

**A STUDY ON REMOVAL OF AMMONIA FROM THE
WASTE WATER OF FENCHUGANJ NATURAL GAS
FERTILIZER FACTORY**

BY

RAQUIBUL ALAM



Thesis submitted to the Department of Civil Engineering of
**BANGLADESH UNIVERSITY OF ENGINEERING AND
TECHNOLOGY, (BUET) DHAKA** in partial fulfillment for the degree

of

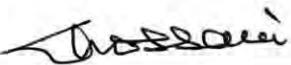
MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

May 2006



The thesis titled “ A STUDY ON REMOVAL OF AMMONIA FROM THE WASTE WATER OF FENCHUGANJ NATURAL GAS FERTILIZER FACTORY” submitted by RAQUIBUL ALAM, Roll no 040304501P, session: April/2003 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Science in Environmental Engineering on 22nd May, 2006.

BOARD OF EXAMINERS


Dr. Md. Delwar Hossain : Chairman
Professor
Dept. of Civil Engineering (Supervisor)
Bangladesh University of Engineering and Technology, Dhaka


Dr. Md. Mazharul Hoque : Member
Professor and Head
Dept. of Civil Engineering (Ex-Officio)
Bangladesh University of Engineering and Technology, Dhaka


Dr. M. Ashraf Ali : Member
Associate Professor
Dept. of Civil Engineering
Bangladesh University of Engineering and Technology, Dhaka


Mr. Md. Khoda Bux : Member
Project Director
BAMWSP (External)
14, Shaheed Capt. Monsur Ali Sarani
Kakrail, Dhaka

DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma (except for publication)

A handwritten signature in black ink, appearing to read "Raquibul Alam", is written over a horizontal line.

Raquibul Alam

To
My Loving Parents

ACKNOWLEDGEMENT

First of all, the author would like to express his deepest gratitude to the most powerful, the gracious Almighty Allah for giving knowledge, energy and patience to completing the thesis work successfully.

The author wishes to express his deepest gratitude to Dr. Md. Delwar Hossain, Professor, Department of Civil Engineering, BUET for his continuous guidance, invaluable suggestions, constructive comments and endless encouragement throughout the research work and the preparation of this thesis.

The author is grateful to Md Ekramun Nabi, Assistant professor, Department of Chemistry, and Muhammad Alamgir Toimoor, Assistant Professor, Department of English, Shah Jalal University of Science & Technology, Sylhet, whose suggestion and comments contributed to this thesis.

Contribution of the Department of Civil & Environmental Engineering, Shah Jalal University of Science & Technology, Sylhet by providing laboratory facilities for performing thesis work is highly acknowledged. Thanks are also expressed to Mr. Nazrul Islam, Laboratory Officer of Environmental Engineering Laboratory, Shah Jalal University of Science & Technology, Sylhet; Md Abdul Khaleque, Deputy Chief Chemist and Md Abu Faker, Chemist, Technical Service Department, Inspection and Quality Control (Laboratory), Natural Gas Fertilizer Factory Limited for their help and cooperation.

Finally, the author records with deep appreciation, the patience, understanding and encouragement shown by his parents and younger brother, Saiful Alam throughout the period of this study.

ABSTRACT

The Natural Gas Fertilizer Factory Ltd. (NGFFL), Fenchuganj, Sylhet was established in December 1961 to meet the urea demand of the country. The effluent from the plant contains high concentration of ammonia and oil and grease. Before 1986, all effluents were discharged directly into the Kushiara River. In 1986 two lagoons were constructed. The less contaminated effluent collected in lagoon 2 is subjected to equalization and dilution (with uncontaminated effluent of the plant) before discharging into the Kushiara River. Highly contaminated effluent from the plant are collected and stored into a two-chambered pit near the urea plant. Lube oil is collected through siphon and oil trap. After separation of lube well, ammonia-contaminated effluent is taken in the second pit from where it is pumped to lagoon 1 through a 4 km pipeline. The contents of lagoon 1 is diluted by river water, and then slowly released in to the Kushiara River.

An attempt has been made to characterize the liquid waste of NGFFL, to identify any changes of water quality of Kushiara River due to discharge of industrial effluent from NGFFL, to assess the efficiency of the present treatment facilities of NGFFL, and to assess effectiveness of different methods to remove ammonia from wastewater of NGFFL.

The physical, chemical and biological characteristics of the wastewater of the two lagoons were determined through extensive laboratory tests and compared with effluent discharge standard. Wastewater samples were collected from the lagoons once a month from March 2005 to December 2005. Dissolved solid contents of the lagoons were within the limit, but suspended solid contents exceeded the Bangladesh Standards for industrial effluent. COD and BOD_5 were well below the Bangladesh Standard. Dissolved Oxygen of the wastewater was found to be between 2.0 to 3.0 mg/L, which do not satisfy the standard (4.5 -8 mg/L). Oil and grease concentrations were found in the range of 28 to 68 mg/L, much higher than the standard (10 mg/L) for discharge into the inland surface water. Chromium and nitrate were found to be slightly higher than the standard limit for some samples. Ammonia nitrogen concentration was very high in lagoon 1, which is being directly discharged into the Kushiara River.

River water quality was analyzed in the month of December. Ammonia nitrogen was found to be 0.44 mg/L and 0.18 mg/L at the 300 yards and 1500 yards downstream of the effluent discharge point, respectively. The efficiency of lagoon 2 was analyzed and found that the lagoon 2 is not efficiently reducing ammonia.

Several techniques to remove of ammonia from wastewater were studied in the laboratory. It has been found that Lagooning after pH control could be a good option. About 60% removal of ammonia was achieved within one day by keeping the wastewater in a small container after raising the pH to 11.0. Use of Sulfonile resin as cation exchanger was not found to be a cost effective option to remove ammonia. The air-stripping method achieved very good ammonia removal. Different materials were used as

.0014, .001 and .0009 for coal, plastic ring, stone chips and wood chips, respectively. Best result was found for plastic ring for its higher surface area. Wood chips did not give good result, because the chips amalgamate with each other and hence reduces the surface area. Aeration after controlling pH was also found to be very effective in removing ammonia.

On the basis of wastewater analysis of NGFFL, it is clear that new treatment plant or improvement of the existing lagoons is essential. For reducing ammonia concentration in the existing lagoons, NGFFL authority could make provision of aeration in the lagoons. Since NGFFL uses huge amount of air for producing fertilizer, NGFFL authority can transfer air through a bypass line for aeration of the lagoons. Air stripping appears to be the most effective options for treatment of plant effluent. But it requires a huge amount of calcium oxide to adjust pH. Alternatively, biological treatment of the wastewater involving nitrification and denitrification may be considered.

CONTENTS

	Page No
ACKNOWLEDGEMENT	v
ABSTRACT	vi
CONTENTS	viii
LIST OF FIGURES	xii
LIST OF TABLES	xvi
LIST OF ABBREVIATIONS	xvii
CHAPTER ONE: INTRODUCTION	1
1.1 General	1
1.2 Scope of the Study	3
1.3 Objective of the Study	4
1.4 Organization of the Thesis	4
CHAPTER TWO: LITERATURE REVIEW	6
2.1 Introduction	6
2.2 Fertilizer Factories in Bangladesh	7
2.3 Natural Gas Fertilizer Factory (NGFFL), Fenchuganj, Sylhet	10
2.3.1 Existing treatment options of wastewater of NGFFL	11
2.4 Wastewater Quality And Their Impacts	13
2.4.1 Temperature	13
2.4.2 pH	14
2.4.3 Ammonia	15
2.4.4 Nitrites	15
2.4.5 Nitrates	15
2.4.6 Total alkalinity/ temporary hardness	15
2.4.7 Dissolved Oxygen	15
2.4.8 Biochemical Oxygen Demand (BOD)	16
2.4.9 Chemical Oxygen Demand (COD)	16
2.4.10 Chromium (Cr)	17
2.4.11 Phosphate	17
2.4.12 Organic Compounds	17

2.5 Nature and Characteristics of Ammonia and Its Effects on Fish	19
2.5.1 History	20
2.5.2 Production	20
2.5.3 Properties	22
2.5.4 Detection and determination	23
2.5.5 Effects on fish	23
2.6 Treatment of Ammonia from Effluent	25
2.6.1 Land application	25
2.6.1.1 Lagooning after pH adjustment	25
2.6.1.2 Waste- stabilization ponds	26
2.6.2 Physico-chemical processes	26
2.6.2.1 Break point chlorination	26
2.6.2.2 Diffused-aeration	27
2.6.2.3 Air stripping	27
2.6.2.4 Steam stripping	39
2.6.2.5 Selective ion exchanger	39
2.6.3 Nitrification in aerated lagoons	40
2.7 Overview	42
CHAPTER THREE: METHODOLOGY AND STUDY DESIGN	43
3.1 Introduction	43
3.2 Sample Collection	43
3.2.1 Selection of sampling points	43
3.2.2 Sampling method	43
3.2.3 Frequency of sampling	44
3.3 Analysis of Wastewater of NGFFL	44
3.4 Wastewater Treatment for Ammonia Removal	45
3.4.1 Aeration and air stripping	45
3.4.2 Ion exchange	48
3.4.3 Lagooning after pH adjustment	49
3.5 Overview	50

CHAPTER FOUR: WATER AND WASTEWATER QUALITY MONITORING AND ANALYSIS	51
4.1 Introduction	51
4.2 Analysis of Wastewater of NGFFL	51
4.2.1 Temperature	51
4.2.2 pH	52
4.2.3 Total Solids	53
4.2.4 Alkalinity	54
4.2.5 Chemical Oxygen Demand (COD)	55
4.2.6 Biochemical Oxygen Demand (BOD)	56
4.2.7 Dissolved Oxygen (DO)	57
4.2.8 Oil and grease	58
4.2.9 Phosphate (PO_4)	58
4.2.10 Sulfate (SO_4)	59
4.2.11 Chromium (Cr^{+6})	60
4.2.12 Nitrate	60
4.2.13 Ammonia nitrogen	61
4.3 Effect of Effluent Discharge on Kushiara River	62
4.4 Efficiency of The Existing Lagoon	66
4.5 Overview	67
CHAPTER FIVE: REMOVAL OF AMMONIA	68
5.1 Introduction	68
5.2 Ion Exchange Resin	68
5.3 Lagooning After pH Adjustment	69
5.4 Aeration	70
5.4.1 Effect of volume	70
5.4.2 Effect of pH	72
5.5 Air Stripping	74
5.5.1 Effect of packing height	74
5.5.2 Effect of pH on air stripping	76
5.5.3 Effect of air-water ratio	79

5.5.4 Effect of initial concentration	81
5.5.5 Effect of packing materials	84
5.5.6 Effluent concentration prediction	84
5.5.7 Ammonia in the air	86
5.6 Overview	87
CHAPTER SIX: CONCLUSIONS AND RECOMMENDATION	88
6.1 Conclusions	88
6.2 Recommendation for Policy Making	89
6.3 Recommendation for Further Study	90
BIBLIOGRAPHY	91
Appendix A	94
Appendix B	98

LIST OF FIGURES

		Page No
Figure 2.1	Lagoon 2	11
Figure 2.2	Treated effluent of lagoon-2 is slowly discharging into Awlachhara canal	11
Figure 2.3	4 Km pipeline carrying the wastewater to lagoon 1	11
Figure 2.4	Lagoon 1	11
Figure 2.5	Proposed treatment system of NGFFL liquid waste	13
Figure 2.6	Ammonia structure	19
Figure 2.7	Distribution of ammonia (NH_3) and ammonium ion (NH_4^+) as a function of pH	24
Figure 2.8	Air stripping unit	28
Figure 2.9	Visualization of two film theory	30
Figure 2.10	Resistance to motion encountered by a molecule being absorbed	31
Figure 2.11	Equilibrium curves for ammonia in water as a function of temperature based on Henry's law	32
Figure 2.12	Materials balance for con-current flow	33
Figure 2.13	Air requirements for ammonia stripping as a function of temperature	34
Figure 2.14	Generalized flooding and pressure drop correlation	36
Figure 2.15	Fouling of packing materials	37
Figure 2.16	Influence of temperature on hydraulic retention time required achieving nitrification in a completely suspended aerated lagoon under optimum conditions	42
Figure 3.1	Effluent drainage system of NGFFL	44
Figure 3.2	Aeration Experiment	45
Figure 3.3	Different types of materials used as packing materials	47
Figure 3.4	Air stripping experiment	47
Figure 3.5	Soil –covered Artificial Lagoon	49
Figure 4.1	Temperature at various sampling points in the year 2005	52

Figure 4.2	pH at various sampling points in the year 2005	53
Figure 4.3	Dissolved solids at various sampling points in the year 2005	54
Figure 4.4	Suspended solids at various sampling points in the year 2005	54
Figure 4.5	Alkalinity at various sampling points in the year 2005	55
Figure 4.6	COD at various sampling points in the year 2005	56
Figure 4.7	BOD ₅ at various sampling points in the year 2005	57
Figure 4.8	DO at various sampling points in the year 2005	57
Figure 4.9	Oil and grease at various sampling points in the year 2005	58
Figure 4.10	PO ₄ at various sampling points in the year 2005	59
Figure 4.11	SO ₄ at various sampling points in the year 2005	59
Figure 4.12	Cr ⁺⁶ at various sampling points in the year 2005	60
Figure 4.13	NO ₃ at various sampling points in the year 2005	61
Figure 4.14	Ammonia nitrogen at various sampling points in the year 2005	61
Figure 4.15	Concentration of ammonia nitrogen at the down stream of River Kushiara	62
Figure 4.16	Seasonal variation of temperature	63
Figure 4.17	Seasonal variation of pH	64
Figure 4.18	Seasonal variation of Dissolved solids	64
Figure 4.19	Seasonal variation of suspended solids	64
Figure 4.20	Seasonal variation of COD	65
Figure 4.21	Seasonal variation of BOD ₅	65
Figure 4.22	Seasonal variation of DO	65
Figure 4.23	Influent and effluent concentration of lagoon 2	66
Figure 4.24	Seasonal variation of ammonia nitrogen in lagoon	66
Figure 4.25	Effect of wastewater on a species, near lagoon 1	67
Figure 5.1	Break through curve of ammonia passing through sulfonile resin (30 cc)	69
Figure 5.2	Break through curve of ammonia passing through sulfonile resin (50 cc)	69
Figure 5.3	Wastewater kept in a jar at pH 11.5 (inner side was covered by soil)	70

Figure 5.4	Wastewater kept in a jar at pH 11.5 (inner side was not covered by soil)	70
Figure 5.5	Removal of ammonia by aeration at pH 11.5 (water volume is 200 ml)	71
Figure 5.6	Removal of ammonia by aeration at pH 11.5 (water volume is 350 ml)	71
Figure 5.7	Removal of ammonia by aeration at pH 11.5 (water volume is 750 ml)	72
Figure 5.8	Removal of ammonia by aeration at pH 8.6 (water volume is 200 ml)	72
Figure 5.9	Determination of GK_{eq}/V and relation of GK_{eq}/V with volume of aerated wastewater	74
Figure 5.10	Effect of packing height on removal of ammonia (packing material is coal)	75
Figure 5.11	Effect of packing height on removal of ammonia (packing material is plastic ring)	75
Figure 5.12	Effect of packing height on removal of ammonia (packing material is Stone Chips)	76
Figure 5.13	Effect of packing height on removal of ammonia (packing material is Wood Chips)	76
Figure 5.14	Effect of pH on removal efficiency of ammonia (Packing material is coal)	77
Figure 5.15	Effect of pH on removal efficiency of ammonia (Packing material is plastic ring)	78
Figure 5.16	Effect of pH on removal efficiency of ammonia (Packing material is stone chips)	78
Figure 5.17	Effect of pH on removal efficiency of ammonia (Packing material is wood chips)	79
Figure 5.18	Effect of air: water on removal of ammonia (Packing material is coal)	80
Figure 5.19	Effect of air: water on removal of ammonia (Packing material is plastic ring)	80

Figure 5.20	Effect of air: water on removal of ammonia (Packing material is stone chips)	81
Figure 5.21	Effect of air: water on removal of ammonia (Packing material is wood chips)	81
Figure 5.22	Effect of initial concentration of ammonia on removal of ammonia (packing material is coal)	82
Figure 5.23	Effect of initial concentration of ammonia on removal of ammonia (packing material is plastic ring)	82
Figure 5.24	Effect of initial concentration of ammonia on removal of ammonia (packing material is stone chips)	83
Figure 5.25	Effect of initial concentration of ammonia on removal of ammonia (packing material is wood chips)	83
Figure 5.26	Model prediction curve for coal	85
Figure 5.27	Model prediction curve for plastic ring	85
Figure 5.28	Model prediction curve for stone chips	85
Figure 5.29	Model prediction curve for wood chips	85
Figure 5.30	Verification of predicted model	86

LIST OF TABLES

	Page No
Table 2.1 Ranking of the industrial sectors (top five polluters)	8
Table 2.2 Waste generations by selected fertilizer factories	9
Table 2.3 Fertilizer Plant Nitrogenous fertilizer plant Effluent (liquid waste)	17
Table 2.4 Bangladesh Industrial Effluent Standards	18
Table 2.5 Showing the maximum levels of total ammonia (TAN mg/litre) for fish health	24
Table 5.1 Effluent concentration of ammonia in the air at the outlet	87
Table A-1 Wastewater Quality of NGFFL	94
Table A-2 Seasonal variation of Ammonia –N of lagoon 1 and lagoon 2	95
Table A-3 Water Quality of Kushiara River at the 600 yards down stream	96
Table A-4 Concentration of ammonia at the up stream and down stream of River Kushiara (December, 2005)	97
Table B-1 Lagooning after controlling of pH	98
Table B-2 Aeration Experiment	98
Table B-3 Effect of pH on air stripping unit	99
Table B-4 Effect of influent concentration on air stripping unit	99
Table B-5 Effect of packing height and air to water flow ratio on air stripping unit by keeping pH 10.5	100
Table B-6 Comparison between predicted effluent concentration and effluent concentration by laboratory experiment	101
Table B-7 Ion exchange Experiment (Resin bed volume is 30 cc)	101
Table B-8 Ion exchange Experiment (Resin bed volume is 30 cc)	102
Table B-9 Ion exchange Experiment (Efficiency of the resin bed)	102

LIST OF ABBREVIATIONS

BCIC	Bangladesh Chemical Industries Corporation
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CUFL	Chittagong Urea Fertilizer Factory Ltd
DO	Dissolved Oxygen
ECR	Environmental Conservation Rules
GDP	Gross Domestic Product
HRT	Hydraulic Retention Time
JFL	Jamuna Fertilizer Factory Ltd
NGFFL	The Natural Gas Fertilizer Factory Ltd
PUFL	Polash Urea Fertilizer Factory Ltd
SBR	Sequencing Batch Reactor
TSP	Triple Super Phosphate
UFFL	Urea Fertilizer Factory Ltd
VOC	Volatile Organic Compound
ZFL	Zia Fertilizer Factory Ltd.



CHAPTER ONE

INTRODUCTION

1.1 GENERAL

Industrial pollution is an area of growing environmental concern in Bangladesh. The country still has a relatively small industrial base (including manufacturing, construction, mining and utilities) contributing about 20% of GDP (1996-97). The manufacturing sub-sector accounts for about half of this contribution and it grew at a rate of 5.04% between 1972 and 1992. The growth rate of the manufacturing sector has been projected to be 11% for the year 2000 (World Bank, 1997). As Bangladesh attempts to attain economic development by replacing its agricultural base with industries and rural enterprises with urban centers, pollution and other environmental impacts of industries are becoming critical in development planning (Islam et al, 1994).

Industrialization in Bangladesh (former East Pakistan) began in the 1950s at a very slow pace with the primary focus on agro-based industries such as jute, cotton and sugar. After independence in 1971, there was renewed interest in industrial development within the limited and fragile post-war infrastructure. The most significant industrial growth has been recorded after 1982; particularly the development of the garments, textile and dyeing sectors.

Treatment of industrial waste and effluent has so far been considered a low priority, because policy planners had a feeling of complacency that industrial pollution is still at a very low level. Due to lack of awareness as well as the absence of strong punitive actions, the practice of circulating waste and effluent into water bodies including ponds, canals, creeks and rivers still remains widespread. The serious public health hazards they create are to some extent minimized as the waste and effluents are mostly flushed out into the sea during the rainy season. But excessive localized pollution is already threatening the sustainability of the resource base and having effects on the health of people; most of them are affected or unaware or hardly have any other choices.

The number one toxic chemicals polluter is the tanneries and leather industry, followed by pulp and paper, pharmaceuticals, fertilizer/pesticides and industrial chemicals. In most cases, the chemicals are disposed on land as part of the solid waste, parts of which are then collected and recycled. Exceptions are the pulp and paper and cement factories – these emit most of the chemical to air. Direct emission to water appears to be small – the two significant ones are 18% by the pulp and paper, and 10% by the industrial chemicals (Islam et al, 1994). However, it is quite likely that a significant part of the land pollution eventually ends up in water through direct runoff and seepage. Unfortunately, no information is available on the ultimate fate of these toxic chemicals.

The Natural Gas Fertilizer Factory Ltd. (NGFFL), Fenchuganj, Sylhet is a pride and pioneer enterprise of the Bangladesh Chemical Industries Corporation (BCIC), was established in December, 1961 in the hilly picturesque surroundings of Fenchuganj to meet the urea demand of the country (Khan et al, 2002). It is the outcome of government policy to boost-up fertilizer production and hence achieving self sufficiency in food from indigenous raw materials like natural gas which is quite abundantly available in our country. The factory is located 28 kilometers south – east of Sylhet town at Fenchuganj upazila, 4 kilometers east from the river Kushiara, 5 kilometers south – west of Maizgaon railway station. Total factory area is 419 acres. M/S. Cobe Steel, Japan and M/S Mitsubishi Sojikiasa Ltd. conducted the main construction of the factory. After liberation war of Bangladesh, the ultimate control of the factory was given to Bangladesh Chemical Industry Corporation (BCIC). Presently the factory is well managed by a set of Company Board Directors with central control by BCIC. BCIC keeps it open only to preserve the local employment base. The factory is equipped with its own Power Generation Plant, Water treatment Plant, Inspection and Quality Control Laboratory, Polythene Bag Manufacturing Plant, Bagging, Storage and Dispatch system as well as various Engineering Workshops to carry out normal maintenance of the factory and to ensure steady operation of the plants. Natural gas fertilizer factory Ltd. (NGFFL), Fenchuganj, Sylhet produces urea. The process involves traditional chemical technology and deals with many chemicals. A part of the chemicals disposed as an industrial effluent in Kushiara River, which is responsible for the degradation of river water quality. Among

all the pollutants discharged from a fertilizer factory ammonia has the most severe effect on the receiving water body, soil and air. Ammonia is toxic to fish and aquatic organisms, even in very low concentrations. "When levels reach 0.06 mg/L, fish can suffer gill damage. When levels reach 0.2 mg/L, sensitive fish like trout and salmon begin to die. As levels near 2.0 mg/L, even ammonia-tolerant fish like carp begin to die. Ammonia levels greater than approximately 0.1 mg/L usually indicate polluted waters" (EPA, 1986). Also, ammonia is much more toxic to fish and aquatic life when water contains very little dissolved oxygen and carbon dioxide and its pH and temperature is high. Ammonia in aerobic aquatic environment is oxidized to nitrates. The conversion of NH_4^+ to NO_3^- consumes large quantities of dissolved oxygen. Ammonia has a very strong odor that is irritating when it is in the air at a level higher than 50 ppm (Agency for Toxic Substances and Disease Registry, 2004). Low levels of ammonia may harm some people with asthma and other sensitive individuals. A few drops of liquid ammonia on the skin or in the eyes will cause burns. Exposure to larger amounts of liquid ammonia or ammonium ion in the skin, eyes, throat, or lungs may be severely burned. These burns might be serious enough to cause permanent blindness, lung disease, or death. (Agency for Toxic Substances and Disease Registry, 2004).

As Natural Gas Fertilizer Factory Ltd. (NGFFL) produces excessive amount of ammonia as effluent and discharges it into the river Kushiara, so treatment of wastewater of NGFFL is very important.

1.2 SCOPE OF THE STUDY

NGFFL is Bangladesh's oldest urea fertilizer plant. The plant's discharges contain toxic ammonia and pH levels, and substantial residues of grease and oil. They have been clearly identified by downstream villages as the cause of major fish kills, paddy field damage, and health threats. In addition, there have been regular atmospheric releases of ammonia and sulphur di- and trioxide. Before 1986, all effluents were discharged directly into the Kushiara River. Since then the plant has constructed two lagoons, in which the effluent is diluted by adding the staff colony's Wastewater and local spring water. In addition, acidic and alkaline injections are used to neutralize the pH level. Some

separation of oil and grease from the water has been undertaken, and an improved method is currently planned. The cleanup effort has improved ambient quality modestly. Fish kills are now less frequent, and the plant makes sure that communities downstream are warned before periodic cleaning operations discharge large quantities of ammonia and other pollutants into the river (Huq and Wheeler, 1993).

A Case study based on field visits, primary survey and secondary data have been conducted. These studies cover almost all the major polluting parameters present in the wastewater of NGFFL. Due to lack of resources, modern technology, and awareness, not much is being done to trap the harmful pollutants and reuse/recycle these chemicals. An attempt has been made to remove ammonia from wastewater of NGFFL in this study. It is hoped that the study will provide valuable information to the development and management of wastewater of NGFFL.

1.3 OBJECTIVE OF THE STUDY

The overall objective of the research project is to provide suitable treatment option to remove ammonia from the effluent of the Natural Gas Fertilizer Factory Ltd. (NGFFL). The major objectives of the research project are:

- To identify any changes of water quality of Kushiara river due to discharge of industrial effluent from NGFFL.
- To determine the characteristics of liquid waste of NGFFL.
- To assess the efficiency of present treatment facilities of NGFFL
- To assess the effectiveness of different method to remove ammonia from wastewater of NGFFL and to recommend the most suitable option.

1.4 ORGANIZATION OF THE THESIS

The theses comprises of six chapters. The first one is introduction presenting an overall view of the study. Chapter two contains a brief and selective review of the relevant literature that provides different wastewater quality parameters and standards, nature and characteristics of ammonia, different techniques to remove ammonia etc. In chapter three,

methodologies adopted in the research work are described. Chapter four provides an assessment of wastewater quality of NGFFL and water quality at the down stream of river Kushiara. Chapter five investigates the effectiveness of different techniques like aeration, air stripping, ion exchange and lagooning after pH control to remove ammonia from the effluent of wastewater from NGFFL. In chapter six, attempts are made to bring the findings of the study together in the form of conclusions and outline the recommendations for actions and studies to be required in future.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Nitrogen is an essential plant nutrient. It is required in substantial amounts in order to support crop growth and must be adequate to produce economically sufficient yields. When the amount of soil-supplied nitrogen is considered to be deficient for satisfactory crop yields, nitrogen fertilizer is added to supplement the soil-supplied nitrogen.

Fertilizers are compounds given to plants with the intention of promoting growth. They are usually applied either via the soil, for the uptake by plant roots, or by foliar spraying for uptake through leaves. Fertilizers can be organic or inorganic. They can be naturally occurring compounds such as peat or mineral deposits, or manufactured through natural processes such as composting or chemical process such as Haber process. Fertilizers typically provide, in varying proportions, the three major plant nutrients (nitrogen, phosphorus and potassium), the secondary plant nutrients (Calcium, sulfur, magnesium), and some times trace elements (or micro nutrients) with a role in plant nutrition: boron, manganese, iron, zinc, copper and molybdenum (Wikipedia)

The process of manufacturing fertilizer by industrial nitrogen fixation was first developed in Germany during World War I, and fertilizer production has grown exponentially since the 1940s. In recent years, the increasing pace of production and use has been truly phenomenal. The amount of industrially fixed nitrogen applied to crops during the decade from 1980 to 1990 more than equaled all industrial fertilizer applied previously in human history. Until the late 1970s, most industrially produced fertilizer was applied in developed countries. Use in these regions has now stabilized while fertilizer applications in developing countries have risen dramatically. The momentum of human population growth and increasing urbanization ensures that industrial fertilizer production will continue at high and likely accelerating rates for decades in order to meet the escalating demand for food (Peter et al, 1997).

2.2 FERTILIZER FACTORIES IN BANGLADESH

There are eight public fertilizer factories in Bangladesh falling under three categories and operating under the jurisdiction of Bangladesh Chemical Industries Corporation (BCIC):

Ammonia-urea production complexes

- Urea Fertilizer Factory at Ghorashal (UFFL)
- Polash Urea Fertilizer Factory at Ghorashal (PUFL)
- Zia Fertilizer Factory at Ashuganj (ZFL)
- Chittagong Urea Fertilizer Factory at Chittagong (CUFL)
- Natural Gas Fertilizer Factory at Fenchuganj (NGFL)
- Jamuna Fertilizer Factory at Jamalpur (JFL)

Triple Super Phosphate (TSP) production Complex

- T. S. P. Complex at Chittagong

Ammonia Sulphate production complex

- Ammonia Sulphate Complex

In addition, there is one private sector plant belonging to KAFCO (DOE, 1994). Limited data is available on the type of waste generated, and physical and chemical characteristics of effluent produced in both urea and phosphate plants. A study conducted by Islam et al, 1994 shows that (table 2.1) the rank of fertilizer factory as a pollutant in context of water pollution is fifth in Bangladesh. The acidic and alkaline waste generated from fertilizer factories affects aquatic life. Ammonia present in the waste is toxic to fish. The amines have high oxygen and chlorine values. Rainwater runoff from storage areas carries dissolved and suspended solids, urea dust, and other materials such as, chromium and nickel. Phosphate from T.S.P. complex can accelerate the growth of algae and other aquatic weeds. Ammonia and urea dust may affect land areas around the fertilizer plants. Other substances found in the effluent of fertilizer factories that are toxic to aquatic life are urea, hydrogen sulfide, hydrogen cyanide, arsenic, methanol and fluorides. Sometimes fine carbon particle in the effluent reduces dissolved oxygen content of the receiving stream.

Table 2.1 Ranking of the industrial sectors (top five polluters)

Rank	Industrial sector	Emission (tons/year)	Percent contribution	Cumulative percent
Air pollution				
1	Food industry	146356.06	38.7%	38.7%
2	Cement/Clay	62725.88	16.6%	55.3%
3	Pulp and paper	51963.92	13.7%	69.0%
4	Textile	39831.01	10.5%	79.5%
5	Tobacco	16992.22	4.5%	84.0%
Water pollution				
1	Pulp and paper	91768.10	47.4%	47.4%
2	Pharmaceuticals	30866.72	15.9%	63.3%
3	Metal	27174.61	14.0%	77.3%
4	Food industry	23403.39	12.1%	89.4%
5	Fertilizers/pesticides	12715.00	6.6%	96.0%
Toxic metals emission				
1	Metal	1071.92	28.3%	28.3%
2	Cement/Clay	688.90	18.2%	46.6%
3	Tanneries/leather	659.38	17.4%	64.0%
4	Fertilizers/pesticides	407.30	10.8%	74.8%
5	Textile	192.46	5.1%	79.8%
Toxic chemicals emission				
1	Tanneries/leather	13630.55	20.6%	20.6%
2	Pulp and paper	10132.96	15.3%	35.9%
3	Pharmaceuticals	8362.393	12.6%	48.6%
4	Fertilizers/pesticides	8226.275	12.4%	61.0%
5	Industrial chemicals	5713.782	8.6%	69.6%

(Islam et al, 1994)

In addition to pollution, several occupational hazards have taken place in fertilizer factories primarily due to lack of safety measures. Workers are subjected to noise pollution and various health risks from breathing urea dust gaseous ammonia.

Fertilizer factories regularly report waste and pollution related data to BCIC. The waste produced at selected factories with information on treatment and disposal has been summarized in Table 2.2.

Table 2.2 Waste generations by selected fertilizer factories

Waste Type	CUFL	ZFL	UFL	PUFFL	JFCL	T.S.P. Complex	Treatment	Disposal
Solid waste								
Catalyst waste/dust			0.05 m ³ /d			1.8 m ³ /year	None	Underground dumping in plastic bags, Sale
Urea dust		0.81 ton/d		No data	216 kg/d		Some scrubbing	Dispersed by air & water
Solid scraps	No data	No data	No data	No data	No data	No data	None	Dumped in scrap yard
Contaminated sludge					31 m ³ /d		Dilution	Drained into river
Liquid waste								
Combined effluent	3756 m ³ /d		10920 MT/d	10 ton/d	5160 ton/d	8,040 m ³ /d	Dilution Aeration PCT	Dumped in the river
P ₂ O ₅						100 ppm	system (UFL)	
F						80 ppm	Lagooning Treatment (JFCL)	
SO ₄						50 ppm	Dilution	Drained into river
Ammonia		40 kg/d					None	Stored in vessels
G. V. Solution			960.3 0	MT/d			Treatment (JFCL)	To basin equalization
Sanitary wastewater					240 ton/d			
Gaseous Waste								
SA Plant exhaust gas						70,000 NM ³ /h	Demister	Through chimney into air
SO ₂						900 ppm		
SO ₃						210 ppm		
Rock grinding plant exhaust gas				No data		2.650 NM ³ /h w/ 62 NM ³ /h dust	Dust collector	Through chimney into air
Ammonia	No data	201.6 NM ³ /d			504 kg/d		Some scrubbing and recovery	Dispersed into air
Formaldehyde vapor					1.25 ppm		Some scrubbing	Vented to air
Flue gas with CO ₂				No data			Partially recovered	Vented to air

(Islam et al, 1994)

2.3 NATURAL GAS FERTILIZER FACTORY (NGFFL), FENCHUGANJ, SYLHET

The effluents are grouped into three categories based on the level of contamination and for easy wastewater management:

- Non-contaminated effluent ($300\text{ m}^3/\text{hr}$). This non-contaminated effluent comes from following two sources: Colony wash ($200\text{ m}^3/\text{hr}$) and Intake overflow ($100\text{ m}^3/\text{hr}$). This $300\text{ m}^3/\text{hr}$ non-contaminated water will be used as diluents to less contaminated water. It will also act as sewage seeding to ammonia-contaminated water.
- Less contaminated effluent ($515\text{ m}^3/\text{hr}$). The average quantity of less contaminated effluents collected from different plants are Ammonia plant ($90\text{ m}^3/\text{hr}$), Urea plant ($75\text{ m}^3/\text{hr}$), Power plant & Ammonium Sulfate plant ($170\text{ m}^3/\text{hr}$) and cooling water blow down ($180\text{ m}^3/\text{hr}$). and
- Highly contaminated effluent with oil and Ammonia ($5\text{ m}^3/\text{hr}$).

Before 1986, all effluents were discharged directly into the Kushiara River. Presently the factory disposes its effluent in two ways. Less contaminated effluent collected from different plants is first taken into Lagoon-2 (Figure 2.1), adjacent to the factory where it is subjected to the bio-degradation and evaporation of ammonia. The spatiality of this area is that a number of hilly springs are flowing in and around the factory. Two main streams (Canal-1 & 2) are flowing through the factory. These two main streams meet at a point near the factory colony and finally flow in name ‘Awlachhara Khal’ and cover a distance of 4.0 Km. to Kushiara River. The year average flow of this canal is about 4000 MT/hr. The less contaminated effluent of Lagoon-2 is subjected to equalization, natural evaporation and bio-degradation and is dropped to this Awlachhara canal for further dilution before discharging into the river (Figure 2.2).

Oil and highly contaminated effluent are collected from the plant and stored into the two-chambered pit near Urea plant. Lube oil is collected through siphon and oil trap. The lube oil is sent to lube oil purification unit. The collected oil is purified and reused in the factory. The lube oil collected from different drains by oil trap is sold as sweep oil. After separation of lube oil ammonia contaminated effluent is taken in the second pit where



Figure 2.1: Lagoon 2



Figure 2.2: Treated effluent of lagoon-2 is slowly discharging into Awlachhara canal

from it is pumped to lagoon-1 (Figure 2.4) through 4 Km pipeline (Figure 2.3). This effluent is not allowed to any surface drain. In the lagoon, it is subjected to evaporation and bio-degradation. The lagoon water is diluted by fresh water from the intake pump station. After dilution, the lagoon water is slowly released to the river Kushiara.



Figure 2.3 4Km pipeline carrying the wastewater to lagoon 1



Figure 2.4: Lagoon 1

2.3.1 Existing Treatment Options of Wastewater of NGFFL

The major pollutants of fertilizer waste are ammonia, urea, acids, alkali and wash water. There are a lot of technologies and treatment options available for treatment of ammonia, urea, acids and alkali contaminated water. According to the Environmental Management

Plan of NGFFL, following steps are needed for treatment: Neutralization, Equalization, Dilution and Bio-degradation.

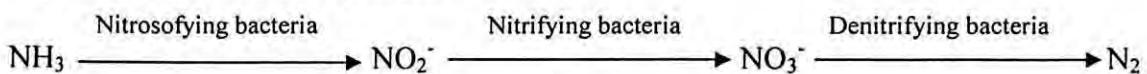
Neutralization: It is necessary when waste contains excess acid or alkali. Regeneration of cation and anion bed resins is the main sources of acid/alkali water. Acid and alkali wash water of resin beds are stored in concrete tanks, neutralized, monitored and feed to the drain. As both acid/alkali waste of same volume are regenerated from demineralization plant no financial involvement will be necessary.

Equalization: This means retaining of wastes in a basin/lagoon for some predetermined time so that the effluent discharged from different plants/sections at different time is well mixed and becomes fairly uniform in its characteristics. Since characteristics of fertilizer waste vary from time to time/shift to shift and also discharge rate is not uniform or continuous, the waste stream must have equalization before it is subjected to further treatment. The present plant has an equalization lagoon (Lagoon-2) for holding less contaminated discharge from its various section/plants where following further treatment can be done: Dilution, Evaporation and Bio-degradation.

Dilution: The non-contaminated effluent of the factory is fed to the lagoon-2 to dilute the less contaminated effluent of this lagoon.

Evaporation: The effluent in this lagoon will be held for a considerable period of time when ammonia of the effluent will be evaporated and pollution level of lagoon-2 will further be lowered.

Bio-degradation: Ammonia is biodegradable to NO_2^- , NO_3^- and finally to nitrogen. During its holding time in the lagoon, it will be subjected to bio-degradation and ammonia and urea contents of effluent water will be further reduced. The biological treatment in combination with domestic sewage is advantageous from the point of economics, availability of supplementary nutrients and seeding with microorganisms. The bio-degradation of NH_3 and urea both in aerobic and anaerobic condition will occur in lagoons as per as following reaction:



The management plan of NGFFL includes aeration and seeding with sewage for this ammonia contaminated water of effluent pond. As a result of aeration, the ammonia content of this pond will reduce greatly. After aeration, biodegradation rate of ammonia will be enhanced and ammonia level will further reduce at lagoon-1. After this treatment effluent from this pond will be pumped to lagoon-1 as per previous practice. The effluent water in lagoon-1 will be retained for a period for operations like dilution, equalization, and bio-degradation as discussed in process for lagoon-2. Total effluent treatment system with proposed seeding and aeration system is shown in Figure 2.5.

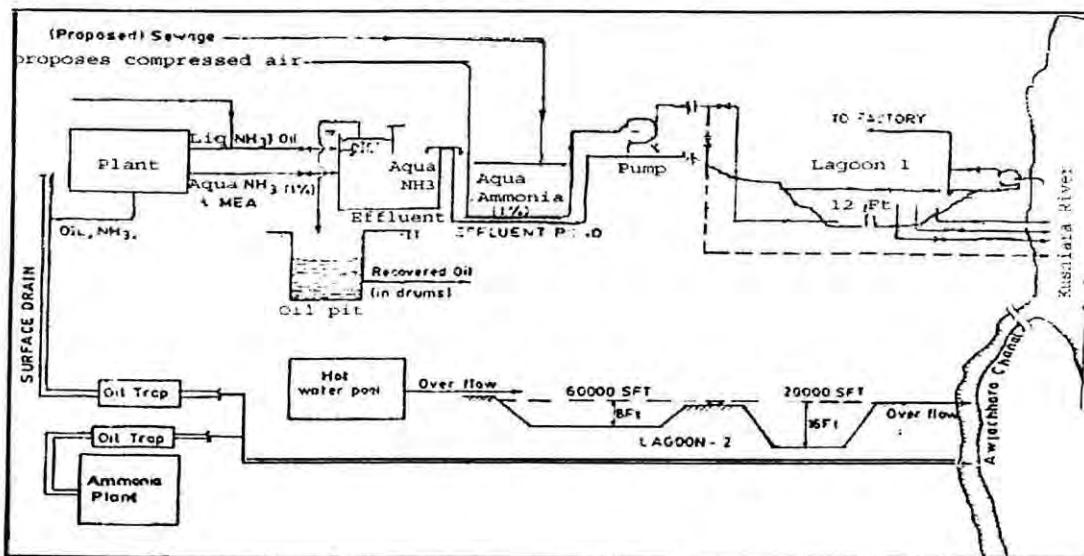


Figure 2.5: Proposed treatment system of NGFFL liquid waste

2.4 WASTEWATER QUALITY AND THEIR IMPACTS:

Wastewater quality is one of the primary factors affecting the natural water body. Many abnormal behaviors exhibited by fish can be attributed to poor water quality. Upon determining that fish has a problem, the first thing to suspect is water quality. The Bangladesh Industrial effluent standards are shown in table 2.3 and 2.4. The wastewater qualities those should be considered for the fertilizer industry are as follows:

2.4.1 Temperature

Water temperature has an inverse relationship to the amount of oxygen contained in that water. The higher the water temperature, the lower the oxygen saturation level would be

the result. The 'saturation level' is the maximum amount of oxygen in water at a given temperature. Fish and most aquatic organisms are cold-blooded. Consequently, their metabolism increases as the water warms and decreases as it cools. Each species of aquatic organism has its own optimum (best) water temperature. If the water temperature shifts too far from the optimum, the organism suffers. Cold-blooded animals can't survive temperatures below 0 °C (32 °F), and only rough fish like carp can tolerate temperatures much warmer than about 36 °C (97 °F). Fish are not the only organisms requiring specific temperatures. Diatoms seem to grow best at a temperature of 15-25 °C, green algae at 25-35 °C, and blue-green algae at 30-40 °C. Warm water also makes some substances, such as cyanides, phenol, xylene and zinc, more toxic for aquatic animals. If high water temperatures are combined with low dissolved oxygen levels, the toxicity is increased.

2.4.2 pH

The balance of positive hydrogen ions (H^+) and negative hydroxide ions (OH^-) in water determines how acidic or basic the water is. In pure water, the concentration of positive hydrogen ions is in equilibrium with the concentration of negative hydroxide ions, and the pH measures exactly 7. Most fishes can tolerate pH values of about 5.0 to 9.0, but serious anglers look for waters between pH 6.5 and 8.2. When acid waters (waters with low pH values) come into contact with certain chemicals and metals, they often make them more toxic than normal. As an example, fish that usually withstand pH values as low as 4.8 will die at pH 5.5 if the water contains 0.9 mg/L of iron. The pH of sea (salt) water is not as vulnerable as fresh water's pH to acid wastes. This is because the different salts in sea water tend to buffer the water with Alka-Seltzer-like ingredients. Normal pH values in seawater are about 8.1 at the surface and decrease to about 7.7 in deep water. Many shellfish and algae are more sensitive than fish to large changes in pH, so they need the sea's relatively stable pH environment to survive. Shallow waters in subtropical regions that hold considerable organic matter often vary from pH 9.5 in the daytime to pH 7.3 at night. Organisms living in these waters are able to tolerate these extremes or swim into more neutral waters when the range exceeds their tolerance.

2.4.3 Ammonia

Ammonia is the most important parameter in context of fertilizer factory. Details of ammonia is discussed in section 2.5

2.4.4 Nitrites

Nitrite (NO_2^-) is the by-product of Nitrosomonas bacteria breaking down ammonia in alkaline water. Nitrous Acid (HNO_2) is the by-product of Nitrosomonas bacteria breaking down ammonium in acid water. These reactions are the first steps in the Nitrogen Cycle. There is again an exponential relationship with pH. As pH decreases below pH 7, the amount of nitrous acid increases and becomes more toxic. A test for these molecules should read 0.0 PPM.

2.4.5 Nitrates

(NO_3^-) and (HNO_3) respectively are the molecular by-products of Nitrobacter Bacteria breaking down Nitrites and Nitrous Acid respectively. This is the second step in the Nitrogen Cycle. Unless found in large quantities, both are considered non-toxic. To control the amount of nitrates and nitric acid, make water changes or add plants.

2.4.6 Total Alkalinity

Alkalinity is not a pollutant. It is a total measure of the substances in water that have "acid-neutralizing" ability. Alkalinity indicates a solution's power to react with acid and "buffer" its pH — that is, the power to keep its pH from changing. Alkalinity is important for fish and aquatic life because it protects or buffers against pH changes (keeps the pH fairly constant) and makes water less vulnerable to acid rain. The main sources of natural alkalinity are rocks, which contain carbonate, bicarbonate, and hydroxide compounds. Borates, silicates, and phosphates may also contribute to alkalinity.

2.4.7 Dissolved Oxygen

Dissolved oxygen (DO) is oxygen that is dissolved in water. It gets there by diffusion from the surrounding air; aeration of water that has tumbled over falls and rapids; and as a waste product of photosynthesis. Fish and aquatic animals cannot split oxygen from water (H_2O) or other oxygen-containing compounds. If water is too warm, there may not be enough oxygen in it. Oxygen levels also can be reduced through over fertilization of

water plants by run-off from farm fields containing phosphates and nitrates (the ingredients in fertilizers). Under these conditions, the numbers and size of water plants increase a great deal. Then, if the weather becomes cloudy for several days, respiring plants will use much of the available DO. When these plants die, they become food for bacteria, which in turn multiply and use large amounts of oxygen. It is impossible to accurately predict minimum DO levels for specific fish and aquatic animals. For example, at 5 °C (41 °F), trout use about 50-60 milligrams (mg) of oxygen per hour; at 25 °C (77 °F), they may need five or six times that amount. Fish are cold-blooded animals, so they use more oxygen at higher temperatures when their metabolic rate increases. Numerous scientific studies suggest that 4-5 parts per million (ppm) of DO is the minimum amount that will support a large, diverse fish population. The DO level in good fishing waters generally averages about 9.0 parts per million (ppm). When DO levels drop below about 3.0 parts per million, even the rough fish die.

2.4.8 Biochemical Oxygen Demand (BOD)

BOD is typically reported as 5 day BOD and ultimate BOD at 20° C and reported as milligrams of oxygen consumed per liter (mg O₂/L). BOD₅ is to monitor wastewater treatment facilities and surface water quality. BOD is the biochemical oxygen demand of the water and it is related to the concentration of the bacterial facilitated decomposable organic material in the water. A sample with a 5 day BOD between 1 and 2 mg O₂/L indicates very clean water, 3.0 to 5.0 mg O₂/L indicates moderately clean water and > 5 mg O₂/L indicates a nearby pollution source. BOD is a laboratory test that requires an oxygen-sensing meter, incubator, nitrifying inhibitors, and a source of bacteria.

2.4.9 Chemical Oxygen Demand (COD)

COD is used as a measure of the oxygen equivalent of the organic matter content of the sample. Only the organic matter that is susceptible to oxidation by strong chemical oxidant. COD is typically used when there are industrial wastewater sources, comparing biological to chemical oxidation in the selection of treatment process and performances, or depending on the waste stream it can provide insight into the concentration of reduced inorganic metal inorganic, such as ferrous iron, sulfide, and manganese.

2.4.10 Chromium (Cr)

The impact of chromium is not clearly defined, but it is known to adversely impact aquatic organisms.

2.4.11 Phosphate

The element phosphorus is necessary for plant and animal growth. Nearly all fertilizers contain phosphates (chemical compounds containing the element, phosphorous). When it rains, varying amounts of phosphates wash from farm soils into nearby waterways. Phosphates stimulate the growth of plankton and water plants that provide food for fish. This may increase the fish population and improve the waterway's quality of life. If too much phosphate is present, algae and waterweeds grow wildly, choke the waterway, and use up large amounts of oxygen. Many fish and aquatic organisms may die.

2.4.12 Organic Compounds

Oil and grease, organic carbons, phenolic compounds, and detergents are included in this group. Oil and grease includes a wide array of hydrocarbon compounds, some of which are toxic to aquatic organisms at low concentrations.

Table 2.3 Fertilizer Plant Nitrogenous fertilizer plant Effluent (liquid waste)

Parameters	Standard presence in a unit of mg/l
Ammonia As Nitrogen	50 (New) 100 (Old)
Total Kjeldahl Nitrogen	250 (New)
pH	6.5 – 8
Chromium (as total Cr)	0.5
Hexavalent Chromium	0.1
Suspended Solids	100
Oil and Grease	10

Source: DOE, 1997

Table 2.4 Bangladesh Industrial Effluent Standards

sl. No.	Parameters	Unit	Discharge to			
			Inland surface water	Public sewer	leading to secondary treatment Plant	Irrigable land
1	Ammonical nitrogen(as N)	mg/l	50	75		5
2	Ammonia (as free NH ₃)	mg/l	5	5		15
3	Arsenic(as As)	mg/l	0.2	0.05		0.2
4	BOD ₅ at 20°C	mg/l	50	250		100
5	Boron	mg/l	2	2		2
6	Cadmium(as Cd)	mg/l	0.05	0.5		0.5
7	Chloride	mg/l	600	600		600
8	Chromium (as total Cr)	mg/l	0.5	1.0		1.0
9	COD	mg/l	200	400		400
10	Chromium (as hexavalent Cr)	mg/l	0.1	1.0		1.0
11	Copper (as Cu)	mg/l	0.5	3.0		3.0
12	Dissolved oxygen (DO)	mg/l	4.5-8	4.5-8		4.5-8
13	Electro- Conductivity (EC)	μmho/cm	1200	1200		1200
14	Total dissolved solids	mg/l	2100	2100		2100
15	Flouride (as F)	mg/l	2	15		10
16	Sulfide (as S)	mg/l	1	2		2
17	Iron (as Fe)	mg/l	2	2		2
18	Total kjeldhal nitrogen (as N)	mg/l	100	100		100
19	Lead (as Pb)	mg/l	0.1	1		0.1
20	Manganese (as Mn)	mg/l	5	5		5
21	Mercury (as Hg)	mg/l	0.01	0.01		0.01
22	Nickle (as Ni)	mg/l	1.0	2.0		1.0
23	Nitrate (as elementary N)	mg/l	10.0	Not yet set		10
	Nitrite (as elementary N)	mg/l	50	50		50
24	Oil & grease	mg/l	10	20		10
25	Phenolic compounds (as C ₆ H ₅ OH)	mg/l	1.0	5		1
26	Dissolved Phosphorus (as P)	mg/l	8	8		15
27	Radioactive substance	mg/l	(to be specified by Bangladesh Atomic Energy Commission)			
28	pH	mg/l	6-9	6-9		6-9
29	Selenium (as Se)	mg/l	0.05	0.05		0.05
30	Zinc (as Zn)	mg/l	5	10		10
31	Total dissolved solids	mg/l	2100	2100		2100
32	Temperature (summer/winter)	°C	40/50	40/50		40/50
33	Suspended solids	mg/l	150	500		200
34	Cyanide	mg/l	0.1	2.0		0.2

Source: DOE, 1997

2.5 NATURE AND CHARACTERISTICS OF AMMONIA AND ITS EFFECTS ON FISH

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 . At standard temperature and pressure ammonia is a gas. It is toxic and corrosive to some materials, and has a characteristic pungent odor. An ammonia molecule is not flat, but has the shape of a compressed tetrahedron known as a trigonal pyramid. This shape gives the molecule an overall dipole moment and makes it polar so that ammonia very readily dissolves in water. The nitrogen atom in the molecule has a lone electron pair, and ammonia acts as a base. In acidic or even neutral aqueous solutions, it can bond to a hydronium ion (H_3O^+), releasing a water molecule (H_2O) to form the positively charged ammonium ion (NH_4^+), which has the shape of a regular tetrahedron. The degree to which ammonia forms the ammonium ion depends on the pH of the solution.

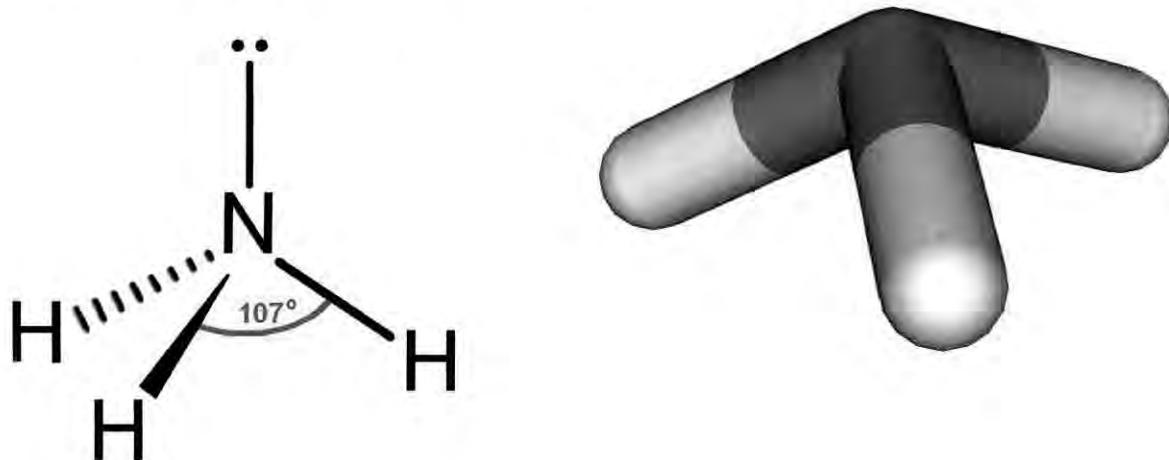


Figure 2.6 Ammonia structure (Wikipedia)

The main uses of ammonia are in the production of fertilizers, explosives and polymers. It is also an ingredient in certain household glass cleaners. Ammonia is found in small quantities in the atmosphere, being produced from the putrefaction of nitrogenous animal and vegetable matter. Ammonia and ammonium salts are also found in small quantities in rainwater, while ammonium chloride (sal-ammoniac) and ammonium sulfate are found in volcanic districts; crystals of ammonium bicarbonate have been found in Patagonian

guano. Ammonium salts also are found distributed through all fertile soil and in seawater. Substances containing ammonia or that are similar to it are called ammoniacal.

2.5.1 History

Gaseous ammonia was first isolated by Joseph Priestley in 1774 and was termed by him alkaline air. In 1777 Karl Wilhelm Scheele showed that it contained nitrogen, and Claude Louis Berthollet, in about 1785, ascertained its composition. The Haber process to produce ammonia from the nitrogen contained in the air was developed by Fritz Haber and Carl Bosch in 1909 and patented in 1910. It was first used on an industrial scale by the Germans during World War I. The ammonia was used to produce explosives to sustain their war effort.

2.5.2 Production

Today the Haber process is the most important method for production of ammonia. In this process, nitrogen and hydrogen gases combine directly on an iron catalyst at a pressure of 200 bar (20 MPa, 3000 lbf/in²) and a temperature of 500 °C to produce ammonia.



Compared to older methods, the feedstocks of the Haber process are relatively inexpensive—nitrogen makes up 78% of the atmosphere, while hydrogen can be readily produced from natural gas.

2.5.3 Properties

Ammonia is a colourless gas with a characteristic pungent smell; it is lighter than air, its density being 0.589 times that of air. It is easily liquefied and the liquid boils at -33.7 °C, and solidifies at -75 °C to a mass of white crystals. Liquid ammonia possesses strong ionizing powers ($\epsilon = 22$), and solutions of salts in liquid ammonia have been much studied. Liquid ammonia has a very high standard enthalpy change of vaporization (23.35 kJ/mol, c.f. water 40.65 kJ/mol, methane 8.19 kJ/mol, phosphine 14.6 kJ/mol) and can therefore be used in laboratories in non-insulated vessels at room temperature, even

though it is well above its boiling point. It is miscible with water. All the ammonia contained in an aqueous solution of the gas may be expelled by boiling. The aqueous solution of ammonia is basic. The maximum concentration of ammonia in water (a saturated solution) has a density of 0.880 g cm^{-3} and is often known as '.880 Ammonia'. It does not sustain combustion, and it does not burn readily unless mixed with oxygen, when it burns with a pale yellowish-green flame. At high temperature and in the presence of a suitable catalyst, ammonia is decomposed into its constituent elements. Chlorine catches fire when passed into ammonia, forming nitrogen and hydrochloric acid; unless the ammonia is present in excess, the highly explosive nitrogen trichloride (NCl_3) is also formed.

The ammonia molecule readily undergoes nitrogen inversion at normal pressures, that is to say that the nitrogen atom passes through the plane of the three hydrogen atoms as if it were an umbrella turning inside out in a strong wind. The energy barrier to this inversion is 24.7 kJ/mol in ammonia, and the resonance frequency is 23.79 GHz, corresponding to microwave radiation of a wavelength of 1.260 cm. The absorption at this frequency was the first microwave spectrum to be observed (Wikipedia).

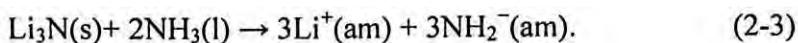
Formation of salts

One of the most characteristic properties of ammonia is its power of combining directly with acids to form salts; thus with hydrochloric acid it forms ammonium chloride (sal-ammoniac); with nitric acid, ammonium nitrate, etc. However perfectly dry ammonia will not combine with perfectly dry hydrogen chloride, moisture being necessary to bring about the reaction.



Acidity

Although ammonia is well-known as a base, it can also act as an extremely weak acid. It is a protic substance, and is capable of dissociation into the amide (NH_2^-) ion, for example when solid lithium nitride is added to liquid ammonia, forming a lithium amide solution:



Formation of other compounds

Amines can be formed by the reaction of ammonia with alkyl halides. The hydrogen in ammonia is capable of replacement by metals, thus magnesium burns in the gas with the formation of magnesium nitride Mg_3N_2 , and when the gas is passed over heated sodium or potassium, sodamide, NaNH_2 , and potassamide, KNH_2 , are formed.

Ammonia as a ligand

Ammonia can act as a ligand in transition metal complexes. It is a pure σ -donor, in the middle of the spectrochemical series, and shows intermediate hard-soft behaviour. For historical reasons, ammonia is named **ammine** in the nomenclature of coordination compounds. Some notable ammine complexes include:

- Hexamminecopper(II), $[\text{Cu}(\text{NH}_3)_6]^{2+}$, a characteristic dark blue complex formed by adding ammonia to solution of copper(II) salts.
- Diamminesilver(I), $[\text{Ag}(\text{NH}_3)_2]^+$, the active species in Tollens' reagent. Formation of this complex can also help to distinguish between precipitates of the different silver halides: AgCl is soluble in dilute (2 M) ammonia solution, AgBr is only soluble in concentrated ammonia solution while AgI is insoluble in aqueous solution of ammonia.
- Ammine complexes of chromium(III) were known in the late 19th century, and formed the basis of Alfred Werner's theory of coordination compounds. Werner noted that only two isomers (fac- and mer-) of the complex $[\text{CrCl}_3(\text{NH}_3)_3]$ could be formed, and concluded that the ligands must be arranged around the metal ion at the vertices of an octahedron. This has since been confirmed by X-ray crystallography.
- An ammine ligand bound to a metal ion is markedly more acidic than a free ammonia molecule, although deprotonation in aqueous solution is still rare. One

example is the Calomel reaction, where the resulting amidomercury(II) compound is highly insoluble.

2.5.4 Detection and Determination

Ammonia and ammonium salts can be readily detected, in very minute traces, by the addition of Nessler's solution, which gives a distinct yellow coloration in the presence of the least trace of ammonia or ammonium salts. Beside this method, another methods those are being used to determine ammonianitrogen are by direct phenate addition, by distillation, by volumetric analysis and by ammonia selective electrode.

2.5.5 Effects on Fish

Ammonia is extremely toxic and even relatively low levels pose a threat to fish health. Fish and all other animals, including ourselves, as part of normal metabolism, produce ammonia. Such is the toxicity that most animals immediately convert it to a less harmful substance, usually urea, and excrete it in urine. Fish shortcut this process and continually excrete metabolic ammonia directly into the surrounding water via special cells in the gills. In a natural environment, such as seas, lakes and rivers, it would be immediately diluted to harmless levels.

Raised levels affect fish health in several different ways. At low levels (<0.1 mg/liter NH₃) it acts a strong irritant, especially to the gills. Prolonged exposure to sub-lethal levels can lead to skin and gill hyperplasia . Gill hyperplasia is a condition in which the secondary gill lamellae swell and thicken, restricting the water flow over the gill filaments. This can result in respiratory problems and stress and as well as creating conditions for opportunistic bacteria and parasites to proliferate. Elevated levels are a common precursor to bacterial gill disease.

At higher levels (>0.1 mg/liter NH₃) even relatively short exposures can lead to skin, eye, and gills damage. Elevated levels can also lead to ammonia poisoning by suppressing normal ammonia excretion from the gills. If fish are unable to excrete this metabolic waste product there is a rise in blood-ammonia levels resulting in damage to internal organs. Ammonia (NH₃) is highly toxic, whereas the ammonium ion is significantly less

toxic. All test kits measure total ammonia-nitrogen (TAN) that is ammonia plus ammonium. However it is possible to determine the actual ammonia level if we know (a) TAN, (b) the water temperature and (c) the water pH. Distribution of ammonia (NH_3) and ammonium ion (NH_4^+) as a function of pH is shown in figure 2.7.

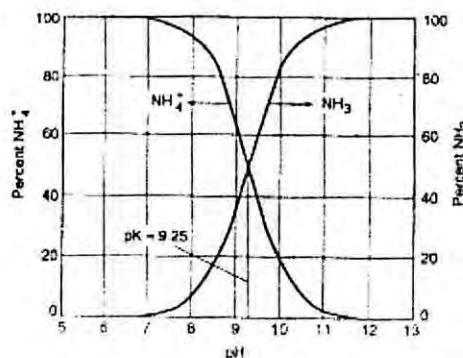


Figure 2.7: Distribution of ammonia (NH_3) and ammonium ion (NH_4^+) as a function of pH (Metcalf and Eddy, 2005)

Table 2.5 shows the maximum acceptable level of TAN at a given pH and temperature. For example at pH 7.5 and a water temperature of 20°C a TAN of 2 mg / liter would be fairly safe as only 1.2% would exist as un-ionized ammonia. As a rule of thumb it is best to aim for a zero level of total ammonia at all times. In normal circumstances any readings above 0.1 mg/liter TAN should be considered as unacceptable and steps taken to reduce it.

Table 2.5 Showing the maximum levels of total ammonia (TAN mg/liter) for fish health

pH	Temperature, °C					
	5	10	15	20	25	30
6.5	50	34	23	16	11	8
7	16	11	7	5	4	3
7.5	5	3	2	2	1	1
8	1.6	1.1	0.7	0.5	0.4	0.3
8.5	0.5	0.4	0.3	0.2	0.1	0.1
9	0.2	0.1	0.09	0.07	0.05	0.04

Source: www.fishdoc.co.uk

2.6 TREATMENT OF AMMONIA FROM EFFLUENT

Treatment methods for removal of various pollutants encountered in the waste streams of fertilizer Industry are briefly describe here. Choice of any method is predicated upon waste characteristics, availability of land and affordable investment. The first step in waste management is to examine the practicability of the in plant waste management options. The next step is to characterize the waste streams and set the level of pollutant concentration in the treated effluent to be achieved. And finally chose an appropriate method of treatment. Wastewater streams containing ammonia can be treated by any of the following process (Mahajan, 1985):

1. Land application- lagooning and stabilization ponds
2. Physico-chemical- breakpoint chlorination, air stripping, ion exchange and reverse osmosis
3. Biological- nitrification, denitrification and algal-bacterial flocculating system.

2.6.1 Land Application

Lagooning and stabilization ponds represent low-cost methods of treatment of industrial liquid waste. Their efficiencies for nitrogen removal are, how ever, limited.

2.6.1.1 Lagooning after pH adjustment

Biological nitrogen control can be carried out with the use of lagoons. The Lagoon treatment/ removal rates are highly variable and dependent on Wastewater application rates, pH, temperature, dissolved oxygen and organic content of soil. It has recently been observed that ammonia can be removed by merely retaining Wastewater in an earthen tank after pH adjustment. Pilot-plant studies using actual ammonia-urea effluent indicate that there was an appreciable reduction of ammonia after period of 24 h. After 48 h ammoniacal nitrogen increased due to conversion of urea into ammonia. The lagooning method does not ensure ammonia reduction to 50 mg/L but can be very useful where plant upsets or shutdowns are frequent (Mahajan, 1985).

2.6.1.2 Waste- Stabilization ponds

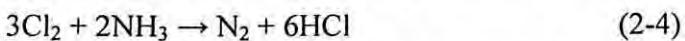
Stabilization ponds work on the natural process of bacterial and algal symbiosis. The nitrogen is recovered in the form of increased biomass. It is necessary, however, to provide a carbon source in the form of carbon di-oxide for obtaining higher efficiencies of conversion. This method is quite workable for ammonia-urea, but suffers from the disadvantages of the high cost of harvesting and disposal of algae and quite extensive land area requirement.

2.6.2 Physico-Chemical Processes

They include methods such as break-point chlorination, air and steam striping, ion exchange, and reverse osmosis. They precede biological treatment and are normally followed when the concentration of ammonia is high.

2.6.2.1 Break Point Chlorination

This method involves addition of sufficient chlorine to Wastewater to bring about oxidation of nitrogenous material to nitrogen gas. The overall reaction rate is dependent on contact time, temperature and pH of the effluent. Nitrogen can be reduced to appreciably low levels, but there is a large-scale wastage of chlorine, especially at lower concentration levels of nitrogen. Other impurities in water like phenol, sulphide, nitrite and organic materials if present, can lead to different products including chlorinated hydrocarbons which are carcinogenic. The overall reaction is



At the breakpoint, all ammonia-nitrogen is reduced to zero. According to EPA, break point chlorination can bring about 95-99 percent ammonia-nitrogen removals. For complete removal, chlorine to ammonia-nitrogen ratio required is rather high (9:1). The absorption rate of chlorine in Wastewater to form hydrochlorous acid is low. The latter reacts with ammonia to produce chloramines that are in turn converted into nitrogen gas on further chlorination. The disadvantages of this method are: 1) it requires sophisticated pH control, 2) Operating cost due to large quantities of chemicals required, 3) downstream dechlorination may be necessary and 4) carcinogenic chlorinated-

hydrocarbons may be produced. The process however can reduce ammonia-nitrogen concentration to value as low as 0.1 mg/L, is comparatively insensitive to temperature and can be adjusted readily to varying flow rates of liquid waste.

2.6.2.2 Diffused-aeration

A diffused-aeration air stripper is a vessel with air diffusers in the bottom of the vessel. Air from the diffusers rises through the water and exits at the top of the vessel. The contaminated water to be air stripped enters the top of the vessel and exits at the bottom. Transfer of the VOCs from the water to the air occurs as the bubbles rise through the water. Transfer of the VOCs from the water to the air can be improved by increasing the vessel depth and by producing smaller bubbles. This kind of air stripper is not as efficient as the other two kinds and is not used as often. Its main advantages are its simplicity, ability to handle high-suspended solids, and resistance to fouling. Information on diffused aeration is available in the literature (Kavanaugh and Trussell, 1980; Patterson, 1985).

2.6.2.3 Air stripping

Ammonia stripping is a simple desorption process used to lower the ammonia content of a wastewater stream. Some wastewaters contain large amounts of ammonia and/or nitrogen-containing compounds that may readily form ammonia. It is often easier and less expensive to remove nitrogen from wastewater in the form of ammonia than to convert it to nitrate-nitrogen before removing it (Culp et al., 1978). Ammonia (a weak base) reacts with water (a weak acid) to form ammonium hydroxide. In ammonia stripping, lime or caustic is added to the wastewater until the pH reaches 10.8 to 11.5 standard units, which converts ammonium hydroxide ions to ammonia gas.

Air stripping involves the mass transfer of volatile contaminants from water to air. This process is typically conducted in a packed tower or an aeration tank. The typical packed tower air stripper includes a spray nozzle at the top of the tower to distribute contaminated water over the packing in the column, a fan to force air countercurrent to the water flow, and a sump at the bottom of the tower to collect decontaminated water. Auxiliary equipment that can be added to the basic air stripper includes an air heater to improve removal efficiencies; automated control systems with sump level switches and

safety features, such as differential pressure monitors, high sump level switches, and explosion-proof components; and air emission control and treatment systems, such as activated carbon units, catalytic oxidizers, or thermal oxidizers. Packed tower air strippers are installed either as permanent installations on concrete pads or on a skid or a trailer.

Aeration tanks strip volatile compounds by bubbling air into a tank through which contaminated water flows. A forced air blower and a distribution manifold are designed to ensure air-water contact without the need for any packing materials. The baffles and multiple units ensure adequate residence time for stripping to occur. Aeration tanks are typically sold as continuously operated skid-mounted units. The advantages offered by aeration tanks are considerably lower profiles (less than 2 meters or 6 feet high) than packed towers (5 to 12 meters or 15 to 40 feet high) where height may be a problem, and the ability to modify performance or adapt to changing feed composition by adding or removing trays or chambers. The discharge air from aeration tanks can be treated using the same technology as for packed tower air discharge treatment. A typical air-stripping unit has been shown in figure 2.8.

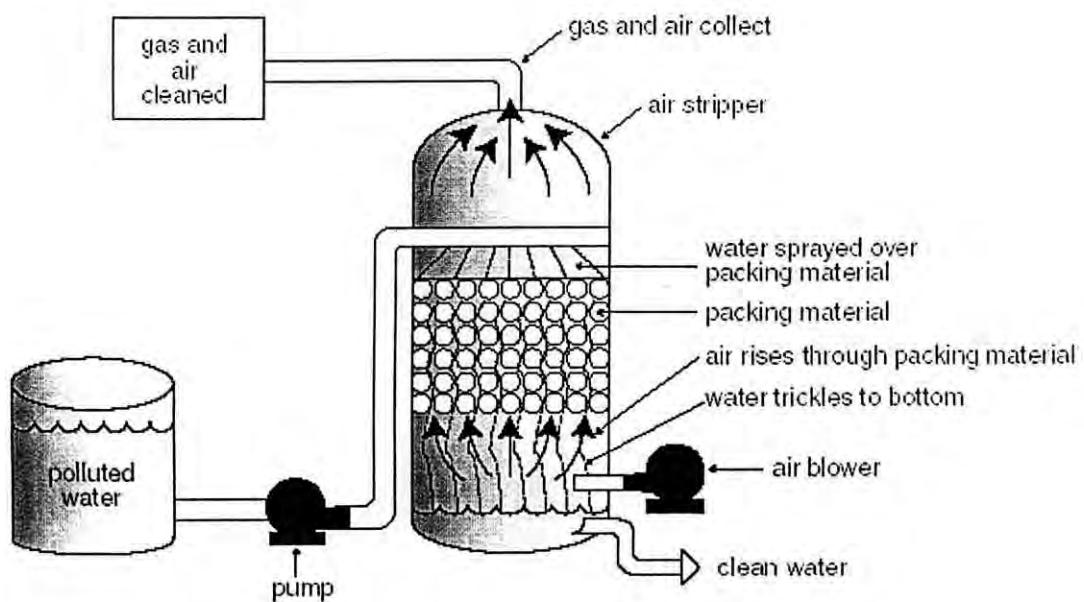


Figure: 2.8 Air stripping unit (EPA, 2001)

Modifying packing configurations greatly increase removal efficiency. A recent innovation is the so-called low-profile air stripper that contains a number of trays in a very small chamber to maximize air-water contact while minimizing space.

Air strippers can be operated continuously or in a batch mode where the air stripper is intermittently fed from a collection tank. The batch mode ensures consistent air stripper performance and greater energy efficiency than continuously operated units because mixing in the storage tanks eliminates any inconsistencies in feed water composition.

Different aspects of air stripping

Two film theory

The most widely used model for describing the absorption or desorption process is the two-film, or Double-resistance, theory, which was first proposed by Whitman in 1923. From this mechanism, the rate of mass transfer was shown to depend on the rate of migration of a molecule in either the gas or liquid phase. The two-film model starts by assuming that the gas and liquid phases are in turbulent contact with each other, separated by an interface area where they meet. The mass-transfer zone is comprised of two films, a gas film and a liquid film on their respective sides of the interface. These films are assumed to flow in a laminar, or streamline, motion. In laminar flow, molecular motion occurs by diffusion, and can be categorized by mathematical expressions. This concept of the two-film theory is illustrated in Figure 2-9. According to the two-film theory, for a molecule of substance A to be absorbed or desorbed, it must proceed through a series of five steps. The molecule must:

1. Migrate from the bulk-gas phase to the gas film or bulk liquid phase to liquid film.
2. Diffuse through the gas film or liquid film.
3. Diffuse across the interface
4. Diffuse through the liquid film or gas film
5. Mix into the bulk liquid or gas

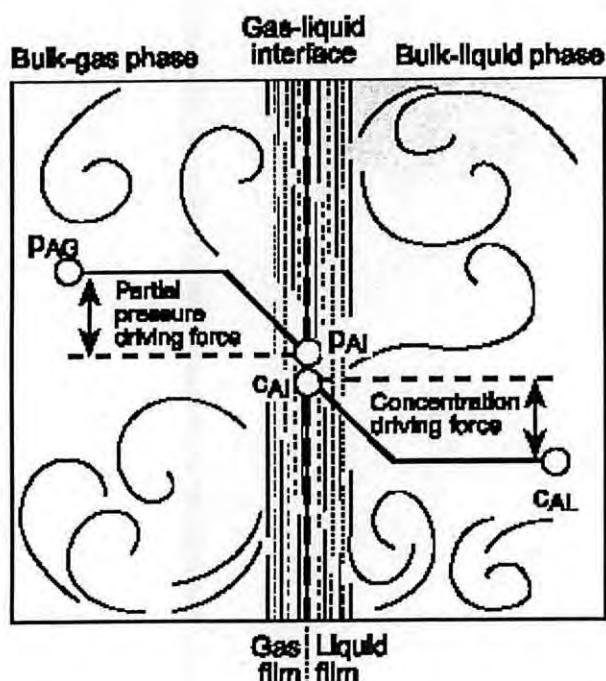


Figure 2.9: visualization of two film theory
<http://yosemite.epa.gov>)

The theory assumes that complete mixing takes place in both gas and liquid bulk phases and that the interface is at equilibrium with respect to pollutant molecules transferring in or out of the interface. A gas concentration is expressed by its partial pressure. Similarly, the concentration in the liquid changes from C_{AI} at the interface to C_{AL} in the bulk liquid phase as mass transfer occurs. The rate of mass transfer from one phase to the other then equals the amount of molecule A transferred multiplied by the resistance molecule A encounters in diffusing through the films.

$$N_A = K_g (p_{AG} - p_{AI}) \quad (2-5)$$

$$N_A = K_l (C_{AI} - C_{AL}) \quad (2-6)$$

N_A = rate of transfer of component A, g-mol/hm² (lb-mole/hft²)

K_g = mass-transfer coefficient for gas film, g-mol/hm² Pa (lb-mole/hft² atm)

K_l = mass-transfer coefficient for liquid film, g-mol/hm² Pa (lb-mole/hft² atm)

p_{AG} = partial pressure of solute A in the gas

p_{AI} = partial pressure of solute A at the interface

C_{AI} = concentration of solute A at the interface

C_{AL} = concentration of solute A in the liquid

The mass-transfer coefficients, K_g and K_l , represent the flow resistance the solute encounters in diffusing through each film respectively (Figure 2-10). As the value for a mass transfer coefficient increases, the amount of pollutant transferred (per unit of time) from one phase to another phase increases. An analogy is the resistance electricity encounters as it flows through a circuit.

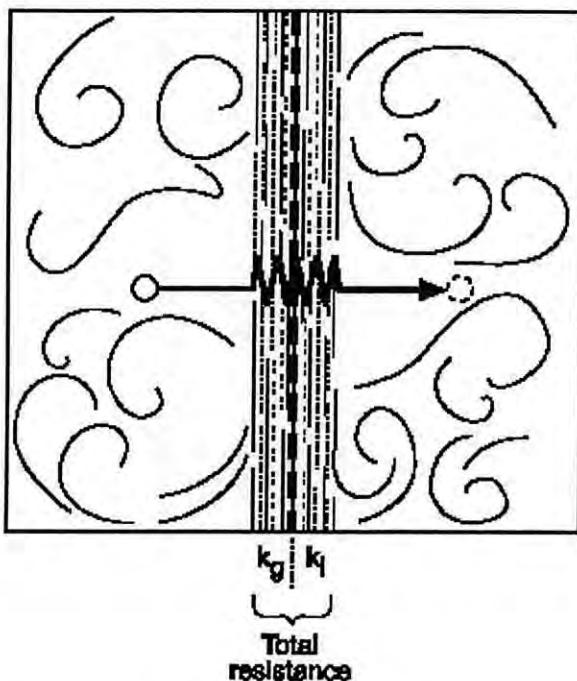


Figure 2.10: Resistance to motion encountered by a molecule being absorbed
(<http://yosemite.epa.gov>)

Henry's law constant

The value of the Henry's law constant plays an important part in determining the required air to water ratio in the stripper. It can also be important in the determination of the number of transfer units and the height of a transfer unit through its effect on the stripping factor. Reliable data on Henry's constants (H) are not easy to find, especially since these constants are dramatically affected by temperature and other solutes present in the water. In general "H" increases with temperature and concentration of inorganic salts

in the water. The effect of temperature should always be considered whereas the effect of inorganic salts is usually neglected since this represents a conservative assumption.

Henry's law is usually expressed as:

$$yP = H'x \quad (2-7)$$

where y is the mole fraction in the gas phase, x is the mole fraction in the liquid phase, P is the total pressure and H' is Henry's constant. By considering the Henry's constant to be in pressure (atmospheres) units and that the total pressure is always very close to one atmosphere:

$$y = H x \quad (2-8)$$

The numerical values of H and H' are the same since $P=1$.

Equilibrium diagram

An equilibrium diagram is a plot of the mole fraction of solute in the liquid phase, denoted as x , versus the mole fraction of solute in the gas phase, denoted as y . Equilibrium lines for the NH_3 and water system are plotted in Figure 2.11. Figure 2.11 also illustrates the temperature dependence of the stripping process.

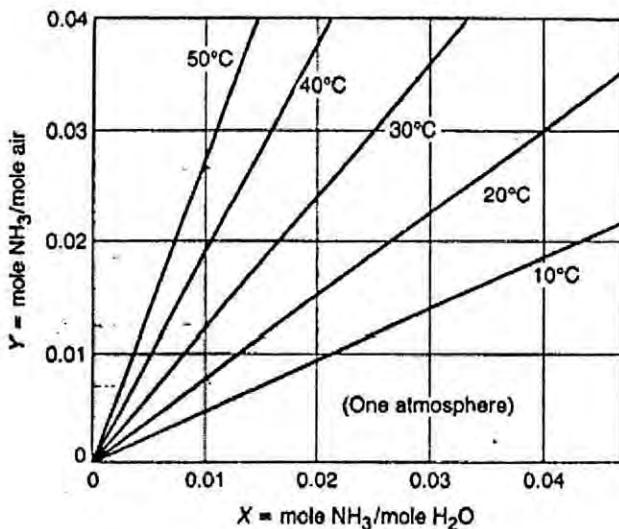


Figure 2.11: Equilibrium curves for ammonia in water as a function of temperature based on Henry's law
(Metcalf and Eddy, 2005)

Material Balance

In designing or reviewing the design of an absorption control system, the first task is to determine the flow rates and composition of each stream entering the system. From the law of conservation of mass, the material entering a process must either accumulate or exit. In other words, "what comes in must go out."

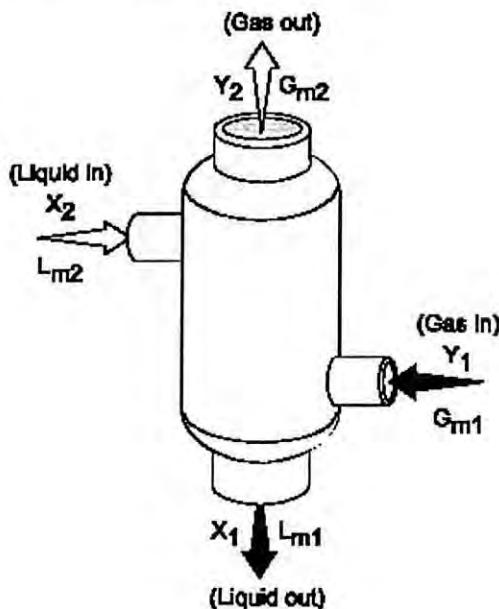


Figure 2.12: Materials balance for concurrent flow (<http://yosemite.epa.gov>)

X = mole fraction of solute in pure liquid

Y = mole fraction of solute in inert gas

L_m = liquid molar flow rate, g-mol/h (lb-mole/hr)

G_m = gas molar flow rate, g-mol/h (lb-mole/hr)

An overall mass balance across the absorber in Figure 2.12 yields Equation:

lb-mole in = lb-mole out

$$G_m(\text{in}) + L_m(\text{in}) = G_m(\text{out}) + L_m(\text{out}) \quad (2-9)$$

For convenience, the top of the stripping unit is labeled as point 2 and the bottom as point 1. This changes Equation 2-9 to Equation 2-10.

$$G_{m1} + L_{m2} = G_{m2} + L_{m1} \quad (2-10)$$

In this same manner, a material balance for the contaminant to be removed is obtained as expressed in Equation 2-11.

$$Gm_1 Y_1 + Lm_2 X_2 = Gm_2 Y_2 + Lm_1 X_1 \quad (2-11)$$

Equation 2-11 can be simplified by assuming that as the gas and liquid streams flow through the absorber, their total mass does not change appreciably (i.e., $Gm_1 = Gm_2$ and $Lm_1 = Lm_2$).

Therefore, Equation 2-11 can be reduced to Equation 2-12.

$$(Y_2 - Y_1) = Lm/Gm (X_2 - X_1) \quad (2-12)$$

Equation 2-12 is the equation of a straight line. When this line is plotted on an equilibrium diagram, it is referred to as an **operating line**. This line defines operating conditions within the air stripper: what is going in and what is coming out. The theoretical ratio for air stripping ammonia from wastewater for various temperatures is plotted on figure 2.13 is derived by assuming the process to be 100 percent efficient with a stripping tower of finite height- obviously unachievable in practice.

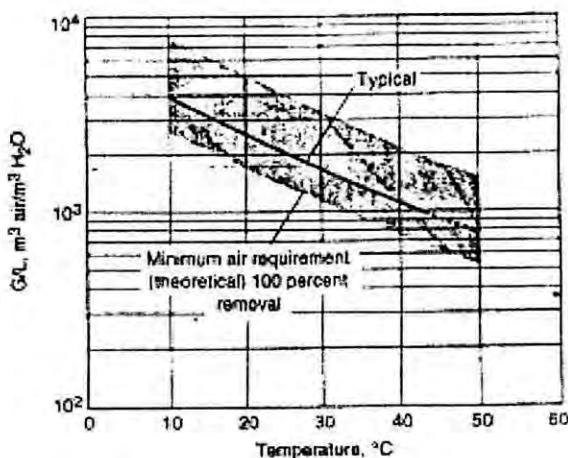


Figure 2.13: Air requirements for ammonia stripping as a function of temperature (Metcalf and Eddy, 2005)

Flooding velocity

The main parameter affecting the size of a packed column is the gas velocity at which liquid droplets become entrained in the exiting gas stream. A packed column, operating at set gas and liquid flow rates, by decreasing the diameter of the column, the gas flow rate

(m/s or ft/sec) through the column will increase. If the gas flow rate through the column is gradually increased (by using smaller and smaller diameter columns), a point will be reached where the liquid flowing down over the packing begins to be held in the void spaces between the packing. This gas-to-liquid ratio is termed the **loading point**. The pressure drop of the column begins to increase and the degree of mixing between the phases decreases. A further increase in gas velocity will cause the liquid to completely fill the void spaces in the packing. The liquid forms a layer over the top of the packing and no more liquid can flow down through the tower. The pressure drop increases substantially, and mixing between the phases is minimal. This condition is referred to as **flooding**, and the gas velocity at which it occurs is the **flooding velocity**. Using an extremely large-diameter tower would eliminate this problem. However, as the diameter increases, the cost of the tower increases.

Normal practice is to size a packed column diameter to operate at a certain percent of the flooding velocity. A typical operating range for the gas velocity through the columns is 50 to 75% of the flooding velocity. It is assumed that, by operating in this range, the gas velocity will also be below the loading point.

A common and relatively simple procedure for estimating flooding velocity (thus, setting a minimum column diameter) is to use a generalized flooding and pressure drop correlation. One version of the flooding and pressure drop relationship for a packed tower is in the **Sherwood correlation**, shown in Figure 2-14. The "X" axis (or abscissa) is a function of the physical properties of the gas and liquid streams. The "Y" axis (ordinate), is also a function of the gas and liquid properties as well as the packing material utilized. The graph is used to predict what conditions will cause flooding to occur. Since flooding is an unacceptable operating condition, this sets a minimum tower diameter for a given set of gas/liquid conditions. Knowing minimum unacceptable diameter, a larger, operating diameter can be specified.

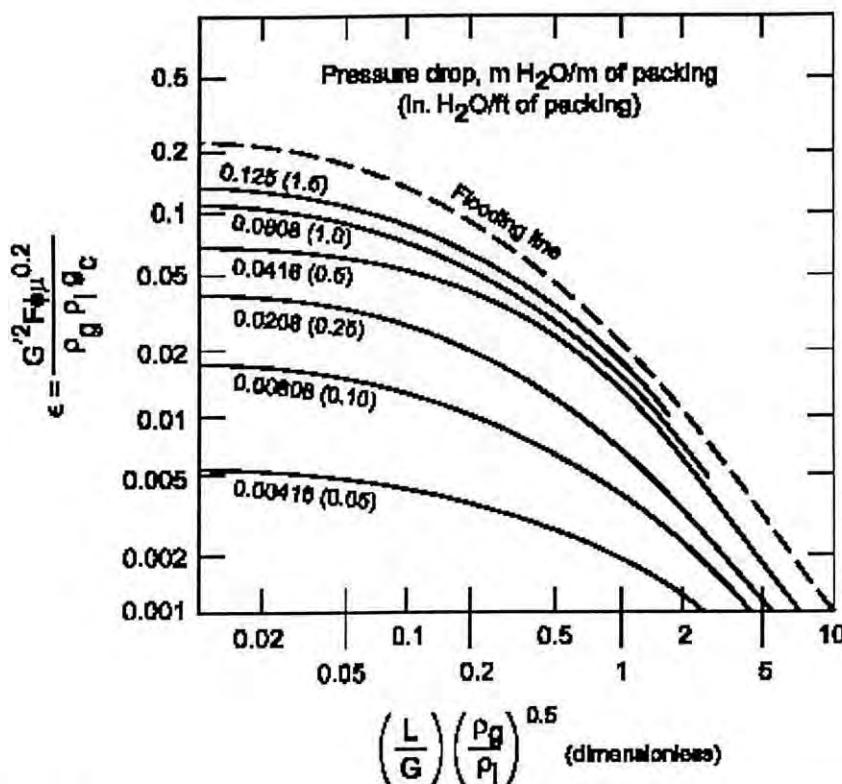


Figure 2-14: Generalized flooding and pressure drop correlation (Calvert et al, 1972)

Mass transfer efficiency

There are several ways to predict the mass transfer performance of given packing under the required operating conditions. In every case, the required height of packing will be the product of HTU times NTU. (Packed height = number of transfer units * height of a transfer unit). The values of HTU and NTU to be used will depend on the stripping factor and the inherent efficiency of the packing. NTU is a variable that relates exclusively to the stripping factor and the degree of removal. HTU relates to the stripping factor, liquid load, and the packing efficiency. The equation to determine the value of NTU_{ol} (number of transfer units) for a VOC stripper is:

$$NTU_{ol} = (S/S-1) \ln [(1-1/S)X_{in}/X_{out} + 1/S] \quad (2-13)$$

S = stripping factor, X_{in} = inlet concentration, X_{out} = outlet concentration

At values of $S = 12$ or above, the previous equation can be approximated by

$$NTU_{ol} = \ln (X_{in} / X_{out})$$

The height of a transfer unit (HTU) is defined as,

$$HTU = L/K_{La}A$$

L = liquid volumetric flow rate, K_{La} = volumetric mas transfer coefficient, A = cross-sectional area of tower.

Fouling and plugging of packings

There are a number of variables that cause plastic packing to foul. The total surface area of the packing per unit volume is one important variable. However, the most important variables that cause fouling are the chemistry of the system conditions of the process. The shape of the packing elements, although important to the gas/liquid contacting, has been proven to have little effect on plugging or fouling problems.

A very common example is the precipitation of iron oxides onto plastic packing surfaces in air stripping units. These strippers are generally used to remove organic contaminants from source waters to acceptable limits. Oxygen from the air is simultaneously



Figure 2.15 : Fouling of packing materials
(Source: Jaeger Products, Inc)

transferred into the water and this promotes the conversion of iron to oxidation states that are insoluble in water. These insoluble iron oxides precipitate out of the water and the crystals attach themselves to any available surface. As soon as a crystal attaches itself, it becomes a "seeding" site for other crystals to adhere and grow. A complicating factor is that the heavily aerated water is also an excellent medium for bacterial growth. Bacteria colonies in the water attach themselves to the packing and provide numerous sites for

colonies in the water attach themselves to the packing and provide numerous sites for inorganic deposition and vice versa. Some forms of bacteria will use the iron oxides as a nutrient. Paradoxically, the high mass transfer efficiency provided by the packing promotes the deposition of the oxides and bacterial growth. Packings with high surfaces will be more efficient but would tend to promote fouling as well.

The chemical of choice for removal of biological fouling is an oxidant or a free radical generator. Ozone is both an oxidant and a free radical generator. Other oxidants that are commonly used include potassium permanganate and hydrogen peroxide. Chlorine can also be used as a radical producer. Inorganic fouling by basic salts and oxides (for example calcium carbonate, iron oxide, calcium hydroxide, etc.) can be removed by weak acid solutions. Mineral acids, such as phosphoric and nitric, are frequently used. Organic acids can also be used effectively. A sequestering agent can work in these applications but it would be significantly slower. Inorganic fouling by neutral or acidic salts and oxides (for example calcium sulfate, iron sulfate, calcium chloride, etc.). Acids will not be effective in removing fouling caused by these compounds. The best solution here is a combination of a sequestering agent with colloidal agents that can break crystal-crystal bonds and disperse the pieces. These fouling compounds are the most difficult to remove.

Limitations

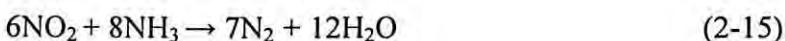
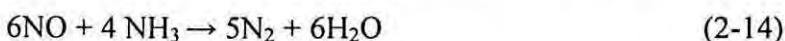
The following factors may limit the applicability and effectiveness of the air stripping process:

- The potential exists for inorganic (e.g., iron greater than 5 ppm, hardness greater than 800 ppm) or biological fouling of the equipment, requiring pretreatment or periodic column cleaning.
- Effective only for contaminated water with VOC or semi volatile concentrations with a dimensionless Henry's constant greater than 0.01.
- Consideration should be given to the type and amount of packing used in the tower
- Process energy costs are high.

- Compounds with low volatility at ambient temperature may require preheating of the feeding water.
- Air strippers transfer contaminants from one medium to another. There is no destruction of the contaminant. Consequently, the risks of emitting pollutants into the air must be carefully evaluated. Often, the air stream (or off-gas) is treated before it is emitted to the atmosphere.

2.6.2.4 Steam stripping

Steam streaming is preferred when the ammonia concentration in water is as high as 3-4 percent. The quantity of system required for this, however, is very high. For handling 13500 m³/day of liquid waste, as much as 250 tones/h of steam are required, which makes this process quite costly. In another process using steam stripping, the stripped gases are reheated and the NH₃ used to catalytically convert NO_x pollutants to nitrogen gas. Organic substances, if present, can also get selectively removed.

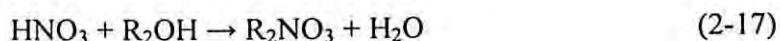
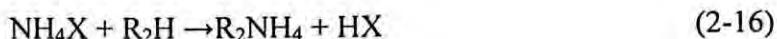


The ratio of NH₃ to NO_x employed is 0.7

2.6.2.5 Selective ion exchanger

Naturally occurring zeolite clinoptilolite removes NH₄⁺ ions selectively. The bed can be regenerated by rinsing with a slightly alkaline salt solution and reused. NaOH, CaCl₂, or HNO₃ giving concentrated NH₄OH, NH₄Cl, NH₄NO₃, respectively, can also achieve regeneration. Though the zeolite is fairly selective, Ca⁺² does interfere during the exchange process. The removal efficiency may vary from 75 to 95 percent.

A process, which is promising from the viewpoint of recovery of ammonium nitrate, involves the use of moving bed continuous-flow counter-current ion-exchange beds. It removes contaminants as well recovering useful end products. The process makes use of separate anion and cation exchange systems, one selective to NO₃⁻ and other to NH₄⁺.



HNO_3 is obtained from the cationic bed and water from the anionic bed. On generation using a weak base, NH_4OH in anionic and HNO_3 in cationic beds, one gets NH_4NO_3 of concentration varying from 10 to 15 percent. The drawbacks of the processes are: Lack of efficient treatment of the regenerated bed, High initial capital cost, other ions interfere, not been used for very high load such as fertilizer effluents.

2.6.3 Nitrification in Aerated Lagoons

Nitrification is defined as the oxidation of ammonia to nitrate. The oxidation occurs in two steps – the oxidation of ammonia to nitrite by the bacterium Nitrosomonas followed by the oxidation of nitrite to nitrate by the bacterium Nitrobactor. The stoichiometric equations for nitrification are being chemosynthetic autotrophs; nitrifying bacteria derive their energy from ammonia and nitrite and their carbon from carbon dioxide.

Below a pH of 8.5, almost all of the ammonia in solution will exist as the ammonium ion. The conversion of ammonium to nitrite results in the formation of hydrogen ions. If the pH of the wastewater is less than 8.3, which is typical for domestic wastewaters, the hydrogen ions produced are neutralized by bicarbonate ions in the wastewater.



This reaction results in the decrease in bicarbonate alkalinity as well as an increase in the carbon dioxide concentration, both occurrences of which lowers the pH. If the wastewater has a relatively low alkalinity, the change in pH can be dramatic. In turn, the low pH can significantly reduce the rate of nitrification. Below a pH of 7.2, the rate falls precipitously, approaching zero at a pH of 6. Wastewaters with low alkalinity require the addition of alkalinity to support uninhibited nitrification. In addition to pH, nitrification is very sensitive to temperature, the dissolved oxygen concentration, and toxic materials.

During warm weather months, some nitrification generally occurs in most aerated lagoons treating domestic wastewaters. However, such nitrification is usually

unpredictable and cannot be depended upon to meet effluent limits. The reason is that the organisms responsible for nitrification are slow growers and more sensitive to environmental factors than are those that remove BOD_5 .

Figure 2.16 illustrates the impact that temperature has on nitrification. The curves, which was prepared by using the kinetics used by Downing et al. (1964), Downing and Knowles (1966), and Parker (1975), predicts the Hydraulic Retention Time (HRT) required in an aerated lagoon to achieve an effluent ammonia nitrogen concentration of 2 mg/L if all the biomass is maintained in suspension, if sufficient alkalinity is present to meet the requirement for nitrification, if the dissolve oxygen is maintained at 2 mg/L, if there are no toxic materials present, and if the influent conditions do not vary. Obviously, these limitations are not met on a consistent basis in the real world; hence even longer retention times would typically be required. Since cold weather temperatures in lagoons in the Southeast may drop to as low as 8 to 10°C, an HRT of at least 6 to 7 days would be required for year-round nitrification. Considering the fact that the completely-suspended biomass conditions require aeration power of about 6 W/m^3 of basin volume (30 hp/106 gal), such retention times are excessive from the stand point of power usage. Power for solids suspension would be about three times that required to meet the oxygen demand. Therefore, for aerated lagoons to be considered as viable processes for nitrification, the lagoon process must be modified so that the solids age can be uncoupled from the HRT. This can be accomplished either through sedimentation in clarifiers with solids recycle or through the retention of solids by use of sequencing batch reactor (SBR) technology. However, there are available add-on processes that can be used to nitrify effluents of aerated lagoons. These include the intermittent sand filter, a process for which long term performance records are available that demonstrate its success as a nitrifier and polisher with respect to TSS and BOD_5 .

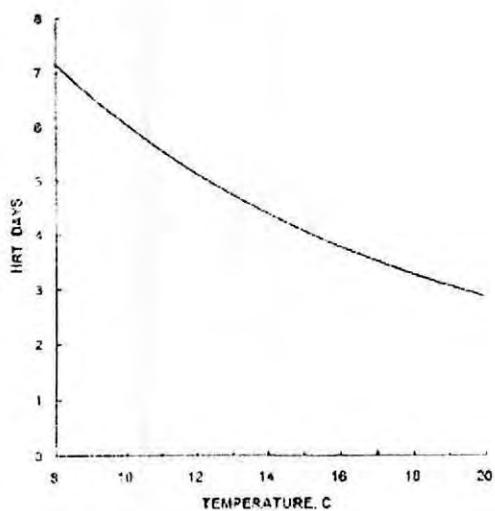


Figure 2.16 Influence of temperature on hydraulic retention time required achieving nitrification in a completely suspended aerated lagoon under optimum conditions. (Linvil, 2003)

2.7 OVERVIEW

This chapter describes brief and selective review of different wastewater quality parameters and different techniques to remove ammonia. Among the different wastewater quality parameters, those, which were dealt with in this research work, have been described in this chapter. Obviously attention is given on Ammonia. Among the different treatment techniques, emphasize is given on air stripping though it is used in this research work. This chapter also gives a brief description on fertilizer factories of Bangladesh, especially on NGFFL. Environmental Management Plan (EMP) for NGFFL has also been described in brief.

CHAPTER THREE

METHODOLOGY AND STUDY DESIGN

3.1 INTRODUCTION

The Methodology of this work may be broadly classified into three categories: 1) Collection of representative samples, 2) details analysis in the laboratory to evaluate the quality of NGFFL effluent and its effect on river Kushiara and 3) laboratory investigation to remove ammonia by physical and chemical method.

3.2 SAMPLE COLLECTION

3.2.1 Selection of Sampling Points

This study includes visit to NGFFL area for proper selection of sampling stations. Presently the factory disposes its effluent in two ways. Less contaminated effluent collected from different plants is taken into Lagoon-2 and highly contaminated effluent is pumped to lagoon-1 through 4 Km pipeline. The lagoon water is slowly released to the river Kushiara. Details have been discussed in chapter two. The samples were collected from lagoon 1 and lagoon 2 to observe the characteristics of wastewater of NGFFL and the efficiency of the existing lagoons. Samples were also collected from upstream and down stream of the river to observe its impact on river Kushiara. Effluent drainage system of NGFFL is shown in figure 3.1.

3.2.2 Sampling Method

Proper collection of waste samples for analysis is of great importance. Representative combined samples were tested in the laboratory for the assessment of existing pollutants. Combined samples were prepared by mixing equal volume of two samples collected from two points of each sampling locations. The samples collected were transported to laboratory and all possible efforts were made to minimize the time lag between collection and analysis so that no significant change may occur in the quality of the samples.

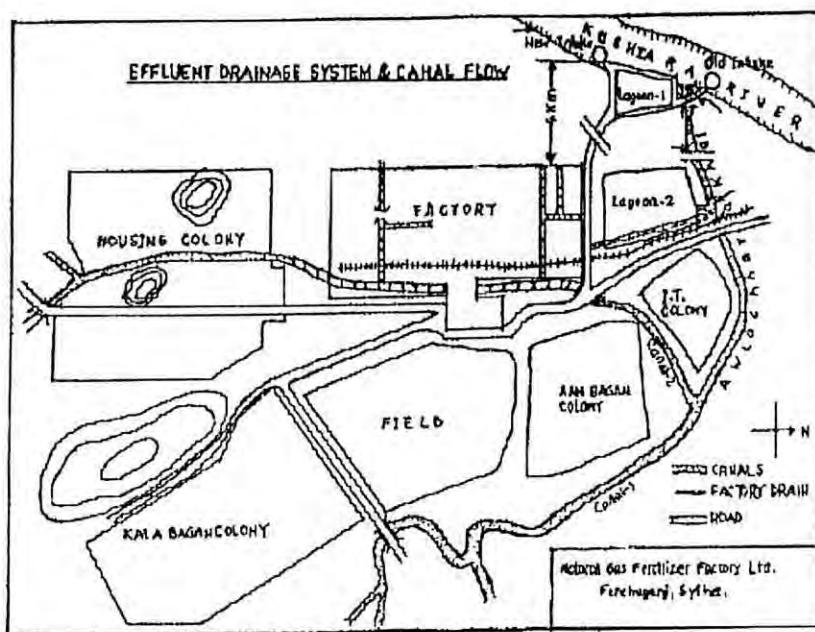


Figure 3.1 Effluent drainage system of NGFFL

3.2.3 Frequency of Sampling

To study the effluent quality of the NGFFL waste, laboratory analysis were conducted for four months. (March, July, October and December 2005). The samples were collected once in a month. On rainy days sampling was avoided.

3.3 ANALYSIS OF WASTEWATER OF NGFFL

Characteristics of the wastewater samples were determined through extensive laboratory analysis. The wastewater parameter determined included temperature, suspended solids, and dissolved solids, pH, alkalinity, ammonia nitrogen, BOD_5 , COD, oil and grease, chromium, sulfate, phosphate and nitrate for chemical quality.

Temperature and pH were measured electrometrically. Digital pH meter (HANNA, HI 98204) was used for the determination of pH and temperature of the samples. Two buffer solutions containing pH 4.0 and 7.0 were used to calibrate the digital pH meter. The concentrations of dissolved species were determined by DR-4000 spectrophotometer UV-visible at the following wavelengths: NO_3^- —was determined at $\lambda=400$ nm (cadmium reduction method, using NitraVer 5 Nitrate reagent, Hach 8171), ammonia nitrogen at $\lambda=425$ nm (Nessler method, using Nessler reagent, Mineral Stabilizer and Polyvinyl

Alcohol Dispersing Agent, Hach 8038), SO_4^- was determined at $\lambda=450$ nm (Sulfa Ver 4 method, Hach-8051), Orthophosphate at $\lambda=890$ nm (Phos ver 3 Ascarbic acid method, Hach 8048), Cr^{+6} at $\lambda=540$ nm (1,5-Diphenylcarbohydrazide Method, using Chroma Ver 3 reagent Hach-8023). Oil and grease was analyzed by soxhlet extraction method. DO was measured by Winklers method and total alkalinity was measured by titration with Methyl-orange. BOD_5 was measured by incubation in the dark at 20°C for 5 days. Suspended solids and Dissolved solids were dried to a constant weight at 105°C and weighed. KMnO_4 was used to determine COD as it attacks the carbonaceous and not the nitrogenous matter.

3.4 WASTEWATER TREATMENT FOR AMMONIA REMOVAL

In this study, different treatment methods such as aeration, air stripping, ion exchange, Lagooning after pH control were applied.

3.4.1 Aeration and Air Stripping

In this laboratory-scale study, aeration methods were applied to remove ammonia from wastewater, which contains high concentration of ammonia. For the aeration experiments, three experiments with working volume of 200 cc, 350 cc and 750 cc were performed in three measuring cylinders (250 cc, 500 cc and 1000cc). pH was adjusted to 11.5 to convert the NH_4^+ ion to NH_3 gas. Forced air was introduced directly into the liquid phase via a vacuum pump. The aeration rate was maintained 15 l/min for each experimental set. Another experiment was done without changing the pH of raw wastewater sample.



Figure 3.2: Aeration Experiment

Air-stripping towers

For the air-stripping experiments, one stripping tower of polyvinyl Chloride tube (6.5 feet height X 2 inch internal diameter) was constructed. The tower was packed with plastic ring of 0.5 inch dia, wood chips of 0.75 inch, stone chips of 0.75 inch and coal chips of 0.75 inch to promote the down flow of liquid in a thin, gentle stream. Five hundred to seven hundred ml of wastewater was used for each experiment. The effluent was collected from the bottom of the tower to measure the concentration of ammonia after collecting 100 and 300 ml of water each time. Average was taken as the final concentration. Forced air was introduced directly into the column. The airflow rate was maintained 15 l/min for each experimental set. The pH levels were maintained 10.5 for each experiment to convert the ammonium ion to ammonia gas by adding Calcium Oxide. As the pump capacity was fixed, different air to liquid flow ratio was maintained by changing the water flow rates. A hand-operated valve was used to regulate the wastewater flow rate. The effect of pH over 10.5, air-water flow ratio, nature of packing materials and height of materials and initial concentration of ammonia on air stripping unit were investigated.

An attempt has been made to find out the stripping constant. For each combination of airflow rate, water flow rate and effluent concentration, the fraction remaining after stripping was calculated by dividing the effluent concentration by the influent concentration. The fractional results were plotted on log scale against the volumetric air-to-water ratio. An exponential curve was fitted to the data. When there is no airflow, the stripping factor is zero, the effluent concentration should theoretically be equal to the influent concentration. Therefore, the y-intercept should be one. So the curve fit was forced through it. Empirically derived stripping constants were obtained from the exponential equations of the curve fitted lines

The stripping constants can be used to predict treatment performance. The first-order decay model was used to determine stripping constant:

$$C_e/C_i = e^{-Kq} \quad (3-1)$$

C_e = effluent water concentration

C_i = influent water concentration

K = stripping constant

q = volumetric air-to-water ratio



Figure 3.3: Different types of materials used as packing materials



Figure 3.4: Air stripping experiment (Laboratory setup)

3.4.2 Ion Exchange

The experiment was conducted using 30 cc and 50 cc of sulfonile cation exchanger in two columns (of 100cc burette). The form of ammonia in water depends on the pH of the solutions. In acidic and neutral pH solutions, ammonia exists in the form of ammonium salt. So pH was adjusted to 6.5. The ammonia-contaminated water having concentration of 892 mg/L was passed through the system. Ammonia concentration was measured after collecting every 10 ml of sample at the outlet.

Efficiency of the resin in a column in removing ammonium ion was determined in terms of the following parameters (Hoque, 2003):

Number of Bed volume (BV) upto ammonia Maximum Concentration Level (MCL), which is the ratio of the quantity of water treated (ΣQ) upto ammonia MCL in the effluent and the volume (V) of the resin packed in the column i.e. $BV = (\Sigma Q/V)$.

Quantity of exchanged ammonium ion by the resin, which is calculated through the equation:

$$\text{Exchanged ammonium ion (mg/g)} = \frac{\text{Influent ammonia-N concentration} - \text{Avg. effluent Ammonia-N concentration upto MCL, mg/L}}{\text{Weight of the resin, gm}} \times \frac{\text{Effluent volume upto MCL, L}}{\text{Weight of the resin, gm}}$$

Overall ammonia-N removal efficiency of the resin, which is calculated through the equation:

$$\text{Efficiency (\%)} = \frac{\text{Influent ammonia-N concentration} - \text{Avg. effluent Ammonia-N concentration upto MCL, mg/L}}{\text{Influent ammonia-N concentration, mg/L}} \times 100$$

3.4.3 Lagooning after pH Adjustment

Very encouraging results are obtained from some laboratory and pilot plats studies conducted by National Environmental Engineering Research Institute in the removal of ammonia by simply lagooning the wastewater. It was found that considerable reduction in the ammonia content can be accomplished just by retaining the ammoniacal wastewater in an earthen tank, about 1 m deep, for a day or two, after a pre-treatment of wastewater by lime to increase the pH to 11.0 (Rao and Datta, 2002). On the basis of this idea, to observe the effect of an earthen lagoon to remove ammonia at pH 11.0, two experiments were done. For one experiment the inner side of the jar was covered with soil (collected from lagoon of NGFFL). At the same time the inner side of another container remained uncovered (i.e. not covered by soil). Depth of wastewater in the containers was 9 cm and surface area was 113 cm^2 . Concentration of ammonia was measured with time (days).



Figure 3.5: Soil –covered Artificial lagoon

3.5 OVERVIEW

This chapter describes locations and frequency of sampling, and procedure of the research work. This chapter also describes different treatment techniques to remove ammonia from wastewater that have been used in this research work. All these experiments have been done in Water Supply Engineering Laboratory of Department of Civil and Environmental Engineering at Shah Jalal University of Science and Technology, Sylhet. Necessary data on water quality parameter of Kushiara River and the concentration of ammonia of lagoon 1 and lagoon 2 (from January 2004 to April 2006) were collected from NGFFL laboratory to analyze the seasonal variation.

CHAPTER FOUR

WATER AND WASTEWATER QUALITY MONITORING AND ANALYSIS

4.1 INTRODUCTION

Wastewater treatment facilities include physical, chemical and biochemical processes. An understanding of the nature of wastewater is important in design and operation of collection, treatment, and disposal facilities and in the engineering management of environmental quality. Laboratory data are, therefore, essential before a sound engineering design can be made. To obtain laboratory data, samples were collected for laboratory experiment as described in chapter three. Data was also collected from NGFFL laboratory. From those data the characteristics of wastewater of NGFFL and its impact on river Kushiara have been evaluated. The different tests performed were temperature, suspended solids, and dissolved solids for ascertaining physical qualities; pH, alkalinity, ammonia nitrogen, BOD_5 , COD, oil and grease, chromium, sulfate phosphate and nitrate for chemical quality.

4.2 ANALYSIS OF WASTEWATER OF NGFFL

It is already mentioned that NGFFL has two lagoons. Samples have been collected from those two lagoons for laboratory analysis of different wastewater quality parameters. Experimental analysis has been described in this section.

4.2.1 Temperature

The test results of temperature of different sampling points are presented in table A-1 in appendix A. The fluctuations of temperature at different times and locations in 2005 are shown in figure 4.1. Temperature was found higher in month of July and lower in month of December. NGFFL authority uses spray tower to control temperature. Figure 4.1 indicates that temperature of wastewater of the lagoon mainly depend on the ambient temperature of the environment.

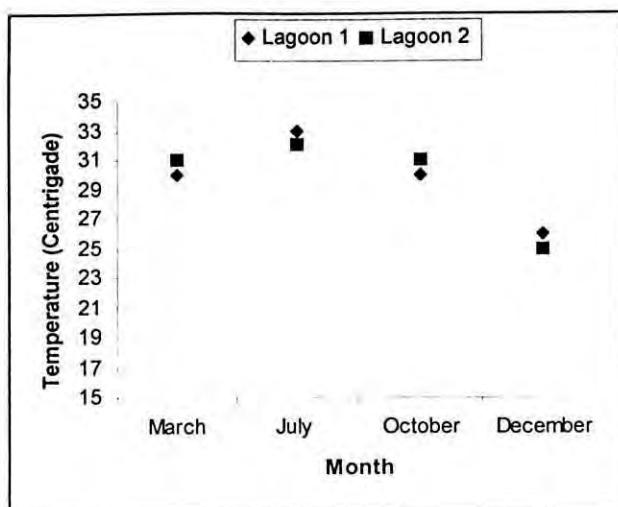


Figure 4.1: Temperature at various sampling points in the year 2005

4.2.2 pH

pH is a very important factor that must be considered to remove ammonia from wastewater. The test results of pH of different sampling points are presented in table A-1 in appendix A. The fluctuations of pH at different times and locations in 2005 are shown in figure 4.2. In 2005, pH was found to vary from 7.6 to 8.7 in the wastewater of NGFFL. pH is higher due to the presence of higher concentration of ammonia in the water. Bangladesh Industrial Effluent Standards (DOE, 1997) for pH is 6.5 to 8.0. Among the eight samples, six samples show that pH levels exceeded the standard limit. However there is a benefit, i.e. as pH of the wastewater is high, if we want to treat ammonia of wastewater by air-stripping then less amount of chemicals will be needed to raise pH of the wastewater.

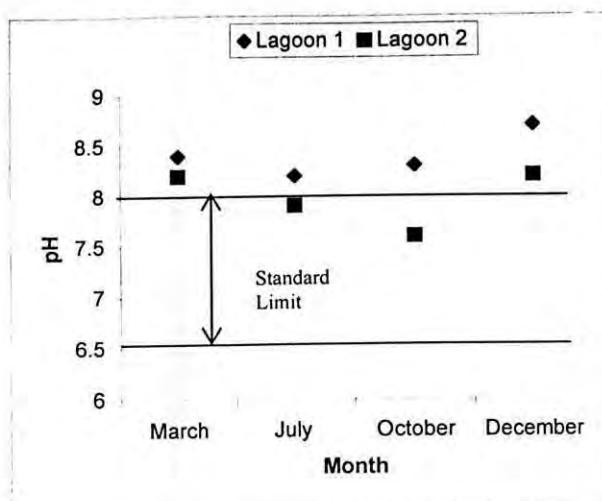


Figure 4.2: pH at various sampling points in the year 2005

4.2.3 Total Solids

The test results of Dissolved Solids of the different sampling points are presented in table A-1 in appendix A. The fluctuations of Dissolved Solids at different times and locations in 2005 are shown in figure 4.3. Maximum concentrations of Dissolved Solids were found in winter season (i.e. in month of December-January). In 2005, concentration of Dissolved Solids was found to vary from 576 to 1456 mg/L. Bangladesh Industrial Effluent Standards (DOE, 1997), for Dissolved Solids is 2100 mg/L. For the year 2005, Dissolved Solids were found within the limit.

The test results of Suspended Solids of the different sampling points are presented in table A-1 in appendix A. The fluctuations of Suspended Solids at different times and locations in 2005 are shown in figure 4.4. In 2005, concentration of Suspended Solids was within the range of 445 to 950 mg/L. Bangladesh Industrial Effluent Standards (DOE, 1997) for Suspended Solids is 100 mg/L. For the year 2005, the Suspended Solids were found above the limit in all the samples. Highest amount of Suspended Solids were found in lagoon 1 in wet season (July-05). The reason may be the surface run off of water into the lagoon.

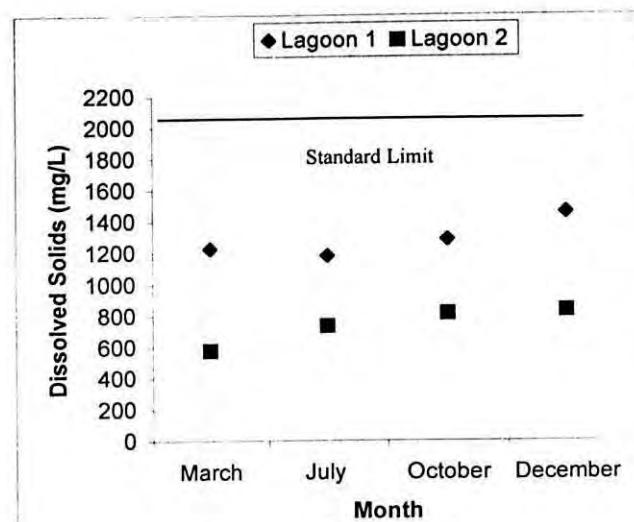


Figure 4.3: Dissolved Solids at various sampling points in the year 2005

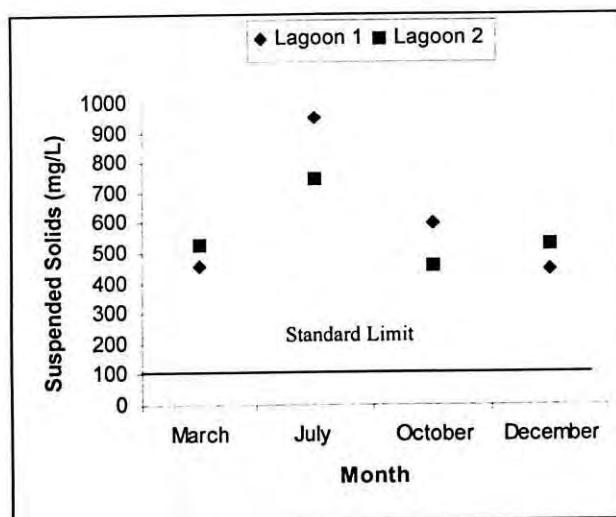


Figure 4.4: Suspended Solids at various sampling points in the year 2005

4.2.4 Alkalinity

The test results of Alkalinity of different sampling points are presented in table A-1 in appendix A. The fluctuations of Alkalinity at different times and locations in 2005 are

shown in figure 4.5. In 2005, concentration of alkalinity was found to vary from 218 to 850 mg/L.

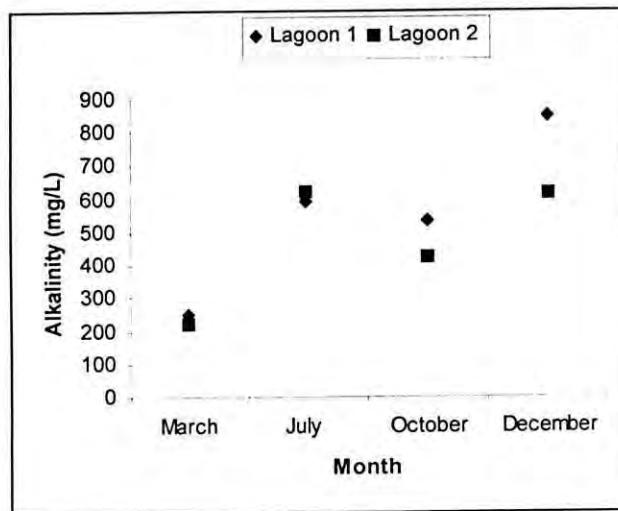


Figure 4.5: Alkalinity at various sampling points in the year 2005

4.2.5 Chemical Oxygen Demand (COD)

The major advantage of the COD test is the short time required for evaluation. Hence it may be used as a substitute for the BOD test in many instances. The test results of COD of different sampling points are presented in table A-1 in appendix A. The fluctuations of COD at different times and locations in 2005 are shown in figure 4.6. In 2005, concentration of COD was found to vary from 24.3 to 46.5 mg/L. Bangladesh Industrial Effluent Standards (DOE, 1997), for COD is 200 mg/L. For the year 2005, the COD was found below the limit in all the samples.

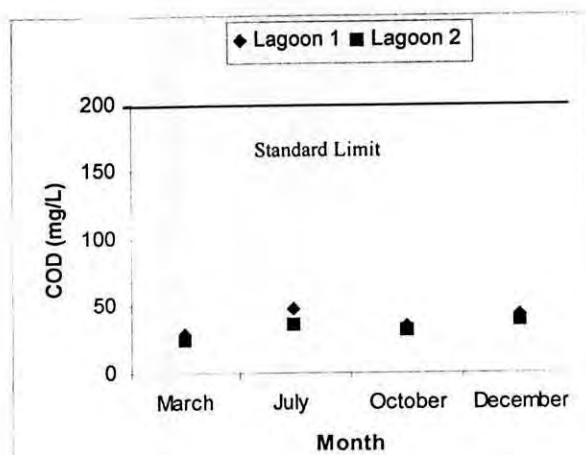


Figure 4.6: COD at various sampling points in the year 2005

4.2.6 Biochemical Oxygen Demand (BOD)

The BOD test is widely used to determine the pollution strength of domestic and industrial wastes in terms of the oxygen that they will require if is discharged into natural water bodies in which aerobic condition exists. The test results of BOD_5 at different sampling points are presented in table A-1 in appendix A. The fluctuations of BOD_5 at different times and locations in 2005 are shown in figure 4.7. In 2005, concentration of BOD_5 was found to vary from 4.5 to 8.4 mg/L. Comparatively high amount of BOD_5 were recorded during dry season. Bangladesh Industrial Effluent Standards (DOE, 1997), for BOD_5 is 50 mg/L. For the year 2005, the BOD_5 was found below the limit in all the samples. As the wastewater of NGFFL contains little amount of organic matter, so heterotrophic organism (Denitrifying bacteria) may not be present in the wastewater. The denitrification requires addition of some quantity of carbonaceous matter. But less amount of BOD_5 indicates that there is a little possibility of denitrification in the existing lagoons.

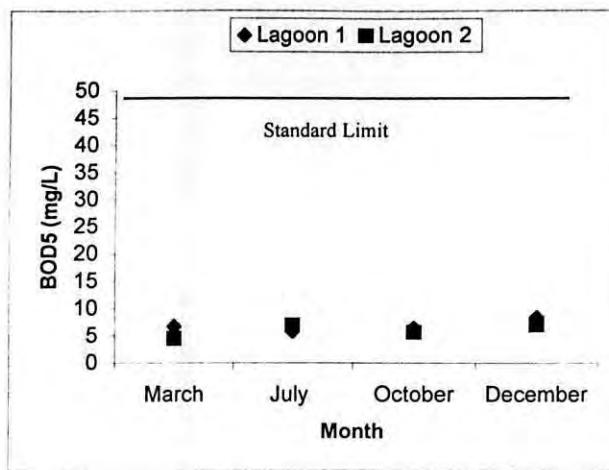


Figure 4.7: BOD₅ at various sampling points in the year 2005

4.2.7 Dissolved Oxygen (DO)

The test results of DO of different sampling points are presented in table A-1 in appendix A. The fluctuations of DO at different times and locations in 2005 are shown in figure 4.8. In 2005, concentration of DO was found to vary from 2.1 to 3.1 mg/L in the wastewater. Bangladesh Industrial Effluent Standards (DOE, 1997), for DO is 4.5 to 8.0 mg/L. For the year 2005, the DO was found below the limit in all the samples.

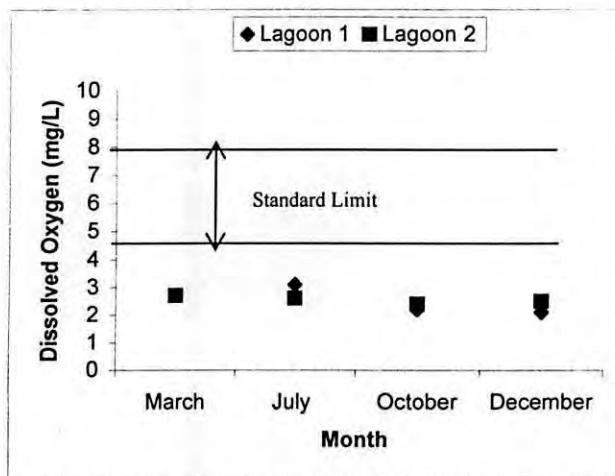


Figure 4.8: DO at various sampling points in the year 2005

4.2.8 Oil and Grease

The test results of Oil and grease of the different sampling points are presented in table A-1 in appendix A. The fluctuations of Oil and grease at different times and locations in 2005 are shown in figure 4.9. Lube oil used in NGFFL is the main source of oil and grease. In 2005, oil and grease in wastewater were recorded 28 to 56 mg/L. Bangladesh Industrial Effluent Standards (DOE, 1997), the amount of oil and grease should not exceed 10 mg/L before discharging it into inland surface water or into irrigable land. For the year 2005, the oil and grease was found above the limit in all the samples.

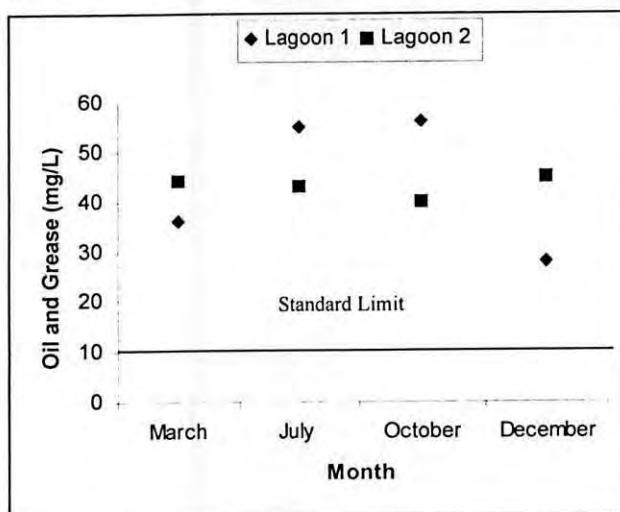


Figure 4.9: Oil and grease at various sampling points in the year 2005

4.2.9 Phosphate (PO_4)

The test results of PO_4 of the different sampling points are presented in table A-1 in appendix A. The fluctuations of PO_4 at different times and locations in 2005 are shown in figure 4.10. In 2005, concentration of PO_4 was found to vary from .075 to 0.98 mg/L in the wastewater. NGFFL uses 23 kg Sodium Phosphate/ month, which is the major source of PO_4 in wastewater.

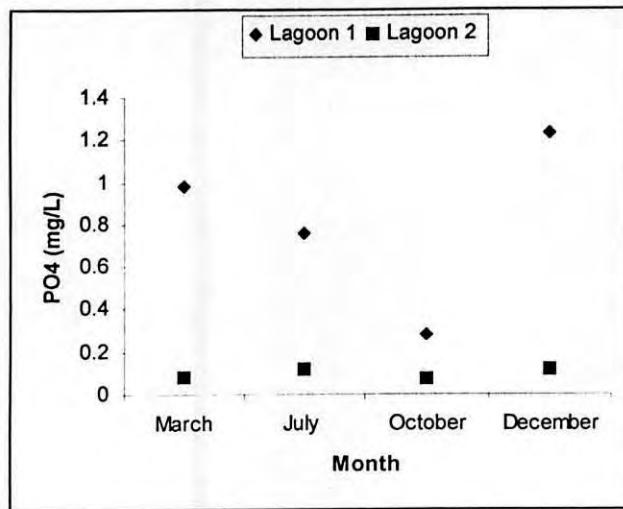


Figure 4.10: PO₄ at various sampling points in the year 2005

4.2.10 Sulfate (SO₄)

The test results of SO₄ of different sampling points are presented in table A-1 in appendix A. The fluctuations of SO₄ at different times and locations in 2005 are shown in figure 4.11. In 2005, concentration of SO₄ was found to vary from 6.7 to 19.8 mg/L in the wastewater. NGFFL uses 19.2 MT alum/ month and 12 MT sulfuric acid/month, which is the major source of SO₄ in wastewater.

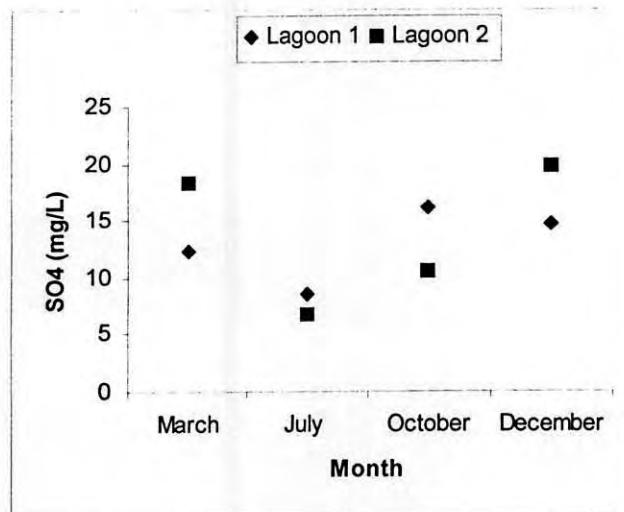


Figure 4.11: SO₄ at various sampling points in the year 2005

4.2.11 Chromium (Cr⁺⁶)

The test results of Cr^{+6} of different sampling points are presented in table A-1 in appendix A. The fluctuations of Cr^{+6} at different times and locations in 2005 are shown in figure 4.12. In 2005, concentration of Cr^{+6} was found to vary from 0.01 to 0.156 mg/L in the wastewater. NGFFL uses 50 kg Sodium dichromate / month which is the major source of Cr^{+6} in wastewater. Bangladesh Industrial Effluent Standards (DOE, 1997), for Cr^{+6} is 0.1 mg/L. For the year 2005, the concentration of chromium was found above the limit in three samples.

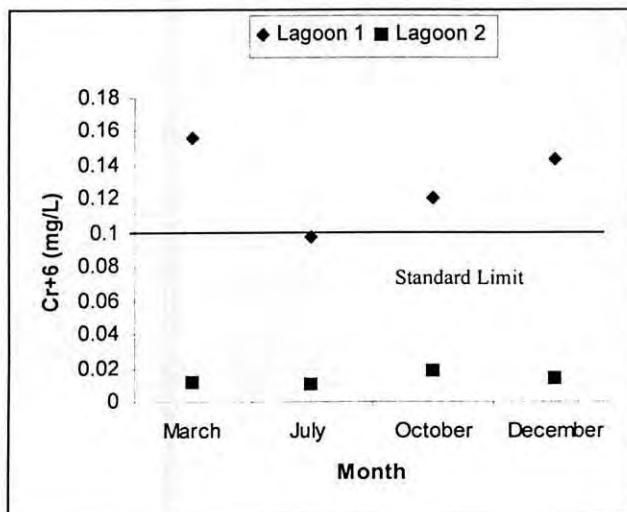


Figure 4.12: Cr^{+6} at various sampling points in the year 2005

4.2.12 Nitrate

The test results of NO_3 of different sampling points are presented in table A-1 in appendix A. The fluctuations of NO_3 at different times and locations in 2005 are shown in figure 4.13. In 2005, concentration of NO_3 was found to vary from 4.5 to 15.2 mg/L in the wastewater. NGFFL discharges huge amount of ammonia in the wastewater. NO_3 may come from the oxidation of ammonia. Bangladesh Industrial Effluent Standards (DOE, 1997), for nitrate is 10 mg/L. For the year 2005, the nitrate was found above the limit in three samples.

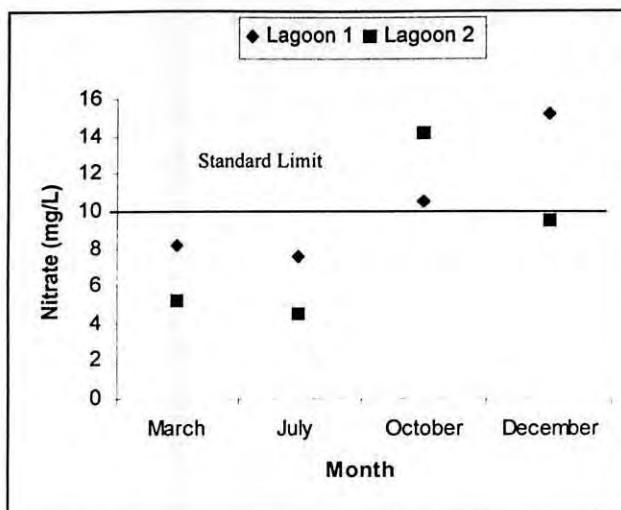


Figure 4.13: NO₃ at various sampling points in the year 2005

4.2.13 Ammonia Nitrogen:

The test results of Ammonia nitrogen of different sampling points are presented in table A-1 in appendix A. The fluctuations of Ammonia nitrogen at different times and locations in 2005 are shown in figure 4.14. Lagoon 1 contains highly concentrated ammonia. Maximum concentration of ammonia in lagoon 1 was found 1710 mg/L in month of December. Bangladesh Industrial Effluent Standards (DOE, 1997), for ammonia nitrogen is 100 mg/L. For the year 2005, the ammonia nitrogen was found above the limit in all samples.

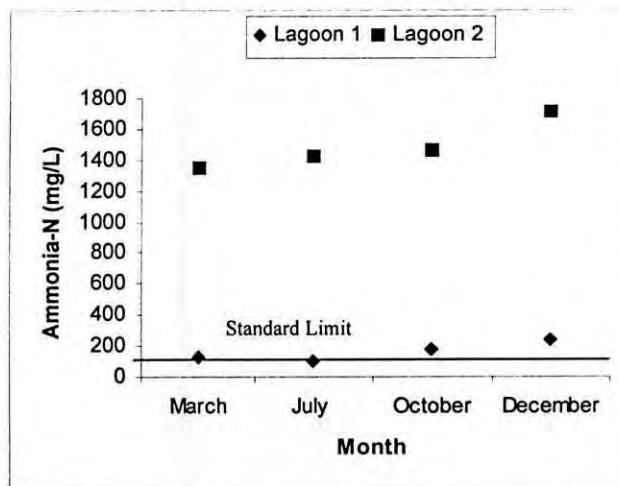


Figure 4.14: Ammonia nitrogen at various sampling points in the year 2005

4.3 EFFECT OF EFFLUENT DISCHARGE ON KUSHIARA RIVER

According to Bangladesh effluent standard, the effluent concentration of ammonia nitrogen should not exceed 50 mg/L for new industry and 100 mg/L for old industry. As ammonia nitrogen discharged into Kushiara River is over Bangladesh Effluent Standard, laboratory analysis was done in the month of December 2005 to observe the condition of the river at the downstream of the factory discharge. Detailed result are shown in table A-4 in appendix A, and also graphically represented in figure 4.15. Ammonia nitrogen was found 0.44 mg/L at 300 yards downstream of the river from the discharging point, which gradually decreased with distance. At the down stream of Kushiara River pH was found to vary from 7.2 to 7.8 (table A-4), which keeps ammonia at a tolerable state according to table 2.5.

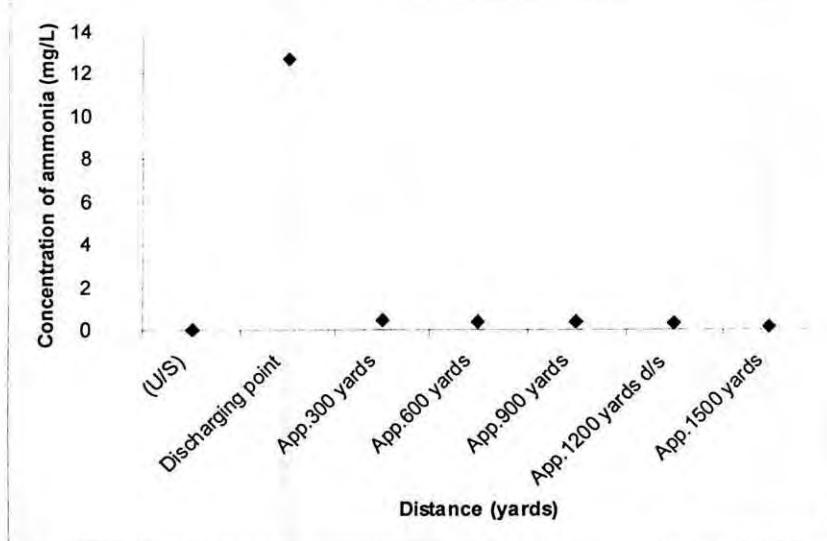


Figure 4.15: Concentration of ammonia nitrogen at the down stream of River Kushiara

Data of water quality at the 600 yards down Stream of Kushiara River has been collected from NGFFL authority of last two years (i.e. from January 2004 to April 2006). Detailed result are shown in table A-3 in appendix A, and also graphically represented from figure 4.16 to 4.22. Temperature was found to vary all through the year (Figure 4.16). Average temperature of river Kushiara for last two year is 26.17°C (Geometric mean is 25.99°C and standard deviation is 3.05°C). pH of down stream of river was found steady through out the year (Figure 4.17). Average pH of river Kushiara for last two year is 7.73

(Geometric mean is 7.73 and standard deviation is 0.13). According to Bangladesh Standard (DOE, 1997), pH for inland surface water is 6.5 to 8.5 for recreational, fishing, irrigation and industrial purposes. So the water of the river Kushiara is suitable for above mentioned purposes. Suspended Solids were found to vary through out the year (Figure 4.18). Average suspended solids of river Kushiara for last two year is 321.96 mg/L (Geometric mean is 189.32 mg/L and standard deviation is 317.35 mg/L). Dissolved Solids were also found to vary all through the year (Figure 4.19). Average Dissolved solids of river Kushiara for last two years is 178.39 mg/L (Geometric mean is 168.50 mg/L and standard deviation is 59.47 mg/L). COD of down stream of river was found fluctuated through out the year (Figure 4.20). Average COD of river Kushiara for last two year is 15.56 mg/L (Geometric mean is 14.97 mg/L and standard deviation is 4.53 mg/L). BOD₅ of down stream of river was found steady through out the year (Figure 4.21). Average BOD₅ of river Kushiara for last two year is 1.84 mg/L (Geometric mean is 1.75 mg/L and standard deviation is 0.57 mg/L). Dissolved Oxygen of down stream of river was found steady all through the year (Figure 4.22). Average Dissolved Oxygen of river Kushiara for last two year is 7.35 mg/L (Geometric mean is 7.31mg/L and standard deviation is 4.53 mg/L). Ammonia nitrogen and oil were not found or found as trace level at the 600 yards down Stream of Kushiara River.

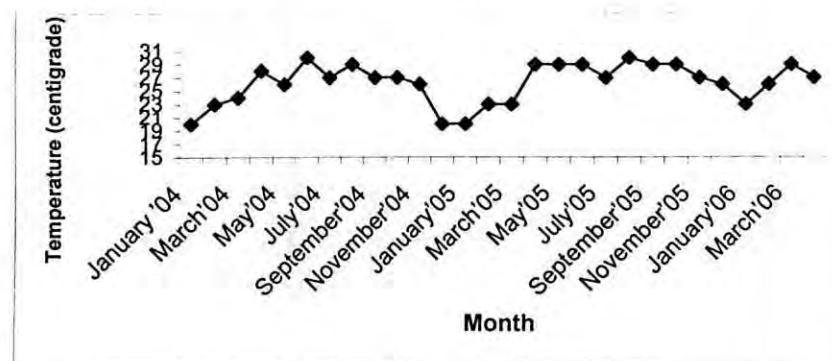


Figure 4.16: Seasonal variation of temperature at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

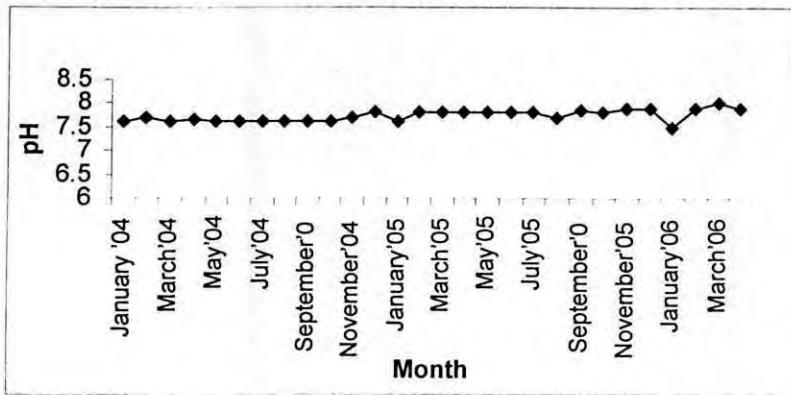


Figure 4.17: Seasonal variation of pH at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

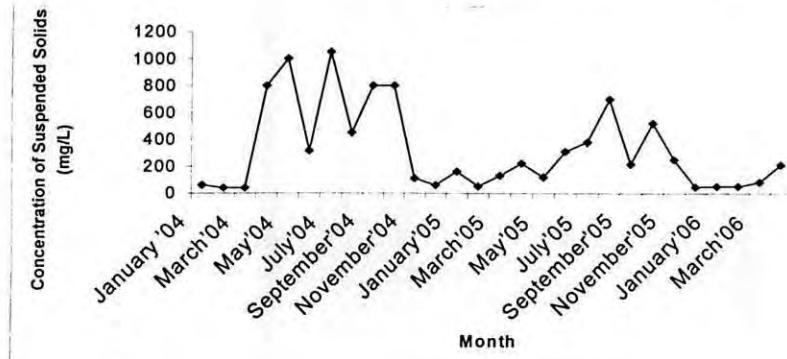


Figure 4.18: Seasonal variation of Suspended Solids at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

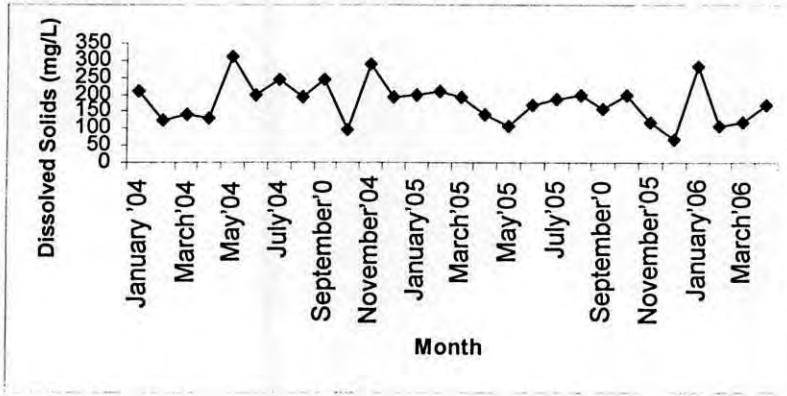


Figure 4.19: Seasonal variation of Dissolved Solids at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

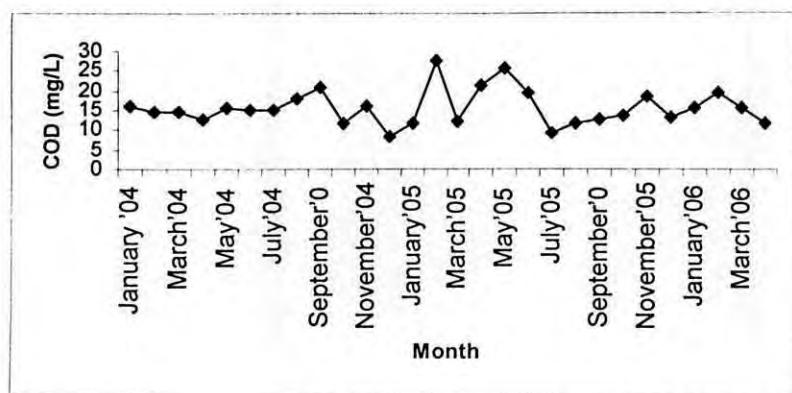


Figure 4.20: Seasonal variation of COD at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

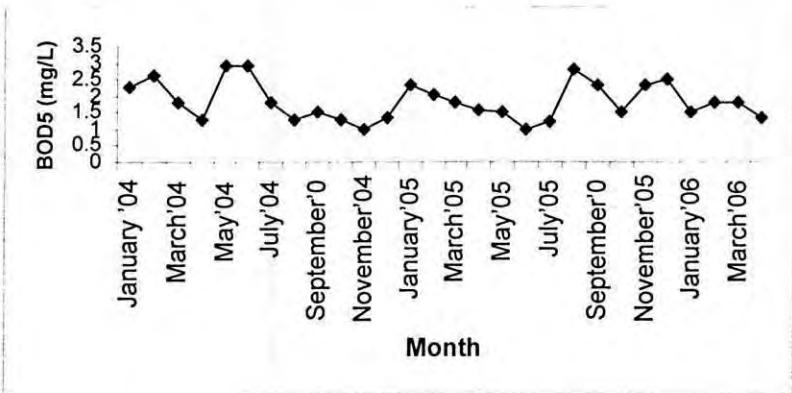


Figure 4.21: Seasonal variation of BOD₅ at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

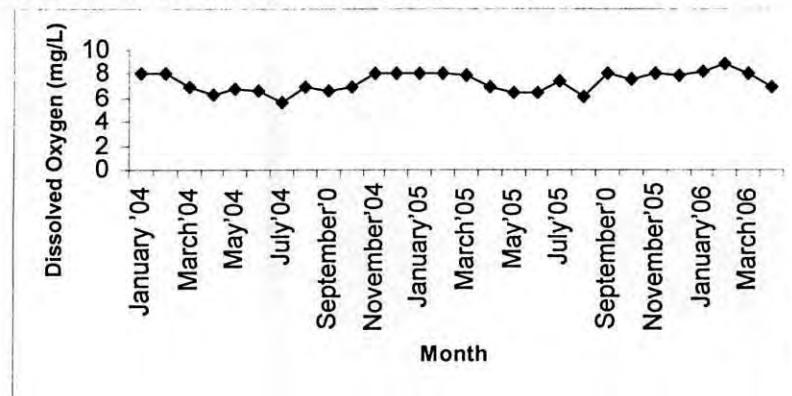


Figure 4.22: Seasonal variation of DO at 600 yards downstream of factory discharge (Source: NGFFL laboratory)

4.4 EFFICIENCY OF THE EXITING LAGOON:

Seasonal variation of ammonia-nitrogen of lagoon 1 is shown in figure 4.24 and in table A-2 in Appendix A. The influent and effluent concentration of lagoon 2 is shown in figure 4.23. Maximum influent concentration of a month is considered. As the retention time of wastewater is 1 day in the lagoon 2, the effluent concentration was taken after one day, which holds maximum influent concentration. Average influent concentration of lagoon 2 for last two years is 283.52 mg/L (Geometric mean is 205.74 mg/L and standard deviation is 256.06 mg/L). Where as average effluent concentration of lagoon 2 for last two years is 221.56 mg/L (Geometric mean is 189.91 mg/L and standard deviation is 148.88 mg/L). It is evident that, lagoon 2 is not working properly. Sometimes effluent concentration is higher than the influent concentration. Average concentration of lagoon 1 for last two years is 1045.82 mg/L (Geometric mean is 1008.65 mg/L and standard deviation is 277.84 mg/L), which is directly discharging into river Kushiara.

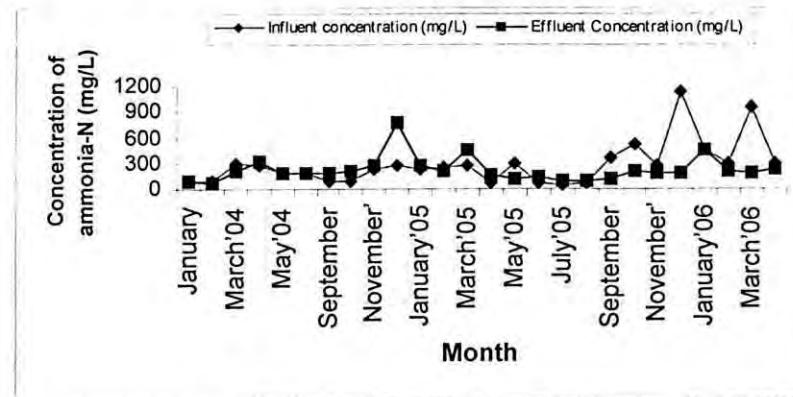


Figure 4.23: influent and effluent concentration of lagoon 2 (Source: NGFFL laboratory)

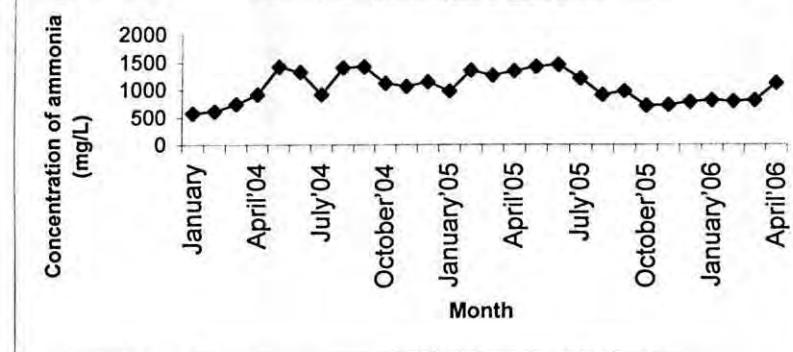


Figure 4.24: Seasonal variation of ammonia nitrogen in lagoon 1 (Source: NGFFL laboratory)

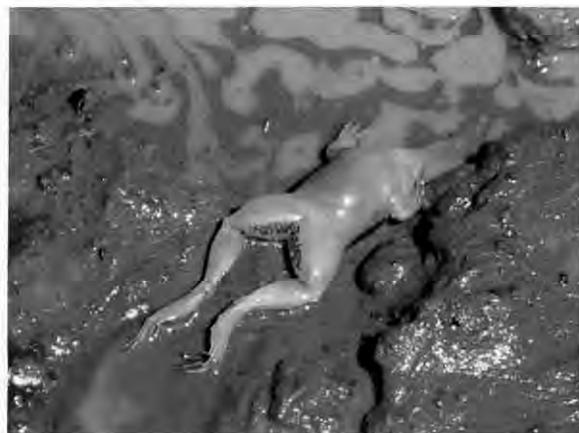


Figure 4.25: Effect of wastewater on a species, near lagoon 1

4.5 OVERVIEW:

The analysis results of different wastewater quality parameters of lagoon 1 and lagoon 2 that were tested in this research work are shown graphically. The analysis of seasonal variation of water quality of Kushiara River at 600 yards downstream has also been shown graphically in this chapter. It is clear that the major two contaminants of NGFFL are ammonia- nitrogen and oil and grease. But the data collected from NGFFL laboratory reveal that wastewater of NGFFL does not influence the water quality of Kushiara River a lot. So the question that has arisen from this chapter is, whether treatment of ammonia from wastewater of NGFFL is essential or not. If we consider the seasonal ammonia variation of wastewater of NGFFL, we will find that NGFFL discharges wastewater which contains ammonia at a concentration several times greater than the standard limit of Bangladesh. In this context, if NGFFL authority wants to maintain the Environmental Conservation Rules 1997, they must treat ammonia in their wastewater. For this reason, this research work is very important to keep the river Kushiara safe in near future. On the other hand there are two lagoons. Among them, lagoon 2 is not working properly. Environmental Management Plan should be implemented to increase the efficiency of the existing two lagoons.

CHAPTER FIVE

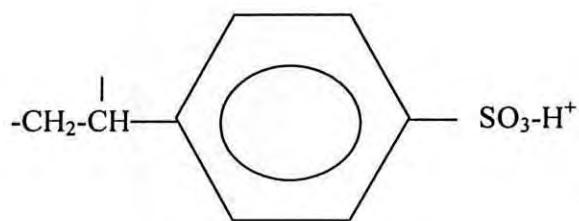
REMOVAL OF AMMONIA

5.1 INTRODUCTION

The major industries contributing to ammonia in liquid wastes are fertilizer and coke-oven units (Mahajan, 1985). In both these, the concentration of ammonia in liquid wastes is high and needs to be treated. Urea-producing fertilizer units give rise to urea in liquid effluents. It is imperative, therefore, that with increase in fertilizer production, steps be undertaken to tackle pollution problem. This can be done through in-built pollution control system in modern plants and whenever possible by incorporating pollution abatement systems in older plants.

5.2 ION EXCHANGE RESIN

Sulfonile resin was used as cation exchanger. To study the efficiency of the resin on ammonia-Nitrogen removal, experiments were conducted with raw wastewater of NGFFL. The influent concentration of ammonia nitrogen was 892 mg/L. pH was adjusted to 6.5 to convert free ammonia to ammonium ion. Experimental data are shown in table B-7, B-8 and B-9 in appendix B. Figure 5.1 and 5.2 present the relationship between bed volume and effluent ammonia-N concentration. Efficiency of the bed and ammonium ion exchanged by resin was determined as it is described in section 3.4.2. Efficiency of the resin was found around 95%. And the exchanged ammonium ion by the resin was found 0.51 mg/gm. Though the efficiency of the resin is high to remove of ammonia from the wastewater but as the concentration of ammonia in the wastewater of NGFFL is very high so large amount of resin will be needed to treat ammonia from the wastewater of NGFFL, which may not be cost effective. On the other hand there are other ions which may interfere the process.



Sulfonile resin

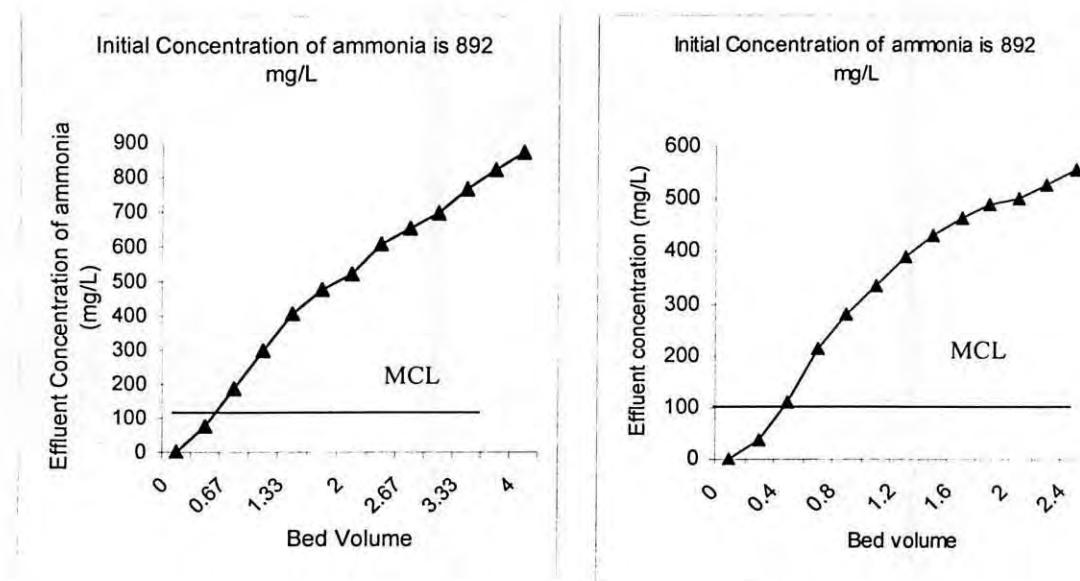


Figure 5.1 Break through curve of ammonia passing through sulfonile resin (30 cc)

Figure 5.2 Break through curve of ammonia passing through sulfonile resin (50 cc)

5.3 LAGOONING AFTER pH ADJUSTMENT

Laboratory experiment was conducted to remove ammonia by simply keeping the wastewater. It was found that considerable reduction in the ammonia content can be accomplished just by retaining the ammonia-contaminated wastewater in a container. The experiment was also done for earthen container (which inner side was covered by soil). The removal of ammonia of the earthen container is slightly better than the container which inner side was not covered by soil. Details have been shown in figure 5.3 and 5.4 and table B-1 in appendix B. 58.77% to 62.8% removal was achieved within 1 day, and

88.6% to 90.12% removal was found after 10 days. As the two experiments gave almost the same results, there is a very little possibility of biological treatment of ammonia due to earthen lagoon after rising of pH to 11.5.

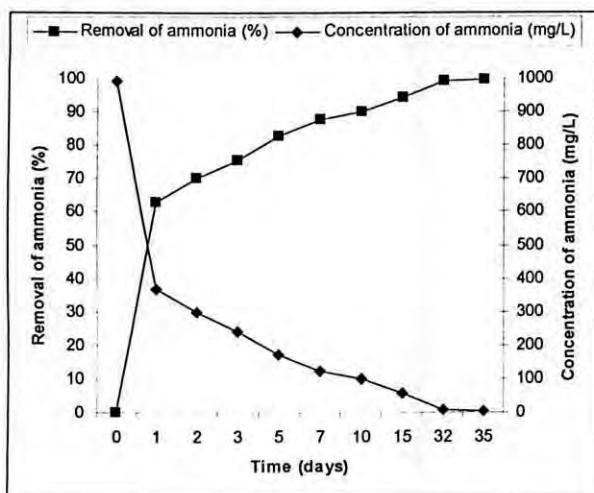


Figure 5.3: Wastewater kept in a jar at pH 11.5 (inner side was covered by soil)

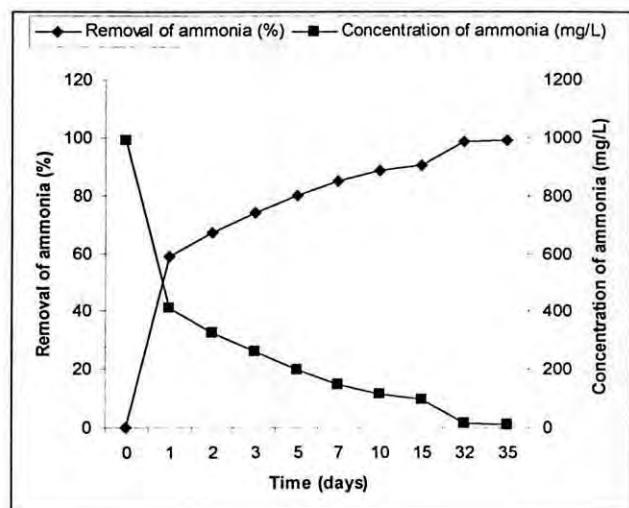


Figure 5.4: Wastewater kept in a jar at pH 11.5 (inner side was not covered by soil)

5.4 AERATION

The results for the experiments concerning the direct aeration of ammonia-contaminated wastewater are presented from figure 5.5 to 5.8 and in table B-2 in appendix B. Effect of volume of wastewater and pH on aeration was observed.

5.4.1 Effect of Volume

Aeration was done for 200 ml (dia of the aeration cylinder is 4 cm), 350 ml (dia of the aeration cylinder is 5 cm) and 750 ml (dia of the aeration cylinder is 6 cm) of sample. pH was adjusted to 11.5 to covert NH_4^+ to NH_3 gas. Aeration rate for each experiment was 15 l/min. 99%, 97% and 80% removal of ammonia were achieved respectively for 200, 350 and 750 ml of wastewater after 300 minutes. Volume of water is an important factor. Mass transfer rate is larger for smaller volume of water comparing to that of larger volume of water when the aeration rate is same.

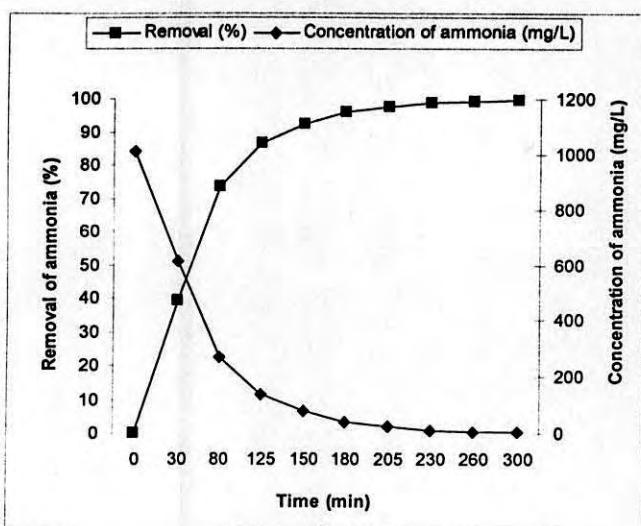


Figure 5.5: Removal of ammonia by aeration at pH 11.5 (water volume is 200 ml)

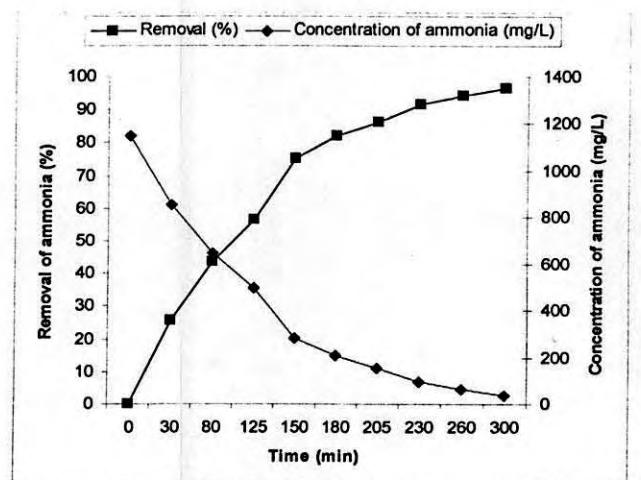


Figure 5.6: Removal of ammonia by aeration at pH 11.5 (water volume is 350 ml)

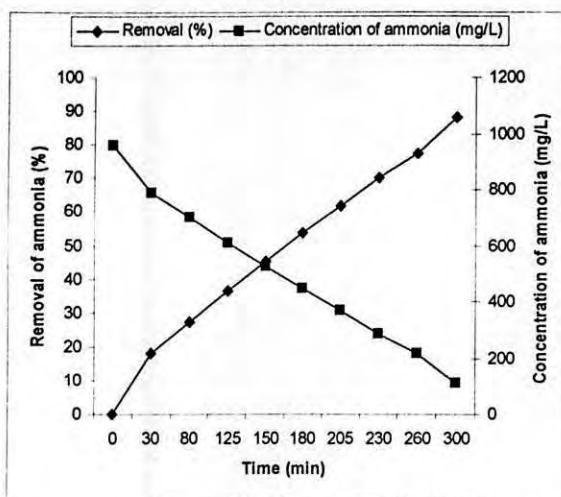


Figure 5.7: Removal of ammonia by aeration at pH 11.5 (water volume is 750 ml)

5.4.2 Effect of pH

A higher influent pH resulted in higher removal efficiency; a removal of 99% was achieved in approximately 300 minute when the pH was 11.5. At a pH 8.1 (without controlling the pH of the sample), the removal efficiency had reached only 67% after 300 minute (figure 5.8). So it can be said that, pH is an important factor to remove ammonia by aeration. pH should be adjusted before aeration. Without controlling pH aeration will not be effective.

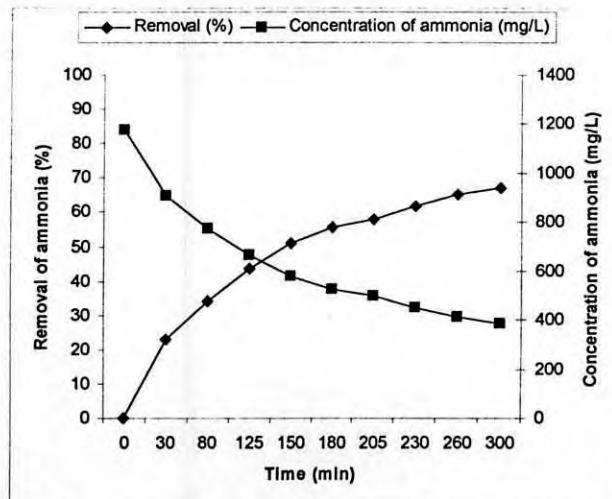


Figure 5.8: Removal of Ammonia by Aeration at pH 8.1 (water volume is 200 ml)

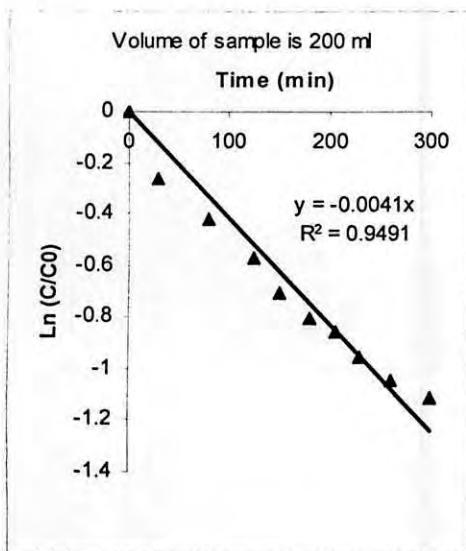
If the system is at equilibrium, the Henry's law constant may be estimated with the following equation:

$$-\ln(C/C_0) = (GK_{eq}/V)t \quad (5-1)$$

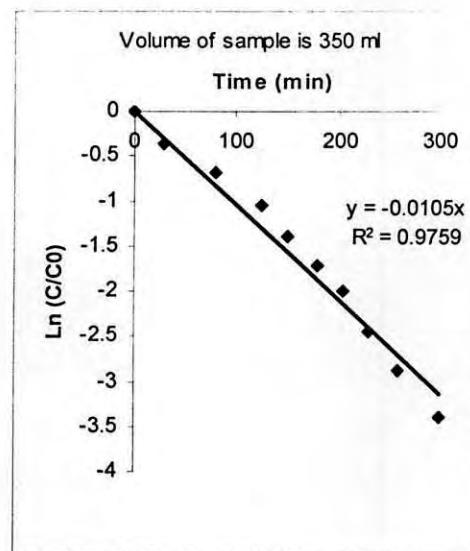
where:

- C = concentration at time, t (min)
- C_0 = concentration at $t = 0$
- G = volumetric gas flow rate (ml/min)
- V = liquid volume in the batch reactor (ml)
- K_{eq} = Henry's law constant (mg/L-gas)/(mg/L-liquid)
- t = time (min)

A plot of $-\ln(C/C_0)$ as a function of t will have a slope equal to GK_{eq}/V . Figure 5-9 (a-c) shows the value of ' GK_{eq}/V ' for different sample volume and Figure 5-9 (d) shows the relationship between volumes of aerated sample Vs GK_{eq}/V . Values of K_{eq} will be valid when the depth and surface area are as it is described at the beginning of this section.



(a)



(b)

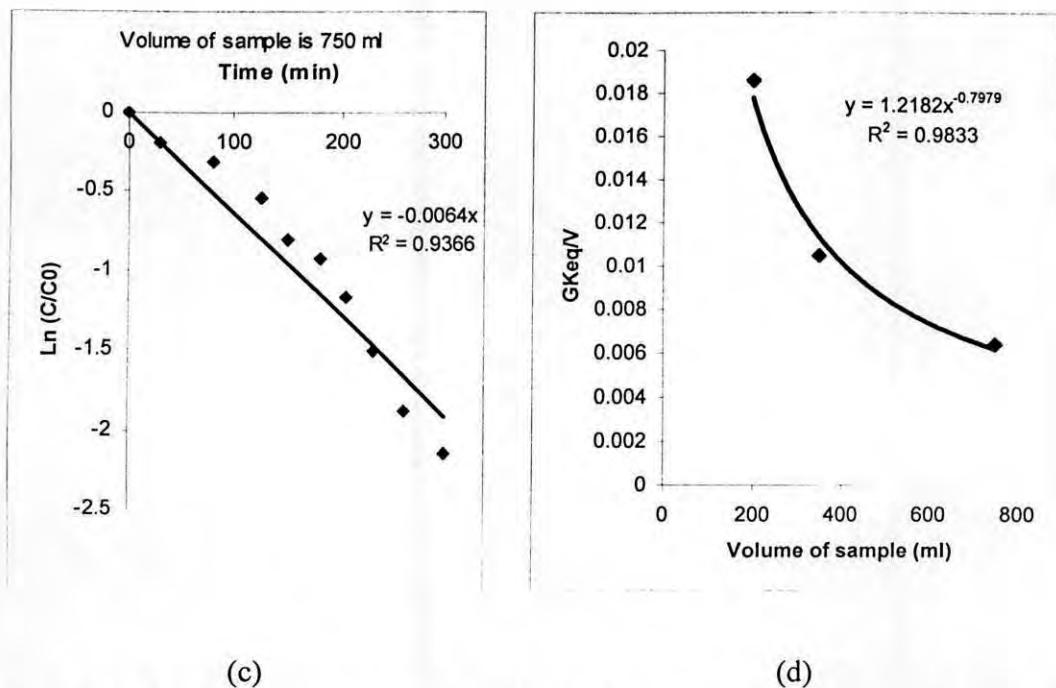


Figure 5.9: Determination of GK_{eq}/V and relation of GK_{eq}/V with volume of aerated wastewater

5.5 AIR STRIPPING

The effect of nature of packing materials, height of materials, pH over 10.5, air-water flow ratio, and initial concentration of ammonia on air stripping unit were investigated.

5.5.1 Effect of Packing Height

Packing height has a great influence on stripping process. Laboratory experiments show that removal efficiency increased with the increase of packing height due to the increment of contact time between air and water. Without packing materials, with a constant air-water ratio 2000, the removal was found around 50%. pH of the wastewater was adjusted to 10.5. In case of plastic ring, only 63.59% removal was found for 1 feet height of packing materials and removal efficiency was being gradually increased and gave 91.60% removal for 5 feet height. Same results were found for other three materials. Coal, stone chips, and wood chips gave 60.89%, 60.73% and 60.43% removal for 1 feet height and 87.82%, 85.24% and 84.5% removal for 5 feet height respectively. The effect

of packing height for various packing materials has been shown in figure 5.10 to 5.13 and table B-5 in appendix B.

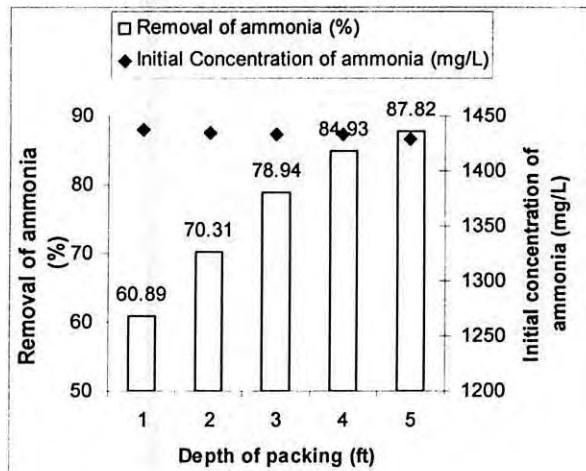


Figure 5.10: Effect of packing height on removal of ammonia (packing material is coal)

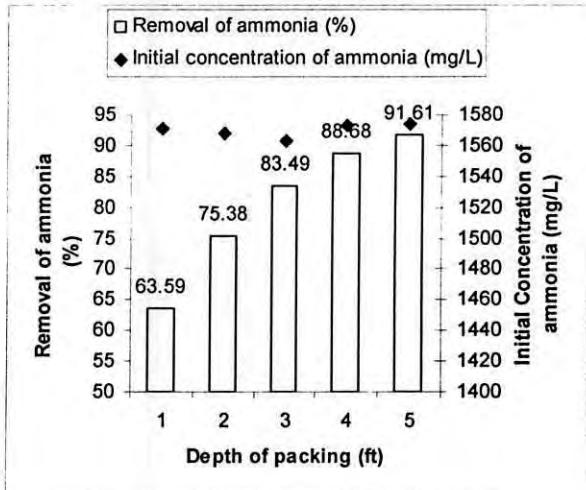


Figure 5.11: Effect of packing height on removal of ammonia (packing material is plastic ring)

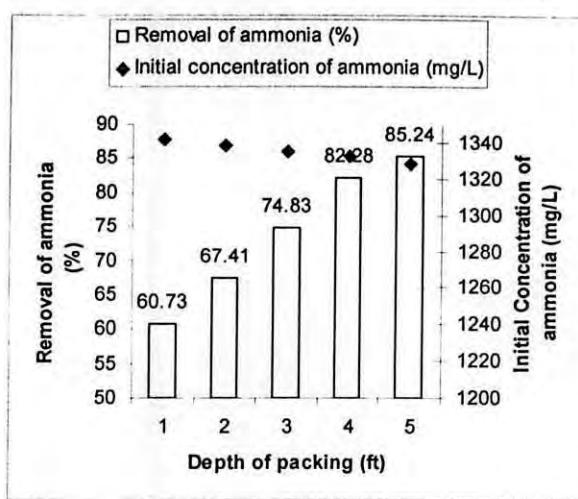


Figure 5.12: Effect of packing height on removal of ammonia (packing material is stone chips)

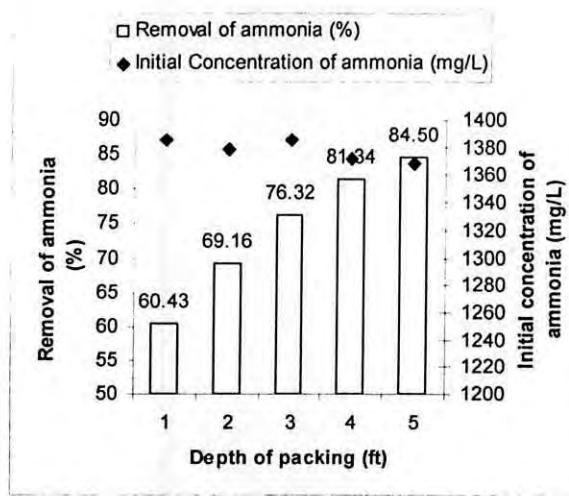


Figure 5.13: Effect of packing height on removal of ammonia (packing material is Wood Chips)

5.5.2 Effect of pH on Air Stripping

According to the literature before stripping the pH of the sample has to be raised above 11.0. Above pH 10.5, the effectiveness of the stripping has been studied. Because controlling of pH involves a lot of chemicals like calcium oxide. The effect of pH on the ammonia removal efficiency of the air-stripping method is shown in figure 5.14 to 5.17

and in table B-3 in appendix B. The best result obtained from the study was 88.94%, 94.15%, 87.8% and 87.4% ammonia reduction by coal, plastic ring, stone chips and wood chips respectively at or over pH 11.5. Above pH 10.5, the ammonia removal efficiency was not greatly influenced by pH. For example, in case of coal as a packing material at pH 10.5 with an air flow rate 15 l/min, 87.8 % removal efficiency was achieved, while at pH 11.5 with the same air flow rate 88.9% removal was achieved. But it is evident from the experiment that more calcium is required to raise the pH 11.5 than pH 10.5. Such large additions of lime would increase the formation of heavy calcium carbonate scale within the stripping tower and as a result the efficiency of the system would decrease and severe maintenance problem would occur (USEPA, 1973). However, since the effects of pH on removal efficiency were not found to be significant at levels above pH 10.5, there appears to be some reason for raising the level any higher. That is, the experiment results show the most efficient to be 10.5.

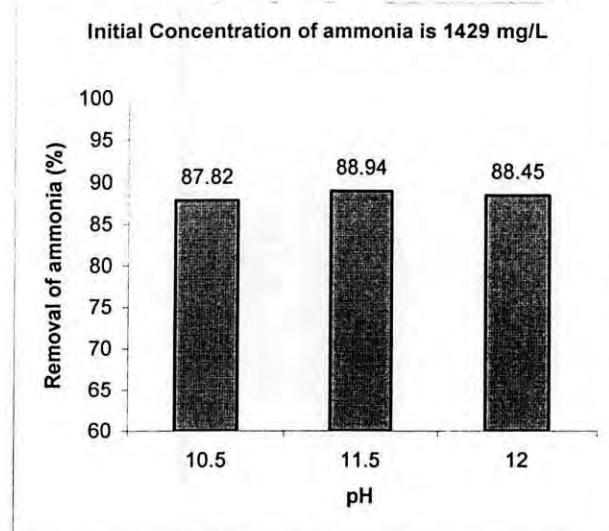


Figure 5.14: Effect of pH on removal efficiency of ammonia (Packing material is coal)

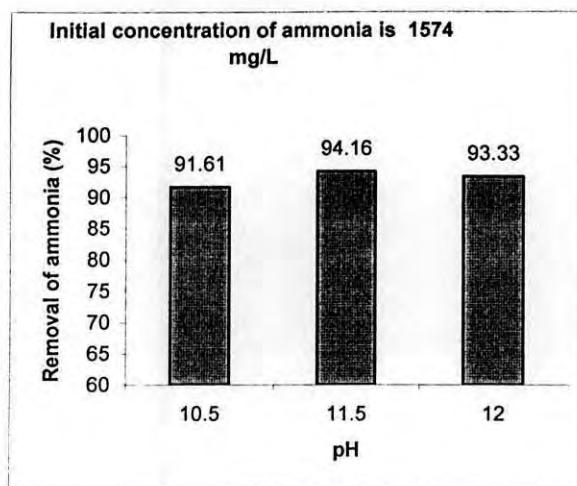


Figure 5.15: Effect of pH on removal efficiency of ammonia (Packing material is plastic ring)

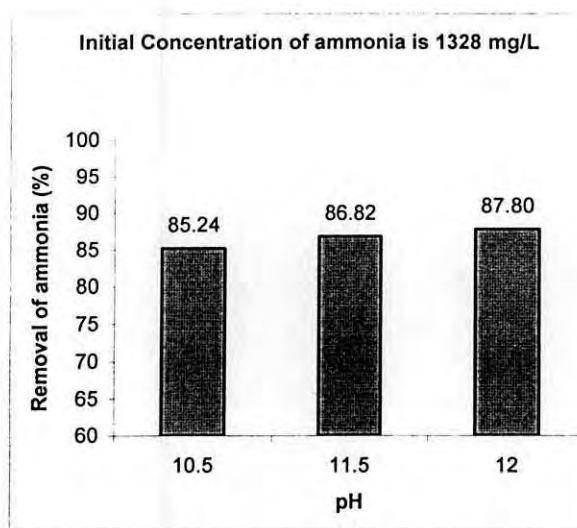


Figure 5.16: Effect of pH on removal efficiency of ammonia (Packing material is stone chips)

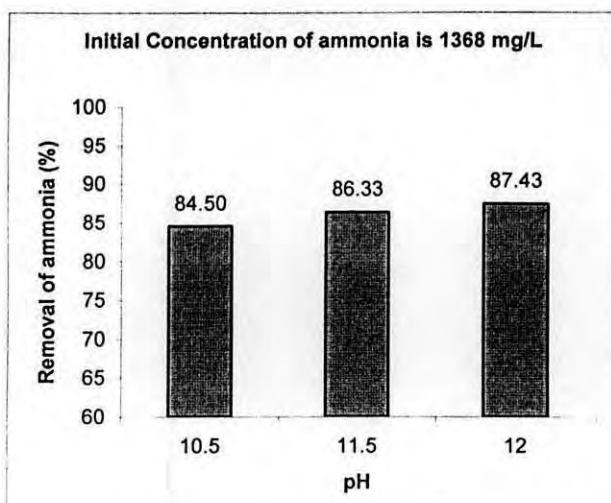


Figure 5.17: Effect of pH on removal efficiency of ammonia (Packing material is wood chips)

5.5.3 Effect of Air-Water Ratio

The effect of air-water ratio on removal efficiency is presented in figure 5.18 to figure 5.21 and in table B-5 in appendix B. All the result shows very high levels of ammonia removal. An increase of air to water flow ratio from 1250 to 2000 (air flow is constant) facilitated the stripping process. In case of coal, plastic ring, stone and wood chips; removal efficiency was increased from 72.84% to 87.82%, 78.7% to 91.60%, 70% to 85.3% and 69.5% to 84.5% respectively by increasing the air to water flow ratio 1250 to 2000. In all the cases, packing depth was 5 feet and pH was adjusted to 10.5.

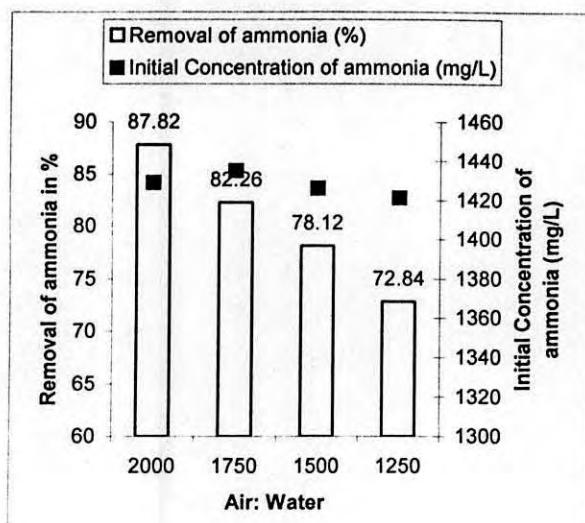


Figure 5.18: Effect of air: water on removal of ammonia (Packing material is coal)

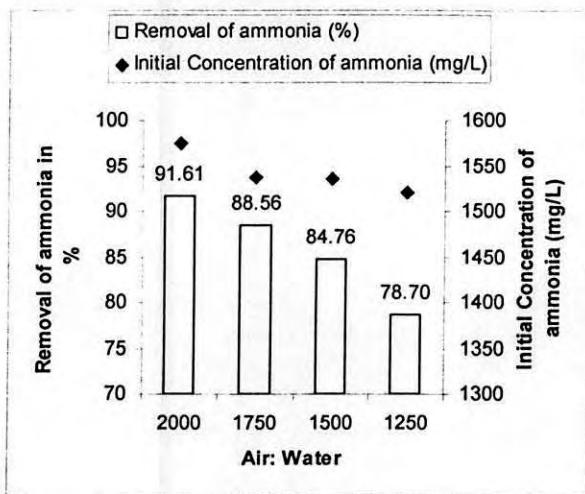


Figure 5.19: Effect of air: water on removal of ammonia (Packing material is plastic ring)

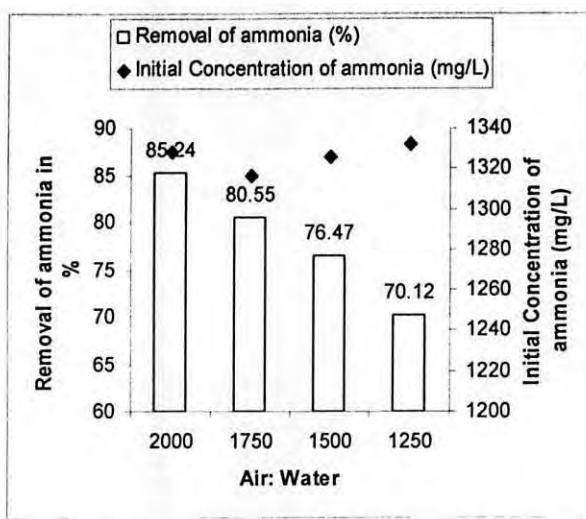


Figure 5.20: Effect of air: water on removal of ammonia (Packing material is stone chips)

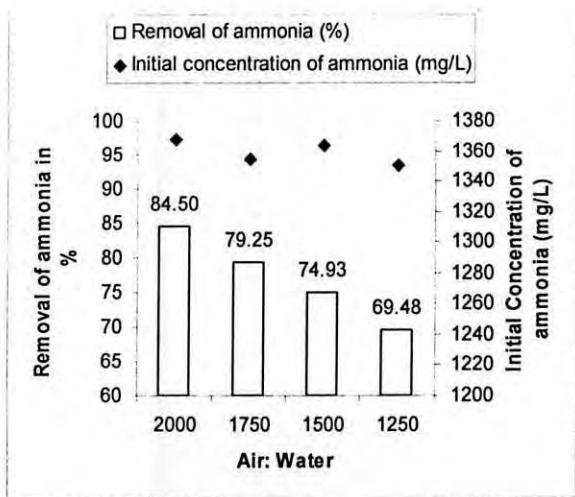


Figure 5.21: Effect of air: water on removal of ammonia (Packing material is wood chips)

5.5.4 Effect of Initial Concentration

Effect of initial concentration on stripping unit was investigated. Effect of initial concentration did not influence the efficiency (in terms of removal) a lot. Influent concentration was varied from 80 mg/L to 1574 mg/L. In case of coal, plastic ring, stone and wood chips the removal efficiencies were in the range of 86.21% to 91.76%, 90.43% to 92.39%, 80% to 88.31%, and 83.72% to 88.20% respectively. Air to water flow ratio

was maintained 2000 and packing depth in all the cases were 5 feet and pH was adjusted to 10.5. The detail results have been shown in figure 5.22 to 5.25 and in table B-4 in appendix B.

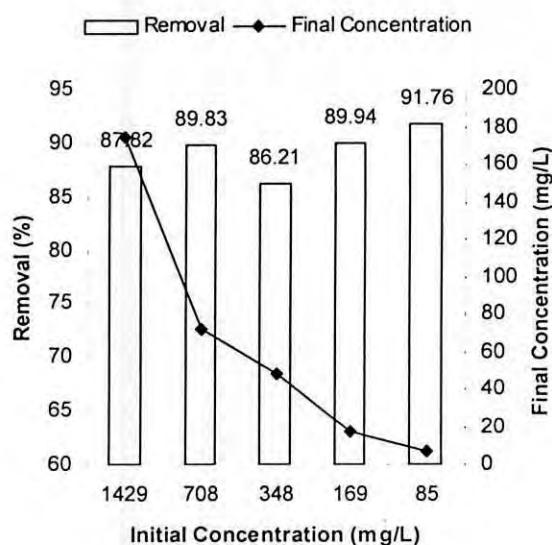


Figure 5.22: Effect of initial concentration of ammonia on removal of ammonia (packing material is coal)

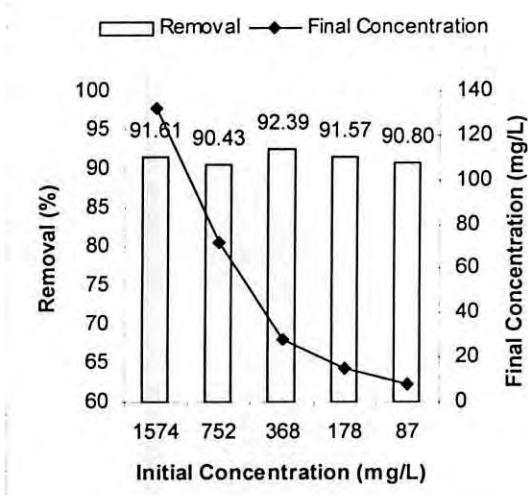


Figure 5.23: Effect of initial concentration of ammonia on removal of ammonia (packing material is plastic ring)

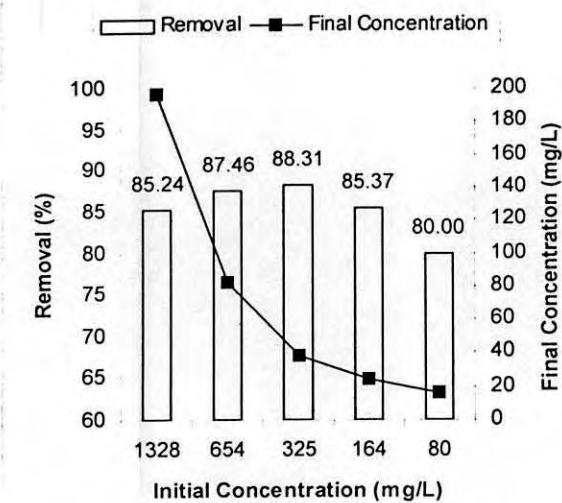


Figure 5.24: Effect of initial concentration of ammonia on removal of ammonia (packing material is stone chips)

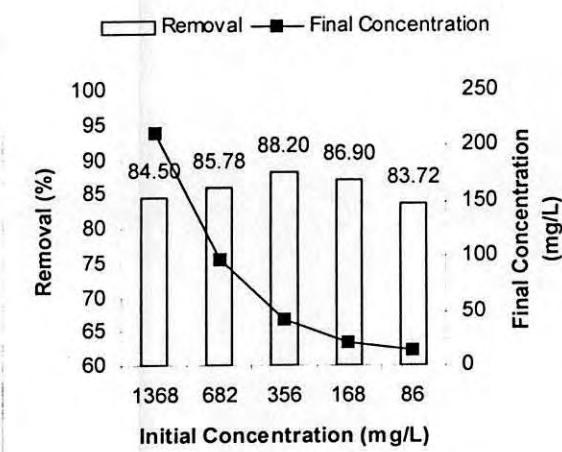


Figure 5.25: Effect of initial concentration of ammonia on removal of ammonia (packing material is wood chips)

5.5.5 Effect of Packing Materials

Packing can be divided into four main classes—broken solids, shaped packing, grids and structured packing. The packing size influences the height and diameter of a column, pressure drop and cost of packing. Generally as the packing size is increased, the cost per unit volume of packing and the pressure drop per unit height are reduced, and the mass transfer efficiency is reduced. Quality of packing materials has an influence over efficiency of stripping column. Among the four types of packing materials used as packing materials, plastic ring gave the best performance due to its high surface area. Among the other three materials, coal gave comparatively better performance. It may be due to its adsorbing property. Wood as packing materials was not found suitable because they amalgamated with each other within a very short time and reduced the surface area. Stone is a heavy material. So it will increase the cost of the building of column. Coal may be a good option. It gives good performance. But the major drawback is its self-weight. Plastic ring will be the best choice to use as packing materials. It is lighter, gave the maximum surface area and can be produced locally.

5.5.6 Effluent Concentration Prediction

The first-order decay model was used to determine stripping constant according to the equation 3.1. Fitted curves are presented in figure 5.26 to 5.29. Stripping constant was found .001, .0014, .001 and .0009 for coal, plastic ring, stone chips and wood chips respectively. The equation with the empirically derived stripping constants was used to predict effluent water concentration. A curve of experimental concentration vs. predicted concentration has been plotted in figure 5.30 to evaluate the accuracy of the model.

From the model prediction curves, equation 5.2, 5.3, 5.4 and 5.5 have been generated to find out the value of effluent concentration of ammonia when the packing materials are coal, plastic ring, stone chips and wood chips respectively. Those equations will be valid only when the pH of the raw water is adjusted to 10.5 and the height of the packing materials is 5 feet. To verify the prediction model, some known concentration of ammonia contaminated Wastewater was passed through the air-stripping unit by keeping the air-water ratio 2000.

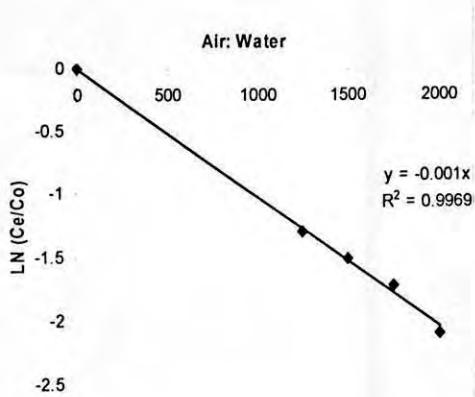


Figure 5.26: Model prediction curve for coal

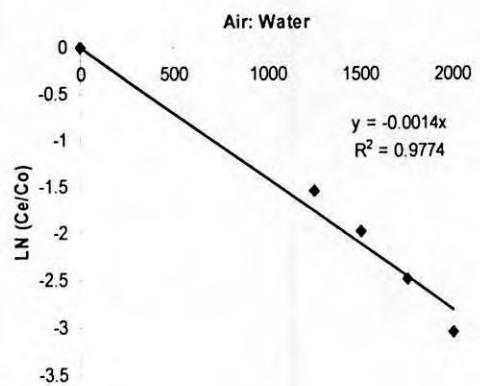


Figure 5.27: Model prediction curve for plastic ring

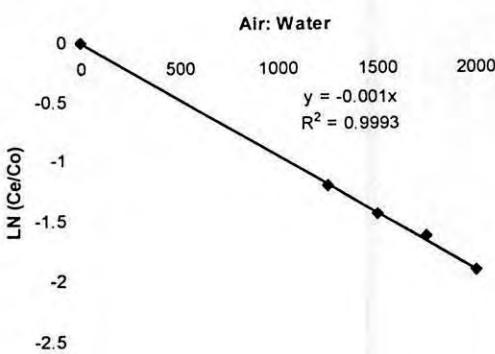


Figure 5.28: Model prediction curve for stone chips

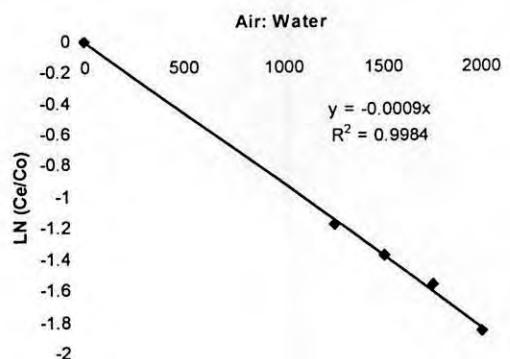


Figure 5.29: Model prediction curve for wood chips

The effluent concentration of ammonia was measured by both experimentally and using the equations. Detailed are shown in table B-6 in appendix B. From figure 5.30, it is clear that the predicted effluent concentration is more accurate when the effluent concentration is below 50 mg/L. Closeness of the points towards the 45° line indicates that this model is suitable to predict effluent concentration of ammonia nitrogen.

$$C_e = C_i e^{-0.001q} \quad (5-2)$$

$$C_e = C_i e^{-0.0014q} \quad (5-3)$$

$$C_e = C_i e^{-0.001q} \quad (5-4)$$

$$C_e = C_i e^{-0.0009q} \quad (5-5)$$

Where

C_e = effluent water concentration

C_i = influent water concentration

q = volumetric air-to-water ratio

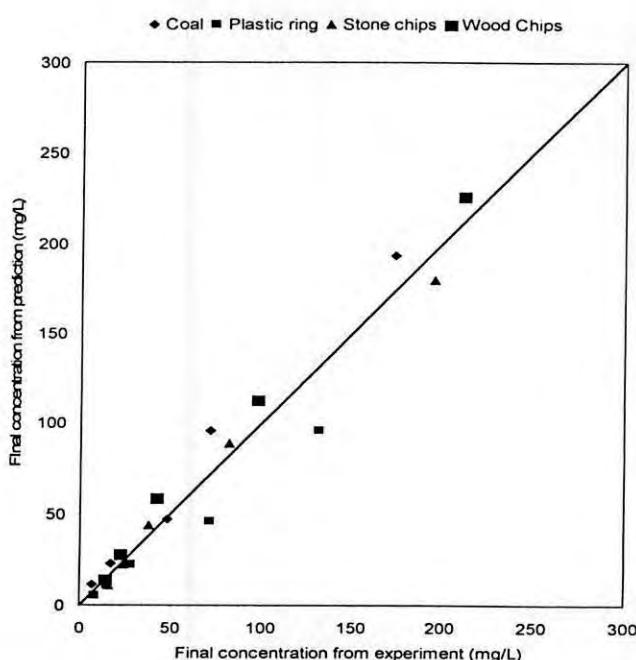


Figure 5.30: verification of predicted model

5.5.6 Ammonia in the Air

In air stripping unit, water is treated and becomes free from ammonia. But it posses a great threat to the ambient air. In different condition of the experiment, amount of ammonia that has been discharged into the air is summarized in table 5.1. It is clear that huge amount ammonia (828 to 1401 ppm) has been found at the outlet of the stripping unit by using mass balance equation. At the same time, it is obvious that air-water ratio has a great influence on ammonia emission in the air. For example, in case of plastic ring,

at the outlet of the stripping unit, 1055 and 1401 ppm of ammonia was found for air – water ratio 2000 and 1250 respectively. Recovery of ammonia as either ammonium sulfate or nitrate by scrubbing with sulfuric or nitric acid can be a solution.

Table 5.1: Effluent concentration of ammonia in the air at the outlet

Air: Water	Packing materials	Ye (ppm)
2000	Coal	918.46
1750	Coal	992.69
1500	Coal	1086.87
1250	Coal	1211.66
2000	Plastic ring	1055.201
1750	Plastic ring	1139.03
1500	Plastic ring	1269.27
1250	Plastic ring	1401.26
2000	Stone chips	828.51
1750	Stone chips	886.60
1500	Stone chips	989.41
1250	Stone chips	1093.51
2000	Wood chips	846.03
1750	Wood chips	897.41
1500	Wood chips	997.14
1250	Wood chips	1098.163

5.6 OVERVIEW

This chapter describes the results of different techniques that have been used to remove ammonia. Among all the treatment techniques, air stripping gave the best result. Over 90% removal was found by this method. A large amount of calcium oxide is needed to adjust the pH before air stripping. Aeration was also found effective. But it also needs pre-adjustment of pH. Laboratory experiments show that though ion exchange is a very efficient method, as the wastewater contains a large amount of ammonia it will not be cost effective. Huge amount of resin will be needed to treat the wastewater. NGFFL has two lagoons. In chapter four, it has been shown that lagoon 2 is not working properly. But laboratory experiment shows that lagooning after pH control will be a very effective method.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATION

6.1 CONCLUSIONS

The objectives of the study were to identify any changes of adjacent river water quality due to the discharge of industrial effluent from NGFFL into the Kushiara River, to characterize the liquid waste of NGFFL, to analyze the efficiency of present treatment facilities of NGFFL, and to provide suitable treatment option to remove ammonia from the effluent of NGFFL according to Bangladesh Standards for Industrial Effluent. The wastewater quality of NGFFL and condition of river Kushiara were observed in the months of March, July, October, and December 2005. The aeration, air stripping, lagooning, and ion exchange to remove ammonia from wastewater of NGFFL were observed.

The following conclusion can be drawn from this research work:

- Several techniques to remove ammonia were studied in the laboratory. The air-stripping method achieved very high rates of ammonia removal and the results indicated that it could be a great solution for waste management problems currently being incurred by the fertilizer factory. Its use requires a large addition of lime, a high airflow rate and the provision of a tower containing some packing materials. Different materials were used as packing materials. Stripping constants were found .001, .0014, .001 and .0009 for coal, plastic ring, stone chips and wood chips respectively at pH 10.5. Best result was found using plastic ring for its higher surface area. Wood did not give good result, because they amalgamate with each other and hence reduce the surface area.
- Aeration after controlling pH has been found very effective. But using raw water without controlling pH was not found effective. So pH should be adjusted before aeration.
- Ion exchange method was applied using Sulfonile resin as cation exchanger. But result was not satisfactory. The resin becomes exhausted within very short period of time.

- Lagooning after pH control may be a good option. About 60% of removal was achieved within one day by keeping the wastewater in a small container at pH 11.5.
- The major pollutants discharged from NGFFL into river Kushiara are ammonia, oil and grease, and suspended solids. Dissolve solids were found within the limit, but suspended solids were found higher than the Bangladesh Standard for Industrial effluent. COD and BOD_5 were found well below Bangladesh Standards limit. Dissolved Oxygen of the wastewater was found to be 2.0 to 3.0 mg/L at every wastewater sampling points, which do not satisfy the standard limit (4.5 -8 mg/L). Oil and grease were found within the range of 28 to 68 mg/L whereas the standard limit is 10 mg/L before discharging into the inland surface water. Ammonia nitrogen was found very high in lagoon 1, which is directly discharging into the river Kushiara.
- River water quality was analyzed in the month of December. Ammonia nitrogen was found 0.44 mg/L (pH was 7.2) and 0.18 mg/L (pH was 7.3) at 300 yards and 1500 yards down stream respectively. As pH was just around 7.5 and temperature ranged from 20 to 30°C , which keeps ammonia at a tolerable state, it can be said that the fishes of Kushiara River are not affected by ammonia nitrogen. But attention should be given on ammonia treatment as it is discharging with a high concentration into river Kushiara.
- The efficiency of lagoon 2 was analyzed and it was found that the lagoon 2 is not suitable for treatment of ammonia. There may be several reasons behind it. Firstly, the retention time may not be enough. Secondly, the lagoon is not properly seeded.

6.2 RECOMMENDATION FOR POLICY MAKING

On the basis of wastewater analysis of NGFFL, it is clear that new treatment plant or improvement of the existing lagoons is essential. From this research work, it is obvious that air stripping would be the most effective option. But the major problem is that, it requires a huge amount of calcium oxide to adjust pH. In fact, research shows almost every treatment option demands pH adjustment. If NGFFL authority wants to adjust pH

of their wastewater, air stripping would be the best choice. If they are unable then an alternative should be found out. It has been said earlier that ion exchange would not be feasible. They can think about biological treatment. pH and alkalinity of the wastewater is suitable for biological treatment. But major problem is lacking of BOD in wastewater. Because by biological treatment, ammonia will be converted to nitrite and nitrate. Then organic matter (BOD) will be needed to convert nitrate into nitrogen by heterotrophic organism. Otherwise nitrate will cause eutrophication problem. NGFFL uses huge amount of air to generate fertilizer. They can transfer air through a bypass line to the lagoons. This research suggests if they provide aeration in their lagoons then considerable amount of ammonia reduction can be achieved.

6.3 RECOMMENDATION FOR FURTHER STUDY

- Mass transfer coefficient is an important parameter for air stripping unit, which has not been found out. An attempt can be made to find out this parameter. As the dia of the packing tower was small, the liquid was poured into the column through only one point. Spray nozzle can be used to increase the efficiency of the bed. Airflow was being maintained at 15 l/minute. It can be changed to observe the effectiveness of airflow rate on the removal efficiency of ammonia. Diameter of column can also be changed.
- Only Sulfonile resin was used as ion exchange bed. Other cation exchanger can be used to compare the efficiency of different cation exchangers.
- The organisms responsible for nitrification are slow-growers and more sensitive to environmental factors than are those that remove BOD₅, so biological treatment of ammonia removal was not investigated in this study. Biological treatment for removal of ammonia can be studied.

BIBLIOGRAPHY

1. Agency for Toxic Substances and Disease Registry, (2004), "Toxicological profile for ammonia. Atlanta," GA: U.S. Department of Health and Human Services, Public Health Service.
2. AWWA, (1990), "Water Quality and Treatment," McGraw- Hill, New York.
3. Calvert, S., Goldschmid, J., Leith, D., and Mehta. D., (1972), "Wet Scrubber System Study," Vol. 1 Scrubber Handbook. EPA-R2-72-118a. U.S. Environmental Protection Agency.
4. Culp, L.; Wesner, George M; and Culp, L., (1978), "Handbook of Advanced Wastewater Treatment," 2nd ed. Van Nostrand Reinhold Co., NY.
5. DOE, (1997), "The Environment Conservation Rules" Department of Environment, Ministry of Environment and Forest, Government of the People's Republic of Bangladesh.
6. Downing, A. L. et al. (1964). "Nitrification in the activated sludge process." Journal, Institute of Sewage Purification.
7. Downing, A. L. and Knowles, G. (1966). "Population dynamics in biological treatment plants." 3rd International Conference on Water Pollution Control, Munich, Germany.
8. EPA (2001), "A Citizen's Guide to Air Stripping". United States Environmental Protection Emergency, Office of Solid Waste Response Agency (5102G), EPA 542-F-01-016.
9. Hoque, M. A. (2003), "A study on the effectiveness of activated alumina in removing arsenic from ground water." M.Sc. Engg. thesis submitted to the department of Civil Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka.
10. <http://en.wikipedia.org/wiki/Ammonia>, Ammonia.
11. <http://yosemite.epa.gov>, "Design Review of Absorbers Used for Gaseous Pollutants," North Carolina University Ralcligh, NC 27695.
12. Hug, (1999), "Fertilizer production and use in Bangladesh", www.fadinap.org

13. Huq M, Wheeler D, (1993), "Pollution reduction without formal regulation: Evidence from Bangladesh" Environment Department Divisional Working Paper #1993-3.
14. Islam F, Rumi S, Juhaina J, (1994), "Industrial Pollution in Bangladesh," www.worldbankgroup.org.
15. Jaeger Products, Inc., 1611 Peachleaf, Houston, TX 77039, jadmin@jaeger.com/1006foul.htm
16. Kavanaugh, M., and Trussell R. R., (1980), "Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water", Journal AWWA, December, pp. 684-692.
17. Khan, M.N.A., Datta, P., Dakua, A.S.M. S.I, (2002), "An assessment of Water Quality Deterioration of the River Kushiara due to Effluent Discharge from Natural Gas Fertilizer Factory", Fenchuganj, B.Sc. Engg. Thesis, CEE Dept, Shahjalal University of Science & Tech., Sylhet.
18. Linvil G. Rich, (2003) "Nitrification in aerated lagoons and with intermittent sand filters," Technical Note Number 6, Clemson University Clemson, SC 29634-0919 USA
19. Mahajan S P (1985), "Pollution Control in Process Industries", Tata McGraw-Hill Publishing Company Limited, New Delhi.
20. McCabe, W.L., Smith J.C., and Harriott P., (1993)." Unit Operations of Chemical Engineering", McGraw-Hill, New York.
21. Metcalf and Eddy, Inc (2005), "Wastewater Engineering Treatment and Reuse", 4th Edition, McGraw-Hill, New York.
22. Parker, D. S. (1975),"Process Design Manual for Nitrogen Control. Technology Transfer Manual", U. S. Environmental Protection Agency, Washington, DC.
23. Patterson, J., (1985). "Industrial Wastewater Treatment Technology", Butterworths, Boston, 2nd ed., Chap. 18.

24. Peter M., Chair V., John A., Robert W., Gene E., Pamela A., David W., William H., and David G., (1997), "Human Alteration of the Global Nitrogen Cycle: Causes and Consequences, Ecological Applications," www.esa.org.
25. Quality Criteria for Water, (1986) U.S. Environmental Protection Agency, EPA#440/5-86-001.
26. Rao, M.N. and Datta, A.K (2002), "Waste Water treatment" second edition, Oxford & IBH publishing Co Pvt. Ltd., New Delhi.
27. Treybal, R., (1980). "Mass-Transfer Operations". McGraw-Hill, New York, 3rd ed., pp. 275- 313.
28. USEPA (1973), "Nitrogen Removal by ammonia Stripping," EPA/670/2-73-040. US Environmental Protection Agency, Washington, DC.
29. Whitman, W., G. (1923). "The two-film theory of gas absorption". Chem. Metal. Eng. 29: 146-148.
30. Wikipedia, the free encyclopedia
31. World Bank. (1997), "Industrial Pollution in Bangladesh: A Detailed Analysis, Workshop Discussion Paper", the World Bank Dhaka Office.
32. [Www.fishdoc.co.uk](http://www.fishdoc.co.uk), Ammonia and water quality

APPENDIX-A
WATER AND WASTEWATER QUALITY

Table A-1 Wastewater Quality of NGFFL

Wastewater Parameters	Quality	March		July		October		December	
		Lagoon 1	Lagoon 2						
Temperature (°C)		30	31	33	32	30	31	26	25
pH		8.4	8.2	8.2	7.9	8.3	7.6	8.7	8.2
Dissolved Solids (mg/L)		1226	576	1178	732	1284	812	1456	832
Suspended Solids (mg/L)		458	524	950	745	598	456	445	526
Alkalinity (mg/L)		252	218	592	623	537	426	850	618
COD (mg/L)		28.6	24.3	46.5	35.6	34.3	30.5	42	38
BOD ₅ (mg/L)		6.7	4.5	5.8	6.9	6.4	5.6	8.4	7.0
Dissolved Oxygen (mg/L)		2.7	2.7	3.1	2.6	2.2	2.4	2.1	2.5
Oil and grease (mg/L)		36	44	55	43	56	40	28	45
Phosphate (mg/L)		0.98	0.08	0.75	0.12	0.28	0.075	1.23	.12
Sulfate (mg/L)		12.4	18.3	8.5	6.7	16.2	10.5	14.6	19.8
Chromium (mg/L)		0.156	0.012	0.098	0.01	0.12	0.018	0.143	0.014
Nitrate (mg/L)		8.2	5.2	7.5	4.5	10.5	14.2	15.2	9.5
Ammonia-N (mg/L)		131	1346	105	1428	170	1457	235	1710

- Experiments have been done in the Water Supply Engineering laboratory of Civil and Environmental Engineering at Shah Jalal University of Science and Technology, Sylhet

Table A-2 Seasonal variation of Ammonia –N of lagoon 1 and lagoon 2

Month	Lagoon 2		Lagoon 1
	Influent concentration		(mg/L)
	(mg/L)	Effluent Concentration	
January '04	86	92	576
February'04	86	73	610
March'04	295	206.5	740
April'04	277	314.7	913
May'04	175	175	1420
June'04	182	182.6	1320
July'04	3729.8	654.6	913
August'04	3486.2	228.3	1400
September'04	81	182	1420
October'04	99	202	1120
November'04	220	270	1063
December'04	280	780	1140
January'05	226	273	980
February'05	249.6	210	1350
March'05	265.0	459.9	1260
April'05	72.0	163.0	1340
May'05	304.0	105.0	1420
June'05	68.0	128.0	1450
July'05	49.0	96.0	1210
August'05	58.0	98.0	910
September'05	358.0	117.0	980
October'05	515.0	214.0	710
November'05	280.0	171.0	724
December'05	1131.0	180.0	782
January'06	452.0	452.0	810
February'06	304.0	208.0	792
March'06	955.0	182.0	810
April'06	304.0	226.0	1120

- Data have been collected from laboratory of NGFFL

Table A-3 Water Quality of Kushiara River at the 600 yards down stream

Month	pH	Temperature	Ammonia	Dissolved	Suspended	COD	Dissolved	Oil	BOD ₅
		(°C)	-	Solids (mg/L)	Solids (mg/L)	(mg/L)	Oxygen (mg/L)	and grease (mg/L)	
			Nitrogen (mg/L)						
January '04	7.6	20	-	210	60	16.2	8.0	-	2.3
February'04	7.7	23	-	125	40	14.7	8.0	-	2.6
March'04	7.6	24	-	140	40	14.7	7.0	-	1.8
April'04	7.65	28	-	130	800	12.6	6.3	-	1.3
May'04	7.6	26	-	310	1000	15.7	6.8	-	2.9
June'04	7.6	30	-	200	315	14.8	6.6	-	2.9
July'04	7.6	27	-	240	1050	15.10	5.6	-	1.8
August'04	7.6	29	-	190	450	18.0	6.9	-	1.3
September'04	7.6	27	-	240	800	20.9	6.6	-	1.5
October'04	7.6	27	-	95	800	11.6	6.9	-	1.27
November'04	7.7	26	-	290	110	15.9	8.0	-	1.01
December'04	7.8	20	Trace	190	60	8.08	8.06	-	1.37
January'05	7.6	20	-	200	160	11.5	8.06	-	2.35
February'05	7.8	23	-	210	50	27.5	8.07	-	2.02
March'05	7.8	23	Trace	190	130	12.0	7.84	-	1.8
April'05	7.8	29	-	140	220	21.42	7.00	-	1.6
May'05	7.8	29	-	110	120	25.7	6.47	-	1.49
June'05	7.8	29	-	170	310	19.5	6.47	-	0.99
July'05	7.8	27	-	185	380	9.3	7.46	-	1.23
August'05	7.7	30	-	200	700	11.42	6.09	-	2.78
September'05	7.85	29	-	160	215	12.5	8.0	-	2.35
October'05	7.8	29	-	200	520	13.63	7.63	-	1.52
November'05	7.9	27	-	120	250	18.35	8.04	-	2.33
December'05	7.9	26	-	70	45	13.11	7.83	-	2.5
January'06	7.5	23	-	280	50	15.3	8.3	-	1.5
February'06	7.9	26	-	110	50	19.2	8.89	-	1.78
March'06	8.0	29	-	120	80	15.36	8.0	-	1.79
April'06	7.9	27	-	170	210	11.65	7.0	-	1.34

- Data have been collected from laboratory of NGFFL

Table A-4: Concentration of ammonia at the up stream and down stream of River Kushiara (December, 2005):

Sampling points	pH	NH ₃ -N (mg/L)
Sampling point 1 (U/S)	7.5	0.03
Sampling point 2 (Discharging point)	7.8	12.7
Sampling point 3 (App.300 yards d/s)	7.2	0.44
Sampling point 4 (App.600 yards d/s)	7.4	0.38
Sampling point 5 (App.900 yards d/s)	7.3	0.34
Sampling point 6 (App.1200 yards d/s)	7.4	0.26
Sampling point 7 (App.1500 yards d/s)	7.3	0.18

- Experiments have been done in the Water Supply Engineering laboratory of Civil and Environmental Engineering at Shah Jalal University of Science and Technology, Sylhet



APPENDIX-B

REMOVAL OF AMMONIA

Table B-1: Lagooning after controlling of pH (at pH 11.0)

Time (day)	Inner side was covered by soil	Inner side was uncovered by soil
	(mg/L)	(mg/L)
0	992	992
1	369	409
2	297.6	326
3	243.25	260
5	172.75	198
7	121	148
10	98	113
15	58	98
32	8	14
35	2	8

Table B-2: Aeration Experiment

Time (Minute)	Concentration of Ammonia-N (mg/L)	Concentration of Ammonia-N (mg/L)	Concentration of Ammonia-N (mg/L)	Concentration of Ammonia-N (mg/L)
	at pH 11.5 (Volume of sample is 200 ml)	at pH 8.1 (Volume of sample is 200 ml)	at pH 11.5 (Volume of sample is 350 ml)	at pH 11.5 (Volume of sample is 750 ml)
0	1008	1177	1148	958
30	612	905	802	786
80	267.9	775	575	698
125	137	664	398	557
150	80.2	578	284	426
180	40.9	525	206	378
205	26.1	498	156	298
230	11.325	452	98	212
260	6.525	412	64	145
300	3.125	387	38	112

Table B-3: Effect of pH on air stripping unit

	Concentration	Coal chips	Plastic ring	Stone chips	Wood chips
	Initial (mg/L)	1429	1574	1328	1368
pH 10.5		174	132	196	212
pH 11.5	Final (mg/L)	158	92	175	187
pH 12.0		165	105	162	172

Table B-4: Effect of influent concentration on air stripping unit

Coal chips		Plastic ring		Stone chips		Wood chips	
Initial Concentration (mg/L)	Final Concentration (mg/L)						
1429	174	1574	132	1328	196	1368	212
708	72	752	72	654	82	682	97
348	48	368	28	325	38	356	42
169	17	178	15	164	24	168	22
85	7	87	8	80	16	86	14



Table B-5: Effect of packing height and air to water flow ratio on air stripping unit at pH 10.5

Experiment No	NH ₃ -N (mg/L)	Air/liquid ratio	Packing materials	Height of the packing (ft)	Effluent concentration (mg/L)
1	1437	2000	Coal	1	562
2	1435	2000	Coal	2	426
3	1434	2000	Coal	3	302
4	1433	2000	Coal	4	216
5	1429	2000	Coal	5	174
6	1435	1750	Coal	5	256
7	1426	1500	Coal	5	312
8	1421	1250	Coal	5	386
9	1571	2000	Plastic ring	1	572
10	1568	2000	Plastic ring	2	386
11	1563	2000	Plastic ring	3	258
12	1573	2000	Plastic ring	4	178
13	1574	2000	Plastic ring	5	132
14	1538	1750	Plastic ring	5	176
15	1535	1500	Plastic ring	5	234
16	1521	1250	Plastic ring	5	324
17	1342	2000	Stone chips	1	527
18	1338	2000	Stone chips	2	436
19	1335	2000	Stone chips	3	336
20	1332	2000	Stone chips	4	236
21	1328	2000	Stone chips	5	196
22	1316	1750	Stone chips	5	256
23	1326	1500	Stone chips	5	312
24	1332	1250	Stone chips	5	398
25	1385	2000	Wood chips	1	548
26	1378	2000	Wood chips	2	425
27	1385	2000	Wood chips	3	328
28	1372	2000	Wood chips	4	256
29	1368	2000	Wood chips	5	212
30	1354	1750	Wood chips	5	281
31	1364	1500	Wood chips	5	342
32	1350	1250	Wood chips	5	412

Table B-6: Comparison between predicted effluent concentration and effluent concentration by laboratory experiment

	Stripping constant	Initial concentration (mg/L)	Final concentration by experiment (mg/L)	Final concentration by Empirical formula (mg/L)
Coal	0.001	1429	174	193.39
		708	72	95.82
		348	48	47.10
		169	17	22.87
		85	7	11.50
Plastic Ring	0.0014	1574	132	95.72
		752	72	45.73
		368	28	22.38
		178	15	10.83
		87	8	5.29
Stone chips	0.001	1328	196	179.73
		654	82	88.51
		325	38	43.98
		164	24	22.19
		80	16	10.83
Wood chips	0.0009	1368	212	226.13
		682	97	112.73
		356	42	58.85
		168	22	27.77
		86	14	14.22

Table B-7: Ion exchange Experiment (Resin bed volume is 30 cc)

Influent Ammonia-Nitrogen concentration, mg/ml	Volume (ml), ΣQ	Resin bed Volume, cc V	Bed Volume $\Sigma Q/V$	Effluent Ammonia-Nitrogen concentration mg/ml
0.892	10	30	0.33	0.076
0.892	20	30	0.67	0.187
0.892	30	30	1	0.298
0.892	40	30	1.33	0.406
0.892	50	30	1.67	0.476
0.892	60	30	2	0.522
0.892	70	30	2.33	0.608
0.892	80	30	2.67	0.654
0.892	90	30	3	0.698
0.892	100	30	3.33	0.767
0.892	110	30	3.67	0.822
0.892	120	30	4	0.872

Table B-8: Ion exchange Experiment (Resin bed volume is 50 cc)

Influent Ammonia-Nitrogen concentration, mg/ml	Volume (ml), ΣQ	Resin bed Volume, ml V	Bed Volume $\Sigma Q/V$	Effluent Ammonia-Nitrogen concentration mg/ml
0.892	10	50	0.2	0.035
0.892	20	50	0.4	0.112
0.892	30	50	0.6	0.214
0.892	40	50	0.8	0.278
0.892	50	50	1	0.336
0.892	60	50	1.2	0.392
0.892	70	50	1.4	0.432
0.892	80	50	1.6	0.463
0.892	90	50	1.8	0.488
0.892	100	50	2	0.502
0.892	110	50	2.2	0.525
0.892	120	50	2.4	0.557

Table B-9: Ion exchange Experiment (Efficiency of the resin bed)

Influent Ammonia-Nitrogen concentration, mg/l	Resin bed Volume, ml V	Area under curve (mg)	Effluent volume upto MCL, ml	Avg. Effluent ammonia-nitrogen concentration, mg/l	Unit wt of the resin gm/cc	Exchanged ammonium ion by the resin mg/gm	Efficiency of resin
892	30	0.5472	11.9	45.98319	.65	0.516287	0.948449
892	50	0.8182	19.53	41.89452	.65	0.510848	0.953033

- Area under curve (mg) where effluent ammonia-N concentration is below MCL is obtained from cumulative effluent volume of wastewater vs. effluent concentration of ammonia-N
- Average effluent ammonia-N concentration (mg/L) = Area under curve/Effluent volume upto MCL
- Efficiency of the bed (%) = (Influent ammonia-N conc.- Avg. effluent ammonia-N concentration) / Influent ammonia-N concentration
- Bed Volume (BV) = Effluent volume upto MCL / Resin bed volume

