ADSORPTION COLUMN STUDIES TO PREDICT THE FLOW OF NUTRIENTS THROUGH HETEROGENOUS POROUS MEDIA UNDER EQUILIBRIUM AND ISOTHERMAL CONDITIONS

A Dissertation Presented

by

VIJAI B. PANDEY

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 2012

Food Engineering
In 1972, Vijai B. Pandey completed a doctoral dissertation in the Department of Agricultural Engineering at the University of Massachusetts Amherst. He was not allowed to defend that dissertation, and he left without receiving a degree. He did not pursue the matter at that time because he needed to go to work to provide for his family.

In 2011, Mr. Pandey contacted the then Dean of the Graduate School, John R. Mullin, and other senior University administrators. Mr. Pandey argued that an injustice had been done to him in 1972, and he requested an opportunity to defend his dissertation. Dean Mullin convened a tribunal of three distinguished faculty to consider Mr. Pandey’s request. After a thorough investigation, the tribunal concluded that Mr. Pandey should have been allowed to defend in 1972 and very likely would have passed and received the degree.

Because organizing a defense of a 1972 dissertation submitted to a long-defunct department was impractical, a decision was made to award the degree by an exercise of the Dean’s discretionary authority, in the interest of equity and fairness.

John J. McCarthy
Acting Dean of the Graduate School
ACKNOWLEDGEMENTS

I would like to thank Mr. Douglas Hayes and his son Mr. Donald Hayes, the owners of the Pine Crest Duck Farm, Sterling, Massachusetts for allowing me to conduct the field studies on their farm. A great appreciation is extended to Mr. Roger Kniskern for endless help in taking water samples in the observation wells and ponds and for installation and testing the soil columns in the laboratory. Thanks are also to Mr. Percy Wheeler for all the help in the fabrication of cylinders for the soil columns. I express great sense of gratitude to my Advisor Dr. J. T. Clayton and the members of the Dissertation committee, Drs. T. H. Feng, Donald Dean Adrian and C. S. Chen for their noble guidance and inspiration. I further express my great sense of gratitude to Drs. D. D. Lindsey and James Kittrell for their help and guidance. I would also like to thank my beloved Grandfather, Grandmother, Father, Mother and Nani, who could not live to see my accomplishments.
ABSTRACT

ADSORPTION COLUMN STUDIES TO PREDICT THE FLOW OF NUTRIENTS THROUGH HETEROGENOUS POROUS MEDIA UNDER EQUILIBRIUM AND ISOTHERMAL CONDITIONS

SEPTEMBER 2012

VIJAI B. PANDEY, M.TECH., INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR, INDIA

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor J.T. Clayton

Because of the endangerment of life of the human beings due to the environmental pollution, a serious study of the pollution of the environment is most vital. Because of increasing surface water pollution there is great hazard of ground water pollution. About half the United States of America derives drinking water from aquifers and much of the projected demand is expected to be met from subsurface sources. Therefore, a study was needed to determine the process of ground water contamination due to nutrients, especially Nitrogen, its degree and Length and Time of Travel and factors inhibiting its flow through soil.

The present study was undertaken at the ‘Pine Crest Duck Farm’ at Sterling, Massachusetts, where the nature of the soil was Gravely Sandy Loam and Three unlined (from the side and bottom) waste stabilization ponds existed and there was a great danger of ground water contamination due to Nitrogen in the vicinity of ponds and further. In the field, observation wells were installed along the radial line and bi-monthly samples of water were taken to monitor the levels of B.O.D., Ammonium, Nitrate and Nitrite Nitrogen.

Since the Adsorption of the Nitrogen by the soil is great inhibitor in the movement of the Nitrogen through soil profiles, this study was undertaken to study the adsorptive capacity of the soil in ‘Bench Tests’ and to test the applicability and validity of various adsorption isotherms of nitrogen in the soil; to develop a dimensional model or prediction equation for the nitrogen in the soil under natural flow conditions by studying the effects of varying concentration and flow rates on the adsorptive capacity of the soil, based on the principles of similitude; to correlate adsorption values in bench and column tests; and to determine the length and time of travel of nitrogen through soil.
The soil from the Farm was obtained from a depth of six feet with enough care so that original structure was maintained. Adsorptive capacity of the soil was determined through series of ‘Bench Tests’ and ‘Soil Adsorption Columns’ in the laboratory under temperature controlled chambers. From the Bench Tests Adsorption values of the soil at various concentrations of Ammonium, Nitrate and Nitrite Nitrogen were determined and validity and applicability of Adsorption isotherms were confirmed.

To study the Adsorption Process under natural flow conditions ‘Soil Adsorption Column Tests’ were done by using never done before Dimensional Model Analysis of Factors affecting Adsorption and getting dimensionless numbers and further obtaining ‘Break Through Curves’ at different Concentration and flow rates and Adsorption Values were obtained for Ammonium Nitrogen and Nitrite Nitrogen. Finally, Component and Prediction Equations were obtained for Ammonium Nitrogen and Nitrate Nitrogen.

By knowing the Adsorption Values of the soil Length and Time of Travel of Ammonium and Nitrate Nitrogen through soil was calculated at various Concentration Levels. A mathematical Prediction Equation was also obtained between Bench and Column Tests and Length of Time of Travel, to predict the adsorption values under natural flow conditions by just performing less time consuming Bench Tests.

It was also found that under equilibrium Bench Test conditions and natural flow conditions, adsorption of Ammonium, Nitrate and Nitrite Nitrogen increased with increasing solution concentration and adsorption of Ammonium Nitrogen was considerably higher than Nitrate and Nitrite Nitrogen. It was further found that for solution concentrations of 20, 40, 60, 80 and 100 mg/l Ammonium Nitrogen and nitrate nitrogen will travel one foot distance in 183 and 115 days; 168 and 111 days; 148 and 98 days; 145 and 81 days; 130 and 98 days; and 127 and 97 days respectively. It was determined that at the present time contamination of shallow water wells does not pose Nitrogen contamination problem and installation of these wells beyond 300 feet radial distance from the waste stabilization ponds was safe.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I - INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Objectives</td>
<td>4</td>
</tr>
<tr>
<td>II - REVIEW OF LITERATURE</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Past and Present Attempts to Investigate the Flow of Nitrogen through Soil</td>
<td>6</td>
</tr>
<tr>
<td>2.2 Adsorption Phenomena, Breaking-through Curves, Types and Factors Affecting Adsorption</td>
<td>11</td>
</tr>
<tr>
<td>2.2.1 Adsorption Phenomena</td>
<td>11</td>
</tr>
<tr>
<td>2.2.2 The Break-through Curve</td>
<td>12</td>
</tr>
<tr>
<td>2.2.3 Types of Adsorption</td>
<td>14</td>
</tr>
<tr>
<td>2.2.4 Factors Affecting Adsorption</td>
<td>15</td>
</tr>
<tr>
<td>2.3 Adsorption Column Studies</td>
<td>15</td>
</tr>
<tr>
<td>III - THEORETICAL CONSIDERATIONS</td>
<td>25</td>
</tr>
<tr>
<td>3.1 Mathematical Models of Adsorption</td>
<td>25</td>
</tr>
<tr>
<td>3.1.1 Langmuir’s Model</td>
<td>26</td>
</tr>
<tr>
<td>3.1.2 Brunauer, Emmet, Teller or B.E.T. Model</td>
<td>29</td>
</tr>
<tr>
<td>3.1.3 The Freundlich Model</td>
<td>30</td>
</tr>
<tr>
<td>3.2 Dimensional Model of Adsorption Process</td>
<td>30</td>
</tr>
<tr>
<td>3.2.1 Component Equations</td>
<td>34</td>
</tr>
</tbody>
</table>
3.2.2 Development of Dimensional Model or Prediction Equation ..................................35

3.3 Length and Time of Travel of Nitrogen ........................................................................36

IV – EXPERIMENTAL METHODS AND MATERIALS .........................................................38

4.1 Field Installation and Experimentation .......................................................................38

4.1.1 Installation Technique .........................................................................................39

4.1.2 Sampling Technique ..........................................................................................39

4.1.3 Soil for the Experiment ......................................................................................42

4.2 Laboratory Experimentation .....................................................................................42

4.2.1 Bench Tests .........................................................................................................42

4.2.2 Column Tests .....................................................................................................45

V – RESULTS AND DISCUSSION ....................................................................................52

5.1 Bench Tests .............................................................................................................52

5.1.1 Adsorption of Ammonium Nitrogen .................................................................52

5.1.2 Adsorption of Nitrate Nitrogen .........................................................................56

5.1.3 Adsorption of Nitrate Nitrogen .........................................................................59

5.2 Column Tests ..........................................................................................................63

5.2.1 Variation of Adsorption at Varying Concentration and Flow Rates at Constant $D_p/L \times \Delta t g^{1/2}/L^{1/2}$ (2291.5) .........................................................................................63

5.2.2 Variation of Adsorption with Varying Concentration and Length of Columns at Constant Froude Number (3.1 x $10^{-7}$) .........................................................69

5.3 Dimensional Model or General Prediction Equation ...............................................73

5.3.1 Prediction Equation for $\text{NH}_4\text{-N}$ ................................................................73

5.3.2 Prediction Equation for $\text{NO}_3\text{-N}$ ..................................................................75

5.4 Biological Transformation of Ammonium .................................................................76

5.5 Elution of the Column .............................................................................................80
5.6 Bench Tests and Column Tests ................................................................. 82

5.6.1. Length and Time of Travel of Nitrogen .............................................. 83

5.7 Field Studies ......................................................................................... 85

5.7.1. Ammonium Nitrogen ........................................................................ 85
5.7.2 Nitrate Nitrogen ................................................................................. 87
5.7.3 Nitrite Nitrogen .................................................................................. 87
5.7.4 Biochemical Oxygen Demand ............................................................ 90
5.7.5 Variation of Water Table in the Observation Wells ......................... 92
5.7.6 Coliform, Solids, and pH ................................................................. 92

VI – CONCLUSION ...................................................................................... 95

APPENDICES

A. PREDICTION EQUATION FOR NH$_4^-$N .............................................. 98
B. PREDICTION EQUATION FOR NO$_3^-$N .............................................. 100
C. LENGTH AND TIME OF TRAVEL OF AMMONIUM NITROGEN .......... 101

BIBLIOGRAPHY ........................................................................................... 102
LIST OF TABLES

Table                                                                                       Page
1. Physical and Chemical Characteristics of the Soil .........................................................43
2. Concentration and Flow Levels used in the Column Test – 1 ...........................................49
3. Concentration and Flow Levels used in the Column Test – 2 ...........................................50
4. Adsorption of NH$_4^+$ on the Soil .......................................................................................54
5. Adsorption of NO$_3$ on the Soil (p$_H$ below 7.0) ...............................................................57
6. Adsorption of NO$_3$ on the Soil (p$_H$ above 7.0) ...............................................................58
7. Adsorption of NO$_2$ on the Soil ............................................................................................62
8. Effect of Froude’s Number (V/$\sqrt{gL}$) on Dimensionless Term A/C at Varying
   Concentrations and Flow Rates for NH$_4$-N .......................................................................65
9. Effect of Froude’s Number on Dimensionless Term A/C at Varying Concentrations
   and Flow Rates for NO$_3$-N .................................................................................................68
10. Effect of $\frac{dp}{L} x \frac{\Delta g^{1/2}}{L^{1/2}}$ on A/C for NH$_4$-N at Varying Concentrations and Column
    Length (Froude’s Number = 3.1 x 10$^{-7}$) .........................................................................70
11. Effect of $\frac{dp}{L} x \frac{\Delta g^{1/2}}{L^{1/2}}$ on A/C for NO$_2$-N at Varying Concentrations and Column
    Lengths (Froude’s Number = 3.1 x 10$^{-7}$) .......................................................................71
    Conditions .................................................................................................................................77
13. B.O.D. of Ground Water at Various Sampling Locations ..................................................91
<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. A Schematic Representation of Moving Adsorption Zone and Resulting 'Break-through Curve'</td>
<td>13</td>
</tr>
<tr>
<td>2. Linear Forms of Adsorption Isotherms</td>
<td>28</td>
</tr>
<tr>
<td>3. Typical Observation Well Locations at the Pond in a Sectional View</td>
<td>40</td>
</tr>
<tr>
<td>4. Orion Digital Water Meter Used in Determining $p^H$ and Nitrate Concentration</td>
<td>41</td>
</tr>
<tr>
<td>5. A Typical Adsorption Column</td>
<td>47</td>
</tr>
<tr>
<td>6. Soil Adsorption Columns in Constant Temperature Room</td>
<td>48</td>
</tr>
<tr>
<td>7. Adsorption Isotherm for Ammonium on the Soil</td>
<td>55</td>
</tr>
<tr>
<td>8. Langmuir's Isotherm for Ammonium on the Soil</td>
<td>60</td>
</tr>
<tr>
<td>9. Adsorption Isotherm for Nitrite on the Soil</td>
<td>61</td>
</tr>
<tr>
<td>10. Typical NH₃ Adsorption Curve for Columns with Varying Concentration and Flow Rates</td>
<td>64</td>
</tr>
<tr>
<td>11. Variation of Froude's Number with A/C at Constant $\frac{D}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}$</td>
<td>67</td>
</tr>
<tr>
<td>12. Variation of A/C with Respect to $\frac{D}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}$ at Constant Froude's Number</td>
<td>72</td>
</tr>
<tr>
<td>14. Extent of Nitrification in a Column of Ammonium (Column Test A-1)</td>
<td>78</td>
</tr>
<tr>
<td>15. Extent of Nitrification on a Column of Ammonium (Column Test A-2)</td>
<td>79</td>
</tr>
<tr>
<td>16. Elution Performance of Column Number 4 for Ammonium Nitrogen</td>
<td>81</td>
</tr>
</tbody>
</table>
17. Time of Travel of Ammonium and Nitrate Nitrogen at Varying Concentrations ......84

18. Concentration of Ammonia Nitrogen in Ground Water ........................................86

19. Concentration of Nitrate Nitrogen in Ground Water ...........................................88

20. Concentration of Nitrite Nitrogen in Ground Water ...........................................89

21. Depth of Water Table at Various Locations of Observation Wells .......................93
CHAPTER I

INTRODUCTION

"Shall we surrender to our surroundings or shall we make our peace with nature and begin to make reparations for the damage we have done to our air, to our land and to our water? Restoring nature to its natural state --- has become a common cause of all the people---."

President Richard M. Nixon

Lest the life of human beings be endangered due to environmental contamination, a serious study of the pollution of the environment is most vital. Increasing air and water pollution are posing a severe threat to human health and survival. Breathing in fresh and clean air and drinking pure water is becoming less possible for mankind day by day. Therefore, scientific and engineering studies into the causes and effects of environmental contamination are important, if the best possible remedies are to be found.

Water pollution is perhaps no more important than air pollution but for the present case, discussion will be limited to ground water pollution. Pollution of surface waters is mainly caused by organic wastes, chemical wastes from the industry, application of insecticides, pesticides and fertilizers for agriculture purposes, silt from agricultural operations and engineering projects, run-off from watersheds and feed lots and municipal sewage.

Because of surface water pollution there is a great hazard of ground water pollution. About half the United States of America derives drinking
water from aquifers and much of the projected demand is expected to be met from subsurface sources. There is much yet to be learned regarding the degree of contamination of these sources and degree of public health threat they pose. Environment Protection Agency has already taken initiative to protect the ground water with intent to remedy the predominance of surface water related activities within the agency. However, the movement of agency in proclaiming effective laws, setting up standards and funding for ground water research has been less than satisfactory.

How ground water pollution takes place is the leading question at this point. Water plays a good role as a carrier in the movement of contaminants and if enough water is available, either in the form of precipitation or liquid waste solution, the contaminants will move through the soil profile. As the contaminants move downward, their concentration decreases. This is mainly due to the adsorption of contaminants by soil particles, although dilution and dispersion are also effective to some extent. If the concentration of contaminants is not totally reduced within the aeration zone, they will travel farther and contaminate the ground water.

Various geologic and hydrologic factors affect the movement of contaminants underground. Moderately high topographical conditions, good permeability of the soil and low precipitation rate or liquid waste application rate enhance the movement of contaminants underground. For liquid waste solutions, low viscosity and infiltration rate will cause underground movement.
On the basis of the above discussion, it may be presumed that groundwater contamination due to nitrogen may take place in the vicinity of waste stabilization ponds and lagoons. Groundwater contamination due to nitrogen (11, 14, 26, 43, 62, 70, 71), phosphorus and Alkyl Benzene Sulphonate (14, 27, 62, 75) has been well documented and it is a potentially very serious problem, since many rural water supplies are from surface wells and groundwater is also used for industrial purposes. High nitrate concentrations in water cause disease (methemoglobinemia in children) if used for drinking purposes.

Since the movement of nitrogen in the vicinity of waste stabilization ponds has been demonstrated by Chang (14), Legrand (43), Preul (62), Singh (70), Smith (71) and Steward (73), it may be realized that investigation of the degree and nature of groundwater contamination due to nitrogen will be of high practical significance. The present study was done on the waste stabilization ponds of 'Pine Crest Duck Farm,' Sterling, Massachusetts. This farm has three ponds which are unlined from the side and bottom. The gravelly sandy loam nature of soil in the vicinity of ponds increases the possibility of groundwater contamination by nitrogen in the vicinity of ponds. Since adsorption is the greatest inhibitor to the movement of nitrogen through soil profiles, the study of the adsorptive capacity of the soil will be highly valuable. The adsorptive capacity of the soil was studied through series of bench tests and column tests. From the bench tests the nature of adsorption process was determined and the values of constants in different isotherms were determined. Through column tests the adsorption values were obtained under natural flow conditions and dimensional prediction equations were obtained to predict the adsorption at varying
concentration and flow rates of nitrogen. By knowing the adsorption values it was possible to calculate the length and time of travel of nitrogen through soil medium. Thus, knowing the amount of time taken to travel a particular distance in the soil, possible predictions could be made regarding the possibility of ground water contamination due to nitrogen in the other areas under similar conditions.

Hence, a study relating to ground water contamination by nitrogen and its adsorption on the soil was felt highly desirable and important. The study would also help in determining the safe location of sub-surface wells from waste treatment ponds.

1.1 Objectives

The specific objectives of this scientific study were:

1. To study the adsorptive capacity of the soil (Duck Farm) in bench tests and to test the applicability and validity of Langmuir, Freundlich and B.E.T. isotherms of adsorption for the adsorption of nitrogen on the soil.

2. To develop a dimensional model or prediction equation for the adsorption of nitrogen on the soil under natural flow conditions by studying the effect of varying concentrations and flow rates on the adsorptive capacity of the soil, based on the principles of similitude.

3. To look into the possibility of correlating bench test and column test data to aid in predicting the adsorption values by knowing only bench test adsorption values in order to save
the time taken in column tests.

(4) To determine the length and time of travel of nitrogen by knowing the values of adsorption under natural flow conditions.

(5) To find out the variability of nitrogen concentrations in the ground water in the vicinity of ponds by means of observation wells, installed in the apparent direction of ground water flow.
CHAPTER II

REVIEW OF LITERATURE

"The river Rhine, it is well known
Doth wash your city at Cologne:
But tell me, Nymphs, what power divine
Shall henceforth wash the river Rhine?

Samuel Taylor Coleridge

An Overview

All the literature reviewed has been divided into three parts. The first part contains the past and present works to investigate the groundwater pollution due to travel of nitrogen through soil mass. The second part is devoted to the understanding of adsorption phenomena on the soil and its main role in controlling the movement of contaminants, break through curve, types and factors affecting adsorption. The third part extensively deals with the column studies used to study the adsorption of various kinds of nutrients on various kinds of adsorbents. Selected mathematical models have also been included in section 3.

2.1 Past and Present Attempts to Investigate the Flow of Nitrogen

Through Soil

Since very few researchers have ventured to work in the area of groundwater contamination due to nitrogen the availability of literature is very limited. The occurrence of nitrogen contaminated ground water has been well documented (11, 14, 26, 43, 54, 62, 70, 71). Expressing his concern regarding the ground water contamination Legrand (43) commented that "The
upper part of the zone of saturation in populated parts of the earth may be considered as a galaxy in which millions of enclaves of contaminated water are scattered in uncontaminated water." The likelihood of ground water contamination in the vicinity of waste stabilization ponds has been predicted by Preul (62). Nitrogen contamination by barnyard leachets was reported by Gillham and Weber (26). During the five month study period they found that 4.4 pound nitrogen leached to ground water under stony loam till overlying dolomitic limestone bed rock. They further concluded that 4.4 pound of nitrogen leached is considerably small amount but would require $1.4 \times 10^4$ cu.ft. of water to dilute to be acceptable for disposal in the streams (5 mg/l-N). Stewart et al. (73) demonstrated the movement of nitrogen from feed lots to ground water in Colorado, U.S.A. Similar conclusions were drawn by Smith (71) and Legrand (43). In a survey of wells in Minnesota by Minnesota Department of Public Health in 1951 showed high concentrations of nitrates in the well water (44).

Therefore, there seems to be a clear danger of ground water contamination by nitrogen in the vicinity of waste stabilization ponds. The permissible nitrate level in drinking water is 10 mg/l and 45 mg/l when reported as nitrogen and nitrate respectively (62). Nitrates are responsible for health problems and industrial problems. Dying of fabrics, brewing of beer and growing of fish and other aquatic life is affected by the presence of nitrates (44). In addition, if taken in excessive quantities nitrate may be poisonous to humans (44). Nitrate develops a serious disease in the bloodstream of babies under six months called infant cyanosis or methemoglobinemia. In Iowa, in 1945, incidents of this condition were first
associated with high nitrate levels in water used in formula preparation (44). In 1949, in a nine state survey 262 cases of infant cyanosis were reported (21). Minnesota recorded 138 cases, including 14 deaths with nitrate contaminated wells (44). Free ammonia in the ground water may be the evidence of recent pollution. Nitrites are usually not found in ground water in excess of 0.1 mg/l as nitrogen and is considered insignificant for drinking water purposes (62, 63).

Preul (62) found concentrations of nitrates, nitrites, ammonia nitrogen, phosphate and A.B.S. (Alkyl Benzene Sulphonate) in the ground water in the vicinity of waste treatment ponds in Minnesota. From his studies he showed that ammonia nitrogen varied form 0.1 mg/l to 0.9 mg/l with a mean of 0.5 mg/l while nitrite nitrogen was not found in excess of 0.1 mg/l.

Nitrate nitrogen he reported, was 0.1 mg/l and phosphate levels were very low. He further concluded that ammonium nitrogen was reduced from the mean of 12 mg/l found in raw waste water to 0.5 mg/l in ground water. He also found that in the upper and lower reaches of ponds concentration levels were very low in the ground water samples.

Brink (11), while studying the water pollution from agriculture due to livestock production and commercial use of fertilizers found a five-year average consumption from 1956 to 1960 to be 10 kg N/hectare/yr for fertilizer and 15 kg N/hectare/yr for manure. Between the years of 1966 and 1970, he further found that while no change in nitrogen consumption from manure occurred while nitrogen consumption from fertilizers significantly increased to 80 kg N/hectare/yr on the average. He also found that ground water contamination of total nitrogen varied from 1.7 mg/l to 9.4 mg/l at
the depths of 3.6 meter and 2.9 meter respectively. The \textit{NH}_4-\textit{N} concentration were found to be 0.1 mg/l to 4.5 mg/l at the depths of 9.8 meter and 1.1 meter respectively. He predicted severe contamination of ground water in the future. Stollar et al. (75) also discovered contamination of ground water on the farmlands in the flood plains of Kansas river.

From the above discussion, it is obvious that soil mechanisms such as adsorption, and possibly biological transformation are effective to some extent. Preul and Schroepfer (63) in another study positively established that adsorption and biological actions are the greatest inhibitor to the movement of nitrogen through soil. They conducted a series of bench tests and column tests to establish the adsorption capacity of the various soils (Zimmerman sand, Hayden silt and Milaca clay). From bench tests they demonstrated that under equilibrium conditions the Freundlich isotherm as given below applies for \textit{NH}_4-\textit{N}.

\[ A = K C^{1/n} \]  \hspace{1cm} [1]

where

\[ A = \text{adsorption of } \textit{NH}_4-\textit{N}, \mu g-\textit{NH}_4-\textit{N} \text{ per gram of soil} \]

\[ C = \text{concentration of } \textit{NH}_4-\textit{N} \text{ in the solution at equilibrium or initial concentration, mg/l} \]

\[ K, n = \text{constants} \]

They also suggested that under the flow conditions through a soil bed the rate of adsorption was found to vary in the following manner:

\[ \frac{C}{C_0} = e^{(k/q)} \]  \hspace{1cm} [2]
where
\[ C = \text{effluent concentration of } \text{NH}_4 \text{ mg/l} \]
\[ C_o = \text{influuent concentration of } \text{NH}_4 \text{, mg/l} \]
\[ q = \text{\mu g } \text{NH}_4 \text{ adsorbed} \]

Since Preul and Schroepfer (63) conducted studies with predominantly clay, silt and sandy soils, the applicability of their data is limited to mainly these soils. In natural field conditions soil strata may be formed with different kinds of soils and hence the use of their data is limited. In the column tests they used only two concentrations of ammonium nitrogen, i.e. 10 mg/l and 50 mg/l and flow rates were varied from 200 ml/day to 1,170 ml/day. Since only two concentrations were used, the adsorptive capacity of the soil beyond 50 mg/l concentration could not be assessed. Also they limited their studies to only ammonium nitrogen and thus adsorptive capacity of the soil for nitrate nitrogen remains yet to be determined. Furthermore, there is no statistical evidence supporting the significance of the fitted data and reproducibility is suspected. Therefore a need existed to find out the adsorptive capacity of heterogeneous soil beds as is the practical case under field conditions.

Preul (62) attempted to calculate the length and time of travel of ammonia nitrogen for Zimmerman sand and Hayden silt. He took arbitrary percolation rate and determined that ammonia nitrogen will travel 10 ft. length of sand and silt in 16.7 and five years respectively. These data cannot be applied to field conditions. Thus length and time of travel of ammonia nitrogen and nitrate nitrogen at various concentrations are yet to be determined.
Ray et al. (65) studied the movement of ammonium nitrogen in four different kinds of soils in Minnesota, Viz Nicollet loam, Anoka Lamy fine sand, Fayette silt loam and Barnes loam. They concluded that the movement of ammonia nitrogen is closely related to the movement of water and other factors such as texture of the soil, organic matter and cation exchange capacity of the soil are also of great importance. Their studies did not include the effect of various concentrations and moisture tension on the migration pattern of ammonia nitrogen in the soils.

Tyler et al. (81) studied the movement of nitrogen in simulated cross section of field soil. They used soil boxes in which nitrogen fertilizers were applied four inches below the soil surface. After three days soils were brought to field capacity to a depth of two feet by flooding with irrigation water. Two weeks later samples were taken and they found that downward movement of ammonium nitrogen was very little. This was due to the fact that ammonium ion has greater affinity to soil particles and also nitrification helped in changing ammonium into nitrate and nitrites.

Since adsorption is the main inhibitor to the movement of nutrients it is very necessary to include a brief discussion about adsorption phenomena, break-through curves, types and factors affecting adsorption.

\subsection*{2.2 Adsorption Phenomena, Break-through Curves, Types and Factors Affecting Adsorption}

\subsubsection*{2.2.1 Adsorption Phenomena}

Adsorption has been defined in several ways. Mantell (49) defines "Adsorption concerns itself with the concentration, as a result of surface
forces existing on a solid, of gases, vapors, liquids or solutes (i.e. solids dissolved in a solvent, dispersed materials and colloids)." Adorption is a surface phenomenon in which molecules or atoms of one phase are accumulated on the other phase. The material getting adsorbed is known as adsorbate and material on which adsorbate is adsorbed is known as adsorbent. Generally the adsorbent is solid material and porous. Sometimes confusion arises between adsorption and absorption. The adsorption as described earlier is accumulation of adsorbate on the surface of adsorbent and it may be with or without chemical reaction. On the other hand in absorption adsorbate molecules penetrate the adsorbent structure thus producing a solid solution. Hence a general term 'sorption' may be used when a gas, vapor or liquid is taken up by a solid (49, 90).

Mantell (49) reports that C. W. Scheele (1773) and Fontana (1777) were first to observe the occurrence of adsorption in the removal of gases from the air by charcoal. Since then attempts were made to evolve a theoretical basis for this phenomenon. According to Mantell (49), "Lowitz (1785) discovered that charcoal would effectively remove coloring matter from various solutions when the coloring matter was of an organic nature." And today adsorption has found a great place in physical, chemical and biological sciences. Various kinds of adsorption processes are detailed elsewhere (49).

2.2.2 The Break-through Curve

The adsorption process could be very well illustrated by break-through curve (90) as given in Figure 1 in which abscissa is either time or volume of water treated and ordinate is the ratio of effluent in influent concentration. Referring to Figure 1, in the beginning all the solute is adsorbed
Fig. 1. A Schematic Representation of Moving Adsorption Zone (A.Z.) and Resulting Break-through Curve (90).
by top layers and whatever escapes is totally adsorbed by the bottom layers so adsorption zone is concentrated at the top end and at point 1 effluent is practically solute free. At the point 2 when top layers are totally exhausted and have very little capacity to adsorb, adsorption zone moves to the middle of the column and at point 2 more and more solute escapes in the effluent. At point 3 adsorption zone has moved to the bottom of the column as the result of inability of the above layers to adsorb any solute and column is practically in equilibrium with influent water and beyond this very little adsorption will take place. This point is known as break 'point.' At point 4 adsorption zone tends to move out from the column and effluent solute concentration is practically the same as influent solute concentration and at this point column is totally exhausted. The point 4 is called as 'exhaustion point.' The total amount of solute adsorbed could be calculated by calculating the area on the left of the break-through curve.

2.2.3. Types of Adsorption

There are three kinds of adsorption: physical, chemical and exchange adsorption (49, 90).

If there is weak interaction between solid and liquid molecules then the adsorption will be called physical adsorption. In these molecules of liquid are free to move to any other site as the result of weak attraction. This kind of adsorption is also known as van der Walls adsorption.

In chemical adsorption there is strong interaction between solid and liquid and molecules are not free to move. This is also known as 'activated adsorption' because in this activation energy is required in much similar way as in the chemical reactions (49).
In exchange adsorption the concentration of ions on the surface is due to electrostatic (forces) attraction to charged sites at the surface (90). Thus in this kind displacement of ions takes place.

Adsorption mainly takes place in three steps--film diffusion, pore diffusion and internal adsorption (88, 90). In film diffusion molecules of adsorbate are transported through a surface film on the surface of adsorbent. In pore diffusion the molecules are diffused in the adsorbent pores as a result of concentration difference. In internal adsorption, adsorption takes place on the interior surface of the adsorbent.

2.2.4 Factors Affecting Adsorption

Factors affecting adsorption have been detailed elsewhere (49, 89, 90) but main factors affecting are surface area, concentration of solute, pH, nature of adsorbate, mass flow rate, temperature, presence of other ions, nature of adsorbent, contacting system and mode of operation (49, 79, 89, 90).

2.3 Adsorption Column Studies

Fixed bed and fluidized columns of different adsorbents have been in use for long time for different adsorption processes.

Thiele (77) presented a good brief review of all the work done on adsorption columns. According to him "all authors assume that the solid is contained in a vessel of uniform cross section and that at any cross section at a given time the concentration in the solid and fluid are uniform, so that there is no loss in generality in basing all formulas on unit cross section. And authors have not taken into account any heat effects."

De Vault (21) presented an equation to show the distribution of a single solute in a column of adsorbent. The equation is given as follows:
\[
\frac{dv}{dx}c = a + Mf'(c) \tag{3}
\]

where

- \( V \) = volume of solution poured into column since initial time
- \( x \) = distance at any point in the column
- \( c \) = amount of solute per unit volume of solution, as a function of solution passed and position in the column
- \( M \) = amount of granular solid per unit volume
- \( b \) = amount of solute adsorbed on unit amount of solid as a function of solution passed and position in column
- \( f(c) \) be the isotherm of system under consideration
- \( \alpha \) = pore volume per unit bulk volume of granular solid
- \( f'(c) \) = derivative of \( f(c) \) with respect to \( c \)

The above equation assumes equilibrium at all points in the column.

De Vault's equation works good if it is applied for the cases where solute is already adsorbed on the solid uniformly and elution of the column results in depicting the distribution. But when solid is initially free from adsorbate or solute ambiguous results will be obtained (77).

Hougen and Marshall (32) developed an analytical method for calculating time-position-temperature concentrations for solids and gases during the adsorption. For isothermal conditions Hougen and Marshall expressed the solution of the analytical equations obtained through material balance in terms of four dimensionless groups as below (32):

\[
\frac{\eta}{\eta_o} = 1 - e^{-bt} \int_0^{ax} e^{-ax} J_o(2i\sqrt{bax}) \, d(ax) \tag{4}
\]

\[
\frac{w}{w_o} = e^{-ax} \int_0^{bt} e^{-bt} J_o(2i\sqrt{axbt}) \, d(bt) \tag{5}
\]
where

\[ i = \sqrt{-1} \]

\[ J_0 = \text{Bessel function of the first kind and zero order} \]
\[ y_o = \text{mass of adsorbate per unit mass of entering gas} \]
\[ w_o = \text{mass of adsorbate per unit of mass of adsorbent in equilibrium with entering gas} \]
\[ t = \text{time} \]
\[ y = \text{adsorbate content of fluid stream} \]
\[ w = \text{adsorbate content of solid} \]
\[ x = \text{longitudinal distance in bed} \]
\[ a = \frac{1}{H_d} \]
\[ H_d = \text{height of mass transfer unit} \]
\[ b = \beta c, \beta = \frac{G}{\rho B H_d} \]
\[ G = \text{mass velocity of adsorbate free fluid flowing} \]
\[ \rho = \text{bulk density of solid} \]
\[ c = \text{constant} \]

Hougen and Marshall developed series of charts to aid in the solution of above equations (32).

Michaels (52) introduced the concept of exchange zone method to predict the concentration history in a fixed bed adsorber. Exchange zone is an arbitrary zone in which the majority of the exchange takes place and which descends through the exchanger bed at constant velocity (65). By the use of this method laboratory data could be correlated for the design of large-ion exchange units.
J. B. Rosen (67) derived appropriate partial integrodifferential equations and obtained the solution to predict the effluent concentration of an initially empty column. The proposed equation is as below:

$$\frac{3c}{\delta x} = -2 \sum_{n=1}^{\infty} \int_{0}^{y} \left[ \frac{3c}{\delta \lambda} + v \frac{3^2 c}{\delta x \delta \lambda} \right] \exp \left[ \frac{1}{2} n^2 \pi^2 (\lambda-y) \right] d\lambda$$  \hspace{1cm} [6]

where

- \(c\) = concentration of solute to fluid
- \(x\) = bed length parameter, dimensionless
- \(y\) = contact time parameter, dimensionless
- \(v\) = film resistance parameter, dimensionless
- \(\lambda\) = variable of integration

Rosen considered a linear isotherm of adsorption and obtained the solution in the form of dimensionless family of curves.

Thomas (78) presented a solution based on the second order kinetics to predict the concentration history in a zeolite column. The solution is given as below:

$$\frac{c}{c_o} = \frac{I_o(2\sqrt{k_1k_2\gamma s}) + \phi(k_2\gamma,k_2,s)}{I_o(2\sqrt{k_1k_2\gamma s}) + \phi(k_1s,k_2\gamma) + \phi(k_1,\gamma,k_2s)}$$  \hspace{1cm} [7]

where

- \(c\) = concentration of the exchangeable cation at any time
- \(c_o\) = initial concentration of exchangeable cation
- \(I_o\) = zeroth order Bessel function
- \(k_1, k_2\) = velocity constants
- \(\gamma\) = \(c_o(t-1/R)\)
- \(s\) = \(Mla/Rv_o\)
\[ t = \text{time} \]
\[ l = \text{distance along the bed} \]
\[ R = \text{constant flow rate} \]
\[ M = \text{overall density of zeolite as packed in the column} \]
\[ a = \text{initial exchange capacity of zeolite} \]
\[ v_o = \text{fractional free space in the zeolite column} \]

The hardest thing in the preceding equation is to get reaction rates \( k_1 \) and \( k_2 \) but Thomas has suggested that "these quantities will probably be best obtained by fitting equation (25) to break through data on a column run under known conditions." Equation (25) as referred in the preceding sentence could be obtained from Thomas' original paper (78).

Acrivos (1) proposed a method of characteristics to predict the concentration history of the solute in a uniformly packed bed. Under isothermal conditions for one dimensional plug flow, neglecting diffusion along the \( x \) axis the basic equations are given (1).

\[
\begin{align*}
\frac{\partial c}{\partial x} + \varepsilon \frac{\partial c}{\partial t} &= -(1 - \frac{c}{\rho}) R(c, w, v) \\
\frac{\partial v}{\partial x} &= -\frac{1}{\rho} R(c, w, v) \\
\frac{\partial w}{\partial t} &= R(c, w, v)
\end{align*}
\]

where

\[ c = \text{concentration of adsorbate in fluid stream} \]
\[ w = \text{amount of adsorbate on bed} \]
\[ v = \text{superficial velocity of fluid through bed} \]
\[ \varepsilon = \text{fractional void volume of bed} \]
\[ \rho = \text{molar density of fluid (constant)} \]
\( R(c, w, v) = \) rate of adsorption which in general would be an arbitrary function of \( c, w \) and \( v \)

\( x = \) distance along axis of bed

\( t = \) time

The solution of the above equations is given elsewhere (70) and according to Acrivos (1) this method is more accurate and dependable as its accuracy is checked and improved at each step.

Chi and Wasan (15) modified Hougen and Marshall's model. They pointed out that Hougen-Marshall model could not take into account nonlinear isotherm which is true for many systems and secondly Hougen and Marshall did not present their solutions for the cases where adsorbent is coated on a supporter (15). Chi and Wasan model includes the isothermal adsorption process for any equilibrium relationship. The equations obtained by Chi and Wasan (15) are given as below:

\[
\begin{align*}
\frac{3Y}{\partial n} t &= -(Y-Y^*) \\
\frac{3w}{\partial t} n &= (Y-Y^*) \\
Y^* &= f(w)
\end{align*}
\]  \([9]\)

where

\( Y = \) humidity

\( n = \) dimensionless bed length

\( t = \) dimensionless time

\( Y^* = \) equilibrium humidity at the surface of adsorbent

\( w = \) adsorbate content in the adsorbent

Lindstorm et al. (46) developed a mathematical model for the movement of herbicides in soils based on Fick's law, conservation of energy and an
adsorption isotherm. The model is given as below:

\[ C_t = KCxx - UCx \]  

where

- \( C \) = Concentration of chemical in pore water
- \( K = \frac{K_0}{1 + aR} \)
- \( U = \frac{U_0}{1 + aR} \)
- \( K_0 \) = diffusion coefficient of the chemical in the soil water complex
- \( U_0 \) = average water velocity in the interparticle voids at dept x
- \( R = \exp(\Delta G/kT) \)
- \( \Delta G \) = free energy sorption term
- \( k \) = Boltzman's constant
- \( T \) = absolute temperature
- \( a \) = ratio of surface area of chemically active sites to the total particle surface area

Assuming initial concentration to be zero Lindstorm et al. (46) obtained two solutions: One for the continuous fluxing input and the other for the flux plug type input boundary condition.

While working on the adsorption of chlorine by charcoal in charcoal adsorption columns Bohart and Adams (6) proposed a mathematical equation which predicts the amount of chlorine adsorbed at any time. The model is given as below (6, 92):

\[ \frac{W}{W_s} = \frac{1 - \exp\left(-\frac{N_T t}{t_s}\right)}{1 + \exp\left(-\frac{N_T t}{t_s}\right)[\exp\left(N_T x/L\right) - 1]} \]
where

\[ W = \text{amount of chlorine adsorbed} \]

\[ W_S = \text{adsorption capacity (maximum) of charcoal for chlorine} \]

\[ N_t = \frac{k_A \cdot L}{V_L} \]

\[ K_A = \text{rate transfer coefficient} \]

\[ L = \text{length of the column} \]

\[ V_L = \text{superficial linear velocity} \]

\[ t_s = \text{time corresponding to } W_S \]

\[ t = \text{time} \]

\[ x = \text{distance along the column} \]

The greatest implication in the above model is that the value \( W_S \) must be known which is the maximum amount of adsorbate adsorbable by adsorbent at any concentration of adsorbate and in most of the cases it is difficult to find out the same by extrapolation of \( W \) and \( t \) curve and experiments must be performed to get this value.

Later on Wheeler and Robell (92) used Bohart and Adams' model to predict the poisoning wave patterns in a fixed bed catalytic flow reactor.

Theodore Vermulen (83) defined two dimensionless terms—solution capacity parameter and column capacity parameter and obtained mathematical solution for predicting effluent concentration histories in fixed bed. The solution obtained by Vermulen predicts the break-through curves for solid diffusion under irreversible cases.

Various methods are known for interpreting experimental data for linear equilibrium cases where either external or internal diffusion alone controls the rate in the ion exchange columns. Heister et al. (29) developed
interpretive techniques for nonlinear equilibrium cases of fixed beds, where
the rate is controlled by a combined diffusion mechanism. They also derived
a completely general correlation method for adding the mass transfer resis-
tances under nonequilibrium conditions. In terms of individual coefficients
and interfacial concentrations, the rate equation for external (fluid film)
diffusion is given (91) as below:

$$\frac{dq_A}{dT} = (k_{fA}) a \frac{n}{B_d} [C_A - (C_A)_i]$$  \[12\]

where

$q_A$ and $C_A$ = concentration of components A on the coexisting solid
and fluid phases respectively

$(k_{fA})$ = mass transfer coefficient for external diffusion

$a$ = transfer area per unit volume of the bed

$n$ = fraction of the voids in the column

$B_d$ = bulk density of the resin

$T$ = time

and for intraparticle diffusion:

$$\frac{dq_A}{dT} = (k_p)_A a[q_A)_i - q_A]$$  \[13\]

where

$k_p$ = mass transfer coefficient for internal diffusion

Hajek (28) obtained the following equation to predict the concentration
distribution of a solute in a one dimensional soil flow system. The equation
is given as below:

$$\frac{C}{C_o} = \frac{1}{2} \left[ \text{erfc} \left( \frac{1}{2\sqrt{n'E}} \right) \right]$$  \[14\]
where

\[ C = \text{initial concentration in influent} \]

\[ C_o = \text{concentration in the effluent} \]

\[ n' = \frac{D}{Vx} \]

\[ D = \text{dispersion coefficient} \]

\[ V = \text{flow velocity} \]

\[ x = \text{distance from the influent end} \]

\[ E = \frac{Vt}{bx} \]

\[ b = 1 + \frac{K_d B D}{B} \]

\[ B_d = \text{bulk density of the soil} \]

\[ K_d = \text{distribution coefficient} \]

\[ B = \text{volumetric moisture content} \]

It is evident from the literature that most of the work done on adsorption columns in the area of chemistry and chemical engineering is with ion exchange columns.

In the treatment of water and waste waters use of fluid bed adsorption principles has recently gained much attention. It is not feasible to cover the studies done on fluidized columns in this section. Weber and Morris (86) and Weber and Keinath (91) have extensively studied the kinetics of adsorption and mass transfer of pollutants in a fluidized column respectively. Kasten and Amundson (35) and Wilkins and Thodos (78) studied the theory and mechanics of fluidized bed operations. Trulson (80) used packed columns to recover ammonia. The ammonia was removed in between aerobic and anaerobic steps by countercurrent desorption. Nutt et al. (56) used two stage fluidized beds for the control of nitrogen in the waste water.
CHAPTER III

THEORETICAL CONSIDERATIONS

"Dimensional analysis is a technique for expressing the behavior of a physical system in terms of the minimum number of independent variables and in a form that is unaffected by changes in the magnitude of the units of measurement."

R. E. Johnstone
and M. W. Thring

Literature review provides a sound basis to apply and evaluate certain adsorption models. This chapter has been divided into three parts. The first part deals with the adsorption models—their usefulness and applicability to water and waste waters. The second part is devoted to dimensional analysis of adsorption phenomena to aid in experimental design and to provide better understanding of adsorption process. The third part gives the procedures regarding the calculation of length and time of travel of nitrogen through soil to ground water.

Mathematical Models of Adsorption

When a solid adsorbent is brought into contact with a liquid adsorbate (solute) in a solution, the adsorbate tends to get deposited on the surface of adsorbent. As a result of this deposition the concentration of solute keeps on decreasing to a point after which no solute will get deposited on the surface of adsorbent. This final concentration of the solute to the solution is known as equilibrium concentration. The amount of solute deposited on the surface of solid adsorbent is known as the amount of solute adsorbed and is generally expressed as amount of solute adsorbed per unit
weight of adsorbent. Now for a given solute and unit weight of adsorbent the amount adsorbed at equilibrium is a function of final concentration and temperature which means, if,

\[ X = \text{amount adsorbed per weight of adsorbent} \]
\[ C = \text{equilibrium concentration of solute} \]
\[ T = \text{temperature} \]

then,

\[ X = f(C, T) \]

And if concentration of solute is varied at constant temperature, then

\[ X = f(C) \text{ at } T = \text{constant} \]

And, thus if amount adsorbed is plotted against the equilibrium concentration at constant temperature, the plot is known as 'adsorption isotherm.' The adsorption isotherm is simplest and easiest way of expressing experimental data at a particular constant temperature. These isotherms are very helpful in providing theoretical footing for the development of adsorption equations for a system. In the literature many adsorption isotherms could be found but for the present case only Freundlich's, Langmuir's and B.E.T. isotherms are discussed because it is felt that these models could be successfully applied in the case of water and waste waters. Freundlich's model was successfully applied by Preul and Schroepfer (63) but applicability of B.E.T. and Langmuir's model has rarely been attempted. Therefore, a brief discussion of these models is worth presenting.

3.1.1 Langmuir's Model

Langmuir (40) proposed a theory based on the three basic assumptions (40, 90).
(i) adsorption is a phenomenon in which adsorbed layer is unimolecular or one molecule thick;

(ii) the adsorption energy is constant;

(iii) the molecules do not move across the surface or get replaced by other molecules.

Langmuir conducted experiments by using mica, glass and platinum as adsorbent and various kinds of gases as adsorbate and verified the theory. It is expected that Langmuir's model will be equally applicable to water and waste waters. In Figure 2 (90) linear forms of Freundlich, Langmuir and B.E.T. models are given. A convenient form of Langmuir model is given as below (49, 89, 90).

\[
\frac{C}{X} = \frac{1}{bX_m} + \frac{C}{X_m}
\]

[15]

or

\[
\frac{1}{X} = \frac{1}{X_m} + \frac{1}{bX_m} \cdot \frac{1}{C}
\]

[16]

where

\(X\) = moles of adsorbate per gram of adsorbent at concentration \(C\)

\(X_m\) = moles of solute required to form a complete monolayer

\(C\) = concentration of adsorbate in solution at equilibrium

\(b\) = constant related to the energy of adsorption

It is obvious from the two equations that if \(\frac{1}{X}\) is plotted against \(\frac{1}{C}\) then the slope of the straight line will give \(\frac{1}{bX_m}\) and the intercept would be \(\frac{1}{X_m}\). Yet Zeise tested the validity of Langmuir's equation (25). Weber and Morris (89) experimentally proved the applicability of Langmuir's model for the adsorption of alkylbenzenesulphonates on carbon.
Fig. 2. Linear Forms of Adsorption Isotherms (90).
3.1.2 Brunauer, Emmet, Teller or B.E.T. Model

Brunauer, Emmet and Teller (12) proposed a model with the following assumptions (49, 90).

(i) adsorbate gets deposited in multimolecular layers and each layer obeys the Langmuir model;

(ii) adsorption takes place from one layer to another and until and unless the adsorption in the preceding layer is finished, the second layer does not start;

(iii) after the first layer every other layer has equal adsorption energies.

The simplified form of B.E.T. model is given as below (90):

\[
\frac{C}{(C_s-C)X} = \frac{1}{AX_m} + \frac{A-1}{AX_m} \cdot \frac{C}{C_s}
\]  

[17]

where

- \( C_s \) = saturation concentration of solute
- \( A \) = constant energy of interaction with the surface

It is obvious from the above equation that a plot of left hand side values against \( C/C_s \) will result in a slope of \( A-1/AX_m \) and an intercept of \( 1/AX_m \).

In B.E.T. model since assumptions (ii) and (iii) are very approximate because adsorption does take place in different layers at the same time and energy of adsorption beyond the first layer is not constant, therefore for the case of water and waste waters the applicability is very much doubted.
3.1.3 The Freundlich Model

The Freundlich isotherm (24) which is also called Bemmelen isotherm is the simplest and more convenient to apply. The isotherm is given as below:

\[ \frac{x}{m} = kc^n \]  \hspace{1cm} [18]

where

- \( x \) = amount of adsorbate adsorbed
- \( m \) = weight of the adsorbent
- \( c \) = concentration of adsorbate in the solution at equilibrium
- \( k, n \) = constants

The preceding equation could also be written as below:

\[ \log \frac{x}{m} = \log k + n \log c \]  \hspace{1cm} [19]

and if \( \log \frac{x}{m} \) is plotted against \( \log c \), the constants \( k \) and \( n \) could be evaluated. Preul and Schroepfer (63) demonstrated that under bench test conditions, Freundlich's isotherm is applicable for the adsorption of \( \text{NH}_4^+ \)-N on Zimmerman sand, Hayden silt and Milaca clay. For dilute solutions Freundlich's model is very useful. It is also useful when the nature and identity of the adsorbate is not known as in the adsorption of colored substances from sugar solutions.

3.2 Dimensional Model of Adsorption Process

It is obvious from the review of literature that most of the researchers have used classical approach to define adsorption process in a system. There is no evidence in the literature of any attempt to apply dimensional analysis principle to adsorption processes for water and waste waters. However, Langhar (39), Murphy (55) and Bridgman (10) have suggested that it is possible to study the physical and chemical processes by dimensional analysis.
Development of the present dimensional model will aid in expressing the effect of varying concentrations and flow rates on the adsorption of ammonium and nitrate nitrogen. In addition this will help in predicting the adsorption values more practically and quickly in lack of column tests. The development of dimensional model follows as below.

Main Variables Affecting Adsorption

In chapter II various factors affecting adsorption process have been enumerated. However, main variables considered to be affecting adsorption effectively could be given as further. Let

\[ A = \text{adsorption of N, mg/l (for a particular weight of the soil)} \]
\[ C = \text{initial concentration of N, mg/l} \]
\[ V = \text{superficial velocity of flow, ft/sec} \]
\[ D_p = \text{effective particle size, ft} \]
\[ g = \text{acceleration due to gravity, ft/sec}^2 \]
\[ B_D = \text{bulk density of the soil, gm/cm}^3 \]
\[ \rho_l = \text{density of liquid, lb/ft}^3 \]
\[ \mu = \text{viscosity of the liquid, lb/ft-sec} \]
\[ L = \text{length of the column, ft} \]
\[ \Delta t = \text{elapsed time, seconds} \]

Under isothermal conditions the density and viscosity are constant. Also keeping the bulk density of the soil constant for a particular case, effective size of the particles represents the soil term. It must be remembered at this point that dimensional analysis approach is totally different from classical or mathematical approach and hence dimensional prediction equations are more practical, easy and quick in providing solution to
a problem than the previous one. Then, according to dimensional analysis principles (5, 17, 32) the variables could be arranged as

\[ A = F(C, V, D_p, L, g, \rho_1, \mu, \Delta t) \] \hspace{1cm} [20]

At this point one might raise the question as to why mass transport coefficient, \( K \) has not been included in the variables in the preceding equation. The direct answer to this question is that inclusion of \( K \) will duplicate the same variables which already have been included in the previous equation. This fact will be obvious from the following discussion. It is well known fact that mass transfer coefficient is the function of physical properties and geometry of the system and functional relationship is given as below (38, 50):

\[ K = f(V, \rho_1, \mu, D, L) \] \hspace{1cm} [21]

where

\[ D = \text{diffusivity} \]

\[ L = \text{some characteristic length dimension} \]

Now, for dilute solution diffusivity, \( D \) is constant for all practical purposes (31, 37, 45, 50). Now if we take a careful look at the above equation and the one preceding to the same we will find out that all the factors which affect mass transfer coefficient have already been included and therefore inclusion of mass transport coefficient \( K \) in the proposed dimensional equation will merely duplicate the variables and the principle of dimensional analysis would be violated (37, 39, 45, 55) because main aim of dimensional analysis is to represent the system with minimum number of effective variables without any duplication. Therefore the functional relationship proposed is sound, simple, adequate and valid (37, 45).
The function relationship is rewritten as below on the basis of above discussion:

\[ A = F_1(C, V, L, g, D_p, \Delta t) \]  \[22\]

Since total number of variables involved in the problem is seven and number of fundamental dimensions involved is three, therefore according to dimensional analysis four dimensionless groups \((7 - 3 = 4)\) could be obtained.

In the present case dimension system used is MLT, where

- \(M\) = dimension of mass
- \(L\) = dimension of length
- \(T\) = dimension of time

Now, on the basis of above, the following scheme could be formed in which dimensional relation between fundamental quantities and variables is obtained.

<table>
<thead>
<tr>
<th>Fundamental Variable</th>
<th>Dimension Tried</th>
<th>Dimensional Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass, ( C )</td>
<td>([C] = ML^{-3})</td>
<td>(M = [CL^3])</td>
</tr>
<tr>
<td>Length, ( L )</td>
<td>([L] = L)</td>
<td>(L = [L])</td>
</tr>
<tr>
<td>Time, ( g )</td>
<td>([g] = LT^{-2})</td>
<td>(T = [L^{1/2}/g^{1/2}])</td>
</tr>
</tbody>
</table>

Now, with the help of above developments dimensionless groups could be obtained as described herein.

- \([A]\) = \(ML^{-3} = [CL^3L^{-3}]\)  
  So, \(A/C\) = \( \pi_1 \) group

- \([V]\) = \(LT^{-1} = [L^{1/2}g^{-1/2}]\)  
  So, \(\frac{V}{\sqrt{gL}}\) = \( \pi_2 \) group

- \([D]\) = \(L\) = \(L\)  
  So, \(D_p/L\) = \( \pi_3 \) group

- \([t]\) = \([L^{1/2}/g^{1/2}]\)  
  So, \(\Delta t g^{1/2}/L^{1/2}\) = \( \pi_4 \) group

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
So, functional relationship between groups may be written as below:

\[ \pi_1 = \phi(\pi_2, \pi_3', \pi_4) \] \hspace{1cm} [23]

or

\[ \frac{A}{C} = \phi\left( \frac{V}{\sqrt{gL}} \cdot \frac{D_p}{L} \cdot \frac{\Delta tg^{1/2}}{L^{1/2}} \right) \] \hspace{1cm} [24]

where

\[ \frac{V}{\sqrt{gL}} = \text{Froude's number} \]

Further, in order to reduce the number of experiments and for the sake of convenience, it is customary to combine two or more dimensionless groups. Therefore, \( \pi_3' \) and \( \pi_4 \) could be easily combined and let resulting dimensionless number be called \( \pi_3 \). So, new relationship could be written as below:

\[ \pi_1 = \phi(\pi_2, \pi_3) \] \hspace{1cm} [25]

or

\[ \frac{A}{C} = \phi\left( \frac{V}{\sqrt{gL}} \cdot \frac{D_p}{L} \cdot \frac{\Delta tg^{1/2}}{L^{1/2}} \right) \] \hspace{1cm} [26]

3.2.1 Component Equations

Two component equations may be obtained from the functional relationship between dimensionless groups by conducting laboratory studies in soil columns.

1. Variation of adsorption at different concentrations and flow rates when \( \frac{D_p}{L} \cdot \frac{\Delta tg}{L^{1/2}} \) is constant. In terms of \( \pi \) groups this may be written as

\[ (\pi_1)^3 = f_{1}(\pi_2, \bar{\pi}_3) \] \hspace{1cm} [27]

in which the bar denotes constant values. The above relationship could be
established by plotting \( \pi_1 \) against \( \pi_2 \).

(2) Variation of adsorption with varying concentration and length of soil columns when Froude number \( (V/\sqrt{gL}) \) is constant. And in terms of \( \pi \) groups this could be written as

\[
(\pi_1)^2 = f_1(\pi_2, \pi_3) \tag{28}
\]

Equations such as equations \([27]\) and \([28]\), determined by holding all but one of the Pi terms in the function constant are called component equations \((55)\).

3.2.2 Development of Dimensional Model or Prediction Equation

From the component equations \([27]\) and \([28]\), a general prediction equation could be obtained. Experimental data demonstrated that for \([27]\) and \([28]\) a log-log and log-linear relationship exists between \( \pi_1 \) and \( \pi_2 \), and \( \pi_1 \) and \( \pi_3 \) respectively. Therefore component equations may be combined to form the general prediction equation by multiplication as described by Murphy \((55)\).

\[
\pi_1 = C(\pi_1)^3(\pi_1)^2 \tag{29}
\]

In order to determine \( C \) it is assumed that the component equations are simply multiplied to form the general prediction equation.

\[
F(\pi_2, \pi_3) = f_1(\pi_2, \pi_3)f_2(\pi_2, \pi_3) \tag{30}
\]

And if this is true then the first set of tests with \( \pi_3 \) constant will give

\[
F(\pi_2, \pi_3) = f_1(\pi_2, \pi_3)f_2(\pi_2, \pi_3) \tag{31}
\]

from which

\[
f_1(\pi_2, \pi_3) = \frac{F(\pi_2, \pi_3)}{f_2(\pi_2, \pi_3)} \tag{32}
\]
The second set of tests, with \( \pi_2 \) constant gives, from equation [30]

\[
F(\pi_2, \pi_3) = f_1(\pi_2, \pi_3) f_2(\pi_2, \pi_3) \tag{33}
\]

from which

\[
f_2(\pi_2, \pi_3) = \frac{F(\pi_2, \pi_3)}{f_1(\pi_2, \pi_3)} \tag{34}
\]

values of \( f_1(\pi_2, \pi_3) \) and \( f_2(\pi_2, \pi_3) \) from equations [32] and [34] are substituted into equation [30] to give

\[
F(\pi_2, \pi_3) = \frac{F(\pi_2, \pi_3) F(\pi_2, \pi_3)}{f_2(\pi_2, \pi_3)f_1(\pi_2, \pi_3)} \tag{35}
\]

However, the denominator of equation [35] is found from equation [30] with both \( \pi_2 \) and \( \pi_3 \) constant:

\[
F(\pi_2, \pi_3) = f_1(\pi_2, \pi_3) f_2(\pi_2, \pi_3) \tag{36}
\]

Hence the prediction equation obtained is

\[
F(\pi_2, \pi_3) = \frac{F(\pi_2, \pi_3) F(\pi_2, \pi_3)}{F(\pi_2, \pi_3)} \tag{37}
\]

The component equations and prediction equation obtained are given in the chapter 'Results and Discussion.'

3.3 Length and Time of Travel of Nitrogen

By knowing the soil characteristics and adsorptive capacity it is possible to calculate the length and time of travel of ammonia nitrogen and nitrate nitrogen through soil mass. The following procedure was suggested by Preul (62).
If,

\[ A = \text{adsorptive capacity of the soil from column tests, } \mu\text{gN/gm soil} \]
\[ C = \text{initial solution concentration, mg/l} \]
\[ P = \text{percolation rate, inches/day} \]

Then,

\[ \text{amount of nitrogen in percolation flow per day} \]
\[ = P \text{ (inch./day)} \times 1 \text{ sq.ft.} \times 2.36 \text{ l/inch.sq.ft.} \times C \text{(mg/l)} \]
\[ = \text{flow of nitrogen, mg/day} \]

Further, if

\[ V = \text{volume of the soil column} \]
\[ B.D. = \text{bulk density of the soil} \]

Then,

\[ \text{adsorptive capacity of the soil column} \]
\[ = A \text{(mg/gm)} \times V \text{ (cu.ft.)} \times B.D. \text{ (gm/cu.ft.)} \]
\[ = \text{mg of nitrogen adsorbed} \]

Now, it is easy to calculate the time of travel for a particular length of travel in the soil.

\[ \text{Time of Travel} = \frac{\text{Nitrogen adsorptive capacity of the soil}}{\text{Amount of nitrogen in percolation flow}} \]
\[ = (\text{mg} \times \frac{\text{day}}{\text{mg}}) \]
\[ = \text{days} \]

Thus the time of travel of NH\textsubscript{4}-N and NO\textsubscript{3}-N at various solution concentrations could be easily calculated.
CHAPTER IV
EXPERIMENTAL METHODS AND MATERIALS

"An aimless person is like an arrow which has left the bow without any aim."

Vijai B. Pandey

The experimental work has been divided into two parts—field experiments and laboratory experiments. Field studies were mostly centered on the measurement of the variability of B.O.D. (Biochemical Oxygen Demand) and concentration of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen in the observation wells located in the vicinity of waste stabilization ponds. Timely determinations of coliform and solids (total and volatile) were also done. Laboratory studies were devoted to the study of adsorption of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen on the soil under isothermal and equilibrium conditions.

4.1 Field Installation and Experimentation

'Pine Crest Duck Farm,' where the field studies were carried on, is located in Sterling, Massachusetts. It has three waste stabilization ponds which are about five years old. At the time of this study all the ponds were equipped with mechanical aerators. The wastes from duck houses and processing plant flow by gravity to primary pond (area = 4,992 sq.ft.) and from there to secondary (area = 4,640 sq.ft.) and tertiary (area = 12,640 sq.ft.) pond.

Due to high concentrations of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen in the waste stabilization ponds it was suspected that
ground water contamination due to nitrogen might have taken place. Therefore, observation wells were installed on predetermined ground water flow path. Since the type of the soil in the area is gravelly sandy loam distances between observation wells were kept arbitrary. A total number of ten observation wells were installed. Figure 3 gives a sectional view showing the location of observation wells and ponds. Observation well number A was installed to check the background level concentrations of nutrients as a base to check the ground water contamination by waste stabilization ponds.

4.1.1 Installation Technique

Before the installation of observation wells, locations of ponds and radial line (on which wells were located were determined by plane table surveying and elevations of various installation locations were taken and reduced levels were determined. The observation wells were installed by drilling a four inch diameter hole and then sliding 1.25 inch diameter P.V.C. pipe. The holes were backfilled with original soil and observation wells were protected from the entrance of any foreign material or water.

4.1.2 Sampling Technique

Before taking a sample from an observation well it was pumped for a short time in order to obtain representative ground water samples. A small hand pump was used to draw the samples from the observation wells. As far as possible, samples were taken bimonthly. Samples were taken to the laboratory and analyzed for B.O.D., ammonium nitrogen, nitrate nitrogen, nitrate nitrogen and $p^H$. $MH_4-N$ and $NO_2-N$ were determined by Hach (84) method and $NO_3-N$ and $p^H$ were determined by Orion Digital Meter (Figure 4). Total
Distances Between Observation Wells:

- AB = 30 feet
- BC = 114 feet
- CD = 20 feet
- DF = 175 feet
- FG = 30 feet
- GH = 20 feet
- HI = 20 feet
- IJ = 20 feet

Fig. 3. Typical Observation Well Locations in a Sectional View.
Fig. 4. Orion Digital Meter Used in Determining $p^H$ and Nitrate Concentration.
solids, volatile solids and coliform were determined monthly. In the determination of these procedures as given in "Standard Methods for the Examination of Water and Waste Water" (46, 72) were used. At each sampling time the ground water depths were also measured at all the locations of observation wells.

4.1.3 Soil for the Experiment

For the bench and column type experiments soil was obtained from a depth of six feet with enough care so as original structure was maintained. The soil sampling sites were randomly selected around the ponds in the neighborhood of observation wells. Physical and chemical properties of the soil were determined before using for the bench and column studies. Table 1 gives such properties of the soil. Standard techniques (4, 13, 58, 60) were used for these determinations discussion of which will be superfluous here.

4.2 Laboratory Experimentation

Two types of experimental procedures were used: (i) a bench test in which nitrogen and soil solutions were shaken twice a day for a predetermined length of time and (ii) column tests in which nitrogen bearing solutions were percolated through soil columns. Each of these methods will be discussed separately.

4.2.1 Bench Tests

The bench technique was selected because (i) it is easy and simple to use; (ii) it excludes flow parameters; (iii) it is adoptable to small volume of work thus making the investigation of variable parameters simpler and easier and (iv) it requires very few facilities. The basic purposes of this
Table I. Physical and Chemical Characteristics of the Soil

<table>
<thead>
<tr>
<th>Soil Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Particle size (% retained)</td>
<td></td>
</tr>
<tr>
<td>1) Clay, less than 0.005 mm</td>
<td>2.13</td>
</tr>
<tr>
<td>2) Silt, 0.005 mm</td>
<td>5.51</td>
</tr>
<tr>
<td>3) Very fine sand, 0.05 - 0.1 mm</td>
<td>3.74</td>
</tr>
<tr>
<td>4) Fine sand, 0.10 - 0.25 mm</td>
<td>11.96</td>
</tr>
<tr>
<td>5) Medium sand, 0.25 - 0.5 mm</td>
<td>48.36</td>
</tr>
<tr>
<td>6) Coarse sand, 0.50 - 1 mm</td>
<td>7.19</td>
</tr>
<tr>
<td>7) Fine gravel, 1 - 2 mm</td>
<td>21.10</td>
</tr>
<tr>
<td>2. Effective particle size, mm</td>
<td>0.19</td>
</tr>
<tr>
<td>3. Soil reaction, (pH)</td>
<td>6.5</td>
</tr>
<tr>
<td>4. Organic matter, %</td>
<td>1.2</td>
</tr>
<tr>
<td>5. Specific gravity</td>
<td>2.66</td>
</tr>
<tr>
<td>6. Bulk density, gm/CC</td>
<td>1.69</td>
</tr>
<tr>
<td>7. Percolation rate, inches/day</td>
<td>0.11</td>
</tr>
<tr>
<td>8. Uniformity coefficient</td>
<td>1.65</td>
</tr>
</tbody>
</table>
test were:

(i) to separate physical and chemical effects from biological effects;

(ii) to determine the adsorptive capacity of the soil to aid in the planning and design of column tests;

(iii) to test the applicability and validity of Langmuir, Freundlich and B.E.T. isotherms for the present case of water and waste waters.

4.2.1.1 Test on Ammonium Nitrogen

The test procedures were adopted from Preul and Schroepfer (63) with required modifications. All the soil used in this bench test was disinfected by heating for 24 hours at 100°C temperature and adding one millilitre of chloroform per litre of solution to minimize biological action. The contact of soil and solutions was made in a bottle. One hundred gram of disinfected soil was put in a bottle containing 150 ml solution of NH₄⁺. In this test five concentrations of NH₄⁺ used were 20, 40, 60, 80 and 100 mg/l. Two test periods of five and eight days were used and two replicates of each concentration were given. Thus in all twenty (5 x 2 x 2) solution bottles were used. Each bottle was shaken twice daily for five minutes for the specified test period. The tests were conducted in constant temperature chamber at 15.5°C generally found in sub-surface soils (63). Solutions were prepared using distilled water and adding desired quantity of NH₄HCO₃ to make a desired concentration and phosphate buffer was used to provide a constant pH. At the end of test period the mixtures were removed from the controlled temperature room and determinations of pH were made by 'Orion pH Meter' as
shown in Figure 4. Ammonium nitrogen concentrations were also determined (84). Thus from the resulting decrease of NH$_4$ concentration adsorption per dry weight of soil was determined. Concentrations of nitrate and nitrite nitrogen were also spot-checked to assure about possible nitrogen transformation and in all the cases they were <0.1 mg/l. Applicability of adsorption models were also tested (as described earlier) and values of constants were determined which are discussed in the next chapter.

4.2.1.2 Test on Nitrate Nitrogen

The test procedures were the same as for NH$_4$-N except that in this case in five day period tests $P^H$ was kept above seven and in eight day period $P^H$ was kept below seven. Five concentrations of nitrate used were 20, 40, 60, 80 and 100 mg/l. Solutions were prepared from KNO$_3$, and same replications and test periods were used in this test as were for NH$_4$-N. Applicability of adsorption isotherms was tested and values of constants were determined.

4.2.1.3 Test on Nitrite Nitrogen

All the test and determination procedures for this test were the same as for ammonium nitrogen. In this case concentrations of nitrite was kept as 1, 3, 10, 20 and 100 mg/l and solutions were prepared by KNO$_2$. In this case too applicability of Langmuir, Freundlich and B.E.T. adsorption isotherms were tested. Nitrite nitrogen determinations were made by using Hach Chemical Company's method (84).

4.2.2 Column Tests

The main purpose of performing column tests was to find out the adsorptive capacity of the soil under practical field conditions simulated in the laboratory to aid in determining the length and time of travel of nitrogen
through soil. Secondly column tests will establish the adsorption phenomena under natural water flow conditions.

The soil columns were fabricated from a 4 inch diameter and 1/8 inch thick, transparent acrylic plastic pipes. Columns were connected to supply solution by a 1/4 inch diameter plastic pipe and flow rates were controlled with the help of microflow meters. All the columns were housed in a constant temperature incubator maintained at 15.5°C temperature. All the columns were secured with a continuous stand of wood. Figure 5 shows a typical soil adsorption column and Figure 6 provides a view of column arrangements inside the incubator (constant temperature room). In all the columns a uniform bulk density of soil (1.69) was maintained.

Since in most of the cases flow is saturated through the soil in the vicinity of ponds, column studies were done under saturated flow conditions.

Procedure:

The procedure adopted here is that used by Preul and Schroepfer (54).

(i) Before putting the soil in the columns disinfection was done by heating the soil at 100°C temperature for twenty-four hours.

(ii) All the supply lines and collection bottles were disinfected by sulfuric acid and deionized water.

(iii) The soil was put in the columns carefully to avoid any unnecessary gap or void tube.

(iv) Chloroform was added to feed solutions at the rate of 1 mg/l of solution to check any possible biological action.

(v) After soil was put in the columns, they were leached with deionized water to establish flow conditions.
Fig. 5. A Typical Adsorption Column.
Fig. 6. Soil Adsorption Columns in Constant Temperature Room.
(vi) Then feed solutions were allowed to pass at certain concentrations and flow rates as described later on.

All the column tests were carried out inside of an incubator maintained at 15.5°C temperature. Separate column tests were carried out for ammonium nitrogen and nitrate nitrogen. For each of these the following two types of tests were conducted as described in chapter 3 under the section 'Dimensional Model of Adsorption Process.'

4.2.2.1 Column Test 1 - Effect of Varying Concentration and Flow Rate on Adsorption at Constant $D_p/L \times \Delta \tau g^{1/2}/l^{1/2}$ of 2291.5

For this experiment length of all the soil columns was kept four feet. For each ammonium nitrogen and nitrate nitrogen following concentration and flow levels were selected.

<table>
<thead>
<tr>
<th>Column Number</th>
<th>Concentration mg/l</th>
<th>Flow Rates ml/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>1,000</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>1,200</td>
</tr>
<tr>
<td>6 (control)</td>
<td>150</td>
<td>2,000</td>
</tr>
</tbody>
</table>

Column 6 was kept as control to investigate the possible effect of biological actions. Samples of effluent was collected weekly and analyzed for $\text{NH}_4^-\text{N}$ and $\text{NH}_3^-\text{N}$ and $p^H$. Thus total number of columns used in this experiment was
twelve - six for NH$_4$-$N$ and six for NO$_3$-$N$. Break-through curves were obtained and adsorption of NH$_4$-$N$ and NO$_3$-$N$ was determined. Component equations were obtained for NH$_4$-$N$ and NO$_3$-$N$ as will be discussed in the next chapter.

4.2.2.2 **Column Test 2 - Effect of Varying Concentration and Length of the Column on Adsorption at Constant Froude's Number (3.1 x 10$^{-7}$)**

In this experiment length of columns was varied in such a manner that Froude's number was constant at 3.1 x 10$^{-7}$. The details of concentration levels, flow rates and column lengths are given in Table 3 as below.

**Table 3. Concentration and Flow Levels used in the Column Test 2**

<table>
<thead>
<tr>
<th>Column Number</th>
<th>Length of Column, ft.</th>
<th>Concentration, mg/l</th>
<th>Flow Rate, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>20</td>
<td>536</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>40</td>
<td>599</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>60</td>
<td>657</td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
<td>80</td>
<td>709</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>100</td>
<td>758</td>
</tr>
<tr>
<td>6 (control)</td>
<td>4.0</td>
<td>150</td>
<td>758</td>
</tr>
</tbody>
</table>

Thus for this experiment twelve columns were used - six for NH$_4$ and six for NO$_3$-$N$. Samples of effluent were taken periodically and analyzed for NH$_4$-$N$ and NO$_3$-$N$. Break-through curves were obtained and adsorptive capacity of the soil was calculated. Component equations were obtained for NH$_4$-$N$ and NO$_3$-$N$.

In the determinations of NH$_4$-$N$ and NO$_3$-$N$ and pH, Hach method (84) and Orion Digital Meter (Figure 4) were used respectively.
Experiments were terminated after columns reached equilibrium. To be assured of the fact that only physical adsorption occurred, column 4 (NH\textsubscript{4}-N) of column test 1 was eluted with distilled water and complete reversibility was demonstrated. Depending upon the adsorption values obtained length and time of travel of NH\textsubscript{4}-N and NO\textsubscript{3}-N were calculated. A sample calculation is given in Appendix C.

In all the cases of column flow, flow was in the laminar range as demonstrated by Reynolds number. At the minimum and maximum flow of 400 and 2000 ml/day Reynolds number was 8.34 \times 10^{-7} and 4.13 \times 10^{-6} respectively and these values are in the laminar range.
CHAPTER V
RESULTS AND DISCUSSION

"It's very difficult to change the events but you can always change your attitude towards them."

Dr. S. Radhakrishnan

All the results obtained in this study are discussed broadly under seven main sections: Section one deals with the results and discussion of the bench tests. Section two deals with the results and pertinent discussion of column tests. Section three discusses the dimensional model of adsorption for ammonium and nitrate as a result of column studies. Section four contains the results and discussion of biological transformation of ammonium. Section five involves the results of column elution. Section six discusses bench and column test correlation and the length and time of travel of $\text{NH}_4^-$N and $\text{NO}_3^-$N. And finally section seven discusses the results obtained in the field studies.

5.1 Bench Tests

5.1.1 Adsorption of Ammonium Nitrogen

As discussed in the preceding chapter that two test periods were used (5 days and 8 days), it was positively established that equilibrium has fairly reached in the eight day test period and all the values of adsorption given at equilibrium are eight day test period values. At solution concentrations of 20, 40, 60, 80 and 100 mg/l the adsorption values obtained were 11.25, 22.5, 36.38, 45.75 and 58.15 microgram per gm of soil respectively. The data
is given in Table 4.

5.1.1.1 **Freundlich's Isotherm**

The data was plotted on log-log paper to demonstrate the applicability of Freundlich's isotherm in Figure 7. The data followed the straight line and thus validity of Freundlich's isotherm as given below was proven.

\[ A = kC^{1/n} \]  \[38\]

where

\[ A = \text{amount of adsorbate adsorbed per weight of adsorbent,} \] 
\[ \mu g/gm \]

\[ C = \text{solution concentration, mg/l} \]

\[ k, n = \text{constants} \]

By regression analysis the values of k and n were found to be 0.5206 and 0.9748 respectively. A high correlation coefficient of 0.999 proved that fit of the data was highly significant.

5.1.1.2 **Langmuir's Isotherm**

To prove the applicability of Langmuir's isotherm \(1/X\) was plotted against \(1/C\) in Figure 8 and resulting straight line obviously proved that data follows Langmuir's isotherm. By regression analysis the values of constant b was found to be \(6.1795 \times 10^{-3}\) and \(X_m\) was \(5.9229 \times 10^{-6}\).

Thus Langmuir's isotherm as given below was found to be valid.

\[ \frac{1}{X} = \frac{1}{X_m} + \frac{1}{bX_m} \cdot \frac{1}{C} \]  \[39\]

where all the terms have already been defined. The correlation coefficient was found to be 0.992.
Table 4. Adsorption of $\text{NH}_4^+$ on the Soil

<table>
<thead>
<tr>
<th>Initial Concentration ($C_i$, mg/l)</th>
<th>Final Concentration ($C_f$, mg/l)</th>
<th>H</th>
<th>Adsorption $\mu$g/gm of Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>16.0</td>
<td>7.1</td>
<td>11.25</td>
</tr>
<tr>
<td>40</td>
<td>26.0</td>
<td>7.2</td>
<td>22.50</td>
</tr>
<tr>
<td>60</td>
<td>37.75</td>
<td>7.2</td>
<td>36.38</td>
</tr>
<tr>
<td>80</td>
<td>52.50</td>
<td>7.3</td>
<td>45.75</td>
</tr>
<tr>
<td>100</td>
<td>63.75</td>
<td>7.4</td>
<td>58.15</td>
</tr>
</tbody>
</table>
Fig. 7. Adsorption Isotherm for Ammonium on the Soil.
5.1.1.3 B.E.T. Isotherm

To prove the applicability of B.E.T. isotherm $C/(C_s - C)X$ was plotted against $C/C_s$ and the plot resulted in scattered distribution of points and thus data could not be linearized. This proved that B.E.T. isotherm does not apply at all. This fact is attributed to the multimolecular theory on the basis of which this isotherm was derived. Also this isotherm makes many assumptions which may not be true in practical cases.

In general the adsorption of $\text{NH}_4^+ - \text{N}$ increased as solution concentration increased. The results also proved that Freundlich and Langmuir isotherms successfully apply to the case of water and waste water. Spot checks, at the end of the test period showed concentration of $\text{NO}_3^- - \text{N}$ and $\text{NO}_2^- - \text{N}$ less than 0.1 mg/l and thus biological transformation was minimized and only physical adsorption took place.

5.1.2 Adsorption of Nitrate Nitrogen

In this test, out of two test periods in one (5 days) $p^H$ was kept above 7 and in the other $p^H$ was kept below 7 to possibly see the effect of $p^H$ on nitrate adsorption. For the $p^H$ below 7 adsorption values obtained were 8.25, 15.0, 21.75, 24.0 and 34.28 micrograms per gram of soil at solution concentrations of 20, 40, 60, 80 and 100 mg/l respectively. For the $p^H$ above 7, at the same concentration adsorption values were 4.88, 5.2, 5.62, 3.0 and 6.0 micrograms per gram of soil respectively. The data for both the cases is given in Table 5 ($p^H$ below 7) and Table 6 ($p^H$ above 7).

From the above results it is very clear that adsorption of nitrate nitrogen is $p^H$ dependent and as $p^H$ was kept above 7 very insignificant adsorption resulted and when $p^H$ was kept below 7 significant adsorption took place.
Table 5. Adsorption of $\text{NO}_3^-$ on the Soil

($p_H$ below 7.0)

<table>
<thead>
<tr>
<th>Initial Concentration ($C_i$, mg/l)</th>
<th>Final Concentration ($C_f$, mg/l)</th>
<th>$p_H$</th>
<th>Adsorption ($\mu g/gm$ of Soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>17.0</td>
<td>6.7</td>
<td>8.25</td>
</tr>
<tr>
<td>40</td>
<td>32.0</td>
<td>6.3</td>
<td>15.0</td>
</tr>
<tr>
<td>60</td>
<td>48.0</td>
<td>6.5</td>
<td>21.75</td>
</tr>
<tr>
<td>80</td>
<td>65.5</td>
<td>6.2</td>
<td>24.00</td>
</tr>
<tr>
<td>100</td>
<td>80.15</td>
<td>6.1</td>
<td>34.28</td>
</tr>
</tbody>
</table>
Table 6. Adsorption of NO$_3^-$ on the Soil

\((p^H \text{ above 7.0})\)

<table>
<thead>
<tr>
<th>Initial Concentration ((C_i), \text{ mg/l})</th>
<th>Final Concentration ((C_f), \text{ mg/l})</th>
<th>(p^H)</th>
<th>Adsorption (\mu g/\text{gm of Soil})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>19.25</td>
<td>7.0</td>
<td>4.88</td>
</tr>
<tr>
<td>40</td>
<td>39.75</td>
<td>7.1</td>
<td>5.20</td>
</tr>
<tr>
<td>60</td>
<td>59.50</td>
<td>7.1</td>
<td>5.62</td>
</tr>
<tr>
<td>80</td>
<td>79.50</td>
<td>7.3</td>
<td>3.00</td>
</tr>
<tr>
<td>100</td>
<td>99.75</td>
<td>7.2</td>
<td>6.00</td>
</tr>
</tbody>
</table>
5.1.2.1 Freundlich's Isotherm

The adsorption data given in Table 5 was plotted on log-log paper and a straight line was obtained. The values of k and n were found to be 0.6582 and 1.1835 respectively. Regression analysis gave a high correlation coefficient of 0.993. Therefore validity and applicability of Freundlich's isotherm were demonstrated.

5.1.2.2 Langmuir's Isotherm

The adsorption data (for $pH$ below 7.0) was fitted to Langmuir's isotherm and linearization resulted which proved that Langmuir's isotherm is valid. The value of b and $X_m$ was found to be $3.9476 \times 10^{-3}$ and $2.1237 \times 10^{-6}$ respectively. A correlation coefficient of 0.997 was obtained from regression analysis and thus data followed Langmuir's isotherm (Figure 8).

5.1.2.3 B.E.T. Isotherm

The data was tried to fit but it could not be linearized and thus B.E.T. isotherm cannot be used to represent adsorption phenomena for water and waste water systems.

Hence, on the basis of above discussion it could be said that adsorption data of NO$_3$-N followed Freundlich's and Langmuir's isotherm.

5.1.3 Adsorption of Nitrite Nitrogen

In this test at concentrations of 20, 40, 60, 80 and 100 mg/l the adsorption values obtained were 1.45, 3.08, 6.78, 12.32 and 45.25 micrograms per gram of soil. The plot of data is given in Figure 9.

In this case data very well followed Freundlich's and Langmuir's isotherms but did not fit B.E.T. isotherm. The values of k and n in Freundlich's isotherm were 1.3590 and 1.3416 respectively and correlation coefficient was 0.998. For
Fig. 8. Langmuir's Isotherm for Ammonium on the Soil.
Fig. 9. Adsorption Isotherm for Nitrite Nitrogen on the Soil.
Table 7. Adsorption of $\text{NO}_2^-$ on the Soil

<table>
<thead>
<tr>
<th>Initial Concentration ($C_i$, mg/l)</th>
<th>Final Concentration ($C_f$, mg/l)</th>
<th>$pH$</th>
<th>Adsorption $\mu g/gm$ of Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.12</td>
<td>7.1</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>3.04</td>
<td>6.9</td>
<td>3.08</td>
</tr>
<tr>
<td>10</td>
<td>5.58</td>
<td>7.2</td>
<td>6.78</td>
</tr>
<tr>
<td>20</td>
<td>11.80</td>
<td>6.8</td>
<td>12.32</td>
</tr>
<tr>
<td>100</td>
<td>69.75</td>
<td>6.7</td>
<td>45.25</td>
</tr>
</tbody>
</table>
Langmuir's isotherm the values obtained for \( b \) and \( X_m \) were 3.2464 \( \times 10^{-2} \) and 8.7993 \( \times 10^{-7} \) respectively. The value of correlation coefficient was 0.995 which showed significant relationship.

From the above results it is obvious that adsorption of \( \text{NH}_4^- - \text{N} \) was more as compared to nitrate or nitrite nitrogen. This is due to the fact that \( \text{NH}_4^+ \) ion has greater affinity for the soil particles and therefore tends to get adsorbed in larger quantities. It is also very obvious that Freundlich and Langmuir models applied equally well to the adsorption data.

5.2 Column Tests

As discussed in Chapter III column experiments were designed on the basis dimensional analysis performed and were aimed to derive an experimental dimensional model for the adsorption process.

5.2.1 Variation of Adsorption at Varying Concentration and Flow Rates at Constant \( \frac{D_p}{L} \times \Delta t \frac{1}{2} / L \frac{1}{2} \) (2291.5)

5.2.1.1 Ammonium Nitrogen

In Figure 10 effluent concentration to influent concentration ratio \( (C_o/C_i) \) of \( \text{NH}_4^- - \text{N} \) has been plotted against throughput volume flow per weight of the soil in the column. These kinds of curves are also called as 'break-through' curves. The adsorption values were obtained by computing the areas on the left hand side of these curves. For column numbers 1, 2, 3, 4, 5 and 6 adsorption values obtained were 18.4, 36.3, 48.2, 63.00, 70.5 and 103.4 micrograms per gram of soil respectively. This is very obvious from the above results that as solution concentration increased adsorption increased. Table 8 gives effect of Froude's number \( (V/sL) \) on dimensionless term \( A/C \) where \( A \) and \( C \) are as defined in Chapter III. The values of \( A/C \) were plotted against Froude
Fig. 10. Typical NH₄ Adsorption Curve for Columns with Varying Concentration and Flow Rates.

C₀/C₄ = Effluent NH₄-N/Influent NH₄

Throughout Volume Flow/Column Weight in Litres/h/m Soil

Col. 1
Col. 2
Col. 3
Col. 4
Col. 5
Col. 6
Table 8. Effect of Froude’s Number \( \left( \frac{V}{\sqrt{gL}} \right) \) on Dimensionless Term A/C at Varying Concentrations and Flow Rates for NH\(_4\)-N

<table>
<thead>
<tr>
<th>Column Number</th>
<th>Flow Rate ml/day</th>
<th>Influent Concentration NH(_4)-N mg/l</th>
<th>( p^H )</th>
<th>( \frac{V}{\sqrt{gL}} )</th>
<th>A/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>20</td>
<td>7.2</td>
<td>1.64 x 10(^{-7})</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>40</td>
<td>7.4</td>
<td>2.46 x 10(^{-7})</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>60</td>
<td>7.3</td>
<td>3.27 x 10(^{-7})</td>
<td>0.28</td>
</tr>
<tr>
<td>4</td>
<td>1,000</td>
<td>80</td>
<td>7.5</td>
<td>4.09 x 10(^{-7})</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>1,200</td>
<td>100</td>
<td>7.6</td>
<td>4.91 x 10(^{-7})</td>
<td>0.16</td>
</tr>
<tr>
<td>6</td>
<td>2,000</td>
<td>150</td>
<td>7.7</td>
<td>8.11 x 10(^{-7})</td>
<td>0.10</td>
</tr>
</tbody>
</table>
number on log-log paper and a straight line resulted. Such a plot is given in Figure 11. From the figure it is evident that as Froude's number increased A/C exponentially decreased. By regression analysis the following relationship was obtained between A/C and Froude's number for ammonium nitrogen:

$$\frac{A}{C} = (4.9769 \times 10^{-10}) \times \left(\frac{V}{\sqrt{gL}}\right)^{-1.3468} \tag{40}$$

It should be recalled here that this is one of the component equations for ammonium nitrogen which characterizes the effect of increasing Froude's number and concentration on the adsorption of ammonium nitrogen. The correlation coefficient for this relationship was 0.995 which proved that very significant relationship exists between the two dimensionless groups.

5.2.1.2 Nitrate Nitrogen

Similar break-through curves were obtained for nitrate nitrogen and adsorption values were computed in the similar fashion. The total adsorption of nitrate nitrogen in micrograms per gram of soil was 12.5, 24.0, 32.0, 34.9, 53.2 and 79.2 respectively for column numbers 1, 2, 3, 4, 5 and 6. It is worth noting here that adsorption increased with increasing solution concentration and flow rate.

In Table 9, values of flow rates, Froude's number and A/C are given. In Figure 11 A/C is plotted against Froude's number on log-log paper. By regression analysis the equation of straight line was obtained to emphasize the effect of Froude's number on the adsorption. The relationship obtained was as given below:

$$\frac{A}{C} = (3.8107 \times 10^{-10}) \times \left(\frac{V}{\sqrt{gL}}\right)^{-1.3376} \tag{41}$$
\[
\frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}} = 2291.5
\]

Fig. 11. Variation of Froude's Number with A/C at Constant \( \frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}} \).
Table 9. Effect of Froude's Number on Dimensionless Number A/C at Varying Concentrations and Flow Rates for NO$_3$-N

<table>
<thead>
<tr>
<th>Column Number</th>
<th>Flow Rate ml/day</th>
<th>Influent Concentration NO$_3$-N mg/l</th>
<th>pH</th>
<th>$\frac{V}{\sqrt{gL}}$</th>
<th>A/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>20</td>
<td>6.6</td>
<td>1.64 x 10^{-7}</td>
<td>0.44</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>40</td>
<td>6.5</td>
<td>2.46 x 10^{-7}</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>60</td>
<td>6.4</td>
<td>3.27 x 10^{-7}</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>1,000</td>
<td>80</td>
<td>6.3</td>
<td>4.09 x 10^{-7}</td>
<td>0.12</td>
</tr>
<tr>
<td>5</td>
<td>1,200</td>
<td>100</td>
<td>5.9</td>
<td>4.91 x 10^{-7}</td>
<td>0.12</td>
</tr>
<tr>
<td>6</td>
<td>2,000</td>
<td>150</td>
<td>5.5</td>
<td>8.11 x 10^{-7}</td>
<td>0.07</td>
</tr>
</tbody>
</table>
The previous relationship was highly significant as was demonstrated by
high correlation coefficient of 0.994. This equation is one of the component
equations discussed in Chapter III.

5.2.2 Variation of Adsorption with Varying Concentration and Length of
Columns at Constant Froude Number (3.1 x 10^-7)

5.2.2.1 Ammonium Nitrogen

In this test column lengths were varied and flow was adjusted in such a
manner as to keep Froude's number constant at 3.1 x 10^-7. The break-through
curves obtained were similar in pattern as described in section 5.2.1.1. The
adsorption values for column lengths of 2.0 ft., 2.5 ft., 3.00 ft., 3.5 ft.,
4.0 ft. and 4.0 ft. (control) were respectively 16.7, 33.0, 50.4, 58.3, 71.6
and 104.0 micrograms per gram of soil. It is obvious here that adsorption
values increased with increasing length of the columns.

In Table 10, effect of varying \( D_p / L \times \Delta t g^{1/2} / L^{1/2} \) is shown on the dimen-
sionless number \( A/C \) and in Figure 12 the plot of \( A/C \) with respect to \( D_p / L \times \Delta t g^{1/2} / L^{1/2} \) is shown on a semilog paper, resulting in a straight line. By
regression analysis the following relationship was obtained between these
two dimensionless groups:

\[
\frac{A}{C} = 0.21345 \times 10^{0.0001(\frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}})} \quad [42]
\]

The above relationship was found statistically significant as high
value of correlation coefficient was obtained as 0.985. The preceding equa-
tion is second component equation obtained for ammonium nitrogen.
Table 10. Effect of $\frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}$ on A/C for NH$_4$-N at Varying Concentration and Column Lengths

(Froude's Number = 3.1 x 10$^{-7}$)

<table>
<thead>
<tr>
<th>Column Length ft.</th>
<th>Influent Concentration NH$_4$-N mg/l</th>
<th>H</th>
<th>$\frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}$ (x 10$^{-2}$)</th>
<th>A/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>20</td>
<td>7.1</td>
<td>32.395</td>
<td>0.44</td>
</tr>
<tr>
<td>2.5</td>
<td>40</td>
<td>7.3</td>
<td>27.814</td>
<td>0.40</td>
</tr>
<tr>
<td>3.0</td>
<td>60</td>
<td>7.2</td>
<td>24.684</td>
<td>0.38</td>
</tr>
<tr>
<td>3.5</td>
<td>80</td>
<td>7.3</td>
<td>20.985</td>
<td>0.33</td>
</tr>
<tr>
<td>4.0</td>
<td>100</td>
<td>7.5</td>
<td>18.323</td>
<td>0.33</td>
</tr>
<tr>
<td>4.0 (control)</td>
<td>150</td>
<td>7.6</td>
<td>18.323</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Table 11. Effect of $\frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}$ on A/C for NO$_3$-N at Varying Column Lengths and Concentrations

(Froude's Number = 3.1 x 10$^{-7}$)

<table>
<thead>
<tr>
<th>Column Length ft.</th>
<th>Influent Concentration NO$_3$-N mg/l</th>
<th>pH</th>
<th>$\frac{D_p}{L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}$ ($x 10^{-2}$)</th>
<th>A/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>20</td>
<td>6.5</td>
<td>32.395</td>
<td>0.31</td>
</tr>
<tr>
<td>2.5</td>
<td>40</td>
<td>6.3</td>
<td>27.814</td>
<td>0.28</td>
</tr>
<tr>
<td>3.0</td>
<td>60</td>
<td>6.4</td>
<td>24.684</td>
<td>0.24</td>
</tr>
<tr>
<td>3.5</td>
<td>80</td>
<td>6.2</td>
<td>20.985</td>
<td>0.24</td>
</tr>
<tr>
<td>4.0</td>
<td>100</td>
<td>5.8</td>
<td>18.323</td>
<td>0.21</td>
</tr>
<tr>
<td>4.0 (control)</td>
<td>150</td>
<td>5.7</td>
<td>18.323</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Fig. 12. Variation of A/C with respect to $\frac{D}{L} \times \frac{\Delta \rho \sqrt{g} L^{1/2}}{L^{1/2}} \times 10^{-2}$ at constant Froude's Number.
5.2.2.2 Nitrate Nitrogen

'Break-through' curves in this test were obtained for all the columns as shown in Figure 13. By computing the areas on the left of these curves the adsorption values in micrograms per gram of soil were respectively 11.7, 22.6, 32.5, 41.9, 46.5 and 73.2 at column lengths of 2.00, 2.5, 3.0, 3.5, 4.0 and 4.00 ft. (control). It should be noted here too that with increasing column lengths adsorption of nitrate nitrogen increased.

In Figure 12 A/C is plotted against \( \frac{D_p}{L} \times \Delta t g^{1/2}/L^{1/2} \) on a semilog paper and data was linearized significantly. By regression analysis the following relationship was obtained:

\[
\frac{A}{C} = 0.13536 \times 10^{0.001D_p/L} \times \frac{\Delta t g^{1/2}}{L^{1/2}}
\]  

[43]

A correlation coefficient of 0.98 signifies the significant relationship. This relationship is the second component relationship for nitrate nitrogen. It is very obvious from Figure 12 that as dimensionless number \( \frac{D_p}{L} \times \Delta t g^{1/2}/L^{1/2} \) increases A/C increases and it could be said that with increasing length and concentration adsorption increases.

5.3 Dimensional Model or General Prediction Equation

From the component equations obtained for ammonium nitrogen and nitrate nitrogen in the preceding section a dimensional model was developed. It may be recalled that this model or prediction equation was obtained as per procedures described in Chapter III.

5.3.1 Prediction Equation for NH₄⁻N

At present the final prediction equation will be given. However, in Appendix A the procedure by which it was obtained is given. The general pre-
Figure 13. Break-through curves for nitrate nitrogen with varying lengths of columns.

Throughput volume flow/column weight in litters/kgm soli

C/C = Effluent NO₃-N/Influent NO₃-N

Col. 4 (3.5 ft.)
Col. 3 (3.0 ft.)
Col. 2 (2.5 ft.)
Col. 1 (2.0 ft.)
The prediction equation for \( \text{NH}_4^-\text{N} \) is:

\[
\frac{A}{C} = (2.9364 \times 10^{-10}) \times \left(\frac{V}{\sqrt{gL}}\right)^{-1.3468} \times (10)^{0.001} \left(\frac{D_p}{L} \times \Delta t g^{1/2} / L^{1/2}\right)
\]

[44]

The preceding prediction equation will predict the adsorptive capacity of the soil at any value of Froude number and \( D_p / L \times \Delta t g^{1/2} / L^{1/2} \) and concentration within confounding of this experiment. A sample check is also given in Appendix A.

5.3.2 Prediction Equation for \( \text{NO}_3^-\text{N} \)

The development of prediction equation for \( \text{NO}_3^-\text{N} \) may be found in Appendix B. The general prediction equation obtained is:

\[
\frac{A}{C} = (2.2483 \times 10^{-10}) \times \left(\frac{V}{\sqrt{gL}}\right)^{-1.3376} \times (10)^{0.001} \left(\frac{D_p}{L} \times \Delta t g^{1/2} / L^{1/2}\right)
\]

[45]

With the help of above prediction equation one would be able to predict the adsorptive capacity of the soil at any value of Froude number and \( D_p / L \times \Delta t g^{1/2} / L^{1/2} \) and concentration within the range of this experiment. In Appendix B, the method by which the preceding dimensional model was obtained is given along with a sample check.

The preceding two dimensional prediction equations for \( \text{NH}_4^-\text{N} \) and \( \text{NO}_3^-\text{N} \) are very practical and quick in providing the adsorption values for known Froude number, concentration and dimensionless parameter \( D_p / L \times \Delta t g^{1/2} / L^{1/2} \). These prediction equations are good to calculate the values of adsorption within the range of 'break-through point and exhaustion point' of the break-
through curve and would provide ambiguous results if applied to calculate the values of adsorption at infinite time or time beyond the exhaustion point. Once the values of adsorption between break and exhaust point are determined, equilibrium values could be estimated asymptotically. The range of these prediction equations is also limited by the range of two dimensionless parameters involved.

5.4 Biological Transformation of Ammonium

As explained in Chapter IV, two control columns of NH$_4^+$ were used to see the effect of biological transformation of ammonium. Table 12 gives the values of total nitrogen (NH$_4^+$ + NO$_2^-$ + NO$_3^-$), ammonium and nitrate and nitrite (combined) nitrogen and Figure 14 represents the extent of nitrification. Nitrification is a process of enzymic oxidation brought about by two distinct groups of bacteria and takes place in two coordinated steps. The two special groups of bacteria involved are nitrite (nitrosomonas) and nitrate (nitrobacter) bacteria. The biological nitrification may be shown simple and diagrammatically in the following manner:

$$2\text{NH}_4^+ + 3\text{O}_2 \rightarrow \text{Nitrosomonas} \quad \text{Oxidation} \quad 2\text{NO}_2^- + 2\text{H}_2\text{O} \times 4\text{H}^+ + \text{Energy}$$  \[46\]

$$2\text{NO}_2^- + \text{O}_2 \rightarrow \text{Nitrobacter} \quad \text{Oxidation} \quad 2\text{NO}_3^- + \text{Energy}$$  \[47\]

It is obvious from the above reaction that NH$_4^+$ is transformed into NO$_2^-$ by nitrosomonas and then nitrobacter transforms nitrite to nitrate. The second reaction usually follows so closely on the first as to prevent any appreciable accumulation of nitrites.

The shaded area in Figure 14 represents the extent of nitrification.
Table 12. Biological Transformation of Ammonia Nitrogen under Column Flow Conditions (Length of Column = 4 ft.)

<table>
<thead>
<tr>
<th>Volume of Flow litres</th>
<th>NH$_4$ (mg/l)</th>
<th>NO$_3$ + NO$_2$ (mg/l)</th>
<th>Effluent Nitrogen (NH$_4$ + NO$_2$ + NO$_3$) (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>45</td>
<td>4.5</td>
<td>49.5</td>
</tr>
<tr>
<td>12</td>
<td>88.5</td>
<td>12.0</td>
<td>100.5</td>
</tr>
<tr>
<td>24</td>
<td>148.5</td>
<td>0.5</td>
<td>149.0</td>
</tr>
<tr>
<td>36</td>
<td>148.5</td>
<td>0.9</td>
<td>149.4</td>
</tr>
<tr>
<td>48</td>
<td>148.5</td>
<td>0.9</td>
<td>149.4</td>
</tr>
<tr>
<td>60</td>
<td>148.5</td>
<td>0.9</td>
<td>149.4</td>
</tr>
<tr>
<td>120</td>
<td>148.5</td>
<td>0.9</td>
<td>149.4</td>
</tr>
</tbody>
</table>
Fig. 14. Extent of Nitrification in a Column of Ammonium (Column Test A-1).
Fig. 13. Extent of Nitritation in Column for Ammonium (Column Test A-2)

Flow Rate = 759 ml/day

Effluent Nitrogen (NH₄⁺)

Effluent Nitrogen (NH₄⁺ + NO₂⁻ + NO₃⁻)

Influent Total Nitrogen (NH₄⁺)
It is obvious from Figure 14 in the initial stages of flow nitrification increased as a result of availability of oxygen through influent and active participation of nitrifying bacteria. But in the latter stages the nitrification was insignificant and this could be attributed to the fact that due to saturation of the soil and high flow rate, anaerobic conditions developed and resulted in the inactivation of nitrosomonas and nitrobacter. It is well known that aeration, temperature and moisture affect the nitrification vigorously. And very poor aeration, very low (below freezing) or very high temperature (above 125°F) and higher degree of saturation result in ceasing the nitrification (6). It could also be seen that nitrification tends to result in an increase in soil acidity and resulting pH in this case was 5.5. Figure 15 also signifies above discussed facts for another control column (length 3.5 ft.).

5.5 Elution of the Column

In order to prove that mechanism of adsorption was totally physical adsorption rather than chemical adsorption column number four of Table 8 was eluted after the flow-through tests were completed. Similar flow rate was used as in the original test and distilled water was used for the elution. Elution performance is given in Figure 16. Referring to Figure 10 and break-through curve of column 4, it is seen that curve in Figure 16 is the mirror image of the one in Figure 10. Therefore complete reversibility was demonstrated and thus it was proved that mechanism of adsorption was only of physical nature.
FIG. 16. ELUTION PERFORMANCE OF COLUMN NUMBER 4 FOR NH₄-N.
5.6 Bench Tests and Column Tests

Since bench tests are less time consuming and simpler to perform an attempt was made to find out a significant relationship between them. Since adsorption values in bench tests and column tests are not very close to each other, therefore such a relationship will be of high significance in order to save time and avoid extremely difficult column experiments. Generally the column adsorption values are higher than the bench test values and this may be due to the fact that in column operations which are continuous flow operations the adsorbent is continuously in contact with fresh adsorbate in solution and thus adsorbate concentration in contact with the adsorbent remains constant and therefore adsorption is effectively increased. In bench tests the concentration of adsorbate in solution keeps on decreasing which results in lowering the effectiveness of adsorbent to adsorb the adsorbate.

For NH$_4$-N the adsorption values were related in the following manner:

$$A_B = 2.64 \ A_C^{0.8185}$$  \hspace{1cm} [48]

where

$A_B$, $A_C$ are adsorption values in bench and column tests respectively. A correlation coefficient of 0.995 proved high degree of significance.

For NO$_3$-N the following relationship was found statistically significant as demonstrated by a correlation coefficient of 0.997. The relationship is:

$$A_B = 1.5636 \ A_C^{0.9897}$$  \hspace{1cm} [49]

With the help of such a relationship for the similar soil conditions by just performing bench tests adsorption values in natural flow conditions
could be determined and thus length and time of travel of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ could be determined easily in shortest possible time. The value of constants will considerably vary for different kinds of soils.

5.6.1 Length and Time of Travel of Nitrogen

By using the values of adsorption of ammonium and nitrate nitrogen obtained in sections 5.2.1.1 and 5.2.1.2 respectively, it was possible to calculate the time of travel of these nutrients for one foot depth of soil at varying solution concentrations. It was calculated that for solution concentrations of 20, 40, 60, 80, 100 and 150 mg/l ammonium nitrogen and nitrate nitrogen will travel one foot in the soil in 183 and 115 days; 168 and 111 days; 148 and 98 days; 145 and 81 days; 130 and 98 days; 127 and 97 days respectively.

For ammonium nitrogen the time of travel was plotted on log-log paper in Figure 17 and following relationship was obtained by regression analysis:

$$T = 330.98 \ C^{-0.1934}$$

where

$T =$ time of travel, days

$C =$ initial concentration, mg/l

The above relationship was found statistically significant as 'F' value was found 94.94 which is very highly significant at 10% level.

In the similar manner by plotting the time of travel against initial concentration on log-log paper (Figure 17), for nitrate nitrogen, a fairly significant relationship was obtained as below:

$$T = 159.771 \ C^{-0.1148}$$

where
Fig. 17. Time of Travel of Ammonium and Nitrate Nitrogen at Varying Concentrations.
T = time of travel in days

C = initial concentration

From the above results, it is obvious that as solution concentration increases the time of travel decreases and that time of travel for ammonium nitrogen is more as compared to nitrate nitrogen. Since NH$_4^+$ has greater affinity to soil particles and therefore its adsorption is more as compared to NO$_3^-$ and thus it takes more time to travel.

A sample calculation for calculating the length and time of travel for ammonium nitrogen is given in Appendix C. It should be noted here that for similar soil conditions by knowing the concentration of NH$_4$-N and NO$_3$-N in surface waters, length and time of travel of nitrogen could be fairly well estimated by using preceding two equations. Also by using the relationship between bench test and column test data, it will be easier to estimate adsorption by just performing the bench tests and then length and time of travel of nitrogen could be estimated easily.

5.7 Field Studies

In the field studies, ground water samples were taken from the observation wells and also from the ponds. The variation of concentration of NH$_4$-N, NO$_3$-N, NO$_2$-N, B.O.D. will be discussed as the discussion proceeds.

5.7.1 Ammonium Nitrogen

In Figure 18 concentrations of NH$_4$-N in ground water is plotted against increasing length from the edge of the pond. Secondary pond was selected as the reference for the measurement of distances along the radial line and the first points in Figure 18 refer to concentration levels in this pond. Concentration levels in this pond varied from 120.7 mg/l to 141.1 mg/l with a
Fig. 18: Concentration of Ammonium Nitrogen in Ground Water.
mean of 130.4 mg/l. The background level concentration of NH$_4$-N in the ground water ranged from 14.8 mg/l to 33.2 mg/l with a mean of 28.45 mg/l. It is apparent from Figure 18 that NH$_4$-N concentration of ground water reduced to background level within a distance of 280 feet. Thus concentration of NH$_4$-N decreases as the distance from the pond increases and it is felt that certain mechanisms such as adsorption and possibly biological transformation are effective to a great extent. It should also be noted that in the month of April, 1971 NH$_4$-N levels were considerably lower, and this may be attributed to the dilution by melting of snow and possibly by rain.

5.7.2 Nitrate Nitrogen

In Figure 19 variation of NO$_3$-N concentration with the length is represented. The NO$_3$-N in the reference pond varied from 1.5 mg/l to 64.5 mg/l with a mean of 18.7 mg/l. In the background level the variation was from 1.2 mg/l to 15.8 mg/l with a mean of 12.6 mg/l. From Figure 19 it is obvious that variation of NO$_3$-N concentration is not in a set fashion and this does not increase with increasing distance. This is because of the lack of nitrification of NH$_4$-N in the ground water. Since there is practically no oxygen in the bottom of the ponds and in the path of flow below the zone of aeration, the reduction of NO$_3$-N concentration in the ground water may be subject to adsorption, dilution or denitrification.

5.7.3 Nitrite Nitrogen

As explained in earlier section ammonium is converted to nitrite and then to nitrate through biological transformation under aerobic conditions and generally accumulation of nitrite does not occur. In this reference pond concentrations of NO$_2$-N varied from 0.06 mg/l to 0.5 mg/l with a mean of 0.26 mg/l.
Figure 19. Concentration of Nitrate Nitrogen in Ground Water.
Fig. 20. Concentration of Nitrite Nitrogen in Ground Water.
In Figure 20 the variation of nitrite nitrogen is plotted against the length and it is important to note that within a distance of 200 ft. nitrite fastly reduced to background level.

From the field studies of variation of NH$_4^-$-N, NO$_3^-$-N and NO$_2^-$-N concentrations with respect to length and calculations of length and time of travel by means of adsorption data, it could be said that within next twenty years there is no serious danger involved regarding ground water pollution within 300 ft. of pond distance. Although no significant correlation between field studies and theoretical calculations is possible at this point, but significant conclusions could be derived independently from each of them that ground water pollution is not very serious problem in the vicinity of ponds and subsurface water supplies will not be affected at all due to operations of duck farm if the present level of treatment of duck waste is maintained for many years.

5.7.4 Biochemical Oxygen Demand

Since B.O.D. is the indicator of the degree of pollution it was found necessary to determine the B.O.D. of ground water samples. In the reference pond B.O.D. varied from 425 parts per million to 756 parts per million with a mean of 653 parts per million. In the background level samples the variation was from 2 parts per million to 12.5 parts per million with a mean of 6.1 parts per million. In Appendix D B.O.D. is given at different locations. It is quite interesting to note that B.O.D. reduced to nil within 200 ft. length from the edge of the pond. The five day B.O.D. was measured by 'Hach Manometric Method' (84).
Table 13. B.O.D. of Ground Water at Various Sampling Locations

<table>
<thead>
<tr>
<th>Month</th>
<th>A</th>
<th>C</th>
<th>D</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>Ref. Pond</th>
</tr>
</thead>
<tbody>
<tr>
<td>August '70</td>
<td>-</td>
<td>120.0</td>
<td>92.0</td>
<td>15.0</td>
<td>5.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>756</td>
</tr>
<tr>
<td>September '70</td>
<td>12.5</td>
<td>150.0</td>
<td>144.0</td>
<td>12.0</td>
<td>6.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>October '70</td>
<td>5.0</td>
<td>30.0</td>
<td>15.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>680</td>
</tr>
<tr>
<td>November '70</td>
<td>2.0</td>
<td>35.0</td>
<td>10.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>780</td>
</tr>
<tr>
<td>December '70</td>
<td>5.0</td>
<td>22.0</td>
<td>11.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>600</td>
</tr>
<tr>
<td>April '71</td>
<td>6.0</td>
<td>18.0</td>
<td>9.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>675 425</td>
</tr>
</tbody>
</table>
5.7.5 Variation of Water Table in the Observation Wells

In Figure 22, the depth of water table is plotted for various locations of observation wells. It is to be noted that as the length from the reference pond increased the depth of water table increased and thus appropriate direction of ground water flow was observed from point A to J. From August, 1970 to December, 1970 water table depths increased but in the month of April due to snow melting and rainfall depths in the observation wells were very low.

5.7.6 Coliform, Solids and \( p^H \)

The coliforms were determined to check as to whether significant amount of coliform are present in the ground water and moreover coliform is used as the index of degree of pollution. In the reference pond coliform density varied from \( 1.4 \times 10^4 \) per 100 ml to \( 2.3 \times 10^6 \) per 100 ml with a mean of \( 2.1 \times 10^4 \) per 100 ml. In the ground water samples taken at points C and D the mean density was found to be \( 1.4 \times 10^3 \). The mean coliform density in the upper reach and lower reaches (stations F,G,H,I,J) was found about 60 per 100 ml which was surprisingly very low. The low coliform density could be attributed to the fact that soil mechanisms such as adsorption and dilution were effective. Further it was also felt that sampling technique from the observation wells (for coliform analysis) may not have been totally reliable as coliform density is greatly affected by outside environment.

No solids either total or volatile were detected in the ground water samples. However, in the reference pond total solids varied from 1.4 percent to 0.8 percent and volatile solids were less than 0.04 percent. The \( p^H \)
Fig. 22. Depth of Water Table at Various Locations of Observation Wells.
in the ground water varied from 6.5 to 7.1 with a mean of 6.9. In the reference pond $p^H$ varied from 6.4 to 6.8 with a mean of 6.6.
CHAPTER VI

CONCLUSION

"Untruth can never exist and truth never ceases to exist."

Lord Krishna

As a result of this study the following main conclusions could be drawn.

1. Adsorption of NH$_4^+$, NO$_3^-$ and NO$_2^-$ on the soil could be estimated by Freundlich's isotherm or Langmuir's isotherm under equilibrium batch conditions. The Freundlich isotherm follows:

\[ A = K C^{1/n} \]

and Langmuir's isotherm could be represented as:

\[ \frac{1}{X} = \frac{1}{X_m} + \frac{1}{bX_m} \cdot \frac{1}{C} \]

However, statistical results showed that Freundlich's model fitted the adsorption data more closely but not significantly than Langmuir's isotherm.

2. Under natural flow conditions the adsorption of NH$_4^+$ and NO$_3^-$ could be estimated by the following 'Dimensional Models' or 'Prediction Equations'.

For ammonium the dimensional model is:

\[ \frac{A}{C} = (2.9364 \times 10^{-10}) \left( \frac{V}{\sqrt{gL}} \right)^{-1.3468} (10)^{0.0001} (\frac{D_p}{L} \times \frac{\Delta t g}{L^{1/2}}) \]

and for nitrate the model is:
\[
\frac{A}{C} = (2.2483 \times 10^{-10}) \left( \frac{V}{\sqrt{\gamma g L}} \right)^{-1.3376} 0.0001 \frac{D_p}{L} \times \frac{\Delta t}{L^{1/2}}
\]

(3) Under equilibrium batch and natural flow conditions, adsorption of \( \text{NH}_4^+ \), \( \text{NO}_3^- \) and \( \text{NO}_2^- \) increases as solution concentration increases. And under normal conditions, adsorption of \( \text{NH}_4^+ \) was considerably higher than \( \text{NO}_3^- \) and \( \text{NO}_2^- \).

(4) Adsorption and biological action are chief factors which inhibit the movement of nitrogen through soil depending upon the soil conditions. And mainly the physical adsorption on the soil may be an important mechanism in the inhibition of nitrogen travel when the nitrogen is in the form of \( \text{NH}_4^+ \).

(5) The length and time of travel of nitrogen may be successfully estimated by the expressions obtained in this study based on laboratory and field conditions. At a concentration of 20 mg/l, \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) will travel one foot distance in the soil in 183 and 115 days respectively.

(6) From the relation developed between adsorption and batch conditions and natural flow conditions, it should be possible to establish adsorption values in flow condition by only performing bench tests. This would aid in determining the time and length of travel of nutrients under natural flow conditions. The relationship is

For \( \text{NH}_4^-\text{N} \):

\[
A_B = 2.6401 A_C^{0.8185}
\]
where subscripts B and C indicate bench tests and column tests.

For NO$_3$-N:

\[ A_B = 1.5636 A_C^{0.9897} \]

(7) Nitrate and nitrite contamination of shallow ground water does not appear to pose a severe threat to ground water pollution in the vicinity of waste stabilization ponds on the basis of this study. It could also be concluded that installation of shallow drinking water wells after 300 feet radial distance from the waste treatment ponds will be quite safe.
APPENDIX A

PREDICTION EQUATION FOR NH$_4$-N

Component equations obtained are:

\[ \pi_{13} = (4.9769 \times 10^{-10}) \pi_2^{-1.3468} \pi_3 = 2291.5 \]

\[ \pi_{12} = 0.21345 \times 10^{0.0001\pi_3} \pi_2 = 3.1 \times 10^{-7} \]

Now, according to procedure discussed in Chapter III section 3.2.2 prediction equation is:

\[ \pi_1 = \frac{(4.9769 \times 10^{-10})(0.21345)^{-1.3468}}{0.21345 \times 10^{0.0001 \times 2291.5}} \]

\[ = (2.9364 \times 10^{-10}) \pi_2^{-1.34679} 10^{0.0001\pi_3} \]

Recalling that,

\[ \frac{A}{C} = \pi_1 \]

\[ \frac{V}{\sqrt{gL}} = \pi_2 \]

\[ \frac{D_p}{L} \times \frac{\Delta t g}{L^{1/2}} = \pi_3 \]

the prediction equation could be written as:

\[ \frac{A}{C} = (2.9364 \times 10^{-10}) \left( \frac{V}{\sqrt{gL}} \right)^{-1.34678} \left( \frac{D_p}{L} \times \frac{\Delta t g}{L^{1/2}} \right)^{0.0001} \]

Check:

\[ \frac{V}{\sqrt{gL}} = 2.46 \times 10^{-7} \text{ and } \frac{D_p}{L} \times \frac{\Delta t g}{L^{1/2}} = 2291.5 \]
\( \frac{A}{C} \) obtained is (by computer) \( 0.3963 = 0.40 \)

Now, going to Figure 10 at \( \frac{V}{\sqrt{gL}} \) the value of \( \frac{A}{C} \) is also 0.4. Therefore, this dimensional model or prediction equation is valid and justified.
APPENDIX B

PREDICTION EQUATION FOR NO₃⁻N

Component equations obtained are:

\[
\begin{align*}
\pi_{13} &= (3.8107 \times 10^{-10}) (\pi_2)^{-1.3376} \pi_3 = 2291.5 \\
\pi_{12} &= 0.13536 \times 10^{0.0001 \pi_3} \pi_2 = 3.1 \times 10^{-7}
\end{align*}
\]

Now, according to procedures described in Chapter III section the prediction equation is:

\[
\pi_1 = \frac{(3.8107 \times 10^{-10}) (0.13536)\pi_2^{-1.3376} 0.0001\pi_3}{0.13536 \times 10^{22915}}
\]

\[
= (2.2483 \times 10^{-10}) \pi_2^{-1.3376} 0.0001\pi_3
\]

Substituting for \(\pi_1, \pi_2\) and \(\pi_3\) the prediction equation becomes:

\[
\frac{A}{C} = (2.2483 \times 10^{-10}) \left(\frac{V}{\sqrt{gL}}\right)^{-1.3376} 0.0001 \frac{D_p}{L} \times \frac{\Delta \tau g^{1/2}}{L^{1/2}}
\]

Check:

At \(\frac{V}{\sqrt{gL}} = 2.46 \times 10^{-7}\) and \(\frac{D_p}{L} \times \frac{\Delta \tau g^{1/2}}{L^{1/2}} = 2291.5\)

\(\frac{A}{C}\) computed is 0.2641 = 0.264 and from Figure 10 for nitrate nitrogen at \(\frac{V}{\sqrt{gL}} = 2.46 \times 10^{-7}\) the \(\frac{A}{C}\) is read as 0.27 and this proves that prediction is valid and justified.
APPENDIX C

LENGTH AND TIME OF TRAVEL OF AMMONIUM NITROGEN

From section 5.2.1.1.1 for solution concentration of 20 mg/l the adsorption is 18.4 microgram per gm of soil.

The procedure given in section 3.2 of Chapter III is followed:

\[
\begin{align*}
A &= 18.4 \text{ mg/gm} \\
C &= 20 \text{ mg/l} \\
P &= 0.11 \text{ inch/day}
\end{align*}
\]

Then, amount of nitrogen in percolation flow:

\[
\begin{align*}
&= 0.11 \times 2.36 \times 20 \\
&= 5.192 \text{ mg/day}
\end{align*}
\]

Further,

\[
\begin{align*}
B.D. &= 1.69 \\
\text{Specific Gravity} &= 2.66
\end{align*}
\]

Assuming one foot of soil length and one square foot surface area, adsorptive capacity of the soil column of 1 cu. foot volume

\[
\begin{align*}
&= 0.0184 \text{ (mg/gm) x 1 (cu.ft.) x 4790249 (gm/cu.ft.)} \\
&= 948.47 \text{ mg}
\end{align*}
\]

So, time of travel

\[
\begin{align*}
&= \frac{948.47}{5.192} \\
&= 182.68 \text{ days} \\
&= 183 \text{ days}
\end{align*}
\]
BIBLIOGRAPHY


