UNIVERSITY OF NAIROBI

Department of Civil Engineering

AMMONIA REMOVAL BY USE OF NATURAL KENYAN ZEOLITE
(Hydrated Ferrous Sodium Potassium Aluminosilicate)

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Reg. No: F/56/8172/99

Supervisor: Prof. B. N. K. Njoroge.

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A thesis submitted in partial fulfilment for the award of
Master of Science in Civil Engineering.

Declaration

This thesis is my original work and has not been submitted for a degree in any other university.

S. G. Mwamachi____________________Date 4/11/2003
Candidate.

This thesis has been submitted for examination with my approval as University supervisor.

Prof. B.N. K Njoroge____________________Date November, 4, 2003

DEDICATION

To every person who wishes to contribute to the knowledge of Science, or Knowledge generally; never at any moment in your life feel that you are too old to read...the time and effort sets you apart from the majority and opens the door to the esoteric club of the very elite.

Acknowledgements

In accomplishing a work of this nature one must feel greatly indebted to a number of people without whose invaluable contributions this work would not have been possible.

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Thank you all for your great help!

Abstract.

A series of batch experiments were conducted to ascertain the ability of a natural Kenyan zeolite (a crystalline aluminosilicate) to remove ammonia from synthetic wastewater samples composed of Ammonium hydroxide (NH_4OH). Estimated ammonia uptake was favoured by low sorbate concentration, small particle size of sorbent, high temperature and an alkaline medium. The sorption kinetics studies strongly indicated that the sorption process was largely governed by intraparticle pore diffusion. The equilibrium data fitted the Langmuir sorption model showing the formation of monolayer coverage of ammonium ions on the particle's surface. The Langmuir correlation of the equilibrium data suggested that ion exchange might have been the dominant sorption mechanism. The average ammonia ion (NH_4^+) sorption capacity was observed to be about 0.7 mg/g of zeolite.

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1.0 INTRODUCTION.

1.1 General.

Ammonia nitrogen removal from waste-water is still a major concern in controlling pollution **[Hendricks and Bosman, 1980; Reed, 1983; Panzer, 1984]**. The problem with ammonia in wastewater is related primarily to the oxygen demand that can be exerted if it is discharged to the environment **[Metcalf and Eddy,Inc, 1979]**; in streams and lakes ammonia can cause serious depletion of the dissolved oxygen content as it is oxidized to nitrate. Ammonia is toxic to fish especially at high pH values, 20mg/l (as N) being lethal. A river is unlikely to recover as a fishery resource if the level remains above 5mg/l **[Walters and Wint, 1981]**. Ammonia in the ground water can be converted to nitrate and might have negative effects when used for human consumption **[Pal, 1983; Lemley *et al.*, 1985]**. Ammonia proliferates eutrophication processes, mainly in open water bodies and hinders efficient chlorination in drinking water.

Ammonia nitrogen can be removed from wastewater in five ways: (1) Nitrification and denitrification; (2) Ammonia stripping; (3) Ion exchange; (4) Break point chlorination followed by treatment on activated carbon and (5) Algae ponds.

Biological nitrification and denitrification and algae ponds are considered less suitable for low temperature regions. Also, nitrification and denitrification are biological methods and therefore not applicable for municipal wastewater containing toxic substances. This process seems difficult to control and automize, and furthermore takes up a great deal of space. However, the cost of the process is rather moderate and new developments have shown that it is not even necessary to add methanol to the denitrification step. Due to the control and the sensitivity to the variations, it seems most useful to apply the process on larger sewage plants **[Jørgensen, *et al.*, 1976]**. The removal of ammonia nitrogen by stripping and break-point chlorination is implemented to a limited scale due to extensive work and expenses involved **[Morris and Isaac, 1983]**.

The ion exchange process, using the ammoniun selective ion exchanger Clinoptilolite, is slightly more expensive than nitrification and denitrification, and has the disadvantage that an elution liquid, which must be discharged is produced **[Jørgensen *et al.*, 1976]**. The cost of chemical regeneration of Clinoptilolite remains high and represents more than 50 to 60% of the total process costs even with regenerant reuse **[Koon *et al.*, 1971]**. In an effort to find a more economical means of regenerating Clinoptilolite, the possibility of using nitrifying bacteria to assist in the regeneration process has been investigated **[Semmens *et al.*, 1971]**. Early studies indicated that when ammonium-saturated Clinoptilolite was exposed to nitrifying bacteria in salt solutions, ammonia was displaced into solution by ion exchange and then the liberated ammonia was available for oxidation to nitrate by the nitrifying bacteria.

The capacity of geological materials to attenuate potential pollutants has been studied by many researchers in the past four decades. A potential application of such research is the design and evaluation of compacted soil or clay liners for attenuation of chemical constituents of leachates from waste management facilities, such as landfills and surface impoundments. In this research, the use of a natural zeolite as a sorbent for the removal of ammonia in wastewater will be investigated using batch sorption studies.

The zeolite, identified as an aluminosilicate of iron, sodium and potassium, is a naturally occuring material mined in quarries in Murang'a District of Kenya. The zeolite stone is creamish-white in colour, relatively soft (you can cut it with a machette), has a density greater than that of water and, like all zeolites, a porous structure. In terms of chemical composition or mineral content, it is very rich in Iron, Fe^{2+}, Sodium, Na^{+} and potassium, K^{+}. It is expected that some of these ions are present as counterions and that the same mechanisms that render Clinoptiloite a good ion exchange resin for ammonia will abound in in this zeolite. Also, because of its porous nature and high surface area, some of the ammoniun ion removal is expected to be through the process of adsorption.

1.2 Research Objectives.

The following are the objectives of this study:-

- To explore the potential of a naturally occurring Kenyan zeolite to remove ammonia from synthetic wastewater.
- To compare the ammonia removal capacity obtained in this study with that from similar other researches so as to assess the viability of this material to remove ammonia.
- To determine the nature of the sorption process involved.

2.0 LITERATURE REVIEW

2.1 Overview.

The literature comprising this section of this report has been carefully selected for a number of reasons. First, before discussing how ammonia (a form of Nitrogen) can be removed from wastewater, it was thought important to discuss the sources and the various forms of nitrogen, and how they exist and interrelate to each other in nature. This information is presented in the form of the Nitrogen Cycle, Fig. 2-1.

The various methods of ammonia removal have been discussed to some detail, along with their advantages and disadvantages and cost implications. This is to give a fair comparison between the various methods and to lend perspective to this study which is an attempt to find a cheaper way of treating wastewater containing toxic ammonia.

The theories of Adsorption and Ion Exchange have also been presented to some fairly good detail. This is because adsorption and ion exchange are some of the major properties of zeolites, a group of aluminosilicates to which the material under investigation belongs. The main forces and mechanisms behind these phenomena have been outlined, together with some of the reactions that take place and the sorption equilibrium models that they follow.

Zeolites, as a class of natural and synthetic minerals have been introduced. This is to give an insight into the nature of the material under study and to enable to predict or postulate how it might behave in the presence of an aqueous solution containing ammonium (NH_4^+) ions.

Finally, the research is introduced and its aim outlined. As the last item in this section, this is intended to give some measure of continuity with the proceeding sections that deal with research methodology; results and discussion and; conclusions and recommendations.

2.2 How Nitrogen Exists in Wastewater.

Before discussing ammonia removal processes in detail, it will be helpful to review the forms in which nitrogen can exist in the environment, the principal sources of nitrogen in wastewater, and the various means that have been used or proposed for the removal of nitrogen in its alternative forms.

2.2.1 Forms of Nitrogen.

Nitrogen in wastewater can exist in four forms: organic nitrogen, ammonia nitrogen, nitrite nitrogen, and nitrate nitrogen **[Metcalf and Eddy, Inc., 1979].** Organic nitrogen and ammonia nitrogen are the principal forms in untreated wastewater. In nature, in the nitrogen cycle (see fig 2-1), organic nitrogen and ammonia nitrogen are converted first to nitrite and then to nitrate. The overall reaction starting with ammonia is:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$

For this reaction to go to completion, 4.57g of oxygen are required per g of ammonia nitrogen. This oxygen demand is often identified as the nitrogenous oxygen demand (NOD). The reaction also requires alkalinity to go to completion. It should be noted that 7.1g of alkalinity (as $CaCO_3$) will be required per gram of ammonia nitrogen **[Metcalf and Eddy, Inc., 1979]**.

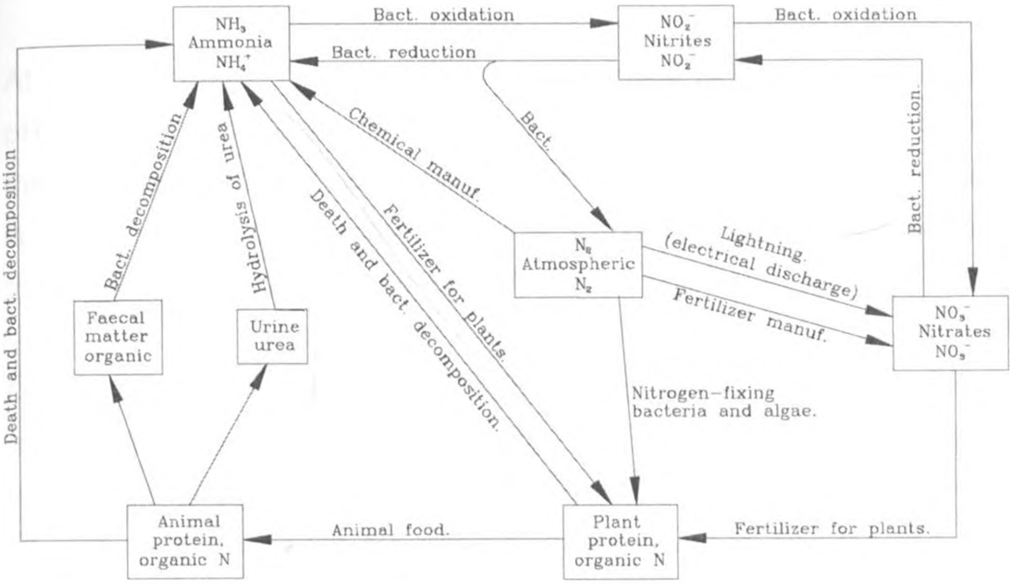

Fig 2-1 Nitrogen cycle

The various forms of nitrogen that are present in nature and the pathways by which the forms are changed are depicted in the Figure 2-1. The nitrogen present in fresh wastewater is primarily combined in proteinacious matter and urea. Decomposition by bacteria readily changes the form to ammonia. The age of wastewater is indicated by the relative amount of ammonia that is present. In an aerobic environment, bacteria can oxidize the ammonia nitrogen to nitrites and nitrates. The predominance of nitrate nitrogen in wastewater indicates that the waste has been stabilized with respect to oxygen demand. Nitrates, however, can be used by algae and other aquatic plants to form plant protein which, in turn, can be used by animals to form animal protein. Death and decomposition of the plant and animal protein by bacteria again yields ammonia. Thus, if nitrogen in the form of nitrates can be reused to make protein by algae and other plants, it may be necessary to remove or reduce the nitrogen that is present to these levels.

Ammonia nitrogen exists in aqueous solution as either the ammonium ion or ammonia, depending on the pH of the solution, in accordance with the following equilibrium equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

At pH levels above 7, the equilibrium is displaced to the left; at levels below pH 7, the ammonium ion is predominant. Ammonia is determined by raising the pH, distilling off the ammonia with the steam produced when the sample is boiled, and condensing the steam that absorbs the gaseous ammonia. The measurement is made colourimetrically.

Organic nitrogen is determined by the Kjeldahl method. The aqueous sample is first boiled to drive off the ammonia, and then it is digested. During the digestion the organic nitrogen is converted to ammonia. Total kjeldahl nitrogen is determined in the same manner as organic nitrogen, except that the ammonia is not driven off before the digestion step. Kjeldahl nitrogen is therefore the total of the organic and ammonia nitrogen **[Metcalf and Eddy, Inc., 1979].**

Nitrite nitrogen (NO_2^--N) is relatively unimportant in wastewater or water-pollution studies because it is unstable and is easily oxidised to the nitrate form. Nitrate nitrogen (NO_3^--N) is the mostly highly oxidised form of nitrogen found in wastewaters. The nitrate concentration is also usually determined by colourimetric methods **[Metcalf and Eddy, Inc., 1979].**

2.2.2 Sources of Nitrogen.

Nitrogen enters the aquatic environment from both natural and manmade sources. Natural sources include precipitation, dustfall, nonurbarn runoff, and biological fixation. As a result of the activities of human beings, the quantities of nitrogen contained in precipitation, dustfall, and nonurban runoff have all increased. Other sources deriving from human activities include runoff from urban areas, municipal wastewaters, drainage from agricultural lands and feedlots, industrial wastes, and septic tank leachate. The total nitrogen concentration in untreated wastewater varies from 20 to 85mg/l. Of this total, about 40 percent is organic nitrogen and 60 percent is ammonia nitrogen

[Metcalf and Eddy, Inc., 1979]. The forms of nitrogen in treated wastewater depend on both the type and the degree of treatment **[U. S. EPA, 1975]**.

2.3 Methods of Ammonia Removal from Wastewater.

Ammonia nitrogen can be removed from wastewater in five ways: (1) Nitrification and denitrification; (2) Ammonia stripping; (3) Break point chlorination followed by treatment on activated carbon; (4) Algae ponds and aquatic plants and, (5) Ion exchange. These methods are discussed briefly in the sections that follow.

2.3.1 Nitrification – Denitrification.

The nitrification-denitrification process is probably the best method of ammonia removal for the following reasons: (1) high potential removal efficiency, (2) high process stability and reliability, (3) easy process control, (4) low land-area requirements, and (5) moderate cost **[Metcalf and Eddy, Inc., 1979]**. The removal of ammonia with this process is carried out in two steps. In the first step the ammonia is aerobically converted to the nitrate NO_3^- form (nitrification). In the second step, the nitrates are converted to nitrogen gas (denitrification).

Nitrification is the biological oxidation of ammonia to nitrate with nitrite formation as an intermediate step. The microorganisms involved are the autotrophic species *Nitrosomonas* and *Nitrobacter* which carry out the reaction in two steps:

$$2NH_4^+ + 3O_2 \xrightarrow{Nitrosomonas} 2NO_2^- + 4H^+ + 2H_2O$$

$$2NO_2^- + O_2 \xrightarrow{Nitrobacter} 2NO_3^-$$

The above two equations can be combined and with simplification, to yield the following overall energy reaction:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + 2H_2O$$

Nitrifying organisms are present in almost all aerobic biological treatment processes, but usually their numbers are limited. Nitrification can be accomplished in most of the suspended growth activated sludge processes. All that is required is the maintenance of conditions suitable for growth of nitrifying organisms.

Denitrification is the conversion of nitrates by microorganisms to nitrogen. Usually a carbon source is required for this process to go to completion. In cases where a carbon source is not available in the wastewater, methanol has been used as a carbon source. Various industrial effluents can also be used as a carbon source. Denitrification uses Biochemical Oxygen Demand (BOD) as a carbon source for synthesis and energy and nitrate as an oxygen source.

$$NO_3^- + BOD \longrightarrow N_2 + CO_2 + H_2O + OH^- + \text{new cells.}$$

Since biological denitrification generates one hydroxyl ion while nitrification generates two hydrogen ions, it may be advantageous to couple the nitrification and denitrification processes to provide “internal” buffering capacity **[Eckenfelder Jr, 2000].**

Because of the high cost of most organic carbon sources, a number of processes have been developed or are currently under development in which the carbon oxidation nitrification-denitrification processes are combined into a single process without any intermediate steps. These processes appear to hold promise as an effective means for nitrogen removal. Specific advantages include: (1) reduction in the volume of air needed to achieve nitrification and BOD_5 removal; (2) potential elimination of the supplemental organic carbon sources (e.g. methanol) required for complete denitrification, and (3) elimination of the intermediate clarifiers required in a staged nitrification-denitrification system **[Metcalf and Eddy, Inc., 1979]**.

In the combined processes, either the endogenous decay of the organisms or the carbon in the wastewater is used to achieve denitrification. The procedure that has been used to achieve denitrification by using the carbon in the wastewater involves a series of alternating aerobic and anoxic stages without intermediate settling. This can be accomplished, for example, in oxidation ditches by controlling the rotor oxygenation levels, or in alternating contact process in which two separate tanks are used.

The nitrification-denitrification process suffers the disadvantages that nitrification is frequently inhibited, or in some cases prevented by the presence of toxic organic or inorganic compounds in wastewater. Too, large volumes of air are required to achieve complete nitrification of the wastewater and sometimes an external source of carbon may be required to achieve denitrification. The process is also very sensitive to variations and needs constant monitoring and control.

2.3.2 Ammonia Stripping.

The air stripping of ammonia from wastewater is a modification of the aeration process used for the removal of gases dissolved in water. Ammonium ions in wastewater exist in equilibrium with ammonia as shown in the equation below:

$$\mathbf{NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-}$$

As the pH of the wastewater is increased above 7, the equilibrium is shifted to the left; and the ammonium ion is converted to ammonia, which may be removed as a gas by agitating the wastewater in the presence of air. This is usually accomplished in a packed tray tower equipped with an air blower.

In the application of the ammonia stripping process, a number of problems have been encountererd. When lime, $Ca(OH)_2$, is used to raise the pH, calcium carbonate scaling forms within the tower and feed lines. The amount and nature (soft to extremely hard) of the calcium carbonate scale formed varies with the characteristics of the wastewater and local environmental conditions. The process is also adversely affected by temperature, performing very poorly in low temperatures. As the temperature decreases, the amount of air required increases significantly for the same degree of removal. In addition to these operational problems, the discharge of ammonia to the atmosphere near large bodies of water or snow-covered areas can create serious nitrogen pollution problems.

2.3.3 Break point Chlorination.

Chlorine reacts with water to form hypochlorous acid, HOCl, which is a powerful oxidizing agent and ionizes in water to form the hypochlorite ion (OCl^-). Hypochlorus acid readily reacts with ammonia to form a series of chloroamines (monochloroamine, dichloroamine and trichloroamine in that order) in stepwise successive reactions. With continued addition of chlorine, most of the chloroamines are oxidized to nitrogen at the breakpoint. The following representative equation can be used to describe the overall reaction with ammonia at breakpoint.

$$\mathbf{2NH_3 + 3HOCl \longrightarrow N_2 + 3H_2O + 3HCl}$$

From the above equation, the stoichiometric mass ratio of chlorine as Cl_2 to ammonia as N is found to be 7.6 : 1. In practice, the ratio has been found to vary from about 8 : 1 to 10 : 1. From both laboratory and full-scale testing programs, it has been found out that the optimum pH operating range for breakpoint chlorination is between 6 and 7. If breakpoint chlorination is accomplished outside this range, it has been observed that the chlorine dosage required to reach breakpoint increases significantly and that the rate of reaction is slower **[Metcalf and Eddy, Inc., 1979].** Unlike the air stripping of ammonia, temperature does not appear to have a major effect on this process in the ranges normally encountered in wastewater treatment.

The breakpoint chlorination process can be applied for the removal of ammonia nitrogen from treatment plant effluents either alone or in conjuction with other processes. Usually, to avoid the large chlorine dosages required when used alone, it is used in conjuction with other processes, such as selective ion exchange or multimedium filtration. For optimum performance and to minimize plant costs, flow equalization is usually necessary. The process has the disadvantage that the effluent has to be dechlorinated to avoid discharging toxic chlorinated compounds to the atmosphere. This is usually accomplished by use of activated carbon columns.

2.3.4 Algae Ponds and Aquatic Plants.

In recent years a great deal of attention has been focused on wastewater treatment and recycling via aquaculture and wetland methods as a means for reducing treatment expenses **[Bastian and Reed, 1979; O'Brien, 1981; Edwards, 1985; Kawasaki *et al.*, 1982; Brix, 1986, Gersberg *et al.*, 1986].** Earlier methods of wastewater treatment include a few aquatic plants: (a) microscopic algae and other unicellular organisms which grow in many variations of oxidation ponds; (b) water hyacinths are grown mainly in large water bodies and are capable of removing high levels of BOD_5, small concentrations of suspended solids (SS), nitrogen, and significant removal of refractory trace elements; (c) Thai Pak Bung plants *(Ipomoea aquatica)* **[Hashimoto, 1984]** and (d) duckweed are grown on mainly stagnant and relatively small water bodies **[Hauser, 1984; Oron *et al.*, 1986].**

The use of aquatic plants is a constructive approach for ammonia removal from wastewater bodies. Instead of releasing the nitrogen (generally to the atmosphere), it is trapped by the aquatic plants to produce protein rich biomass. The direct conversion of ammonia into plant protein in aquatic plants is a relatively high level efficient route compared to other alternatives. Due to ammonia preference uptake, the process of plant protein is shortened; in lieu of assimilation and reduction phases via nitrate, protein is produced in the plant directly from ammonia **[Oron *et al*, 1988]**.

Utilizing floating plants appears to be highly competitive with existing secondary treatment methods and may significantly reduce the overall treatment expenses. Re-use of the renovated effluent for irrigation can have a significant impact in dry areas **[DeBoer, 1983; Crook, 1985]**. The byproducts of an aquaculture and waste treatment process can be used for energy generation **[Wolverton and McDonald, 1981]** and alternative animal food sources with a relatively high nutrition value, **[Shelef *et al*., 1978; Gaigher *et al*; Hashimoto, 1984]**.

2.3.5 Ion Exchange.

Ammonia nitrogen can be removed by ion-exchange. Ion exchange is a unit process by which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. The treatment of a wastewater by ion exchange involves a sequence of operating steps In a continuous process, the exchange material is placed in a bed or packed column, and the water to be treated is passed through it until the available sites are filled and the contaminant appears in the effluent. This process is defined as the breakthrough **[Eckenfelder Jr, 2000]**. At this point treatment is stopped and the bed is backwashed to remove dirt and to regenerate the resin. After regeneration, the bed is rinsed with water to wash out the residual regenerant. The bed is then ready for another treatment cycle.

Although both natural and synthetic ion exchange resins are available, synthetic resins are used more widely because of their durability. Nevertheless, some natural resins (zeolites) have found application in the removal of ammonia from wastewater. Of the natural zeolites that have been investigated Hector Clinoptilolite has proved to be one of the most effective **[Applebaum, 1968].** One of the novel features of this resin is the regeneration system employed. Upon exhaustion, the zeolite is regenerated with lime $Ca(OH)_2$. The ammonium ion removed from the zeolite is converted to ammonia because of the high pH. At this point, the regenerating solution is passed through a stripping tower for removal of the ammonia. The stripped liquid is collected in a tank for subsequent reuse. The advantage with this system is that there is no process waste containing ammonia for which ultimate disposal must be provided.

A pressing problem that must be solved is the formation of calcium carbonate precipitates within the zeolite exchange bed and in the stripping tower and piping appurtenances. Another serious problem associated with application of ion exchange to the treatment of wastewater effluents is resin binding caused by the residual organic matter found in effluent from biological treatment. This problem has been solved partially by prefiltering the wastewater or by using scavenger exchange resins before application to the exchange column **[Mercer *et al*, 1969].**

To make ion exchange economical for advanced wastewater treatment, it would be desirable to use regenerants and restorants that would remove both the inorganic anions and the organic material from the spent resin. Chemical and physical restorants found to be successful in removal of organic material from resins include sodium hydroxide, hydrochloric acid, methanol, and bentonite.

2.3.6 How Ammonia Wastewater is treated in Kenya.

Currently, there is no specialised treatment for ammonia wastewater in Kenya. Ammonia wastewater is treated in much the same way as domestic wastewater, often in municipal wastewater treatment plants. The major methods of ammonia removal and their limitations have already been discussed in the foregoing sections. From these sections it emerges there is need for alternative and cheaper treatment methods, hence the current study.

2.4 Theory Of Adsorption.

The process in which chemicals become associated with solid phases is generally referred to as sorption. This phase transfer process may involve interacting either vapour molecules or dissolved molecules with adjacent solid phases **[Schwarzenbach, R. P., 1993].**

A solid surface in contact with a solution tends to accumulate a surface layer of solute molecules because of the unbalance of surface forces. The solute molecules are called the sorbate and the solid is called the sorbent. If the bonds that form between the sorbate and the sorbent are very strong, the process is almost always irreversible, and chemical *ad*sorption or chemisorption is said to have occurred. On the other hand, if the bonds that are formed are very weak, as is characteristic of van der Waals forces, physical *ad*sorption is said to have occurred **[Metcalf and Eddy, Inc., 1979]**.

2.4.1 Adsorption Forces and Mechanisms.

Adsorption from solution at the solid-liquid interface is a complex and imperfectly understood phenomenon. Before any adsorption studies are discussed, it is imperative to have an understanding of the physiochemical forces and mechanisms thought to be responsible for the adsorption of ions and molecules.These physiochemical forces can be broken into eight categories as listed below **[Reinbold et al., 1979 ; Griffin and Roy, 1985].**

2.4.1.1 London-van der Waals.

These are attractive forces arising from momentary dipoles about atoms or molecules caused by small perturbations of electronic motions. These dipoles induce small dipoles in neighbouring atoms of opposite sign. Although the momentary dipoles and the induced dipoles are constantly changing position and sign, the net result is a weak attraction (4 to 8 kJ/mol for small molecules and atoms). These forces are important in adsorption of organics and are generally attributed to the non-ideal behaviour in gases. They also have been partially treated by quantum mechanical perturbation theory, which uses polarizabilities, ionization potentials, and the magnetic susceptibilities of the interacting atoms to explain various phenomena such as adsorption.

2.4.1.2 Coloumbic-electrostatic-chemical.

An electrostatic force results from a charged surface due to isormorphous substitution in the mineral lattice (permanent charge) or protonation of surface oxygen and OH groups (pH-dependent charge) and an oppositely charged species, which maintains the electroneutrality of the surface. In layer silicates, substitution of octahedrally or tetrahedrally coordinated cations by cations of lower valence results in a net negative charge. This excess charge can bring about the the formation of a diffuse layer of positively charged atoms or molecules about the colloid; the density of this layer is greater at the surface, and then decreases exponentially to the level of the bulk solution. This type of reaction is important in adsorption of organic ions and ionized organic molecules.

2.4.1.3 Hydrogen Bonding.

A hydrogen atom is bonded to two or more other atoms; the "bond" is generally concieved as an induced dipole phenemenon. No universal agreement has been reached on the best description of the hydrogen bond **[Huheey, 1978]**, but it may be considered as the assymetric electronic distribution of the 1s electron of the hydrogen atom by very electronegative atoms (e.g, F,O,S,Cl). Hydrogen bonding is probably more than simply an exaggerated dipole-dipole or ion-dipole interaction, since these concepts do not account for molecular geometry in some cases **[Huheey, 1978; Cotton and Wilkinson, 1980]**. In reality, hydrogen bonds may be delocalized covalent bonds, i.e, resonance bonds or multiple-center bonds **[Huheey, 1978]**. The energy of this attraction ranges from 8 to 42 kJ/mol.

2.4.1.4 Ligand exchange-anion penetration-coordination.

Many atoms or molecules form coordinated complexes with ligands that range in complexity from simple linear molecules to extensive chelate complexes. These complexes may in turn be bonded to surfaces by hydrogen bonding or by polyvalent cation bridges linking the complex to a charged surface. The possible geometrical arrangements of coordinated complexes bonded to mineral faces are diverse. The bonded coordinated complexes may be displaced by other coordinated complexes that better satisfy electroneutrality requirements (i.e, are stronger complexing agents while being constrained by steric limitations. The energy of ligand exchange reactions with inorganic ions ranges from 8 to 60 kJ/mol.

2.4.1.5 Chemisorption.

In this adsorption process an actual chemical bond, usually covalent, is formed between the molecule and surface atoms. A molecule undergoing chemisorption may lose its identity as the atoms are rearranged forming new compounds at the demand of the unsatisfied valences of the surface atoms. The enthalpy of chemisorption ($\sim\Delta H > 29$ kJ/mol) is much greater than physical adsorption. The basis of much catalytic activity at surfaces is chemisorption, which may organize molecules into forms that readily undergo reactions. Chemisorption and physical adsorption are often difficult to distinguish from one another because a chemisorbed layer may have a physically adsorbed layer upon it. Moreover, some ligand exchange reactions are chemisorption processes.

2.4.1.6 Dipole-dipole or orientation energy.

This interaction results from the attraction of a permanent dipole for another permanent dipole. The resulting energy of attraction is less than 8 kJ/mol.

2.4.1.7 Induction or dipole-induced dipole.

This type of interaction results from the attraction of an induced dipole brought about by either (1) a permanent dipole or (2) a charged site or species. The energy of attracion is less than 8 kJ/mol, but this force often adds to coloumbic interactions.

2.4.1.8 Hydrophobic effect.

The exact nature of this adsorption mechanism is uncertain. Some investigators believe that hydrophobic adsorption is primarily an entropically driven mechanism brought about by the destruction of the physical cavity occupied by the solute in the solvent, and from the partial loss of structured water molecules about the solute, ordered by van der Waals forces **[Hovath et al., 1976; Sinanoglu and Abdulnur, 1965]**. Other researchers feel that the hydrophobic effect is the result of simple partitioning. Non polar organic solutes tend to migrate from the aqueuos phase to hydrophobic surfaces on the adsorbent **[Dzombak and Luthy, 1984; Chiou et al., 1983; Griffin and Roy, 1985].**

2.4.2 Sorption Isotherms.

When assessing the equilibrium proportion of a particular chemical's presence in association with solids for any particular volume of an aquatic environment, one must consider how the total sorbate concentration associated with the sorbent, q_e (mol.kg^{-1}), depends on the total chemical concentration in the solution, C_e (mol.L^{-1}). Such a relationship is commonly referred to as a sorption isotherm. The term isotherm is used to indicate that one is considering sorption at a constant temperature. Depending on the dominating mechanism(s), sorption isotherms may exhibit different shapes. Experimentally determined isotherms can commonly be fit with a relationship of the form

$$q_e = KC_e^n$$

This equation is known as the **Freundlich isotherm**; K is referred to as the Freundlich constant; and n is a measure of the non-linearity involved.

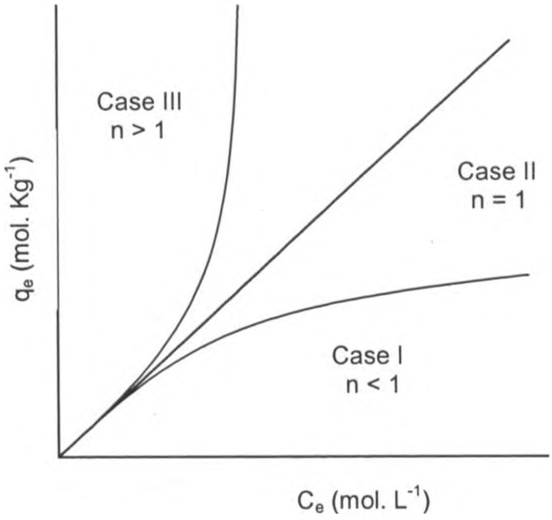

Fig. 2-2. Three types of observed relationships between concentrations of a chemical in sorbed state, q_e, and the dissolved state, C_e.

From the above equation, three types of curves can be drawn. Case I in Fig.2-2 (n < 1) reflects the situation in which at higher and higher sorbate concentrations, it becomes more and more difficult to sorb additional molecules due to saturation of the adsorbing surface or active sites. Case II (n = 1) reflects those situations in which the attractiveness of the solid for the sorbate remains the same for all levels of C_e. This is the so-called **linear isotherm** case. Case III (n > 1) describes a contrasting situation in which previously sorbed molecules lead to a modification of the surface which favours further sorption. Such effects have been seen for surface active compounds like alkyl benzene sulphonates, where the sorbent becomes coated with the sorbate and increasingly exhibits a non polar nature.

The Freundlich isotherm described in the preceding paragraphs is more usually expressed in the form

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

where,

q_e = mass of sorbate sorbed per gram of sorbent

C_e = concentration remaining in solution

and *k* and *n* are constants depending on temperature, the adsorbent, and the substance to be adsorbed.

Another isotherm commonly used to describe sorption phenomena is the **Langmuir isotherm**. This isotherm takes the form of Case I in Fig. 2-2 and can be viewed as a special case of the Freundlich isotherm. The Langamuir equation is based on an equilibrium between condensation and evaporation of adsorbed molecules, considering a monomolecular adsorption layer:

$$q_e = \frac{abC_e}{1 + aC_e}$$

This can be expressed in linear form as,

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{ab}\frac{1}{C_e}$$

where,

b = amount adsorbed to form a complete monolayer on the surface and *a* = constant which increases with increasing molecular size.

Since most wastewaters contain more than one substance which will be adsorbed, direct application of Langamuir equation is not possible. Morris and Weber have developed relationships from the Langamuir equation for competitive adsorption of two substances **[Morris and Weber, 1964]**:

$$q_{eA} = \frac{a_A b_A C_{eA}}{1 + a_A C_{eA} + a_B C_{eA}}$$

$$q_{eB} = \frac{a_B b_B C_{eB}}{1 + a_A C_{eA} + a_B C_{eB}}$$

More complex relationships could similarly be developed for multicomponent mixtures. It should be noted that although the equilibrium capacity for each individual substance adsorbed in a mixture is less than that of the substance alone, the combined adsorption is greater than that of the individuals alone. In industrial application of activated carbon, contact times of less than 1 h are usually used. Equilibrium is probably closely realized when high carbon dosages are employed, since the rate of adsorption increases with carbon dosage.

2.4.3 Influence of Molecular Structure and other Factors on Adsorbability

Most wastewaters are highly complex and vary widely in the adsorbabilty of the compounds present. Molecular structure, solubility, etc., all affect the adsorbability. These effects are shown in Table 2.1 and are based on adsorption on carbon **[Eckenfelder Jr, 2000].**

TABLE 2.1

Influence of molecular structure and other factors on adsorbability.

1. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

2. Branched chains are usually more adsorbable than straight chains. An increasing length of the chain decreases solubility.

3. Substituent groups affect adsorbability:

Hydroxyl	Generally reduces adsorbability. Extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule. Glyoxylic acid more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double bonds	Variable effects as with carbonyl.
Halogens	Variable effects.
Sulphonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

4. Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.

5. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

6. Unless the screening action of the sorbent pores intervenes, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

7. Molecules with low polarity are more sorbable than highly polar ones.

2.5 Theory of Ion Exchange.

Ion exchange refers to the process by which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. Ion exchange can be used for the removal of undesirable or recovery of useful anions and cations from a wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange also takes place in living materials because cell walls, cell membranes, and other physiological structures have charges.

An ion exchange resin is a natural or synthetic material with electrically charged sites at which one ion may replace another. Natural soils contain solids with charged sites that exchange ions, and certain minerals called **zeolites** have exhibited remarkable ion exchange properties. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds into a porous three-dimensional structure. The degree of cross-linking between organic chains determines the internal pore structure, with higher cross-link density giving smaller pore sizes. From a kinetic view point, a low degree of cross-linking would enhance diffusion of ions through larger pores. However, physical strength decreases and swelling in water increases as cross-link density is lowered. The functional ionic groups are usually introduced by reacting by reacting the polymeric matrix with a chemical compound containing the desired group. Exchange capacity is determined by the number of functional groups per unit mass of resin.

2.5.1 Types of Ion Exchange Resins.

Basically, there are two types of ion exchange resins: cationic and anionic. Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions. Cation exchange resins have acidic functional groups, such as sulphonic, whereas anion exchange resins contain basic functional groups, such as amine. Ion exchange resins are often classified by the nature of the functional group as strong-acid, weak-acid, strong-base, and weak-base. The strength of the acidic or basic character depends upon the degree of ionization of the functional groups, as with soluble acids or bases. Thus, a resin with sulphonic acid groups would act as a strong-acid cation exchange resin. The various types of ion exchange resins are listed below:

2.5.1.1 Strong-Acid Cation Resins.

Strong-acid resins are so named because their chemical behaviour is similar to that of a strong acid. The resins are highly ionized in both the acid ($R–SO_3H$) and salt ($R-SO_3Na$) form.

2.5.1.2 Weak-Acid Cation Resins.

In a weak–acid resin, the ionizable group is a carboxylic acid (-COOH) as opposed to the sulphonic acid group (SO_3H^-) used in strong acid resins. These resins behave like weak organic acids that are weakly dissociated.

2.5.1.3 Strong-Base Anion Resins.

Like strong-acid resins, strong base resins are highly ionized and can be used over entire pH range. These resins are used in the hydroxide (OH) form for water deionization.

2.5.1.4 Weak-Base Anion Resins.

Weak-base anion resins are like weak-acid resins, in that the degree of ionization is strongly influenced by pH.

2.5.1.5 Heavy-Metal Selective Chelating Resins.

Chelating resins behave like weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins tend to form stable complexes with the heavy metals. In fact the functional group used in these resins is an EDTA compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

2.5.2 Ion Exchange Reactions (Kinetics).

The ion exchange reactions that occur depend upon chemical equilibria situations in which one ion will selectively replace another on the ionized exchange site. Cation exchange on the sodium cycle can be illustrated by the following reaction:

$$Na_2.R + Ca^{2+} \rightleftarrows Ca.R + 2Na^+$$

where R represents the exchange resin. When all the exchange sites have been substantially replaced with calcium, the resin can be regenerated by passing a concentrated solution of sodium ions through the bed. This reverses the equilibrium and replaces the calcium sodium.

A 10 percent brine solution is usually used for regeneration:

$$2Na^+ + Ca.R \rightleftarrows Na_2.R + Ca^{2+}$$

Similar reactions occur for cation exchange on the hydrogen cycle:

$$Ca^{2+} + H_2.R \rightleftarrows Ca.R + 2H^+$$

Regeneration with 2 to 10 percent H_2SO_4 yields:

$$Ca.R + 2H^+ \rightleftarrows H_2.R + Ca^{2+}$$

Anion exchange similarly replaces anions with hydroxyl ions:

$$SO_4^{2-} + R.(OH)_2 \rightleftarrows R.SO_4 + 2OH^-$$

Regeneration with 5 to 10 percent sodium hydroxide will renew the exchange sites:

$$R.SO_4 + 2OH^- \rightleftarrows R.(OH)_2 + SO_4^{2-}$$

In addition to the factors of concentration, the nature of the exchanger, and the exchanging ions, such factors as temperature and particle size of the exchanger are also of considerable importance to the kinetics of ion exchange. The degree of ion exchange depends on several factors:

- The size and valence (charge) of the ions entering into the exchange.
- The concentration of ions in the water or solution.
- The nature (both physical and chemical) of the ion exchange substance.
- The temperature.

2.5.3 Ion Exchange Capacity.

The performance and economics of ion exchange are related to the capacity of the resin to exchange ions and to the quantity of regenerant required. The total capacity of the ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of milliequivalents per dry gram of resin or in terms of milliequivalents of wet resin. In some cases capacity has been expressed as kilograms of $CaCO_3$ per unit of bed volume or as mass of ions per unit volume of bed. In like manner,the quantity of ions to be removed from the wastewater is expressed as equivalents per liter of wastewater to be treated **[Eckenfelder Jr, 2000]**.

In a fixed-bed exchanger, there is a relationship between the operating capacity of the bed and the quantity of regenerant employed. Resin utilization is defined as the ratio of the quantity of ions removed during treatment to the total quantity of ions that could be removed at 100 percent efficiency. The regenerant efficiency is the quantity of ions removed from the resin compared to the quantity of ions present in the volume of regenerant used. The resin utilization will increase as the regenerant efficiency decreases **[Eckenfelder Jr, 2000]**.

2.6 The zeolites.

Zeolites are crystalline aluminosilicates with base-exchange and molecular sieve properties, having three-dimensional, microporous lattice framework structures of tetrahedral oxide units. They are also compounds isomorphous to crystalline aluminosilicates wherein the aluminium or silicon atoms in the framework are partly or wholly replaced by atoms of other elements, e.g. gallium, germanium, phosphorous or boron **[IPC 7, 2001]**

2.6.1 Historical Background.

The word 'zeolite' was first coined in 1756 by the Swedish mineralogist, Cronstedt, who discovered the mineral stilbite. Stilbite turned out to lose water when heated with a blowpipe flame, a process now known as intumescence **[Berkout,2001]**. He called this mineral a 'zeolite', from the Greek 'zeo', to boil, and 'lithos', stone, because many zeolites appear to boil when heated **[Berkout, 2001]**. Since then, zeolites have been recognised as a separate group of minerals, one of the most abundant on earth , and 48 separate species have been discovered so far **[Berkout, 2001]**. Synthesis of zeolites has been reported from 1862 on, although it wasn't until the 1940s, with the availability of x-ray diffraction techniques, that the synthesised products could be assigned completely. In 1956, the first fully characterised synthesis of a zeolite not occurring in nature was reported and many other have followed in its wake.

Over the past few decades, zeolites have found numerous applications in industry. Hundreds of thousands of tons of zeolites are used every year, as water softeners, in detergents, as catalysts, as adsorbents or desiccants, or even as soil conditioners, to control soil pH, moisture content and manure malodour. Zeolites research covers an even wider area, including catalytic and ion-exchange properties of zeolites, zeolite synthesis and the behaviour of molecules adsorbed on the zeolite surface to name but a few.

2.6.2 Zeolite formation, Synthesis and Nomenclature.

Natural zeolites are formed by the hydrothermal alteration of suitable precursors e.g. volcanic glass, clay minerals, vitric tuffs, or biogenic silica. The process is usually accomplished in the presence of water with a high pH. Zeolite formation occurs in nature over a wide range of circumstances. These include lakes, soils, the sea bed, in hot springs or deep underground. The final product depends on the prevailing ambient conditions e.g. of pressure and temperature.

Synthetic zeolites are crystallised from an inhomogeneous gel, consisting of water, a silica source, and an alumina source, at a high pH. The final product, i.e. its crystalline structure, its Si/Al ratio and its water content, is defined by the conditions applied. These include temperature, pressure, pH and reactant concentration, and range from relatively mild (ambient temperature and pressure) to harsh (high pressure, temperature upto 350°C).

The nomenclature of zeolites is rather haphazard. Natural zeolites such as sodalite, faujasite, and mordenite, were named by the mineralogists who first described them. Synthetic zeolites were given names by researchers who first synthesised them, but not with a uniform system. Some synthetic zeolites were named after their natural counterparts; others were given different names, even for structurally similar zeolites. To make matters worse, nomenclature has in some cases changed over the years. At the moment, some system has emerged, but there is no relation between zeolite names and structure.

Natural zeolites are called by their mineralogical names, sometimes abbreviated to three letters; e.g. Mor for Mordenite. Synthetic zeolites are denoted by one or more letters, sometimes followed by numbers. When zeolites are ion-exchanged, the new cation is usually put infront of the name: thus NaY denotes a zeolite Y with sodium counterions, CsMor is Mordenite exchanged with Caesium. Other cations can also be included in the name e.g. HZSM-5 for H^+ exchanged zeolite ZSM-5, MVX for zeolite X with the dye MV^{2+} or KNaA, to denote a partial ion-exchange.

2.6.3 The Molecular Structure of Zeolites.

Zeolites are a group of crystalline aluminosilicates, with group **I** or **II** elements as counter ions. They consist of a framework of $\mathbf{[SiO_4]^{4-}}$ and $\mathbf{[AlO_4]^{5-}}$

tetrahedra, linked to each other at the corners by sharing their oxygens. This leads to the following empirical formula for zeolites,

$$\mathbf{M_{x/n}O.Al_2O_3.xSiO_2.yH_2O}$$

or more precisely as,

$$\mathbf{M_{x/n}[(Al_xSi_y)_{2(x+y)}].pH_2O}$$

Where,

- M are monovalent (Na, K, Li) and / or bivalent (Ca, Mg, Ba, etc) cations;
- n is the charge of the cation;
- $1 < y/x < 6$;
- $1 < p/x < 4$.

The oxide tetrahedra make up three-dimensional network, with lots of voids and open spaces. It is these voids that define the many special properties of zeolites. The channel-like, 3-D crystal structure of zeolites provides a large internal surface area (between 500 and 1000m^2/g) for chemical exchange reactions and adsorption of various materials. Because the channels are all the same size and shape, they can be used as molecular sieves, as well as ion exchangers and adsorbents.

2.7 Zeolite Properties.

The properties of a zeolite are largely governed by the mineral content and the large internal network of voids, known as supercages or nanocages. Shapes and dimensions of these cages show a tremendous variety. But not only the supercages are important; size and shape of the apertures linking these voids play an important part in the determination of the zeolite properties, since the size of these windows determine what molecule can penetrate inside the zeolite. The main properties of zeolites include the following:-

- Water sorption / desorption;
- The Si/Al ratio;
- Ion Exchange;
- Adsorption;
- Molecular sieve effects, and
- Catalytic properties.

2.7.1 Water Sorption/Desorption.

One of the special zeolite properties is the ability to host other molecules within its framework. In untreated natural and synthetic zeolites, this is water: hence the H_2O in the formula. The water molecules in the zeolite channels are bonded by forces of dipole interactions from the cations forming their close surrounds. This water is lost relatively easily (the intumesence process mentioned earlier) often without any change in the 3-D structure of the zeolite; which has now room to host other molecules.

2.7.2 The Si/Al ratio.

The Si/Al ratio is the measure of the amount of Silicon in relation to that of Aluminium in the zeolite sample. The Si/Al ratio determines the zeolite framework which influences most, if not all of the zeolite properties. The Si/Al ratio varies (1:1 – 6:1 – N:1), but is never less than 1. The number of cations present in a zeolite is defined by the Si/Al ratio, because only an **$[AlO_4]^{5-}$** unit needs a charge balancing cation. **Al-O-Al** bonds are not formed because this would lead to a disadvantageously close proximity of negative charges: therefore, the Si/Al ratio must be 1 or greater. If it is closer to 1, the framework structure has a rather high net charge, there are many counterions present, and the zeolite is highly hydrophilic. On the other hand, a very high Si/Al ratio renders a strongly hydrophobic zeolite, with barely counterions at all. Obviously, this also means that a zeolite with a high Si/Al ratio has rather few ion exchange sites. The Si/Al ratio also determines the window sizes in the zeolite structure. The unit cell dimensions decrease upon increase of the Si/Al ratio, because the **Si-O** bond is shorter than the **Al-O** bond (1.62 Å and 1.75 Å, respectively), which leads to the smaller dimensions of the cages and sometimes to subtle differences in behaviour.

2.7.3 Ion Exchange.

The presence of the trivalent aluminium ions gives rise to a surplus of negative charge; hence the need for counter ions. The number of counter ions present in the unit cell thus depends on the Si/Al ratio. In natural zeolites, the most common counter ions are Na^+ and Ca^{2+}. These counter ions reside within the 3-D network. They are easily traded in for other ions by ion exchange. Through ion exchange, other metal ions can be introduced; this might influence the supercage size, thereby modifying the molecular sieving or catalytic properties of the zeolite, or promote intersystem crossing.

2.7.4 Adsorption.

Zeolites are able to adsorb other molecules because of the charge imbalance arising from the presence of the trivalent aluminium ions in their structures. Adsorption of molecules within the zeolite is influenced by the polarity, or electrical field strength within the zeolite. This depends on, among other things, the net charge on the framework (defined by the Si/Al ratio), the size and shape of the supercage, the presence of other adsorbed molecules, and the number and size of the counter ions.

2.7.5 Molecular Sieve effects.

Perhaps the most unique feature zeolites have is their ability to act as molecular sieves. Within the supercages, guest molecules can reside. The strictly defined, uniform shape and size of these cages make sure only molecules of a certain size or smaller can penetrate within the zeolite and adsorb there. This property allows for the very efficient use of zeolites in separation processes. Other materials, such as alumina, carbon, or porous glass, have molecular sieve properties as well, but none so versatile as zeolites have. The main reason for this is the poor pore size distribution in these other materials.

2.7.6 Catalytic Properties.

A catalyst is a substance that takes part in a chemical reaction but is left unchanged at the end of it. This is accomplished by formation intermediary surface complexes that greatly influence the activation energy, hence the reaction rate. Because of the high net charge on zeolite mineral surfaces, they are able to take part in catalytic reactions through the formation of intermediary surface complexes.

2.8 Research Introduction.

The limitations of the various methods of ammonia removal have already been discussed in the preceding sections. Ammonia removal by sorption processes (adsorption / ion exchange) seems preferable over the other methods since it is stable, suits automation and quality control, and is easy to maintain. Up to now, the most common sorbent used has been activated carbon, but economic considerations and availability of the material has prompted the search for other materials. A lot of research has been carried out in this regard and it has been found out that zeolites have a high affinity for ammonia. Of all zeolites tested, it is Clinoptilolite which has been put to industrial use **[Ciambeli et al, 1985; Torii, 1978].**

The aim of this research therefore, is to explore the potential of a cheap and locally available zeolite to remove ammonia from wastewater. The research is carried out through batch sorption studies.

3.0 MATERIALS AND RESEARCH METHODOLOGY.

3.1 Introduction.

Batch experiments were conducted to investigate the adsorption of ammonium ions (NH_4^+) on a natural Kenyan zeolite which was identified as Ferrous Sodium Potassium Aluminosilicate by chemical and x-ray diffraction techniques. Save for investigations into the effect of temperature, all experiments were conducted at room temperature (which was found to be fairly constant at 25±1°C). Kinetic and equilibrium studies were conducted and the effect of temperature and initial pH on these investigated. Various relationships between the various parameters involved were drawn and the results of these are discussed in chapter four (4). A full account of the materials used and the research methodology employed is discussed in the sections that follow.

3.2 Materials and Equipment.

3.2.1 The Sorbent.

The sorbent, mined from quarries in Murang'a in Kenya and locally known as "chokaa" (swahili for 'chalk') was bought at Gikomba market where it is sold in small lumps retailing at Kshs 2/= each. Though it may have other undocumented uses, its principal buyers are expectant mothers who chew it as a source of iron! The material is creamish white to whitish grey in colour, it has a specific gravity of between 2.2 and 2.4. Its suspension pH is 6.2, which shows it is weakly acidic.

The lumps, which are relatively soft, were crushed to smaller particles by manual means. The pulverised material was then placed in an oven at 103°C for 24 hrs to drive off moisture. It was then sieved into different particle size ranges. Each sieved fraction was washed thoroughly with ammonia-free distilled water to remove foreign impurities and the finer particles i.e. dust. The washed fractions of the material were then placed in an oven at 103°C for 12 hours, after which they were cooled in a desiccator to the room temperature. The fractions were then stored in separate airtight bottles, ready for use.

The chemical analysis of the zeolite sample is given in Table 4.1. The analysis was carried out at the Mines and Geological Department, Ministry of Environment and Natural Resources. The sample is rich in Na^+, K^+, and Fe^{++}, suggesting the chemical name Hydrated Ferrous Sodium Potassium Aluminosilicate.

3.2.2 The Sorbate.

The sorbate used was Ammonium Hydroxide solution. It was of analytical grade and bought at Manigate (K) Ltd. A stock solution of Ammonium Hydroxide (0.2N) was prepared by diluting 15ml of concentrated ammonia solution (25%, sp.gr 0.91, 13N) and diluting to one litre. Appropriate volumes of this were diluted to 1L to yield the required ammonium ion concentration. These are given below:

The original Ammonium Hydroxide solution (25%, sp.gr 0.91, 13N) contained 0.25 x 910 g = 227.5 g NH_3 per litre. Therefore 1 ml = 0.2275 g NH_3 = 0.2409 g NH_4^+. 15 ml of this solution = 3.4125 g NH_3 = 3.6132 g NH_4^+. This diluted to one litre makes a 0.2 N NH_3 solution, the stock solution used in this study. To obtain the desired ammonium ion concentration the stock solution was diluted thus: 1 ml = 3.4125 mg NH_3 = 3.6132 mg NH_4^+. Therefore, the volume of the stock solution to be diluted to one litre to achieve the desired NH_4^+ ion concentration is equal to that concentration divided by 3.6132. The results are entered in the table 3.1. The 5 to 60mg/l concentration range was chosen to cover that of ammonia in normal domestic wastewater.

Table 3.1: Volume of stock solution to be diluted to one litre to achieve the desired ammonium ion concentration.

Desired ammonium ion concentration (mg/l)	Volume of stock solution to be diluted one litre (ml).
5	1.384
10	2.768
15	4.151
20	5.535
25	6.919
30	8.303
35	9.687
40	11.070
45	12.454
50	13.838
55	15.222
60	16.606

3.2.3 Reagents and Equipment.

All the reagents used were of analytical grade. They were bought from Laborama and Manigate (K) Ltd, both situated on Kijabe street, Nairobi, Kenya. Ammonia-free distilled water was used for making synthetic water samples and for preparation of reagents. The ammonia-free distilled water was prepared according to Standard methods **[APHA-AWWA-WCPF, 1975]**. A full list of the reagents involved in the determination of ammonia nitrogen using the distillation-titrimetric technique of the Standard Methods **[APHA-AWWA-WCPF, 1975]** and appendix E of this report.

All glassware used was of Pyrex. Before each experiment, all glassware were cleaned with dilute nitric acid and repeatedly with ammonia-free distilled water followed by drying in an oven. An all Pyrex distillation apparatus was used to distil the ammonia off the synthetic water samples prior to the determination of the residual ammonium ion concentration.

3.3 Experimental Procedures.

3.3.1 Analytical Methods.

Standard methods **[APHA-AWWA-WCPF, 1975]** were adopted for the determination of the residual ammonium concentration and for the preparation of the various reagents involved. The ammonium ion concentration was determined by distillation and titrimetric technique. This is the preferred method as the ammonia concentrations involved were generally greater than 5 mg /l **[APHA-AWWA-WCPF, 1975]**. The ammonia in the distillate was collected in 50 ml of indicating boric acid solution and titrated with 0.02N H_2SO_4 titrant until the colour turned a pale lavender **[APHA-AWWA-WCPF, 1975]**. At least 400 ml of distillate were collected.

3.3.2 Kinetic Studies.

Conical flasks of 250 ml capacity were used in the kinetic experiments. Synthetic water samples (100 ml) of known ammonium ion (NH_4^+) concentration were introduced into the flasks. Carefully weighed amounts of the sorbent material were added to the flasks, which were then tightly stoppered and shaken at 100 r.p.m on an electric shaker for a prescribed length of time. After the required time, the samples were filtered and analysed for residual ammonium ion concentration by distillation followed by titration with standard sulphuric acid (0.02N) **[APHA-AWWA-WCPF, 1975]**.

The first step was to determine the optimal dose of the sorbent to be used in subsequent experiments. 100 ml solutions of 25 mg NH_4^+ l^{-1} were shaken with varying amounts of sorbent of particle size range 0.6 – 1.2 mm for prescribed lengths of time. It was noted that, the difference in the percentage removal of ammonium ions from solution between 5.0, 7.5, and 10.0 g of sorbent was less than 1.5%. Therefore, 5.0 g of sorbent per 100 ml of solution was adopted as the optimal mass of the sorbent. All subsequent experiments were carried out using this mass of sorbent.

Kinetic experiments were carried out to determine the equilibrium time and to investigate the nature and rate of the sorption process. The experiments were carried out for a duration of three hours. The adsorption times used were 15, 30, 60, 120, and 180 minutes. For adsorption dynamics, experiments were carried out for durations of 1, 3, 5, 7, 10, 13, 15, 20, 25, 30, 60, 120, and 180 minutes – using particle size range 0.3 – 0.6 mm and 100 ml samples of 25 mg NH_4^+ l^{-1} solution. The variables in the kinetic studies included particle size, pH, initial concentration and temperature. These results are found in appendix A and are discussed in Chapter Four (4).

3.3.3 Equilibrium Studies.

After the establishment of the optimal conditions, batch experiments were conducted for the development of adsorption isotherms. For all the four different particle size ranges, it was found out that equilibrium was established well before two hours had elapsed. This was used as the shaking time for all the equilibrium experiments. Experiments were carried out for ammonium ion concentrations of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 mg /l. In each case, 100 ml of sample was taken and shaken with 5.0 g of sorbent in tightly stoppered conical flasks of 250 ml capacity. For investigations into the effect of temperature and pH only particle size range 0.3 – 0.6 mm was used. The experiments into the effect of temperature were carried out in a fridge chamber with conical flasks having an electrical stirrer fitted into their stoppers and connected externally to a power source by means of wires. Equilibrium studies results are found in appendix B and are discussed in Chapter Four (4).

3.3.3 Blank and Control Experiments.

Control experiments were carried out with the sorbate (which was agitated in conical flasks for 1 hour) and carried out through the whole process of distillation and titration. Blank tests were carried out on ammonia-free distilled water and taken through the same process as the control tests.

Three types of control experiments were carried out: (1) the sorbate was agitated without the sorbent for a predetermined length of time and then taken through the whole process of distillation and titration to determine the residual ammonium ion concentration; (2) samples of the sorbate were distilled and titrated without any agitation; and (3) samples of ammonia-free distilled water were taken through the process of distillation and titration. In addition to the above, 100 ml samples of the sorbate were titrated directly with standard titrant (0.02 N H_2SO_4) in the presence of a few drops of the mixed indicator solution. These experiments were carried out using concentrations of 12.5 and 25 mg/l NH_4^+

3.4 Material Analysis at Mines and Geological Department.

The Mines and Geological Department of the Ministry of Environment and Natural Resources uses the X-ray Powder Diffraction method for mineral identification and an Atomic Absorption Spectrophotometer for the chemical analysis.

3.4.1 X-ray Powder Diffraction Method:

The X-ray powder diffraction method is based on Braggs law which states that, when a monochromatic x-ray beam with wavelength λ is incident on lattice planes in a crystal at an angle θ, diffraction only occurs when the distance *d* travelled by the rays reflected from successive planes differs by a complete number *n* of wavelengths. Braggs law can be summarised by the equation below:

$$n\lambda = 2d\sin\theta$$

The sample to be identified is first ground and made into a paste using acetone. The paste is then smeared onto a slide which is inserted into the x-ray diffraction machine. By varying the angle θ, the Bragg's law conditions are satisfied by different d spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a pattern which is characteristic of the sample. Where a mixture of different phase is present, the diffractogram is formed by addition of the individual patterns.

The widths of peaks in a particular phase pattern provides an indication of the average crystalline size. Large crystals give rise to large peaks, while the peak width increases as crystal size reduces.

3.4.2 Atomic Absorption Spectrophotometry.

This method determines the chemical composition of the sample. The sample is dried at room temperature, ground and sieved using Mesh No 100. A representative sample weighing 1g is then digested in a mixture of concentrated acids. The acids used are conc. Nitric acid, conc. Hydrochloric acid, conc. Hydrofluoric acid and Boric acid. When the digestion is complete the mixture is diluted to 50% using Boric acid. An atomic absorption spetrophotometer (Varian Techtron) is then used to determine the chemical composition of the sample.

4.0 RESULTS AND DISCUSSION.

4.1 Effect of the Sorbent Properties on the Sorption Process.

The chemical analysis of the zeolite sample is given in Table 4.1 below.

Table 4.1. Chemical analysis of the zeolite sorbent.

Constituent	% by weight.
SiO_2	57.47
Al_2O_3	12.30
CaO	0.74
MgO	0.42
Na_2O	3.10
K_2O	2.60
TiO_2	1.05
MnO	0.13
Fe_2O_3	7.70
LOI	5.8

The Si/Al ratio for the zeolite is 4.12 by mole ratio. This suggests that the zeolite has a fairly high net charge, there are many counterions present, and the zeolite is quite hydrophilic. The mineralogical content of the zeolite suggests that sorption of ammonium ions could be through a combined mechanism of ion exchange and adsorption on the particles surface. This is because the particles of Aluminosilicates present two surfaces to the external media **[Schwarzenbach, 1993]**. First, the edges of the particles of these minerals are somewhat like aluminium oxides in their behaviour and respond to pH changes like pure aluminium oxides e.g. Kaolinite **[Williams and Williams, 1978]**. On the other hand, the faces of these particles have a "siloxane" structure (—Si—O—Si—) which does not leave any free hydroxyl groups (—Si—OH) to participate in proton exchange reactions with the bulk solution. Instead, the faces exhibit a charge due to cation substitutions for the aluminium or silicon atoms within the internal structure. These "isormophic" substitutions often involve cations of lower total positive charge (e.g., Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}). The result is a fixed and permanent charge deficiency that looks like a negative surface charge to the surrounding solution. This negative charge deficiency is what is called the cation exchange capacity or (CEC), and is the major attractive force behind the presence of any counterions in the zeolite. Because of the charges arising from the proton-exchange reactions on hydroxyl groups on the edges of the aluminosilicate crystals, these minerals may exhibit both a CEC and an anionic exchange capacity (AEC) at the same time.

The sorption of ammonium ions on the zeolite is expected to show Langmuirian behaviour if at all the sorption process proceeds through the mechanisms postulated above. As the ammonium ions exchange with the counterions present in the zeolite, the amount sorbed asymptotically appproaches a constant value set by the total charge density (in this case, the cation exchange capacity of the mineral). This appears to be borne out by the plot of the sorption isotherms, Fig-4-10.

4.2 Control Experiments Results.

Control experiments were carried out to establish the suitability of the distillation–titration procedure and the efficiency of the quick-fit assemblage of distillation apparatus in the determination of the ammonia-nitrogen concentration. Also, whether there were any losses to the sorption process and where they occurred and; whether there were any extraneous sources of ammonia that interfered with the experimental results. The results are presented in appendix E.

These results demonstrate that the distillation–titration technique is an accurate method of ammonia nitrogen concentration determination especially for concentrations above 5 mg/l. Also, that the 400 ml volume of distillate collected was enough to capture all the ammonia in the sample.

There appears to be a little loss in the agitation process but it can also be attributed in part to some of the errors involved in the experimentation process. Possible errors include: the failure to locate the end-point accurately as this is a visual observation, for instance, one's observation of "pale lavender" (the end-point in this titration) may not be exactly the same for the next titration, or one might overshoot or underestimate the end-point by a few drops. Another source of error is in the reading of measurements off the measuring instruments like burettes, pipettes, measuring cylinders, etc. Given that the most sensitive had an accuracy of 0.1 ml, it is not possible to measure volumes of say 8.93 ml. There are also errors incurred as the sample is transferred from, say the measuring cylinder to the conical flask and then to the distillation flask – invariably there is some loss as there's always some little liquid left sticking to the sides of glass vessels. Given this array of errors, it was decided to use the initial concentrations given by the dilution of the stock solution, i.e. 5, 10, 25, 30 mg/l etc. Granted, there is some error in this but the use of a figure less than this to cater for any losses might also be a little sanctimonious. The reaction with the sorbent was a very fast one, and this alone could have stymied some of the errors. For example, if the sorbent could reduce the initial concentration to a half by reaction with the sorbate in less than one minute, the loss involved in shaking the sample for the remainder of the hour is greatly arrested.

The ammonia nitrogen concentration was determined using the following formula:

$$mg/l\ Ammonia\ N = [(A - B) \times 280] / ml\ sample,$$

where, A = ml 0.02 N H_2SO_4 titration for sample and,

B = ml 0.02 N H_2SO_4 titration for blank (ammonia-free distilled water).

Since the blank showed no trace of ammonia, the formula reduced to:

mg/l Ammonia N = (A x 280) / ml sample

4.3 Kinetics of the Sorption Process.

Sorption is a time dependent process. In a solid-aqueous solution exchange, transfer of the sorbate from the bulk solution to the sorbent particle must proceed through at least two stages: transfer of the sorbate from the bulk liquid to the surface of the sorbent particle; and, migration of the sorbate from the surface of the sorbent to the sorption site within the particle. Kinetic experiments demonstrate that the first step is appreciably more rapid than the second; so the latter is normally the primary rate-determining step; knowledge of which, is very important in the design of a sorption process.

Kinetic studies on the sorption of ammonium ions on the zeolite were conducted with particle size range 0.3 – 0.6 mm and a solution of ammonium hydroxide containing 25 mg NH_4^+ l^{-1}. These results are entered in Table 4.2. The rate constant for the sorption process at room temperature (25±1°C) was determined using the following equation **[Lagergren, 1898]**:

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303}.t$$

where, q_e and q (both in mg/l) are amounts of sorbate sorbed at equilibrium and at time t (min), respectively, and k_{ad} (min^{-1}) is the rate constant for the sorption process.

The value of k_{ad} for sorption of the ammonium ions at room temperature was calculated from the slope of the linear plot of log (q_e – q) vs t **[Fig. 4-1]** and noted in Table 4.2. It may be concluded from the results that the reaction taking place is of first order.

Table 4.2. Results of the Kinetic Studies on the Sorption Process (C_o = 25mgl).

Time (min)	Time $(min)^{1/2}$	C_e (mg/l)	q_e (mg/g)	q (mg/g)	(qe – q) (mg/g)	$Log(q_e-q)$ (log)
1	1	11.49	0.360 (Obtained after two hours of shaking).	0.270	0.090	-1.046
3	1.732	10.02		0.300	0.060	-1.222
5	2.236	9.43		0.311	0.049	-1.310
7	2.646	8.84		0.323	0.037	-1.432
10	3.162	8.25		0.335	0.025	-1.602
12	3.606	7.66		0.347	0.013	-1.886
15	3.873	7.00		0.360	0.000	-
20	4.472	7.00		0.360	0.000	-

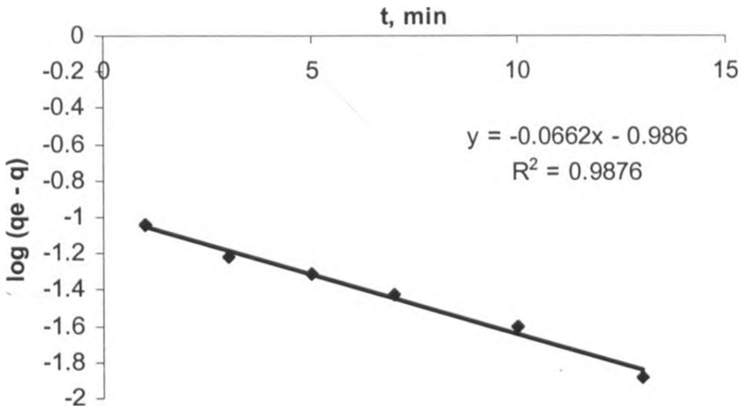

Fig.4-1. Lagergren plot [25±1°C] for removal of ammonium ions by zeolite sorbent. (Conditions: 5.0g Sorbent per 100ml solution containing 25 mg $NH_4^+l^{-1}$, 0.3 – 0.6 mm particle size, 8.8 – 9.0 pH).

The possibility that the diffusion of sorbate ions from solution into the pores of the sorbent is the rate-controlling step was investigated by determining the relative sorption rate or intraparticle diffusion constant. The relative sorption rate, described by coefficient, k_p, is obtained by plotting the amount of sorbed solute per unit weight of sorbent, q, against the square-root of time ($t^{1/2}$) **[Morris and Weber, 1963].** The straight line plot (Fig.4-1) indicates intraparticle diffusion **[McKay et al., 1980].** The relative sorption rate should be proportional to the first power of concentration for the processes controlled by external film diffusion **[Korczak and Kurbiel, 1989]**. This was not investigated in this study but in most turbulent situations, as with constant agitation, it can be proved that the timescales of such external diffusion are on the order of seconds. Obviously, if the solution outside the particles is mixed at all, there will not be much time spent by molecules reaching the aggregate exterior **[Schwarzenbach, 1993]**.

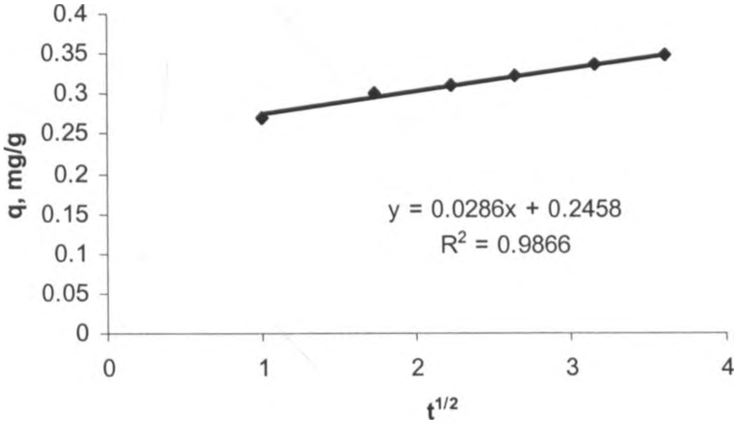

Fig. 4-2. Weber and Morris plot for the rate constants of pore diffusion of ammonium ions during its sorption on zeolite sorbent. (Conditions: 5.0g Sorbent per 100ml solution containing 25 mg $NH_4^+l^{-1}$, 0.3 – 0.6 mm particle size, 8.8 – 9.0 pH, temp 25±1oC).

The rate constant for intraparticle diffusion, k_p, at room temperature was determined from the slope of the graph of q_e vs $t^{1/2}$ and is given in Table 4.2. The average value of the pore diffusion coefficient or effective diffusivity, D*, at room temperature was determined by using the following equation **[Schwarzenbach, 1993]**:

$$t_{\frac{1}{2}} \approx \frac{0.03R^2}{D*}$$

where, $t_{1/2}$ (min) is the time for sorption of half amount of sorbate, r_o (cm) is the radius of the sorbent particles (in this case an average of 0.0225cm). The value of $t_{1/2}$ was obtained from the plot of remaining concentration vs time Fig. 4-3 and was found to be 51 seconds. The value of D* (Table 4.3) was found to be of the order 10^{-7} indicating that the process is governed by diffusion but pore diffusion is not the only rate-controlling step **[Michelson et al., 1975]**.

Table 4.3. Adsorption Kinetic parameters at room temperature.

K_{ad} (min^{-1})	k_p ($mg\ g^{-1}\ min^{-1/2}$)	D* ($cm^2\ s^{-1}$)
1.52×10^{-1}	2.86×10^{-2}	2.97×10^{-7}

The kinetic profiles in Figs. 4-3, 4-6 and 4-9 reveal an early period of extensive exchange followed by a slowly proceeding uptake by the particles. This suggests a very strong electrostatic attraction for the ammonium ions and that there was a rapid NH_4^+ ion concentration build-up in the diffuse double layer around the sorbent particles. Therefore, the timescales of diffusion through the diffuse double layer might be infinitesimally low as to render diffusion through the particle's pores as the rate-limiting step. Also, this result seems to suggest ion exchange as possibly the dominant sorption mechanism.

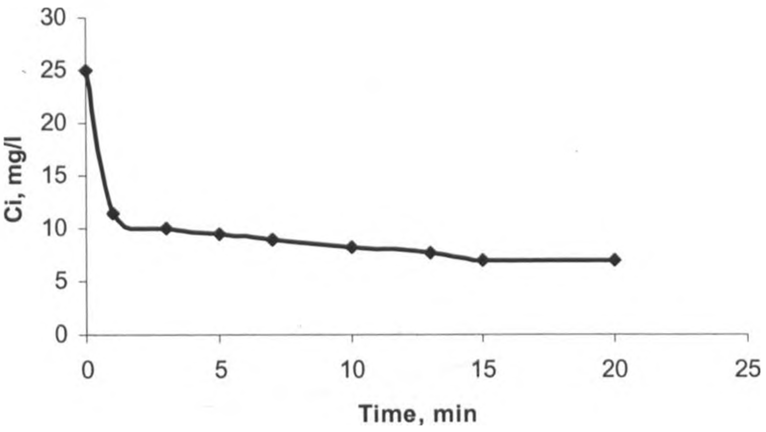

Fig. 4-3. Plot of remaining concentration, Ci, against time, min, for sorption of ammonium ions on zeolite sorbent. (Conditions: 5.0g Sorbent per 100ml solution containing 25 mg $NH_4^+l^{-1}$, 0.3 – 0.6 mm particle size, 8.8 – 9.0 pH, temp 25±1°C).

4.4 Effect of Sorbent Dosage.

The effect of zeolite dosage is presented in Figs. 4-4 and 4-5. Fig. 4-4 indicates that the sorption increased with increasing dosage upto a certain value (about 75% sorption) and then there was no further increase in sorption. Fig. 4-5 show that the specific sorption capacity decreased with increasing sorbent dosage.

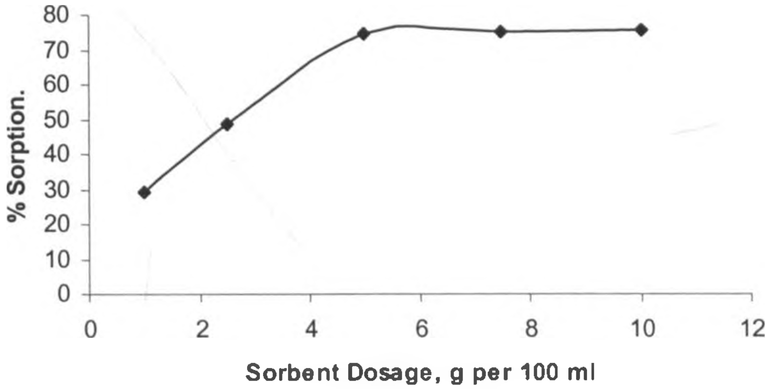

Fig. 4-4. Plot of percentage sorption of ammonium ions from solution vs sorbent dosage. (Conditions: 25 mg $NH_4^+l^{-1}$, Particle size 0.6 – 1.2mm, temp 25±1°C, Contact time 3h)

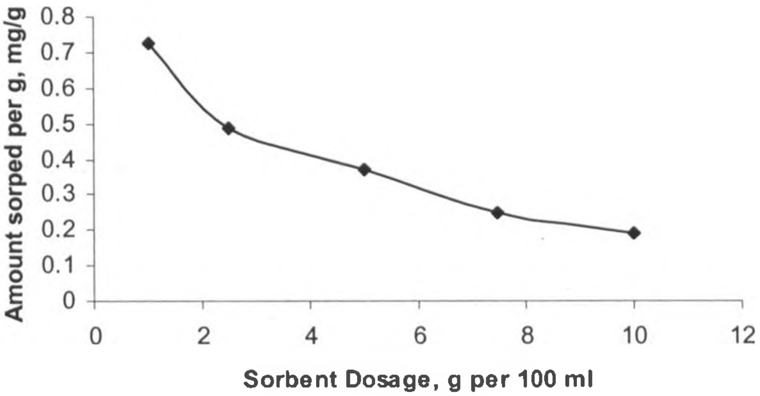

Fig. 4-5. Plot of specific sorption capacity vs sorbent dosage. (Conditions: 25 mg $NH_4^+l^{-1}$, Particle size 0.6 – 1.2mm, temp 25±1°C, Contact time 3h)

These results can be explained in terms of the increased number of sorption sites as the sorbent dosage is increased. 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 equilibrium concentration, this difference is zero **[Metcalf and Eddy, Inc., 1979].** As the sorbent dosage is increased, more ammonium ions are sorbed from solution, lowering the concentration of the bulk liquid and increasing the percent adsorption or removal. Equilibrium, therefore, is established at a lower concentration.

4.5 Effect of Sorbent Particle size.

The effect of particle size is presented in Figs. 4-6. These kinetic profiles show that the sorptive capacity increased with decrease in particle size. In a sorption system where the diffusion of the sorbate from the surface of the sorbent is the rate-limiting step, the rate of sorption will vary with the diameter of the sorbent particles **[Cheremisinoff and Ellerbusch, 1978]**. This can be attributed to the larger surface area and closer proximity of sorption sites in smaller particles than in larger ones. The variation of particle size also affected the rate of the sorption process Figs. 4-6. The rate decreased with increase in particle size, thus equilibrium was achieved much faster with smaller particles **[Table 4.4]**. With a solution containing 25 mg NH_4^+ per litre, removals of over 70% were achieved with particle size range 0.3 – 0.6 mm in only 15 minutes.

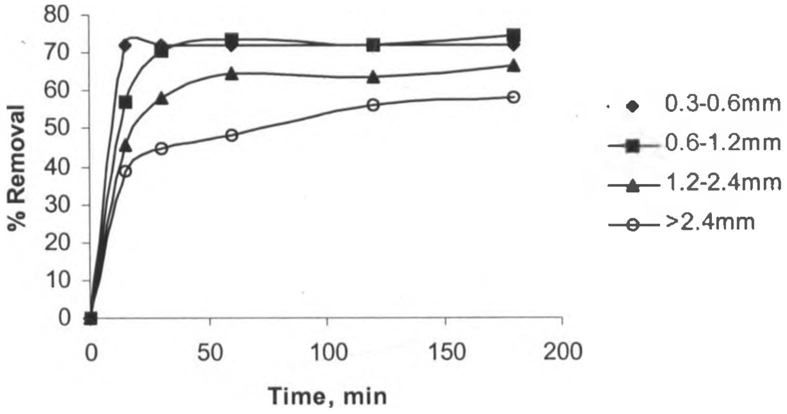

Fig. 4-6. Plot of percentage removal vs time for different particle size ranges of zeolite sorbent. (Conditions: 5.0g sorbent per 100ml solution containing 25 mg $NH_4^+l^{-1}$, 8.8 – 9.4 pH, temp 25±1°C)

4.6 Effect of Initial Sorbate Concentration on the Sorption Process.

The initial concentration of sorbate affected the sorptive capacity and the rate of sorption of ammonium ions. As indicated in Fig. 4-10 the amount of ammonium ions sorbed increased with increase of equilibrium concentration which is an indicator of the initial sorbate concentration. The rate of increase was rapid at low concentrations (5 – 20 mg/l) and tended to slow down as the concentration increased. In theory, in a system where intraparticle diffusion is the rate-limiting step, adsorption rate dependence upon solution concentration is limited. It has been proven **[Zorgoski et al., 1976]** that in such systems linear variations of the rate with concentrations occurs only at low concentrations. As sorbate concentration increases, the concentration equilibrium around the particle forms rapidly and the process becomes dependent upon the slow intraparticle transport of the sorbate **[Korczak and Kurbiel, 1989]**.

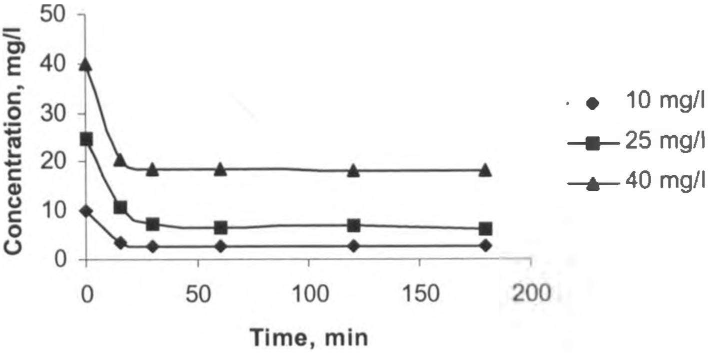

Fig. 4-7. Plot of remaining concentration, mg/l, vs time, min for various initial concentrations. (Conditions: 5.0 g sorbent per 100 ml solution, Particle size 0.6 – 1.2mm, temp 25±1°C)

Kinetic experiments on sorbent particle range 0.6 – 1.2 mm (Fig. 4-7) show that the initial concentration decreased with time with equilibrium being established quite rapidly, within 30 – 60 minutes. For concentrations lower than 25 mg/l removals of over 70% were achieved within the first 45 minutes of sorption, Fig. 4-8. Fig. 4-9 shows the equilibrium variation of percentage removal with increase of initial concentration. The percentage removal decreased almost linearly with increasing initial concentration of ammonium ions. This can be viewed in terms of an increase in the number of sorbate ions against a limited number of sorption sites.

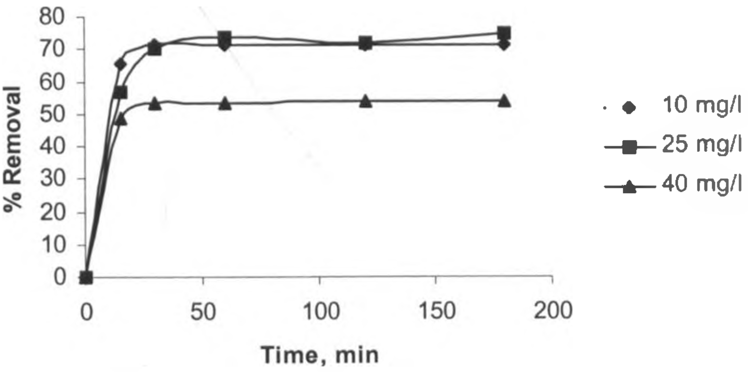

Fig. 4-8. Plot of percentage removal vs time, min, for various initial concentrations. (Conditions: 5.0 g sorbent per 100 ml solution, Particle size 0.6 – 1.2mm, temp 25±1°C)

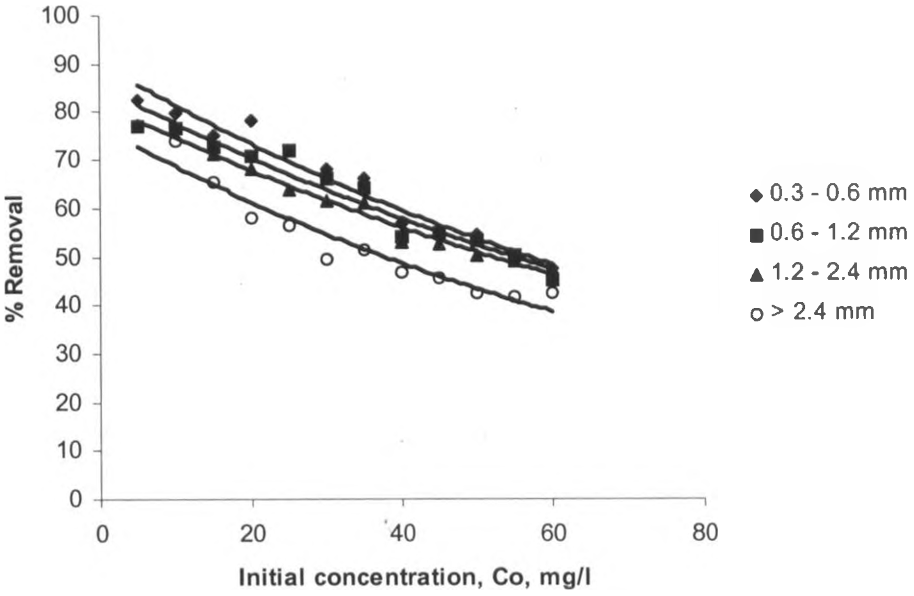

Fig. 4-9. Plot of equilibrium percentage removal vs initial sorbate concentration. (Conditions: 5.0 g sorbent per 100 ml solution, temp 25±1°C)

4.7 Time of Equilibrium.

The kinetic profiles depicted in the foregoing sections i.e. Fig. 4-6 give an insight into the time taken to reach equilibrium for each of the four particle size ranges. The equilibrium time varied with the sorbent particle size and ranged from 15 to 150 minutes. This variation can be explained in terms of the surface area and the time taken for the ammonium ions to diffuse to sorption sites within the sorbent particles. The smaller the particles sizes the greater the surface area and the shorter the route taken by the sorbate particles to reach the sorption sites. On the basis of kinetic equilibrium times, different contact times for the different particle size ranges were adopted for the equilibrium experiments. These, together with the equilibrium times are entered in Table 4.4.

Table 4.4. Results of equilibrium and contact times obtained from kinetic profiles.

Particle size (mm)	Equilibrium time (min)	Contact or shaking time(min)
0.3 – 0.6	15 –30	60
0.6 – 1.2	45 - 75	120
1.2 – 2.4	60 - 90	120
>2.4	120 -150	180

4.8 Sorption Equlibrium Isotherms.

Equilibrium studies were carried out for all the four sorbent particle size ranges to assess the adsorption equilibrium that they followed. The Langmuir isotherm models was considered. The isothermal plots for all the four sorbent fractions are given in Fig. 4-10.

To estimate Q_{max} the linearized form of Langmuir isotherm as given below was used:

$C_e/q_e = 1/Q_{max}.b + C_e/Q_{max}$ **[Langmuir model]**

where C_e is the sorbate concentration at equilibrium in mg/l, q_e is the amount of ammonium ions sorped per unit weight of sorbent in mg/g, Q_{max} is the maximum sorbate sorbed per unit weight of sorbent in mg/g, and b is a constant.

The sorption data seems to follow the Langmuir sorption model Fig. 4-11.

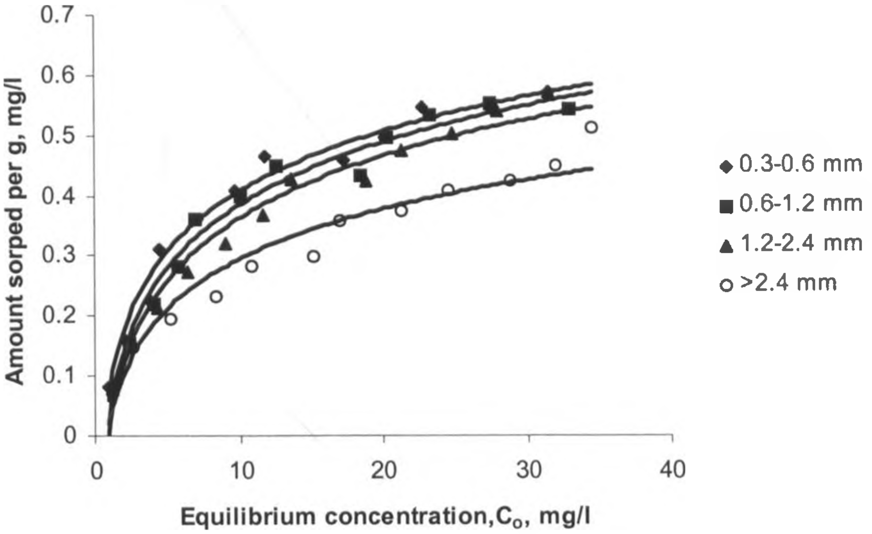

Fig. 4-10. Isothermal plots for different particle size ranges. (Conditions: 5.0 g sorbent per 100 ml solution, temp 25±1°C)

Further, the degree of fitness of the Langmuir isotherm was examined in terms of a dimensionless equilibrium parameter R_L **[Hall et al., 1966]** using the following equation:

$$R_L = \frac{1}{1+b.C_o}$$

where b is the Langmuir constant (Table 4.5) and C_O is the initial concentration. The value R_L denotes an unfavourable ($R > 1$), linear ($R = 1$) or favourable ($R < 1$) process. The values of R_L for the concentration range (5 – 60 mg/l) used were found to be between 0 and 1 showing favourable adsorption of ammonium ions on zeolite sorbent (Table 4.6).

Table 4.5. Langmuir adsorption parameters.

Particle	Langmuir isotherm		
size (mm)	Q_{max} (mg/g)	b (l/mg)	Corr. r^2 –
0.3 – 0.6	0.680	0.154	0.992
0.6 – 1.2	0.693	0.123	0.985
1.2 – 2.4	0.723	0.096	0.984
>2.4	0.597	0.091	0.949

Table 4.6. Langmuir equilibrium values, R_L.

Particle size (mm)	R_L range
0.3 – 0.6	0.098 to 0.655
0.6 – 1.2	0.119 to 0.619
1.2 – 2.4	0.148 to 0.675
> 2.4	0.155 to 0.687

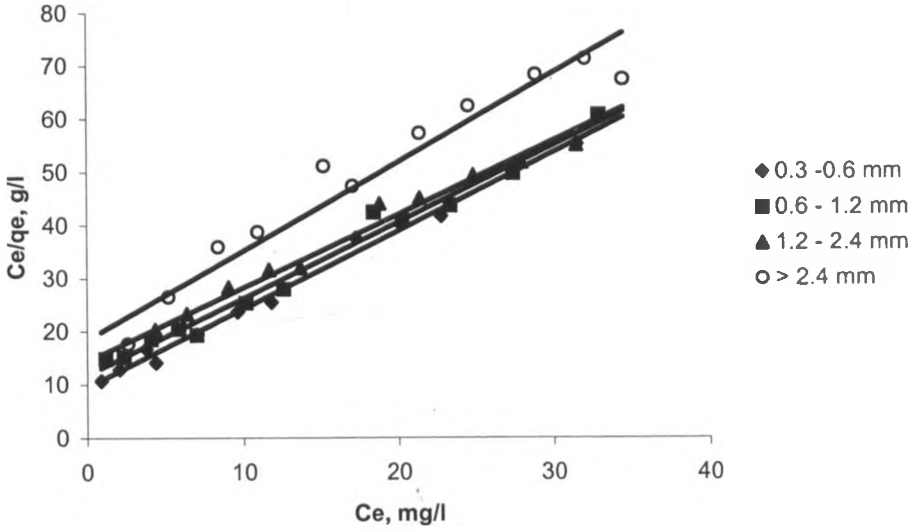

Fig. 4-11. Linearized Langmuir isotherms for different particle size ranges (Conditions: 5.0 g sorbent per 100 ml solution, temp 25±1°C)

This Langmuir correlation of the sorption isotherms may be explained by postulating what might be happening on the zeolite surface when it comes into contact with ammonium ions. From the mineralogical content in Table 4.1, the zeolite has a large amount of Sodium, Na^+, and Potassium, K^+, ions.

some of these may be present as counterions on the zeolite surface. It can therefore be assumed an ion exchange reaction takes place between the counterions on the zeolite surface and the ammonium ions in solution. Since potassium is higher on the ion exchange selectivity series than ammonia, it can be assumed that bulk of the ion exchange reaction is between NH_4^+ and Na^+. In the diffuse double layer surrounding the sorbent particles, the ion exchange reaction may be represented thus:

$$\mathbf{NH_4^+ + Na{:}Surface \rightleftharpoons NH_4{:}Surface + Na^+}$$

(the colon here indicates association without bond formation). An equilibrium constant expression for this ion exchange reaction can be written thus:

$$K_{ie} = \frac{[NH_4 : Surface][Na^+]}{[NH_4^+][Na : Surface]}$$

where concentrations are used in place of activities. (A complete equilibrium expression will include activity coefficients for the charged species; however, since this equation involves monovalent ions both in the bulk medium and near the surface, such activity coefficients virtually cancel one another out in the equilibrium quotient). K_{ie} reflects the preference of NH_4^+ relative to the competing ions, in this case represented by Na^+. Recognising that the accumulation of counter cations around the negatively charged particles must be a constant equal to the product of surface charge density σ_{ie} (mol. m^{-2}) and the specific particle surface area A (m^2. Kg^{-1}), we can write

$$\sigma_{ie} = \mathbf{[NH_4{:}Surface] + [Na{:}Surface]}$$

where **[NH₄:Surface]** and **[Na:Surface]** have units of moles per kilogram. The term in **[Na:Surface]** can now be eliminated from the equilibrium constant expression:

$$K_{ie} = \frac{[NH_4 : Surface][Na^+]}{[NH_4^+](\sigma_{ie}.A - [Na : Surface])}$$

Rearranging this expression, it is found,

$$[NH_4 : Surface] = \frac{(\sigma_{ie}.A)(K_{ie})[NH_4^+]}{[Na^+] + (K_{ie})[NH_4^+]}$$

By dividing the right-hand terms by $[Na^+]$ the equation becomes,

$$[NH_4 : Surface] = \frac{(\sigma_{ie}.A)\left(K_{ie}/[Na^+]\right)[NH_4^+]}{1 + \left(K_{ie}/[Na^+]\right)[NH_4^+]}$$

This is an expression analogous to the one of the Langmuir isotherm with α or Q_{max} [maximum sorbed] = σ_{ie}.A and $b = K_{ie}/[Na^+]$ and $C_e = [NH_4^+]$, the equilibrium concentration of ammonium ions.

The equilibrium experiments were conducted with solutions of alkaline pH (actually > 9.0; i.e. 10.6 for 25 mg/l). The pK_a value for NH_4^+ at 25°C = 9.26. Consequently, the solid – water distribution coefficient may only have involved the concentration of ammonium ions near the solid surface and those in the bulk solution.

Thus, at low values of $[NH_4^+]$, [Na+] >> K_{ie} $[NH_4^+]$ and the above equation reduces to

$[NH_4^+$:Surface] = (σ_{ie}.A)(K_{ie}/[Na+])$[NH_4^+]$

i.e it take the form,$q_e = kC_e$. This means that at low ammonium ion concentrations we should expect the sorption isotherms to be linear. This was indeed the result as Fig.4-12 shows for initial concentrations of 5 – 20mg/l. At high $[NH_4^+]$ concentrations the sorbed concentration asymptotically approaches a constant value set by the cation exchange capacity (CEC) of the solid surface – this was also the observed result Fig.4-10.

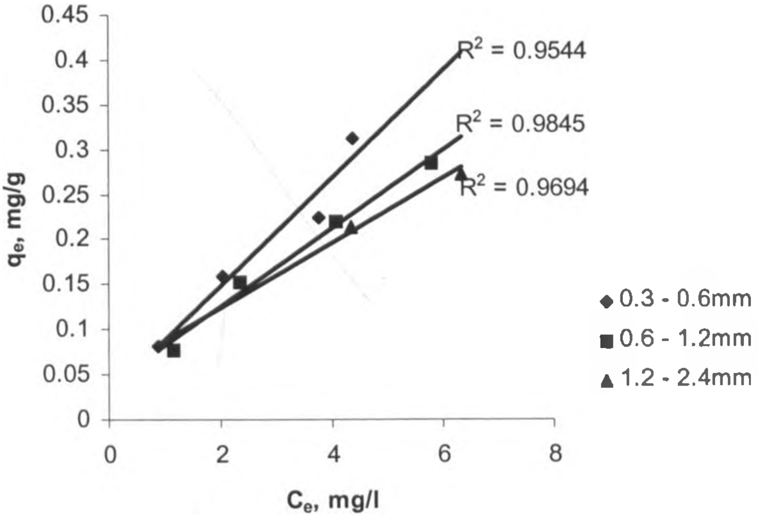

Fig. 4-12.Sorption isotherms at low concentrations (C_o = 5 – 20mg/l) for different particle size ranges. (Conditions: 5.0 g sorbent per 100 ml solution, temp 25±1°C)

Given the mineral content of the zeolite, the overall sorption process may not have been limited to the exchange between ammonium and sodium ions as depicted above. There is the possibility of other complimentary reactions, such as the partial substitution of potassium (K^+) ions or any orther counterions present e.g. Ca^{2+}, Mg^{2+}, direct adsorption of ammonium ions due to the negative charges on the zeolite surface arising from isomorphic substitutions and the protonation of hydroxyl moeities, etc. However, if ion exchange was the dominant mechanism, the overall result is a somewhat Langmuirian kind of sorption.

4.8 Effect of Temperature on Equilibrium.

The effect of temperature on equilibrium was carried out at 14°C and at room temperature, 25±1°C. The results presented in Figs.4-13, suggest that the sorption of ammonium ions on the zeolite sorbent is endothermic. The rate and extent of sorption increased with temperature appreciably. For instance, the % removal for an initial concentration of 5 mg/l was 71.2% at 14°C and 82.4 at 25°C. For 10 mg/l, the removal was 70.9% at 14°C and 79.6% at 25°C.

When H+ and OH- are presumed to be the potential-determining ions, it can be shown that the surface charge of oxides increases with temperature for constant ionic strength. This, in turn reflects on the extent of sorption. However, it should be noted that the direction and magnitude of the temperature dependency will depend on the specific solute-sorbent system. For example, an early paper by **Jurinak and Bauer (1956)** reported that the sorption of zinc by calcite was exothermic; the amount of zinc sorbed decreased with increasing temperature. In contrast **Kuo and Mikkelsen (1979)** studied the sorption of zinc by soils at temperatures ranging from 10° to 35°C and found that zinc sorbed endothermically; increased sorption was associated with higher temperatures.

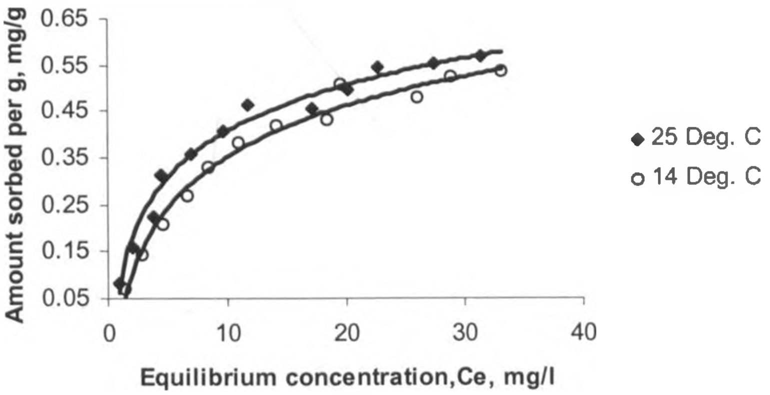

Fig. 4-13. Sorption isotherms at 14 and 25°C for particle size range 0.3 – 0.6mm. (Conditions: 5.0 g sorbent per 100 ml solutions of varying concentrations.)

Sorption at the solid-liquid interface tends to occur when the attractive forces between the surface and ionic solutes are greater than those between solutes and the solvent **[Zottlemeyer and Micale, 1971]**. The sorption of an ionic or polar solute is often the result of a thermodynamically favourable change in the enthalpy (ΔH) **[Hasset et al., 1981]** or sometimes of a favourable change in the entropy (ΔS) of the system in which the -T ΔS term of the **Gibbs-Helmholtz** equation compensates for the positive value of ΔH **[Thomas,**

1961], where T is the temperature of the system. Thus, the sorption behaviour of ionic or polar solutes will probably show some temperature dependency.

Table 4.7. Langmuir adsorption parameters at 14 and 25 °C.

Temp. (°C)	Langmuir isotherm		
	Q_{max} (mg/g)	b (l/mg)	Corr. r^2 –
14	0.728	0.087	0.981
25	0.680	0.154	0.992

The constants for Langmuir and Freundlich isotherms at different temperatures are entered in Table 4.7. These figures show that Langmuir is the favourite isotherm.

4.9 Effect of Solution pH on Equilibrium.

The effect of solution pH is presented in Fig. 4-14.

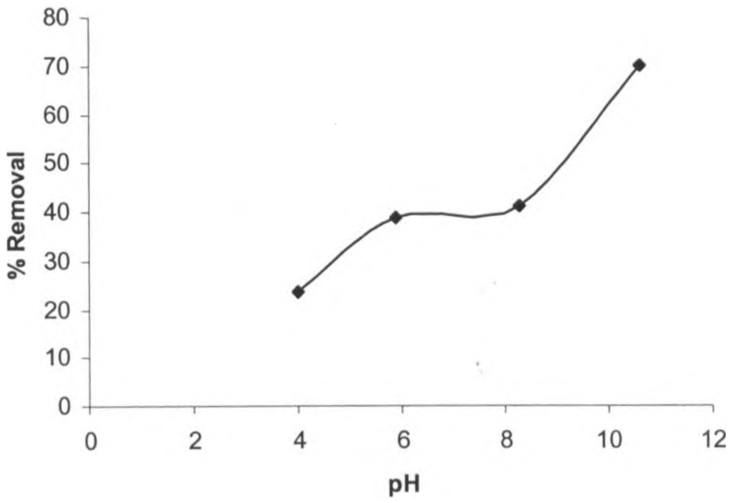

Fig. 4-14. Effect of pH on the sorption process (Conditions: 5.0 g sorbent per 100 ml solutions of 25 mg/l, particle size range 0.3 – 0.6mm, Temp 22±1°C.)

The graph shows that the % removal of ammonium ions at equilibrium from a solution containing 25 mg/l NH_4^+ while varying the pH. The figure shows that the NH_4^+ ion removal increased with increasing pH. However, the rate of removal was sluggish between pH 5.9 and 8.3 leading to a “saddle” on the graph. This can be explained in terms of the interactions of NH_4^+ ions with the sorbent surface as the pH is varied.

For natural solids that are oxides or oxyhydroxides (eg. Quartz, SiO_2; geothite, FeOOH; alumina, Al_2O_3), their water-wet surface is covered by hydroxyl groups. These hydroxyl moieties can undergo proton-exchange reactions with the aqueous solution much like dissolved acids:

$$\mathbf{Surface \equiv M - OH_2^+ \quad \leftrightarrows \quad Surface \equiv M - OH + H^+}$$

$$\mathbf{Surface \equiv M - OH \quad \leftrightarrows \quad Surface \equiv M - O^- + H^+}$$

where M refers to an atom like Si, Fe, or Al at the particle surface, and $\equiv$ refers to the attachments of that atom to the solid. From the above reactions, it is easy to see that the abundance of $\mathbf{\equiv MOH_2^+}$ and $\mathbf{\equiv MO^-}$ species on the solid surface control the surface charge. Neglecting other specifically sorbed species, the concentration of this charge, σ_{ie} (mol charges. m^{-2}) can be estimated:

$$\sigma_{ie} = [\equiv \mathbf{MOH_2^+}] - [\equiv \mathbf{MO^-}]$$

where the surface species concentrations are given in units of mole per meter squared of exposed surface. When these two surface species are present in equal concentration, the surface exhibits zero net charge (also the surface potential, ψ = 0); we call the solution pH that establishes this condition, the pH of zero point of charge or pH_{zpc} **[Schwarzenbach, 1993]**. Thus, at low pH the concentration of the $\mathbf{\equiv MOH_2^+}$ species is dominant leading to the electrostatic repulsion and low sorption of the similarly charged NH_4^+ ions. At higher pH values the surface is negatively charged $[\equiv \mathbf{MO^-}]$ and NH_4^+ ions are readily accepted by the surface. It has been observed that at pH values near the pH_{zpc}, the changes in the net surface charge, is very low, especially for solutions of low ionic strength. Obviously, this effect on σ_{ie} would feed back onto the extent of sorption, this is probably what is happening on the "saddle" part of the curve.

5.0 CONCLUSIONS AND RECOMMENDATIONS.

The following conclusions and recommendations were made from the experimental observations:

5.1 Conclusions.

- The zeolite is an Aluminosilicate of Iron, Sodium and Potassium, possibly ***Hydrated Ferrous Sodium Potassium Aluminosilicate*** as its chemical name.

- The zeolite seems to have some fairly good potential for ammonia removal but this needs to be investigated further as per the recommendations in section 5.2.

- The sorptive capacity seems to be around 4 mmol 100 g^{-1}. This is about half of that of Clinoptilolite as obsverved by **Jørgensen, *et al.* (1976).** Clinoptilolite has been used commercially as an ion exchange resin for ammonia removal.

- The zeolite seems to work by a combination of ion exchange and adsorption. The reaction with ammonia is very fast with intra-particle diffusion being the rate limiting step.

- The uptake of the ammonium ions is favoured by high temperatures, small sorbent particle size, low sorbate concentrations and an alkaline medium.

- The equilibrium data fitted the Langmuir sorption model. This shows that a monolayer of ammonium ions formed on the particle surface and suggests ion exchange as the possible dominant mechanism.

5.2 Reccomendations.

- The sorptive capacity or the cationic exchange capacity (CEC) should be investigated further through dynamic studies in laboratory ion exchange columns.

- The effect of the presence of other ions on the sorptive capacity needs to be investigated.

APPENDICES.

6.1 APPENDIX A: RATE (KINETIC) STUDIES (Temp. 25 ± 1°C).

Appendix A1: *Ammonia Removal as a function of time (1.0g of sorbent, particle size 0.6-1.2mm in contact with 100ml solutions of 25 mg/l ammonium ions).*

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	99.5	7.3	20.54	0.446	0.446	17.84
30	99.5	6.5	18.29	0.671	0.671	26.00
60	99.5	6.3	17.73	0.727	0.727	29.10
120	99.0	6.0	16.98	.0.802	0.802	32.1
180	99.5	6.3	17.73	0.727	0.727	29.1
Blank	100	No trace of ammonia in distilled water.				

Appendix A2*: Ammonia Removal as a function of time (2.5g of sorbent, particle size 0.6-1.2mm in contact with 100ml solutions of 25 mg/l ammonium ions).*

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	98.5	5.4	15.35	0.965	0.386	38.6
30	98.5	5.0	14.21	1.079	0.432	43.16
60	99	4.8	13.58	1.142	0.457	45.68
120	99	4.5	12.73	1.227	0.491	49.08
180	98	4.5	12.85	1.212	0.486	48.60
Blank	100	No trace of ammonia in distilled water.				

Appendix A3: *Ammonia Removal as a function of time (5.0g of sorbent, particle size 0.6-1.2mm in contact with 100ml solutions of 25 mg/l ammonium ions).*

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	96.0	3.5	10.76	1.424	0.280	56.96
30	94.5	2.5	7.41	1.759	0.350	70.36
60	97	2.3	6.64	1.836	0.367	73.44
120	96.5	2.4	6.96	1.804	0.360	72.16
180	97.0	2.2	6.35	1.865	0.370	74.60
Blank	100	No trace of ammonia in distilled water.				

Appendix A4: *Ammonia Removal as a function of time (7.5g of sorbent, particle size 0.6-1.2mm in contact with 100ml solutions of 25 mg/l ammonium ions).*

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	94	2.3	6.85	1.815	0.245	72.60
30	95	2.2	6.48	1.852	0.247	74.08
60	95	2.2	6.48	1.852	0.247	74.08
120	95	2.1	6.19	1.881	0.251	75.24
180	94	2.1	6.26	1.874	0.250	74.96
Blank	100	No trace of ammonia in distilled water.				

Appendix A5: *Ammonia Removal as a function of time (10.0g of sorbent, particle size 0.6-1.2mm in contact with 100ml solutions of 25 mg/l ammonium ions).*

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	92.0	2.0	6.09	1.891	0.189	75.64
30	92.0	2.0	6.09	1.891	0.189	75.64
60	93.0	2.0	6.02	1.898	0.190	75.92
120	93.0	2.0	6.02	1.898	0.190	75.92
180	92.0	2.0	6.09	1.891	0.189	75.64
Blank	100	No trace of ammonia in distilled water.				

Appendix A6: Ammonia Removal as a function of time (5.0g of sorbent, particle size 1.2-2.4mm in contact with 100ml solutions of 25 mg/l ammonium ions).

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	97.0	4.7	13.57	1.143	0.229	45.72
30	96.0	3.6	10.50	1.450	0.290	58.00
60	97.0	3.05	8.80	1.620	0.324	64.80
120	96.0	3.1	9.04	1.596	0.319	63.84
180	97.0	2.9	8.37	1.663	0.333	66.52
Blank	100	No trace of ammonia in distilled water.				

Appendix A7: Ammonia Removal as a function of time (5.0g of sorbent, particle size >2.4mm in contact with 100ml solutions of 25 mg/l ammonium ions).

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	97.0	5.3	15.30	0.970	0.194	38.80
30	97.0	4.8	13.86	1.114	0.223	44.56
60	97.0	4.5	12.99	1.201	0.240	48.04
120	97.5	3.8	10.91	1.409	0.282	56.36
180	97.5	3.5	10.51	1.449	0.290	57.96
Blank	100	No trace of ammonia in distilled water.				

Appendix A8: Ammonia Removal as a function of time (5.0g of sorbent, particle size 0.3 – 0.6mm in contact with 100ml solutions of 25 mg/l ammonium ions).

Time (min)	Volume of Sample (ml)	Acid Titre (0.02N H_2SO_4) (ml)	Final conc., Ce, (mg/l)	Amount of NH_4^+ sorbed, X, (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	96.0	2.4	7.00	1.800	0.360	72.0
30	96.0	2.4	7.00	1.800	0.360	72.0
60	96.0	2.4	7.00	1.800	0.360	72.00
120	96.0	2.4	7.00	1.800	0.360	72.0
180	96.0	2.4	7.00	1.800	0.360	7.200
Blank	100	No trace of ammonia in distilled water.				

***Appendix A9**: Ammonia Removal as a function of time (5.0g of sorbent, particle size 0.6 – 1.2mm in contact with 100ml solutions of 10 mg/l ammonium ions).*

Time (min)	**Volume of Sample (ml)**	**Acid Titre (0.02N H_2SO_4) (ml)**	**Final conc., Ce, (mg/l)**	**Amount of NH_4^+ sorbed, X, (mg)**	**Amount sorbed per unit weight, qe (mg/g)**	**Removal efficiency %**
15	97.0	1.2	3.46	0.654	0.131	65.40
30	97.0	1.0	2.89	0.711	0.142	71.10
60	97.0	1.0	2.89	0.711	0.142	71.10
120	97.0	1.0	2.89	0.711	0.142	71.10
180	97.0	1.0	2.89	0.711	0.142	71.10
Blank	100	No trace of ammonia in distilled water.				

***Appendix A10**: Ammonia Removal as a function of time (5.0g of sorbent, particle size 0.6 – 1.2mm in contact with 100ml solutions of 40 mg/l ammonium ions).*

Time (min)	**Volume of Sample (ml)**	**Acid Titre (0.02N H_2SO_4) (ml)**	**Final conc., Ce, (mg/l)**	**Amount of NH_4^+ sorbed, X, (mg)**	**Amount sorbed per unit weight, qe (mg/g)**	**Removal efficiency %**
15	96.0	7.0	20.42	1.958	0.392	48.95
30	97.0	6.5	18.76	2.124	0.425	53.10
60	98.0	6.5	18.57	2.143	0.429	53.58
120	97.5	6.4	18.38	2.162	0.432	54.05
180	98.0	6.4	18.29	2.171	0.434	54.28
Blank	100	No trace of ammonia in distilled water.				

6.2 APPENDIX B: EQUILIBRIUM STUDIES (Temp. 25 ± 1°C).

***Appendix B1**: Equlibrium Studies on particle size 0.3 – 0.6mm (5.0g of sorbent shaken for one hour with 100ml solutions of varying concentrations of ammonium ions).*

Initial conc.C_o (mg/l)	**Volume of sample (ml)**	**Acid titre (ml)**	**Final conc. C_e (mg/l)**	**Amt. sorbed, q_e (mg/g)**	**Ce/qe (g/l)**	**Log qe Log 10**	**Log Ce Log 10**	**Removal %**
5	97	0.3	0.88	0.082	10.73	-1.086	-0.056	82.40
10	96	0.7	2.04	0.159	12.83	-0.799	0.310	79.60
15	97	1.3	3.75	0.225	16.67	-0.648	0.574	75.00
20	96	1.5	4.38	0.312	14.04	-0.505	0.641	78.10
25	96	2.4	7.00	0.360	19.44	-0.444	0.845	72.00
30	96	3.3	9.63	0.407	23.66	-0.390	0.984	67.90
35	95	4.0	11.79	0.464	25.41	-0.333	1.072	66.30
40	96	5.9	17.21	0.457	37.65	-0.340	1.236	56.98
45	96	6.9	20.13	0.497	40.50	-0.304	1.304	55.27
50	96	7.8	22.75	0.545	41.74	-0.264	1.357	54.50
55	96	9.4	27.42	0.551	49.76	-0.259	1.438	50.15
60	96	10.8	31.50	0.570	55.26	-0.244	1.498	47.50

***Appendix B2**: Equlibrium Studies on particle size 0.6 – 1.2mm (5.0g of sorbent shaken for two hours with 100ml solutions of varying concentrations of ammonium ions).*

Initial conc.C_o (mg/l)	**Volume of sample (ml)**	**Acid titre (ml)**	**Final conc. C_e (mg/l)**	**Amt. sorbed, q_e (mg/g)**	**Ce/qe (g/l)**	**Log qe Log 10**	**Log Ce Log 10**	**Removal %**
5	97.0	0.4	1.15	0.077	14.94	-1.114	0.061	77.00
10	96.0	0.8	2.33	0.153	15.27	-0.815	0.367	76.70
15	96.5	1.4	4.06	0.219	18.54	-0.660	0.609	72.93
20	96.5	2.0	5.80	0.284	20.42	-0.547	0.763	71.00
25	96.5	2.4	6.96	0.360	19.33	-0.444	0.843	72.16
30	97.0	3.5	10.10	0.398	25.38	-0.400	1.004	66.33
35	96.0	4.3	12.54	0.449	27.93	-0.348	1.098	64.2
40	97.5	6.4	18.38	0.432	42.55	-0.365	1.264	54.05
45	95.5	6.9	20.23	0.495	40.87	-0.305	1.306	55.04
50	96.0	8.0	23.33	0.533	43.77	-0.273	1.368	53.34
55	97.0	9.3	26.85	0.563	47.69	-0.249	1.429	51.18
60	97.0	11.4	32.91	0.542	60.72	-0.266	1.517	45.15

***Appendix B3**: Equlibrium Studies on particle size 1.2 – 2.4mm (5.0g of sorbent shaken for two hours with 100ml solutions of varying concentrations of ammonium ions).*

Initial conc.C_o (mg/l)	Volume of sample (ml)	Acid titre (ml)	Final conc. C_e (mg/l)	Amt. sorbed, q_e (mg/g)	Ce/qe (g/l)	Log qe Log 10	Log Ce Log 10	Removal %
5	97.0	0.4	1.15	0.077	14.94	-1.114	0.061	77.00
10	96.0	0.8	2.33	0.153	15.27	-0.815	0.367	76.70
15	97.0	1.5	4.33	0.213	20.33	-0.672	0.636	71.13
20	97.0	2.2	6.35	0.273	23.26	-0.564	0.803	68.25
25	96.0	3.10	9.04	0.319	28.34	-0.496	0.956	63.84
30	96.5	4.00	11.61	0.368	31.55	-0.434	1.065	61.30
35	96.5	4.7	13.64	0.427	31.94	-0.370	1.135	61.03
40	97.0	6.5	18.76	0.425	44.14	-0.372	1.273	53.10
45	97.0	7.4	21.36	0.473	45.16	-0.325	1.300	52.53
50	98.0	8.7	24.86	0.503	49.42	-0.298	1.396	50.28
55	96.0	9.6	28.0	0.540	51.85	-0.268	1.447	49.09
60	97.0	10.9	31.46	0.571	55.10	-0.243	1.498	47.57

***Appendix B4**: Equlibrium Studies on particle size > 2.4mm (5.0g of sorbent shaken for two hours with 100ml solutions of varying concentrations of ammonium ions).*

Initial conc.C_o (mg/l)	Volume of sample (ml)	Acid titre (ml)	Final conc. C_e (mg/l)	Amt. sorbed, q_e (mg/g)	Ce/qe (g/l)	Log qe Log 10	Log Ce Log 10	Removal %
5	97.0	0.4	1.15	0.077	14.94	-1.114	0.061	77.00
10	97.0	0.9	2.60	0.148	17.57	-0.830	0.415	74.00
15	97.0	1.8	5.20	0.196	26.53	-0.708	0.716	65.33
20	97.0	2.9	8.37	0.233	35.92	-0.633	0.923	58.15
25	97.5	3.8	10.91	0.282	38.72	-0.550	1.038	56.36
30	97.0	5.3	15.17	0.297	51.08	-0.527	1.181	49.43
35	97.0	5.9	17.03	0.359	47.44	-0.445	1.231	51.34
40	97.0	7.4	21.36	0.373	57.27	-0.428	1.330	46.60
45	97.0	8.5	24.54	0.409	62.44	-0.388	1.390	45.47
50	97.0	10.0	28.87	0.423	68.25	-0.374	1.460	42.26
55	97.0	11.1	32.04	0.450	71.20	-0.347	1.506	41.75
60	97.5	12.0	34.46	0.511	67.44	-0.292	1.537	42.57

6.3 APPENDIX C: EFFECT OF TEMPERATURE (14°C).

***Appendix C**: Equlibrium Studies on particle size 0.3 – 0.6mm at 14°C (5.0g of sorbent shaken for two hours with 100ml solutions of varying concentrations of ammonium ions).*

Initial conc.C_o (mg/l)	Volume of sample (ml)	Acid titre (ml)	Final conc. C_e (mg/l)	Amt. sorbed, q_e (mg/g)	Ce/qe (g/l)	Log qe Log 10	Log Ce Log 10	Removal %
5	97.0	0.5	1.44	0.071	20.28	-1.149	0.158	71.20
10	96.0	1.0	2.92	0.142	20.58	-0.848	0.465	70.90
15	97.0	1.6	4.62	0.208	22.21	-0.682	0.665	69.21
20	97.0	2.3	6.64	0.267	24.87	-0.573	0.822	66.80
25	96.0	2.9	8.46	0.331	25.56	-0.480	0.927	66.16
30	97.0	3.8	10.97	0.381	28.79	-0.419	1.040	63.43
35	97.0	4.9	14.14	0.417	33.91	-0.380	1.150	59.60
40	97.0	6.4	18.47	0.431	42.85	-0.366	1.266	53.83
45	96.0	6.7	19.54	0.509	38.39	-0.293	1.291	56.58
50	97.0	9.0	25.98	0.480	54.13	-0.319	1.415	48.04
55	97.0	10.0	28.87	0.523	55.20	-0.281	1.460	47.51
60	97.0	11.5	33.20	0.536	61.94	-0.271	1.521	44.67

6.4 APPENDIX D: EFFECT OF SOLUTION pH (Temp 22°C).

***Appendix D**: Equlibrium Studies on particle size 0.3 – 0.6mm (5.0g of sorbent shaken for two hours with 100ml solutions of 25mg/l ammonium ions of varying pH).*

Initial conc.C_o (mg/l)	Volume of sample (ml)	pH	Equilib. pH	Acid titre (ml)	Final conc. C_e (mg/l)	Amt. sorbed, q_e (mg/g)	Removal %
25	97.0	4.0	3.8	6.6	19.05	0.119	23.80
25	97.0	5.9	6.0	5.3	15.30	0.194	38.80
25	97.0	8.3	6.0	5.1	14.72	0.206	41.12
25	97.0	10.6	8.8	2.3	7.51	0.350	69.96

6.5 APPENDIX E: BLANK AND CONTROI EXPERIMENTS RESULTS.

Appendix E1: *Control experiments using an initial ammonium ion concentration of 12.5 mg/l.*

	Expt No.	**Initial conc. (mg/l)**	**Sample volume (ml)**	**Acid Titre (ml)**	**Calculated acid titre (ml)**	**Final conc. (mg/l)**
Direct Titration.	1	12.5	100	4.4	4.46	12.32
	2	12.5	100	4.5	4.46	12.60
Distillation + Titration	1	12.5	100	4.45	4.46	12.46
	2	12.5	100	4.5	4.46	12.60
Agitation (1hr) + Distillation + Titration	1	12.5	100	4.4	4.46	12.32
	2	12.5	100	4.35	4.46	12.18
	3	12.5	100	4.4	4.46	12.32
Blank (Ammonia-free distilled water)	1	0	100	The indicating Boric acid solution did not change colour. Therefore, zero.		
	2	0	100			

***Appendix E2**: Control experiments using an initial ammonium ion concentration of 25 mg/l.*

	Expt No.	**Initial conc. (mg/l)**	**Sample volume (ml)**	**Acid Titre (ml)**	**Calculated acid titre (ml)**	**Final conc. (mg/l)**
Direct Titration.	1	25	100	8.8	8.93	24.64
	2	25	100	8.9	8.93	24.92
	3	25	100	8.9	8.93	24.92
Distillation + Titration	1	25	100	8.9	8.93	24.92
	2	25	100	8.7	8.93	24.36
	3	25	100	8.8	8.93	24.64
Agitation (1hr) + Distillation + Titration	1	25	100	8.8	8.93	24.64
	2	25	100	8.85	8.93	24.78
	3	25	100	8.7	8.93	24.36
Blank (Ammonia-free distilled water)	1	0	100	The indicating Boric acid solution did not change colour. Therefore, zero.		
	2	0	100			

6.6 APPENDIX E: AMMONIA NITROGEN DETERMINATION BY DISTILLATION-TITRATION TECHNIQUE.

6.6A Preliminary Distillation Step.

1. General Discussion.

The sample is buffered at pH 9.5 with a borate buffer to decrease the hydrolysis of cyanates and organic nitrogen compounds and distilled into a solution of boric acid when nesslerization or titration is to be used or into sulphuric acid when the phenate method is to be used. The ammonia in the distillate can be determined either colourimetrically by nesslerization or the phenate method of titrimetrically with standard sulphuric acid and a mixed indicator or a pH meter. The choice between the colourimetric or acidimetric finish depends on the concentration of ammonia.

2. Apparatus.

a. *Distillation apparatus:* Arrange a pyrex flask of 800 – 2000-ml capacity attached to a vertical condenser so that the outlet tip may be submerged in the receiving boric acid solution. Use an all pyrex apparatus or one with condensing units constructed of block tin or aluminium tubes.

b. *PH meter.*

3. Reagents.

a. *Ammonia-free water:* Prepare by ion exhange or distillation methods.

1) Ion exchange – Prepare ammonia-free water by passing distilled water through an ion-exchange column containing a strongly acidic cation-exchange resin mixed with a strongly basic anion-exchange resin. Select resins that will remove organic compounds that subsequently

interfere with the ammonia determination. Regenerate the column according to the instructions of the manufacturer.

2) Distillation – Eliminate traces of ammonia in distilled water by adding 0.1 ml conc. H_2SO_4 to 1 l distilled water and redistilling. Alternatively, treat distilled water with sufficient bromine or chlorine water to produce a free halogen residual of 2 to 5 mg/l and redistill after standing at least 1 hr. discard the first 100ml distillate. Check the redistilled water for the possibility of a high blank.

Since it is virtually impossible to store ammonia-free water in the laboratory without contamination from ammonia fumes, prepare fresh for each batch of samples.

Prepare all reagents with ammonia-free water.

b. *Borate buffer solution:* Add 88 ml 0.1 *N* NaOH solution to 500 ml 0.025 *M* sodium tetraborate ($Na_2B_4O_7$) solution (5.0 g $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7.10H_2O$ /l) an dilute to 1 l.

c. *Sodium hydroxide, 6N*: Dissolve 240 g NaOH in 1 l ammonia-free distilled water.

d. *Dechlorinating agent, N/70*: use 1 ml of any of the following reagents to remove 1 mg/l of residual chlorine in 500ml sample. Prepare the unstable thiosulphate and and sulphate solutions fresh.

1) *Phenylarsine oxide* – Dissolve 1.2 g C_6H_5AsO in 200 ml 0.3 *N* NaoH solution, filter if necessary, and dilute to 1 l with ammonia-free water. (CAUTION: *Toxic – take care to avoid ingestion.*)
2) *Sodium arsenite* – Dissolve 0.9 g $NaAsO_2$ in ammonia-free water and dilute to 1 l. (CAUTION: *Toxic – take care to avoid ingestion.*)
3) Sodium sulphite – Dissolve 0.9 g Na_2SO_3 in ammonia-free and dilute to 1 l.

4) *Sodium thiosulphate* – Dissolve 3.5 g $Na_2S_2O_3.5H_2O$ in ammonia-free water and dilute to 1 l.

e. *Neutralising agent*: Prepare with ammonia-free water.

1) *Sodium hydroxide*, NaOH, 1 *N*.

2) *Sulphuric acid*, H_2SO_4, 1 *N*.

f. *Absorbent solution*: Dissolve 20 g H3BO3 in ammonia-free water and dilute to 1 l.

4. Procedure.

a. *Preparation of equipment:* Add 500 ml ammonia-free water, 20 ml borate buffer, and adjust pH to 9.5 with 6*N* NaOH solution. Add a few glass beads or boiling chips and use this mixture to steam the distillation apparatus until the distillate shows no trace of ammonia.

b. *Sample preparation:* Use a 500-ml sample or portion diluted to 500 ml with ammonia-free water. When the ammonia nitrogen content is less than 100 µg/l, use a sample volume of 1,000 ml. Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual, if necessary neutralise the sample to approximately pH 7 with the dilute acid or base, using a pH meter.

c. Add 25 ml borate buffer and adjust pH to 9.5 with 6*N* NaOH using a pH meter or short-range pH paper.

d. *Distillation:* To minimise contamination, leave the entire distillation apparatus assembled after the steaming-out process until just before starting the sample distillation. Disconnect the steaming-out flask and immediately transfer the sample flask to the distillation apparatus. Distil at a rate of 6 to 10 ml/min with the tip of the delivery tube in a 500-ml erlenmeyer flask containing 50 ml boric acid. Collect at least 300 ml distillate. Lower the collected distillate free of contact with the delivery tube and continue distillation during the last minute or two to cleanse the condenser and delivery tube. Dilute to 500 ml with ammonia-free water.

e. *Ammonia determination:* Determine the ammonia by the nesslerization method, the phenate method, or acidimetric method.

6.6B The Acidimetric Method.

1. General Discussion.

The acidimetric method is used only on samples that have been carried through the preliminary distillation step described in section 5.5A. the following table is useful in selecting sample volume for the distillation and titration method.

Ammonia Nitrogen in sample mg/l	**Sample Volume ml**
5 – 10	250
10 – 20	100
20 – 50	50.0
50 - 100	25.0

2. Apparatus.

Distillation apparatus: See section 5.5A.2*a*

3. Reagents.

a. *Mixed indicator solution:* Dissolve 200 mg methyl red indicator in 100 ml 95% ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in

50 ml 95% ethyl or isopropyl alcohol. Combine the two solutions. Prepare monthly.

b. *Indicating boric acid solution:* Dissolve 20 g H_3BO_3 in ammonia-free distilled water, add 10 ml mixed indicator solution and dilute to 1 l. prepare monthly.

c. *Standard sulphuric acid titrant, 0.02N*: Prepare and standardise as described in Alkalinity, Section 403.3*c* of Standard Methods **[APHA-AWWA-WCPF, 1975]**. For greatest accuracy, standardise the titrant against an amount of sodium carbonate that has been incorporated in the indicating boric acid solution to reproduce the actual conditions of the sample titration. If the acid is 0.02*N*, 1.00 ml = 280 μg/l.

4. Procedure.

a. Proceed as described in the preliminary distillation step (section 5.5A), using indicating boric acid solution as an absorbent for the distillate.

b. Titrate the ammonia in the distillate with standard sulphuric acid (0.02*N* H_2SO_4) titrant until the indicator turns a pale lavender.

c. *Blank.* Carry a blank through all the steps of the procedure and apply the necessary correction to the results.

d. Calculation

mg/l Ammonia N = [(A – B) x 280] / ml sample,

where, A = ml 0.02 N H_2SO_4 titration for sample and,

B = ml 0.02 N H_2SO_4 titration for blank (ammonia-free distilled water).

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