.6

3.3 Experimental procedure

This experiment was divided into two stages. The first stage was an ammonia adsorption capacity study, the effect of particle size, ion concentration and contact time on the adsorptivity of zeolite were examined. The second stage was a zeolite-packed column efficiency study, the factors affecting the ammonia removal efficiency and the regeneration process were investigated.

3.3.1 Batch studies of the adsorption capacity

In this stage, comparative studies were carried out for the three different particle size zeolites (pebble, coarse and powdered). Both kinetic tests as well as equilibrium studies were accomplished to determine the ammonia adsorption capabilities of the samples of diffrently sized particles of zeolite.

a) *Equilibrium experiments* were conducted to study the effect of ammonia concentration on ammonium adsorption capacity of the zeolites. Zeolite samples of 1g were weighed into flasks. These were then placed in contact with 100 ml of a solution containing various ammonia concentrations. In order to provide an adequate mix, they were placed for 1 hour on an end-over-end shaker table at 150 rpm shaking speed. The set up of all the batch studies is shown in Figure 3-2. Each batch test was performed in duplicate.

Two groups of experiment were undertaken to evaluate the effects of various concentrations of the NH4Cl solution and of leachate as follows.

(i)   Ammonium chloride (NH4Cl) solutions were prepared using analytical-grade NH4Cl powder dissolved in distilled water, resulting in a range of initial NH_4^+ concentrations (25, 50, 75, 100, 125, 150, 175 and 200mg NH4-N/l).

(ii)   Leachate was diluted into several levels of NH_4^+ concentrations which corresponded to the initial concentrations of the group in NH4Cl solutions.

The initial and finial solutions were collected and analyzed for ammonium. The difference between the amounts added initially and that in the finial solution was considered to be the amount that had been adsorbed by the zeolite samples.
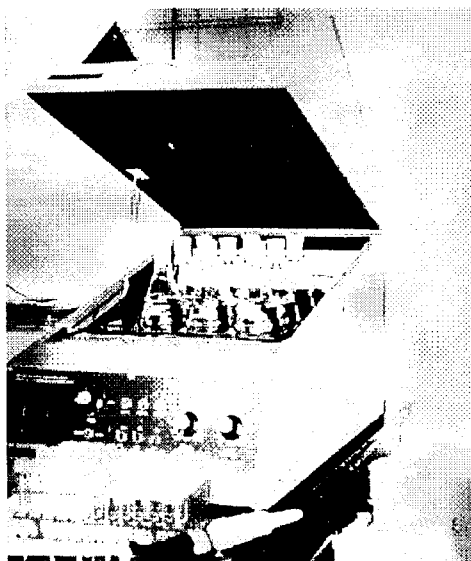
Figure 3-2. The set up for batch studies of zeolite capacity

b) *Kinetic experiments* were undertaken to study the effect of contact time on zeolite adsorption capacity. Tests were performed in 300ml DO bottles. For each batch test, the zeolite samples, of known size range, were accurately weighted (2g per sample). Each sample was placed in contact with 200 ml of solution on a shaker table at 150 rpm shaking speed.

Two sets of experiment were evaluated for leachate and NH_4Cl solution, respectively.

(i)   Ammonium chloride (NH_4Cl, 200mg NH_4-N/l) solution was prepared using analytical-grade NH_4Cl powder dissolved in distilled water.

(ii)   Leachate samples with known initial concentrations of 190.31mg NH_4-N/l.

At time zero the zeolite samples were introduced to the test bottles, and the timer was started. A pipette (Pipetman P10 ml, Gilson) was used to extract 10ml volume samples at several time intervals (5, 10, 15, 30, 45min, 1h, 1.5h, 2h, 2.5h, 3h, 4h, 8h, 12h, 24h and 48h) over the course of the test. These samples were placed in stoppered test tubes for future analysis, in order to find out how much ammonium was taken up by the zeolite samples at each time interval. Each batch test was performed in triplicate.

c) Performance of sodium form zeolite

Another set of batch studies (both kinetic and equilibrium studies) was undertaken by converting the zeolites, to as great an extent as possible, into their sodic homoionic (termed Na-Zeo) forms (Metropoulos *et al.*, 1993). The zeolite samples were treated by exhaustively equilibriating the samples with 1.0 M sodium chloride solution at 70 °C in stirred vessels. The treated zeolites were then washed with distilled water and subsequently oven dried at 110 °C over night. In this part of study, the ion exchange capacities of the Na-Zeo were examined only by means of NH_4Cl solutions.

3.3.2 Packed zeolite column efficiency studies

Based on the results from the previous batch adsorption studies, column studies were conducted. The zeolites with a higher NH_4^+ exchange capacity were selected for the column studies.

The reactors used in these experiments were made of acrylic plastic pipe 35 cm in height and 10.3 cm in inside diameter. The base of the column was fitted with a steel support plate in order to support the zeolite bed and prevent the zeolite from being lost through the reactor. The lower 1.5 cm of the column was transparent. The total volume of each reactor was about 3 L. Both coarse and powder size zeolite particles were selected and packed for the column studies, 2 Kg of each zeolite sample was loaded and shaken well in the column. There was a height of 22 ± 2 cm for each run. The columns were operated in a downflow mode with continuous flow-through of the composting leachate. Two peristaltic pumps (each with two pump heads) were used to feed influent from the center of the top of the reactors and withdraw effluent from the bottom of the reactors. This meant that the same flow rate was used for both feeding and discharging the reactors. The design and dimension of the reactors are shown in Figure 3-3 and Table 3-2, respectively.

Three levels of hydraulic retention time (HRT) were selected (1 hr, 3 hrs and 6 hrs) in order to evaluate the effect of flow rate on ammonia removal abilities. A pair of reactors was set for each run. The columns were replaced and packed with new zeolite in the same condition for each run. Effluent samples were collected at different time intervals (every 30min or 1 h). All the collected samples were placed in stoppered test tubes and stored at 4 °C for future analysis.

The coarse particle packed column (HRT=6) was used to evaluate regeneration efficiency and zeolite life determination. Repeated loading and regeneration was used to determine whether the performance of the zeolite deteriorates over time. Two concentrations of NaCl solutions (0.6M and 1.0M) were used to regenerate the exhausted

zeolite columns. The experiments were carried out in upflow mode as a backwashing procedure with two levels of HRT (30min and 1hr), respectively. To test the completion of the regeneration process, samples were taken at every 0.5-1 bed volumes of regenerating solutions passed intervals during each run. All the samples were stored at 4 °C and the presence of ammonia within effluent was then tested. The absence of ammonia in the effluent indicated the completion of regeneration.

Table 3-2. Operating conditions of zeolite-packed columns used in the flow-through study

Parameter	Coarse-packed	Powder-packed
Diameter (cm)	10.3	10.3
Internal surface area (cm^2)	83.32	83.32
Column height (cm)	35	35
Packed height (cm)	21.5	24
Weight of zeolite (Kg/column)	2	2
Bed volume (L)	2.16	1.93
Influent flowrate (L/hr)		
HRT=1hr	2.07	2.07
HRT=3hr	0.69	0.69
HRT=6hr	0.34	0.34
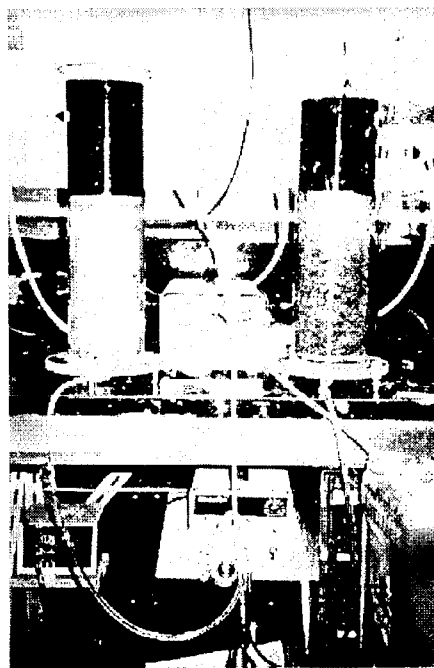
Figure 3-3. Schematic diagram of column experiments set up

3.4 Analytical methods

All the studies were conducted at ambient room temperature (20 ± 2 °C). The synthetic wastewater was prepared by dissolving Analytical Reagent grade NH4Cl in distilled water. The concentration of Ammonia, Nitrate, TKN and Orthro-P was measured using an Automated Ion Analyzer (The Lachat QuickChem® FIA⁺, Zellweger Analytic, Inc., Figure 3-4). Triplicate tests were analyzed for each sample. The method was based on QuikChem® METHOD 10-107-06-1-A, 10-107-04-2-A, 10-116-10-2-A, and 10-115-01-1-A respectively. The analysis techniques used are in accordance with A.P.H.A. Standard Methods based on the absorbance recorded at different wavelengths. Potassium was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) method (Martin *et al.*, 1992) with Liberty 100/200 ICP-OES Spectrometers (Varian Australia Pty. Ltd.) as shown in Figure 3-5.
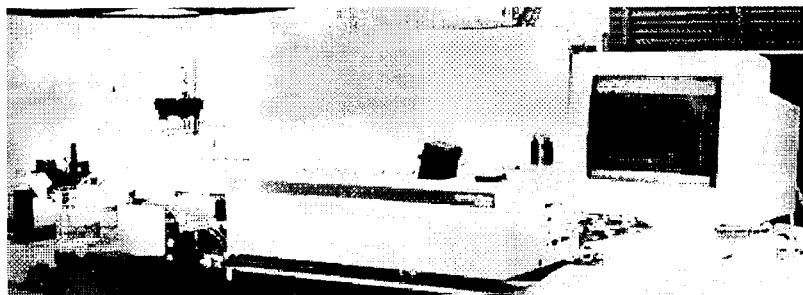
Figure 3-4. The Lachat QuickChem® FIA+ Automated Ion Analyzer
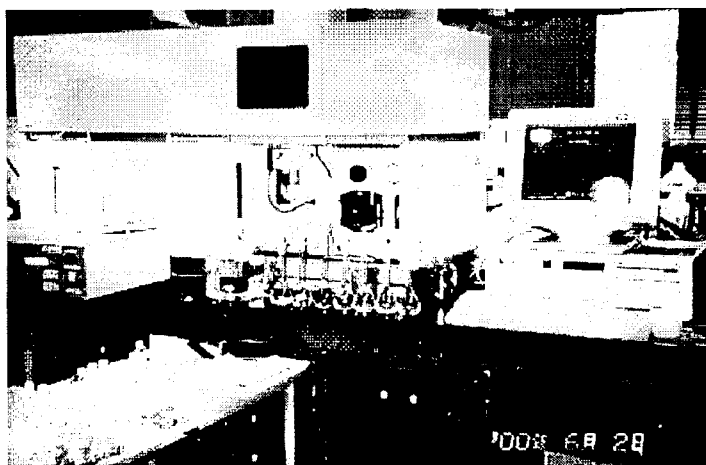
Figure 3-5. Potassium concentrations were determined using Liberty 100/200 ICP-OES Spectrometers

Chapter 4: Results and Discussion

4.1 Batch studies of the adsorption capacity

Results from the batch adsorption studies are discussed in this section. Both equilibrium and kinetic laboratory scale studies were carried out to investigate the ammonium adsorption capabilities of different particle sizes of zeolite and different solution types. The effect of concentration, contact time and competitive cations on zeolite adsorption of ammonium were determined.

4.1.1 Equilibrium experiments

The results for actual initial concentrations used for each set of equilibrium studies are given in Table 4-1. The results for ammonia removal as a function of different particle sizes in contact with different concentrations of solutions for a period of 1 hr are represented in Figure 4-1. Sample calculations for each set can be seen in Appendix A.1. All the data are the average values derived from duplicate samples. For both solutions (NH_4Cl and leachate) used in the experiments, the ammonium adsorption capacities of zeolite increased along with increased concentrations of ammonium in solution. That is, the higher the concentration of the ammonia in solution, the more ammonium was adsorbed by zeolite, and the adsorption rate of zeolite for ammonium also increased. Similar results have also been observed by other researchers as previously mentioned in the literature review (Cooney *et al.* 1999, Dimova *et al.* 1999, Jørgensen *et al.*, 1976 and Singh & Prasad, 1997).

In general, the group which used the NH_4Cl solution had a higher adsorption capacity than the group which used the composting leachate. There was no significant difference between Zeo group and Na-Zeo group treated with the same NH_4Cl solution. The ammonium adsorption capacities observed for pebble, coarse and powdered zeolite and Na-Zeo were 3.33, 4.94, 7.33 and 2.83, 4.68, 6.91 mg NH_4-N/g respectively using the NH_4Cl solution, and 3.06, 3.35, 4.19 mg NH_4-N/g using leachate at the highest concentration (set 8) for each group after 1 hour contact time.

Table 4-1. Experimental conditions for equilibrium experiments

Set	NH4Cl	Leachate
	Initial concentration in NH4Clsolution (mg NH4-N/l)	Initial concentration in leachate (mg NH4-N/l)
1	27.1	39.4
2	57.7	62.9
3	82.7	93.4
4	115.2	121.0
5	138.0	157.2
6	169.4	184.1
7	194.7	210.4
8	219.8	255.2

| ◆ S-pebble | ▣ S-coarse | ▲ S-powder | ◇ S-Na/pebble | □ S-Na/coarse |
| △ S-Na/powder | ○ L-pebble | � L-coarse | + L-powder | |
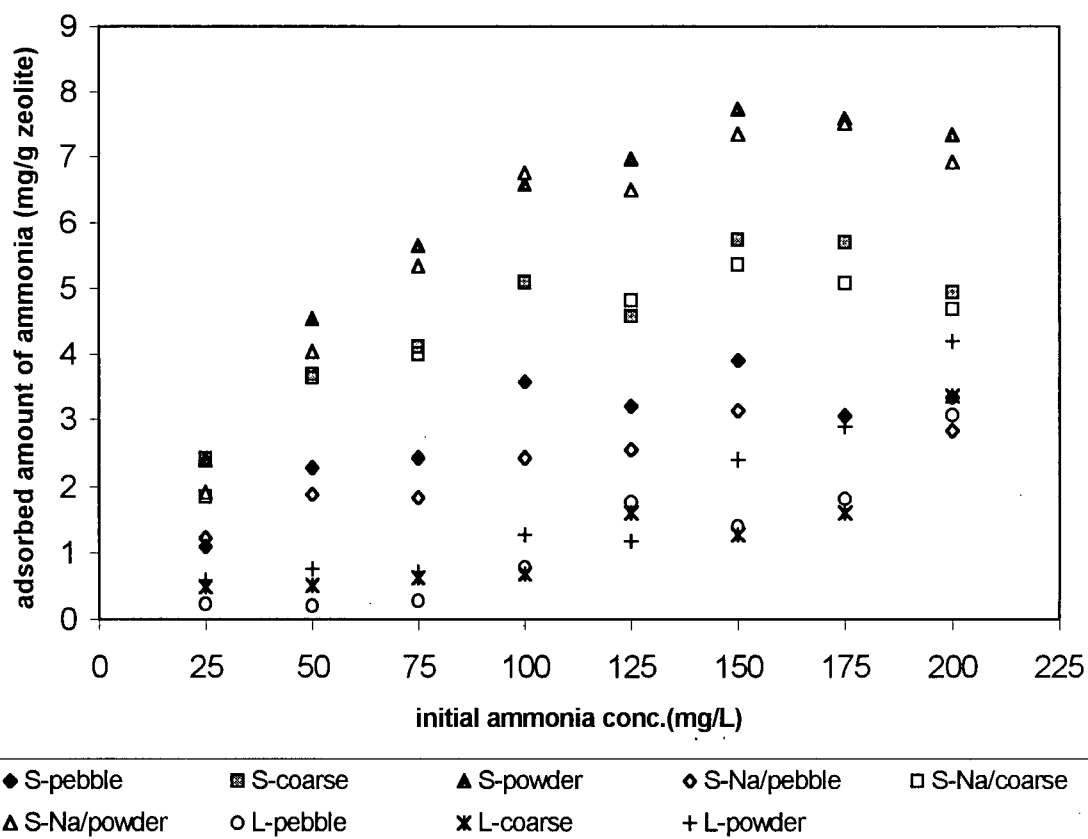
Figure 4-1. Ammonia removal from varying concentration of NH4Cl solution (S) and leachate (L) for different particle sizes of zeolite after an 1 hour contact.

From Figure 4-1, it is also clear that the particle size of the zeolite was an important factor in their ammonium adsorption capacity. The effect of zeolite particle size on the equilibrium study was determined by performing a series of batch tests where all parameters in each set were identical expcept for the grain size of the zeolite. The results show that the uptake of ammonium by zeolite increased significantly with decreasing particle size for all the concentration sets. In each group of batch studies, the smaller the particle size, the higher the ammonium adsorption capacity obtained. This was possibly due to greater available surface area on the smaller size particles of zeolite. The difference was much clearer in the case of the groups (Zeo and Na-zeo) where the NH4Cl solution was used than with the group where the composting leachate was used. Generally, for both groups tested where the NH4Cl solution was used, after 1 hour contact the powdered zeolite had a 1.98-2.92 times higher ratio and coarse zeolite had a 1.43-2.19 times higher ratio than the pebble sized zeolite. This result supports the conclusions reached in a number of previous studies (Hlavay et al., 1982, Jørgensen et al., 1976, Marking and Bills, 1982 and Singh and Prasad, 1997). It should be noted, however, that Cooney et al. (1999) found that ion-exchange equilibrium between the zeolite and the solution containing ammonium is independent of zeolite particle size. The presence or absence of a variation in the ion-exchange behavior of a zeolite with particle size will depend greatly upon both the origin of the material and its pretreatment.

The data obtained in this study were fitted to both Freundlich and Langmuir adsorption isotherms. These are the two most commonly employed types of models used to describe the distribution of ammonium between the resin phase and solution phase (Lahav and Green, 1998, Bernal and Lopez-Real, 1993, Philips, 1998). In essence, the Langmuir model is based on the concept of constant site energy providing a constant cation capacity for each exchange site, and relates the inverse solid concentration to the inverse solution concentration. The Freundlich model describes a logarithmic relationship between the solid and solution concentrations. The Freundlich equation is useful in correlating isotherm data obtained over a wide range of concentrations.

Freundlich isotherm. The Freundlich equation is normally written as:

$$x/m = K\,Ce^{\,1/n} \quad (n > 1) \tag{1}$$

where x/m = amount of solute adsorbed per unit weight of adsorbent

$\quad\quad Ce$ = equilibrium concentration of solute remaining in solution after adsorption is complete

$\quad K,\, n$ = empirical constants.

The constant K may be considered a hypothetical index of NH_4^+-N adsorbed from a solution having a unit equilibrium NH_4^+-N concentration, and may thus be taken to provide a measure of relative NH_4^+-N adsorption capacity of the material being used. The constants in the Freundlich isotherm can be determined by plotting (x/m) versus Ce and making use of Equation (1) rewritten as

$$\log (x/m) = \log K + 1/n \log Ce \tag{2}$$

which should give a linear test plot for adsorption data which follow the Freundlich theory. Value of $\log K$ as intercept and $1/n$ as slope of the equation (Benefield *et al.*, 1982, Tchobanoglous and Burton, 1991); and

Langmuir isotherm. The Langmuir equation is defined as

$$\frac{x}{m} = \frac{abCe}{1 + bCe} \tag{3}$$

where x/m = amount adsorbed per unit weight of adsorbent

$\quad a,\, b$ = empirical constants

$\quad\quad Ce$ = equilibrium concentration of material remaining in solution after adsorption is complete

The constants in the Langmuir isotherm can be determined by plotting $Ce/(x/m)$ versus Ce and making use of Eq.(3) rewritten as

$$Ce/(x/m) = 1/ab + 1/a\,Ce \tag{4}$$

where a and b are constants. If adsorption follows the Langmuir isotherm, a linear trace should result. Values of the constants a and b can be determined from the slope and intercept of the plot. Note that "a" is designated as the Langmuir adsorption maximum and "b" is related to binding energy (Sakadevan and Bavor, 1998).

The Langmuir adsorption isotherm was developed by assuming that (1) a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy and that (2) adsorption is reversible. Equilibrium is reached when the rate of desorption of molecules from the surface equal to the rate of adsorption from solution. The rate at which adsorption proceeds is proportional to the driving force, which is the difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration, this difference is zero. Correspondence of experimental data to the Langmuir equation does not mean that the stated assumptions are valid for the particular system being studied because departures from the assumptions can have a canceling effect (Benefield *et al.*, 1982, Tchobanoglous and Burton, 1991).

Data obtained from equilibrium experiments, expressed as NH_4^+-N adsorbed per unit weight of zeolites (*x/m*) and equilibrium solution concentrations (*Ce*) were fitted to both Freundlich and Langmuir adsorption isotherm equations. Figure 4-2 (a) & (b) show the linear plot for one of the sets; the straight line obtained clearly indicates that adsorption of ammonium by the coarse zeolite follows both adsorption isotherms ($R^2 > 0.977$). The plots of both adsorption isotherms for each set can be seen in Appendix B.1. The regression values for Freundlich and Langumir equations are presented in Table 4-2. For the group where the leachate solution was used, the Freundlich model fit poorly, with a value of $R^2 < 0.849$. Both models fit the experimental results well for the zeo and Na-zeo groups where the NH_4Cl solution was used. In general, the Langmuir isotherm equation ($R^2 > 0.935$) modeled the equilibrium ammonia adsorption better than the Freundlich isotherm equation ($R^2 > 0.768$). The correlation of the Freundlich model gives a quick and simple means for calculating the approximate ammonium concentration for one phase (solid or solution) given for other phase concentration. The Freundlich *K* values and Langmuir *a* values give a measure of the relative ammonia adsorption capacity. Basically, both data values show that the adsorption capacity increased with decreased particle size, which confirmed previous equilibrium results.

In the zeo group, however, the powdered zeolite had a smaller Langmuir adsorption maximum (a values) than the coarse zeolite. This may be due to the very high binding energy (b values) obtained for the powdered zeolite compared with the other sizes of zeolite. No significant differences in ammonium adsorption capacities between zeo and Na-zeo groups were observed; however, the results show that converting zeolite into the sodium form can reduce the binding energy (b values) significantly. The values dropped 30% for pebble size and 70% for powder size after conversion of the zeolite to Na-form, but somehow rose 33% for the coarse size. The high binding strength suggests that less ammonium would be subsequently released from the zeolite. The way the change in binding energy influenced the Langmuir adsorption maximum can be seen from the coarse and powder sets. The significant drop in binding energy from 0.253 to 0.058 within the powdered zeolite and the rise from 0.078 to 0.104 for coarse zeolite reversed the advantage of the Langmuir adsorption maximum from coarse to powdered zeolite. Similar results had been attained by Nguyen and Tanner (1998), who found that zeolite with a lower surface area was more effective in ammonium removal. They suggested that the zeolite surface area might not influence its ammonium removal performance under batch equilibrium conditions. .

In this study, however, the Freundlich K values are not directly related to the Langmuir adsorption maximum (a values). Comparing the results obtained from equilibrium tests and the Langmuir a values, it seems that the Langmuir isotherm truly reflects the adsorption capacity of the equilibrium tests. This suggests that for this study the Langmuir isotherm is more suitable for use in analysis of adsorption capacity. Sakadevan and Bavor (1998) suggested that this might be because the Freundlich equation implies that the affinity for adsorption decreases exponentially with increasing saturation, while the Langmuir equation adheres to the assumption of constant binding energy. Both isotherms are widely used by researchers, but the Langmuir isotherm is used more frequently than the Freundlich isotherm among those references reviewed for this zeolite capacity study (Bernal & Lopez-Real, 1993, Cooney *et al.*, 1999, Green *et al.*, 1996, Jung *ey al.*, 1999, Lahav & Green, 1998, Nguyen & Tanner, 1998, Phillips 1998, and Sakadevan & Bavor, 1998).

In the equilibrium experiments, the ammonium adsorption capacities obtained were generally low, up to 7.73mg N/l, compared to reported capacities (5.7-31.86 mg N/g). This is possibly due to insufficient contact time being allowed in this study (1 hour) for equilibrium to be reached. The contact time chosen for equilibrium studies by other researchers ranged from 1 hour, 2 hours, 2 days to one week (Bernal & Lopez-real, 1993, Haralambous *et al.*, 1992, Olin & Bricka, 1998, Singh & Prasad, 1997 and Sakadevan & Bavor, 1998). Metropoulos *et al.* (1993) found 80% of the ion exchange for ammonium occurred in the first five minutes for clinoptilolite. However, it is known that with an increase in contact time the ammonia removal increases.
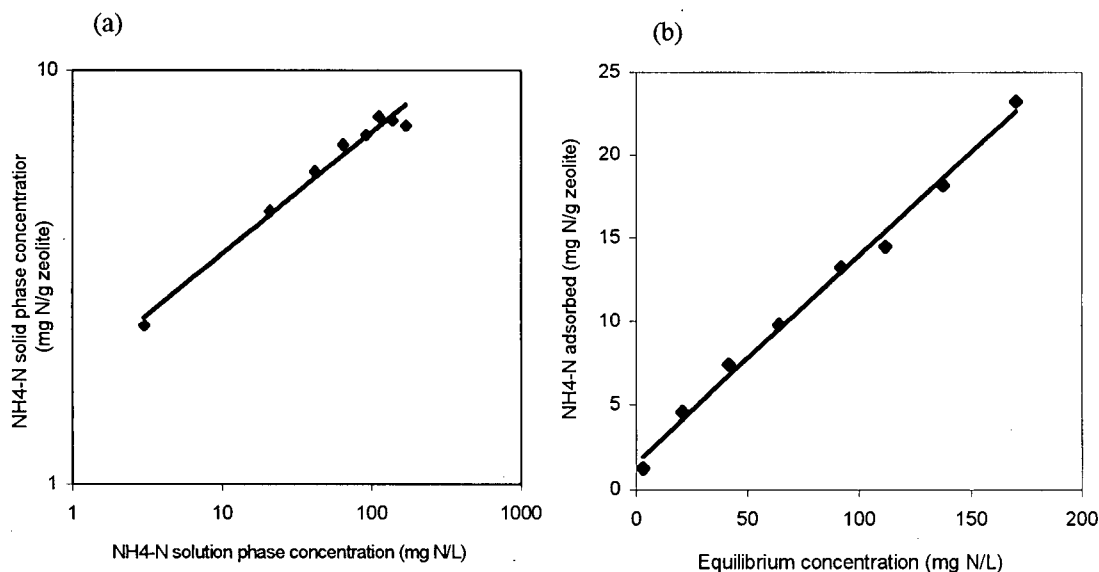
Figure 4-2. The Freundlich (a) and Langmuir (b) adsorption isotherms applied to the equilibrium relationship for ammonium ions exchanged onto coarse zeolite from pure NH4Cl solutions

Table 4-2. Parameter values and coefficients of determination of estimate for the adsorption of ammonium from NH4Cl solution and composting leachate

	Zeoilte	Langmuir			Freundlich	
		a	b	R^2	K	R^2
Zeo	NH4Cl					
	Pebble	3.929	0.037	0.935	0.419	0.787
	Coarse	8.084	0.078	0.993	1.815	0.977
	Powder	5.411	0.253	0.981	2.283	0.908
	Leachate					
	Pebble	-	-	-	0	0.849
	Coarse	-	-	-	0.013	0.768
	Powder	-	-	-	0.013	0.788
Na-zeo	NH4Cl					
	Pebble	3.574	0.026	0.953	0.468	0.930
	Coarse	5.285	0.104	0.983	1.186	0.799
	Powder	8.177	0.058	0.982	1.071	0.835

Note: "-" indicates immeasurable data

4.1.2 Kinetic experiments

Batch kinetic tests were performed to determine the effect of contact time on the ammonium adsorption of zeolite. The initial ammonium concentration in the solution was determined and the amount of adsorbing ammonium ions by each set was calculated as a function of contact time. Results for ammonia removal as a function of contact time for zeolite using the ammonium solution is given in Figure 4-3. Size fractions of the zeolite were also studied to assess the dependence of adsorption rate on particle size. A sample of the calculation method for the accumulated adsorbed ammonia can be seen in Appendix A.2. All the data are the average values derived from triplicate samples.

The results reveal that ammonia removal increased with increasing contact time. The adsorption rate of ammonium by all the sets occurred rapidly at the beginning of contact, and then gradually decreased with increased contact time. Almost 50 % of the equilibrium value of the ammonium uptake was achieved within the first hour for the sets where NH4Cl solutions were used, and about 30 % for the leachate solution sets. After 8

hours of contact with NH4Cl solutions, above 85% of the equilibrium values were observed for sets 1-3 and 7-9, but less than 75% for sets 4-6 in contact with the composting leachate. Generally, the ion exchange for ammonium was very fast initially, then gradually slowed until equilibrium is reached. Dimove et $al.$, (1999) found that after a certain contact time, the ion-exchange velocity becomes practically zero. The reason for this might be that chemical adsorption, which is fast, is initially dominant. Slower physical adsorption then takes place when saturation of the binding sites approaches (Sakadevan and Bavor, 1998).

Equilibrium was achieved within 24 hours for both zeo and Na-zeo groups where NH4Cl solutions were used (set 1-3 & 7-9). The equilibrium for set 4-7 was only obtained after a week. Similar results were obtained by Metropoulos et $al.$ (1993). From the figure, it is clear that zeolite can remove higher amounts of ammonium from NH4Cl solutions than from leachate (at the same contact time point, 30-50 % higher in general). The ammonium adsorption capacities for kinetic tests after equilibrium was achieved are shown in Table 4-3.
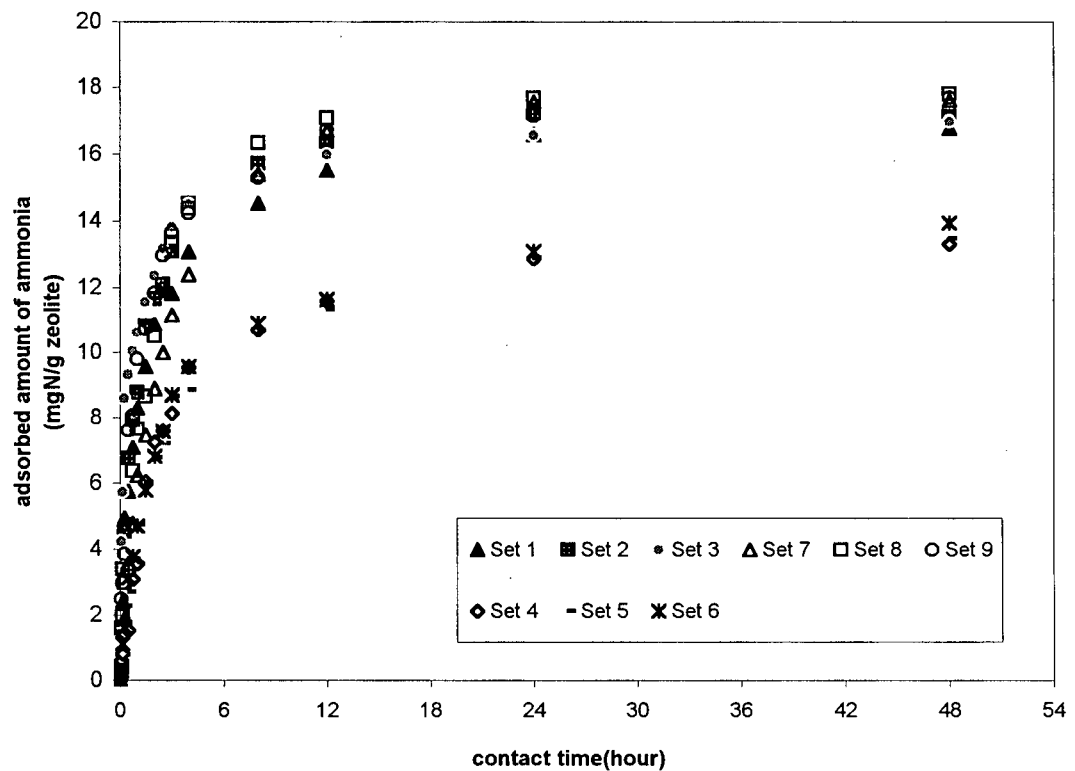
Figure 4-3. Kinetic behavior of the adsorption rate for zeolite

Table 4-3. The ammonium adsorption capacity for kinetic tests after the equilibrium was achieved

Set		Material	Initial solution Concentration (mg NH3-N/l)	Adsorption capacity after 48 hours equilibrium (mg NH3-N/ g zeolite)	Adsorption capacity after 7 days equilibrium (mg NH3-N/ g zeolite)
1	Zeo	Pebble	200	16.77	-
2		Coarse	200	16.81	-
3		Powder	200	16.97	-
4		Pebble	190.31 as leachate	13.31	14.35
5		Coarse	190.31 as leachate	13.47	14.58
6		Powder	190.31 as leachate	13.93	14.53
7	Na-zeo	Pebble	200	17.61	-
8		Coarse	200	17.81	-
9		Powder	200	17.69	-

Note: " − " indicates not measured

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Results show that there was no significant difference between the different particle sizes after equilibrium was achieved. In general, the pretreated zeolite (Na-Zeo) group had a slightly better adsorption capacity than the untreated zeolite group using the NH4Cl solution, 17.61-17.81 mg N/g compared to 16.77-16.97 mg N/g zeolite. Other researchers have reported that the pretreatment of zeolite can improve the ammonium removal performance (Ćurković et al., 1997, Metropoulos et al., 1993 and Semmens & Martin, 1988). As mentioned in the literature review section 2.5.1, adsorption capacities for composting leachate were lower (14.35-14.58 mg N/g zeolite), possibly due to the interference of other ions in the solution. This means that the ammonium adsorption capacity of zeolite yields better results when a synthetic ammonium solution is used. The results of ammonium adsorption capacities in this study were within the capacities for clinoptilolite reported in overseas studies (5.7 to 31.86 mg N/g).

Previous equilibrium experiments indicated that the smaller particle size zeolite had a higher capacity to adsorb ammonium than larger sized particles of zeolite after a 1 hour contact period. In the kinetic studies, however, the influence of particle size on ammonium adsorption capacity of zeolite was more distinct at the beginning of contact but was not significant after equilibrium was reached. This indicates that the effect of zeolite particle size on the ammonium adsorption performance can be reduced by prolonged contact time. This finding agrees with result reported by Marking & Bills (1982) and Nguyen & Tanner (1998). These authors also suggested that the effect of zeolite particle size on ammonium removal performance depends on the contact time.

In order to understand more about this high rate process for the removal of soluble ammonia and the influence of particle size on the ammonium uptake of zeolite, Vermeulen's model was used to identify the rate-controlling mechanism. Generally, the kinetics of ammonium ion exchange using zeolite may be divided into five steps (Cooney et al., 1999b):

1. Diffusion of the counterions through the film solution to the surface of the zeolite;

2. Diffusion of the counterions within the zeolite;

3. Chemical reaction between the counterions and the ion-exchange sites;

4. Diffusion of the displaced ions out of the zeolite;

5. Diffusion of the displaced ions from the zeolite surface into the bulk solution

Step 4 and 5 are the reverse of Step 2 and 1.

The slowest step of the ion-exchange process for a given system controls the speed of ion exchange and is said to be the rate-limiting step.

Two mechanisms generally control the rate of adsorption within porous solids – either film diffusion or particle diffusion. Film diffusion is where the adsorbed species is required to diffuse to the surface of the particle through the stagnant boundary layer. Particle diffusion is where the adsorbed species diffuse through the particle to the adsorption site. Both mechanisms are present in practice, although normally one mechanism (the slower) dominates diffusion kinetics.

It can be shown that for particle diffusion control:

$$\text{Rate} \propto 1/r^2$$

and for film diffusion control:

$$\text{Rate} \propto 1/r$$

where r is the radius of the particle. By using these relationships it is possible to identify the rate-controlling mechanism. Conventional ion-exchange models for particle diffusion control have been used for the analysis of the ion exchanger, zeolite. Vermeulen's model for the fractional attainment of equilibrium, X given particle diffusion control with infinite solution volume boundary conditions, is given by

$$X = [1 - \exp (\frac{-D \pi t}{r^2})]^{1/2} \qquad (5)$$

where D is the diffusion coefficient, t is time, and r is the radius of the particle. Rearranging Equation (5) yields

$$- \ln (1-X^2) = t (\frac{D \pi^2}{r^2}) \qquad (6)$$

The most convenient way to verify this model for the system is to plot time against calculated values for $- \ln (1-X^2)$ for given X values. The diffusion coefficient, D, is obtained from the slope of the line (Helfferich, 1962).

$$X = 1 - \frac{Q_A (t)}{Q_A (o)} \qquad (7)$$

Where $Q_A (t)$ = amount of ion (A) in the ion exchanger at time t; $Q_A (0)$ = initial amount of A in the ion exchanger; X is the fractional attainment of equilibrium.

Figure 4-4 presents the results of set 8 (coarse Na-Zeo in NH4Cl solution) applied to Vermeulen's approximation as an example. Linear regression was performed on the kinetic test data for fitting to Vermeulen's approximation. It is clear from Figure 4-4 (a) that Vermeulen's approximation did not satisfactorily fit the data for contact time after 8 hours ($R^2 = 0.815$). This may be because particle diffusion charges the rate of adsorption onto solid surfaces only at the beginning of the kinetic test. A process of one by one dropping the data point from the far end until a better fit occurred Figure 4-4 (b) revealed that particle diffusion is the rate-controlling mechanism for the exchange of ammonium at the beginning (up to 4 hours). This resulted in a very good fit to this model. The plots of Vermeulen's approximation for each set can be seen in Appendix B.2.

Table 4-4 gives the values of the slop for the first 4 hours of results obtained from kinetic tests for various particle sizes and solution types after fitting of Vermeulen's approximation model. As can be seen, a very good fit to this model ($R^2 = 0.941$-0.995)

was achieved for all the sets, confirming that particle diffusion controls that rate of adsorption at the beginning. In a previous study, Booker *et al.* (1996) found that the adsorption of ammonia into the zeolite was rapid and a very good fit to Vermeulen's approximation model ($R^2 = 0.997$) was achieved for only the first 80 minutes of contact time in a 300 minute test with a zeolite size = 425-600 μm. The found that there was close agreement for the different particle sizes and concentrations, thus providing support for particle diffusion control. The consistency of the diffusion coefficient validates the particle diffusion control. Olin & Bricka (1998) also found only the data from the first 30 min fit satisfactorily with an $R^2 = 0.944$.
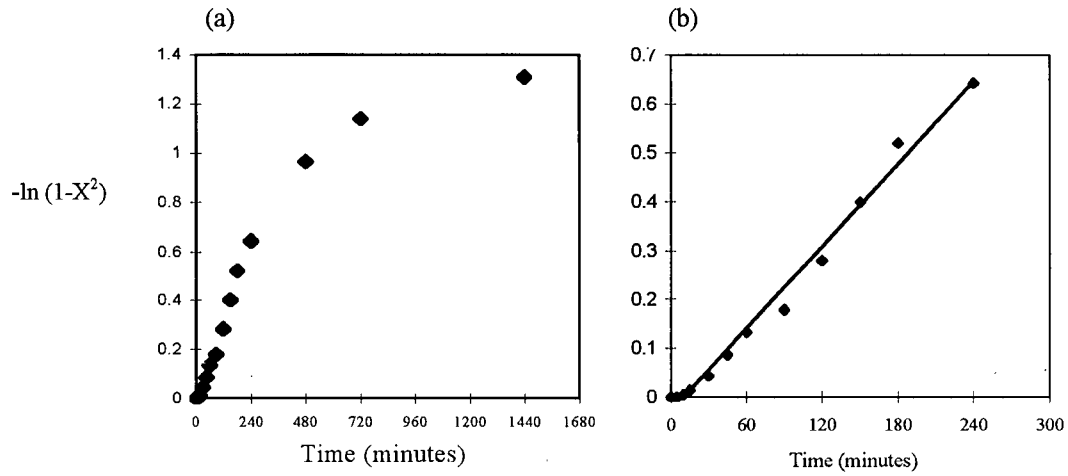
Figure 4-4. (a) Kinetic test result of set 8 applied to Vermeulen's approximation (b) The first 4 hours of the results for set 8 fitted to Vermeulen's approximation model (set 8: coarse zeolite with initial NH4Cl solution)

Table 4-4. Parameters obtained by Vermeulen's approximation for adsorption of ammonium ions onto zeolite for first 4 hours contact

Set		Material	Initial solution Concentration (mg NH3-N/l)	$\dfrac{D\pi^2}{r^2}$	R^2
1	Zeo	Pebble	200	2.60×10^{-3}	0.977
2		Coarse	200	3.04×10^{-3}	0.987
3		Powder	200	2.94×10^{-3}	0.941
4		Pebble	190.31 as leachate	1.34×10^{-3}	0.981
5		Coarse	190.31 as leachate	1.17×10^{-3}	0.977
6		Powder	190.31 as leachate	1.26×10^{-3}	0.995
7	Na-zeo	Pebble	200	1.75×10^{-3}	0.990
8		Coarse	200	2.81×10^{-3}	0.988
9		Powder	200	3.69×10^{-3}	0.963

4.1.3 Influence of wastewater composition on ammonia removal performance of zeolite

Zeolite, especially clinoptilolite, is widely used in wastewater treatment processes for waters with high levels of ammonia. This is due to its greater affinity for ammonium ions, as well as for other ions present in the wastewater (Jorgensen *et al.*, 1976). Its cation selectivity has been reported as:

$$Cs^+ > Rb^+ > K^+ > NH4^+ > Sr^{2++} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$$
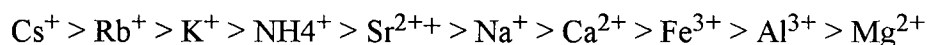
Except for potassium, it is usually the case that the cations which are more amenable to selection by clinoptilolite are not commonly found in wastewaters.

From the results for both the equilibrium and kinetic experiments, it is clear that the ammonia adsorption capacity and adsorption rate for treating composting leachate was low compared with the groups using pure NH_4Cl solutions, despite the effect of particle size. The adsorption capacities for pebble, coarse and powdered zeolite were observed to be 3.33, 4.94 and 7.33 mg NH_4-N/g for the group which used the NH_4Cl solution and 3.06, 3.35 and 4.19 mg NH_4-N/g for those using the leachate solution at the highest concentration (set 8) in the equilibrium experiment (Figure 4-2). About 20% lower adsorption capacities were obtained in the kinetic experiment for the group where leachate was used than where NH_4Cl was used (Table 4-3). Similar results have been reported by others (Dimova *et al.*, 1999, Hlavay *et al.*, 1982, Marking and Bills, 1982, Papadopoulos *et al.*, 1996 and Singh and Prasad, 1997). The values obtained for ammonia adsorption capacity from wastewaters are much lower than the theoretical capacity obtained using synthetic NH_4Cl solutions. This might be due to the presence in the wastewater of other competitive cations such as K^+, Na^+, Ca^{2+}, and Mg^{2+} which approach the ion-exchange site of the zeolite and inhibit the adsorption of ammonia.

In order to investigate the presence of other competitive cations, both the wastewater and zeolite were sent to Norwest Labs before and after treatment for analysis of the ion composition. The method of inductively coupled plasma-optical emission spectrometry (ICP-OES) was used. Table 4-5 shows the results. It can be seen that the concentration of

potassium dropped dramatically from 3800 to 31 mg K/l after saturation with zeolite. In addition, the huge amount of potassium ions accumulated in the treated zeolite indicate a very high concentration of potassium in the composting leachate. This could be the major reason for the low ammonium adsorption capacities obtained in both the equilibrium and kinetic experiments.

Table 4-5. Ion contents of zeolite and wastewater

Component (mg/l)	Leachate	Leachate (treated)	Zeolite	zeolite (treated)
Barium	0.034	0.497	1030	1190
Calcium	16.2	666	9600	8400
Iron	3.14	0.65	8100	7400
Potassium	3800	31	6540	28900
Sodium	280	1820	8130	1100
Strontium	1.16	1.98	223	212

Note: "treated" indicates sample after the treatment of saturating zeolite with leachate

The experimental results for potassium removal as a function of different particle sizes in contact with different concentrations of solutions for 1 hr are represented in Figure 4-5. The influences of initial concentration and particle size on the potassium adsorption of zeolite were the same as the results reported previously for ammonia except for adsorption capacity. The potassium adsorption capacities obtained after 1 hour contact time for pebble, coarse and powdered zeolite were 32.7, 29.05 and 49.3 mg K/g zeolite at the highest concentration (set 8) in the equilibrium test. These were significantly higher than for ammonium (3.06, 3.35 and 4.19 mg N/g). These results confirm that zeolite has a higher affinity for potassium than for ammonium.

The data obtained here were also fitted to both Freundlich and Langmuir adsorption isotherms (Table 4-6). Again, they did not fit the Langmuir model well. Plots for both isotherms can be seen in Appendix B.1. No significant difference between potassium and ammonium was obtained for Freundlich K values. As discussed previously, the Langmuir isotherm appears to truly reflect the adsorption capacity of the equilibrium test

for this study. However, the results indicated that the Langmuir adsorption maximum (a values) for potassium were significantly higher than for ammonium (Table 4-2). Compared to the results for ammonium, the extremely low binding energy (b values close to zero) between potassium and zeolite irregardless of particle size seems to be the main cause of the high Langmuir adsorption maximum obtained for potassium. This gives support to the assumption that in this study potassium is the ion in competition with ammonium for zeolite removal from the composting leachate.
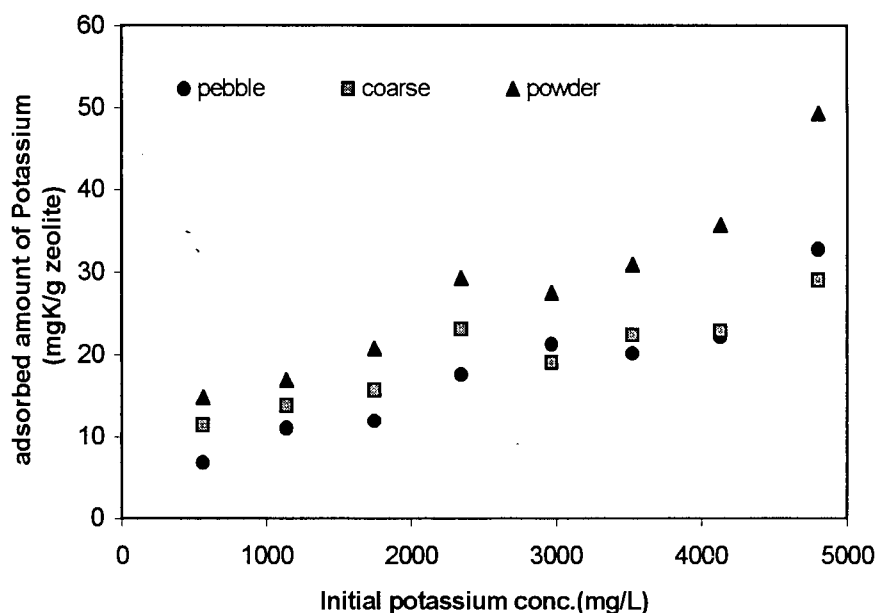
Figure 4-5. Potassium removal by different particle size of zeolite as a function of initial concentration

Table 4-6. Parameter values and coefficients of determination of estimate for the adsorption of potassium

Zeoilte	Langmuir			Freundlich	
	a	b	R^2	K	R^2
Pebble	49.751	0	0.671	0.1247	0.942
Coarse	32.573	0.001	0.891	1.118	0.882
Powder	60.241	0	0.735	0.75	0.875

Potassium removal as a function of contact time of the zeolite using the composting leachate solution is reported in Figure 4-6. The kinetic curves obtained experimentally give a clear picture that the adsorption of potassium into the zeolite occurred rapidly at the beginning of contact, then gradually decreased with increasing contact time. There was no significant difference in adsorption among the different particle sizes. The potassium adsorption capacities after a 48 hours contact period for pebble, coarse and powdered zeolites were 299.81, 306.18 and 316.42 mg K/g zeolite, respectively. The curves show that in the case of potassium, equilibrium was not yet reached after 48 hours of contact time. The potassium adsorption capacities were significantly higher than the ammonium adsorption capacities previously obtained (17.61, 17.81 and 17.69 mg N/g) for the equilibrium tests (Table 4-3). About 35 % of the equilibrium value of the 48 hours total potassium uptake occurred in the first 1 hour and 82-85 % after 8 hours, which is slightly higher than for ammonium.

As in the case of ammonium, the results for potassium adsorption in the kinetic tests were also used to examine the rate-controlling mechanism for potassium uptake by fitting them to Vermeulen's approximation model. A very good fit was achieved ($R^2 > 0.976$) for the first 4 hours of contact time. The consistency of the diffusion coefficients obtained ($D = 1.52 \times 10^{-3}$ for all pebble, coarse and powdered zeolites) validates the idea that the particle diffusion control for potassium is relatively independent of particle size. This corresponds to the kinetic curve results. However, the close agreement of the values for the diffusion coefficient for ammonium and potassium suggests that the adsorption rate of zeolite for both ions is similar. Cooney *et al.*, (1999) assumed that the rate of adsorption onto solid surfaces (zeolite) was independent of differences in particle size.
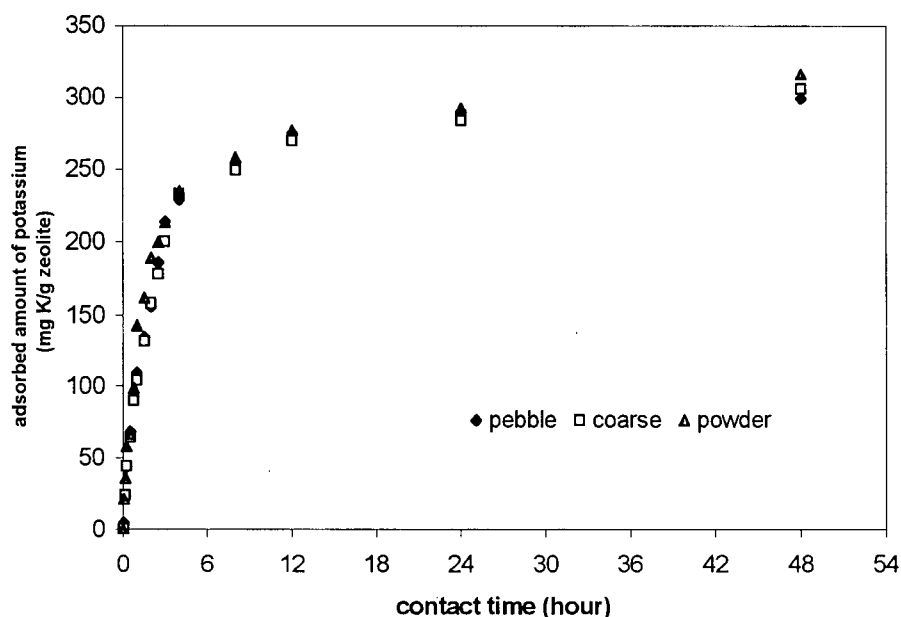
Figure 4-6. Kinetic behavior of the adsorption rate of potassium for zeolite

4.2 Packed zeolite column efficiency studies

According to the results obtained from previous batch adsorption studies, smaller particles had better adsorption capacity and faster adsorption rates in the same reaction time. Although the difference in particle size was not significant when applied to composting leachate, powdered zeolite seemed to have the best adsorption capacity for ammonia removal and was therefore chosen for use in the study of packed zeolite column efficiency. It was also taken into consideration that powdered zeolite has the potential to restrict the flow and cause clogging in the packed columns. Coarse zeolite was therefore also used in the column efficiency studies.

Results from the column tests are presented and discussed in this section. The effect of particle size, hydraulic retention time, operating adsorption capacities, regeneration efficiency, competitive cation (potassium) and comparison with the batch test results are discussed. Zeolite structure and the number of adsorption sites were assumed to remain constant during the experiments. Samples were analyzed in triplicate.

4.2.1 Effect of particle size and hydraulic retention time on ammonia breakthrough curves

The particle size of the zeolite is a very important factor in column performance. Based on the results of the first stage of experiments, both coarse and powdered zeolite were used in the column efficiency studies. In order to determine whether coarse or powdered zeolite were more efficient as the ion exchanger, experiments to determine the number of bed volumes until breakthrough were carried out. The performance of both coarse and powder packed columns in the continuous flow-through composting leachate studies is represented by the breakthrough curves, shown with removal efficiency for different hydraulic retention time (HRT=1, 3 and 6hrs) in Figures 4-7, 4-8 and 4-9, respectively.

For HRT=1hr treatment, it is clear that the effluent concentration of both columns rose rapidly to near the influent concentration (Figure 4-7). A maximum removal of 100% was obtained in the first 2.5 hrs for coarse particle zeolite packed column and 3.5 hrs for powdered zeolite packed column. Removal then decreased rapidly achieving a value of 50% after another one hour of feeding for both columns. After 5 bed volumes of wastewater throughput, less than 10% of ammonia input from wastewater was removed by both columns. The influent concentration was 171.88 mg N/l for this test, if the breakthrough concentration is defined as 18 mg N/l (about 90 % removal efficiency). The coarse zeolite packed column yielded a breakthrough after about 3 bed volumes and the powdered zeolite packed column after 4 bed volumes. Therefore, the estimated operating ammonia removal capacity for the coarse particle zeolite packed column was 0.47mg NH_4-N/g zeolite and 0.61mg NH_4-N/g zeolite for the powdered zeolite packed column.

In the HRT=3hrs test (Figure 4-8) the influent concentration was 194.34 mg N/l. If 90% removal (about 20mg N/l effluent) is used as the breakthrough value, both columns yielded a breakthrough after 3 bed volumes. The estimated operating ammonia removal capacity for the coarse particle zeolite packed column was 0.52mg $NH4$-N/g zeolite and it was 0.62mg $NH4$-N/g zeolite for the powdered zeolite packed column. These results are close to the capacity obtained for the HRT=1hr experiment. However, the overall

performance of the powdered zeolite packed column at HRT=3hr attained over 50% removal from the wastewater with a higher influent ammonia concentration. This was true until the end of the test (approximately 6 bed volumes of feeding).
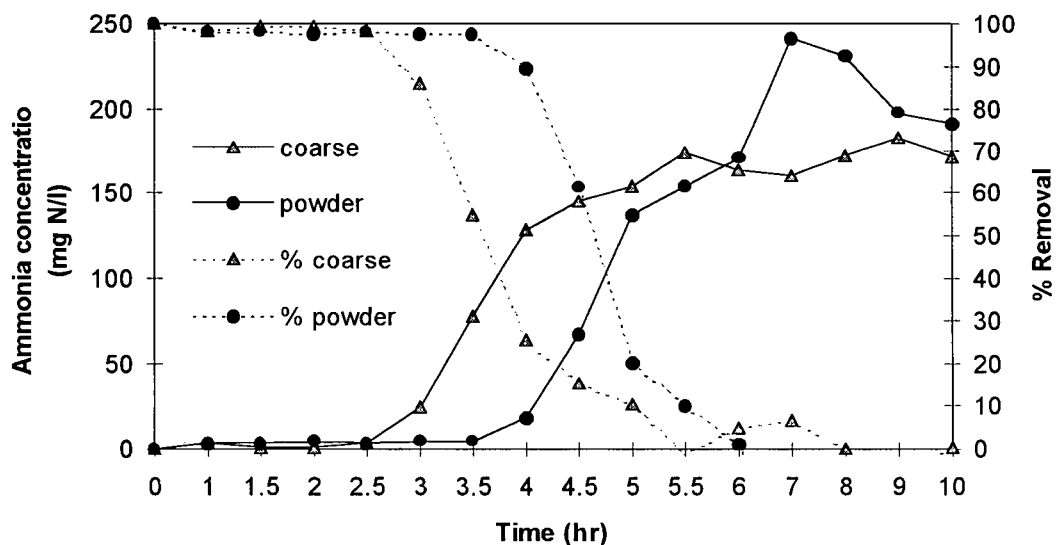
Figure 4-7 Effect of particle size of zeolite on ammonia breakthrough and removal efficiency at HRT = 1hr
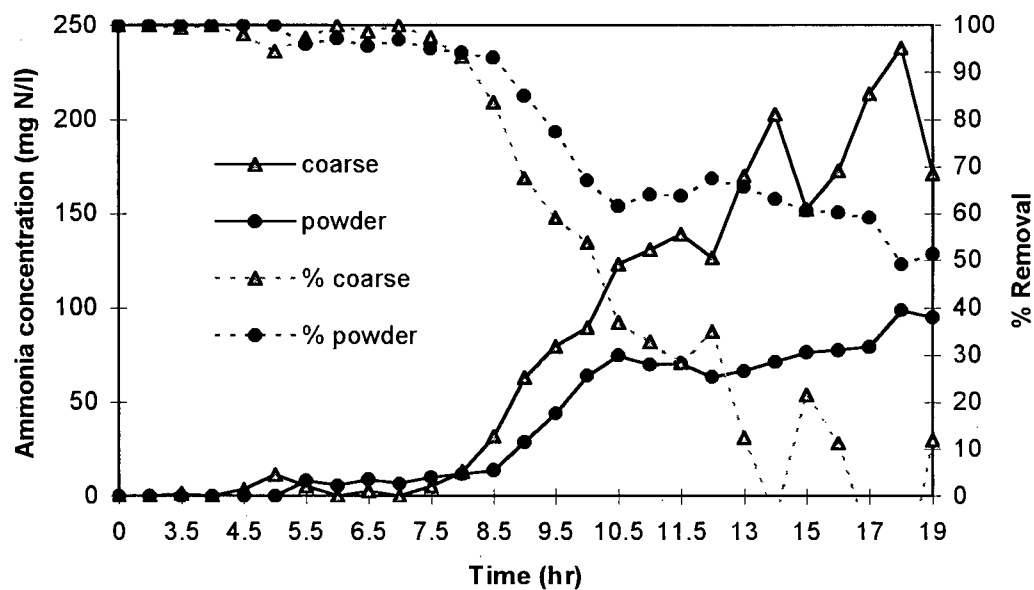
Figure 4-8. Effect of particle size of zeolite on ammonia breakthrough and removal efficiency at HRT = 3hrs

At the slowest wastewater loading flow rate (HRT=6hrs), the ammonia breakthrough for wastewater influent containing 222.43mg NH4-N/l did not occur until after approximately 5 bed volumes flow through for both coarse zeolite and powdered zeolite packed columns (Figure 4-9). Over 98% of the ammonia input from the influent was consistently removed by both columns over approximately 30 hours of loading time. After 5 bed volumes, less than 50% of the ammonia input was removed by the coarse zeolite packed column. The powdered zeolite packed column consistently removed over 90% of the ammonia from wastewater influent even after 6 bed volumes of influent. However, after 35 hr duration, operation of the powdered zeolite packed column had to be stopped due to clogging. The clogging was possibly due to the zeolite channels being filled either with the smaller particles of zeolite or by suspended solids in the wastewater. Using 90% removal (about 22 mg NH4-N/l in the effluent) as the breakthrough value, the ammonia breakthrough capacity of the coarse zeolite packed column was calculated as 1.09mg NH4-N/g zeolite and it was 1.31mg NH4-N/g zeolite for the powdered zeolite packed column.

Figure 4-9. Effect of particle of zeolite on ammonia breakthrough and removal efficiency at HRT = 6hrs

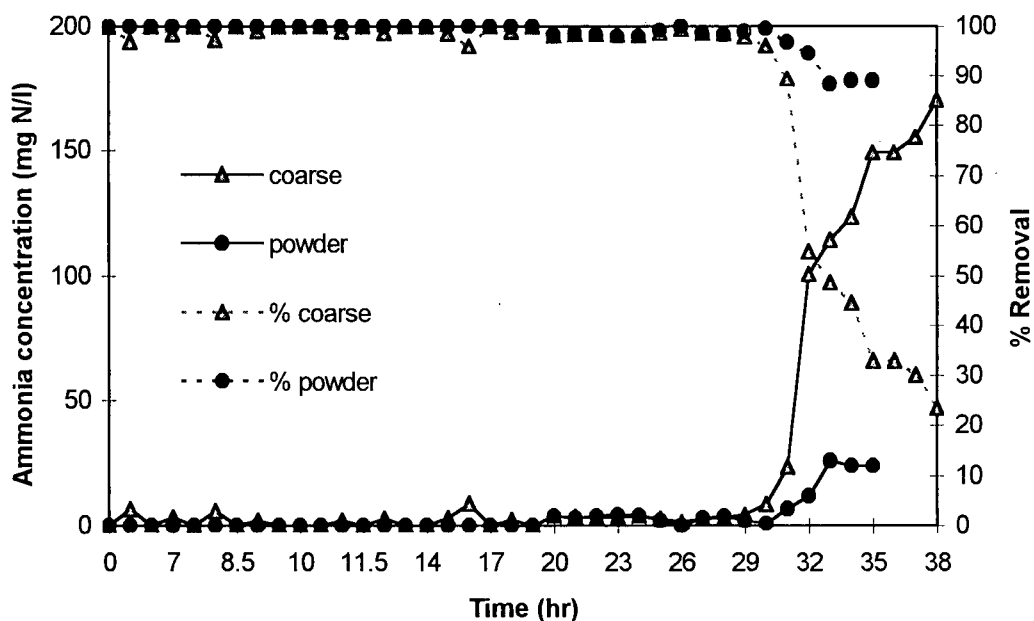From the above breakthrough curve results, it is clear that the removal of ammonium from the influent is dependent upon the relation between the hydraulic retention time and the flow rate through the column. Thus, a lower loading rate yields a comparatively higher adsorption capacity. At the higher flow rate groups (HRT=1 and 3 hrs), in all cases the effluent ammonia concentration rose rapidly after about 3 bed volumes wastewater had passed through, despite the differences in the particle size used for the column. At 90% removal breakthrough, the operating capacities for both groups were about 54% lower than that obtained in the HRT=6hrs test. This behavior suggests that the retention time was insufficient for NH_4^+ exchange to take place between zeolite and NH_4^+ions and for diffusion into the internal structure of the zeolite. Significant flow along the sidewalls may also have occurred, bypassing the zeolite. It suggested that a contact time of less than 6 hrs was too short to achieve a high ammonia removal rate for the zeolite used in this study. HRT=6 hrs was therefore chosen as appropriate for sufficient regeneration in the zeolite life expectancy studies. It should be noted that the effluent ammonia concentration for the powdered zeolite packed column was still at or below breakthrough value for the 35-hr duration of the study. This represented a total volume of about 12L. Thus a capacity calculation based on this volume does not reflect the total capacity of the zeolite because it was insufficient to develop breakthrough; it can, however, be taken as a very conservative estimate of the zeolite capacity.

The studies do show that the particle size of the zeolite used is a very important factor in column performance at different levels of hydraulic retention time. The above results make it clear that the powdered zeolite had a higher apparent ion exchange capacity during breakthrough experiments for each level of loading flow rate. It was to be expected that the coarse zeolite would have a lower NH_4^+ removal capacity than the powdered zeolite due to its lower surface area for NH_4^+ adsorption and diffusion. Generally, the operating capacity for powdered zeolite packed columns was 20% higher than coarse particle packed columns for each level in the HRT test. The improved rate of ion exchange was possibly accompanied by an increase in head loss, but the extent of the head loss was not measured. The powdered zeolite lost its ability as an ion exchanger during the period of column operation as it was saturated with wastewater for over 35

hours. This is in agreement with findings of Nguyen & Tanner (1998) that clinoptilolite displayed disintegration of its structural aggregates after wetting. This will likely limit its use in wastewater treatment. For these reasons, only the coarse zeolite packed column was used for the subsequent regeneration efficiency and zeolite life expectancy studies.

The results of this study suggest that the effect of zeolite particle size on its acutal operating NH_4^+ removal performance (operating capacity) depends on the contact time between the wastewater and the zeolite. This is governed by the wastewater loading flow rate passing through the zeolite beds. The importance of the wastewater loading flow rate on the NH_4^+ removal performance of zeolites has been reported for overseas zeolites (Booker *et al.*, 1996; Nguyen & Tanner, 1998; Singh & Prasad, 1997). The interaction between wastewater flow rate and particle size highlighted the need to conduct flow-through studies to assess the NH_4^+ removal rate of zeolites. In general, the adsorption capacities observed for batch and column experiments did not correspond; the column tests yielded lower adsorption capacities. In this study, the maximum adsorption capacity observed for the batch adsorption experiments was 17.81 mg N/g in NH_4Cl solution and 14.58 mg N/g in leachate. In the column study, however, it was only 1.31 mg N/g. Since the batch adsorption study determines the maximum potential for ammonium adsorption, it is common for the adsorptive capacity to be greater than the actual operating capacity (Booker *et al.*, 1996, Carpio, 2000, Hlavay *et al.*, 1982). This is especially the case when the batch adsorption has been conducted using synthetic wastewater. Hlavay *et al.* (1982) explained that these reasons for this phenomenon are that channeling often occurs in the column, especially in a bigger column, and the ions are not able to reach the ion exchange sites. Olin & Bricka, (1998), also found poor correspondence between parameters obtained from batch and column studies, and argued that scale-up parameters should be obtained using analysis of column performance.

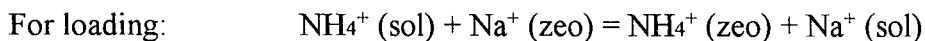### 4.2.2 Determination of regeneration efficiency of zeolite column

Experiments were carried out to test the possibilities of regenerating the zeolite packed columns after ammonia removal. A pair of coarse zeolite packed columns (Column A and B) was operated so as to continuously remove ammonia from the composting leachate. Repeated loading and regeneration cycles were used. Five loading and regeneration cycles were completed. The loading conditions for all runs was the same with a HRT=6hrs for 6 bed volumes influent (36 hrs loading period) in the downflow mode, except for the variability in influent ammonia concentrations in the wastewater samples (composting leachate) in the collecting buckets. The average influent ammonia concentrations for each run were measured and are presented in Table 4-7.

Table 4-7. Average feed ammonia concentrations in composting leachate for each of regeneration efficiency Runs

Run	Average feed ammonia concentration (mg N/l)
1	221.52
2	151.73
3	128.68
4	192.04
5	137.17

The regeneration process involved bringing the exhausted zeolite columns A and B into contact with 1M and 0.6M NaCl regenerant solutions, respectively, after each of the loading cycles was completed (i.e. upon ammonia breakthrough). Runs 1 to 3 were regenerated by applying regenerants at HRT=30 min (2 BV/hr), and Runs 4 & 5 were accomplished at HRT=1hr. A typical loading and regeneration curve for the column study is shown in Figure 4-10.

The loading and regeneration cycles of zeolite can be explained by the following simple equations,

For loading: $NH_4^+ (sol) + Na^+ (zeo) = NH_4^+ (zeo) + Na^+ (sol)$

For regeneration: $Na^+ (sol) + NH_4^+ (zeo) = Na^+ (zeo) + NH_4^+ (sol)$

The effect of differing NaCl concentrations was also examined. The results of Run 1 are shown in Figure 4-10 (a). The zeolite columns were completely saturated with ammonium and greater than 95% ammonia removal from the wastewater was achieved (less than 8.75 mg N/l ammonia in the effluent) after 5 bed volumes. The amount of ammonium removed after 5 BV influent passed through was approximately 2105 mg N/l per column; the corresponding capacity was 1.05 mg N/g zeolite. The exhausted columns were regenerated with two different NaCl solutions in a manner similar to the breakthrough experiments where a continuous feeding of a fresh NaCl solution was used for regeneration in an upflow mode.

The desortpion curves are shown in Figure 4-10 (b). It is clear that the desorption rates are much higher at the beginning and lower at the end of the regeneration. The graph shows that regeneration with 1M NaCl was better than with a lower concentration. 98% of the adsorbed ammonium was recovered within 9 BV when 1M NaCl solution was used, while 10 BV were required with the lower concentration (0.6M NaCl) to recover 95% of the adsorbed ammonium. When using the 1M NaCl solution, the ammonia concentration in the effluent varied between 225.67mg N/l (10.7% of total ammonium adsorbed) at the beginning of the regeneration to 4.58mg N/l at the end (9 BV). With the 0.6M NaCl solution, ammonia concentration in the effluent varied between 207.11mg N/l (9.8% of total ammonium adsorbed) at the beginning of the regeneration to 13.02mg N/l at the end (10 BV). This indicates that a higher sodium concentration could achieve more complete regeneration than a lower sodium concentration given the same regeneration time period.
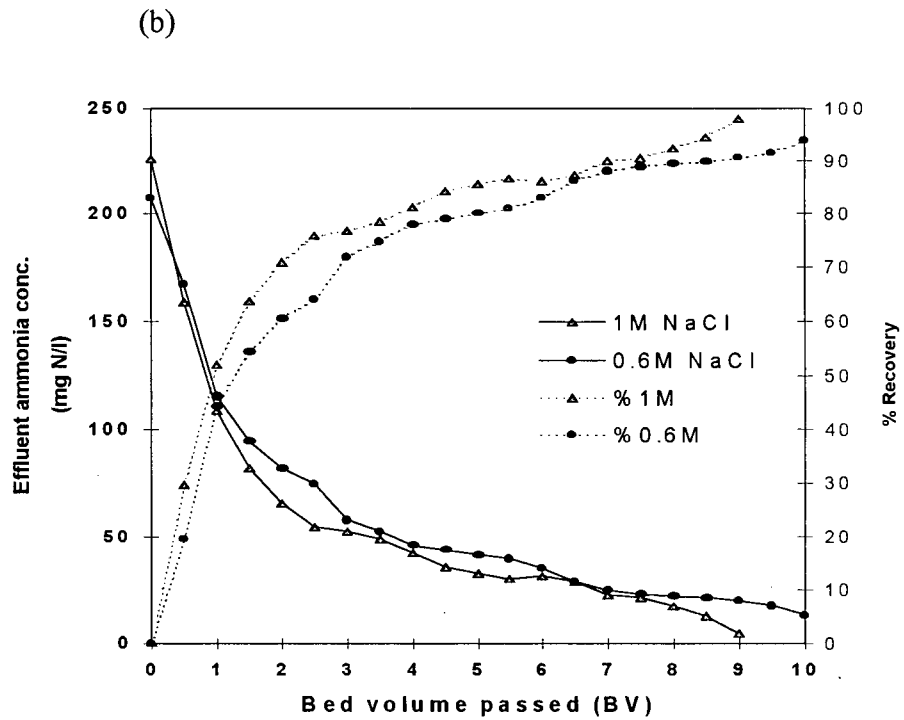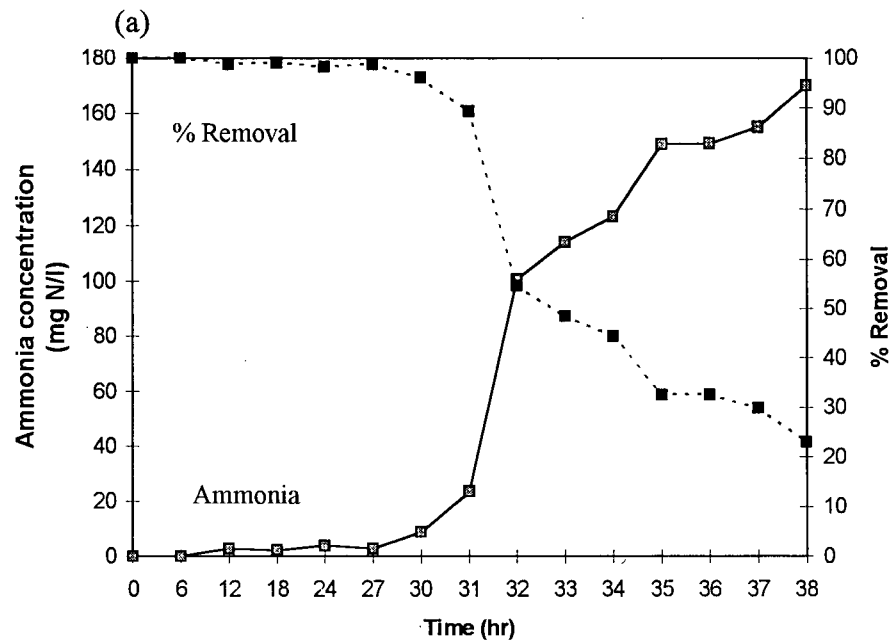
Figure 4-10. (a) Typical loading curve and removal efficiency on ammonia removal for Run1; (b) Typical regeneration plot and recovery efficiency (%) for desorption of adsorbed ammonium with different NaCl concentrations for Run1.

Figure 4-11 represents the ammonia breakthrough curves and removal efficiency of the zeolite columns for each loading test after the different regeneration treatments (Run 2 to Run 5). Runs 2 and Run 3 were repeated cycles of Run 1 followed with 1M and 0.6M NaCl solution regenerated at HRT=30 min. In order to recover as much as possible of the zeolite columns' ammonium exchange capacity before studying the regeneration efficiency at HRT=1 hr for Runs 4 and 5, the zeolite columns were soaked in 1 bed volume of 1M NaCl solution over night followed with 3 bed volumes of 1M NaCl solution at HRT=1 hr.

From Figure 4-11 (a) & (b), it is clear that higher leakage and earlier breakthrough were obtained for Runs 2 and 3 after 4 BV and 3 BV of wastewater, respectively. These were regenerated with higher water velocity (HRT=30 min). The pretreatment of the zeolite columns before commencement of Run 4 seemed to have completely recovered the ammonium exchange capacity of both columns, as 5 BV of influent was obtained before breakthrough for this run. However, poor ammonium removal capacity was obtained for Run 5 after regeneration at HRT=1. The difference between column A and column B was not significant for each run. The detailed results for loading and regeneration are as follows.

Table 4-8 presents the results for ammonia removal and the corresponding capacity for Runs 2 through Run 5 using 90% removal as the breakthrough value. It would appear that the ion exchange capacity of the zeolite columns was reduced when the regeneration treatment was applied, although the column loading conditions remained unchanged for all the runs. Run 2 had an operating capacity that was 48% lower than that obtained for Run 1, although the first regeneration had greater than 95% recovery performance for both columns. Less than 35% of Run 1 operating capacity was obtained for Run 3. This strongly suggests that the regeneration step (both 1M and 0.6M NaCl regenerated zeolite columns at HRT=30 min) did not result in complete recovery of all the ion exchange sites of the resins. After the pretreatment of the zeolite columns before Run 4 commenced, the operating capacity was raised to approximately the capacity of Run 1 (1.05mg N/g). However, after the regeneration of Run 4 (HRT=1hr), a poor operating capacity was

obtained for Run 5; it had 50% less capacity than Run 4. Generally, Runs 2 and 3 had sharper breakthrough curves than Runs 4 and 5. At the end of the operation (36 hrs loading period), Runs 2 and 3 achieved less than 25% ammonium removal efficiency but Runs 4 and 5 still achieved 54.88% - 66.9% ammonium removal efficiency.

Table 4-8. Important parameters measured for ammonium breakthrough of loading cycles

Run	Working influent* (BV)	Adsorbed ammonium mg N/l	Operating capacity mg N/g
2	4	1092.5	0.55
3	3	694.5	0.35
4	5	1881.9	0.94
5	3.5	864.1	0.43

*Working influent refers to the volume of influent applied before breakthrough

Figure 4-12 shows the ammonia concentration and percentage of ammonia recovered during the regeneration period for Runs 2 and 3 at HRT=30 min. The results show that regeneration with 1M NaCl (column A) had approximately 14% higher ammonia concentration in the effluent at the beginning of the regeneration for each run than regeneration with 0.6M NaCl (column B). However, the ammonia concentrations in the effluent were similar for Run 2 (8.5 and 10.63 mg N/l) and Run 3 (10.7 and 14.59 mg N/l) at the end of the regeneration (after 11.5 BV). The results show that 11.5 BV could only recover 85%-95% of the adsorbed ammonium from the resins at a flow rate of 2 BV/h (HRT=30 min). This suggests that more bed volumes of regenerant were necessary to complete the regeneration process at a faster water velocity. In this study, the zeolite columns were not completely regenerated by treatment with either concentration of NaCl solution. This resulted in the insufficient recovery of the ion exchange sites and a decrease in the operating exchange capacity for the zeolite columns during the loading tests (Figure 4-11 & Table 4-8). Obviously, the higher flow rate unfavorably affected the process of ammonium desorption. This is probably due to insufficient contact time which resulted in the ion exchange between the adsorbed ammonium in the zeolite and the sodium ions in the regenerating solution being incomplete.
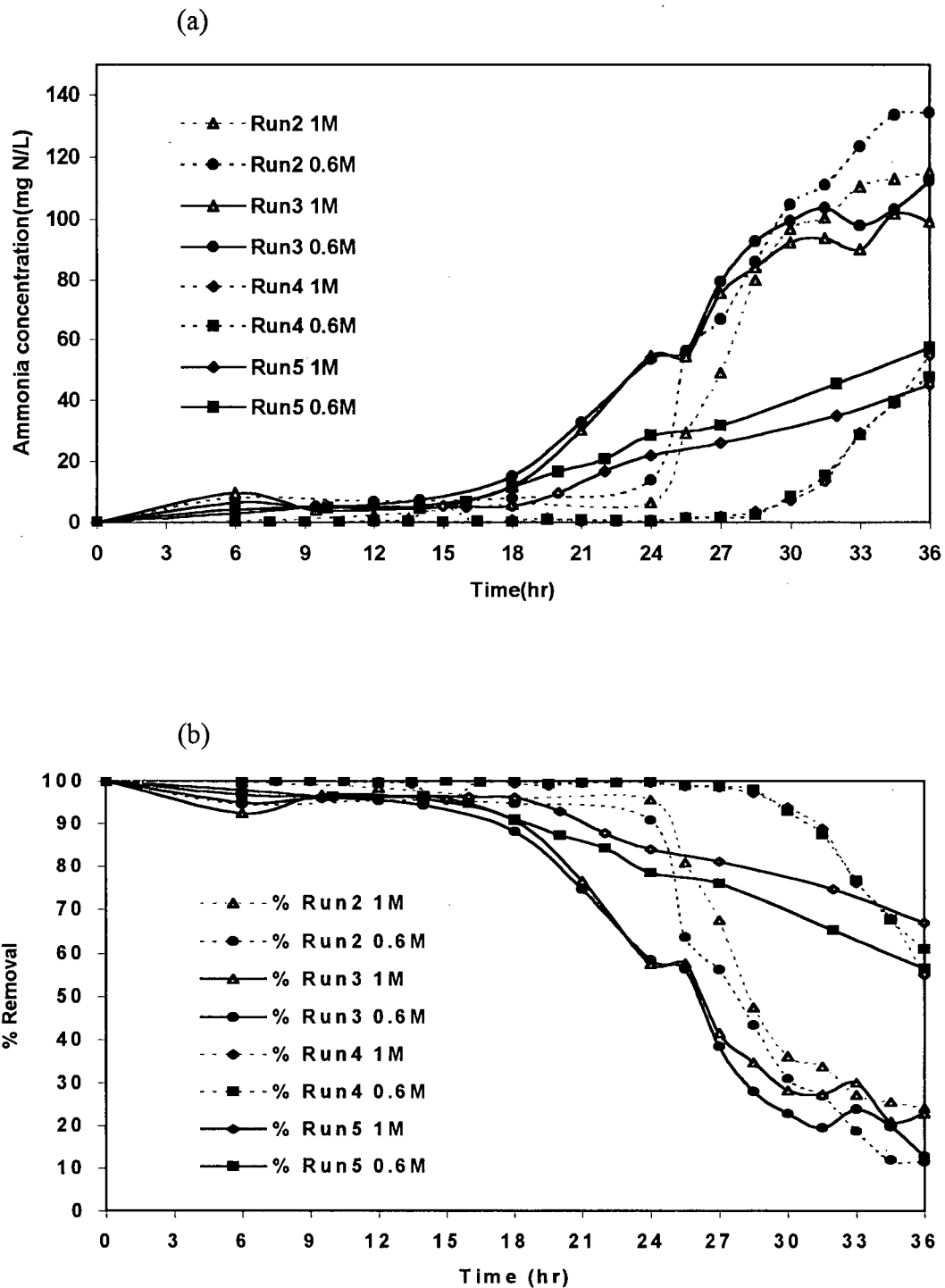
Figure 4-11. Zeolite columns removal of ammonium for loading cycles followed with different concentration and velocity of regenerations. (a) ammonia concentration in effluent during loading period. (b) percentage of ammonia removal in time.
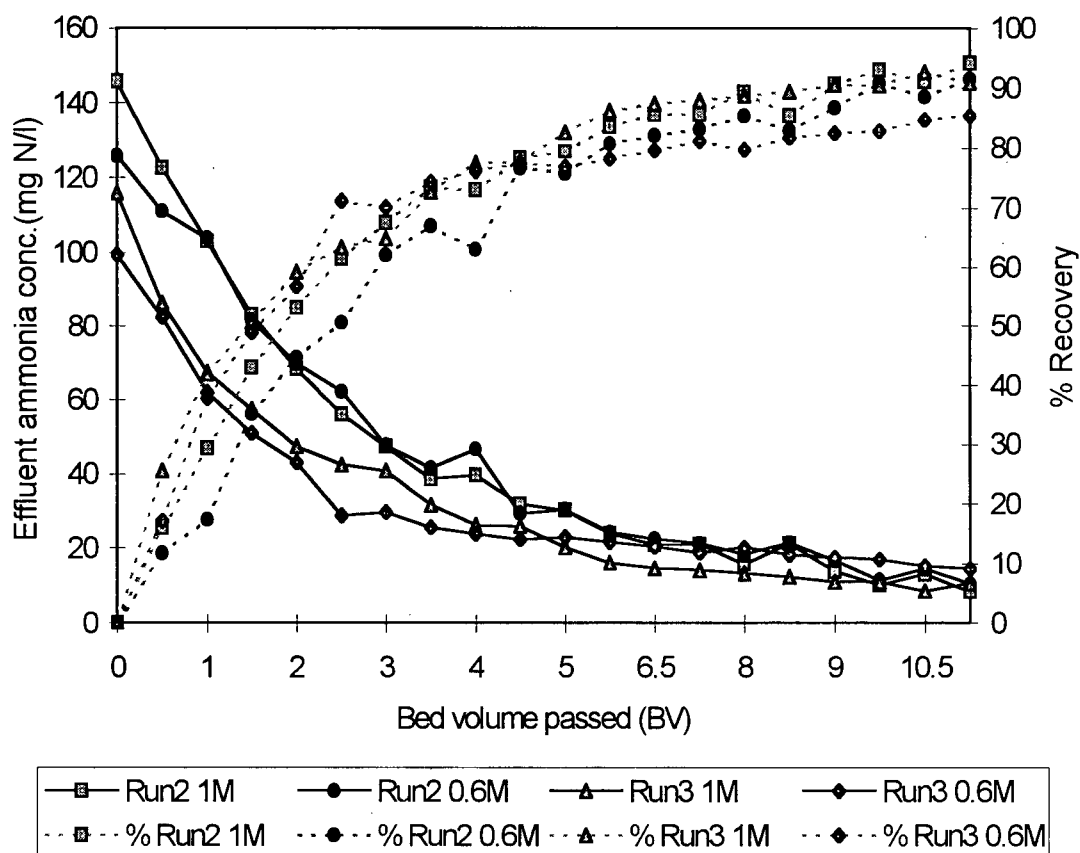
Figure 4-12 Desorption curves of adsorbed ammonium by regenerants with different Na$^+$ concentrations for Run2 & 3 at HRT= 30 min.

The results for lower flow rate regeneration (HRT=1hr) in Runs 4 and 5 are shown in Figure 4-13 (a) & (b) respectively. For Run 4, greater than 96% of the ammonium was recovered within 7 BV when both 1M and 0.6 M NaCl solutions were used. The ammonia concentration in the effluent ranged from 162.09 mg N/l at the beginning of regeneration to 6.81 mg N/l at the end of regeneration for 1M NaCl and from 143.42 mg N/l to 2.44 mg N/l for 0.6M NaCl. About 95% of the ammonium recovery was obtained for both columns for the regeneration of Run 5 after 8 BV of regenerant flow through. In this run, no significant differences between column A and B were observed in terms of ammonia concentration in the effluent at the beginning and the end of regeneration. The ammonia concentration in the effluent ranged from 133.71mg N/l at the beginning of the regeneration to 8.2mg N/l at the end of regeneration for 1M NaCl and ranged from 127.25mg N/l to 6.72mg N/l for 0.6M NaCl. The results of this study therefore suggest

that a lower flow rate can result in better ammonium desorption from the resin during regeneration irregardless of the concentration of the NaCl solutions used. A low flow rate is therefore advisable, since it results in better regeneration and reduces the volume of the regeneration solution required (3.5-4.5 BV less).

Regeneration of the zeolite columns in the five loading cycles was achieved by having the columns in contact with 1M and 0.6M NaCl solutions. Generally, results indicate that the desorption rates were much higher at the beginning and lower at the end of the regeneration period. The overall desorption of ammonium by the 1M NaCl solution was slightly better than for the 0.6M NaCl solution for each run. However, the concentration of NaCl solutions only effected ammonium desorption at the beginning of the regeneration, and was not a significant influence on it at the end of regeneration. This suggests that a solution of 0.6M NaCl is adequate for the regeneration process and is also more cost effective. In fact, a 0.6M NaCl regenerating solution (which is sea-water concentration), was adopted by most of the researchers examined (Bergero et al., 1994, Booker et al., 1996, Cooney et al., 1999, Liberti et al., 1995). It is obvious from the results that a lower flow rate favorably affected the process of ammonium desorption, indicating that sufficient contact time is necessary to allow the diffusion of adsorbed ammonium ions into the regenerating solution. More than 95% of ammonium was recovered with only 7-8 BV of regenerating solution at HRT=1 hr, while 85-95% of recovery was obtained after 11.5-12 BV of regenerating solutions at HRT=30 min. The adsorption-regeneration time ratio was approximately 6:1 for regeneration at HRT=30 min and 5:1 for regeneration at HRT=1. This suggests that the lower flow rate is suitable for regeneration of exhausted zeolite columns since it requires the same length of time while the volume of regenerating solution required is greatly reduced. Similar results were found by Dimova et al. (1999) and Singh & Prasad (1997). However, it should be noted that the regeneration protocols adopted varied widely among the different researchers. The range adopted for loading flow rate were from 30 to 1 BV/hr, and the amount of regenerant needed was from 70-10 BV. Singh & Prasad (1997) have suggested that 85 BV of 0.35 M NaCl solution at a flow rate of 5 BV/hr was sufficient for nearly complete regeneration.
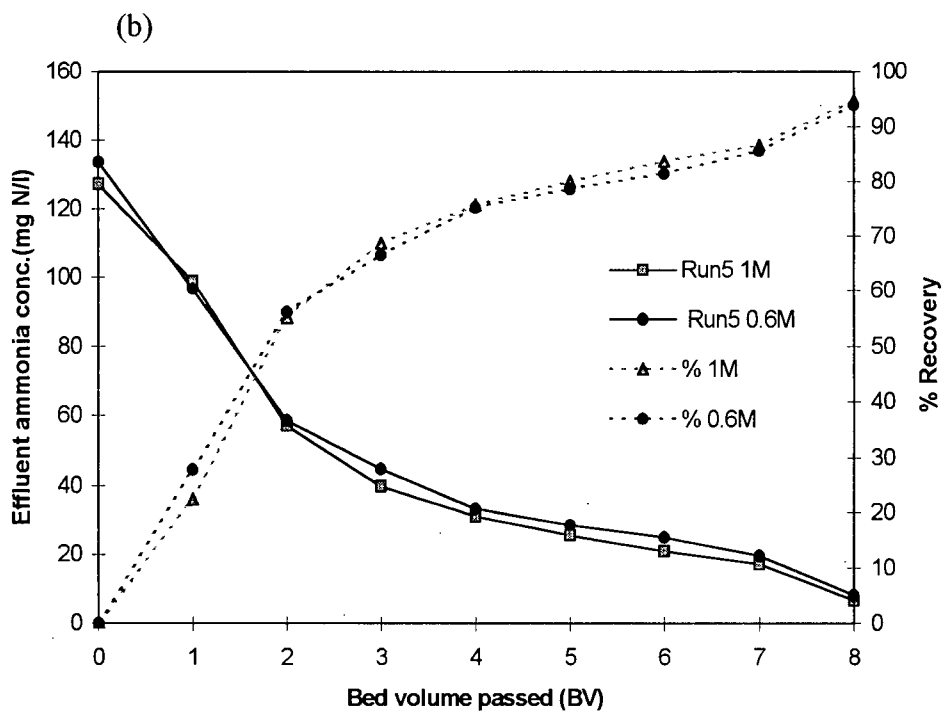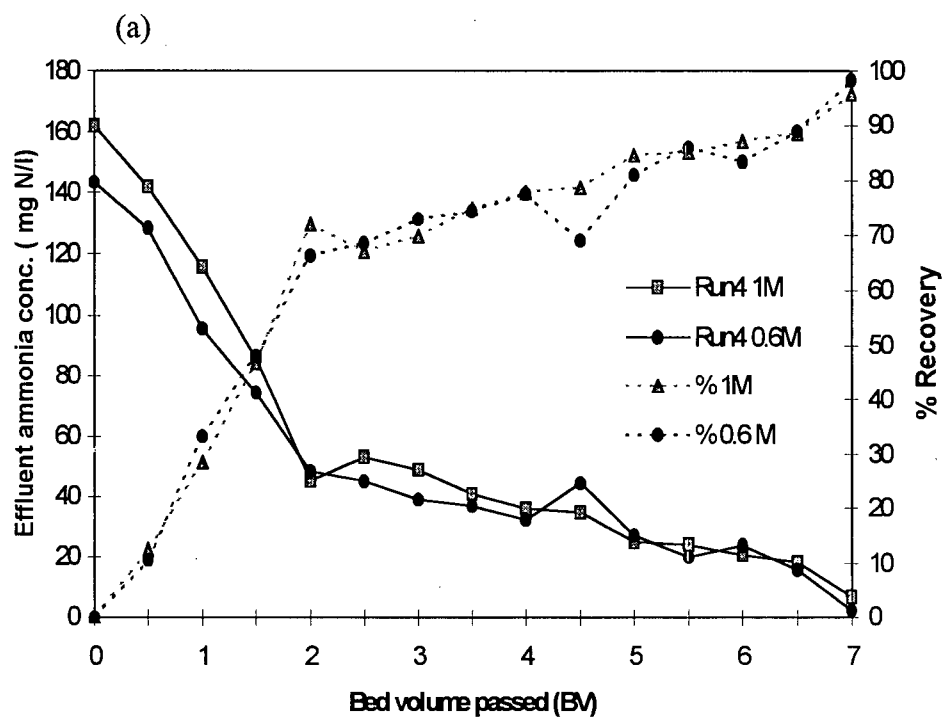
(a)

(b)

Figure 4-13. Regeneration of adsorbed ammonium by regenerants with different Na^+ concentrations at HRT=1 hr (a) Run 4 (b) Run5

4.2.3 Influence of competitive ion on the regeneration efficiency

Although results from these tests show that the regeneration protocol adopted displaced the ammonium adsorbed on the zeolite during the composting leachate loading cycle, the results also indicate that this regeneration treatment did not result in the exhausted zeolite columns recovering their original efficacy. Even though greater than 96-98% of ammonium recovery was obtained at the end of the regeneration of Run 4, the ammonium breakthrough capacity of the zeolite columns had decreased significantly from 0.94mg N/g (Run 4) to 0.43 mg N/g (Run 5). It should be noted that the experimental set-up of these ammonium removal efficiency studies didn't take into consideration the effect of competitive ion accumulation during regeneration. Only ammonium was considered when discussing the recovery of ion exchange sites within the resins. However, as discussed in an earlier section, the composting leachate wastewater used in this study contained very high concentrations of potassium (3500 ± 500 mg /l) compared to ammonium (200 ± 20 mg N/l). It is already known that zeolite has a greater affinity for potassium than for ammonium. Previous batch studies of zeolite adsorption capacity found that the coarse zeolite used in the column studies had an adsorption capacity of 29.05mg K/g for potassium and 3.35mg N/l for ammonium. Since the potassium ions are very selectively held by the zeolite, it may be hard to completely displace all the adsorbed potassium by exposing the zeolite to the NaCl solutions used in the regeneration studies. These unexchanged potassium ions, held in the ion exchange sites of zeolite, might have been responsible for the significant decrease in the zeolite column removal capacity for ammonium. For this reason, the overall desorption performance of potassium ions was also measured and discussed for all the regeneration efficiency study runs.

Figure 4-14 represents the results of adsorption and desorption of potassium during Run 1. Potassium breakthrough for wastewater influent containing 3974 mg/l of potassium did not occur during a 38 hrs loading period (Figure 4-14(a)). The overall removal of potassium was greater than 90 %, corresponding to less than 368.9 mg K/l in the effluent for 12L of loading volume. The amount of potassium removed was therefore

approximately 42919.2 mg K/l per column; the corresponding capacity was 21.5 mg K/g zeolite. Comparing this column capacity with the previous adsorption capacity (29.05 mg K/l) reveals that the column capacity is lower due to the loading period being insufficient for the zeolite column to become saturated with potassium.

The desorption curves are shown in Figure 4-14(b). During regeneration, the potassium concentration in the effluent was 241 mg/l (9.9 % of adsorbed potassium) at the beginning and 246.6 mg K/l (0.6% of total adsorbed potassium) at the end for column A (using 1M NaCl). For column B (using 0.6M NaCl solution), it was 3787 mg K/l (8.8 % of total adsorbed potassium) and 289.28 mg K/l (0.67 % of total adsorbed potassium), respectively. Although the adsorbed potassium was recovered efficiently by both NaCl solutions (greater than 92 % recovery), the potassium leakage in the regeneration effluent was still very high. This meant that a significant amount of potassium ions were still held by the zeolite due to insufficient regeneration. As a consequence, it was expected that this would reduce the overall ion exchange operating capacity of zeolite columns.

Figure 4-15 presents the results for the potassium breakthrough curves and the removal efficiency of the zeolite columns for each loading test after the different regeneration treatments (Run 2 to Run 5). There was no significant difference between column A and B after treatment with either 1M or 0.6M NaCl regenerating solution, respectively, for each run. As in previous ammonium studies, higher leakage and earlier breakthrough were obtained in the higher regeneration flow rate sets (Runs 2 and 3) after 4 bed volumes of wastewater influent passed through. As in the case of ammonium, the results for Runs 4 and 5 indicate that the pretreatment steps before the commencement of these runs seemed to yield a good recovery of the ion exchange capacity of the zeolite columns. Breakthrough was not obtained for Run 4 during a 36 hours loading period and greater than 90 % removal of potassium was reached for Run 5 within 5 BV of influent. A comparison with the results for ammonium removal efficiency (Figure 4-11) shows attainment of a higher removal efficiency for the zeolite columns in the case of potassium ions, confirming again that the zeolite had a higher affinity to potassium than to

ammonium. This means that the presence of potassium ions in the composting leachate used in this study resulted in strong competition for the ammonium ion.

(a)

(b)

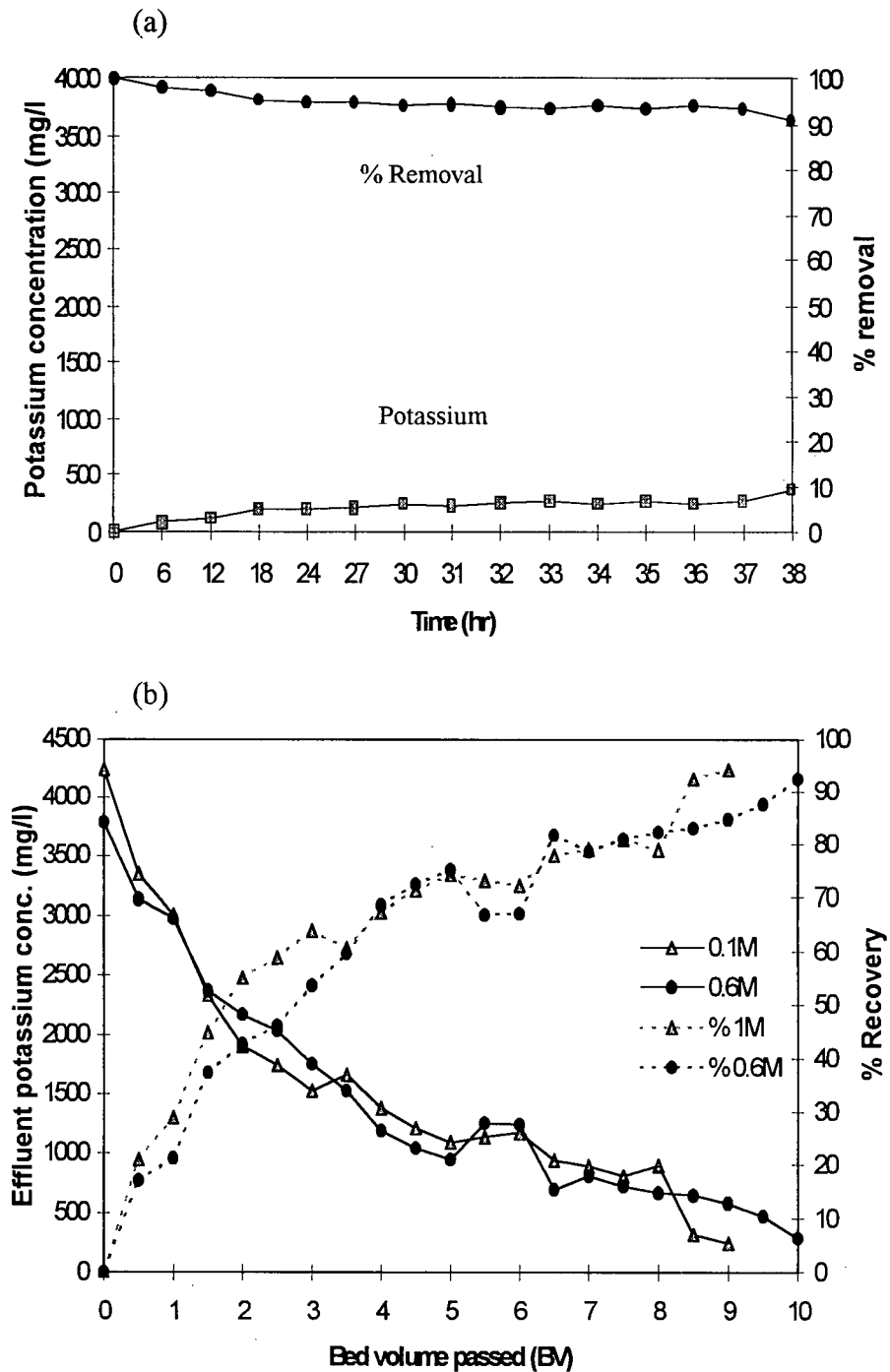Figure 4-14. Adsorption and desorption curves for potassium ions for Run1 at HRT=30 min. (a) loading curve and removal efficiency (b) concentration during regeneration
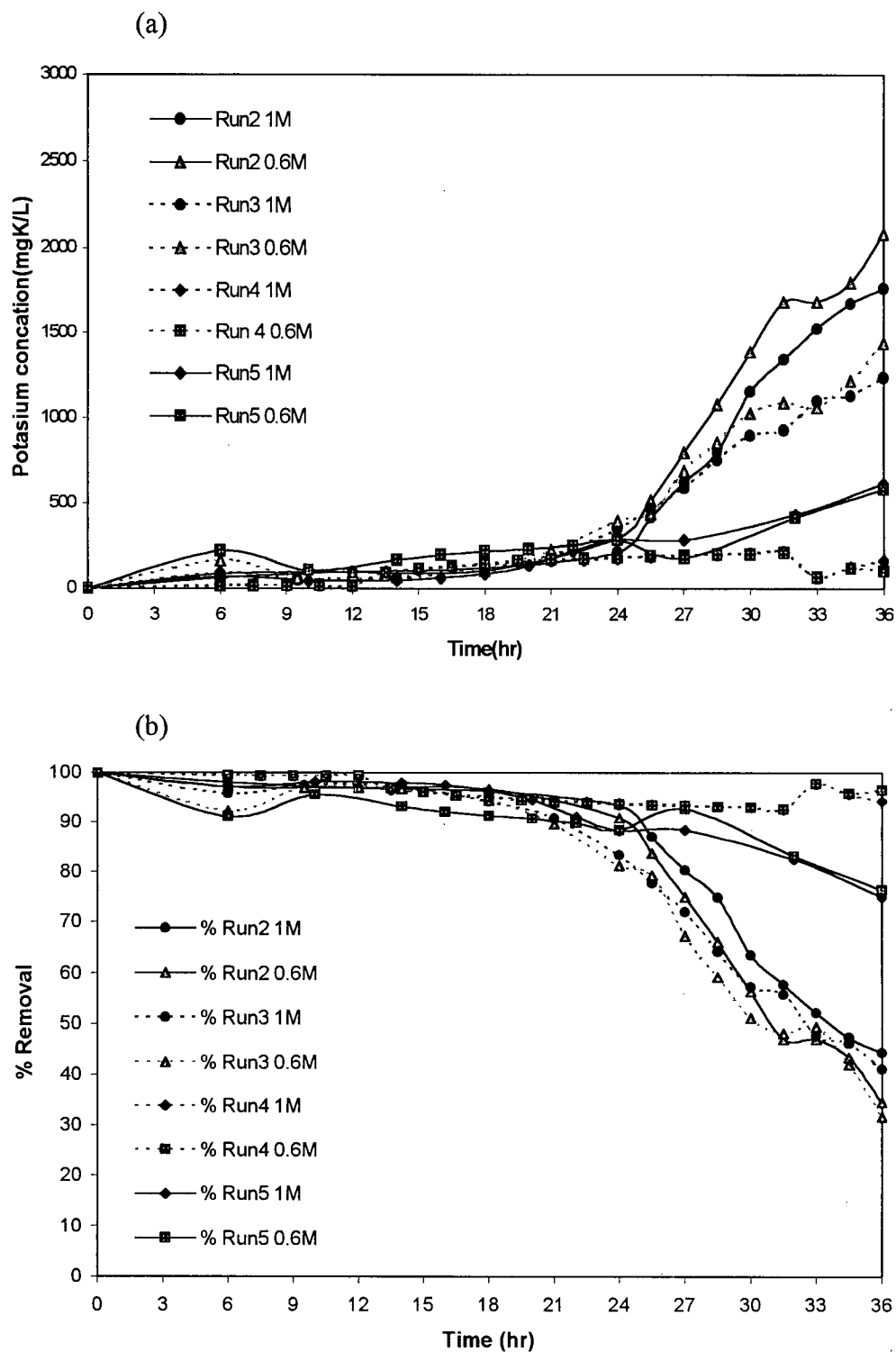
(a)

(b)

Figure 4-15. Potassium removal performance of zeolite columns for loading cycles followed with different concentration and velocity of regenerations. (a) concentration of potassium during loading period (b) percentage of potassium removal in time.

The detail results for potassium removal and the corresponding removal capacities are shown in Table 4-9 based on 90 % removal as the breakthrough value except for Run 4 (95 % used). The capacity for potassium removal of the zeolite columns was gradually reduced with subsequent applications. Run 2 exhibited an operating capacity that was 47 % lower than that obtained for Run 1. These results are similar to the results obtained for ammonium removal capacity (48 % less). The potassium operating capacity for Run 3 was only 35 % of Run 1's capacity, the same as those for ammonium. These results strongly support the view that the reduction in ion exchange capacity obtained for ammonium was due to the incomplete removal of potassium ions during regeneration. The operating capacity obtained from Run 4 was only raised to about 76 % of Run 1's capacity, and an even lower expected capacity was obtained for Run 5 (50 % less capacity than Run 1).

Table 4-9. Important parameters measured for potassium breakthrough of loading cycles

Run	Working influent (BV)	Feeding potassium concentration (mg K/l)	Adsorbed potassium (mg K/l)	Operating capacity (mg K/g)
2	4	3178	22881.6	11.5
3	4	2102	15134.4	7.6
4	6	2860	32604	16.3
5	5	2458	22122	11.1

Since the potassium ions are very selectively held by the zeolite, the incomplete removal of adsorbed potassium results in the accumulation of these ions inside the structure of zeolite where they occupy the ion exchange sites. Consequently, the overall ion exchange capacity of the packed zeolite columns decreased for both the ammonium and potassium ions. The potassium concentration and percentage of potassium recovered for high flow rate regeneration at HRT=30 min (Run 2&3) are presented in Figure 4-16. The desorbed potassium concentrations were different at the beginning of regeneration, probably reflecting the total amount of potassium adsorbed during the loading stage. However, 1M NaCl regenerated more potassium adsorption capacity than did 0.6 M NaCl at the beginning of regeneration, but this advantage was gradually lost. At the end of

regeneration, more than 353 mg K/l of concentration was still measured in the effluent, corresponding to less than 88 % recovery of zeolite column capacity.
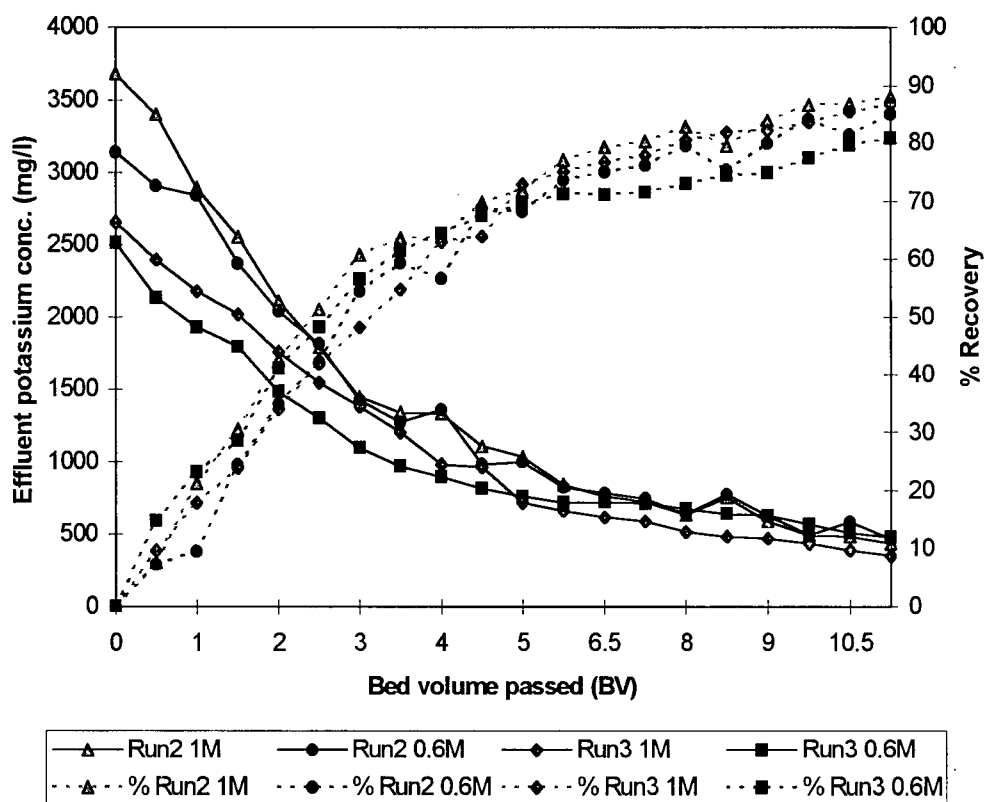
Figure 4-16. Desorption curves of adsorbed potassium by regenerating solution with different sodium concentration at higher flow rate regeneration (HRT=30 min)

Figure 4-17 represents the regeneration efficiency at a lower flow rate for Runs 4 and 5 (HRT=1hr). Again, the higher concentration NaCl solution had better desorption at the beginning of regeneration, but there was no significant difference at the end. Within the volumes of regenerating solutions used for regeneration (7 BV for Run 4 and 8 BV for Run 5), 92-95 % recovery of zeolite capacity for potassium was obtained. The potassium concentration in the effluent at the end of regeneration for Run 4 was 89.2 mg K/l (column A) and 193.6 mg K/l (column B) respectively, and 200.2 and 193.2 mg K/l for

Run 5. Obviously the flow rate significantly affects the process of potassium desorption. The lower flow rate is recommended for the regeneration of exhausted zeolite column given that the time needed is similar to that for the higher flow rate but the usage of regenerating solution is greatly redeuced, as discussed in a previous section. It is concluded that the water velocity had more influence than the concentration of the solution for the regeneration of exhausted zeolite column.s

In general, the leakage of potassium ions in the effluent at the end of each regeneration run was still very high, even though more than 90 % of recovery efficiency was obtained. This indicated that the regeneration process used in this study was adequate to displace the adsorbed potassium from the zeolite. The desorption of appreciable amounts of both ammonium and potassium ions suggested that the regeneration technique was successful only if a sufficient amount of regenerating solution was used. Both 1M and 0.6 M NaCl solutions were very useful as a regenerating solution. In order to reduce operating costs, it is suggested that the 0.6 M NaCl be adopted. It is suggested that the original capacity of zeolite could be recovered with the development of more suitable regeneration techniques, for example using more bed volumes of regenerating solution or an even lower flow rate.

The above results indicate that in this study potassium ions offered strong competition to the ammonium ions. That potassium ions compete with NH_4^+ for exchange sites and therefore reduced the amount of NH_4^+ removed by zeolite has been reported by many researchers (Booker *et al.*, 1996, Green *et al.*, 1996, Jørgensen *et al.*, 1976, Nguyen & Tanner, 1998, and Singh & Prasad, 1997). Dimovas *et al.* (1999) also found that at higher concentration of competing ions, continuous leakage of NH_4^+ was observed during operation and removal capacity decreased.
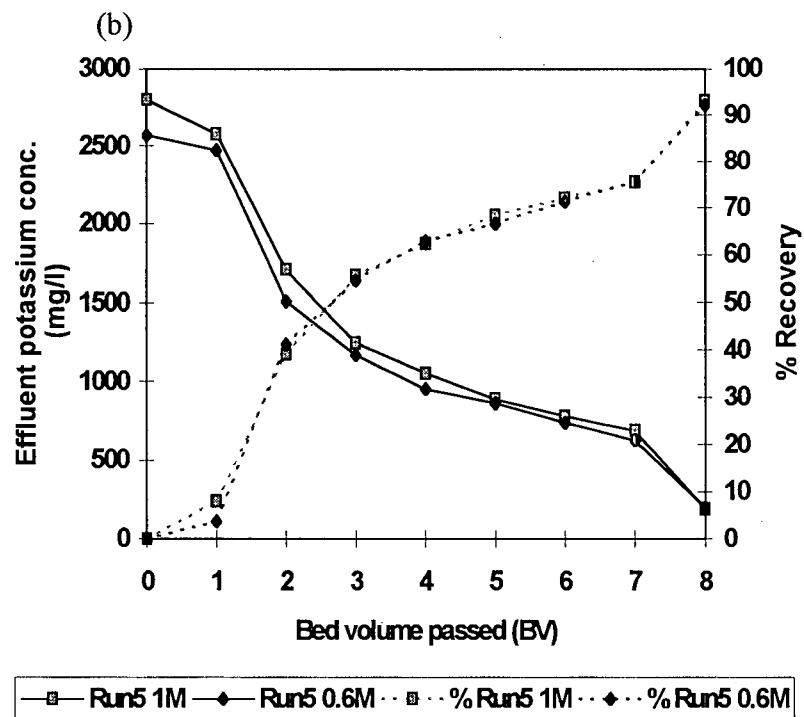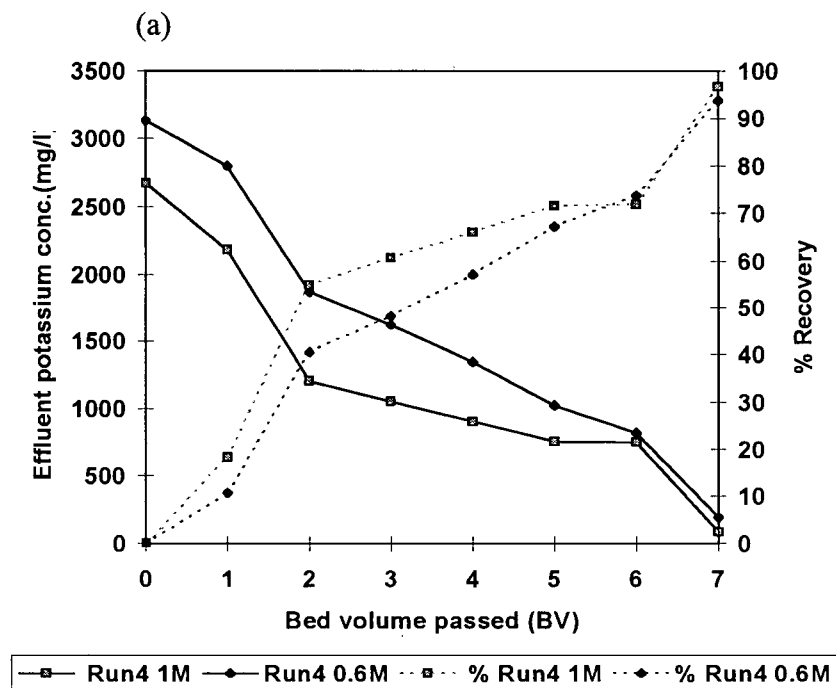
(a)

(b)

Figure 4-17. Regeneration of adsorbed potassium at lower flow rate with different
concentration of regenerating solutions. (a) Run4 (b) Run5

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The feasibility of using Canadian zeolite to remove ammonia in the treatment of leachate from a pilot-scale composting plant for vegetable greenhouse solid waste was studied. Through batch and column experiments, the potential of the zeolite was observed. The following conclusions are drawn from this study.

The maximum NH_4^+ removal capacities for different particle sizes of zeolite were determined through batch adsorption experiments. The capacity determined using synthetic NH_4Cl solution was 16.77-16.97 mg N/g, and for composting leachate it was 14.35-14.58 mg N/g . The capacity was slightly increased to 17.61-17.81 mg N/g if the zeolite was converted to the sodium form. Out of the three different particle sizes of zeolite, powdered zeolite (< 35 mesh size) had the highest ammonium adsorption capacity. This revealed that particle size influences the ammonium uptake capacity. Due to greater surface area, the uptake is larger with a smaller particle size. Equilibrium tests revealed that with an increase in the concentration of ammonia in solution, the adsorption rate of zeolite for ammonium also increased. Results indicated that for this study the Langmuir isotherm better described the equilibrium of ammonium than did the Freundlich model, possibly because of the inherent assumption of constant binding energy.

Results also show that the adsorption capacity increased with increased contact time. The adsorption of ammonium by zeolite occurred rapidly at the beginning of contact, then gradually decreased. Equilibrium was achieved within 24 hours for zeolite with the NH_4Cl solution, but more than 48 hours was necessary with treatment using composting leachate. Above 85 % of the equilibrium values were achieved by zeolite with the synthetic NH_4Cl solution and less than 75 % with the composting leachate. Particle diffusion was identified as the rate-controlling mechanism at the beginning of contact between zeolite and wastewater, a period of up to 4 hours. In the batch experiments, the values for the Diffusion coefficient clarified the not only low but also slow ammonium

adsorption capacities observed for zeolite when treating composting leachate. It was also observed that the influence of particle size on the ammonium adsorption capacity of zeolite was more distinct at the beginning of contact.

The hydraulic retention time was found to greatly effect the zeolite column performance. Lower loading flow rates yielded a higher operating adsorption capacity which revealed that adequate contact time is essential to achieve a specific adsorption capacity. A hydraulic retention time of 6 hours was found to be preferred which yielded an operating capacity of 1.31mg NH_4-N/g zeolite. Although powdered zeolite was found to have the highest ammonium adsorption capacity in earlier batch studies, it was found not to be suitable for column operation as it restricted the flow through after 35 hours continuous operation. The adsorption capacities observed in column tests were lower than in batch studies. This was probably the result of channeling and by-pass which occurred in the scale-up column.

A lower loading flow rate of regenerating solution was preferred for the desorption of adsorbed ammonium ions; the regeneration of original capacity was greater and the volume of regenerating solution required greatly reduced (3.5-4.5 BV). The effect of different NaCl solutions on the desorption of adsorbed ammonium was not significant. A 0.6M NaCl solution regenerated zeolite column at a flow rate of 1 BV/hr was found desirable; this provided good regeneration efficiency and kept the costs to a minimum. More than 95 % of adsorbed ammonium ions were recovered by 7-8 BV of regenerating solution. The adsorption-regeneration time ratio was approximately 5:1. The regeneration protocol adopted was shown to have the ability to displace the ammonium adsorbed on the zeolite. However, the capacity of the packed zeolite column could not be fully regenerated.

It was observed in both the batch and column studies that the presence of competitive ions reduced the ammonium adsorption capacity. The composting leachate wastewater used for this study was found to contain not only high concentrations of ammonium (200 ± 20 mg /l) but also potassium (3500 ± 500mg/l). Zeolite was found to have a greater

affinity for potassium than ammonium. The adsorption capacity was found to be 29.05 mg K/g coarse zeolite in the batch study. The regeneration process adopted in the column study could not completely regenerate the adsorbed potassium. It seems that the potassium ions were strongly held by the zeolite. These accumulated potassium ions inside the structure of the zeolite occupied the ion exchange site and resulted in a decrease in the overall capacity of the zeolite column for either ammonium or potassium.

Through the study of batch adsorption tests and column experiments, zeolite proved to have potential ammonia removal efficiency as ion exchanger sufficient enough for treating composting leachate. However, the presence of competing ion (potassium) had an adverse effect on the amount of ammonia removal by zeolite and the regeneration of exhausted zeolite. More study is required on the reuse of exhausted zeolite in order to reduce the cost for this process.

5.2 Recommendations

The following recommendations are suggested for further study:

For the batch adsorption studies

1. Use synthetic potassium solution to determine the maximum potassium adsorption capacity

2. Evaluation using longer contact time for equilibrium experiment

3. Additional evaluations in the pretreatment of zeolite to increase the adsorption capacity

4. Find the effect of pH values on the zeolite adsorption efficiency

For the column experiments

1. Evaluation the packing of zeolite column to avoid the channeling and by-pass

2. Performing longer loading period to obtain the operating capacity of potassium ions

3. Future research on investigating the usage of exhausted zeolite as slow released fertilizer is recommended

4. Analysis of the cost efficiency should be evaluated to better understand the potential usefulness of zeolite

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This section provides a few samples of data collection and analysis spreadsheets used in the batch studies of the adsorption capacity.

1) Sample calculations for the Equilibrium experiments (example for the group used NH_4Cl solution, Table 4-1 and Figure 4-1)

$$\begin{array}{lcl} \text{Adsorbed amount} & & \text{Initial } NH_4^+ \quad\quad \text{Final } NH_4^+ \quad\quad \text{Volume} \\ \text{of ammonia} & = & \text{conc. in the} \quad - \quad \text{conc. after} \quad x \quad \text{of} \\ \text{(mg N/g zeolite)} & & \text{leachate} \quad\quad\quad\quad \text{1 hr contact} \quad\quad \text{leachate} \end{array}$$

Set	Actual initial conc.(mg/L)	after One hour contact			adsorbed amount of ammonia(mg/g zeolite)		
		pebble	coarse	powder	pebble	coarse	powder
25 a	27.14	18.39	1.33	1.08	0.88	2.58	2.35
b		13.90	4.68	2.60	1.32	2.25	2.45
50a	57.74	33.65	18.80	8.31	2.41	3.89	4.45
b		36.00	22.93	11.46	2.17	3.48	4.63
75a	82.74	62.58	41.79	20.01	2.02	4.10	5.65
b		54.25	41.40	26.13	2.85	4.13	5.66
100a	115.15	81.39	59.81	47.40	3.38	5.53	6.10
b		77.60	68.72	44.46	3.76	4.64	7.07
125a	137.95	107.89	98.12	60.05	3.01	3.98	7.01
b		103.93	86.09	68.85	3.40	5.19	6.91
150a	169.44	129.87	111.69	88.39	3.96	5.78	7.29
b		130.94	112.38	87.81	3.85	5.71	8.16
175a	194.73	169.25	133.64	117.51	2.55	6.11	6.95
b		159.16	141.78	112.60	3.56	5.30	8.21
200a	219.76	191.19	167.01	145.59	2.86	5.28	6.68
b		181.71	173.78	139.88	3.81	4.60	7.99

2) Sample calculations for the Kinetic experiments (example for the group used NH_4Cl solution, powder size zeolite, Table 4-3 and Figure 4-3)

$$\begin{array}{lcl} \text{Adsorbed amount} & & \left\{ \dfrac{\left[\begin{array}{l}\text{Initial } NH_4^+ \quad \text{Final } NH_4^+ \\ \text{conc. in the} - \text{conc. after} \\ \text{leachate} \quad\quad \text{1hr contact}\end{array}\right] \; x \; \begin{array}{c}\text{Volume}\\\text{of}\\\text{leachate}\end{array}}{\text{Mass of zeolite}} + \begin{array}{c}\text{Accumulated adsorbed}\\\text{ammonia conc. of}\\\text{previous sample}\end{array}\right\} \\ \text{of ammonia} & = & \\ \text{(mg N/g zeolite)} & & \end{array}$$

sample ID	NH3(mg N/L)	Vol(L)	NH3(mg-N)	adsorbed amount of NH3 (mg N/g)	A	B	C
0	200.43	0.20	40.086		0	0	0
5A	154.49	0.20	30.898	4.594	4.594		
5B	158.62	0.20	31.724	4.181		4.181	
5C	161.00	0.20	32.200	3.943			3.943
10A	146.31	0.19	27.799	1.550	6.144		
10B	153.43	0.19	29.152	1.286		5.467	
10C	152.00	0.19	28.880	1.660			5.603
15A	125.86	0.18	22.655	2.572	8.716		
15B	134.74	0.18	24.253	2.449		7.916	
15C	120.71	0.18	21.728	3.576			9.179
30A	134.04	0.17	22.787	-0.066	8.650		
30B	119.21	0.17	20.266	1.994		9.910	
30C	125.56	0.17	21.345	0.191			9.370
45A	133.16	0.16	21.306	0.741	9.390		
45B	124.79	0.16	19.966	0.150		10.060	
45C	117.64	0.16	18.822	1.261			10.632
60A	112.97	0.15	16.946	2.180	11.570		
60B	131.72	0.15	19.758	0.104		10.164	
60C	132.79	0.15	19.919	-0.548			10.084
90A	124.23	0.14	17.392	-0.223	11.347		
90B	114.19	0.14	15.987	1.886		12.050	
90C	125.42	0.14	17.559	1.180			11.264
120A	116.16	0.13	15.101	1.146	12.493		
120B	119.12	0.13	15.486	0.251		12.300	
120C	120.20	0.13	15.626	0.966			12.230
150A	107.81	0.12	12.937	1.082	13.574		
150B	118.39	0.12	14.207	0.639		12.940	
150C	118.56	0.12	14.227	0.699			12.929
180A	115.84	0.11	12.742	0.097	13.672		
180B	109.91	0.11	12.090	1.058		13.998	
180C	115.12	0.11	12.663	0.782			13.711
4hrsA	104.77	0.10	10.477	1.133	14.805		
4hrsB	115.06	0.10	11.506	0.292		14.290	
4hrsC	113.58	0.10	11.358	0.653			14.364
8hrsA	106.13	0.09	9.552	0.463	15.267		
8hrsB	105.16	0.09	9.464	1.021		15.311	
8hrsC	99.84	0.09	8.986	1.186			15.550
12hrsA	96.16	0.08	7.693	0.929	16.197		
12hrsB	99.61	0.08	7.969	0.748		16.059	
12hrsC	108.52	0.08	8.682	0.152			15.702
24hrsA	101.98	0.07	7.139	0.277	16.474		
24hrsB	99.32	0.07	6.952	0.508		16.567	
24hrsC	97.07	0.07	6.795	0.943			16.646
48hrsA	101.86	0.06	6.112	0.514	16.987		
48hrsB	102.91	0.06	6.175	0.389		16.956	
48hrsC	102.09	0.06	6.125	0.335			16.980

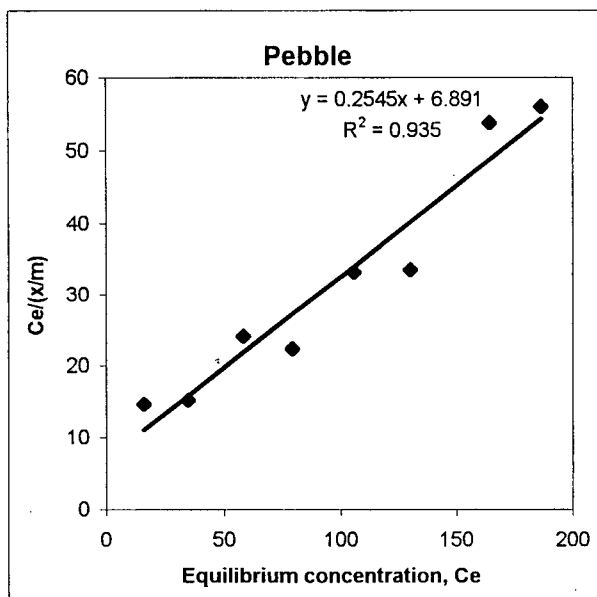# APPENDIX B: Batch Adsorption Tests Graphs

1).Adsorption Isotherms Graphs (examples of sample calculations for the Zeo group used NH4Cl solution same as in Appendix A1.)

- Freundlich isotherm: plotting (x/m) versus Ce
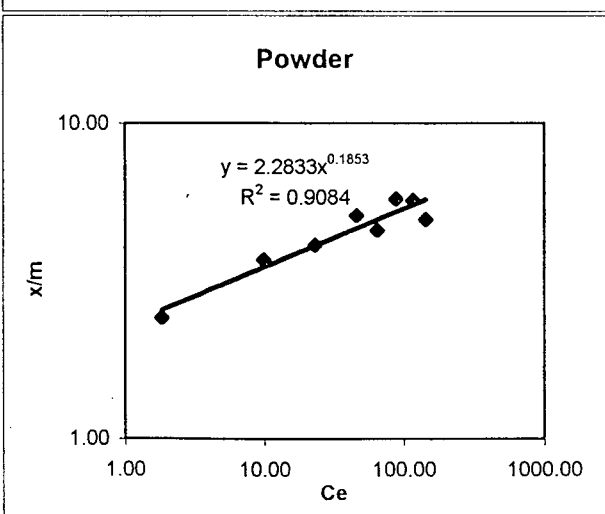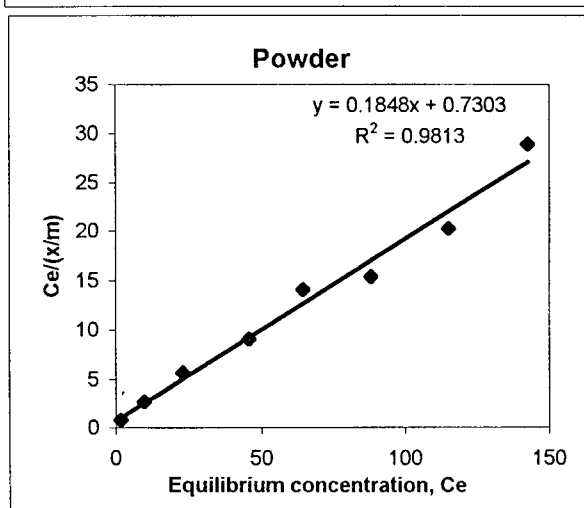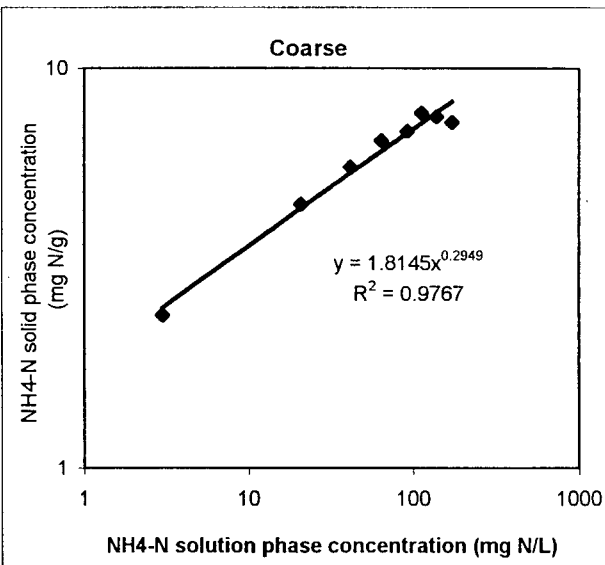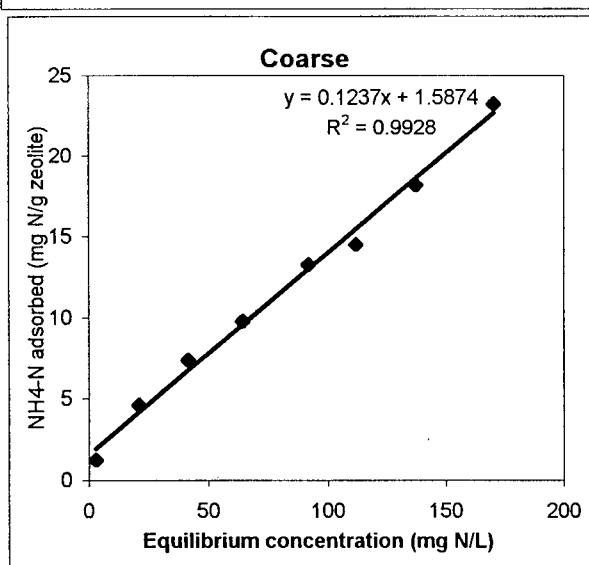- Langmuir isotherm: plotting Ce/(x/m) versus Ce

pebble		
Final conc. Ce(mg/l)	Adsorbed amount x/m (mg/g)	Ce/(x/m)
16.15	1.10	14.677273
34.83	2.29	15.207424
58.42	2.43	24.039095
79.50	3.57	22.267507
105.91	3.20	33.096875
130.41	3.90	33.437179
164.21	3.05	53.837705
186.45	3.33	55.990991
coarse		
Final conc. Ce(mg/l)	adsorbed x/m (mg/g)	Ce/(x/m)
3.01	2.40	1.2520833
20.87	4.54	4.595815
41.60	5.65	7.3619469
64.27	6.58	9.7667173
92.11	6.96	13.233477
112.04	7.73	14.493532
137.71	7.58	18.167546
170.40	7.33	23.246248
powder		
Final conc. Ce(mg/l)	adsorbed x/m (mg/g)	Ce/(x/m)
1.84	2.41	0.7634855
9.89	3.69	2.6788618
23.07	4.11	5.6131387
45.93	5.09	9.0235756
64.45	4.58	14.072052
88.10	5.74	15.348432
115.06	5.70	20.185088
142.74	4.94	28.893725

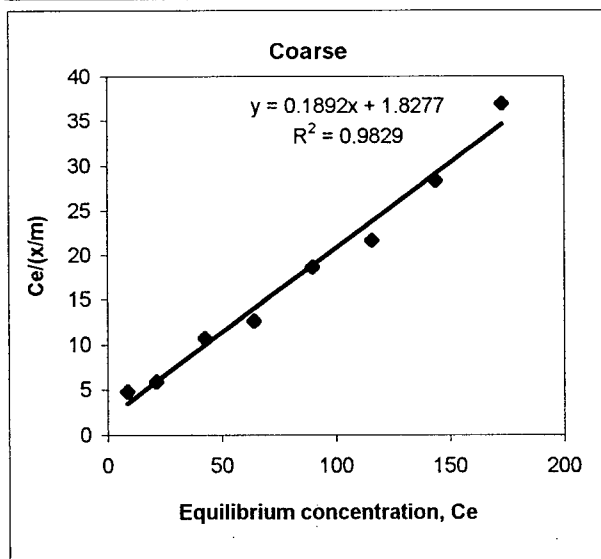Zeolite Vs NH4Cl Solution

Langmuir isotherm   Freundlich isotherm

Pebble

$y = 0.2545x + 6.891$
$R^2 = 0.935$

Ce/(x/m)

Equilibrium concentration, Ce

Pebble

$y = 0.4192x^{0.4296}$
$R^2 = 0.7865$

x/m

Ce

Coarse

$y = 0.1237x + 1.5874$
$R^2 = 0.9928$

NH4-N adsorbed (mg N/g zeolite)

Equilibrium concentration (mg N/L)

Coarse

NH4-N solid phase concentration (mg N/g)

$y = 1.8145x^{0.2949}$
$R^2 = 0.9767$

NH4-N solution phase concentration (mg N/L)

Powder

$y = 0.1848x + 0.7303$
$R^2 = 0.9813$

Ce/(x/m)

Equilibrium concentration, Ce

Powder

$y = 2.2833x^{0.1853}$
$R^2 = 0.9084$

x/m

Ce

Na-Zeo Vs NH4Cl solution

Langmuir isotherm   Freundlich isotherm

Pebble

$y = 0.2798x + 10.879$
$R^2 = 0.9529$

Ce/(x/m) vs Equilibrium concentration, Ce

Pebble

$y = 0.4675x^{0.3609}$
$R^2 = 0.9299$

x/m vs Ce

Coarse

$y = 0.1892x + 1.8277$
$R^2 = 0.9829$

Ce/(x/m) vs Equilibrium concentration, Ce

Coarse

$y = 1.186x^{0.3067}$
$R^2 = 0.7992$

x/m vs Ce

Powder

$y = 0.1223x + 2.1116$
$R^2 = 0.9817$

Ce/(x/m) vs Equilibrium concentration, Ce

Powder

$y = 1.0706x^{0.4185}$
$R^2 = 0.8349$

x/m vs Ce

Zeolite Vs Leachate

Langmuir isotherm

Freundlich isotherm

Pebbel

y = -1.0131x + 294.37
R^2 = 0.4608

Ce/(x/m)

Equilibrium concentration, Ce

Pebble

y = 0.0004x$^{1.6038}$
R^2 = 0.8487

x/m

Ce

Coarse

y = -0.0324x + 116.41
R^2 = 0.0038

Ce/(x/m)

Equilibrium concentration, Ce

Coarse

y = 0.0128x$^{0.9321}$
R^2 = 0.7678

x/m

Ce

Powder

y = -0.079x + 89.71
R^2 = 0.0311

Ce/(x/m)

Equilibrium concentration, Ce

Powder

y = 0.0129x$^{1.0039}$
R^2 = 0.7883

x/m

Ce

96
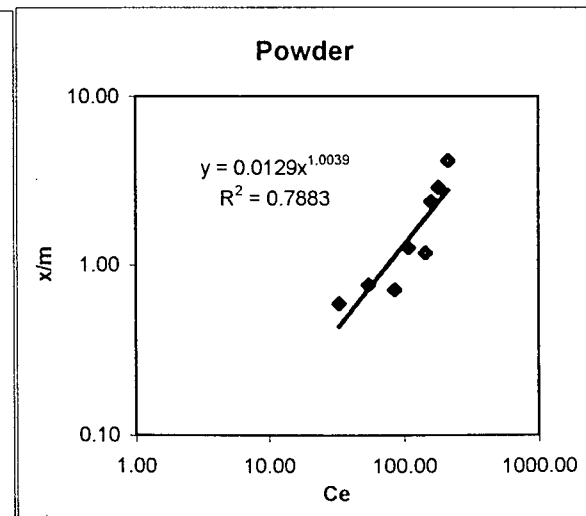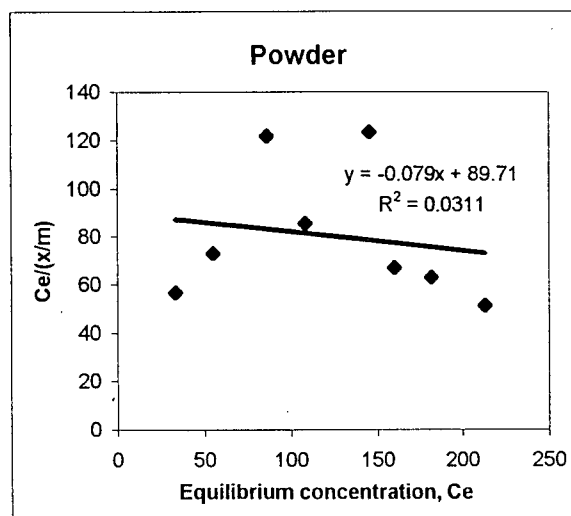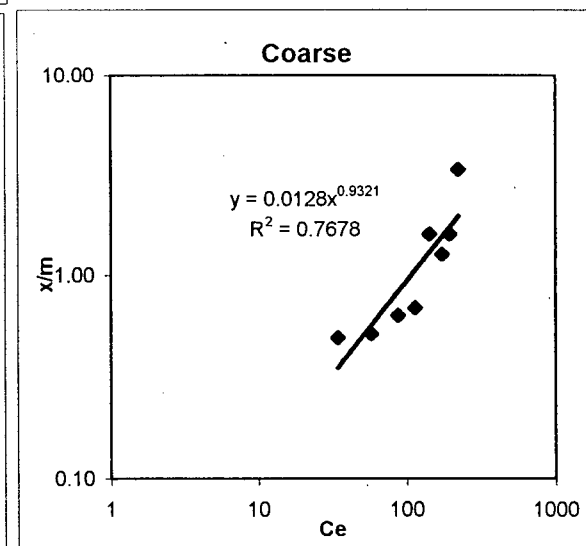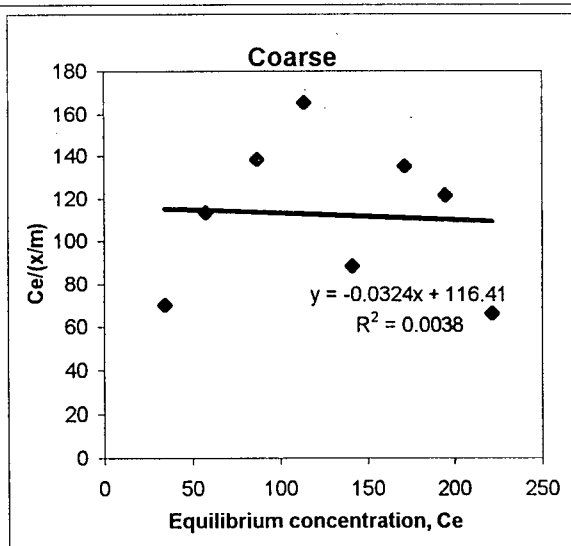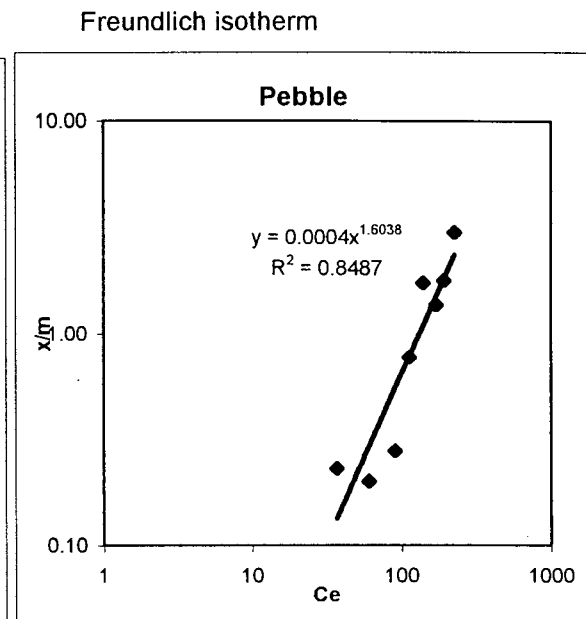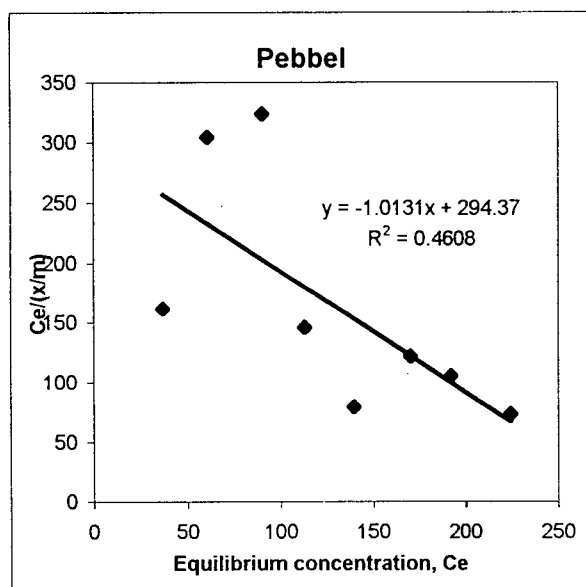
Zeolite Vs Leachate for Potassium

Langmuir isotherm

Pebble

$y = 0.0201x + 79.02$
$R^2 = 0.6709$

X-axis: Equilibrium concentration, Ce
Y-axis: Ce/(x/m)

Freundlich isotherm

Pebble

$y = 0.1247x^{0.6401}$
$R^2 = 0.942$

X-axis: Ce
Y-axis: x/m

Coarse

$y = 0.0307x + 39.698$
$R^2 = 0.8906$

X-axis: Equilibrium concentration, Ce
Y-axis: Ce/(x/m)

Coarse

$y = 1.1175x^{0.3727}$
$R^2 = 0.8816$

X-axis: Ce
Y-axis: x/m

Powder

$y = 0.0166x + 38.477$
$R^2 = 0.7352$

X-axis: Equilibrium concentration, Ce
Y-axis: Ce/(x/m)

Powder

$y = 0.7503x^{0.4708}$
$R^2 = 0.8752$
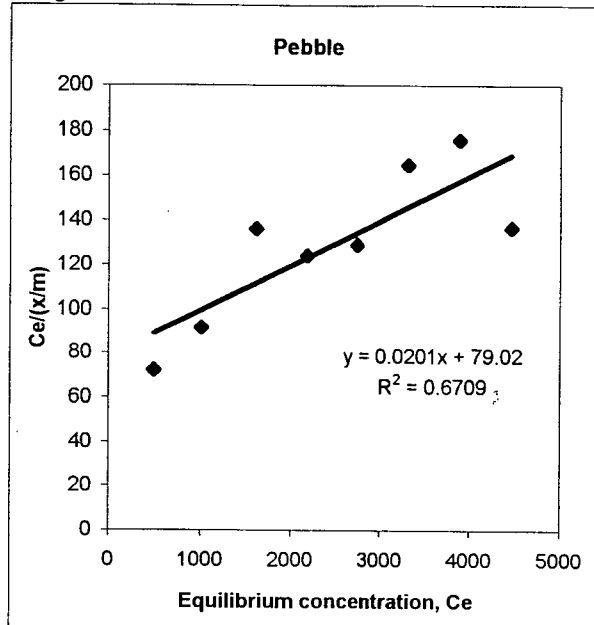
X-axis: Ce
Y-axis: x/m
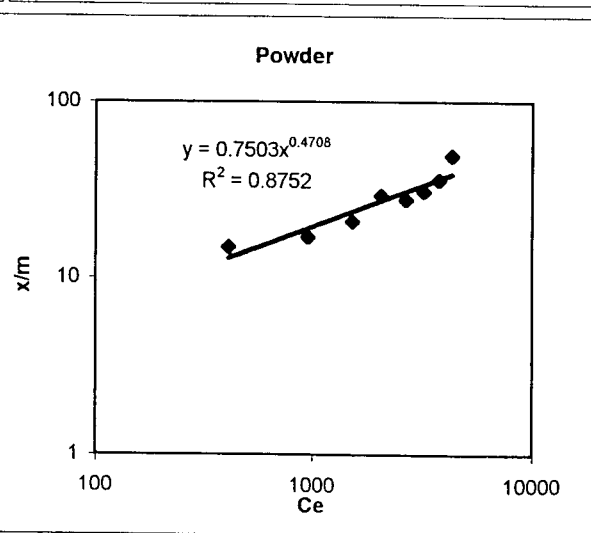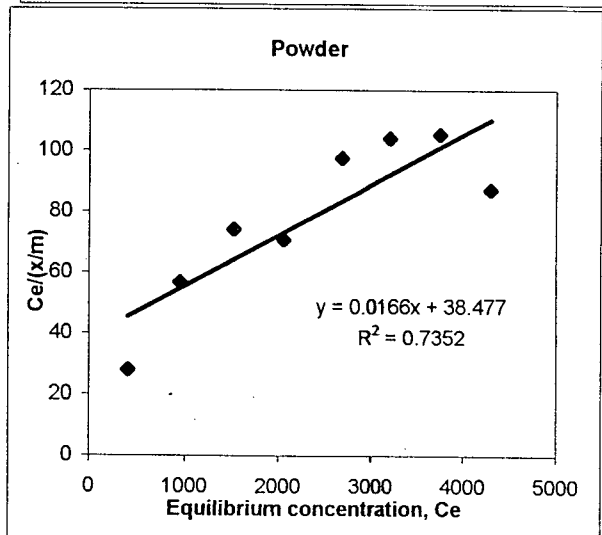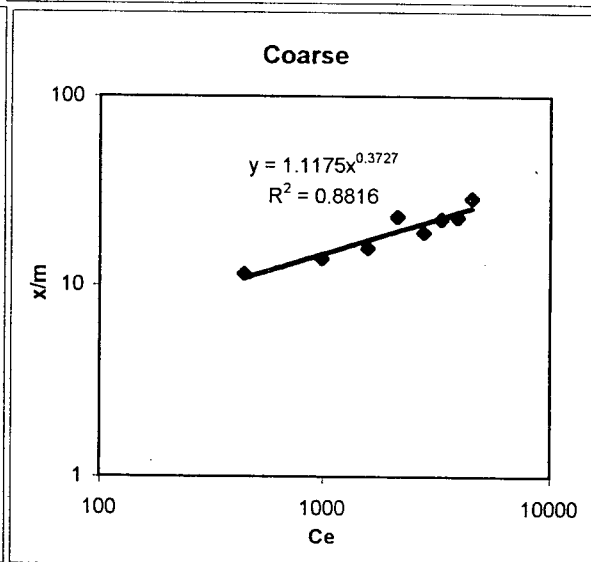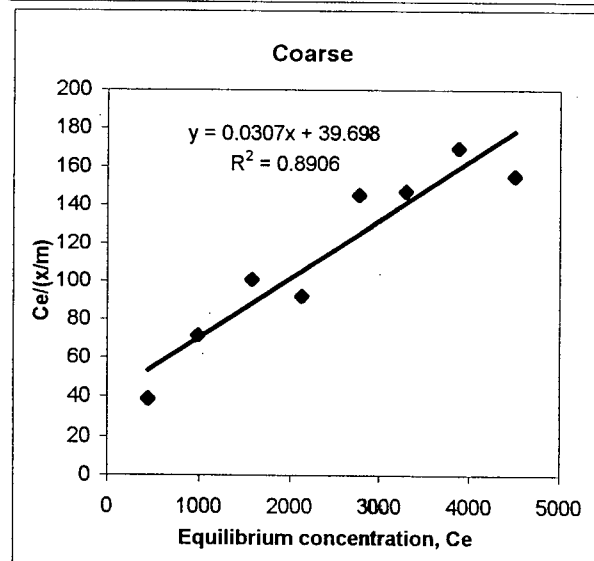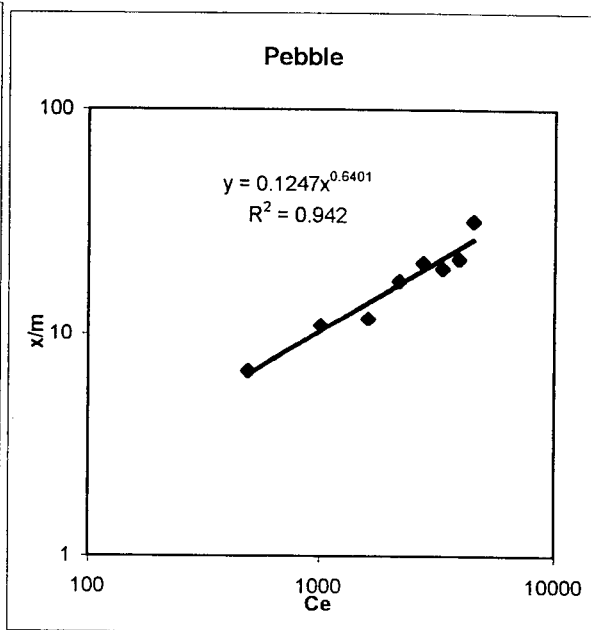
2).Kinetic Test Data applied to Vermeulen's Approximation Model Plots
(examples of sample calculations for the group used NH4Cl solution, powder size zeolite same as in Appendix A2)

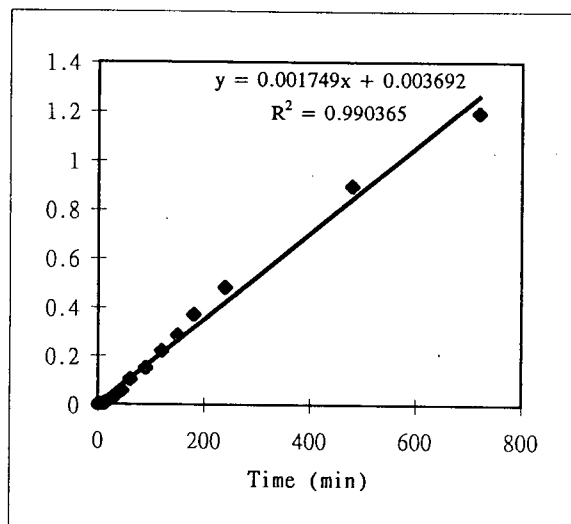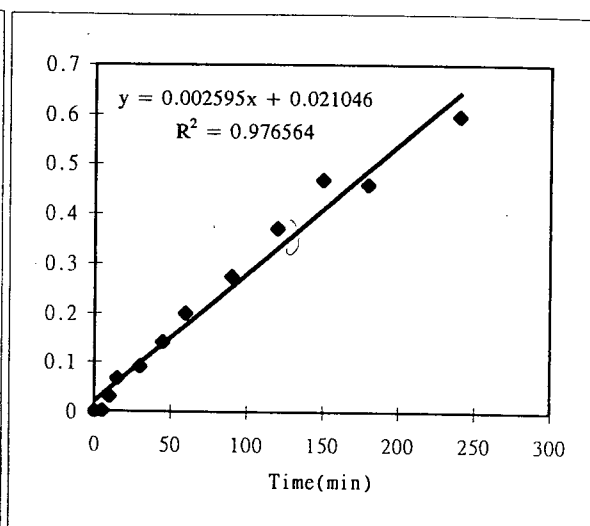| sample ID	NH3(mgN/L)	Vol(L)	NH3(mgN)		X	-ln (1-X^2)
0	200.43	0.20	40.086	40.086	0.000	0.000
5A	154.49	0.20	30.898	31.607	0.212	0.046
5B	158.62	0.20	31.724			
5C	161.00	0.20	32.200			
10A	146.31	0.19	27.799	28.610	0.286	0.086
10B	153.43	0.19	29.152			
10C	152.00	0.19	28.880			
15A	125.86	0.18	22.655	22.879	0.429	0.204
15B	134.74	0.18	24.253			
15C	120.71	0.18	21.728			
30A	134.04	0.17	22.787	21.466	0.465	0.243
30B	119.21	0.17	20.266			
30C	125.56	0.17	21.345			
45A	133.16	0.16	21.306	20.031	0.500	0.288
45B	124.79	0.16	19.966			
45C	117.64	0.16	18.822			
60A	112.97	0.15	16.946	18.874	0.529	0.329
60B	131.72	0.15	19.758			
60C	132.79	0.15	19.919			
90A	124.23	0.14	17.392	16.979	0.576	0.404
90B	114.19	0.14	15.987			
90C	125.42	0.14	17.559			
120A	116.16	0.13	15.101	15.404	0.616	0.477
120B	119.12	0.13	15.486			
120C	120.20	0.13	15.626			
150A	107.81	0.12	12.937	13.790	0.656	0.563
150B	118.39	0.12	14.207			
150C	118.56	0.12	14.227			
180A	115.84	0.11	12.742	12.499	0.688	0.642
180B	109.91	0.11	12.090			
180C	115.12	0.11	12.663			
4hrsA	104.77	0.10	10.477	11.114	0.723	0.739
4hrsB	115.06	0.10	11.506			
4hrsC	113.58	0.10	11.358			
8hrsA	106.13	0.09	9.552	9.334	0.767	0.888
8hrsB	105.16	0.09	9.464			
8hrsC	99.84	0.09	8.986			
12hrsA	96.16	0.08	7.693	8.114	0.798	1.011
12hrsB	99.61	0.08	7.969			
12hrsC	108.52	0.08	8.682			
24hrsA	101.98	0.07	7.139	6.962	0.826	1.148
24hrsB	99.32	0.07	6.952			
24hrsC	97.07	0.07	6.795			
48hrsA	101.86	0.06	6.112	6.137	0.847	1.263
48hrsB	102.91	0.06	6.175			
48hrsC	102.09	0.06	6.125			

Na-Zeo of the first 4 hours
Pebble size

$y = 0.001749x + 0.003692$
$R^2 = 0.990365$

Time (min)

Zeolite of the first 4 hours
Pebble size

$y = 0.002595x + 0.021046$
$R^2 = 0.976564$

Time(min)

Coarse

$y = 0.0028x - 0.0293$
$R^2 = 0.9884$

$-\ln(1-X2)$

Time (minutes)

Coarse

$y = 0.003044x + 0.021387$
$R^2 = 0.986774$

$-\ln(1-X2)$

Time (min)

Powder

$y = 0.003686x + 0.054615$
$R^2 = 0.962532$

Time (min)

Powder

$y = 0.002942x + 0.103401$
$R^2 = 0.941721$

Time (min)
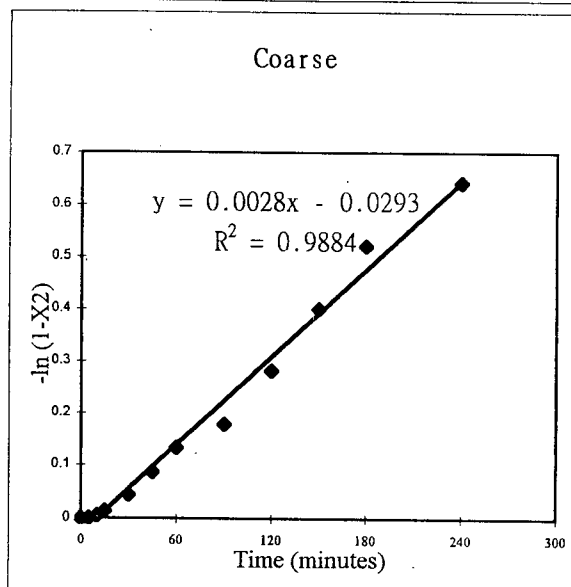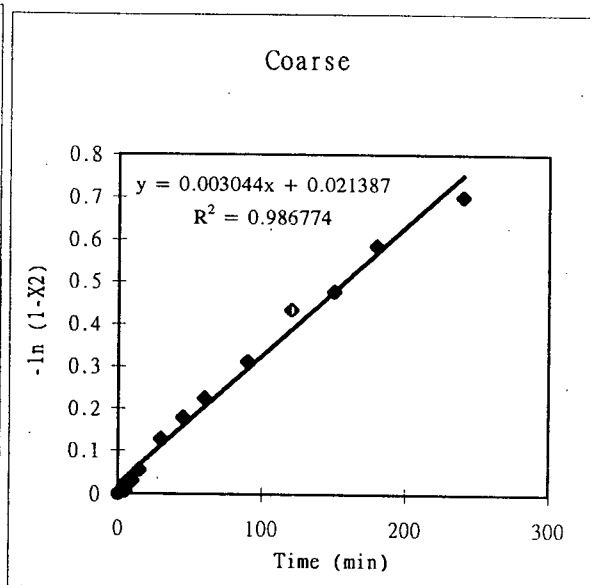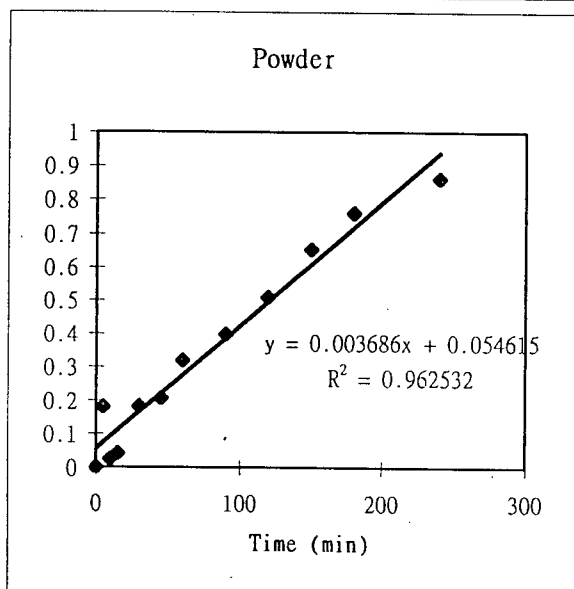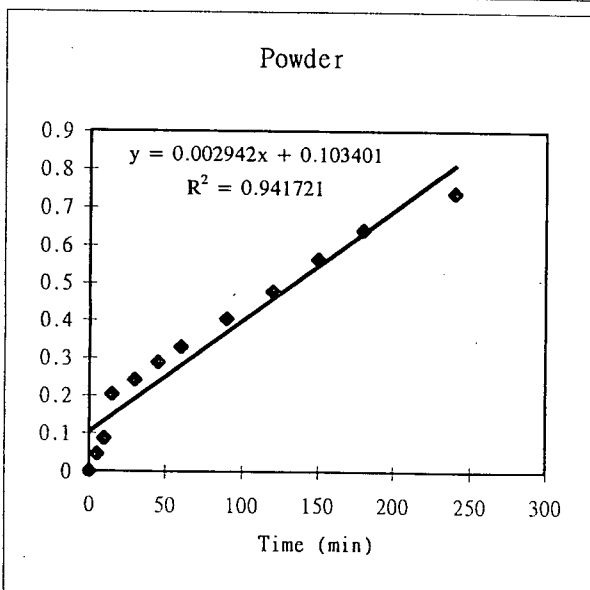
Leachate-Ammonia of the first 4 hours   **Leachate- Potassium**

Pebble

$$y = 0.001336x - 0.016185$$
$$R^2 = 0.981253$$

-ln(1-X2)

Time (min)

Pebble

$$y = 0.001515x - 0.014053$$
$$R^2 = 0.988681$$

Time (min)

Coarse

$$y = 0.001166x - 0.003753$$
$$R^2 = 0.977436$$

-ln(1-X2)

Time (min)

Coarse

$$y = 0.001362x - 0.01424 0$$
$$R^2 = 0.991427$$

Time (min)

Powder

$$y = 0.001261x - 0.010172$$
$$R^2 = 0.994755$$

-ln(1-X2)

Time(min)

Powder

$$y = 0.001599x - 0.004415$$
$$R^2 = 0.976297$$

Time(min)