

**MODELING AND SIMULATION OF ION-EXCHANGE PROCESS  
FOR REMOVAL OF AMMONIUM FROM TREATED  
WASTEWATER USING ZEOLITE**

**A DISSERTATION**

*Submitted in partial fulfillment of the  
requirements for the award of the degree*

*of*

**MASTER OF TECHNOLOGY**

*in*

**CHEMICAL ENGINEERING**

**(With Specialization in Industrial Pollution Abatement)**

**By**

**BHAWNA SINGH**



**DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE  
ROORKEE - 247 667 (INDIA)  
JUNE, 2006**

## DECLARATION

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*I hereby declare that the work, presented in this thesis, entitled “Modeling and Simulation of Ion-Exchange process for removal of Ammonium from treated wastewater using Zeolite” in partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, IIT Roorkee, is an authentic record of my own work carried out from November 2005 to May 2006 under the guidance of Dr.Ing.W.Sternad IGB-Fraunhofer, Stuttgart and Dr.I.D.Mall Professor, Department of Chemical Engineering, IIT Roorkee.*

*The matter embodied in this thesis has not been submitted by me for the award of any other degree or diploma.*

**Date:** June 22, 2006

**Place:** Roorkee.


*Bhawna Singh*  
**(Bhawna Singh)**

## CERTIFICATE

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*This is to certify that the thesis entitled, "Modeling and Simulation of Ion-Exchange process for removal of Ammonium from treated wastewater using Zeolite" being submitted by Miss Bhawna Singh to the Indian Institute of Technology, Roorkee, for the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, is a record of bonafide research work carried out by her under our guidance and supervision and has fulfilled requirement for the submission of this thesis.*

*The results contained in this thesis are original and have not been submitted in part or full, to any other Institute for the award of any degree or diploma.*



**Dr.Ing. W. STERNAD** 3. 1. 05. 06  
Fraunhofer Institut für Grenzflächen-  
Bioverfahrenstechnik, 70569 Stuttgart,  
Germany

Fraunhofer-Institut für Grenzflächen-  
und Bioverfahrenstechnik (IGB)  
Nobelstraße 12  
70569 Stuttgart  
Telefon: +49 (0) 711/970-00  
Telefax: +49 (0) 711/970-4200  
<http://www.igb.fraunhofer.de>



**Dr. I.D.MALL**

Chemical Engineering Department  
Indian Institute of Technology, Roorkee 247667,  
India

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**Bhawna Singh**

## ABSTRACT

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Ammonium removal by ion exchange using natural zeolite has gained much attention within last 20 years. It has various advantages over the conventional biological nitrification-denitrification and air stripping techniques. Ion exchange is stable process, suits automation and quality control, and is easy to maintain. Land requirement with the ion-exchange process is relatively low, making the process, generally a much cheaper option.

The ion exchange kinetics shows a complex behavior. The possible rate controlling mechanisms could be film-diffusion control, particle-diffusion control, and chemical reaction control. When ion exchange is considered for use as an ammonium removal process extensive studies for the process kinetics, evaluation of the variables such as loading rate, contact time, etc. are required.

This thesis work is an effort to determine the reaction kinetics of the ion exchange process using clinoptilolite, a naturally occurring zeolite used for removal of ammonium from waste water and then to extend these results to pilot plant studies for forming a simple model. Evaluation of process is undertaken for ammonium removal ammonium chloride solution.

Equilibrium relationship for ammonium distribution has been determined in batch systems. Freundlich Isotherm is found to be more appropriate for the system giving the equilibrium relation as  $Q = 1.3477C_e^{0.3867}$ . Experiments showed that the process is very rapid and a contact time of 60 min is sufficient for quantitative removal of ammoniacal nitrogen. Also, by increasing the initial concentration of ammoniacal nitrogen, the removal efficiency quickly decreases.

Particle-diffusion is the rate controlling mechanism for the concentration of more than 30 mg/l  $\text{NH}_4\text{-N}$ , however under dilute concentrations the control shifts to film-diffusion controlling. Existing equation characterizing this process are used to predict the experiments.

A continuous system is then made and the physical column data are determined. The simplest model of Tank-in-series is evaluated for the system. Residence Time Distribution (RTD) study gives the approximation for the number of tanks and simple mass balance is used to model the continuous process.

## LIST OF SYMBOLS

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- $\alpha_{B/A}$  selectivity coefficient of B over A
- BOD<sub>5</sub>** biological oxygen demand (mg/l)
- C** ammonium concentration in solution (mg/l)
- C<sub>e</sub>** equilibrium ammonium concentration in solution (mg/l)
- C<sub>n</sub>** ammonium concentration in the liquid phase of the n<sup>th</sup> segment (mg/l)
- C<sub>n-1</sub>** ammonium concentration in the liquid phase of the (n-1)<sup>th</sup> segment (mg/l)
- COD** chemical oxygen demand (mg/l)
- d<sub>o</sub>** equivalent spherical diameter of the particle
- D** diffusion coefficient
- $\varepsilon$  packed bed porosity, and
- k** film mass transfer coefficient
- NH<sub>4</sub>-N** ammoniacal nitrogen
- N** number of ideal stirred tanks
- PMMA** polymethyl methacrylate
- Q** mass of ammonium per unit mass of zeolite (mg/g)
- Q\*** equilibrium mass of ammonium per unit mass of zeolite (mg/g)
- Q<sub>n</sub>** ammonium concentration in the solid phase of the n<sup>th</sup> segment (mg/g)
- r<sub>o</sub>** radius of particle
- $\rho$  packed bed density of the clinoptilolite (g/l)
- t** time
- $\theta$  dimensionless time based on the mean residence time in all N tanks
- U** volumetric flow rate of the solution (l/h)
- V** volume of each column segment (l)
- X** fractional equilibrium on clinoptilolite

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# CHAPTER 1

## INTRODUCTION

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Rapid population increase, decreasing assimilative capacity of water bodies, need for water conservation and growing public awareness in the maintenance of clean environment, bring the need for development of appropriate, cost effective and resource recovery based wastewater treatment systems. The principal objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment. Increasing stringency of effluent quality demands in time have led engineers to search for more effective designs for new plants and upgrades for existing facilities to assure compliance [Baykal et al., 1996].

Environmental problems such as algal blooms have highlighted the effect of excessive amounts of nutrients on natural water systems. The nutrients of concern are primarily nitrogen (ammonium ion and nitrate) and phosphorus (orthophosphate).

### 1.1 SOURCES OF NUTRIENT INPUT

These nutrients can reach water system from a variety of sources, including non-point sources such as agricultural runoff, and point sources such as wastewater treatment plant discharges. The ammoniacal nitrogen may be initially present in, for example, municipal or food industry wastewater, but may also be produced as a result of biological modifications of organic nitrogen during other treatment operations. The industrial context of this problem include oil refineries, coal gasification plants, slaughter houses, dairy plants, distilleries, fertilizer plants and pharmaceutical operations [Weatherley and Miladinovic, 2004].

The principal sources of nutrient input are from agriculture, sewage and atmospheric fallout [Kansal et al.].

#### 1.1.1 Nutrients from agriculture

The majority of nutrients that effect the water come from agriculture. Manure contains amongst other things, nitrogen in the form of nitrates and ammonia. This manure can get

flushed out of the earth and end up in the ground water, rivers and streams and take the nutrients with it. Finally, these nutrients end up in the sea.

### **1.1.2 Nutrients from sewage**

Sewage contains many nutrients, and a great deal of it ends up in the sea. Sewage is commonly delivered to a sewage plant where it is cleaned to varying degrees before it is released into the environment. The resulting sludge is often burnt or deposited in quarries. Some of the resulting sludge from the treatment process is used as fertilizer on arable land. One of the disadvantages with this method is that the sludge is often deposited on the fields at the wrong time of the year so the nutrients leak out into the groundwater and rivers and eventually out into the sea. The sludge also can contain traces of poisons that finally end up in agricultural products.

### **1.1.3 Nutrients in the atmosphere**

The air we breath contains about 80% nitrogen. Plants usually cannot absorb nitrogen directly from the atmosphere, but take it up in the form of ions. Therefore nitrogen in gas form does not directly result in over-fertilization. The blue-green bacteria have the ability to bind nitrogen gas from the atmosphere or decaying compounds into a nitrate. Air pollution is also another important factor. Automobile combustion and incineration in power plants enables the oxygen and nitrogen in the atmosphere to combine and form compounds of nitrogen oxide. These nitrogen oxides are deposited on the land, in rivers and lakes and directly into the sea, partly as dry deposits and partly as rain.

## **1.2 HAZARDS OF NITROGEN**

Nitrogen is a nutrient essential to all forms of life as a basic building block of plant and animal proteins. However, the presence of nitrogen excess in the environment has caused serious distortions of the natural nutrient cycle between the living world and the soil, water, and atmosphere [Rozic et al.,2000]. Ammonium nitrogen decreases the dissolved oxygen, required for the aquatic life and also accelerates the corrosion of metals and construction materials [Celik et al., 2001]. Ammonia at even low concentrations in the aquatic environment can be deleterious to fish and their physiological factors such as growth rate, oxygen consumption and disease resistance. For fish life, ammonium nitrogen concentration

must not be more than 1.5mg/l  $\text{NH}_4^+\text{-N}$  [Sarioglu, 2005]. The eutrophication of water bodies is also to be avoided, because it leads to algal mats and plentiful macrophyte growth, hampered light penetration, undesirable species and low species diversity. Nitrogen in the form of nitrous oxide, nitric oxide, nitrate, nitrite or ammonia/ammonium is soluble in water and can end up in ground water and drinking water [Rozic et al., 2000]. Therefore raw water with high ammonia concentration must be treated before it reaches the consumer and also wastewater before arriving at the receiving water.

### 1.3 WASTEWATER STANDARDS

#### 1.3.1 European Wastewater Standards [Riesen]

**Table 1.1 Normal Requirements**

Parameters	Concentration	Minimum reduction
BOD <sub>5</sub>	25 mg/l O <sub>2</sub>	70-90 %
COD	125 mg/l O <sub>2</sub>	75 %
Total Suspended Solids	35 mg/l	90 %

**Table 1.2 Requirement for discharges in sensitive areas**

Parameters	Concentration maximum	Minimum reduction
Total Phosphorus	2 mg/l P (10,000-100,000 PE) 1 mg/l P ( >100,000 PE)	80 %
Total Nitrogen	15 mg/l N ( 10,000-100,000 PE) 10 mg/l N ( >100,000 PE)	70-80 %

#### 1.3.2 Indian wastewater Standards

**Table 1.3 General standards for discharge (selected parameters)**

Parameter	Inland surface water	Public sewers
Suspended solids, mg/l	100	600
BOD <sub>5</sub> ,mg/l	30	350
COD,mg/l	250	
Ammonical nitrogen (as N),mg/l	50	50
Dissolved phosphates (as P),mg/l	5.0	5.0

**Table 1.4 Industrial Effluent standards (N & P)**

S.no.	Industry	Concentration (mg/l)
1.	Thermal Power Plants	Phosphate 5.0 mg/l
2.	Soda Ash Industry	Ammonical nitrogen, as N (mg/l) 50 Nitrate nitrogen, as N (mg/l) 10
3.	Small Scale Industry	Phosphate (as P) 5.0 mg/l Ammoniacal nitrogen (as N) 50 mg/l
4.	Pharmaceuticals Industry	Phosphate (as P) 5.0 mg/l
5.	Pesticide Industry	Nitrate as NO <sub>3</sub> 50mg/l Phosphate as P 5.0mg/l
6.	Organic Chemicals Manufacturing Industry	Nitrate (as N) 10mg/l
7.	Nitric acid Plant	Oxides of nitrogen-3 kg of oxides of nitrogen per tonne of weak acid
8.	Natural Rubber Processing Industry	Total Kjeldahl nitrogen (as N) 50mg/l Ammoniacal nitrogen (as N) 25mg/l
9.	Integrated Iron & Steel Plant	Ammonical Nitrogen 50mg/l
10.	Fertiliser Industry	Ammonical nitrogen 50mg/l Total kjeldahl nitrogen (TKN) 100mg/l Phosphate as P 5mg/l
11.	Electroplating Industry	Ammonical nitrogen (as N) 50mg/l

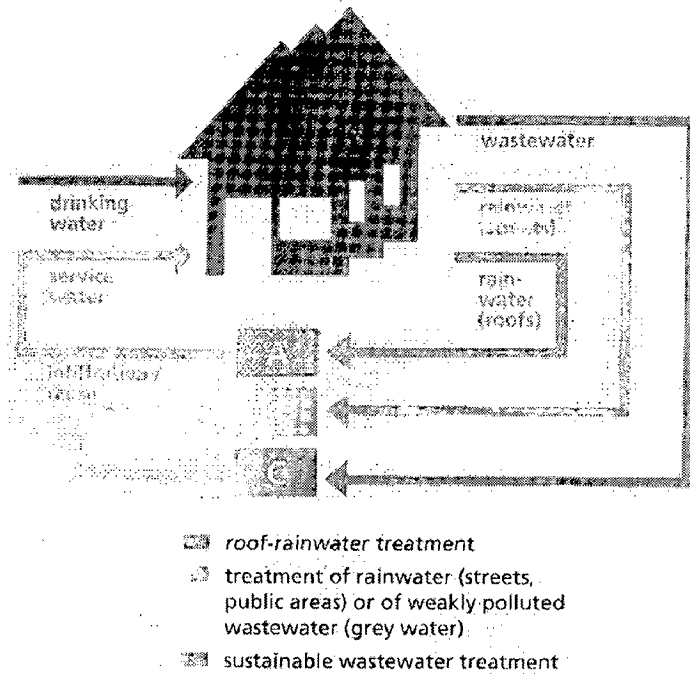
Source: [www.cpcb.nic.in](http://www.cpcb.nic.in)

#### 1.4 DECENTRALIZED WATER MANAGEMENT: DEUS 21 [Mohr, 2005]

On the newly built “Am Römerweg” estate in the Knittlingen district of Pforzheim, Germany, a form of municipal waste water management is being realized for an initial number of 350 citizens (ceremonial beginning on June 8, 2004). This is a new design of semi decentralized urban water and waste water management, firstly providing quality-assured rainwater utilization and secondly employing modern wastewater treatment technology with recovery of valuable substances (fig.1).

Rainwater from roof expanses and residential roads is collected, stored underground, processed and then supplied as utility water via a separate supply circuit. The collection and transportation of domestic wastewater is accomplished by means of a vacuum sewerage system. First of all, the incoming wastewater is separated using a rotating disk filter into a viscous concentrate stream and a solids-free filtrate stream. The concentrate stream is digested in a high-performance anaerobic stage with integrated micro filtration, producing biogas which is utilized as a regenerative energy source. From the digested filtrate water, the

nutrients that are present in relatively high concentration are recovered in an MAP (magnesium ammonium phosphate) precipitation procedure, the N/P fertilizer Struvit is produced, while in an ammonia stripping operation ammonium salt is formed which can be used as nitrogen fertilizer. The remaining organic load in the filtrate water after the anaerobic unit and the recycling stations is passed to the filtrate stream after the primary filtration. This filtrate stream is cleaned either by means of a membrane-supported aerobic technique with upstream denitrification, or by means of anaerobic methane digestion, from whose discharge the nutrients nitrogen and phosphorus are recovered.



**Fig.1: DEUS 21 water circulation**

### 1.5 OBJECTIVE

The present work focuses on the characterization of the kinetics in ion exchange. Existing equations characterizing the process were used to anticipate results of the experiments, which thus verified the model expressed by these equations. On this basis, a simulation of the ion exchange was composed, taking into account the influence of parameters e.g. Temperature, concentration of ammonium and contact time. To find correlations between the parameters and the exchange of ions, batch experiments were carried out. The simulation was then to be modified to describe the ion exchange in a column, similar to the one in which the ion exchange would be operated. This simulation would then help to optimize the operation of the ion exchange and dimensioning the process.



## CHAPTER 2

### LITERATURE REVIEW

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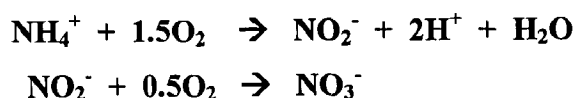
Considering the serious effects of excess ammonia concentration, there arises the need to remove it from the water stream. Further, considering that ammonia is also the main component of nitrogenous fertilizers and as the global demand for nitrogenous fertilizers is in constant rise, the need for recovery as well as removal of ammonia is well justified.

#### 2.1 METHODS OF NITROGEN REMOVAL

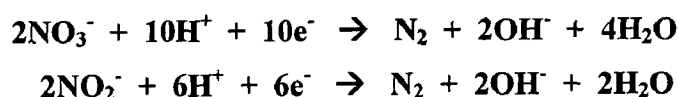
The main nitrogen removal processes are biological nitrification-denitrification, air stripping, chemical treatment and selective ion exchange.

##### 2.1.1. Biological Nitrification-denitrification [Peavy et al., 1985]

The removal involves aerobic nitrification by autotrophic bacteria, nitrosomonas and nitrobacter (i.e., the conversion of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  and further to  $\text{NO}_3^-$ ) with molecular oxygen as the electron acceptor.



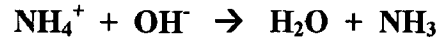
The anoxic denitrification is accomplished by heterotrophic bacteria (i.e., the conversion of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to gaseous nitrogen) with a variety of electron donors, including methanol, acetate, ethanol, lactate and glucose. The anoxic denitrification involves the following reactions:



The nitrification and denitrification processes have to be separated in time or space to function effectively because these are carried out under different conditions and by different microorganisms.

### 2.1.2 Air Stripping [EPA 832-F-00-019, 2000; Peavy et al., 1985]

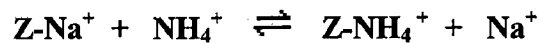
Ammonia (a weak base) reacts with water (a weak acid) to form ammonium hydroxide. In ammonia stripping, lime or caustic is added to the wastewater until the pH reaches 10.8 to 11.5 which converts ammonium hydroxide ions to ammonia gas.



The waste water stream containing ammonia gas is then dispersed in air, allowing the transfer of ammonia from the wastewater to the air.

### 2.1.3 Ion Exchange

Insoluble polyelectrolyte (e.g. zeolites) having free  $\text{Na}^+$  ions, reversibly interchange them with ammonium ions present in the surrounding solution. The ammonium ion is retained by association or chemical reaction with anionic groups in the solid.



The exchange of ions occurs until equilibrium is reached. The zeolite could then be regenerated with NaOH solution, and hence repeatedly used.

Various methods for nitrogen removal are tabulated in Table 2.1

## 2.2 ION EXCHANGE – A BETTER OPTION

Though biological nitrification-denitrification has demonstrated removal of  $\text{NH}_4^+\text{-N}$  down to very low levels, the process is sensitive to process disturbances (pH, temperature, and  $\text{NH}_4^+$  concentration). Also nitrogen peak loads cannot be handled successfully.

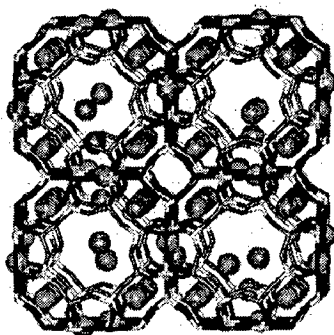
Physical systems like stripping can be used for ammonia removal especially for high loads of ammonia. However, the efficiency of the process of air stripping too is significantly impaired by the low temperature in winter. It is possible to decrease the ammonia level to 1mg/L using air stripping methods. But the requirement of using water over 15°C and carbonate deposition are the disadvantages of this method [Celik et al., 2001]. Also, air

pollution problems may result from ammonia and sulfur dioxide reaction [EPA 832-F-00-019, 2000].

Ammonium removal by ion exchange looks most attractive compared to other processes, when effective, low-cost materials (e.g. natural zeolite – clinoptilolite) are used as exchangers. Ion exchange is stable process, suits automation and quality control, and is easy to maintain [Celik et al., 2001]. Land requirement with the ion-exchange process is relatively low, making the process, generally a much cheaper option. The major problem in ion separations using zeolites is due to their solubility in aqueous media at extreme pH values. Zeolites are almost insoluble between pH 5.5 and 10 [Dorfner, 1991]. Ion-exchange therefore is more competitive because of little influence of the low temperature, taking up relatively little space, and particularly its relative simplicity of application and operation.

### 2.3 ZEOLITES

Zeolites are naturally occurring aluminosilicate minerals. Their structures are build from tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  units cross linked by sharing of oxygen atoms. These possess open frameworks characterized by networks of channels or pores yielding a very high specific surface area (fig.2).

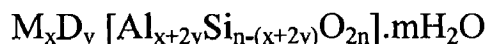


*Fig.2: Micro porous structure of zeolite [Bell, 2001]*

The limiting pore sizes are roughly between 3 and 10 Å in diameter. Largest cavity identified in zeolites is (in faujasite-type zeolite) 11.8 Å. The zeolite frameworks bear a negative charge created by partial substitution of Si by Al. The ion exchange capacity is inversely proportional to the silicon-aluminum ratio. There are enough metal cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Sr}^{2+}$ , present in the interstices of the aluminosilicate framework to make the crystal electrically neutral. Water molecules fill the remaining space in the

interstices of the framework. These alkali and alkaline earth metal cations have certain mobility within the zeolite structure and can be exchanged for other cations. There are more than 50 different natural zeolite types including clinoptilolite which has a high selectivity for ammonium ions [Sherry; Dorfner, 1991].

The general chemical formula of a zeolite is: [Sarioglu, 2005]

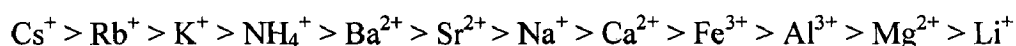


where M = Na<sup>+</sup>, K<sup>+</sup> or other monovalent cations, and D = Mg, Ca, Sr, Ba and other divalent cations.

Zeolites are stable with regard to high temperatures, oxidizing/reducing agents, ionizing radiations, physical attack by swelling, high pH levels.

The main features of zeolites are high level of ion exchange capacity, adsorption, porous structure, molecular sieve, dehydration and rehydration, low density and silica compounds. These are used in a variety of applications e.g. in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. [Bell, 2001]

Clinoptilolite is the most abundant natural zeolite that occurs in relatively large minerable sedimentary deposits in sufficiently high purity in many parts of the world e.g. in Japan, USA, Russia and Hungary.[Sarioglu, 2005] It belongs to the Heulandite group, with a three-dimensional framework of silicon and aluminum tetrahedral, having the typical chemical formula Na<sub>6</sub>[(AlO<sub>2</sub>)(SiO<sub>2</sub>)<sub>30</sub>].24H<sub>2</sub>O. Its maximum exchange capacity varies, having an upper limit of about 2.6 meq/g [Inglezakis et al., 2001]. In nature, the cations present on clinoptilolite are calcium, sodium and potassium. The general selectivity order of natural zeolite among cations is as follows: [Sarioglu, 2005]



The most suitable form of clinoptilolite for ammonium removal is found to be Na form.

**Table 2.1 Treatment methods for nitrogen removal**

S.no.	Method	Principle
1.	<b>Nitrification and Denitrification</b>	The process involves aerobic nitrification by autotrophic bacteria, nitrosomonas and nitrobacter (i.e., the conversion of $\text{NH}_4^+$ to $\text{NO}_2^-$ and further to $\text{NO}_3^-$ ) with molecular oxygen as the electron acceptor. The anoxic denitrification is accomplished by heterotrophic bacteria (i.e., the conversion of $\text{NO}_3^-$ and $\text{NO}_2^-$ to gaseous nitrogen) with a variety of electron donors, including methanol, acetate, ethanol, lactate and glucose.
2.	<b>Air Stripping</b>	In this process, lime or caustic is added to the wastewater until the pH reaches 10.8 to 11.5 which convert ammonium hydroxide ions to ammonia gas. Stream containing ammonia gas is then dispersed in air, allowing the transfer of ammonia from the wastewater to the air.
3.	<b>Ion Exchange</b>	Insoluble polyelectrolyte (e.g. zeolites) having free $\text{Na}^+$ ions, reversibly interchange them with ammonium ions present in the surrounding solution. The ammonium ion is retained by association or chemical reaction with anionic groups in the solid.
4.	<b>SHARON process</b>	This is a biological nitrification process and involves partial nitrification of ammonium to nitrite. which is converted to gaseous $\text{NO}$ , $\text{N}_2\text{O}$ and $\text{N}_2$ .
5.	<b>ANAMMOX process</b>	The anaerobic ammonium oxidation reaction is carried out by two ANAMMOX bacteria. Here, nitrite is the preferred electron acceptor and the main product of anaerobic ammonium oxidation is $\text{N}_2$ , about 10% of the N feed is converted to $\text{NO}_3^-$ .
6.	<b>Combined SHARON and ANAMMOX processes</b>	First, the wastewater containing ammonium is oxidized in the SHARON reactor to nitrite using only 50% of the influent ammonium. The effluent from SHARON reactor containing a mixture of ammonium and nitrite is ideally suited as the influent for the ANAMMOX process where ammonium and nitrite are anaerobically converted to dinitrogen gas and water.
7.	<b>CANON process</b>	This process is based on a partial nitrification and anoxic oxidation of ammonia. Under oxygen-limited condition, ammonium is oxidized to nitrite by aerobic nitrifiers, such as Nitrosomonas and Nitrososira, anaerobic ammonium oxidizers Planctomycete convert ammonium with the produced nitrite to dinitrogen gas and trace amounts of nitrate.
8.	<b>Struvite Crystallisation</b>	It is a techniques to remove and recover N and P by crystallization of N and P in the form of struvite. (magnesium ammonium phosphate or $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), The technique utilizes the addition of $\text{Mg}^{2+}$ ion, the usual limiting reactant in the formation of struvite, as the means for altering the solubility product equilibrium and initiating precipitation.

## **2.4 REMOVAL OF AMMONIUM BY ION EXCHANGE USING ZEOLITE**

Ammonium removal from aqueous solution by ion-exchange has been investigated by many researchers (Koon and Kaufman, 1975; Gaspard et al., 1983; Schoeman, 1986; Haralambous et al., 1992). Koon and Kaufman (1975) were concerned with ammonium removal from municipal wastewater by clinoptilolite. Gaspard et al. (1983) examined the ammonium removal characteristics from drinking water by clinoptilolite. Schoeman (1986) evaluated NH<sub>3</sub>-N removal from an underground mine-water by South African clinoptilolite (Pratley) and compared it with Hector clinoptilolite from the USA. Haralambous et al. (1992) compared natural and synthetic zeolites for ammonium removal from aqueous solution [Demir et al., 2002].

Komarowski & Yu [1997] conducted batch equilibrium and kinetics experiments for ammonium removal using natural Zeolite. They concluded that removal efficiency increases with higher initial ammonium ion concentration and is highest for pH 5.5. From kinetics experiments 90% of ammonium ion removal occurs within 10-15 minutes and equilibrium is reached within 1.5-2 hours. Baykal et al. [1996] investigated operating parameters like water velocity, contact times and effect of Desorption. Aiyuk et al. [2004] investigated the best size range applicable to treated domestic sewage and the dependence of the Zeolite ammonium removal efficiency and the flow rate/HRT. The optimum size ranges from 1-2 mm and 2-2.8 mm. Du et al. [2005] assessed the potential of natural Chinese clinoptilolite for ammonia removal from aqueous solution. In batch study, the effects of contact time, pH and initial ammonium concentration were determined. Baykal et al. [1994] proposed post equalization of peak ammonia loads in a filter with biological activity in combination with an ion exchanger. Gisvold et al. [2000] conducted experiments on a nitrifying biofilter with a Zeolite containing expanded clay aggregate filter media. Experiments indicated that the filter media performed very well at extreme peak loads of ammonium. Sarioglu [2005] carried out both batch and column experiments using naturally occurring Turkish Zeolite. The flow rates and the pH at which the highest adsorption capacities were obtained, were found to be 0.5 ml/min and 4 respectively. Sprynskyy et al. [2005] studied ammonium ion uptake from synthetic aqueous solutions onto raw and pretreated forms of the natural zeolite Transcarpathian clinoptilolite under dynamic conditions. Maximum sorption capacity evaluated under dynamic conditions varies in the interval 13.56-21.52 mg/g, being significantly higher than determined under static conditions. Weatherley et al. [2004] compared the uptake performances of the naturally

occurring zeolite, clinoptilolite and of New Zealand mordenite. The influence of other cations present in the water upon the ammonium uptake was also determined. Rozic et al. [2000] investigated the removal of nitrogen in the form of ammonium ions from aqueous solutions using natural clay and zeolite. The highest removal efficiency was found for the natural zeolite. Milan et al. [1997] studied the treatment of digested piggery manure in an anaerobic fixed bed reactor by ion exchange for ammonia removal using K-zeo, Mg-zeo, Na-zeo and Ca-zeo. Sodium homoionic zeolite followed by calcium homoionic zeolite gave the best results. Demir et al. [2002] investigated the factors affecting the ammonium exchange capacity including the zeolite's particle size, the loading flow rates and the impact of number of regenerations upon ion exchange capacity. Celik et al. [2001] conducted a series of fixed and fluidized bed ion exchange column runs to identify the ability of natural clay minerals, sepiolite and clinoptilolite, to remove ammonia from contaminated drinking water reservoir. Fluidized bed runs with clinoptilolite utilizing water and air as fluidizer resulted in inferior results compared to those of fixed bed runs. Nguyen et al. [1998] compared the capacity of two natural New Zealand zeolites (clinoptilolite and mordenite) to remove ammonium. Mordenite showed more effective ammonium removal than clinoptilolite for synthetic solutions containing high  $\text{NH}_4^+$ -N concentrations. Semmens et al. [1981] presented a very simple computer model capable of predicting the exchange behavior of natural clinoptilolite during service and regeneration. Cooney et al. [1999] designed and operated a pilot scale process to investigate the continuous removal of ammonia from sewage using natural zeolite from Australia. Application of rigorous model for solving overall rate equation closely predicted the ammonium breakthrough and elution profiles for the pilot zeolite column. Inglezakis et al. [2001] investigated the impact of operational and chemical conditions of pretreatment upon the effective capacity of clinoptilolite.

**Table 2.2 Studies on removal of Ammonium using various types of Zeolites**

References	Zeolite	Operation	Results and discussion
Komarowski & Qu, 1997	Australian natural zeolite	Batch study	Ammonium ion removal efficiency was less for wastewater effluent than for solutions of simple ammonium salts. Ammonium ion removal efficiency of natural zeolite depends on the solution characteristics such as initial ammonium ion concentration and pH. It increases with higher initial ammonium ion concentration and is highest for pH 5.5. The Freundlich adsorption model gives a better fit than the Langmuir model in the range of pH 4-7 suggesting lateral interactions between the adsorbed ions. From kinetic experiments 90% of ammonium ion removal occurs within 10-15 minutes and equilibrium is reached within 1.5 – 2 hours.
Baykal et al., 1996	Clinoptilolite	Column study	A contact time over 3 minutes was found to be suitable. Desorption during very low influent concentrations of ammonia following a high load period is demonstrated to be effective and owing to this phenomenon, at very low influent concentrations, effluent levels exceeding that of the influent may be observed. Further clinoptilolite may be used separately in a fixed column or it may be incorporated in filters where biological activity is enhanced. The latter has an additional benefit of further ammonia removal during very low influent ammonia concentrations.
Smith	Resins	Column study	Results of comparison study revealed that one resin yielded the best results. It was determined that lower levels of ammonia influent could be used. Heating the influent to 155 °F increased the volume throughput before breakout occurred. No benefit was achieved by adjusting the pH.
Aiyuk et al., 2004	Clinoptilolite	Column study	The dependence of the zeolite ammonium removal efficiency on the flow rate/hydraulic retention time (HRT) was also investigated. Comparing the chosen zeolite size to finer sizes showed that the finer particles added turbidity to the effluent and increased head loss. The optimum size ranges from 1-2 mm and 2-2.8 mm. From comparison with different flow rates it was found that Breakthrough occurred faster with higher flow rates, i.e. with lower HRTs, and the zeolite



Du et al., 2005	Chinese Clinoptilolite	Batch study	removal efficiency also decreased with higher flow rates. The results show that ammonia removal occurs rapidly within the first 20 min of contact time and the removal capacity of clinoptilolite increases with the increase of initial ammonia concentration. At pH of about 6.0 ammonia removals efficiency can achieve maximum. Column study showed that flow velocity can affect breakthrough capacity of clinoptilolite by changing the hydraulic retention time. Spent regeneration solution can be reused by air-stripping ammonia out of regeneration solution at pH 12-13.
Baykal et al., 1994	Filter media and Clinoptilolite	Column study	The results obtained indicated the dampening peaks of 2/5 times the average value.
Gisvold et al., 2000	Clay aggregate & Zeolite	Column study	Experiments on a nitrifying biofilter with a zeolite containing expanded clay aggregate filter media showed that it can serve as a biofilm carrier for nitrifying biomass as well as an ammonium ion exchanger at the same time. The experiments indicated that the filter media performed very well at extreme peak loads (2-3 times the normal) of ammonium. The ammonium sorbed during the peak was subsequently nitrified at lower loads when the nitrifying capacity was abundant.
Sarioglu, 2005	Turkish zeolite	Batch & Column study	Increasing initial ammonium nitrogen concentration increased the exchange capacity. The flow rates and the pH at which the highest adsorption capacities were obtained, were found to be 0.5 ml/min and 4 respectively. Further, the efficiency of natural zeolite could be increased through conditioning with Na.
Sprynskyy et al., 2005	Transcarpathian clinoptilolite	Column study	Maximum sorption capacity of the Transcarpathian clinoptilolite toward ammonium evaluated under dynamic conditions varies in the interval 13.56-21.52 mg/g, being significantly higher than determined under static conditions. The values of the sorption distribution coefficient and of the retardation factor of ammonium ion front movement were calculated as equal to 215-265 L/kg and 979-1107, respectively. Slowing of the filtration velocity of the initial solution and 12-hour breaks in the sorption process, resulted in improvement of ammonium sorption properties of the natural zeolite, which is probably connected with

Weatherley et al., 2004	Clinoptilolite & New Zealand Mordenite	Batch study	The influence of other cations present in water upon the ammonia uptake was also determined. Mordenite has better removal of ammonium ions for initial liquid concentration greater than 80 mg/L $N-NH_4^+$ . The presence of calcium ion had the most significant effect upon ammonium ion uptake, followed by potassium ion for the equivalent potassium concentration two times less than the calcium concentration. Magnesium ion had the least effect. The mordenite showed smaller reduction in ammonium ion uptake in the presence of the other cations when compared with clinoptilolite.
Rozić et al., 2000	Natural clay & Zeolite	Batch study	The highest removal efficiency was found for the natural zeolite. By increasing the initial concentration of ammoniacal nitrogen, the removal efficiency quickly decreases. Further, the ammoniacal nitrogen removal efficiency is higher for clays in a liquid colloidal state compared to the clays in a dry state.
Milan et al., 1997	K, Mg, Na and Ca forms of zeolite	Continuous study	Sodium homoionic zeolite, followed by calcium homoionic zeolite gave the best results. An increase in the bed height combined with a decrease in the relative flow rate represented the most effective combination to obtain the highest ammonia nitrogen removal.
Demir et al., 2002	Clinoptilolite	Batch & Continuous study	The results indicated that conditioning of the zeolite improves the ion-exchange capacity and that the smaller particle size also causes a higher ion-exchange capacity due to greater available surface area.
Celik et al., 2001	Sepiolite & Clinoptilolite	Continuous study	Clinoptilolite gave superior results than sepiolite. Fluidized bed runs with clinoptilolite utilizing water and air as fluidizer resulted in inferior results compared to those of fixed bed runs. Furthermore, regenerated clinoptilolite was found to be capable of removing ammonia from both synthetic and actual raw

				water at much higher rate than the untreated clinoptilolite.
Nguyen et al., 1998	Clinoptilolite & Mordenite	Batch & Continuous study		Mordenite showed more effective ammonium removal than clinoptilolite for synthetic solutions containing high $\text{NH}_4^+$ concentrations. Also, fine zeolites were more effective than the coarse zeolites in removing wastewater $\text{NH}_4^+$ even after receiving 64 BV of wastewater.
Semmens et al., 1981	Zeolite	Continuous study		Model could evaluate the impact of alternative regeneration conditions on ammonium removal performance during service, etc.
Cooney et al., 1999	Australian zeolite	Continuous study		Application of a rigorous model for solving overall rate equation closely predicted the ammonium breakthrough and elution profiles for the pilot zeolite column. Continuous chemical regeneration effectively restored the exchange sites back to the sodium form. Also, the repeated loading and regeneration cycles were found not to reveal any deterioration of ammonium removal performance.
Inglezakis et al., 2001	Clinoptilolite	Continuous study		An optimal flow rate and a minimum concentration were determined, for a pretreatment that leads to a high effective capacity of the material, while pH adjustment did not result in a higher effective capacity and one washing with 10 Bed Volumes after pretreatment was found to be sufficient.

# CHAPTER 3

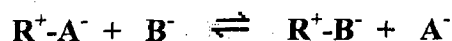
## ION EXCHANGE

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Ion Exchange is a separation process in which the insoluble polyelectrolytes having free ions reversibly interchange them with ions in the surrounding solutions. The solute is retained by association or chemical reaction with ionic groups in the solid. A cation exchanger has negative anionic sites with cations  $A^+$  electrostatically bound but free to undergo exchange with cations  $B^+$  [Dorfner, 1991].



Correspondingly for anion exchanger,



Ion exchange process if left to itself, reaches a state of equilibrium.

### 3.1 ION EXCHANGE EQUILIBRIA

Since ion exchange processes are stoichiometric and reversible, so whenever an ion exchanger is brought into contact with an aqueous solution containing a counterion different from that initially bound to the resin, an exchange of ions occur until equilibrium is reached. Because in ion exchange reactions equivalent amounts of ions participate, the law of mass action describes ion exchange quite adequately [Dorfner, 1991].



apparent exchange constant  $K$  (equilibrium constant)

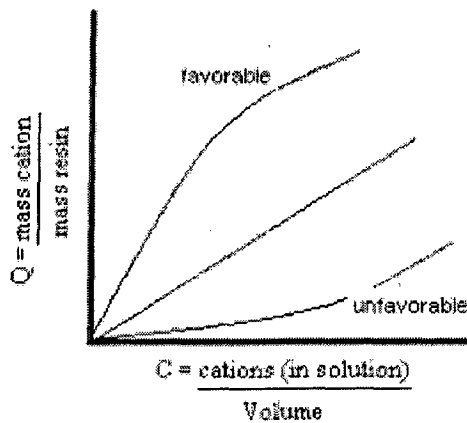
$$K = \frac{[R-B^+][A^+]}{[R-A^+][B^+]}$$

Considering the exchange of univalent ions, the selectivity coefficient is given by,

$$K_A^B = \frac{Y_B(1-X_B)}{X^B(1-Y_B)} = \alpha_{B/A}$$

where, Y and X gives the fraction on zeolite and in solution respectively.

The results of selectivity measurements in ion exchange are illustrated as isotherms with the mass of one of the competing cations in zeolite on y-axis and the mass of same cation in the solution on x-axis. The shape of the curve is significant and factors heavily into design. "Favorable" isotherms permit higher solid loadings at lower solution concentrations.



**Fig.3: Ion-Exchange isotherms**

Several fits have been proposed for isotherms. A linear isotherm seems to work for very dilute solutions, but not for many others. The *Langmuir model* hypothesis assumes the homogenous distribution of exchange sites and without interaction between the exchanged molecules. The *Freundlich model* suggests the energetic distribution of the sites is heterogeneous and describes physical adsorption from liquids [Komarowski & Yu, 1997]

For the ion exchange of ammonium ion on zeolite, isotherms give the amount of the equilibrium concentration of ammonium ion exchanged onto the zeolite per gram of zeolite, Q (mg NH<sub>4</sub><sup>+</sup>-N / g zeolite) as a function of the equilibrium concentration of ammonium ion in bulk solution, C<sub>e</sub>.

### 3.1.1 Langmuir Isotherm

The Langmuir isotherm relates  $Q$  (mg of ammonia adsorbed per gm of zeolite) and  $C_e$  (equilibrium ammonium concentration in solution) as shown:

$$Q = \frac{kbC_e}{(1 + kC_e)}$$

Rearranging the Langmuir equation gives a linear equation,

$$\frac{1}{Q} = \frac{1}{kbC_e} + \frac{1}{b}$$

where,

$Q$  is the amount of ammonium adsorbed per unit weight of zeolite;

$C_e$  is the equilibrium concentration of ammonium in the solution;

$k$  and  $b$  are the constants

### 3.1.2 Freundlich Isotherm

The Freundlich equation is written as,

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

The Freundlich equation can be rearranged to the linear form by taking logarithms on both sides:

$$\log Q = \log k + \frac{1}{n} \log C_e$$

where,

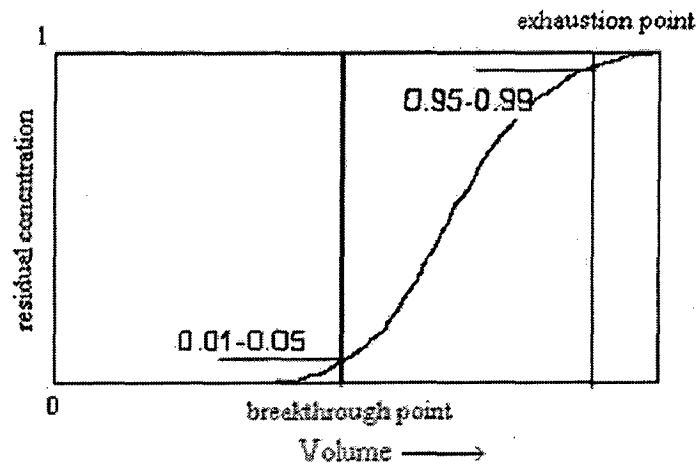
$Q$  is the amount of ammonium adsorbed per unit weight of clinoptilolite;

$C_e$  is the equilibrium concentration of ammonium in the solution;

$k$  and  $n$  are the empirical constants ( $n > 1$ )

### 3.2 BREAKTHROUGH CURVES

Ion exchange is a transient process. The amount of material exchanged within a bed depends both on position and time. Consider the time dependence. As fluid enters the bed, it comes in contact with the first few layers of resin. Counterions exchange occurs, soon the resin near the entrance is saturated and the fluid penetrates farther into the bed before all counterions are exchanged. Thus the active region shifts down through the bed as time goes on. When the exchange of one species of counterion for another in an ion-exchange column reaches a point where new counterions are no longer exchanged, the *breakthrough* occurs [Dorfner, 1991]. Usually, a *breakpoint composition* is set to be the maximum amount of counterion that can be acceptably lost, typically something between 1 and 5 percent.



**Fig.4: Breakthrough Curve**

Breakthrough capacity is the characteristic for a column. The concentration, column length, time, column volume or the volume of solution flowing through the column at constant flow rate can be used as the coordinates of breakthrough curves [Dorfner, 1991].

### 3.3 ION EXCHANGE KINETICS [Helfferich; Dorfner, 1991]

The counter ion species moving from the ion-exchanger into the solution be designated as 'A' and that moving from the solution into the ion-exchanger as species 'B'. In an exchange of counterions A and B, species B must migrate from the solution into the interior of the ion exchanger and species A must migrate from the exchanger into the solution. The rate controlling step was first shown by 'Boyd et.al' to be diffusion either in ion-

exchanger particle itself or in an adherent stagnant liquid layer called the film, in an intermediate range of conditions both mechanisms may effect the rate.

In film model, first introduced by Nernst, a completely stagnant film with a sharp boundary separating it from the completely mixed solution is assumed. Although, a low solution concentration favours film-diffusion control, but it alone does not determines the rate controlling step. The best method for distinguishing between particle and film diffusion control is by '*Interruption tests*' in which the ion-exchange reaction is stopped by removing the particles from the solution for a short period of time, only with particle-diffusion control is the exchange rate higher upon reimmersion than at the moment of interruption, because internal concentration gradients have had time to level out.

Two other possible rate-controlling steps could be passage through the particle solution interface and chemical reaction at the fixed ionic groups, but these are never yet conclusively demonstrated.

Rate of ion-exchange is the information about fractional attainment of equilibrium as a function of time.

### 3.3.1 Particle diffusion control

It assumes that the counterion concentration in the ion-exchanger is very low than the concentration of exchanging counterions in the solution. '*Linear driving force*' approach gives rate as proportional to the system's distance from the equilibrium.

$$\frac{-d \langle C_A \rangle}{dt} = k_p (\langle C_A \rangle - C_A^*)$$

where,

$\langle C_A \rangle$  is the concentration in the ion exchanger

$C_A^*$  is the concentration which the ion exchanger would have if it were in equilibrium with the solution

$k_p \approx D / 0.07 r_0^2$ , D being the diffusion coefficient and  $r_0$  is the particle radius.

For particle diffusion control, the linear driving force equation is much less satisfactory.



An even better approximation to the flux equation is obtained with Vermeulen's 'quadratic-driving-force' relation.

$$\frac{d \langle C_B \rangle}{dt} = \frac{D\pi^2}{r_o^2} \frac{(C_B^{*2} - \langle C_B \rangle^2)}{2 \langle C_B^2 \rangle}$$

where,

$\langle C_B \rangle$  is the counterion concentration in the ion exchanger

$C_B^*$  is the counterions concentration which the ion exchanger would have if it were in equilibrium with the solution.

The fractional conversion of resin is given by,

$$X = \left[ 1 - \exp\left(-\frac{D\pi^2 t}{r_o^2}\right) \right]^{1/2}$$

rearranging above equation,

$$-\ln(1 - X^2) = t \left( \frac{D\pi^2}{r_o^2} \right)$$

The most convenient way to verify this model for a system is to plot time against calculated values for  $-\ln(1-X^2)$  for given X values.

Quadratic driving force approach too has its weaknesses. Firstly, the effective diffusion coefficient D is presumed to be constant, and this is not the case in ion exchange. Secondly, it assumes that the momentary rate is function of solution's concentration and average interparticle concentration. In reality, the momentary rate depends not only on how much A and b is there in the particle, but also on how it is distributed.

### 3.3.2 Film diffusion control

Film diffusion can be approximated by the linear driving force equation, which assumes that equilibrium exists at all times at the fluid-particle interface.

$$\frac{d \langle C_B \rangle}{dt} = k_1(\langle C_A \rangle - C_A^*) = k_2(C_B^* - \langle C_B \rangle)$$

This equation can be solved to give the fractional conversion of resin X as function of time,

$$X = 1 - \exp\left(\frac{-3DCt}{r_o \delta \bar{C}}\right)$$

where,

$\delta$  is the film thickness

C is counterion concentration and  $\bar{C}$  is the concentration in particle.

Since X is a function of the variable, the time required to attain any given conversion is inversely proportional to the diffusion coefficient of the counterions, solution concentration, and is proportional to the particle radius, the film thickness and the concentration of the fixed ionic groups in the particle.

### 3.3.3 Intermediate case

The limit between particle and film diffusion control is not sharp. Rather, if the dimensionless parameter,

$$\frac{\bar{C}D\delta}{CDr_o} (5 + 2\alpha_{A/B}) \approx 1$$

both diffusion steps will affect the rate. It is even possible for an ion-exchange process to switch from predominantly film diffusion control to predominantly particle-diffusion control as exchange progresses.

### 3.3.4 Chemical rate equations

One approach consists in considering ion exchange as formally analogous to a reversible or irreversible chemical reaction of one or the other kinetic order. The most widely used equation of this type is the second order rate law.

$$-\frac{d\langle C_A \rangle}{dt} = k(C_B \langle C_A \rangle - \alpha_{A/B} C_A \langle C_B \rangle)$$

Once it became known that ion exchange is controlled by diffusion rather than by chemical reaction, the rate coefficient  $k$  in above equation was considered to be an '*overall mass transfer coefficient*' and was presumed to be related to film and particle mass transfer coefficients by virtue of additive resistances to the diffusion in two phases. However, unless the equilibrium isotherm is linear, the concept of additive diffusion resistances fails and one single over-all coefficient cannot account for the kinetic behaviour.

### 3.4 ION EXCHANGE OPERATIONS [Dorfner, 1991]

#### 3.4.1 Batch Operation

Batch operation is the simplest ion exchange process. The ion exchanger is contacted with the electrolyte solution in any suitable vessel with stirring or shaking until an exchange equilibrium has been established between the counterions of the exchanger and the ions of the electrolyte. The degree to which this process takes place depends upon the equilibrium constant of the ion exchange system.

#### 3.4.2 Column Operation

It is the most common and most frequently used ion exchange technique. The ion exchanger is packed in column, usually made of glass, and all necessary operations are carried out in the bed. The flow can be descending or ascending. The particular processes of ion exchanger in one cycle are:

- Ion exchange or exhaustion
- Washing of the exchanger bed
- Regeneration or elution

#### 3.4.3 Continuous Operation

Here the exchanger and liquid usually move in counter current columns. The exhausted part of the ion exchanger is continuously removed, with regeneration being performed immediately. In fluidized bed, contactor is designed to operate continuously by transferring the resin from stage to stage down column, while feed flow continues. Resin is

removed from column on time basis that is consistent with the rate of loading to equilibrium in each stage.

### **3.5 DESIGN REQUIREMENTS [Dorfner, 1991]**

The design requirement for ion exchange process plant and equipment are:

- The apparatus must ensure good contact between the resin phase and process solution at all times:
- The residence time of the resin must be much larger than that of process solution.
- To ensure low capital cost and compact plant design, the solution residence times should be short.
- Plant design should ensure efficient sorption, washing and regeneration of the resin to avoid unnecessary reagent loss and solution contamination.
- Mechanical stress must be avoided to prevent abrasion and fracture of ion exchanger polymeric material

# CHAPTER 4

## MATERIALS AND METHODS

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### 4.1 MATERIALS

**Reagents:** All chemicals used in the study were analytical grade reagents. All solutions and dilutions were made using distilled water. Ammonium nitrogen concentration in solution was analyzed by Dr. Lange's LCK 303 and LCK 304 tests.

**Clinoptilolite:** Clinoptilolite for the study was obtained from Daum-Import and Export, Isernhagen-Germany.

### 4.2 EXPERIMENTAL PROGRAMME

#### 4.2.1 Batch Study

Batch Experiments were performed in 250mL flasks. For each batch tests, the clinoptilolite sample of known size range (1-3mm) was accurately weighed. Stock solution of known ammonium concentration was prepared using analytical-grade  $\text{NH}_4\text{Cl}$  powder dissolved in deionized water. Experiments were conducted with ammonium concentration ranging from 2 mg/l  $\text{NH}_4\text{-N}$  to 90 mg/l  $\text{NH}_4\text{-N}$ . For each different concentration solution, the required volume of stock solution was mixed with the deionized water. A known volume of solution was placed in each batch test. The vessels were shaken at 90rpm, using a Kottermann shaker.

At time zero the clinoptilolite was introduced to the test flasks, and the timer was started. Micropipettes were used to extract known volumes of samples at known time intervals over the course of the tests. (Table 5.5 – 5.11) An experiment was also, conducted with different clinoptilolite mass to solution volume ratio, to verify the model. 2g (2.018g) of clinoptilolite was added and shaken with 100 ml of solution. 0.20 ml of solution was withdrawn at each sampling. (Table 5.34)

#### 4.2.2 Ion exchange isotherms

Isotherm for batch system was determined in 250 mL closed conical flasks. Weighed amounts (1 g) of clinoptilolite were introduced into each conical flask, to which 100 mL of ammonium chloride solution with concentrations of between 10 and 150  $\text{NH}_4^+\text{-N}$  mg/L were

added. The flasks were then closed using parafilm. The conical flasks were shaken for over 48 hours at 20°C. The final ammonium concentrations remaining in solution were analyzed. (Table 5.1)

#### **4.2.3 Kinetic Study**

Batch experiments were performed to determine the kinetics of Ion-exchange. Waste water of concentration about 70mg/l NH<sub>4</sub>-N was taken. Measured amount of clinoptilolite was added to known volume of waste water and the vessel was shaken. Concentration of ammonium was noted at the definite time intervals. (Table 4.1- 4.4)

#### **4.2.4 Column Study**

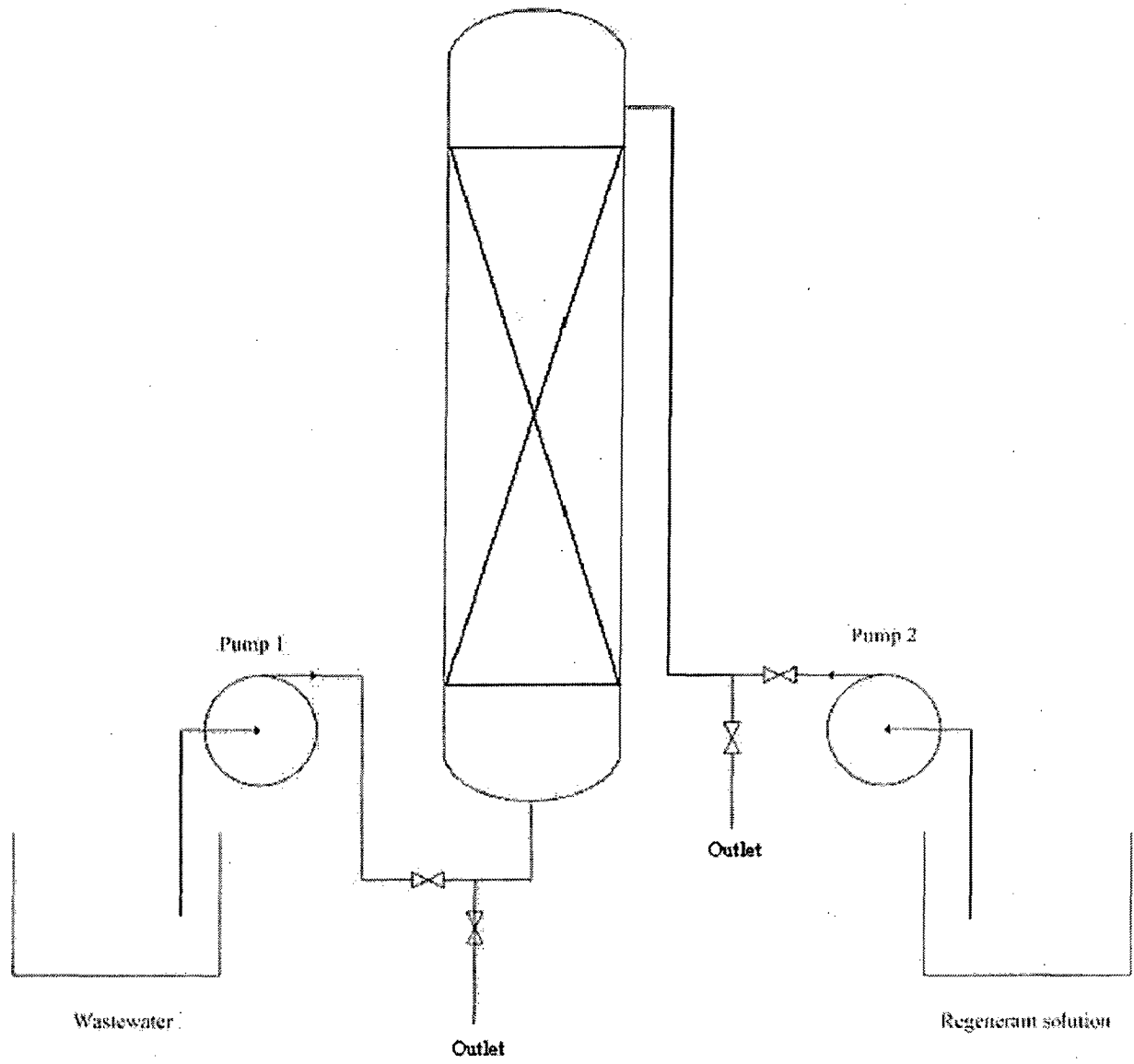
A pilot scale column 110mm in diameter and 125mm in height was fabricated for continuous adsorption of ammonium from waste water. The column was fabricated from PMMA.

The base of the column was fitted with a perforated steel support plate. A polypropylene sheet of 0.2mm mesh was placed over the steel plate to prevent the clinoptilolite being lost through the holes in the base plate. Outlets were positioned along the total column height. The inlet/outlet points were positioned at the top and bottom. The top point was raised above the top of the bed such that the bed was always fully immersed. In the column, 210g of coarse clinoptilolite (4-6mm diameter) was used to support the clinoptilolite bed. About 7.9kg of 1-3mm diameter clinoptilolite was loaded in the column. Backwashing was done to remove the finer sized particles from the bed.

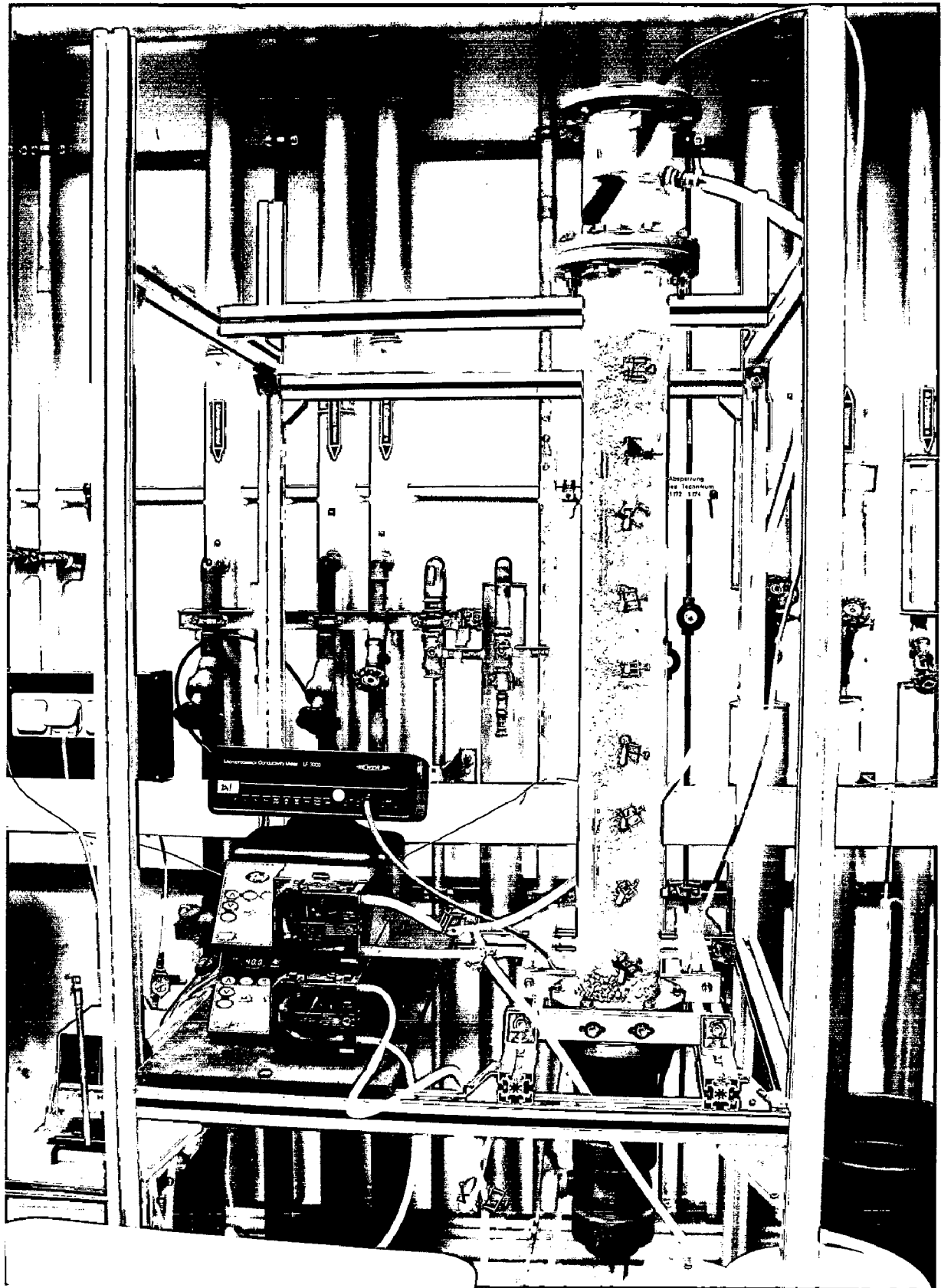
The flow lines for the column were arranged to make upflow loading and downflow regeneration. Two separate Watson Marlow 505U pumps were installed for loading and regeneration. WTW LF3000 conductivity meter was installed to measure the conductivity of the solution.

#### **4.2.5 Residence Time Distribution**

Step input of measured conductivity was introduced to the column at 30 rpm and the exit conductivity rise was measured. Mean residence time in the column was noticed. The output F curves were plotted for the experiments. (Table 6.1-Table 6.2)



**Fig.5: Pilot-scale process flow sheet**



**Fig.6: Pilot plant for ammonium removal**



# CHAPTER 5

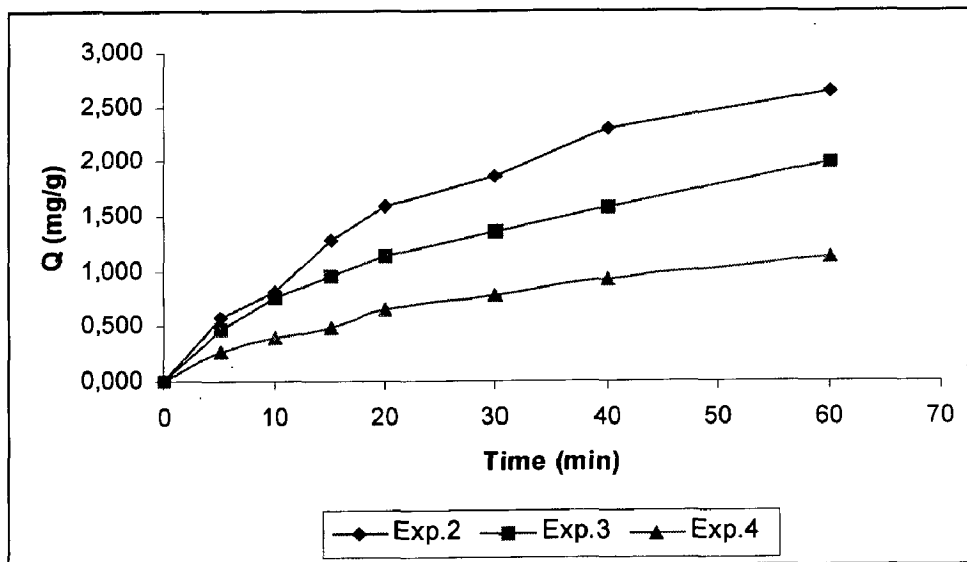
## RESULTS AND DISCUSSIONS

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include:

- Effect of contact time
- Effect of initial ammonium concentration
- Ion exchange isotherm
- Kinetic study
- Batch modeling
- Residence time distribution
- Column modeling

### 5.1 EFFECT OF CONTACT TIME

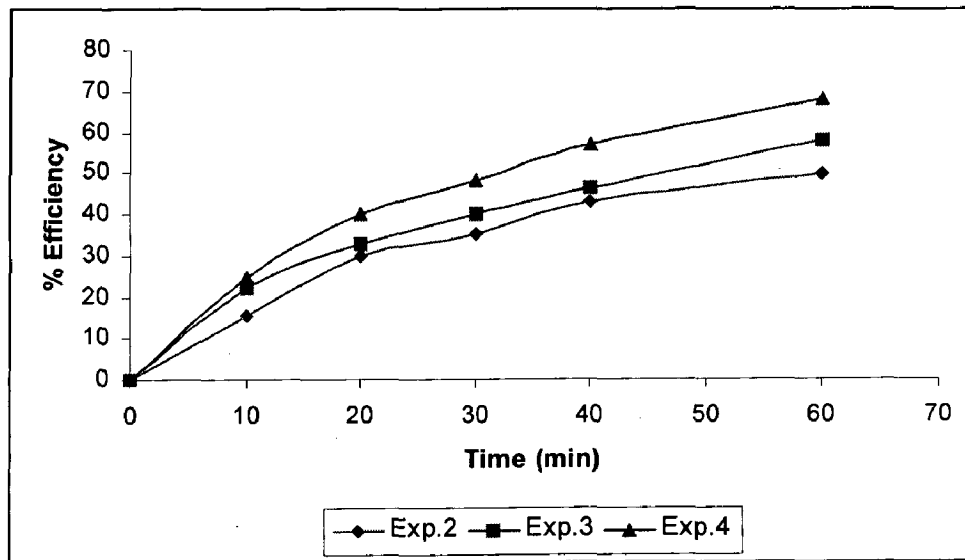
Experimental data revealed that the removal of ammoniacal nitrogen by clinoptilolite was a very rapid process. A stirring time of 60 min was sufficient for quantitative removal of ammoniacal nitrogen. The rate of removal was high for first 20 min and then reduces rapidly as the concentration approached to the equilibrium.



*Fig 5.1 : Q (mg/g) versus Time*

## 5.2 EFFECT OF INITIAL AMMONIUM CONCENTRATION

A maximal ammoniacal nitrogen removal efficiency was achieved at the smallest initial concentration. By increasing the initial concentration of ammoniacal nitrogen, the removal efficiency quickly decreases (Table 5.13). After 60 min, about 50% of ammonium was removed from solution with 90 mg/l NH<sub>4</sub>-N initial concentration, 58% from 46.20mg/l initial concentration solution, and 68% from 18.32mg/l NH<sub>4</sub>-N initial concentration solution.



**Fig 5.2 : % efficiency versus time for different initial concentrations**

## 5.3 ION EXCHANGE ISOTHERM

The Langmuir Isotherm is given by the following equation:

$$Q = \frac{k \cdot b \cdot C_e}{(1 + k \cdot C_e)}$$

where,

Q is the amount of ammonium per unit weight of clinoptilolite (mg/g)

C<sub>e</sub> is the ammonium ion concentration (mg/l) in solution at equilibrium,

b (mg/g zeolite) is the loading capacity, and

k is a constant ( l/mg).

Rearranging the Langmuir equation in a linear form gives,

$$\frac{1}{Q} = \frac{1}{k \cdot b \cdot C_e} + \frac{1}{b}$$

Plotting the experimental data (Table 5.2) using the above equation gives the Langmuir model parameters for best fit as:  $b = 7.6453$  mg/g,

$$k = 0.0979,$$

$$R^2 = 0.986 \text{ (correlation coefficient)}$$

Thus, the Langmuir isotherm for ammonium removal on the clinoptilolite can be represented by the following empirical formula:

$$Q = \frac{0.7485}{1 + 0.0979C_e}$$

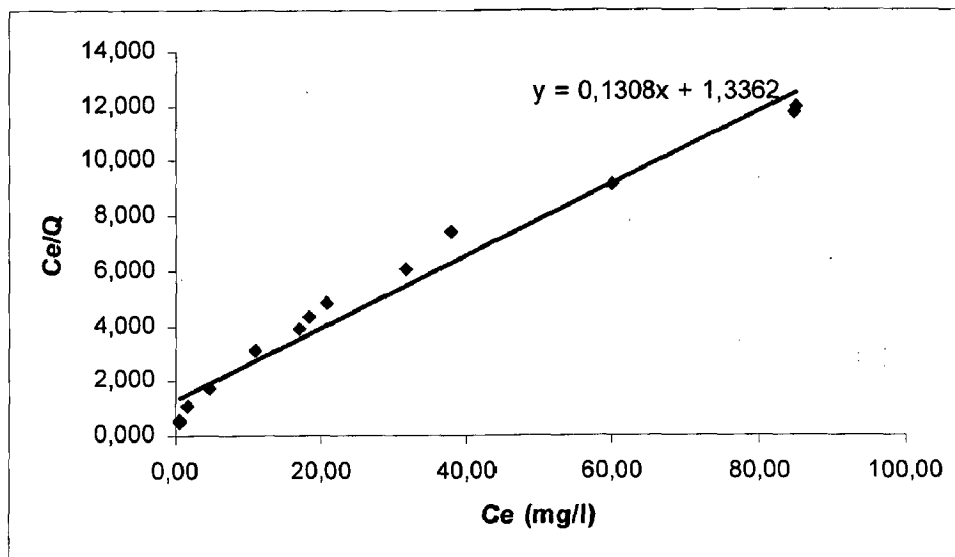


Fig5.3 : C<sub>e</sub>/Q versus C<sub>e</sub>

The Freundlich Isotherm is given by the following equation :

$$Q = k \cdot C_e^{1/n}$$

where,

Q is the amount of ammonium per unit weight of clinoptilolite (mg/g),

$C_e$  is the equilibrium concentration of ammonium in the solution (mg/l),

$K$  and  $n$  are the empirical constants ( $n > 1$ )

Rearranging the Freundlich equation in a linear form gives,

$$\log Q = \log k + \frac{1}{n} \log C_e$$

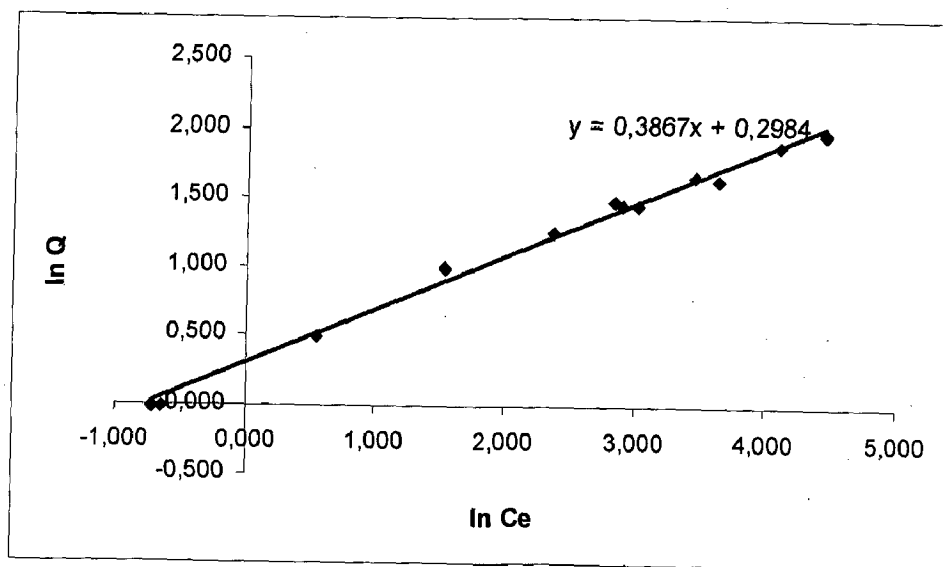
Plotting the experimental data (Table 5.3) using the above equation gives the Freundlich model parameters for best fit as:  $K = 1.3477$ ,

$$1/n = 0.3867, \text{ and}$$

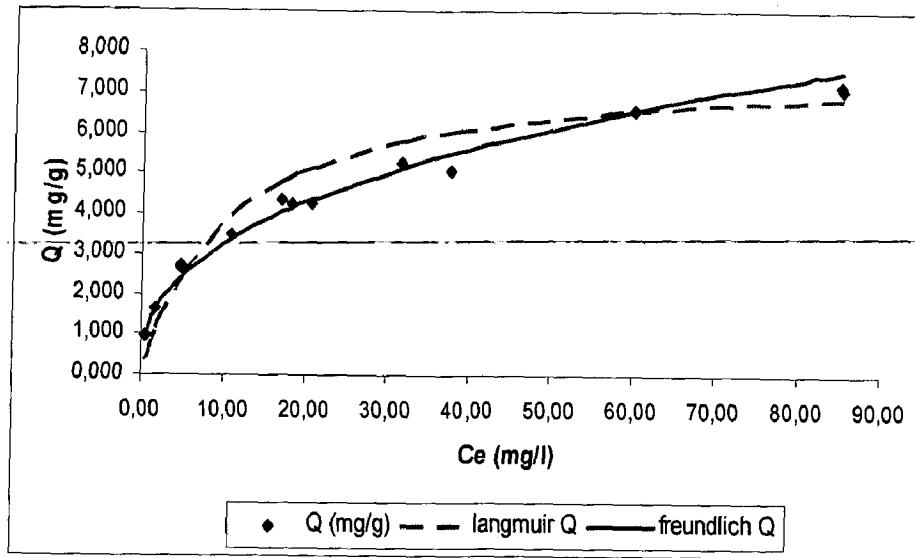
$$R^2 = 0.996 \text{ (correlation coefficient)}$$

Thus, the Freundlich isotherm for ammonium removal on the raw clinoptilolite can be represented by the following empirical formula:

$$Q = 1.3477C_e^{0.3867}$$



*Fig 5.4 : ln Q versus ln C<sub>e</sub>*



**Fig5.5 : Comparison of Langmuir and Freundlich Isotherms**

Comparing the equilibrium values (Table 5.4) obtained from both Langmuir and Freundlich Isotherms, shows that Freundlich model gives better fit to data.

#### 5.4 KINETIC STUDY

The kinetics of ammonium ion exchange using zeolite may be dividing into five steps. [Cooney et al., 1999]

1. Diffusion of counterions through the film solution to the surface of the zeolite (film diffusion).
2. Diffusion of the counterions within the zeolite (particle phase diffusion).
3. Chemical reaction between the counterions and the ion-exchange sites.
4. Diffusion of the displaced ions out of the zeolite.
5. Diffusion of the displaced ions from the zeolite surface into the bulk solution.

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

Conventional ion-exchange model for particle diffusion control for the analysis of clinoptilolite was used. Vermeulen's model for fractional attainment of equilibrium X, given particle diffusion control gives,

$$-\ln(1 - X^2) = t \left( \frac{D\pi^2}{r_o^2} \right)$$

where,

$D$  = diffusion coefficient,

$t$  = time, and

$r_o$  = radius of particle

Values of  $-\ln(1 - X^2)$  for given  $X$  values ( Table 5.14) against time were plotted and hence the diffusion coefficient  $D$  was found as the slope of the line. ( $X$  was based on experimental equilibrium value).

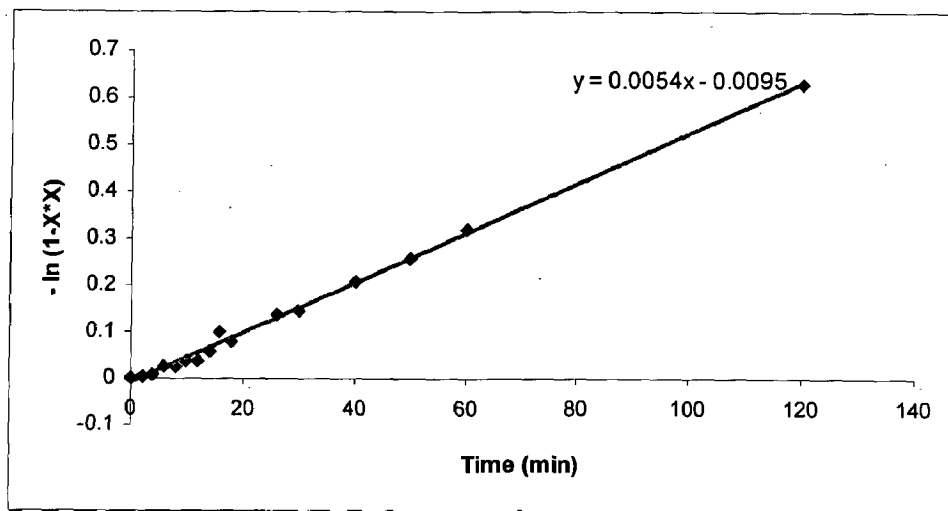


Fig 5.7 :  $-\ln(1 - X^2)$  versus time to find  $D_p$

slope obtained is  $D\pi^2 / r_o^2$  also radius of clinoptilolite particles as found from sieve experiments conducted earlier is 0.5mm. Thus, the diffusion coefficient  $D$  is obtained as,

$$D = 0.0054 r_p^2 / \pi^2$$

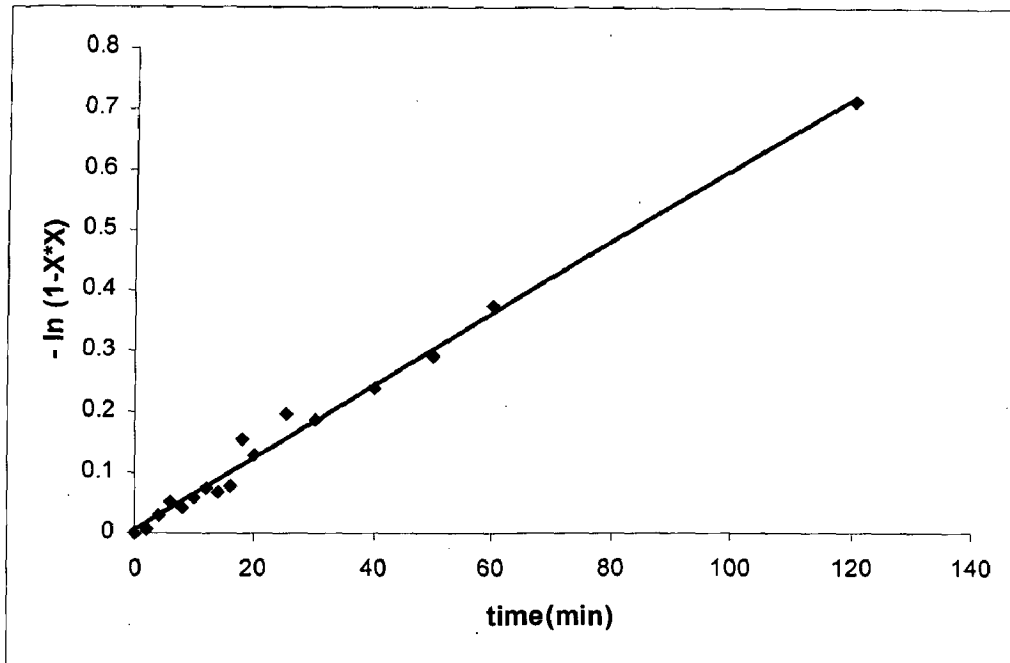
$$= 2.28 \times 10^{-12} \text{ m}^2/\text{s}$$

thus, the mathematical equation giving the process can be written as,

$$\frac{dQ}{dt} = 0.0054 \left( \frac{Q^* - Q}{2Q} \right)$$

$$-\ln(1 - X^2) = t \left( \frac{D\pi^2}{r_o^2} \right)$$

The model was verified by plotting time against calculated values for  $-\ln(1-X^2)$  for given X values for experiment 4.4 (Table 4.5).



**Fig5.6: Verification of Vermeulen's model**

The data fits well to the approximation, verifying the particle diffusion as controlling mechanism for the uptake of ammonia.

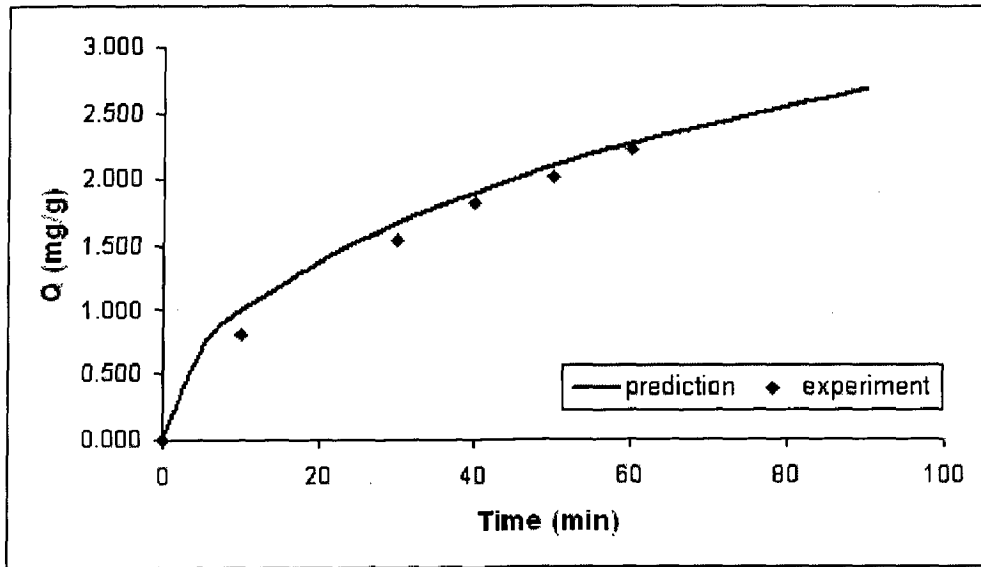
## **5.5 BATCH MODELING**

### **5.5.1 MODEL I: VERMEULEN's MODEL**

Kinetic study on waste water shows that the particle diffusion is the rate controlling mechanism for the exchange of ammonium ions from  $\text{NH}_4\text{Cl}$  solutions onto clinoptilolite. By Vermeulen's model for particle diffusion control, the fractional attainment of equilibrium X, is given by

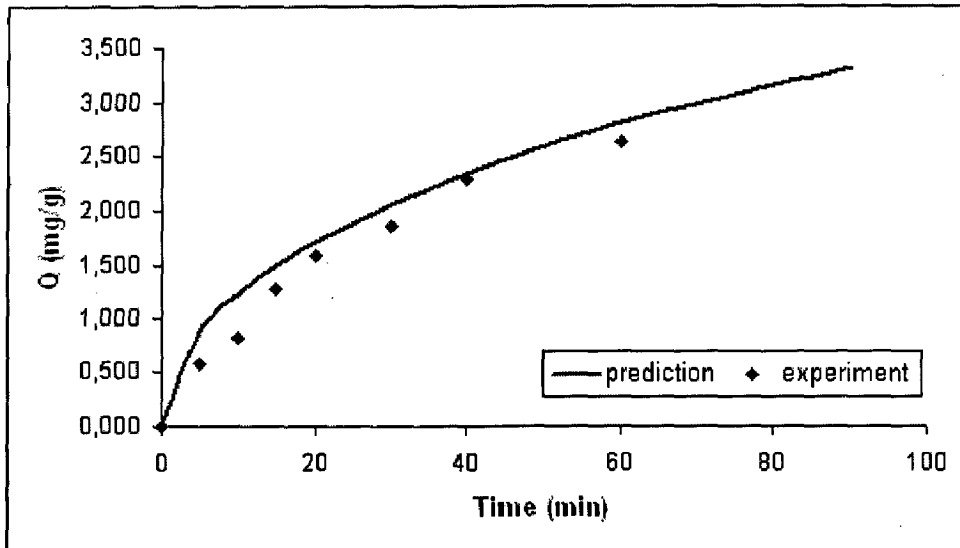
Comparing the experimental values with the solutions given by above mathematical equation, for various experiments is as,

**Experiment 1: (Table 5.15)**



**Fig 5.8 : Predicted and actual Q versus time**

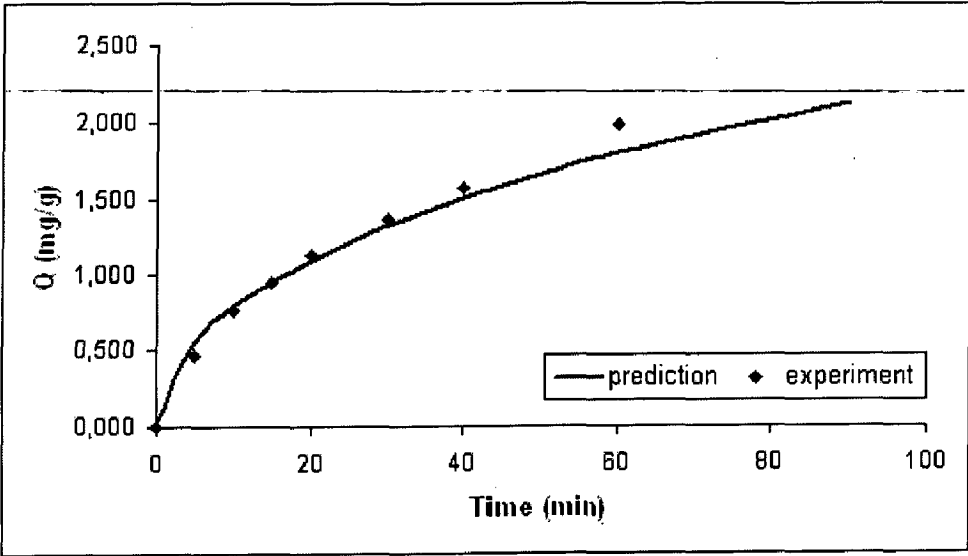
**Experiment 2: (Table 5.16)**



**Fig 5.9: Predicted and actual Q versus time**

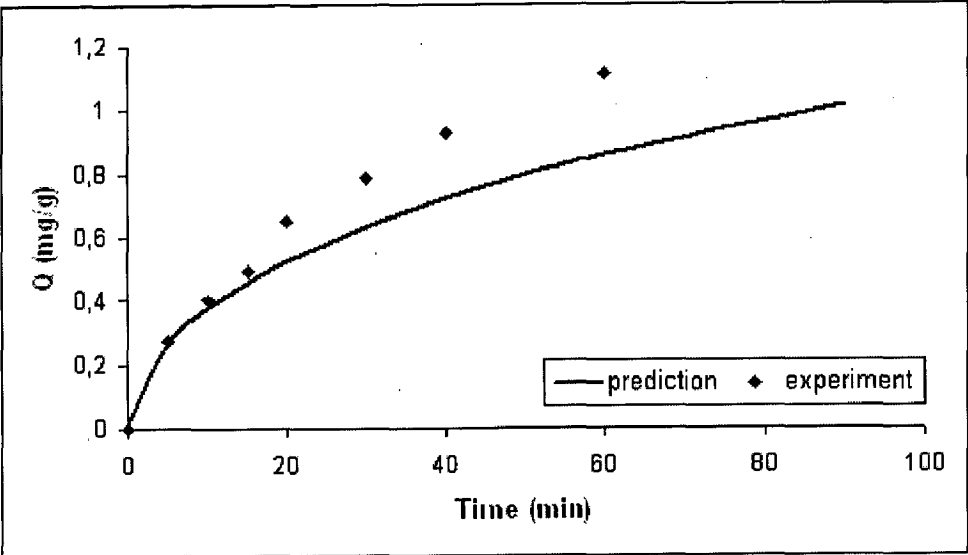


**Experiment 3: (Table 5.17)**



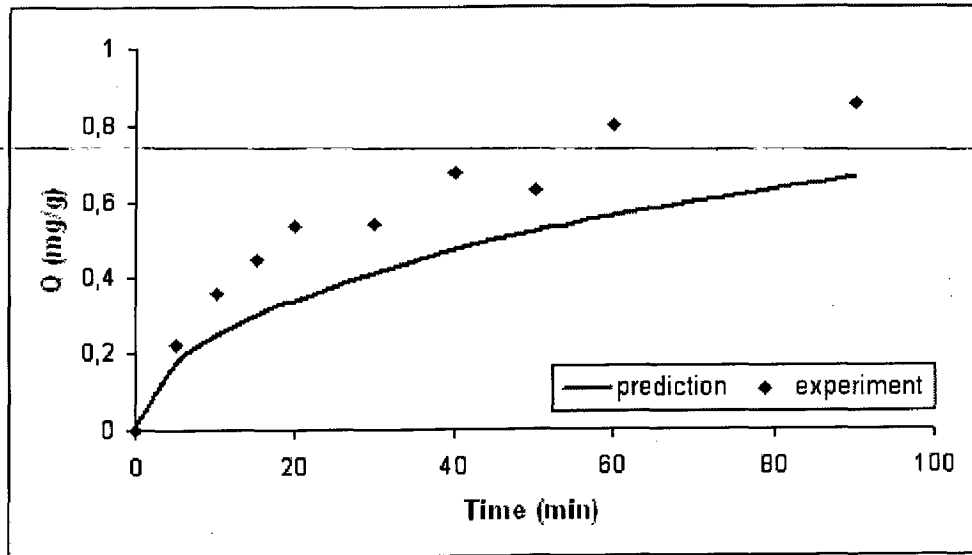
**Fig 5.10 : Predicted and actual Q versus time**

**Experiment 4: (Table 5.18)**



**Fig5.11 : Predicted and actual Q versus time**

### Experiment 5: (Table 5.19)



**Fig 5.12 : Predicted and actual Q versus time**

Comparison shows that the model fits reasonably well for the higher concentration range, but fails for concentration less than 30 mg/l NH<sub>4</sub>-N in solution.

#### 5.5.2 MODEL II : GLUECKAUF & COATES MODEL

This is a simple linear driving force equation widely employed for particle diffusion. It can be written as

$$\frac{dQ}{dt} = 60 \left( \frac{D}{d_o^2} \right) (Q^* - Q)$$

Here, the fractional attainment of equilibrium X, is given by

$$-\ln(1 - X) = t \left( \frac{60D}{d_o^2} \right)$$

where,

D = solid phase diffusivity of the ammonium ions,

t = time, and

d<sub>o</sub> = equivalent spherical diameter of particle

Plotting values of  $-\ln(1-X)$  for given X values (Table 5.20) against time gives diffusion coefficient D as the slope of the line. ( X is based on experimental equilibrium value).

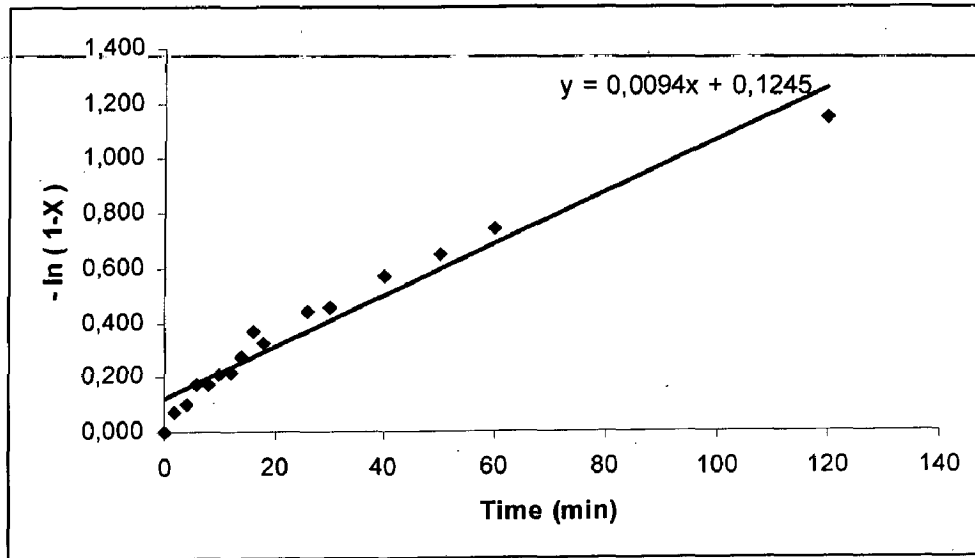


Fig 5.13 :  $-\ln(1-X)$  versus time to find D

slope obtained is  $60 D/ d_0^2$  and also diameter of clinoptilolite particles as found from sieve experiments conducted earlier is 1.0mm. Thus, the diffusion coefficient D is obtained as,

$$D = 0.0094 d_p^2 / 60$$

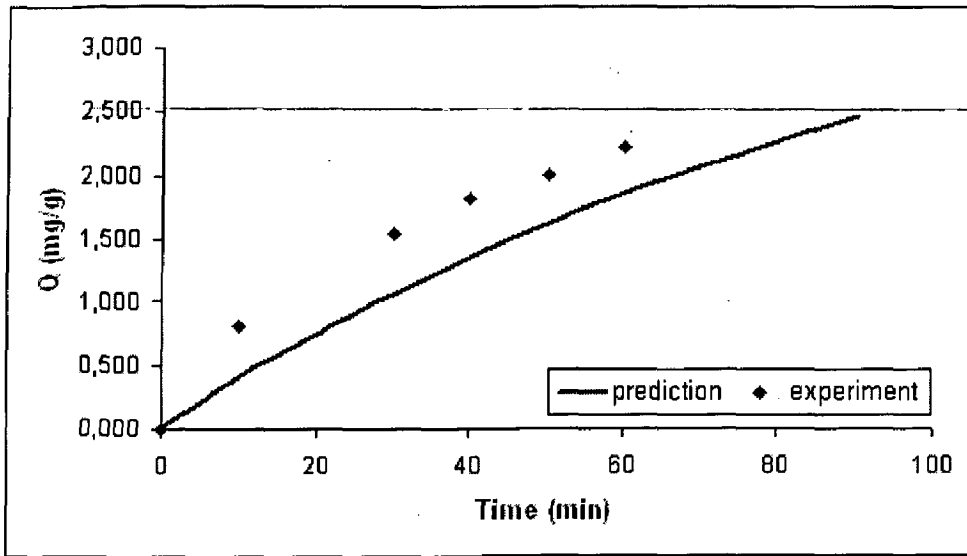
$$= 2.61 \times 10^{-12} \text{ m}^2/\text{s}$$

Thus, the mathematical equation giving the process can be written as,

$$\frac{dQ}{dt} = 0.0094(Q^* - Q)$$

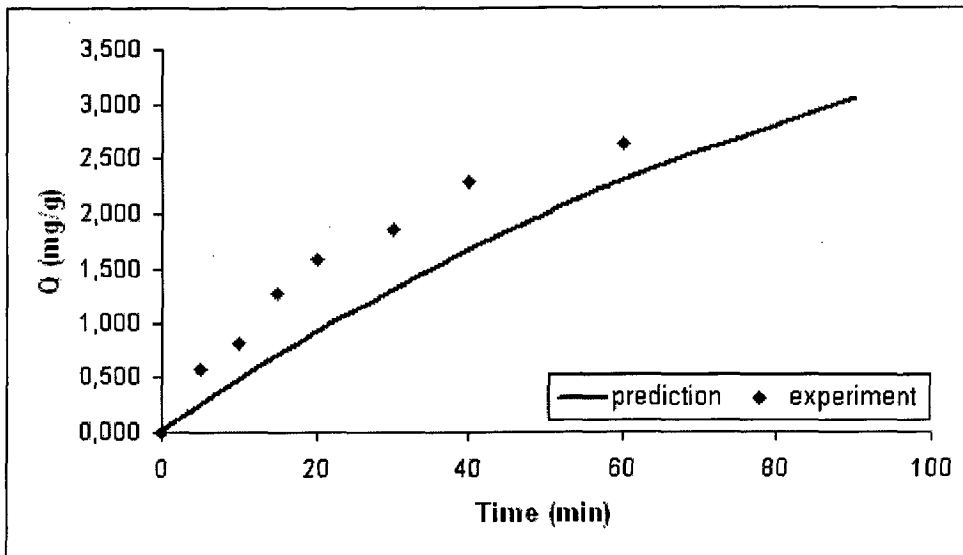
Comparing the experimental values with the solutions given by above mathematical equation, for various experiments is as,

**Experiment 1: (Table 5.21)**



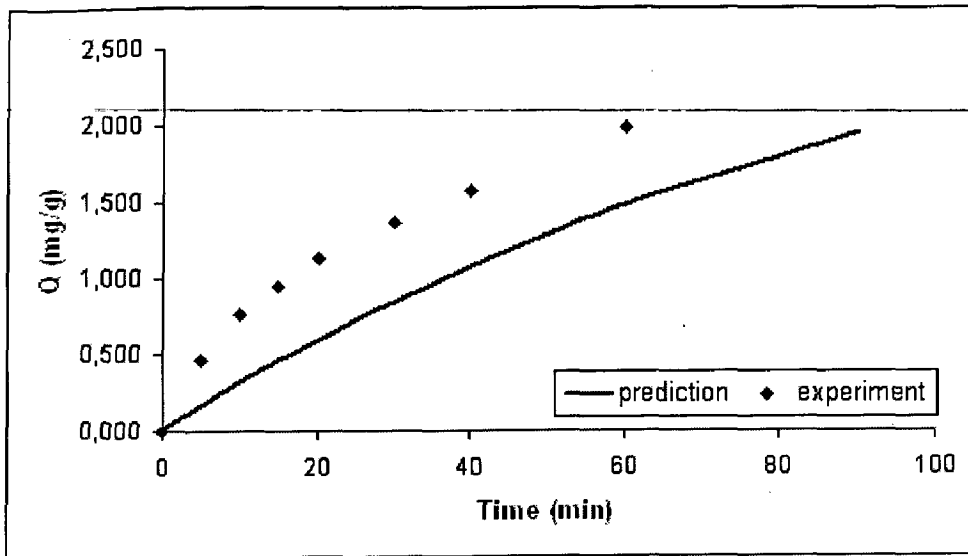
**Fig 5.14 : Predicted and actual Q versus time**

**Experiment 2: (Table 5.22)**



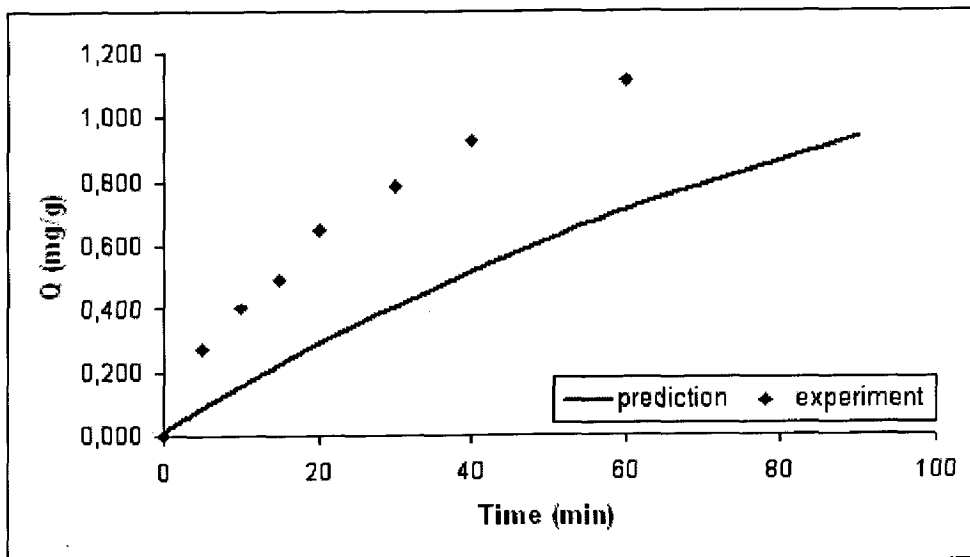
**Fig 5.15 : Predicted and actual Q versus time**

**Experiment 3: (Table 5.23)**



**Fig 5.16 : Predicted and actual Q versus time**

**Experiment 4: (Table 5.24)**



**Fig 5.17 : Predicted and actual Q versus time**

### Experiment 5: (Table 5.25)

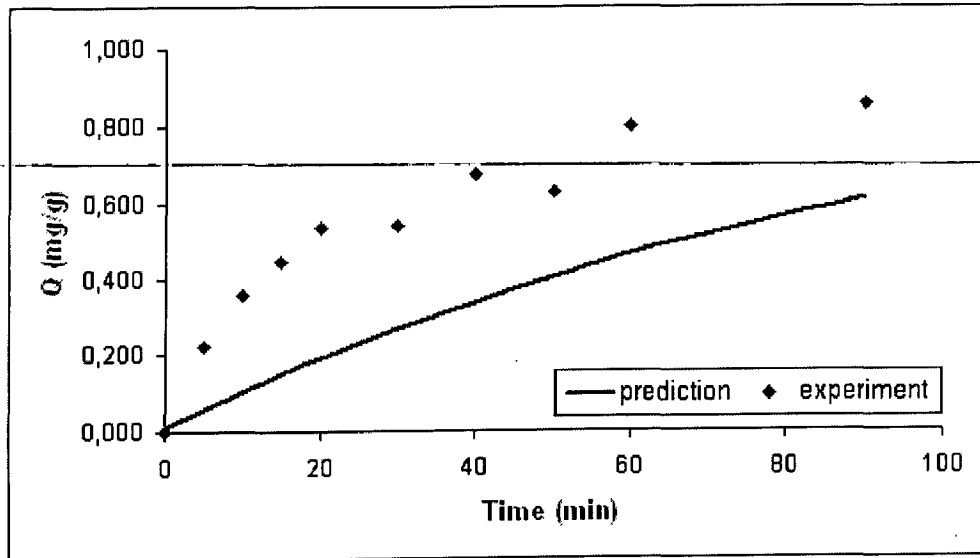


Fig 5.18 : Predicted and actual Q versus time

Comparison shows that the model does not give a better fit.

### 5.5.3 MODEL III : FILM DIFFUSION MODEL

It can be approximated by the linear driving force equation, which assumes that equilibrium exists at all times at the fluid-particle interface. It can be written as

$$\frac{dC}{dt} = k_1(Q - Q^*) = k_2(C^* - C)$$

Here, the fractional attainment of equilibrium  $X$ , is given by

$$-\ln(1 - X) = kt$$

where,

$k$  = film mass transfer constant

$t$  = time

As the film diffusion occurs at low concentration, so mass transfer coefficient was obtained from experimental data of the lowest initial concentration experiment (Experiment 7)

conducted. Plotting values of  $-\ln(1-X)$  for given X values (Table 5.26) against time gives 'k' as the slope of the line.

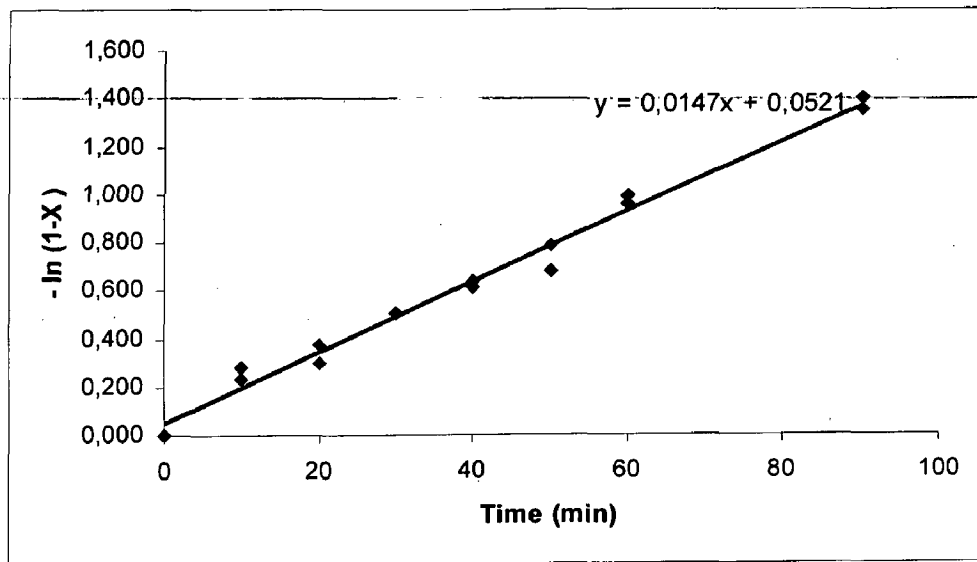


Fig 5.19 :  $-\ln(1-X)$  versus time to find k

slope obtained is mass transfer coefficient k,

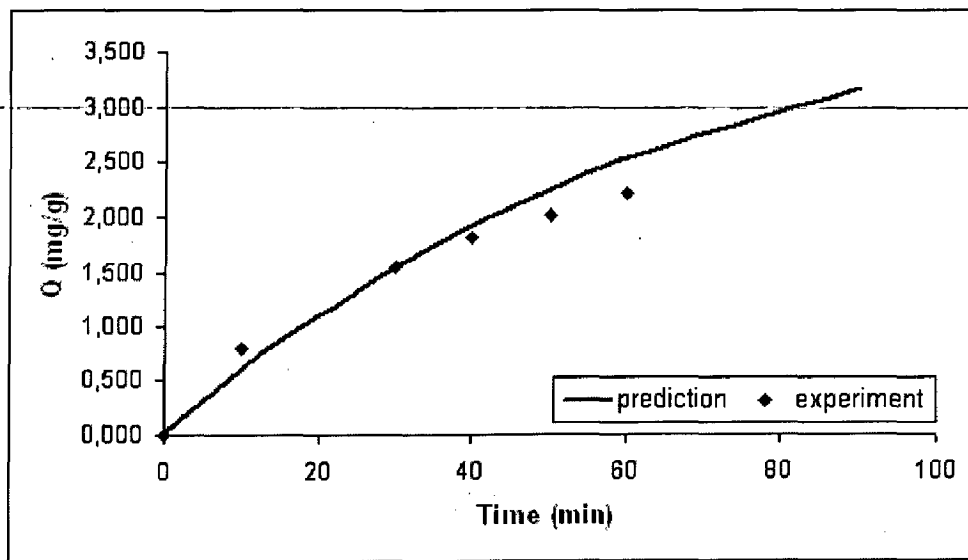
$$k = 0.0147 \text{ s}^{-1}$$

thus the mathematical equation giving the process can be written as,

$$\frac{dQ}{dt} = 0.0147(Q^* - Q)$$

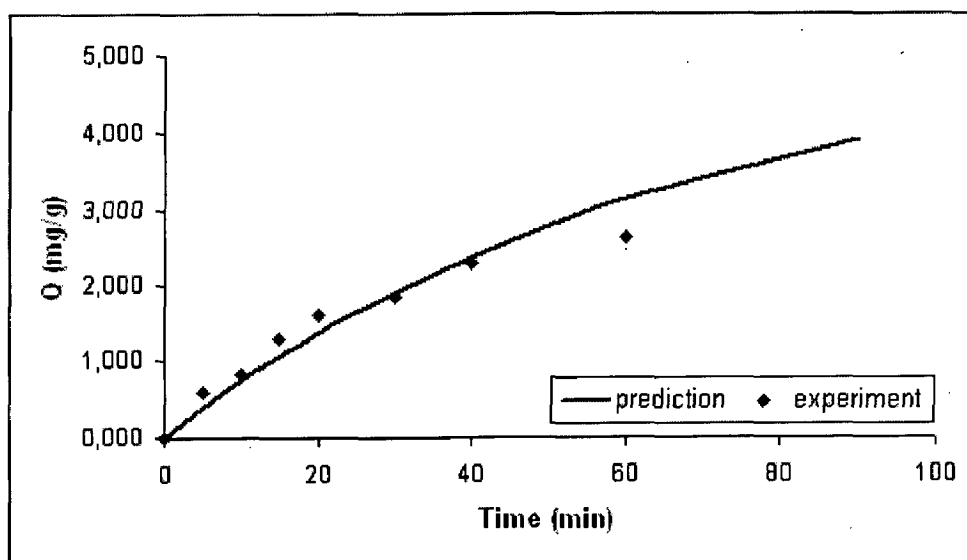
Comparing the experimental values with the solutions given by above mathematical equation, for various experiments is as,

**Experiment 1: (Table 5.27)**



**Fig 5.20 : Predicted and actual Q versus time**

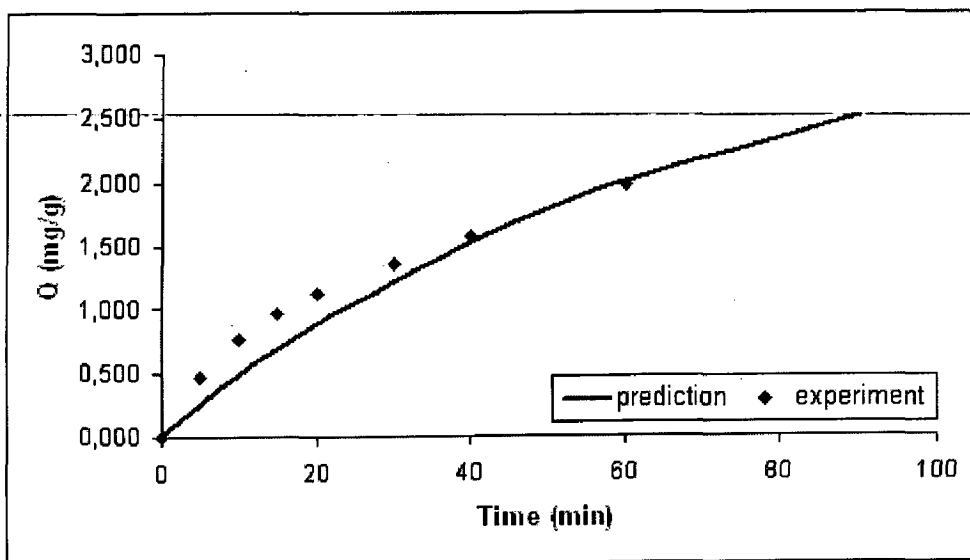
**Experiment 2: (Table 5.28)**



**Fig 5.21 : Predicted and actual Q versus time**

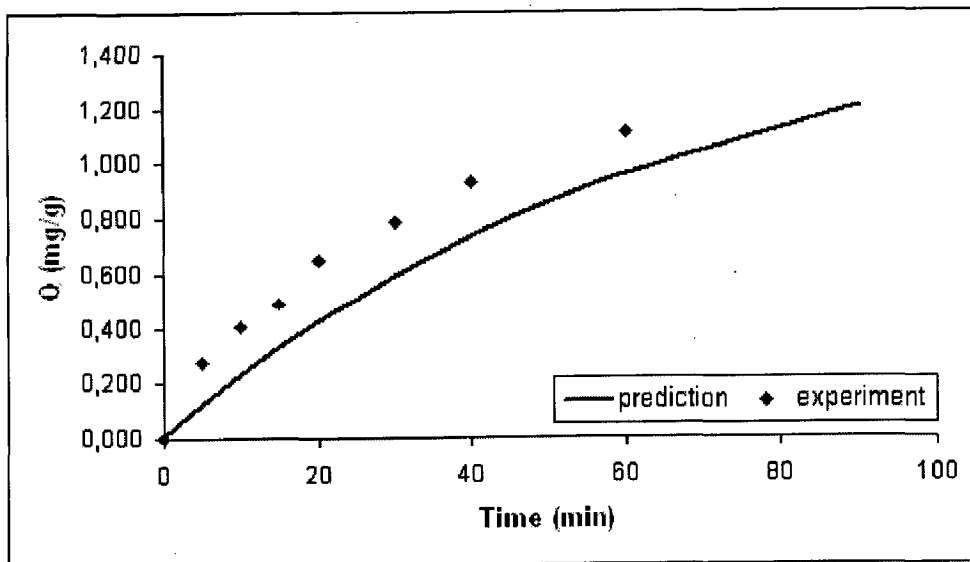


**Experiment 3: (Table 5.29)**



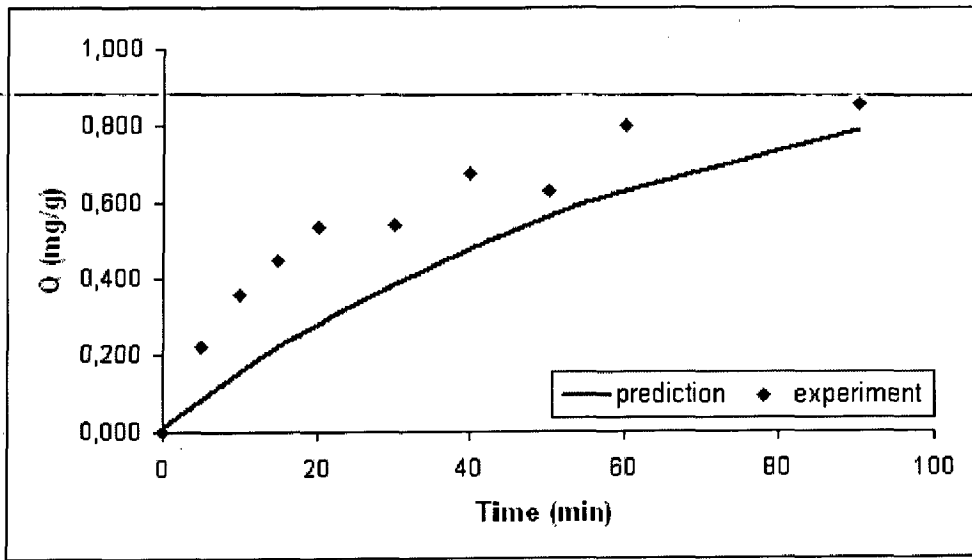
**Fig 5.22 : Predicted and actual Q versus time**

**Experiment 4: (Table 5.30)**



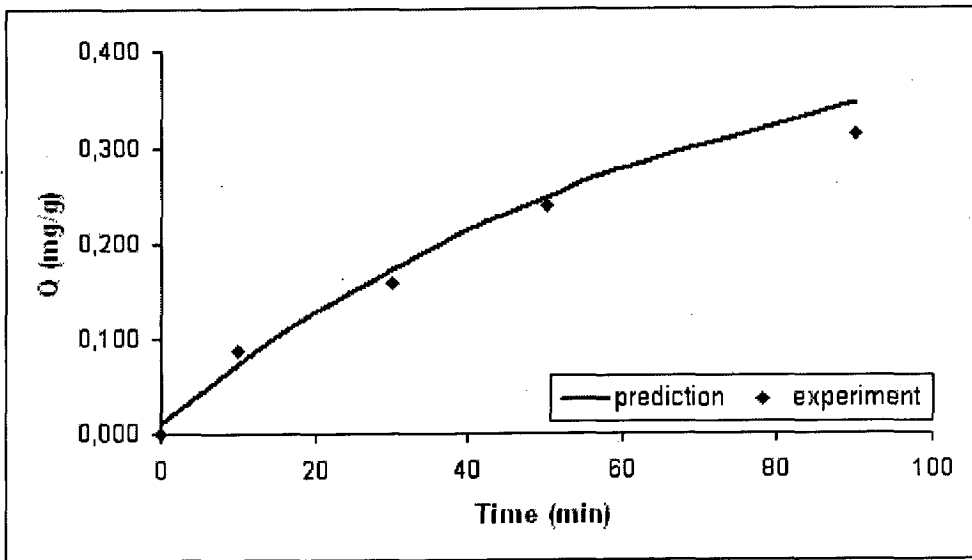
**Fig 5.23 : Predicted and actual Q versus time**

**Experiment 5: (Table 5.31)**



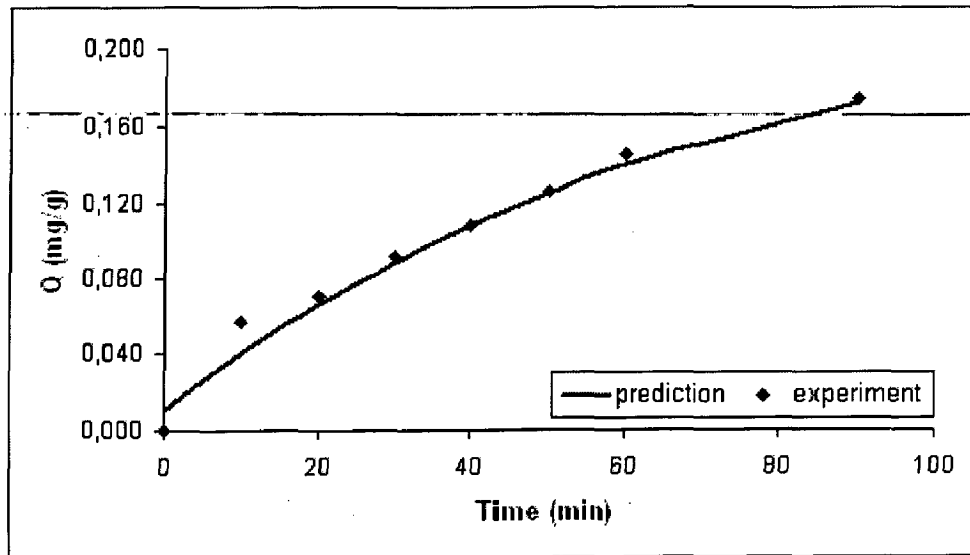
**Fig 5.24 : Predicted and actual Q versus time**

**Experiment 6 I : (Table 5.32)**



**Fig 5.25 : Predicted and actual Q versus time**

### Experiment 7 I : (Table 5.33)



**Fig 5.26 : Predicted and actual Q versus time**

Comparison shows that the model fits reasonably well for the lower concentration range, but fails for concentration more than 10 mg/l NH<sub>4</sub>-N in solution.

Other models like Monod equation and model for adsorption in soil were also checked.

#### **5.5.4 FINAL MODEL**

Model I and Model III collectively fits to the experimental data, with Vermeulen's model proving reasonably well for higher concentration range (more than 30 mg/l) and film diffusion control proving reasonably well for lower concentration range (less than 10 mg/l).

The intermediate range exhibits both particle diffusion and film diffusion substantially. Thus dividing the concentration range into 3 zones as particle diffusion controlling, intermediate and film diffusion controlling:

#### **ZONE I : PARTICLE DIFFUSION CONTROL ( Vermeulen's model )**

$$\frac{dQ}{dt} = 0.0054 \left( \frac{Q^*{}^2 - Q^2}{2Q} \right)$$

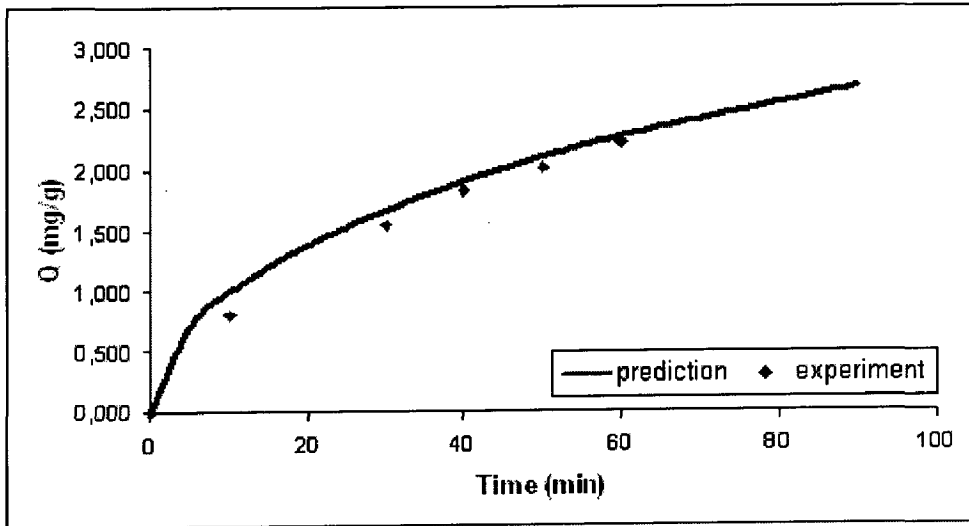
where,

$Q$  =  $\text{NH}_4\text{-N}$  per unit weight of clinoptilolite (mg/g),

$Q^*$  = equilibrium  $\text{NH}_4\text{-N}$  per unit weight of clinoptilolite (mg/g),

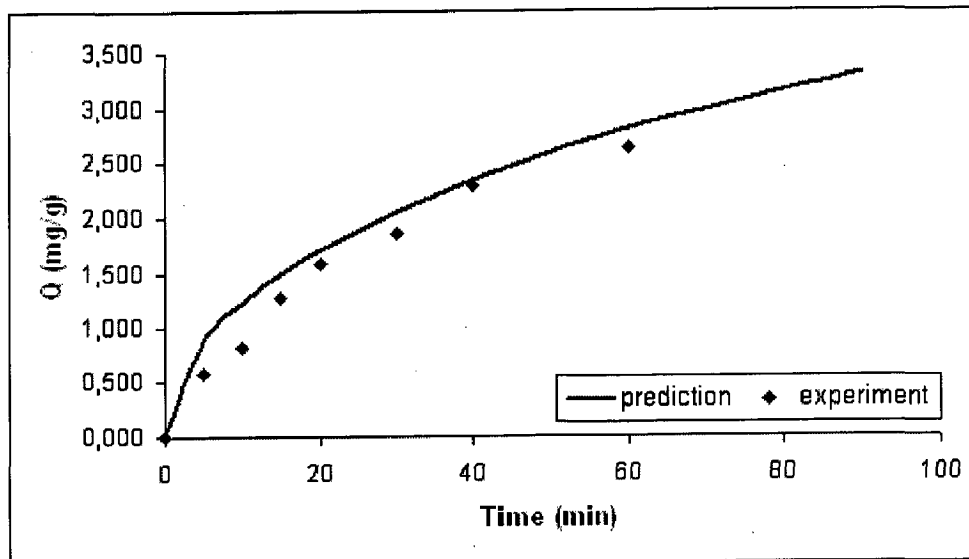
$t$  = time in seconds

**Experiment 1 :**



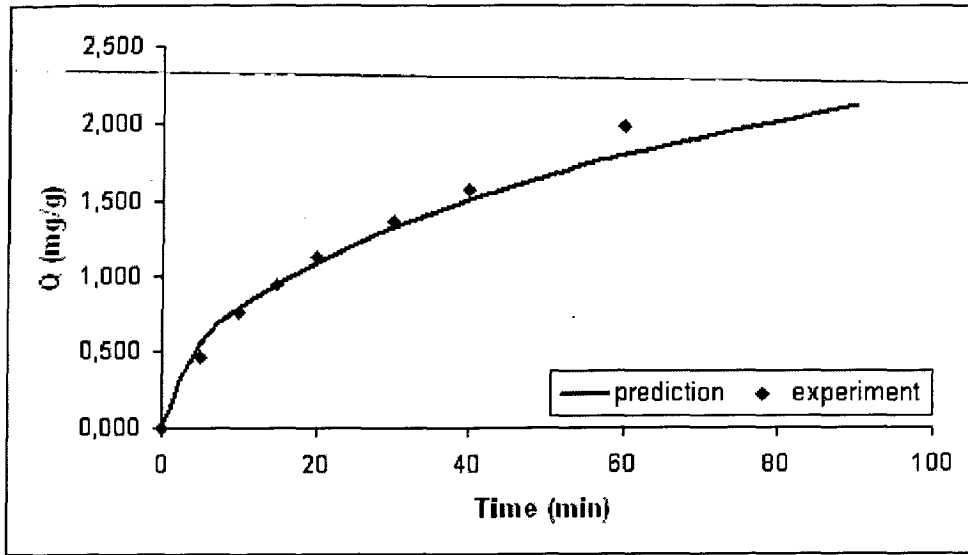
*Fig 5.27 : Predicted and actual Q versus time*

**Experiment 2 :**



*Fig 5.28 : Predicted and actual Q versus time*

**Experiment 3 :**



**Fig 5.29 : Predicted and actual Q versus time**

**ZONE II : INTERMEDIATE ZONE**

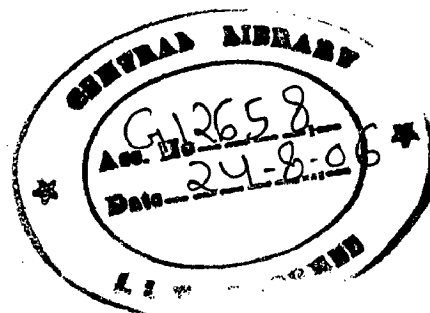
$$\frac{dQ}{dt} = 0.0054k_1 \left( \frac{Q^{*2} - Q^2}{2Q} \right) + 0.0147k_2(Q^* - Q)$$

where,

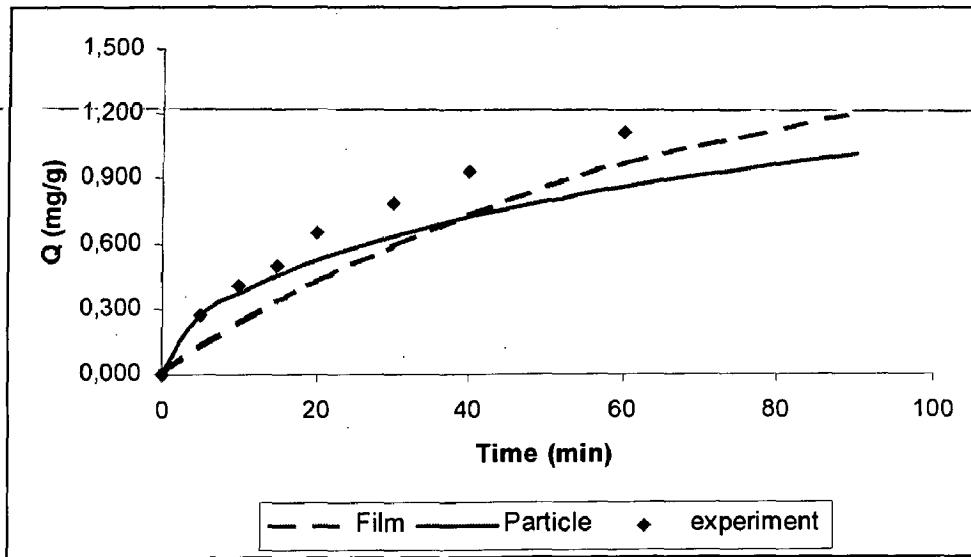
Q = NH<sub>4</sub>-N per unit weight of clinoptilolite (mg/g),

Q\* = equilibrium NH<sub>4</sub>-N per unit weight of clinoptilolite (mg/g),

t = time in seconds and k<sub>1</sub>, k<sub>2</sub> are constants

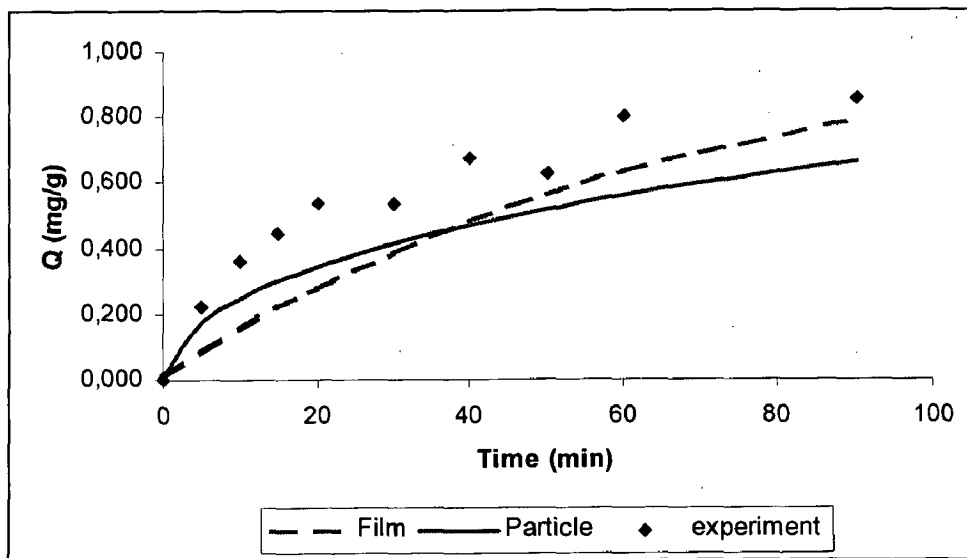


**Experiment 4:**



**Fig 5.30 : Predicted and actual Q versus time**

**Experiment 5 :**



**Fig 5.31 : Predicted and actual Q versus time**

### ZONE III : FILM DIFFUSION CONTROL

$$\frac{dQ}{dt} = 0.0147(Q^* - Q)$$

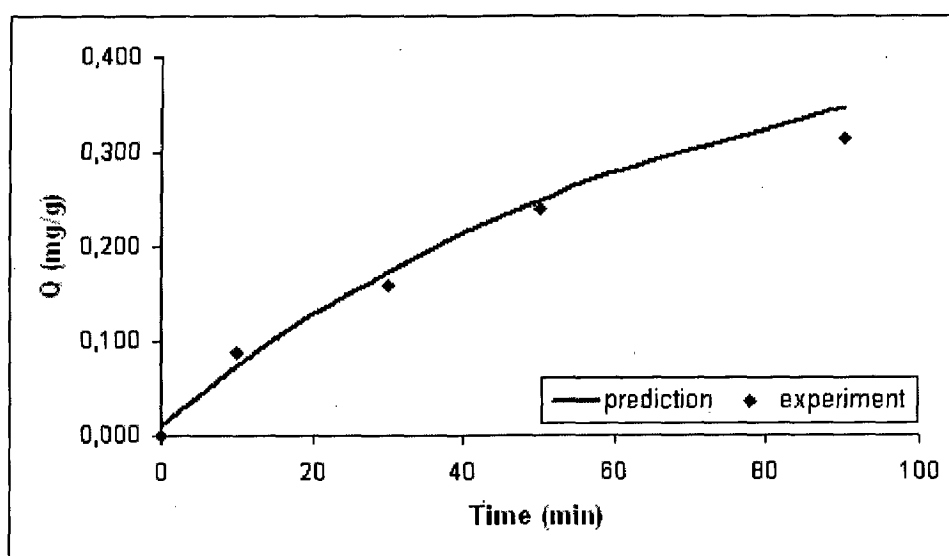
where,

$Q$  =  $\text{NH}_4\text{-N}$  per unit weight of clinoptilolite (mg/g),

$Q^*$  = equilibrium  $\text{NH}_4\text{-N}$  per unit weight of clinoptilolite (mg/g),

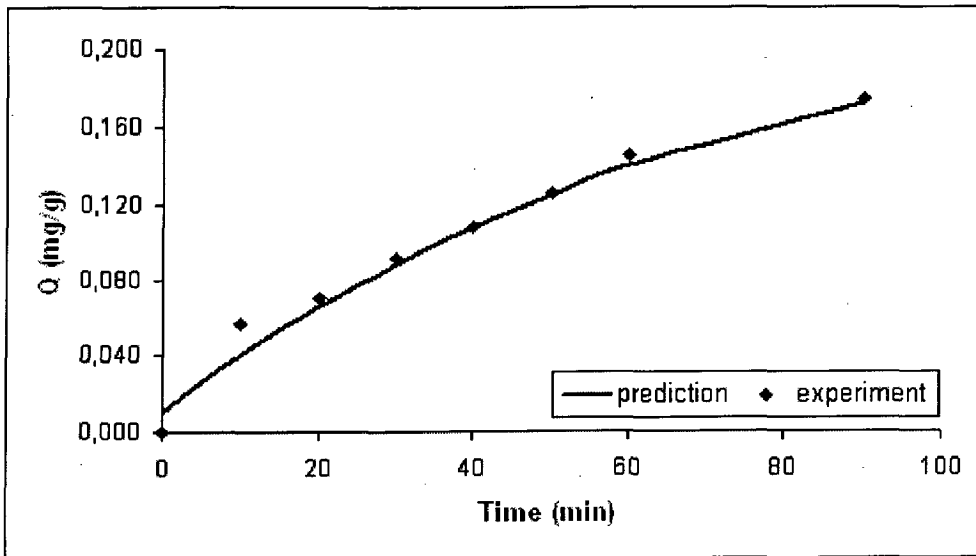
$t$  = time in seconds

#### Experiment 6 I :



*Fig 5.32 : Predicted and actual Q versus time*

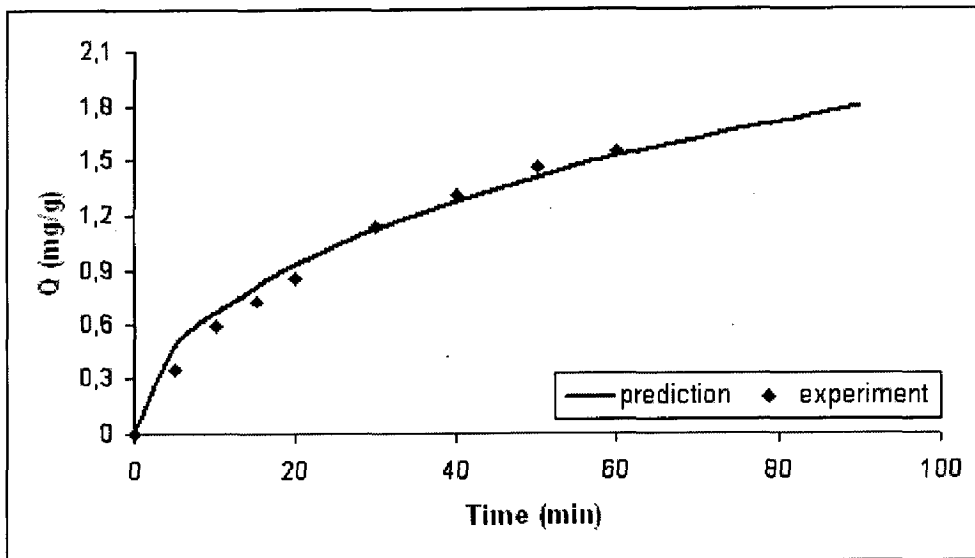
**Experiment 7 I :**



**Fig 5.33 : Predicted and actual Q versus time**

**5.6 MODEL VERIFICATION**

Data obtained from experiment conducted with different clinoptilolite mass to solution volume ratio, verify the model. (Table 5.34)



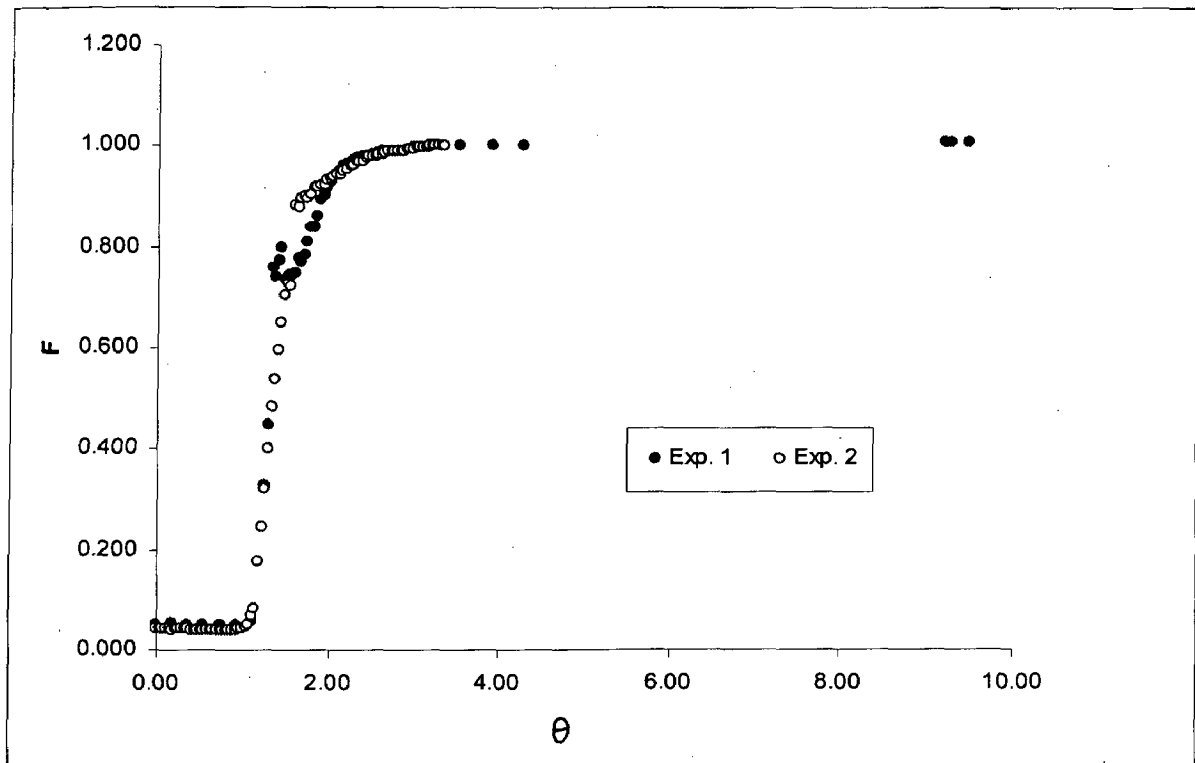
**Fig 5.34 : Predicted and actual Q versus time**

Comparison shows that the model could predict the concentration variation with time, sufficiently accurate for practical use.



## 5.7 RESIDENCE TIME DISTRIBUTION

The elements of fluid take different routes through the reactor and may take different lengths of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the vessel is called the residence time distribution RTD of the fluid.



**Fig 5.35: F curves for the step inputs**

These experimental F curves were then compared with the output F curves from a series of N ideal stirred tanks as,

$$F = 1 - e^{-N\theta} \left[ 1 + N\theta + \frac{(N\theta)^2}{2!} + \dots + \frac{(N\theta)^{N-1}}{(N-1)!} + \dots \right]$$

where,

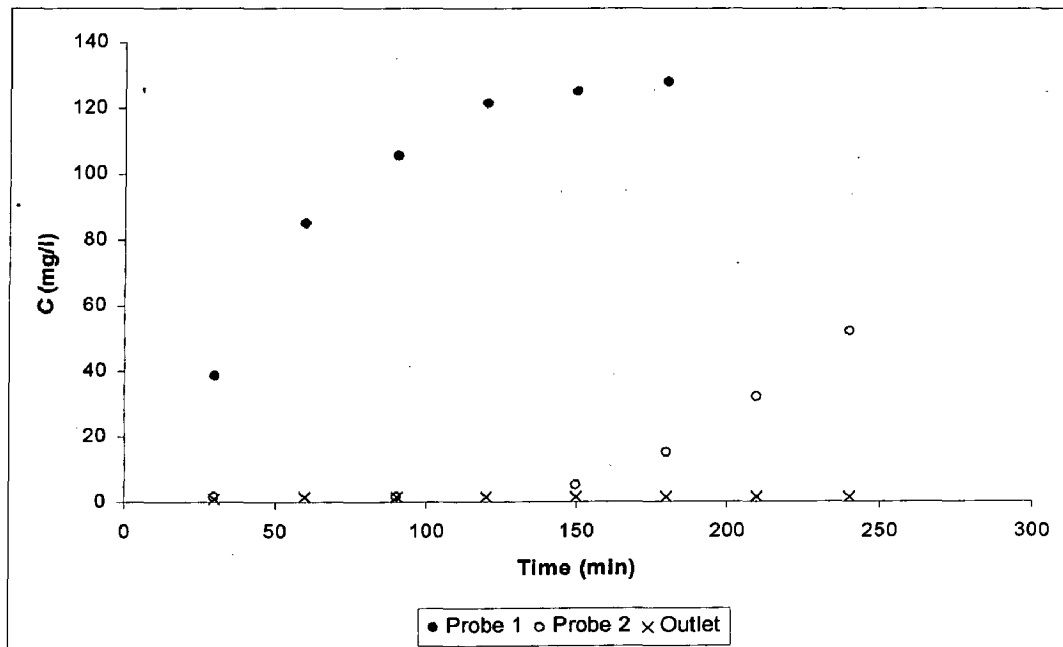
N = number of ideal stirred tanks

$\theta$  = dimensionless time based on the mean residence time in all N tanks

Neglecting the initial time lag, the comparison of time taken to reach 98% of the F value gives an approximation of 6 tanks in series for the column.

## 5.8 COLUMN MODELING

An experiment on column was performed with solution concentration of 145.5 mg/l NH<sub>4</sub>-N introduced at 13.75 l/h. (Table 6.3). The samples were taken from three different outlet points at definite time intervals.



**Fig 5.36: Concentration of NH<sub>4</sub>-N at various probes versus Time**

Initially, the maximum ion exchange occurred at the bottom of the clinoptilolite bed, and slowly the ion exchange increases upward with passage of time keeping the exit ammonium concentration well below the effluent standards.

The clinoptilolite column was modeled as a number of completely mixed reactors in series. The column was segmented into a number of discrete elements of equal volume with both liquid and solid phase concentrations being uniform throughout each element.

A mass balance on n<sup>th</sup> column segment gives, [Semmens et al., 1981]

$$\frac{dC_n}{dt} = \frac{U}{\varepsilon} (C_{n-1} - C_n) - \frac{\rho}{\varepsilon} \left( \frac{dQ_n}{dt} \right)$$

where,

$C_n$  = ammonium concentration in the liquid phase of the  $n^{\text{th}}$  segment (mg/l)

$C_{n-1}$  = ammonium concentration in the liquid phase of the  $(n-1)^{\text{th}}$  segment (mg/l)

$Q_n$  = ammonium concentration in the solid phase of the  $n^{\text{th}}$  segment (mg/g)

$U$  = volumetric flow rate of the solution (l/h)

$\rho$  = packed bed density of the clinoptilolite (g/l)

$\varepsilon$  = packed bed porosity, and

$V$  = volume of each column segment (l)

The residence time distribution gives an approximation of 6 tanks in series for the column. Using 6 tanks as the first guess for the assumption of number of completely mixed reactors in series equivalent to the column, the above model is then to be verified.

# CHAPTER 6

## CONCLUSION AND RECOMMENDATION

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### 6.1 CONCLUSIONS

The following major conclusions can be drawn from the present work:

1. Removal of ammoniacal nitrogen by clinoptilolite is a very rapid process. The rate of removal is high for first 20 min and then reduces rapidly as the concentration approaches to the equilibrium.
2. Maximum ammoniacal nitrogen removal efficiency is achieved at the smallest initial concentration. After 60 min, about 50% of ammonium was removed from solution with 90 mg/l  $\text{NH}_4\text{-N}$  initial concentration, 58% from 46.20mg/l  $\text{NH}_4\text{-N}$  initial concentration solution, and 68% from 18.32mg/l  $\text{NH}_4\text{-N}$  initial concentration solution.
3. The equilibrium curve obtained in the batch study shows that isotherm for ammonium removal on clinoptilolite can be represented by

$$\text{Langmuir form: } Q = \frac{0.7485}{1 + 0.0979C_e}$$

$$\text{Freundlich form: } Q = 1.3477C_e^{0.3867}$$

Freundlich model gives a better fit to the data.

3. Modeling for batch system shows that there occurs a change in controlling mechanism with concentration. Particle diffusion control proves reasonably well for higher concentration range (more than 30 mg/l) and film diffusion control proves reasonably well for lower concentration range (less than 10 mg/l). The intermediate range exhibits both particle diffusion and film diffusion substantially. Thus dividing the concentration range into 3 zones as particle diffusion controlling, intermediate and film diffusion controlling,

$$\text{Particle diffusion control: } \frac{dQ}{dt} = 0.0054 \left( \frac{Q^{*2} - Q^2}{2Q} \right)$$

$$\text{Film diffusion control: } \frac{dQ}{dt} = 0.0147(Q^* - Q)$$

5. Residence time distribution gives an approximation of 6 tanks in series for the column.

6. Mass balance for continuous process in the column gives an equation which could be used to model the process.

$$\frac{dC_n}{dt} = \frac{U}{\varepsilon} (C_{n-1} - C_n) - \frac{\rho}{\varepsilon} \left( \frac{dQ_n}{dt} \right)$$

Continuous experiment shows that the clinoptilolite is good enough to reduce the ammonium concentration (generally 50-150mg/l NH<sub>4</sub>-N in municipal waste water) to well below the effluent standard of 10mg/l NH<sub>4</sub>-N.

## 6.2 RECOMMENDATIONS

1. The validity of the use of batch isotherms in continuous system should be checked. Would equilibrium actually be realized in column? Isotherm should be obtained for column operation.
2. Continuous modeling requires further experiments and verifications. More column experiments should be conducted to calculate and verify the number of tank approximation of the column.
3. Column studies should be carried out at different inlet concentrations, different flow rates to get the characteristic dependence of the ion exchange capacity and other parameters.

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## TABLES

Table 4.1: 4 g (4.006g) of clinoptilolite, 40 ml of waste water.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	67.80	2.712	0.000	0.000
2	2	44.60	1.784	0.928	0.232
3	5	35.20	1.408	1.304	0.326
4	10	27.20	1.088	1.624	0.405
5	15	18.52	0.741	1.971	0.492
6	20	14.70	0.588	2.124	0.530
7	25	15.20	0.608	2.104	0.525
8	30	12.60	0.504	2.208	0.551
9	40	9.79	0.392	2.320	0.579
10	50	8.07	0.323	2.389	0.596
11	60	7.39	0.296	2.416	0.603
12	90	5.95	0.238	2.474	0.618
13	120	5.29	0.212	2.500	0.624
14	180	4.78	0.191	2.521	0.629

Table 4.2: 10g (10.01g) of clinoptilolite, 150 ml of waste water.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	69.40	10.410	0.000	0.000
2	2	61.20	9.180	1.230	0.123
3	4	61.40	9.210	1.200	0.120
4	6	58.60	8.790	1.620	0.162
5	8	59.40	8.910	1.500	0.150
6	10	57.60	8.640	1.770	0.177
7	12	54.60	8.190	2.220	0.222
8	14	57.00	8.550	1.860	0.186
9	16	53.20	7.980	2.430	0.243
10	18	52.00	7.800	2.610	0.261
11	20	45.80	6.870	3.540	0.354
12	25	44.00	6.600	3.810	0.381
13	30	40.00	6.000	4.410	0.441
14	35	35.20	5.280	5.130	0.512
15	40	33.20	4.980	5.430	0.542
16	50	29.00	4.350	6.060	0.605
17	60	23.80	3.570	6.840	0.683

**Table 4.3: 10g of clinoptilolite, 100 ml of waste water.**

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	70.80	7.080	0.000	0.000
2	2	59.20	5.920	1.160	0.116
3	3	59.60	5.960	1.120	0.112
4	5	43.80	4.380	2.700	0.270
5	6	49.60	4.960	2.120	0.212
6	7	43.40	4.340	2.740	0.274
7	8	38.80	3.880	3.200	0.320
8	9	41.20	4.120	2.960	0.296
9	10	40.20	4.020	3.060	0.306
10	11	36.40	3.640	3.440	0.344
11	12	34.60	3.460	3.620	0.362
12	13	34.00	3.400	3.680	0.368
13	14	32.40	3.240	3.840	0.384
14	15	30.80	3.080	4.000	0.400
15	16	30.00	3.000	4.080	0.408
16	17	28.20	2.820	4.260	0.426
17	18	26.80	2.680	4.400	0.440
18	19	26.00	2.600	4.480	0.448
19	20	25.00	2.500	4.580	0.458
20	25	20.10	2.010	5.070	0.507
21	30	17.20	1.720	5.360	0.536
22	35	15.00	1.500	5.580	0.558
23	40	12.50	1.250	5.830	0.583
24	50	10.20	1.020	6.060	0.606
25	60	8.78	0.878	6.202	0.620
26	90	6.19	0.619	6.461	0.646
27	120	5.31	0.531	6.549	0.655

**Table 4.4:** 1g (1.001g) of clinoptilolite, 100 ml of waste water. Equilibrium value was taken after 94 hours.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	70.80	7.080	0.000	0.000
2	2	67.40	6.740	0.340	0.340
3	4	63.60	6.360	0.720	0.719
4	6	61.20	6.120	0.960	0.959
5	8	62.20	6.220	0.860	0.859
6	10	60.60	6.060	1.020	1.019
7	12	59.40	5.940	1.140	1.139
8	14	60.00	6.000	1.080	1.079
9	16	59.20	5.920	1.160	1.159
10	18	54.60	5.460	1.620	1.618
11	20	56.00	5.600	1.480	1.479
12	25	52.80	5.280	1.800	1.798
13	30	53.20	5.320	1.760	1.758
14	40	51.20	5.120	1.960	1.958
15	50	49.40	4.940	2.140	2.138
16	60	47.00	4.700	2.380	2.378
17	120	40.40	4.040	3.040	3.037
18	1440	31.20	3.120	3.960	3.956
19	equilibrium	28.20	2.820	4.260	4.256

**Table 4.5:** Verification of Vermeulen's model. Measured data of experiment with 1g (1.001g) of clinoptilolite and 100 ml of waste water is used (Experiment 4).

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg/g) of zeolite	Conversion X	- ln(1- X <sup>2</sup> )
1	0	70.80	0.000	0.000	0.000
2	2	67.40	0.340	0.080	0.006
3	4	63.60	0.719	0.169	0.029
4	6	61.20	0.959	0.225	0.052
5	8	62.20	0.859	0.202	0.042
6	10	60.60	1.019	0.239	0.059
7	12	59.40	1.139	0.268	0.074
8	14	60.00	1.079	0.254	0.066
9	16	59.20	1.159	0.272	0.077
10	18	54.60	1.618	0.380	0.156
11	20	56.00	1.479	0.347	0.129
12	25	52.80	1.798	0.423	0.197
13	30	53.20	1.758	0.413	0.187
14	40	51.20	1.958	0.460	0.238
15	50	49.40	2.138	0.502	0.291
16	60	47.00	2.378	0.559	0.374
17	120	40.40	3.037	0.714	0.712

**Table 5.1:** Observations for isotherm

S.no.	mass of zeolite (g)	NH <sub>4</sub> -N (mg/l)		NH <sub>4</sub> -N (mg) in solution		mass on zeolite NH <sub>4</sub> -N (mg)	loading on zeolite NH <sub>4</sub> -N (mg/l)
		initial	equilibrium	initial	equilibrium		
1	1.028	18.52	1.71	1.852	0.171	1.681	1.635
2	1.025	46.60	10.80	4.660	1.080	3.580	3.493
3	1.051	65.80	20.60	6.580	2.060	4.450	4.233
4	1.084	92.80	37.80	9.280	3.780	5.500	5.074
5	1.025	10.50	0.53	1.050	0.053	0.997	0.973
6	1.025	10.50	0.49	1.050	0.049	1.001	0.977
7	1.021	32.10	4.61	3.210	0.461	2.749	2.692
8	1.031	32.10	4.61	3.210	0.461	2.749	2.666
9	1.051	62.80	17.00	6.280	1.700	4.580	4.358
10	1.056	62.80	18.20	6.280	1.820	4.460	4.223
11	1.020	85.20	31.70	8.520	3.170	5.350	5.245
12	1.030	12.60	60.00	12.760	6.000	6.760	6.563
13	1.025	158.50	84.80	15.850	8.480	7.370	7.190
14	1.036	158.50	85.00	15.850	8.500	7.350	7.095

**Table 5.2:** Calculations for Langmuir isotherm parameters

S.no.	equilibrium conc. (mg/l) $C_e$	$NH_4-N$ (mg/g) of zeolite (Q)	$C_e / Q$
1	1.71	1.635	1.048
2	10.80	3.493	3.092
3	20.60	4.233	4.867
4	37.80	5.074	7.450
5	0.53	0.973	0.545
6	0.49	0.977	0.502
7	4.61	2.692	1.712
8	4.61	2.666	1.729
9	17.00	4.358	3.901
10	18.20	4.223	4.309
11	31.70	5.245	6.044
12	60.00	6.563	9.142
13	84.80	7.190	11.794
14	85.00	7.095	11.981

**Table 5.3:** Calculations for Freundlich isotherm parameters

S.no.	equilibrium conc. (mg/l) $C_e$	$NH_4-N$ (mg/g) of zeolite Q	$\ln C_e$	$\ln Q$
1	1.71	1.635	0.539	0.492
2	10.80	3.493	2.380	1.251
3	20.60	4.233	3.025	1.443
4	37.80	5.074	3.632	1.624
5	0.53	0.973	-0.635	-0.028
6	0.49	0.977	-0.713	-0.024
7	4.61	2.692	1.528	0.990
8	4.61	2.666	1.528	0.981
9	17.00	4.358	2.833	1.472
10	18.20	4.223	2.901	1.441
11	31.70	5.245	3.456	1.657
12	60.00	6.563	4.094	1.881
13	84.80	7.190	4.440	1.973
14	85.00	7.095	4.443	1.959

**Table 5.4:** Comparison of experimental data with Langmuir and Freundlich isotherms

S.no.	equilibrium conc. (mg/l) Ce	NH <sub>4</sub> -N (mg/g) of zeolite Q	NH <sub>4</sub> -N (mg/g) Langmuir Q	NH <sub>4</sub> -N (mg/g) Freundlich Q
1	0.49	0.977	0.350	1.023
2	0.53	0.973	0.377	1.054
3	1.71	1.635	1.099	1.660
4	4.61	2.692	2.378	2.434
5	4.61	2.666	2.378	2.434
6	10.80	3.493	3.929	3.382
7	17.00	4.358	4.776	4.031
8	18.20	4.223	4.897	4.139
9	20.60	4.233	5.111	4.342
10	31.70	5.245	5.782	5.129
11	37.80	5.074	6.019	5.490
12	60.00	6.563	6.533	6.565
13	84.80	7.190	6.824	7.504
14	85.00	7.095	6.825	7.511

**Table 5.5:** 1g (1.051g) of clinoptilolite, 100 ml of waste water. 0.15ml of solution was withdrawn at each sampling. Equilibrium reading was taken after 72 hours. (Experiment 1)

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	65.80	6.580	0.000	0.000
2	2	62.80	6.271	0.300	0.285
3	4	61.40	6.122	0.440	0.418
4	6	58.60	5.834	0.719	0.684
5	8	58.80	5.845	0.699	0.665
6	10	57.40	5.697	0.838	0.798
7	12	57.20	5.669	0.858	0.816
8	14	55.00	5.442	1.076	1.024
9	16	52.00	5.138	1.373	1.306
10	18	53.40	5.268	1.235	1.175
11	26	49.80	4.905	1.590	1.513
12	30	49.40	4.858	1.629	1.550
13	40	46.40	4.556	1.924	1.831
14	50	44.40	4.353	2.121	2.018
15	60	42.20	4.131	2.336	2.223
16	120	35.00	3.421	3.041	2.894
17	equilibrium	20.60	2.011	4.449	4.233

**Table 5.6:** (1.027g) of clinoptilolite, 100 ml of solution. 0.10 ml of solution was withdrawn at each sampling. (Experiment 2)

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	90.00	9.000	0.000	0.000
2	5	84.00	8.392	0.600	0.584
3	10	81.60	8.144	0.840	0.818
4	15	76.80	7.657	1.319	1.284
5	20	73.60	7.331	1.638	1.595
6	30	70.80	7.045	1.917	1.866
7	40	66.40	6.600	2.355	2.293
8	60	62.80	6.236	2.712	2.641

**Table 5.7:** 1g (1.025g) of clinoptilolite, 100 ml of solution. 0.15 ml of solution was withdrawn at each sampling. (Experiment3)

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	46.20	4.620	0.000	0.000
2	5	41.40	4.134	0.480	0.468
3	10	38.40	3.828	0.780	0.761
4	15	36.40	3.624	0.979	0.955
5	20	34.60	3.439	1.158	1.130
6	30	32.20	3.196	1.397	1.363
7	40	30.00	2.973	1.615	1.576
8	60	25.80	2.553	2.031	1.982
9	120	20.20	1.996	2.585	2.522

**Table 5.8:** 1g (1.020g) of clinoptilolite, 100 ml of solution. 0.15 ml of solution was withdrawn at each sampling. (Experiment 4)

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	18.32	1.832	0.000	0.000
2	5	15.52	1.550	0.280	0.275
3	10	14.20	1.416	0.412	0.404
4	15	13.28	1.322	0.504	0.494
5	20	11.66	1.159	0.665	0.652
6	30	10.28	1.020	0.802	0.786
7	40	8.80	0.872	0.949	0.930
8	60	6.92	0.685	1.135	1.113

**Table 5.9:** 2g (2.160g) of clinoptilolite, 200 ml of solution. 1.00 ml of solution was withdrawn at each sampling. (Experiment 5)

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	12.50	2.500	0.000	0.000
2	5	10.10	2.010	0.480	0.222
3	10	8.62	1.707	0.775	0.359
4	15	7.64	1.505	0.969	0.448
5	20	6.67	1.307	1.160	0.537
6	30	6.65	1.297	1.164	0.539
7	40	5.15	0.999	1.456	0.674
8	50	5.67	1.094	1.355	0.627
9	60	3.74	0.718	1.728	0.800
10	90	3.13	0.598	1.845	0.854
11	120	2.36	0.448	1.992	0.922

**Table 5.10:** 1g of clinoptilolite was added and shaken with 100 ml of solution. More than one parallel experimental sets were run. 0.30 ml of solution was withdrawn at each sampling. (Experiment 6)

**SET I:** 1g (1.011g) of clinoptilolite, 100 ml of solution.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	4.670	0.467	0.000	0.000
2	10	3.790	0.378	0.088	0.087
3	30	3.070	0.305	0.160	0.158
4	50	2.250	0.223	0.241	0.239
5	90	1.480	0.146	0.318	0.314
6	270	0.337	0.031	0.431	0.426

**SET II:** 1g (1.011g) of clinoptilolite, 100 ml of solution.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	4.670	0.467	0.000	0.000
2	10	4.270	0.426	0.040	0.040
3	30	2.800	0.278	0.187	0.185
4	50	2.120	0.210	0.254	0.251
5	90	1.650	0.163	0.301	0.297
6	270	0.351	0.033	0.429	0.424



**SET III:** 1g (1.018g) of clinoptilolite, with 100 ml of solution.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	4.670	0.467	0.000	0.000
2	20	3.740	0.373	0.093	0.091
3	40	2.780	0.276	0.189	0.185
4	60	2.190	0.217	0.247	0.243
5	120	1.425	0.141	0.323	0.317

**SET IV:** 1g (1.022) of clinoptilolite, with 100 ml of solution.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	4.670	0.467	0.000	0.000
2	20	3.450	0.344	0.122	0.119
3	40	2.670	0.265	0.200	0.195
4	60	1.990	0.197	0.267	0.262
5	120	1.200	0.119	0.346	0.338

**Table 5.11:** 1g of clinoptilolite was added and shaken with 100 ml of solution. More than one parallel experimental sets were run. 0.30 ml of solution was withdrawn at each sampling.  
(Experiment 7)

**SET I:** 1g (1.012g) of clinoptilolite, 100 ml of solution.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	2.325	0.233	0.000	0.000
2	10	1.750	0.174	0.058	0.057
3	20	1.600	0.159	0.072	0.072
4	30	1.400	0.139	0.092	0.091
5	40	1.225	0.121	0.110	0.108
6	50	1.050	0.103	0.127	0.125
7	60	0.850	0.083	0.147	0.145
8	90	0.550	0.054	0.176	0.174

**SET II:** 1g (1.012g) of clinoptilolite, 100 ml of solution.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg) in solution	NH <sub>4</sub> -N (mg) on zeolite	NH <sub>4</sub> -N (mg/g) of zeolite
1	0	2.325	0.233	0.000	0.000
2	10	1.850	0.184	0.048	0.047
3	20	1.725	0.171	0.060	0.059
4	30	1.400	0.139	0.092	0.091
5	40	1.250	0.124	0.107	0.106
6	50	1.175	0.116	0.115	0.113
7	60	0.875	0.086	0.144	0.142
8	90	0.575	0.056	0.174	0.171

**Table 5.12:** Equilibrium values using experimental data and isotherm.

Exp. No.	mass of zeolite (g)	volume (ml)	initial conc. NH <sub>4</sub> -N mg/l C <sub>0</sub>	equilibrium conc. NH <sub>4</sub> -N mg/l C <sub>e</sub>	equilibrium loading NH <sub>4</sub> -N mg/g Q*
1	1.051	100	65.800	20.350	4.321
2	1.027	100	90.000	35.150	5.338
3	1.025	100	46.200	11.150	3.424
4	1.020	100	18.320	1.650	1.636
5	2.160	200	12.500	0.550	1.070
6 (I)	1.011	100	4.670	0.065	0.468
6 (II)	1.011	100	4.670	0.065	0.468
6 (III)	1.018	100	4.670	0.060	0.453
6 (IV)	1.022	100	4.670	0.059	0.450
7 (I)	1.012	100	2.325	0.011	0.231
7 (II)	1.012	100	2.325	0.011	0.231

**Table 5.13:** Effect of initial ammonium concentration

S.no.	Time (min)	% Efficiency		
		Exp.2	Exp.3	Exp.4
1	0	0.00	0.00	0.00
2	10	15.32	22.23	24.69
3	20	29.88	33.00	39.85
4	30	34.96	39.81	48.04
5	40	42.96	46.03	56.85
6	60	49.48	57.89	68.03

**Table 5.14:** Calculation of diffusion coefficient using Vermeulen's model. Measured data of experiment with 1g (1.051g) of clinoptilolite and 100 ml of solution was used. (Experiment 5.1).

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg/g) of zeolite	Conversion X	- ln (1- X <sup>2</sup> )
1	0	65.80	0.000	0.000	0.000
2	2	62.80	0.285	0.067	0.005
3	4	61.40	0.418	0.099	0.010
4	6	58.60	0.684	0.162	0.026
5	8	58.80	0.665	0.157	0.025
6	10	57.40	0.798	0.188	0.036
7	12	57.20	0.816	0.193	0.038
8	14	55.00	1.024	0.242	0.060
9	16	52.00	1.306	0.309	0.100
10	18	53.40	1.175	0.278	0.080
11	26	49.80	1.513	0.357	0.137
12	30	49.40	1.550	0.366	0.144
13	40	46.40	1.831	0.433	0.207
14	50	44.40	2.018	0.477	0.258
15	60	42.20	2.223	0.525	0.323
16	120	35.00	2.894	0.684	0.630

**Table 5.15:** Comparison using Vermeulen model for Experiment 1.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.706	
3	10	0.991	0.798
4	15	1.206	
5	20	1.383	
6	30	1.671	1.550
7	40	1.905	1.831
8	50	2.102	2.018
9	60	2.273	2.223
10	90	2.681	

**Table 5.16:** Comparison using Vermeulen model for Experiment 2.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.872	0.584
3	10	1.225	0.818
4	15	1.490	1.284
5	20	1.708	1.595
6	30	2.065	1.866
7	40	2.353	2.293
8	50	2.597	
9	60	2.808	2.641
10	90	3.312	

**Table 5.17:** Comparison using Vermeulen model for Experiment 3.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.559	0.468
3	10	0.785	0.761
4	15	0.955	0.955
5	20	1.096	1.130
6	30	1.324	1.363
7	40	1.509	1.576
8	50	1.666	
9	60	1.801	1.982
10	90	2.124	

**Table 5.18:** Comparison using Vermeulen model for Experiment 4.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.267	0.275
3	10	0.375	0.404
4	15	0.456	0.494
5	20	0.524	0.652
6	30	0.633	0.786
7	40	0.721	0.930
8	50	0.796	
9	60	0.861	1.113
10	90	1.015	

**Table 5.19:** Comparison using Vermeulen model for Experiment 5.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.175	0.222
3	10	0.245	0.359
4	15	0.299	0.448
5	20	0.342	0.537
6	30	0.414	0.539
7	40	0.472	0.674
8	50	0.521	0.627
9	60	0.563	0.800
10	90	0.664	0.854

**Table 5.20:** Calculation of diffusion coefficient using Glueckauf & Coates model. Measured data of experiment with 1g (1.051g) of clinoptilolite and 100 ml of solution was used. (Experiment 5.1).

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg/g) of zeolite	Conversion X	- ln (1- X )
1	0	65.80	0.000	0.000	0.000
2	2	62.80	0.285	0.067	0.070
3	4	61.40	0.418	0.099	0.104
4	6	58.60	0.684	0.162	0.176
5	8	58.80	0.665	0.157	0.171
6	10	57.40	0.798	0.188	0.209
7	12	57.20	0.816	0.193	0.214
8	14	55.00	1.024	0.242	0.277
9	16	52.00	1.306	0.309	0.369
10	18	53.40	1.175	0.278	0.325
11	26	49.80	1.513	0.357	0.442
12	30	49.40	1.550	0.366	0.456
13	40	46.40	1.831	0.433	0.567
14	50	44.40	2.018	0.477	0.648
15	60	42.20	2.223	0.525	0.745
16	120	35.00	2.894	0.684	1.151

**Table 5.21:** Comparison using Glueckauf & Coates model for Experiment 1.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.208	
3	10	0.397	0.798
4	15	0.577	
5	20	0.749	
6	30	1.069	1.550
7	40	1.361	1.831
8	50	1.627	2.018
9	60	1.868	2.223
10	90	2.471	

**Table 5.22:** Comparison using Glueckauf & Coates model for Experiment 2.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.255	0.584
3	10	0.488	0.818
4	15	0.711	1.284
5	20	0.923	1.595
6	30	1.319	1.866
7	40	1.680	2.293
8	50	2.008	
9	60	2.307	2.641
10	90	3.052	

**Table 5.23:** Comparison using Glueckauf & Coates model for Experiment 3.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.167	0.468
3	10	0.316	0.761
4	15	0.459	0.955
5	20	0.595	1.130
6	30	0.849	1.363
7	40	1.080	1.576
8	50	1.290	
9	60	1.482	1.982
10	90	1.959	

**Table 5.24:** Comparison using Glueckauf & Coates model for Experiment 4.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.085	0.275
3	10	0.156	0.404
4	15	0.224	0.494
5	20	0.289	0.652
6	30	0.410	0.786
7	40	0.520	0.930
8	50	0.620	
9	60	0.711	1.113
10	90	0.938	

**Table 5.25:** Comparison using Glueckauf & Coates model for Experiment 5.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.059	0.222
3	10	0.105	0.359
4	15	0.149	0.448
5	20	0.192	0.537
6	30	0.270	0.539
7	40	0.342	0.674
8	50	0.407	0.627
9	60	0.467	0.800
10	90	0.615	0.854

**Table 5.26:** Calculation of film mass transfer coefficient. Measured data of experiment 7 was used.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg/g) of zeolite	Conversion X	- ln (1- X)
1	0	2.325	0.000	0.000	0.000
2	10	1.750	0.057	0.246	0.282
3	10	1.850	0.047	0.203	0.227
4	20	1.600	0.072	0.310	0.371
5	20	1.725	0.059	0.256	0.296
6	30	1.400	0.091	0.395	0.502
7	30	1.400	0.091	0.395	0.502
8	40	1.225	0.108	0.469	0.633
9	40	1.250	0.106	0.458	0.613
10	50	1.050	0.125	0.543	0.783
11	50	1.175	0.113	0.490	0.673
12	60	0.850	0.145	0.627	0.987
13	60	0.875	0.142	0.616	0.958
14	90	0.550	0.174	0.753	1.400
15	90	0.575	0.171	0.742	1.356

**Table 5.27:** Comparison using Film diffusion model for Experiment 1.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.315	
3	10	0.599	0.798
4	15	0.863	
5	20	1.108	
6	30	1.547	1.550
7	40	1.927	1.831
8	50	2.254	2.018
9	60	2.536	2.223
10	90	3.173	



**Table 5.28:** Comparison using Film diffusion model for Experiment 2.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.388	0.584
3	10	0.738	0.818
4	15	1.064	1.284
5	20	1.367	1.595
6	30	1.910	1.866
7	40	2.379	2.293
8	50	2.783	
9	60	3.132	2.641
10	90	3.919	

**Table 5.29:** Comparison using Film diffusion model for Experiment 3.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0,010	0,000
2	5	0,252	0,468
3	10	0,477	0,761
4	15	0,686	0,955
5	20	0,880	1,130
6	30	1,227	1,363
7	40	1,528	1,576
8	50	1,787	
9	60	2,011	1,982
10	90	2,515	

**Table 5.30:** Comparison using Film diffusion model for Experiment 4.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0,010	0,000
2	5	0,125	0,275
3	10	0,232	0,404
4	15	0,332	0,494
5	20	0,424	0,652
6	30	0,590	0,786
7	40	0,733	0,930
8	50	0,856	
9	60	0,963	1,113
10	90	1,203	

**Table 5.31:** Comparison using Film diffusion model for Experiment 5.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.085	0.222
3	10	0.155	0.359
4	15	0.220	0.448
5	20	0.280	0.537
6	30	0.388	0.539
7	40	0.481	0.674
8	50	0.562	0.627
9	60	0.631	0.800
10	90	0.788	0.854

**Table 5.32:** Comparison using Film diffusion model for Experiment 6 I.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.042	
3	10	0.073	0.087
4	15	0.101	
5	20	0.127	
6	30	0.173	0.158
7	40	0.214	
8	50	0.248	0.239
9	60	0.278	
10	90	0.346	0.314

**Table 5.33:** Comparison using Film diffusion model for Experiment 7 I.

S.no	Time (min)	NH <sub>4</sub> -N (mg/g) Q	
		predicted	Experiment
1	0	0.010	0.000
2	5	0.026	
3	10	0.040	0.057
4	15	0.054	
5	20	0.066	0.072
6	30	0.089	0.091
7	40	0.108	0.108
8	50	0.125	0.125
9	60	0.140	0.145
10	90	0.172	0.174

**Table 5.34: Model verification.**

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l) in solution	NH <sub>4</sub> -N (mg/g) Q	
			predicted	Experiment
1	0	65.80	0.010	0.000
2	5	58.80	0.473	0.347
3	10	54.00	0.665	0.584
4	15	51.20	0.809	0.722
5	20	48.60	0.928	0.851
6	30	42.80	1.121	1.136
7	40	39.20	1.278	1.312
8	50	36.20	1.410	1.459
9	60	34.40	1.525	1.547
10	90		1.799	

**Table 6.1: Solution of conductivity 327 $\mu$ S/cm was introduced at 10.3l/h.**

S.no.	Time (min)	$\theta$	$\mu$ S/cm	F	S.no.	Time (min)	$\theta$	$\mu$ S/cm	F
1	0	0.00	17.00	0.052	21	47	1.74	264.90	0.810
2	5	0.19	17.30	0.053	22	48	1.78	274.50	0.839
3	10	0.37	16.98	0.052	23	49	1.82	274.20	0.838
4	15	0.56	16.77	0.051	24	50	1.86	281.60	0.861
5	20	0.74	16.42	0.050	25	51	1.89	292.10	0.893
6	25	0.93	16.58	0.051	26	52	1.93	296.00	0.905
7	30	1.11	19.12	0.058	27	53	1.97	299.80	0.916
8	34	1.26	107.50	0.329	28	54	2.00	304.00	0.929
9	35	1.30	146.30	0.447	29	55	2.04	307.00	0.939
10	36	1.34	248.50	0.760	30	56	2.08	310.00	0.948
11	37	1.37	242.00	0.740	31	57	2.12	312.00	0.954
12	38	1.41	252.60	0.772	32	58	2.15	314.00	0.960
13	39	1.45	261.00	0.798	33	59	2.19	316.00	0.966
14	40	1.48	240.90	0.736	34	60	2.23	317.00	0.969
15	41	1.52	243.90	0.746	35	61	2.26	318.00	0.972
16	42	1.56	242.70	0.742	36	62	2.30	319.00	0.975
17	43	1.60	244.60	0.748	37	63	2.34	319.00	0.975
18	44	1.63	254.50	0.778	38	64	2.38	320.00	0.978
19	45	1.67	251.80	0.770	39	65	2.41	321.00	0.981
20	46	1.71	256.90	0.785	40	66	2.45	321.00	0.981

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41	67	2.49	322.00	0.984	51	85	3.15	326.00	0.997
42	68	2.52	322.00	0.984	52	95	3.53	327.00	1.000
43	69	2.56	323.00	0.987	53	105	3.90	328.00	1.003
44	70	2.60	324.00	0.990	54	115	4.27	328.00	1.003
45	71	2.64	324.00	0.990	55	248	9.20	330.00	1.009
46	72	2.67	324.00	0.990	56	250	9.28	330.00	1.009
47	73	2.71	324.00	0.990	57	255	9.46	330.00	1.009
48	74	2.75	324.00	0.990					
49	75	2.78	324.00	0.990					
50	80	2.97	326.00	0.997					

**Table 6.2:** Solution of conductivity 353 $\mu$ S/cm was introduced at 10.3l/h.

S.no.	Time (min)	$\theta$	$\mu$ S/cm	F	S.no.	Time (min)	$\theta$	$\mu$ S/cm	F
1	0	0.00	15.10	0.043	21	20	0.74	14.56	0.041
2	1	0.04	15.04	0.043	22	21	0.78	14.53	0.041
3	2	0.07	15.00	0.042	23	22	0.82	14.49	0.041
4	3	0.11	14.99	0.042	24	23	0.85	14.45	0.041
5	4	0.15	14.98	0.042	25	24	0.89	14.42	0.041
6	5	0.19	14.66	0.042	26	25	0.93	14.45	0.041
7	6	0.22	14.72	0.042	27	26	0.97	14.73	0.042
8	7	0.26	14.75	0.042	28	27	1.00	15.43	0.044
9	8	0.30	14.84	0.042	29	28	1.04	16.68	0.047
10	9	0.33	14.90	0.042	30	29	1.08	18.10	0.051
11	10	0.37	14.87	0.042	31	30	1.11	23.75	0.067
12	11	0.41	14.55	0.041	32	31	1.15	29.98	0.085
13	12	0.45	14.51	0.041	33	32	1.19	62.30	0.176
14	13	0.48	14.48	0.041	34	33	1.22	87.00	0.246
15	14	0.52	14.65	0.042	35	34	1.26	113.30	0.321
16	15	0.56	14.55	0.041	36	35	1.30	141.20	0.400
17	16	0.59	14.59	0.041	37	36	1.34	171.20	0.485
18	17	0.63	14.50	0.041	38	37	1.37	189.90	0.538
19	18	0.67	14.54	0.041	39	38	1.41	210.90	0.597
20	19	0.71	14.55	0.041	40	39	1.45	230.10	0.652

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41	40	1.48	248.60	0.704	67	66	2.45	346.00	0.980
42	41	1.52	256.00	0.725	68	67	2.49	346.00	0.980
43	42	1.56	255.80	0.725	69	68	2.52	346.00	0.980
44	43	1.60	310.90	0.881	70	69	2.56	347.00	0.983
45	44	1.63	310.00	0.878	71	70	2.60	347.00	0.983
46	45	1.67	316.00	0.895	72	71	2.64	348.00	0.986
47	46	1.71	318.00	0.901	73	72	2.67	349.00	0.989
48	47	1.74	317.00	0.898	74	73	2.71	349.00	0.989
49	48	1.78	319.00	0.904	75	74	2.75	349.00	0.989
50	49	1.82	324.00	0.918	76	75	2.78	349.00	0.989
51	50	1.86	324.00	0.918	77	76	2.82	349.00	0.989
52	51	1.89	325.00	0.921	78	77	2.86	350.00	0.992
53	52	1.93	325.00	0.921	79	78	2.90	351.00	0.994
54	53	1.97	329.00	0.932	80	79	2.93	351.00	0.994
55	54	2.00	331.00	0.938	81	80	2.97	351.00	0.994
56	55	2.04	332.00	0.941	82	81	3.01	352.00	0.997
57	56	2.08	333.00	0.943	83	82	3.04	352.00	0.997
58	57	2.12	333.00	0.943	84	83	3.08	352.00	0.997
59	58	2.15	336.00	0.952	85	84	3.12	352.00	0.997
60	59	2.19	337.00	0.955	86	85	3.15	353.00	1.000
61	60	2.23	339.00	0.960	87	86	3.19	353.00	1.000
62	61	2.26	340.00	0.963	88	87	3.23	353.00	1.000
63	62	2.30	342.00	0.969	89	88	3.27	354.00	1.003
64	63	2.34	342.00	0.969	90	89	3.30	354.00	1.003
65	64	2.38	342.00	0.969	91	90	3.34	354.00	1.003
66	65	2.41	344.00	0.975					

**Table 6.3:** Solution of 145.5 mg/l NH<sub>4</sub>-N was continuously introduced to the column at 13.75l/h. Samples were taken at definite time intervals from different probes.

S.no.	Time (min)	NH <sub>4</sub> -N (mg/l)			
		Probe 1	Probe 2	Probe 9	Outlet
1	30	38.5	1.665		1.070
2	60	85.0			1.720
3	90	105.5	1.725		1.675
4	120	121.5			1.720
5	150	125.0	5.050	1.840	1.710
6	180	128.0	14.800	1.860	1.690
7	210		32.200	1.875	1.715
8	240		52.000	1.865	1.690