Biological and Chemical Treatment of Water for Combating Ammonia: An Integrated Approach

A Thesis submitted in the partial fulfillment of the requirements for the award of the degree

of

DOCTOR OF PHILOSOPHY

by

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(2K17/PhD/AC/15)

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DECLARATION

This is to certify that the Ph.D. thesis entitled "**Biological and Chemical Treatment of Water for Combating Ammonia: An Integrated Approach**" submitted to Delhi Technological University, Delhi, for the award of Doctor of Philosophy is based on the original research work carried out by me under the supervision of **Dr. Raminder Kaur**, Department of Applied Chemistry and co-supervision of **Prof. Jai Gopal Sharma,** Department of Biotechnology, Delhi Technological University, Delhi, India. It is further certified that the work embodied in this thesis has neither partially nor fully been submitted to any other University or Institution to award any degree or diploma.

Place: Delhi, India
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CERTIFICATE

This is to certify that the thesis entitled "**Biological and Chemical Treatment of Water for Combating Ammonia: An Integrated Approach**" by **Mr. Lokesh Kumar (Roll No: 2K17/Ph.D./AC/15)** in fulfillment of the requirements for the award of the degree of **Doctor of Philosophy**, is an authentic record of student's work carried by him under the supervision of **Dr. Raminder Kaur**, Assistant Professor, Department of Applied Chemistry, Delhi Technological University, Delhi and **Prof. Jai Gopal Sharma**, Professor, Department of Biotechnology, Delhi Technological University, Delhi.

This is also certified that the work embodied in this thesis has neither partially nor fully been submitted to any other Institute or University for the award of any other diploma or degree.

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ABSTRACT

Ammonia pollution in water has become a significant concern for environmentalists, chemists, and biologists due to the health hazards. The elevated nitrogen concentrations in the surface waters have primarily resulted from modern agricultural practices, mainly due to nitrogen fertilizers. However, the nitrogen discharge from the point sources, such as sewage treatment plants and industries, also contributes significantly to riverine nitrogen loading. Ammonia exists in the water in both organic and inorganic nitrogen. Organic nitrogen (ON) includes a wide variety of compounds; derived from natural and anthropogenic sources. The natural sources are principally nitrogenous end products of biological metabolism. Agricultural fertilizers also aid in the anthropogenic cause of organic nitrogen. Many bacteria, such as species of *Nitrosomonas*, possess the enzyme urease, which catalyzes the conversion of urea to inorganic nitrogen (IN) forms, like Ammonia (NH_3) or ammonium ion (NH_4^+), that further oxidize to nitrite by the process of nitrification. The wastewater rich in ammonia nitrogen harms the environment significantly, as the ammonia nitrogen may inhibit natural nitrification, cause water hypoxia, result in fish poisoning, and decrease the water purification capacity.

Removal of ammonia-nitrogen from water and wastewater is crucial for water and wastewater treatment operators because it produces potential carcinogenic disinfection by-products when contacting disinfecting agent chlorine. Disinfection by-products (DBPs), in addition to their likely carcinogenic nature, have an objectionable odor in drinking water, such as that of aldehydes and N-chloramines. When chlorine gas is added to water for disinfection, nitrogenous compounds convert to chloramines and are available in water in the form of combined chlorine. The formation of organic chloramines has increased chlorine demand in water and reduced the germicidal efficiency of chlorine and inorganic monochloramines. Organic chloramine includes the species of N-chloramines, N-chloramino acids, N-chloraldimines and N-chloramides. Thus, water treatment utilities must have raw water quality that does not have ammonia-nitrogen contamination.

Appropriate technology is necessary to accelerate nitrification by which ammonia-nitrogen can be converted to stable compound/s such that its adverse effects can be neutralized. This research focuses on the removal of ammonia-nitrogen from water and wastewater. The present study is based on treating two types of water. i.e., one of the Yamuna river water and second municipally treated sewage effluent. Yamuna river water has less ammonia than the municipally treated sewage effluent. The municipally treated sewage effluent (MTSE) samples were treated with cow dung sludge, *yucca* extract, and specific zeolites. Though, the

Yamuna river water samples were treated with zeolites only. A Jar Test Apparatus was used throughout the research experiments performed. The initial quality parameters of ammonia-nitrogen, nitrite, and nitrate were determined before the experiment. Three types of zeolites were utilized in the ammonia-nitrogen treatment of MTSE samples and the Yamuna river water samples. Studies were also performed with synthetically prepared standard ammonium chloride water. Results showed that ammonia-nitrogen was significantly removed and converted to nitrate using cow dung sludge. MTSE samples had an initial ammonia nitrogen content of 34.78 mg/L when treated with 0.0 g/L (Control Sample), 1 g/L, 5 g/L (cow dung), and 100 mg/L, 500 mg/L (*Yucca* extract), respectively, reported conversion to 0.00, 0.00, 0.00, 0.00, 0.88 mg/L ammonia as-N; 17.8, 0.18, 0.09, 18.65, 18.85 mg/L nitrite as-Nand 21.8, 110.1, 133.5, 20.5, 20.8 mg/L nitrate as-NO_3 respectively. It was found that digested cow dung acted catalytically in eliminating the ammonia nitrogen by converting it to nitrate in a short period of nearly eight days, leading to almost 100 % ammonia conversion. However, the *yucca* (plant) extract could not remove/ convert ammonia-nitrogen to any significant value. Based on the experimental results with cow dung sludge, a layout plan for the tertiary treatment of sewage effluents has been proposed in this thesis.

All zeolites were observed to significantly treat ammonia-nitrogen in synthetically prepared ammonium chloride water without having competing ions interference. The sorption capacity of synthetic zeolite 4A was observed as 4.21, 7.68, 9.67, and 11.76 mg/g with 5.0, 10.0, 15.0, 20.0, and 30.0 mg/L ammonia nitrogen synthetic water. The ammonia nitrogen sorption with Clinoptilolite was observed as 3.82, 5.03, 7.09, 7.74, and 10.92 with 5.0, 10.0, 15.0, 20.0, and 30.0 mg/L ammonia nitrogen synthetic water. The removal capacity of Mordenite was found as 4.56, 5.24, 7.20, 8.29, and 9.85 mg/g with 5.0, 10.0, 15.0, 20.0, and 30.0 mg/L ammonia nitrogen synthetic water. However, because competing ions interfere in natural water, their use limits ammonium ions removal. In the case of the Yamuna-river water, ammonia sorption capacity and uptake (%) were observed with clinoptilolite as 0.212 mg/g and 23.24 % with an initial amount of 0.912 mg/L NH3-N and with mordenite zeolites as 0.42 mg/g and 37.5 % with an initial amount of 1.12 mg/L NH_3-N. On the other side, when MTSE samples were treated with zeolites, sorption capacity and uptake (%) were observed. It was observed that with synthetic zeolites, sorption was 5.41 mg/g and uptake was 13.78 %; with clinoptilolite, sorption was 5.19 mg/g and uptake was 13.21 %, and with mordenite zeolites, sorption was 6.46 mg/g, and uptake was 16.45 % with an initial amount of 39.26 mg/L NH_3-N. Based on the present study outcomes, this thesis suggested replacing sand media from Rapid Sand Filters and Slow Sand Filters with Mordenite and Clinoptilolite.

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List of Abbreviations

MTSE	Municipally Treated Sewage Effluent
DNA	Deoxyribonucleic acid
RNA	Ribonucleic acid
AN	Ammonia Nitrogen
BOD	Biological Oxygen Demand
cBOD	Carbon Based BOD
TKN	TatalKjeldahl Nitrogen
NDMA	N-Nitrosodimethylamine
DMA	Dimethylamine
DMCA	Dimethylchloramine
UDMH	Unsymmetrical Dimethylhydrazine
HOCl	Hypochlorous Acid
DBP	Disinfection By-Products
THM	Trihalomethanes
HAA	Haloacetic Acid
HAM	Haloacetamide
DON	Dissolved Organic Nitrogen
DOC	Dissolved Organic Carbon
CHO	Chinese Hamster Ovary
MCRT	Mean Cell Residence Time
SRT	Solid Retention Time
DO	Dissolved Oxygen
IX	Ion Exchange
TMT	Tetramethyltetrazene
FDMH	Formaldehyde dimethyl hydrazone

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1. AMMONIA-NITROGEN POLLUTION IN WATER

Ammonia pollution in water has become a significant concern for Environmentalists, Chemists, and Biologists. Since the early stage of human development, scientists have been keen to research its mitigation measures. An elevated concentration of ammonia-nitrogen concentrations in surface waters concerns modem agricultural practices, particularly nitrogen fertilizers. However, ammonia-nitrogen discharged from point sources and sewage treatment plants significantly increases riverine nitrogen loading. Ammonia exists in water in the form of organic, inorganic nitrogen. Organic nitrogen (ON) includes sewage discharged from municipalities and other anthropogenic sources. The ammonia sources are principally the results of biological metabolism and agricultural fertilizers. Ammonia (NH_3) is a moiety composed of hydrogen nitrogen. It is a pollutant in water in the binary form of ammonium ion (NH_4^+) free ammonia (NH_3), depending on the pH and temperature of the water. Ammonia nitrogen refers to the combined, non-ionized form (NH_3) and the ammonium cation (NH_4^+). Ammonia (NH_3) is an aromatic gaseous, colorless compound soluble in water. Its water solubility is 421 g/liter at 20°C and 706 g/liter at 0°C (Ammonia in Drinking-water, 1996). In water, ammonia changes into ammonium ions (NH_4^+). An ion is a molecule or atom with an electric charge over it by losing or gaining one or more electrons (Equation 1).

$$NH_3 + H_2O \longleftrightarrow NH_4OH \longleftrightarrow NH_4^+ + OH^- \qquad \text{-------(1)}$$

Ammonia is necessary for the formation of DNA, RNA, and proteins. It also plays a crucial role in maintaining the acid-base balance required for the development of the tissues of mammals. It is produced in the human body when food containing protein is broken down into amino acids ammonia, converting it into urea. (Agency for Toxic Substances Disease Registry, 2004). Ammonia in natural water is not directly concerned with human health, but its presence indicates fecal contamination for waterworks operators. Bacteria oxidize ammonia to nitrite (NO_2), and further to nitrate (NO_3) forms in the presence of dissolved oxygen in the water. Unionized ammonia is a toxic compound among the inorganic nitrogenous compounds (NO_2^-, HNO_2, NO_3^-, NH_4^+, and NH_3); aquatic animals can take up directly from ambient water. Ammonium nitrate ions are the least harmful (Camargo and Alonso, 2006).

1.1 SOURCES OF AMMONIA NITROGEN IN THE WATER

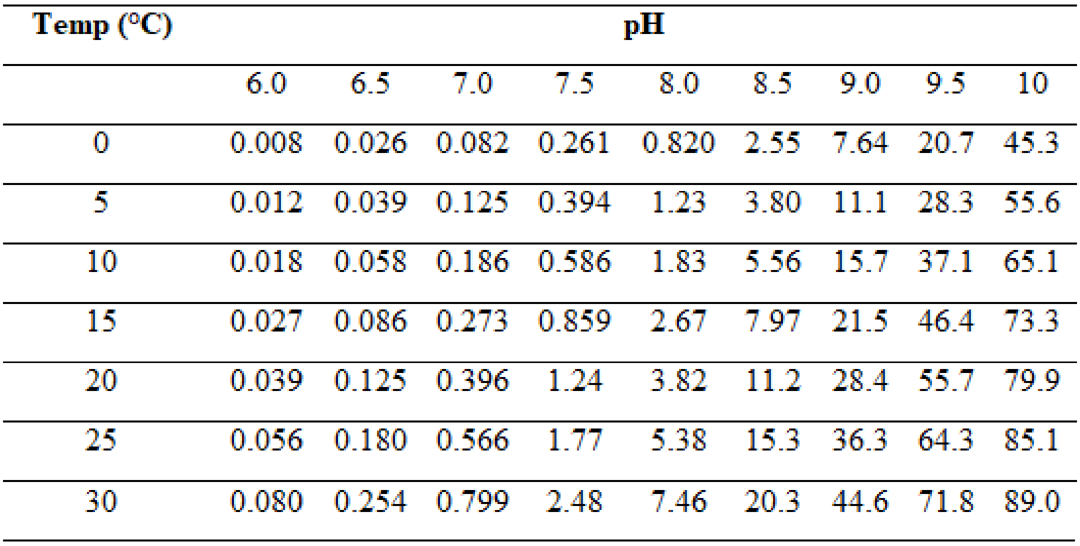
The presence of ammonia nitrogen in natural waters can be because of the intrusion of one or more following pollutant sources into water resources:

- Sewage or fecal matter is drained directly from human residential colonies or discharged from municipal sewage disposal works after partial or secondary treatment.
- Industrial effluents are discharged from leather, pesticide, fertilizer, distillery, and other industries.
- Municipal solid waste disposal leachate.
- Agricultural runoff.

1.2 FORMS OF AMMONIA NITROGEN IN THE WATER

Nitrogen in the form of an unionized or free form (NH_3) ionized form (NH_4^+) is collectively known as ammonia nitrogen (AN). Wastewater contains nitrogen in the form of inorganic ammonium nitrogen organic nitrogen. Ammonia nitrogen can be present in gaseous NH_3 ionic form NH_4^+ (Table 1), depending on the temperature and pH of the water. Organically bonded nitrogen, such as that found in proteins and urea, as well as the breakdown products of amino acids, DNA, peptides, uric acids, enzymes, certain lipids, etc., are all examples of organic ammonia nitrogen.(Eckenfelder et al., 1985). Proteins are a long chain of amino acids. Proteins are broken down into individual amino acids. These organic forms of nitrogen are being converted in the wastewater treatment process. Oxidized forms of inorganic Nitrogen (IN), viz. nitrite (NO_2^-) nitrate (NO_3^-), are the breakdown products of ammonia nitrogen, which ultimately end up getting converted to nitrogen gas released back into the atmosphere.

Table 1: Percent of un-ionized ammonia of ammonia nitrogen present in water for 0 - 30 °C pH 6-10 (Emerson et al., 1975)



Temp (°C)	pH								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10
0	0.008	0.026	0.082	0.261	0.820	2.55	7.64	20.7	45.3
5	0.012	0.039	0.125	0.394	1.23	3.80	11.1	28.3	55.6
10	0.018	0.058	0.186	0.586	1.83	5.56	15.7	37.1	65.1
15	0.027	0.086	0.273	0.859	2.67	7.97	21.5	46.4	73.3
20	0.039	0.125	0.396	1.24	3.82	11.2	28.4	55.7	79.9
25	0.056	0.180	0.566	1.77	5.38	15.3	36.3	64.3	85.1
30	0.080	0.254	0.799	2.48	7.46	20.3	44.6	71.8	89.0

The following are the types of nitrogen found in wastewater:

•Organic Nitrogen-Bound in BOD

•Ammonia Nitrogen-NH_4^+ or NH_3

•Nitrogen Gas-N_{2-}

•Nitrite-NO_2^-

•Nitrate-NO_3^-

• TKN(Total Kjeldahl Nitrogen) -Organic N + ammonia

Nitrogen bound in the amino acids primarily gets released and becomes part of the nitrification process. Some organic nitrogen is never released and goes right through the plant, never leaving its organic form. A nitrogen cycle is shown in Figure 1(Huma & Reserved, 2016).

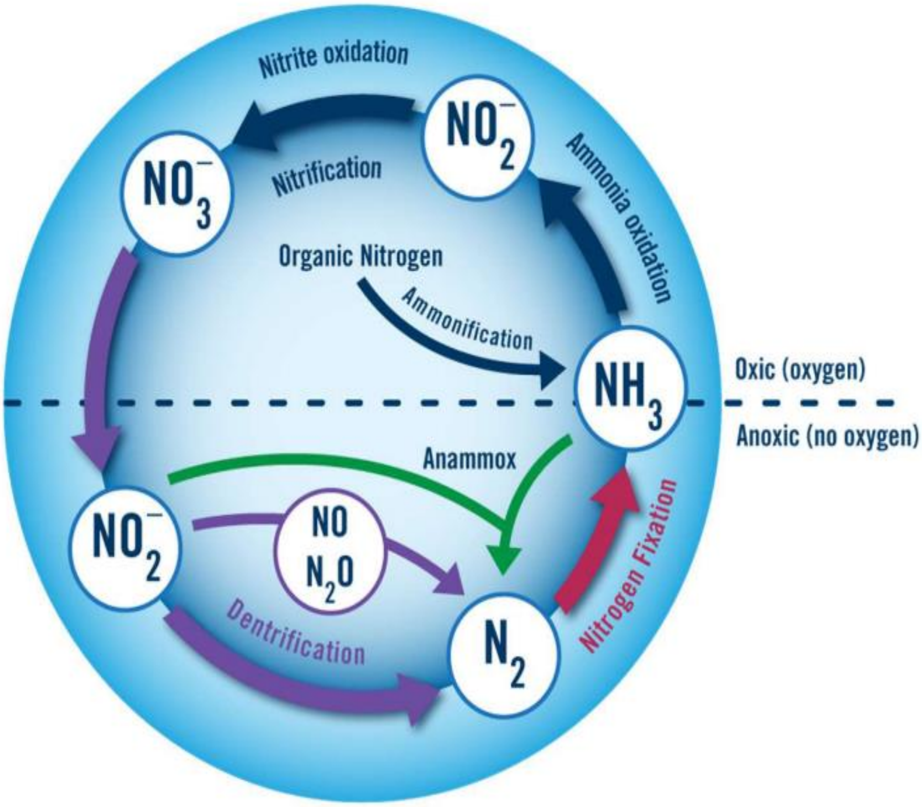


Figure 1: Nitrogen Cycle

The presently available treatment techniques for wastewater, for the removal of ammonia nitrogen, are either highly costly, require a long-time period, or/ cover a large area. Most sewage treatment plants in developing countries are limited to secondary treatment only. A secondary treated sewage effluent contains a substantial amount of ammonia nitrogen, especially in the activated sludge process plants. Disposing wastewater effluent polluted with ammonia-nitrogen into riverine water resources causes significant deterioration of river water quality. Besides, treating the sewage effluent with chlorine gas at municipal waterworks leads to many potentially carcinogenic disinfection by-products. N-Nitrosodimethylamine (NDMA), a potentially cancer-causing disinfection byproduct, can develop when ammonia nitrogen is present (Mitch and Sedlak, 2002). Thus, removing ammonia nitrogen from municipal and industrial wastewater before being discharged is of utmost importance. It is a prime necessity that a cost-effective, simple-to-use technique should be made available to remove ammonia from the vast masses of wastewater, like, in municipal sewage treatment plants, wherein a million gallons of sewage are treated daily.

1.3 BIOLOGICAL NITROGEN CONVERSION

20 to 85 mg/L of total nitrogen, made up of organic nitrogen, ammonia, nitrite, and nitrate-nitrogen, contains 8 to 35 mg/L of organic nitrogen, and 12 to 50 mg/L of ammonia-nitrogen is present in raw home wastewater. About 30 to 40 percent of the organic nitrogen may still be present, with 60 to 70 percent arriving as ammonia or ammonium. We calculate the Total Kjeldahl Nitrogen (TKN) of the influent wastewater as the amount of organic nitrogen or ammonia. (MUNICIPAL Wastewater Treatment Plant Operation, 2008). Bacterial growth is the initial method of nitrogen removal in wastewater. Because it is a component of proteins, amino acids, DNA, certain lipids, etc., nitrogen is incorporated into the structure of cells. The ammonification and nitrification of waste in the water are seen in Figure 2. The general molecular formula for biomass, C5H7O2N, is given in equation 2 and
includes nitrogen (Gerardi, 2002)

$$C_{18}H_{19}O_9N + 0.74NH_4^+ + 8O_2 \rightarrow 1.74C_5H_7O_2N + 9.3CO_2 + 0.74H^+ + 4.52H_2O \qquad \text{---------(2)}$$

Water makes up about 80% of bacteria, while dry stuff makes up 20%. Ninety percent of the dry weight is organic, and the remaining ten percent is inorganic. As can be seen from stoichiometry equations 3, 4, and 5, significant amounts of oxygen are consumed during the oxidation of ammonia by nitrifying bacteria (Gray, 2004). Figure 2 depicts the biological nitrogen conversion of ammonia nitrogen (*The Wastewater Blog*, 2017).

$$2NH_4 + 3O_2 \xrightarrow{\textit{Nitrosomonas}} 2NO_2 + 4H^+ + 2H_2O + \text{Energy} \qquad \text{------(3)}$$

$$2NO_2 + O_2 \xrightarrow{\textit{Nitrobactor}} 2NO_3 + \text{Energy} \qquad \text{------ (4)}$$

The overall reaction:

$$NH_4 + 2O_2 \longrightarrow NO_3 + 2H + H_2O + \text{Energy} \qquad \text{--------(5)}$$

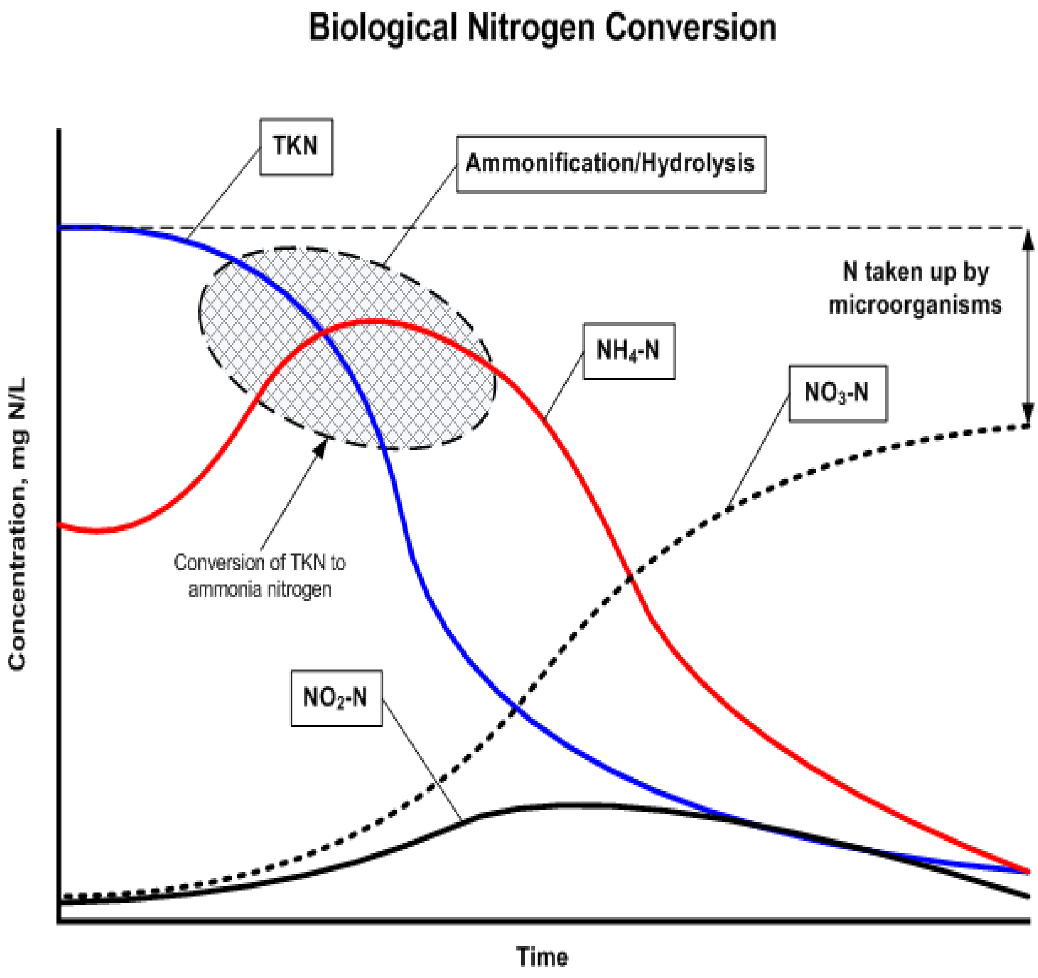


Figure 2: Biological Nitrogen Conversion

1.4 WATER TREATMENT TECHNOLOGIES FOR COMBATING AMMONIA NITROGEN

There are many methods for removing ammonia-nitrogen from water and wastewater. Some of the processes are biological, chemical, thermochemical, and electrochemical. However, biological and chemical processes/ methods are generally feasible.

1.4.1BIOLOGICAL METHODS

Biological methods are the types of wastewater treatment methods by which living organisms (micro-organism-bacterial mass Phyto-micro-organisms-algae) are being used to combat ammonia, nitrogen, and other pollutants. Two types of biological methods are:

i. Biological nitrification Denitrification
ii. Algae Ponds

1.4.1.1BIOLOGICAL NITRIFICATION-DENITRIFICATION

By using bacterial growth, nitrification-denitrification is a method of treating wastewater. Because nitrogen is a component of proteins, amino acids, DNA, certain lipids, etc., it is incorporated into the structure of cells. The general molecular formula of biomass is C5H7O2N, and nitrogen is a component of that formula. The bacteria can use the ammonium in the wastewater to obtain the nitrogen they require to develop. The mole mass calculation reveals that 14 grams of nitrogen are needed to produce 113 grams of biomass. The aerobic process of converting ammonia to nitrate is known as nitrification. Two distinct species carry out the two-step oxidation process known as nitrification (equations 6, 7, and 8, respectively).

- **Nitrification:**

Ammonia-oxidizing bacteria (AOB):

$$NH_3 + O_2 + 2e^- + 2H^+ \rightarrow NH_2OH + H_2O \qquad \text{----------(6)}$$

$$NH_2OH + H_2O + \tfrac{1}{2} O_2 \rightarrow NO_2^- + 2H_2O + H^+ \qquad \text{----------(7)}$$

Nitrite-oxidizing bacteria (NOB):

$$NO_2^- + \tfrac{1}{2} O_2 \rightarrow NO_3^- \qquad \text{-----------(8)}$$

- **Denitrification:**

In the denitrification process, nitrate ions and nitrite ions are used by facultative anaerobes to degrade carbon-based Biochemical Oxygen Demand (cBOD) in anoxic conditions (equation 9).

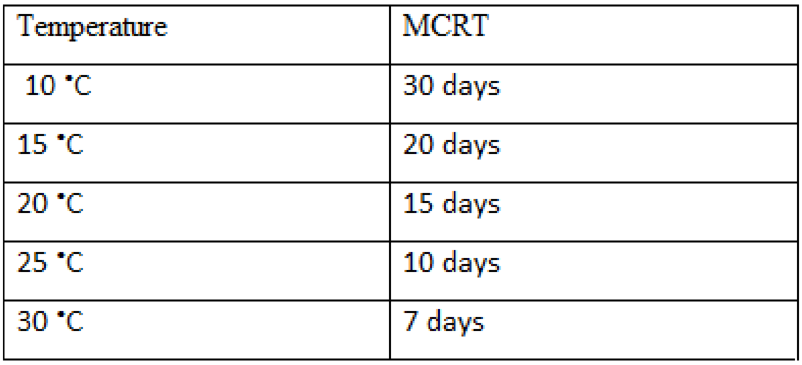
$$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2\,(g) \qquad \text{----------(9)}$$

Nitrosomonas species do the ammonium oxidation to nitrite. Nitrobacter species perform the oxidation of nitrite into nitrate. These organisms are Chemo-Litho-autotrophic organisms. The growth rate for Nitrosomonas is 8 to 10 times faster than that of Nitrobacter. Nitrosomonas are spherical shapes that are of the size of 0.5 to 1,5 µ. It reproduces by binary fission. Nitrobacter is rod-shaped bacteria with a size range from 0.5 to 1.0 µ. Nitrobacter reproduces by budding. Nitrification and denitrification processes depend on the quality of wastewater effluent. Mean Cell Residence Time (MCRT), also known as Solids Retention Time, Mean Cell Alkalinity, Temperature, Dissolved Oxygen, and pH are critical operating factors (SRT). The average number of days that suspended particles are retained in a biological wastewater treatment system is known as the MCRT. The optimum values are as follows:

i. pH value: 7.0 to 8.5
ii. Residual Alkalinity :> 50 mg/L
iii. Dissolved Oxygen :> 2.0 mg/L (at peak loading)
iv. Temperature: 28 °C to 32 °C
v. MCRT: at least four days, preferably > 10 days

At 16 °C, it becomes 50 % rate to that of at 30 °C at 10 °C, approximately 20 % to that of at 30 °C. A relationship between the effect of temperature and MCRT is shown in Table 2(Gerardi, 2002).

Table 2: Tentative co-relation between Temperature MCRT



Temperature	MCRT
10 °C	30 days
15 °C	20 days
20 °C	15 days
25 °C	10 days
30 °C	7 days

To nitrify, BOD. (Biological Oxygen Dem) level in the wastewater needs to be between 20-30 mg/L. Nitrifiers are autotrophs using carbon-di-oxide inorganic carbon for the synthesis of cellular materials. Nitrosomonas Nitrobacter are autotrophic bacteria. Conversely, heterotrophic bacteria classes are Floc Forming bacteria, Filamentous bacteria, Aerobic bacteria, Anaerobic bacteria, Poly-B bacteria, and Facultative bacteria. Heterotrophic bacteria use organic compounds as energy and carbon sources to carry out their life cycles. They remove BOD.

1.4.1.1.1 MERITS OF NITRIFICATION DENITRIFICATION TECHNIQUE

1) Nitrification Denitrification is a chemical-free process of removing ammonia nitrogen from wastewater.
2) It does not require a vast l area to establish its treatment plant compared to algae ponds.
3) It is most effective in treating wastewater for combating nitrogenous pollution in a short period if optimum operating temperature and other conditions are maintained.

1.4.1.1.2DE-MERITSOF NITRIFICATIONDENITRIFICATION TECHNIQUE

1) Nitrification inhibits if the pH value of effluent falls <6.7
2) Inadequate effluent alkalinity <50 mg/L leads to stopping nitrification.
3) The nitrification process ceases if the effluent temperature exceeds 45˚C falls below 5 ˚C.
4) Nitrifiers have a low reproductive rate, so a high MCRT is required for nitrification.
5) In the case of Denitrification, dissolved oxygen (DO) is maintained below 0.3 mg/L in an anoxic zone; as DO increases, the denitrification rate decreases.

1.4.1.2 ALGAE PONDS

Algae ponds are enormous ponds of water spread on a large surface area of land. These ponds can be suitable for wastewater treatment, mostly sewage water. Algae are grown over the water's surface so that algae can utilize ammoniacal nitrogen in their growth. Scotland built the first municipal water treatment plant in the year 1800. Since then, algae ponds have been established worldwide to treat municipal sewage(Mohsenpour et al., 2021).In comparison to the chemical methods, which are typically too expensive to be used in most regions and may cause secondary pollution, the biological tertiary treatment technique seems to function better (Abdel-Raouf et al., 2012). Algae produced in water having nitrogenous pollutants utilize N from a variety of inorganic (e.g., NO_3^-, NO_2^-, and NH_4^+) organic sources (e.g., amino acids, urea, purines, nucleosides)(Cai et al., 2013; Ross et al., 2018). Algae primarily use carbon dioxide to grow in water, employing light energy as a substrate and chlorophyll-a as a necessary catalytic agent to convert CO_2 to organic carbon, symbolized by $(CH_2O)n$. (Equations 10 and 11).

$$nCO_2 + nH_2O \xrightarrow{\text{Chlorophyll-a}} (CH_2O)_n + nO_2 \quad \text{------------} (10)$$

$$CO_2 + H_2O \rightarrow (HCO)_3^- + CO_3^{2-} \quad \text{----------} (11)$$

Algae biomass constitutes carotenoids, carbohydrates, lipids, protein, and vitamins. Algae can result in raising the pH value of ponds above 10. The rapid photosynthesis of pond algae, which absorbs CO2 faster than it can be supplied by bacterial respiration, causes ponds to have a high pH value (above 9). Equations 12 and 13 show how bicarbonate and carbonate ions separate, respectively:

$$2(HCO)_3^- \rightarrow CO_3^{2-} + H_2O + CO_2 \quad \text{----------------} (12)$$

$$CO_3^{2-} + H_2O \rightarrow 2OH^- + CO_2 \quad \text{----------------} (13)$$

Ammonia nitrogen in the form of NH_4^+ion and the formation of nitrate NO_3^- ion is utilized in the biosynthesis of algae (Equations 14 and15, respectively) with the following stoichiometric relationships(Stumm Morgan, 1996):

$$16NH_4^+ + 92CO_2 + HPO_4^{2-} + 92H_2O + 18HCO_3^- \rightarrow C_{106}H_{263}O_{110}N_{16}P + 106O_2 \quad \text{--------} (14)$$

$$16NO_3^+ + 124CO_2 + HPO_4^{2-} + 140\,H_2O \rightarrow \underset{\text{(Algae)}}{C_{106}H_{263}O_{110}N_{16}P} + 138O_2 + 18HCO_3^- \quad \text{-----}(15)$$

Most algae have a range of temperatures. They prefer to grow in some temperate regions. We can see the seasonal succession of algae; for example, green algae are seen when the weather is cold or just starting to warm up in spring. The temperature increases as the season progress to summer, and we see more cyanobacteria. As algae begin to die off in fall, the temperature decreases again, and we may see the population shift back to green algae or diatoms, or a mixture of all these algae. Different algae species up-take nutrients differently at different rates. Some thrive better in some conditions than others.

Over 3,000 years have passed since wastewater was first treated using algae ponds. In 1901, an algal pond system was initially built in the United States in San Antonio, Texas(EPA, 1978, 1973, 1971). Algae ponds have been an essential part of all villages in India since ancient times. Some common algae in wastewater lagoons are *Desmodesmus, Schroederia, Oocystis, Dictyosphaerium, and Chlorella-like*. Algae can be multi-cellular, single-cell, motile, and immotile. Blue-green and green algae, among others, flourish in wastewater treatment ponds. When pond conditions and treatment are ideal, green algae, which give ponds their green hue, predominate. Inadequate pond conditions, such as low dissolved oxygen (DO), high organic loading, warm water temperatures, and insufficient nutrients, are indicated by blue-green algae, which are filamentous. They frequently create obnoxious, smelly carpets. Chlorella, Scenedesmus, Euglena, Chlamydomonas, Actinastrum, and Pedeiastrum are some common green algae types. Green algae that move around suggest a healthy pond that remains close to the surface. Green algae are often found in high-pH, nutrient-rich waste. The treatment pond contains a common species of chlorella.

Blue-green algae are autotrophic organisms that primarily use CO_2 as a carbon source for synthesizing chemical molecules. As a byproduct of photosynthesis, cyanobacteria produce O_2, which serves as a source of oxygen for other pond organisms. Cyanobacteria are found in vast numbers as blooms when environmental conditions are under stress. Cyanobacteria are classified as blue-green algae. The cyanobacteria Oscillatoria, Arthrospira, Spirulina, and Microcystis, are frequently seen. Blue-green algae increase suspended solids concentrations and interfere with settling. Blue-green algae is a sign of unfavorable pond conditions. Low pH and nutrient levels are related to the growth of blue-green algae. Filamentous algae are blue-green algae. Most algal blooms are composed of blue-green algae.EPA recommended detention times for warm climate: 5 – 50 days, and for cold weather: 90-180 days(Vasconcelos and Pereira, 2001; *Wastewater Operator Certification Ponds, Lagoons, Natural Systems Study Guide*, 2015)

1.4.1.2.1 MERITS OF ALGAE POND TECHNIQUE

1. The algae growth in the oxidation pond increases effluent pH, which does microbial disinfection.
2. An average temperature of an algae pond with a detention time of 50-60 days removes 70-80 BOD.

3. About 90-95 % of coliform bacteria get removed in a well-stabilized algae pond.
4. It does not require several human resources. It is a simple technique.
5. The municipality can cultivate useful algae culture in the algae pond beneficial for commercial use.
6. It is a nature-based wastewater treatment solution that does not impart chemical hazards to the environment.
7. In an algae pond, about 60 – 90 % of ammonia nitrogen is removed in summer, while 60 – 70 % is removed during winter(Fallowfield, 2016).

1.4.1.2.2DE-MERITS OF ALGAE POND TECHNIQUE

1. A large area is required for algae pond operation, depending on how much wastewater is treated.
2. Some algae grown in algae ponds, like cyanobacteria algae, fix atmospheric nitrogen for their growth, limiting wastewater nitrogen consumption.
4. It increases the total suspended solids of wastewater.
5. It increases effluent BOD if algae are not filtered well.
6. It increases the sterilization time for chemicals needed.
7. It produces a funny odor in the water.
8. It imparts greenish color to water.

1.5 CHEMICAL METHODS

Chemical methods use chemical agents like alkali, chlorine, alum, organic/ inorganic polymer, and zeolites to treat nitrogenous compounds and other pollutants. Three types of chemical-physical treatment methods are:

A. Ammonia Stripping
B. Chlorination
C. Ion Exchange

1.5.1 AMMONIA STRIPPING

Ammonia stripping converts ammoniacal nitrogen present in ammonium ions (NH_4^+) into molecular gaseous form(NH_3) at an elevated pH and high temperature of wastewater. When ammonia is removed from sewage, lime or caustic is added to the mixture until the pH level reaches 10.8 to 11.5 standard units. This process turns ammonium hydroxide ions into ammonia gas (equation 16) (EPA, 2000):

$$NH_4^+ + OH^- \rightarrow H_2O + NH_3\ (g) \quad \text{-----}(16)$$

According to the following process (equation 17), ammonia nitrogen in water occurs in equilibrium between the molecular (NH_3) and ionic form (NH_4^+):

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \quad \text{------}(17)$$

An equilibrium co-relation between ammonia nitrogen and pH of water is shown in Figure 3, while a co-relationship between pH, temperature, and ammonia-nitrogen concentration is depicted in Figure 4 (Almasvi and Rahimi, 2017; Huang and Shang, 2006). Free ammonia (NH_3)exists in a minimal amount at the acidic pH; adding NaOH to their solutions will increase the ammonia volatilization.

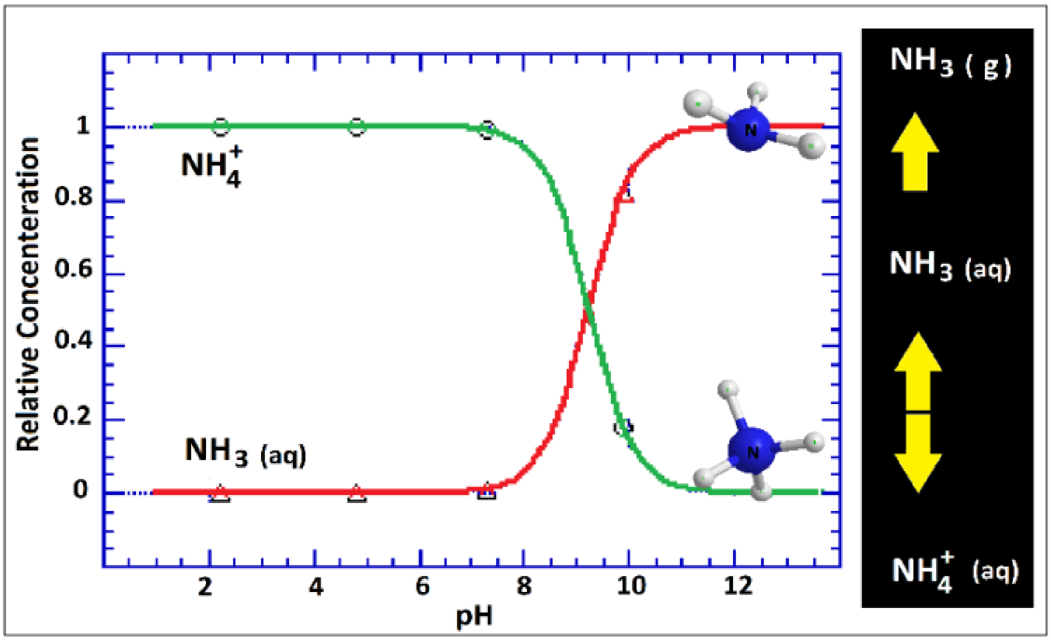


Figure 3: Equilibrium relationship between NH_3 (aq) NH_4^+ with pH

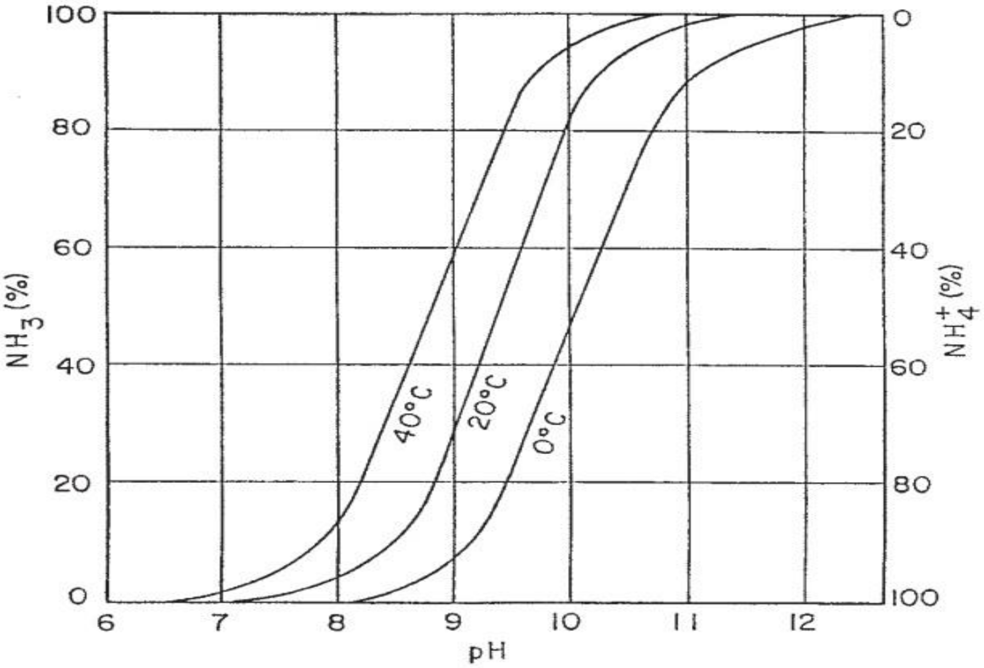


Figure 4: Co-relationship between temperature and pH on the distribution of ammonium ion and ammonia-nitrogen in water

Equation 18 can be used to describe the relationship between molecular ammonia and ammonium ions in water (Deng et al., 2016; El-Gohary et al., 2013; Lei et al., 2007):

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [H^+]/K_a} \quad \text{------------} \ (18)$$

Whereas, $pK_a = 4 \text{ x } 10^{-8} T^3 + 9 \text{ x } 10^{-5} T^2 + 0.0356T + 10.072$ (Bonmatí and Flotats, 2003). $[NH_3]$ is the concentration of molecular ammonia, $[NH_3 + NH_4^+]$ is the concentration of total ammonia, $[H^+]$ is the concentration of hydrogen ions, and [Ka] is the acid ionization constant for ammonium (9.3 at 25 °C). Figure 5 illustrates how Lei et al. (2006) created an ammonia stripping plant for upcoming field applications based on findings from an anaerobic digestion effluent pretreatment system. The effluent is first given a calcium hydroxide treatment. Along with the increase in pH, phosphorus, COD, suspended solids, turbidity, and some ammonia could be eliminated from wastewater during mixture settlement. The supernatant will be handled in the subsequent steps; the sludge could be composted. Second, air stripping removes ammonia from the supernatant, which is then absorbed by H_2SO_4 to create $(NH_4)_2SO_4$. Finally, biogas injection (CO_2 injection) brings the pH of treated wastewater down to around seven while simultaneously purifying the biogas (Lei et al., 2007). Figure 5 displays a schematic of the ammonia stripping process (Lei et al., 2007).

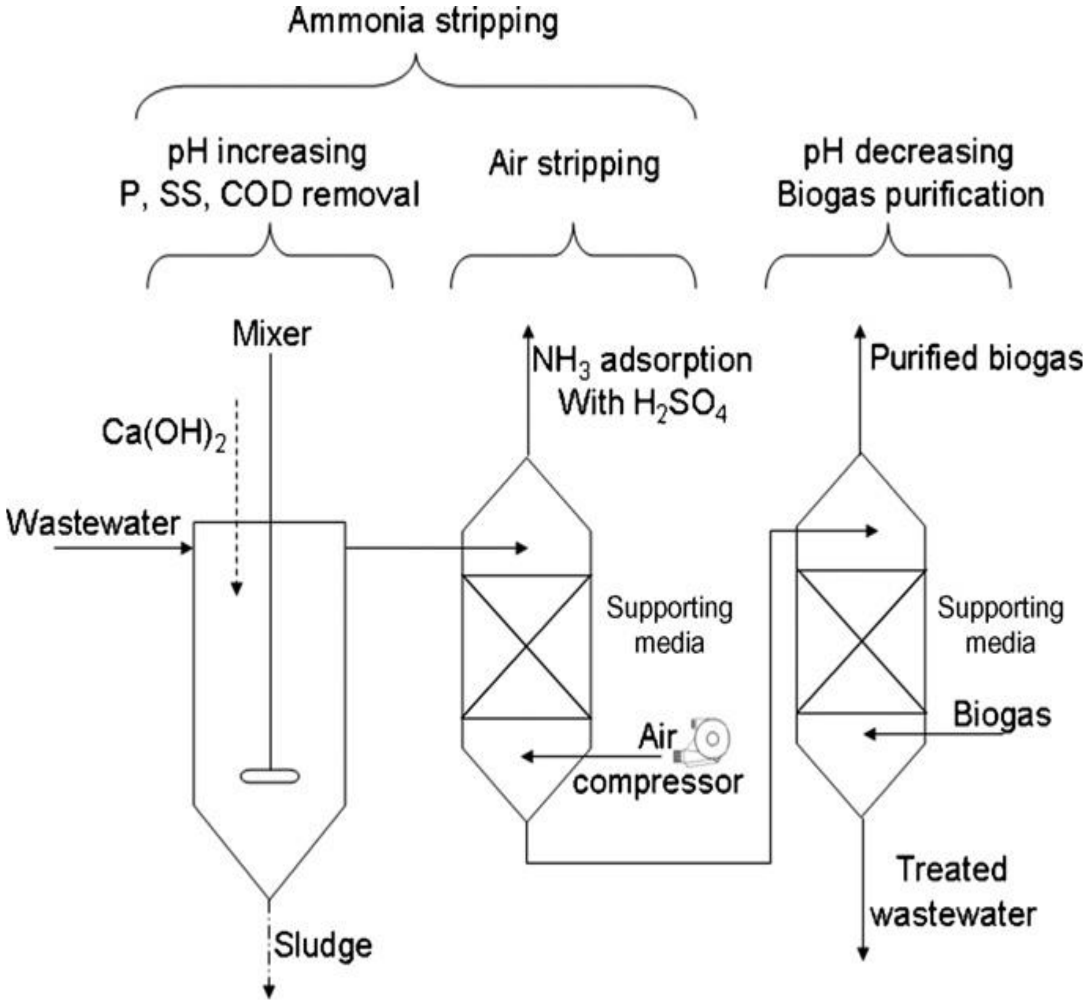


Figure 5: A schematic diagram of ammonia stripping

1.5.1.1 MERITS OF AMMONIA STRIPPING TECHNIQUE

1) The operation of ammonia stripping is simply not affected by wastewater quality fluctuation if air temperature and pH remain stable.
2) This is more likely because of a mechanical process that does not generate backwash.
3) Toxic substances that could impair the functionality of a biological system do not affect it.
4) It is a regulated procedure explicitly designed to remove ammonia.

1.5.1.2 DE-MERITS OF AMMONIA STRIPPING TECHNIQUE

1. The stripping tower receives a pumping of water. Higher electricity and maintenance costs result from this.
2. Removal of scale formation is typical, sometimes removed hydraulically but not all.
3. Cold weather prevents this procedure from being carried out (heated air is required). Ammonia removal is ineffective in cold weather conditions like fogging and icing.
4. Regulations or concerns about air quality may make it inappropriate to release ammonia into the environment at a low level (6 mg/m3).
5. This procedure does not eliminate organically bound nitrogen.
6. This process creates a problem resulting from ammonia and sulfur dioxide atmospheric reactions.
7. Controlling pH requires adding lime, creating operational and maintenance concerns.
8. The higher pH of wastewater leads to corroding the plant's wood packing.

1.5.2 BREAKPOINT CHLORINATION

It is a process of adding chlorine to the water when almost all the micro-biological (algae, protozoa, bacteria, viruses) chemical(inorganic-organic compounds/ moieties) contaminants pollutants get oxidized and destroyed or converted to simpler molecules. Adding chlorine gas (Cl_2) to water causes a mixture of hypochlorous and hydrochloric acids to develop, further dissociate, and create nascent oxygen (Equations 19, 20, and 21, respectively). Nascent oxygen is highly adequate for disinfection purposes(AWWA, 2006):

$$\underset{\text{Chlorine}}{Cl_2} + H_2O \longrightarrow \underset{\text{hypochlorous acid}}{HOCl} + \underset{\text{hydrochloric acid}}{HCl} \quad \text{------------(19)}$$

$$HOCl \longrightarrow H^+ + OCl^- \quad \text{-----------(20)}$$

$$OCl^- \longrightarrow \underset{\text{Nascent Oxygen}}{[O]} + Cl^- \quad \text{-----------(21)}$$

Chlorine as an oxidant for disinfection purposes, oxidation of ammoniacal nitrogen, and other pollutants has been practiced since the early water treatment (Griffin and Chamberlin, 1941). Breakpoint chlorination is the most feasible technique(Figure 6) for water treatment to combat ammoniacal nitrogen("Health Canada," 2020; Robert Spon, 2008). The stoichiometry of the breakpoint chlorination process can be categorized into four zones. In zone 1, chlorine is consumed by reducing agents (H_2S, NO_2^-, Fe^{2+}, and Mn^{2+}) that consume little chlorine. Zone 2 represents additional chlorine combined with total ammonia forming reactive organics resulting formation of monochloramine. In zone 3, higher chlorine dosages transform monochloramine into odorous dichloramine and nitrogen trichloride. In this phase, the total combined chloramine decreases and approaches zero at the breakpoint. The last zone contains free residual chlorine. If the free chlorine is about 85 % of the total residual chlorine, then there are at least nuisance odors. If the combined chlorine residuals exists, it indicates the presence of potential disinfection by-products (haloacetic acid and trihalomethane) which remains in the form of free chlorine residual and develops later on. A system of water disinfection by chlorine gas of a municipal water treatment plant (220 MGD capacity) is shown in Figure 7.

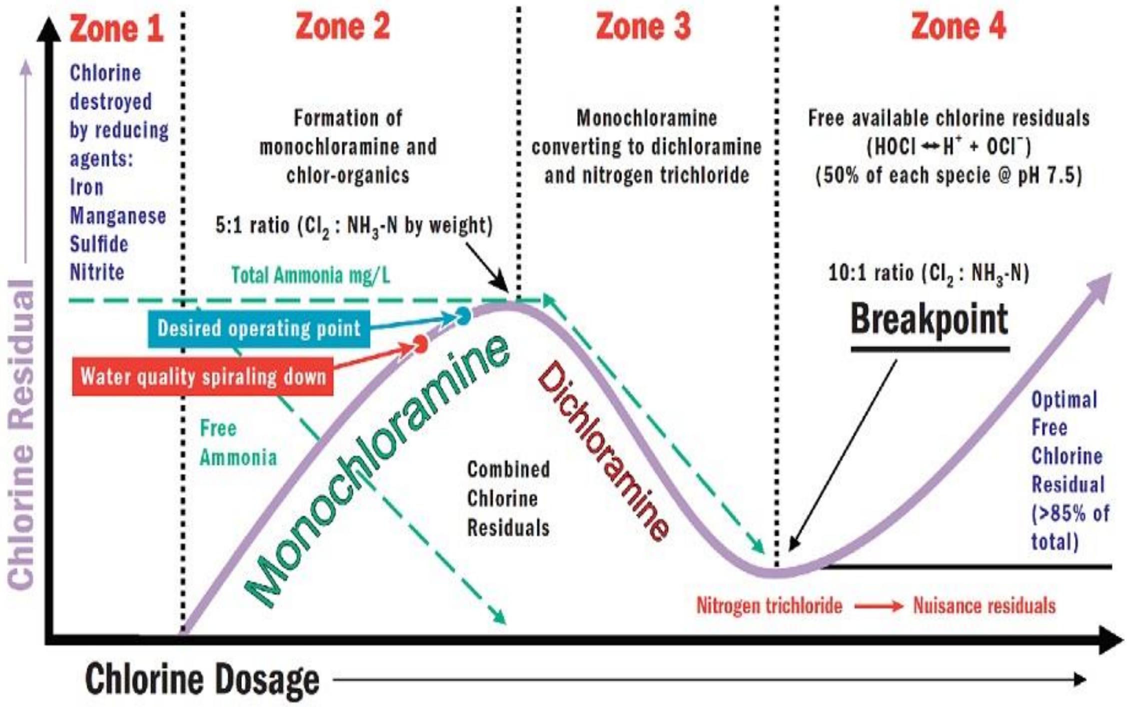


Figure 6: Breakpoint Chlorination Curve Interpretation; Source: Robert Spon, 2008 (Adopted reproduced with permission © Health Canada the Minister of Health, 2020:Appendix-2)

Figure 7: Chlorination system of Water at a Water Treatment Plant in Delhi

1.5.2.1 MERITS OF BREAKPOINT CHLORINATION

- Water treatment using chlorine gas or any of its products is straightforward and does not require a skilled workforce.
- Chlorination of Water does not impart any apparent objectionable color to the water
- The chlorination of water does not require any large area for its application.
- Chlorination is very useful for disinfection and bleaching the color of the water.
- Chlorination neutralizes most nitrogenous and other organic/ inorganic pollutants in water in a short period.

1.5.2.2 DE-MERITS OF BREAKPOINT CHLORINATION

- Chlorination produces Disinfection By-Products (DBPs) when used to treat polluted water.
- The chlorination of water polluted with ammonical/ nitrogenous products produces nitrosamine compounds. Nitrosamine, specifically nitrosodimethylamine (NDMA), is cancerous (Costet et al., 2011).

- Chlorination does not neutralize/oxidize all the pollutants immediately or within half an hour, but the half-life of some contaminants (amines) goes up from 3.2 to 96 hours (How et al., 2017).
- Some microbiological parasites (giardia crypto-sporidium oocysts) cysts are not very amenable to destruction by chlorine. They require extended contact time and a high dosage of chlorine(EPA, 2001).
- High dosages of chlorine in water produce an objectionable odor in water.

1.5.3 ION EXCHANGE/ ZEOLITE PROCESS

Ion exchange can be used to get rid of NH_4^+. The process of exchanging ions from one phase to another is known as ion exchange. Ion exchange in water treatment happens between the influent water and the solid phase of the ion exchanger. Only ions can be used in the ion exchange process. Ion exchange does not remove substances from water that do not ionize. Water and ammonia combine to generate ammonium hydroxide, which then breaks down into ammonium (NH4+) cations according to the following reaction:

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

Reversible chemical processes known as ion exchange (IX) involve the removal of dissolved ions from the solution and replacing them with ions with similar charges. Figure 8 depicts an ion exchange picture (Rowe, 2020). Zeolites are generally used in water treatment for softening, which involves removing calcium and magnesium ions from the water; however, they are increasingly used to remove other dissolved ionic species. Chabasite, mordenite, and clinoptilolite are examples of inorganic zeolites that may also extract ammonia. Some zeolites are more effective at removing ammonia than hardness. They can do so while keeping the pH of drinkable water within the permissible range (6 to 9) without the risk of dumping.

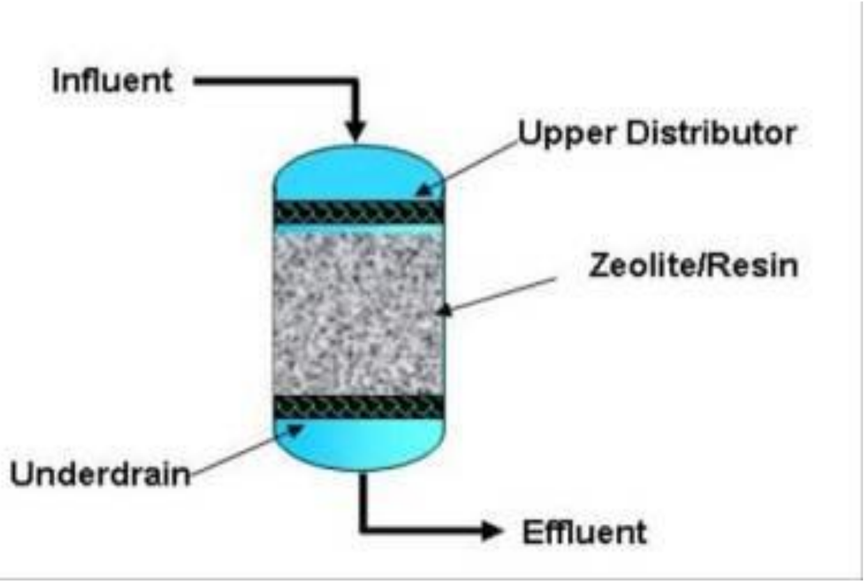


Figure 8: Ion-Exchange System in Water Treatment

Natural zeolites can remove ammonia nitrogen present in the form of ammonium ions (NH_4^+) in water and wastewater. About 30–98% removal has been reported in research studies depending upon the initial ammonium ion concentration, temperature, zeolite type, contact time, particle size, and amount of zeolite loading(Widiastuti et al., 2008).

1.5.3.1 MERITS OF ION EXCHANGE/ ZEOLITE PROCESS TECHNIQUE

1) Natural zeolites are used in agronomic, horticultural, and environmentally safe ways to treat water and waste to reduce ammonia-nitrogen.
2) Although other exchange media are available, they are substantially more expensive than the materials found in natural rock.
3) The nutrient-exchange zeolite added to soil is available for effective plant uptake.
4) Zeolites that undergo natural transformation are employed to filter water. They show good efficacy with up to 97 percent ammonium removal depending on contact time, zeolite loading, initial ammonium concentration, and pH level.
5) Therefore, it is feasible to regenerate the zeolite, reuse it, and reuse the concentrated metal ions that are produced after the renewal of the zeolite, all of which have a remarkable impact on the environment without making new waste.
6) Natural zeolites exhibit outstanding resilience to chemical, biological, mechanical, or thermal changes.
7)

1.5.3.2 DE-MERITS OF ION EXCHANGE/ ZEOLITE PROCESS TECHNIQUE

1) The ion exchange process is not practical for organically bound nitrogen.
2) Ion exchange using the column method is time-consuming for harnessing the full use of zeolites.
3) The backwashing of exhausted zeolites encounters problems that require skilled human resources.
4) Regenerated solution/backwash water contains 2% brine contaminated with high quantities of ammonia and all the other ions that were taken out of the waste stream. Depending on their ionic strength valence, the process is non-discriminatory and may remove other metals in addition to ammonia cations. It is feasible that there could be a hazardous waste liquid to be disposed of in the environment if there are metals in the waste stream. It still needs to be processed for disposal even if it doesn't contain any harmful metals. (D. L. Bish, 2001; Margeta et al., 2013; Russell, 2006; Widiastuti et al., 2008):

1.6 MOTIVATION FOR PRESENT RESEARCH

I The Government of India has amended the Water Act 1974' (Prevention Control of Pollution) with a limiting value of ammonia nitrogen as 5-mg/L for treated sewage effluent to be discharged into the river. However, still existing STPs are producing effluent of higher ammonia concentration. Thus, there is a compulsory requirement for ammonia nitrogen removal in the existing STPs that can be executed with infrastructural modification. A technology, biological or chemical, was required to research that can be beneficial in removing ammonia nitrogen in large masses of sewage/ wastewater.

II Municipal Water Treatment Plants are designed to treat raw water of a specific quality in respect of ammonia-nitrogen. Chlorine gas treatment of ammonia-contaminated natural water with chlorine gas produces hazardous disinfection by-products in the presence of organic pollutants. A sustainable technological modification is required that can be executed in existing treatment plants to mitigate the negative effect of ammonia nitrogen.

1.7 AIM AND OBJECTIVES OF THE PRESENT RESEARCH

The research program aims to develop methods for **biological chemical treatment for combating ammonia in water**, thus mitigating environmental risk. The detailed objectives of the present study were as follows:

- ✓ To diagnose the performance of cow-dung sludge in water treatment for mitigation conversion of ammonia nitrogen into nitrate.
- ✓ To identify the potential use of *Yucca schidigera* plant extract in water treatment for combating ammonia nitrogen.
- ✓ To identify the ammonia adsorption capacity of zeolites in synthetic water.
- ✓ To evaluate the efficiency of Zeolites in Water Treatment for Combating ammonia in both river water treated sewage effluent.
- ✓ To compare the chemical compositional change in zeolites in virgin used states.
- ✓ To propose modifications in the infrastructure of the existing conventional sewage treatment plants to give better final effluent quality, free from ammonia, nitrogen, and nitrite pollution.

1.8 OVERVIEW OF THE THESIS

This thesis focuses on developing sustainable, environmentally friendly measures to remove ammonia-nitrogen from water. Water samples from the Yamuna river and municipally treated sewage effluent have been taken for experimental studies. The citizens of Delhi use the river water for drinking purposes. Sewage effluents are released to a nearby river only after treatment. This research aims to remove ammonia-nitrogen from water and wastewater. The critical review of ammonia nitrogen presented in **Chapter 1** highlighted that ammonia nitrogen is an inevitable part of the nitrogen cycle in nature. Biological and chemical methods convert ammonia nitrogen (NH_3) into ammonium ion (NH_4^+), nitrite ion (NO_2^-), nitrate ion (NO_3^-), nitrous oxide (N_2O), elemental nitrogen gas (N_2). The review also indicated that ammonia nitrogen, the primary form of nitrogen in the water, is the root cause of disinfection by-products in a water treatment utility. Chlorine gas is mainly oxidizing and disinfection agent at water treatment plants. It produces N-Nitrosodimethylamine (NDMA) and many other potential carcinogenic by-products associated with ammonia water. Chapter 1 elaborates on the background of ammonia nitrogen, its origin in water, forms of ammonia nitrogen, and conversion into other states. The hazardous nature of ammonia for aquatic animals and water plants, its association with disinfection precursors, and the formation of disinfection by-products are elaborated on in this chapter. Chapter 1 also elaborates on the water treatment methods to combat ammonia-nitrogen. There are many methods for ammonia-nitrogen treatment, having their own merits and demerits. This chapter critically reviews previously published information on Water Treatment Technologies for combating ammonia-nitrogen. The motivation for the current research aims and objectives are also elaborated on in Chapter 1. **Chapter 2** deals with the experimental part, which includes the materials and methods employed to develop biological and chemical treatment methods for combating ammonia in water. Various characterization techniques used to analyze the parametric values of ammonia nitrogen, Nitrite, Nitrate, pH value, total dissolved solids, electrical conductivity, temperature, etc., have also been discussed in this chapter. **Chapter 3** investigates the performance of cow-dung sludge in water treatment for mitigation and conversion of ammonia nitrogen into nitrate. The potential use of *yucca schidigera*, a plant extract for combating ammonia nitrogen in water treatment, has been discussed in **Chapter 4**. The evaluation of ammonia removal in synthetic water using zeolites is presented in **Chapter 5**. The efficiency of zeolites in water treatment for combating ammonia nitrogen using treated sewage effluents has been elaborated on in **Chapter 6**. The efficiency of zeolites in water treatment for combating ammonia in Yamuna river water has been highlighted in chapter 7. In the last chapter, i.e., **Chapter 8** of the thesis, the overall conclusions of the results obtained in the above study are reported. Moreover, in this thesis, some modifications have been proposed to the existing infrastructure of the sewage treatment plants to increase their operational efficiencies based on experimental results. Recommendations have been made for future studies to guide researchers who want to pursue similar work in water treatment. Finally, the **References** have been added for all cited literature throughout the thesis work.

CHAPTER 2

MATERIAL AND METHODS

CHAPTER 2: MATERIAL AND METHODS

2 MATERIALS

2.1 NATURAL WASTEWATER

Natural wastewater samples were collected in a 10-liter plastic cane from a 40 MGD Municipal Sewage Treatment Plant (STP), Rohini, Delhi. The treated sewage effluent was of milky color and turbid. The said STP is situated about 10 kilometers from the research laboratory. Natural water samples were also collected from the Yamuna river passing through Wazirabad Barrage, Delhi. The said sampling point of the Yamuna river is about 20 kilometers from the research lab at Delhi Technological University. Samples were collected immediately and put on initial chemical analysis. A sampling point of municipally treated sewage effluent (MTSE) and that of the Yamuna river is shown in Figures 9 and 10, respectively.

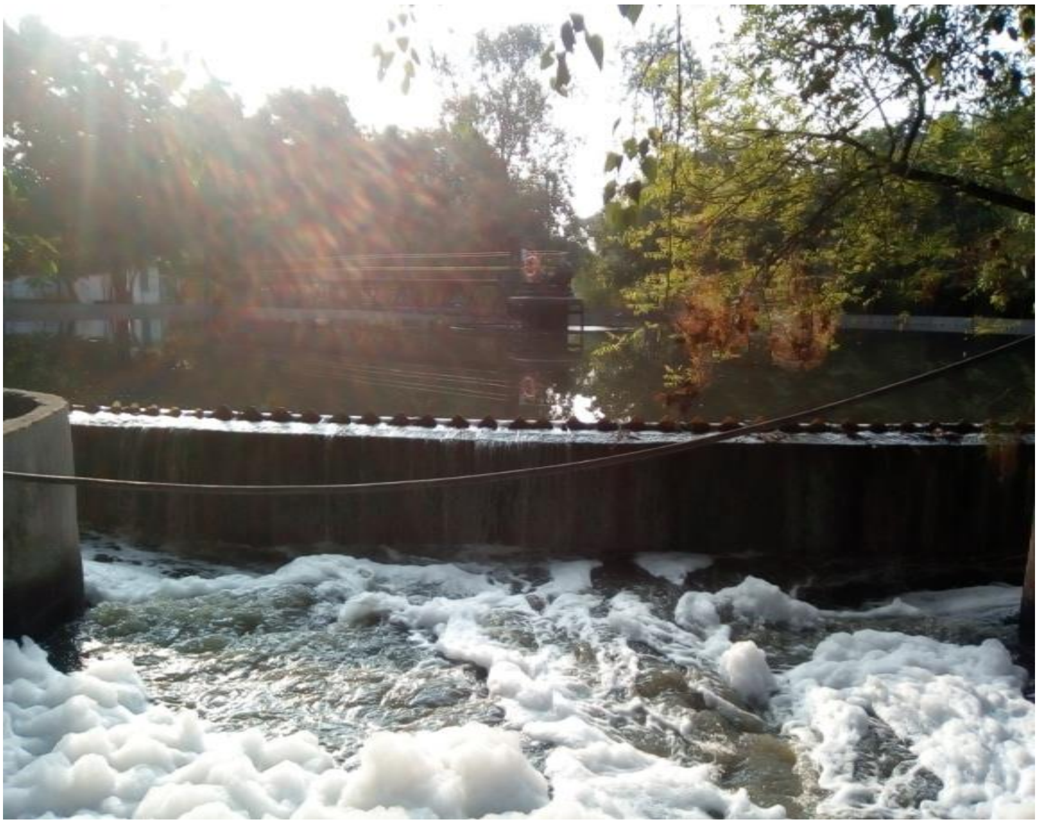


Figure 9: Treated Sewage Effluent for Natural Water

Figure 10: The Yamuna River for Natural Water

2.2 *YUCCA*-EXTRACT

Yucca schidigera, a desert plant, was collected from the Forest Research Institute, Dehradun, Uttrakh State, India. The Yucca plant's stem (about 250 grams) was chopped with a knife into small pieces. Then, the chopped pieces were grounded in a grinder mixture, dried in the open sun for three days, and again ground to make a fine powder. This Yucca powder was sieved through a 150-mesh sieve stored in an airtight container. In the present study, the *Yucca* extract was used in the form of a solution. *Yucca* solution was prepared by mixing and dissolving 50 grams of *Yucca* powder in 700 ml of distilled water. It was taken in a 1-liter beaker, agitated on Jar Apparatus for seven days (about 250 ml water evaporated in the air) so that its contents could dissolve well, filtered through ordinary filter paper, made –up to 500 ml with distilled water using a volumetric flask. Thus, 1 ml of *Yucca* extract produces 100 mg of solution. A picture of the *yucca* plant is shown in Figure11.

Figure 11: ***Yucca*** **Plant**

2.3 COW-DUNG SLUDGE

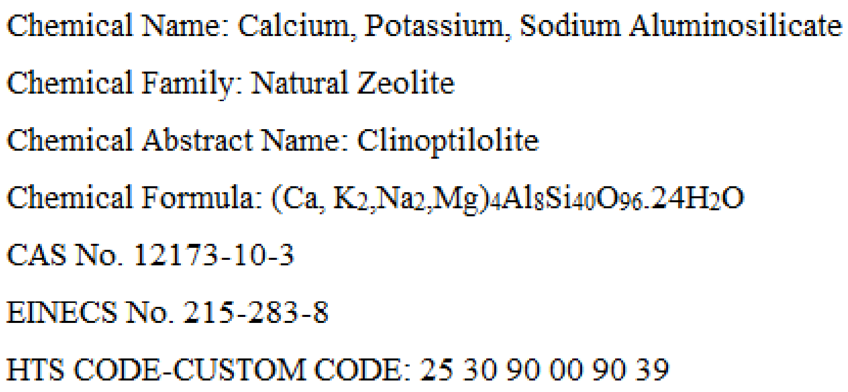
Cowdung sludge was collected locally from a village in Delhi-110036. The cow dung sludge was taken from a heap of cow dung at about a 1-foot depth. The age of the cow-dung pile was about one year. It was contained in a new 500 ml wide-mouth glass bottle previously washed with distilled water, dried, and sterilized in an autoclave. After the material collection, the bottle's mouth was shut and put in the laboratory at room temperature. The cow-dung material was used in a pristine state by weighing on an electronic balance as 1g, 2g, 3g, 4g, and 5g dosed in a 1-liter water sample. Experiments were also performed with cow-dung solutions. 50-gram cow dung was taken in a 500 ml conical flask, dissolved in 200 ml distilled water, then filtered through a broad sieve. The solution was made up to 250 ml in a volumetric flask. This solution gives 1 ml = 0.2 g cow-dung. A material sample of composted cow dung is shown in Figure 12.

Figure 12: Composted cow-dung material

2.4 NATURAL ZEOLITES CLINOPTILOLITE

The firm, M/s Rota Mining Corporation, Istanbul, Turkey, provided clinoptilolite natural zeolites. The general information, mineral composition, chemical composition, and physical properties are depicted in Tables 3, 3(a), 3(b), and 3(c), respectively.

Table 3: General information on clinoptilolite



Chemical Name: Calcium, Potassium, Sodium Aluminosilicate
Chemical Family: Natural Zeolite
Chemical Abstract Name: Clinoptilolite
Chemical Formula: $(Ca, K_2,Na_2,Mg)_4Al_8Si_{40}O_{96}.24H_2O$
CAS No. 12173-10-3
EINECS No. 215-283-8
HTS CODE-CUSTOM CODE: 25 30 90 00 90 39

The mineral composition of clinoptilolite is as follows:

Cristobalite: 0 - 5 % ; Tridymit: 0 - 5 %; Clinoptilolite: 90 - 95 %

Table 3(a): Chemical composition of clinoptilolite

SiO_2	65 - 72 %	Fe_2O_3	0.7 - 1.9 %	MnO	0 - 0.08 %
Al_2O_3	10 - 12 %	MgO	0.9 - 1.2 %	Cr_2O_3	0 - 0.01 %
CaO	2.4 - 3.7 %	Na_2O	0.1 - 0.5 %	P_2O_5	0.02 - 0.03 %
K_2O	2.5 - 3.8 %	LOI*	9 - 14 %	SiO_2/Al_2O_3	5.4 - 7.2 %

* Loss of Ignition

Table 3(b): Physical properties of clinoptilolite

Appearance	Ivory white	Oil Absorption(ml/100g)	57	Solubility	None
Smell	None	Abrasion (mg/100g)	87	pH	7.0 - 8.0
Porosity	45 - 50 %	Single Point Surface Area	39 m^2/g	Softening Point	1150 °C
Hardness	2 - 3 Mohs	Micropore Area	11m^2/g	Melting Point	1300 °C
Mudding Down	None	Mesopore Area	29 m^2/g	Bulk Density	0.6 - 0.8 g/cm^3
Water Absorption	42 - 50 %	Effective Diameter of pores	4 angstroms	Real Density	2.2 - 2.4 g/cm^3
Plasticity	Minor				

<u>CATION EXCHANGE CAPACITY (CEC)</u>: 1.5 - 2.1 meq/g

MAJOR EXCHANGEABLE CATIONS:

Rb, Li, Cs, NH_4, Na, Ca, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Mg, Fe, Co, Al, Cr

(selectivity of above cations is a function of hydrated molecular size relative concentrations)

SELECTIVITY:

$Cs^+ > NH^{4+} > Pb^{2+} > Na^+ > Ca^{2+} > Mg^{2+} > Ba^{2+} > Cu^{2+} > Zn^{2+}$

PRIMARY ADSORBING GASES:

CO, CO_2, SO_2, H_2S, NH_3, HCHO, Ar, O_2, N_2, H_2O, He, H_2, Kr, Xe, CH_2OH

Clinoptilolite zeolite samples are shown in Figure 13.

Figure 13: Clinoptilolite natural zeolites

2.5 NATURAL ZEOLITES MORDENITE

M/s Blue Pacific MINERALS, Twist Road, Nakuru, New Zeal, provided mordenite natural zeolites. The general information, mineral composition, chemical composition (%), chemical composition (ppm), and physical properties are depicted in tables 4, 4(a), 4(b), and 4(c), respectively.

Table 4. General information on mordenite

CAS No. 1318-02-1
HS Code No. 2530.90.00.19k
NSNO Approval No. HSR002544

The mineral composition of mordenite is as follows:

K Feldspar 5 - 20 %; Opal C: < 5 %; Smectite: 5 - 20 % ; Mordenite: 65 - 95 %

Table 4(a): Chemical composition (%) of mordenite

SiO_2	70.79 %	Fe_2O_3	1.61 %	MnO	0.05 %
Al_2O_3	12.97 %	MgO	0.25 %	CaO	1.76 %
Na_2O	1.36 %	P_2O_5	0.02 %	TiO_2	0.18 %
K_2O	4.26 %	LOI*	6.59 %		

* Loss of Ignition

Si/Al Ratio: 4 - 6 (5.46)

Table 4(b): Chemical composition (ppm) of mordenite

Ba	634	Rb	129	Sr	376	Y	40	Zr	161	Nb	11	Th	13	Ga	14
Zn	39	Cu	2	Cr	9	Sc	<1	U	3	La	33	Ce	55	As	6
Pb	0	Cd	0												

Table 4(c): Physical properties of mordenite

Appearance	Off White/ Cream	Solubility	None
Smell	None	pH	8.65 (10 % aqueous)
Porosity	60 %	Hardness	2 - 3 Mohs
Density	0.48 - 0.70 g/cm^3	Micropore SA	~ 88%
Mesopore SA	~ 25%	Total SA	~ 250m^2/g

CATION EXCHANGE CAPACITY (CEC): 130 - 140 meq/100g

TYPICAL SELECTIVITY:

$Cs^+ > K^+ > NH^{4+} > Na^+ > Ba^{2+} > Li^+$

or $NH^{4+} > Na^+ > Mn^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+}$

Mordenite zeolites samples are shown in Figure 14.

Figure 14: Mordenite Natural zeolites

2.6 SYNTHETIC ZEOLITE 4A

The material specifications provided by the firm are as below:
Name of the Firm: Chemicals India, Ahmednagar, Maharashtra 414005 INDIA

GENERAL INFORMATION

4A Zeolite is an ion exchange agent in detergent. It is used as a detergent builder in bars and powders. Hardness-producing minerals in the water, like calcium and magnesium ions, interfere with surfactants' cleaning efficiency. 4A zeolites deplete calcium ion concentration to 2 % of its original level within one minute and magnesium ion within 10-minutes of an average wash cycle. The general information on its chemical composition (%) and physical properties are depicted in Tables 11 and 11(a). Synthetic zeolites 4A samples are shown in Figure 15.

Table 5. Chemical composition (%) of zeolites 4A

SiO_2	32.5 - 33.5 %	Al_2O_3	27.5 - 28.5 %	Na_2O	16.5 - 17.5 %

Table 5(a): Physical properties of zeolites 4A

Appearance: White; Smell: None; pH: 10.7 - 11.7 (5 % suspension); Average particle size,)Max.): 5.0µ; Density: 500 g/l; Calcium-binding capacity: 155 (as mg CaO/g assay); Min Assay content (percent by mass): 77.5 - 79.5; Sieve-residue: 0.5 (50-micron sieve % by mass, Max.)

Figure 15: Synthetic zeolite 4A

2.7 COAGULANTS

2.7.1 AlUMS

Alum solution was prepared from commercially available alum cakes used at waterworks in Delhi. The firm M/s Shree Vam Industries, Plot No. 249-51, GIDC, Kuvada, Rajkot-360023, India, supplied the Alum cakes to the water treatment utility. The Alum cakes had the following characteristics provided by the firm (Table 6):

Table 6: Characteristics of Alum Cakes

Test	**As per DJB PO Specification**	**Observed Results**
Insoluble Matter, % By Mass	0.4 Max	0.3
Iron as Fe, % By Mass	0.7 Max	0.35
Soluble Aluminium Compounds (As Al_2O_3) % By Mass	16.0 Min	16.22
the pH of 5 % Aqueous Solution	2.7 Min	2.88
Free Acidity/ Basicity	0.5 Max	0.45
Lead (as Pb)	20 PPM Max	1.0
Arsenic (as As_2O_3)	4 PPM Max	2.45

10-gram alum cake was dissolved in 1liter of distilled water using a calibrated volumetric flask of 1-liter capacity. This solution produces 1ml= ten ppm.

2.7.2 POLY- ALUMINIUM CHLORIDE (PACL)

PACl was prepared from a commercially available concentrate solution used at waterworks in Delhi. The PACl solutions were supplied by Grasim Industries, Nagda, Madhya Pradesh, India. The PACl had the characteristics provided by the firm as depicted in Table 7:

Table 7: Characteristics of Poly-Aluminum Chloride (PACl)

Parameters	Standard Value
Alumina as Al_2O_3 % by mass	9.5 Min
Basicity % by mass	35 Min
Chloride as Cl^- % by mass	12.5 Max
Sulfate as SO_4^{2-} % by mass	2.7 Max
Specific Gravity at 25 ºC	1.16 Min
Viscosity at 20 ºC mPa	3-30
Mercury as Hg ppm	0.2 Max
Arsenic as As ppm	5 Max
Cadmium as Cd ppm	6 Max
Lead as Pb ppm	30 Max
Iron as Fe Manganese as Mn	100 Max
Chromium as Cr ppm	15 Max
Insoluble % by mass	0.5 Max
pH of 5 % solution	1.8 - 4.5

8.6 ml of PACl concentrate solution was dissolved in 1liter of distilled water using a calibrated measuring flask of 1-liter capacity. This solution produces 1ml= ten ppm.

2.7.3 TANFLOC

Tanfloc is an organic, cationic, low molecular weight polymer of essentially vegetable origin from renewable raw material sources(Black Acacia bark extracts - Mimosa forests). TANFLOC neutralizes the charge in colloidal systems by provoking electric bridges among the particles, stabilizing them, and producing flocks, causing sedimentation.10-gram alum cake was dissolved in 1liter of distilled water using a calibrated volumetric flask of 1-liter capacity. This solution has 1ml= ten ppm.

2.8 APPARATUS AND GLASSWARES

2.8.1 EQUIPMENT INSTRUMENTS

- A Jar Test Apparatus
- The Eppendorf Bio-Spectrometer with the 1-cm light path for measurements of ammonia nitrogen, nitrite- nitrogen, and nitrate nitrogen;
- Hach HQ 440 d Multi Ion Analyser for pH, temperature, electrical conductivity, and total dissolved solids.

2.8.2 GLASSWARES

- Twelve numbers calibrated Nessler's tubes of 100 ml capacity with two stands for water sample color development;
- Five numbers of calibrated measuring flasks of 50 ml, 100 ml, 250 ml, 500 ml, and 1-liter capacity each for preparing standard solutions sample measurements;
- Five calibrated pipettes of 1 ml, 2 ml, 5 ml, 10 ml, and 25 ml capacity, each with two pipettes, stands
- Ten numbers of one-liter capacity long neck beakers for Jar Test Apparatus;
- Five numbers of 25 ml 50 ml capacity injection syringes each for taking water samples from beakers;
- Fifty numbers of 0.45-micron filter cartridges for sample filtration;
- Twenty numbers of 250 ml capacity conical flasks for chloride hardness testing and other purposes;
- Twenty numbers of 250 ml 500 ml capacity reagents glass bottles each for storing stock solutions reagents;
- Ten numbers pipettes, suction pumps/ bulbs

2.9 CHEMICALS REAGENTS

2.9.1 FOR AMMONIA NITROGEN(NESSLERIZATION METHOD)

1. Rochelle Salt (potassium sodium tartrate tetrahydrate- $KNaC_4H_4O_6.4H_2O$)
2. Nessler Reagent prepared with mercuric iodide (HgI_2), potassium iodide (KI), sodium hydroxide (NaOH)
3. Ammonium chloride (NH_4Cl)

2.9.2 FOR NITRITE-NITROGEN (DIAZOTISATION METHOD)

1. Sulfanilic acid(4-aminobenzenesulfonic acid-$C_6H_7NO_3S$)
2. Hydrochloric Acid (HCl)
3. Alpha-Naphthylamine Hydrochloride ($C_{10}H_{10}ClN$)
4. Sodium Acetate ($NaC_2H_3O_2$)
5. Sodium Nitrite ($NaNO_2$)

2.9.3 FOR NITRATE-NITROGEN ULTRAVIOLET SPECTROPHOTOMETRIC SCREENING METHOD)

1. Hydrochloric Acid (HCl)

2.9.4 FOR TOTAL ALKALINITY (TITRIMETRIC METHOD)

1. Sulphuric Acid (H_2SO_4)
2. Sodium Carbonate (Na_2CO_3)
3. Bromocresol Green Indicator ($C_{21}H_{14}Br_4O_5S$)
4. Methyl Red Indicator ($C_{15}H_{15}N_3O_2$)
5. Methyl Orange Indicator($C_{14}H_{14}N_3NaO_3S$)

2.9.5 FOR TOTAL HARDNESS (EDTA TITRIMETRIC METHOD)

1. EDTA (Disodium Ethylene Diamine Tetra Acetate
Dihydrate ($C_{10}H_{14}N_2Na_2O_8$)
2. Ammonia (NH_4OH)
3. Ammonium Chloride (NH_4Cl)
4. Calcium Carbonate ($CaCO_3$)
5. Eriochrome Black T Indicator ($C_{20}H_{12}N_3O_7SNa$)

2.10 METHODS OF TESTING

The content values of ammonia nitrogen, nitrite, and nitrate were analyzed spectrophotometrically by performing tests on the Eppendorf Bio Spectrometer model 2019 Eppendorf AG, made in Germany. Titrimetric methods analyzed the specific change in total alkalinity and total hardness values.

2.10.1 AMMONIA-NITROGEN(NESSLERIZATION METHOD)

Ammonia-nitrogen was tested by the nesslerization method as per test method 4200-NH_3 mentioned in Standard Methods for the Examination of Water Wastewater, 17th Edition. This method determines the amount of ammonia nitrogen present in free and saline (NH_3 + NH_4^+). The filtered sample water gives yellow-brown color with Nessler's reagent in the presence of ammonia nitrogen.

$$2(2KI.HgI_2) + NH_3 + 3KOH \longrightarrow (NH_2)_2HgOH.HgI + 7KI + 2H_2O$$

The yellow-brown color is produced because of ammonia-nitrogen content. It was measured with a spectrophotometer at 425nm.

Reagents:

- Nessler's reagent- Dissolved 100-gram mercuric iodide (HgI_2) 70-gram potassium iodide(KI) in about 100 ml ammonia-free distilled water. Added this solution slowly with constant stirring to a cool solution of 160 grams NaOH in 500 ml water. It was diluted to 1 liter. It kept it in a rubber stoppered pyrex bottle in the dark.
- Ammonia stock solution: Dissolved 19.095-gram ammonium chloride, NH_4Cl (dried at 100 •C) in ammonia-free distilled water made up of five liters with the help of a volumetric flask. The standard solution is stored in a 5-liter reagent glass bottle in a dry place. This is a 1000 mg/L standard solution. 1.0 ml = 1.0 mg N or 1.22 mg NH_3
- Working solutions- The working solutions were prepared from the stock solution by diluting the stipulated amount of stock solution in ammonia-free distilled water.
- Rochelle salt solution: 100 grams of Rochelle salt (potassium sodium tartrate tetrahydrate) was dissolved in 200 ml of distilled water, placed in a reagent glass bottle, and stored in a dark, dry place.

The spectrophotometer was calibrated with standard solutions of ammonia-nitrogen prepared from the stock solution. A calibration graph was obtained in the spectrophotometer with standard strength solutions 0, 0.2. 1.0, 3.0, 5.0, 8.0 mg/L NH_3-N. The absorbance readings were measured at 425 nm wavelength with a 1-cm cuvette path. An ammonia nitrogen-spectrophotometric set-up is shown in Figure 16.

Figure 16: Ammonia nitrogen- Spectrophotometric set-up

50 ml supernatant water sample was filtered through a 0.45-micron filter cartridge. 50 ml or lesser water samples were measured and taken into Nessler's tube depending on the concentration of ammonia nitrogen. High-content water samples (of high concentration) were diluted to 50 ml with ammonia-free distilled water. 2-drops of Rochelle salt solution followed by 1 ml of Nessler's reagent were added to each of the Nessler's tubes, having 50 ml sample/ diluted to 50 ml. A blank sample was also used with sample standards. Rochelle salt solution was added to water samples to eliminate the turbidity interferences caused by calcium magnesium salts. The sample was mixed thoroughly after 10 minutes of reaction time, and absorbance readings were taken at 425nm by using a spectrophotometer. This method determines ammonia nitrogen directly with the calibration curve of standard solutions.

2.10.2 NITRITE-NITROGEN(DIAZOTISATION METHOD)

Nitrite-nitrogen was tested by the diazotization method as per test method 419 NITROGEN (NITRITE) mentioned in Standard Methods for the Examination of Water Wastewater, 15th Edition. This method determines the amount of nitrite (NO_2^-) by forming a reddish-purple azo dye. This color develops at pH from 2.0- 2.5. The reaction is carried out by coupling diazotized sulfanilic acid with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). The reaction mechanism is shown in Figure 17 below(Manivasakam, 2005):

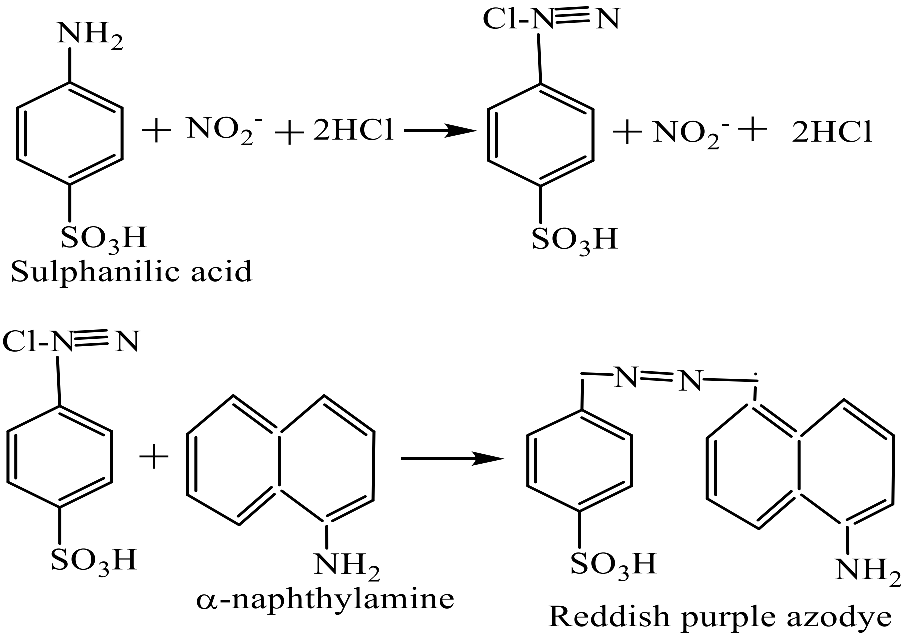


Figure 17: Diazotization of Nitrite (NO_2^-), Reaction- Mechanism

The intensity of the reddish-purple color produced because of nitrite content was measured with the help of a spectrophotometer at 543nm.

Reagents:

1) Sulphanilic acid solution- 6.00-gram sulphanilic acid was dissolved entirely in 100 ml hot distilled water. The solution was cooled and then added 200 ml concentrated HCl, made up to 1liter with distilled water, using a 1-liter capacity measuring volumetric flask and stored.
2) α-naphthylamine hydrochloride solution- To 100 ml distilled water in a beaker, added 10ml concentrated HCl.6-gram naphthylamine hydrochloride was dissolved in it. Diluted to 1liter with distilled water and stored in a refrigerator.
3) Sodium acetate buffer solution 2M-Dissolved 164-gram sodium acetate $NaC_2H_3O_2$ in distilled water diluted to 1liter using a measuring flask.
4) Nitrite stock solution- Dissolved exactly 493 mg sodium nitrite, $NaNO_2$, in distilled water made up to 1liter in a volumetric flask.

1-ml = 100 µg nitrite as N or 328.44 NO_2

The spectrophotometer was calibrated with standard solutions of nitrite-nitrogen prepared from the stock solution. A calibration graph was obtained in the spectrophotometer with standard solutions of strength 0.0, 0.005. 0.01, 0.05, 0.1, 0.3 mg/L NO_2^- as N. The absorbance readings were measured at 543 nm wavelength with a 1-cm cuvette path. The water samples were diluted wherever needed. The nitrite values were obtained directly with the help of the calibration curve. A nitrite nitrogen-spectrophotometric set-up is shown in Figure 18.

Figure 18: Nitrite-nitrogen- Spectrophotometric set-up

2.10.3 NITRATE-NITROGEN (ULTRAVIOLET SPECTROPHOTOMETRIC SCREENING METHOD)

Nitrate-nitrogen was tested by the Ultraviolet Spectrophotometric Screening Method as per test method 4500-NO_3^- NITROGEN (NITRATE) mentioned in Standard Methods for the Examination of Water Wastewater, 18th Edition. This method determines nitrate (NO_3^-) by measuring UV (Ultra Violet) light absorption at 220 nm. Since NO3- does not absorb at 275 nm and dissolved organic matter also absorbs at 220 nm, the NO3- value is corrected using a second test at 275 nm.

Reagents:

1) Hydrochloric acid solution 1N- 83.4-ml of concentrated HCl was diluted to 1000 ml distilled water using a 1-liter measuring volumetric flask and stored.
2) Nitrate stock solution- Dissolved exactly 0.7218 g potassium nitrate, KNO_3 (previously dried in an oven at 105 ºC for 24 h) in distilled water made up to 1liter in a volumetric flask.

   1.0ml = 100 µg NO_3 as N or 4.4267 NO_3

The spectrophotometer was calibrated with standard solutions of nitrate-nitrogen prepared from the stock solution. A calibration graph was obtained in the spectrophotometer with standard solutions of strength 0.0, 4.43. 8.86, 17.72, 22.15 mg/L NO_3^- asNO_3. The absorbance readings were measured at 220 nm and 275 nm wavelength with a 1-cm cuvette path. 50-ml water samples were taken into the Nessler's tube. Samples having a higher content of nitrate were diluted accordingly with distilled water. To each of Nessler's tubes containing samples, a 1-ml solution of 1N HCl was added to prevent interference from hydroxide or carbonate concentrations. Two times the absorbance at 275 nm was subtracted from the reading at 220 nm to obtain absorbance due to NO_3^-.The nitrate values were obtained directly. A nitrate nitrogen- spectrophotometric set-up is shown in Figure 19.

Figure 19: Nitrate nitrogen- Spectrophotometric set-up

2.10.4 TOTAL ALKALINITY (TITRATION METHOD)

Total Alkalinity was tested by the Titration Method as per test method 2320 B mentioned in Standard Methods for the Examination of Water Wastewater, 18th Edition. Alkalinity is a measure of acid-neutralizing capacity that reacts with hydrogen ions. It is brought on by calcium, magnesium, sodium, potassium bicarbonate, carbonate, and hydroxide molecules. Alkalinity is also impacted by silicates, phosphates, and borates. The color change titration procedure measured Alkalinity. Alkalinity was determined by titration with 0.02N H_2SO_4 solution using the mixed indicator.

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

$$2CaCO_3 + H_2SO_4 \rightarrow Ca(HCO_3)_2 + CaSO_4$$

$$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2CO_2\uparrow + 2H_2O$$

Reagents:

1. Sodium carbonate solution 1N- 13.25-gram anhydrous sodium carbonate, Na_2CO_3 (previously dried at 140 ºC for 2 hours), was dissolved in a little distilled water made up to 2250 ml in a volumetric flask.
2. Methyl orange indicator solution- 0.1-gram methyl orange powder was dissolved in 100 ml distilled water.
3. Sulphuric acid solution 1N- 28-ml concentrated sulphuric acid, H_2SO_4 was mixed in a little distilled water made up to 1liter in a measuring volumetric flask with distilled water. This solution was standardized with 1-N Na_2CO_3 solution using methyl as the indicator. (A color change from yellowish to faint orange color indicates the endpoint).
4. Sulphuric acid solution 0.02N- 20-ml solution of 1N-H_2SO_4 was diluted to 1liter in a volumetric measuring flask with carbon dioxide-free distilled water.
   1.0 ml exactly 0.02N H_2SO_4 = 1.0 mg $CaCO_3$
5. Mixed indicator solution- 20-mg methyl red 100-mg Bromo cresol green indicator powder was dissolved in 100-ml 95% ethyl alcohol.

A 25-ml water sample was taken in a 250-ml conical flask, added 25ml distilled water and two drops of mixed indicator. This solution was titrated with 0.02N H_2SO_4. A faint pink color from the greenish color indicated the endpoint.

Calculations:

$$\text{Total Alkalinity (as } CaCO_3\text{) mg/L} = \frac{\text{ml. } 0.02 \text{ N } H_2SO_4 \text{ to total alkalinity endpoint X 1 X 1000}}{\text{ml. sample taken for titration}}$$

2.10.5 TOTAL HARDNESS (EDTA TITRIMETRIC METHOD)

The samples were tested for total hardness by the EDTA Titrimetric Method as per test method 2340 C mentioned in Standard Methods for the Examination of Water Wastewater, 18th Edition. Hardness is a measure of water's capacity to precipitate soap. Calcium and magnesium ions in water cause soap precipitation. EDTA forms soluble complexes with calcium and magnesium ions. Eriochrome black T is the indicator that changes its color from purple to blue at a pH between 8 to 10, indicating the reaction's completion. Total hardness was determined by titration with 0.02N EDTA solution using the Erichrome black T indicator.

$$Ca^{2+} + \underset{\text{(EDTA)}}{H_2Y^{2-}} \longrightarrow CaY^{2-} + 2H^+$$

$$Mg^{2+} + H_2Y^{2-} \longrightarrow MgY^{2-} + 2H^+$$

$$\underset{\text{(wine red)}}{MgD^-} + H_2Y^{2-} \longrightarrow MgY^{2-} + \underset{\text{(blue)}}{HD^{2-}} + H^+$$

Reagents:

1. Calcium standard solution- 1.00-gram pure calcium carbonate (previously dried at 105 °C) was placed in a 2500ml conical flask using 50-ml distilled water. To this solution, added 20.5 ml 1:1 HCl. The solution was warmed for complete dissolution. The solution was transferred to a 1-liter volumetric flask made up with distilled water.

2. Standard EDTA titrant (0.02N)- 3.723-gram AR grade disodium ethylene diamine tetraacetate dihydrate dissolved in distilled water made up to 1 liter in a volumetric flask. The EDTA solution prepared was standardized with a standard calcium solution stored in a pyrex bottle.

   1.0 ml of exactly 0.02N EDTA = 1.0 mg $CaCO_3$

3. Ammonia-Ammonium chloride buffer- 16.9-gram ammonium chloride NH_4Cl dissolved in 143 ml concentrated ammonium solution diluted to 250ml with distilled water.
4. Eriochrome Black T- Mixed 0.5-gram of the dye 100-gram sodium chloride stored in a dry reagent bottle.

A 25-ml water sample was taken in a 250 ml conical flask, added 25 ml distilled water and two drops of an ammonia buffer solution with a few granules of eriochrome black T indicator. This solution was titrated with 0.02N EDTA. A change in blue color from purple indicated the endpoint.

Calculations:

$$\text{Total Hardness (as } CaCO_3\text{) mg/L} = \frac{\text{ml. 0.02 N EDTA to total alkalinity endpoint X 1 X 1000}}{\text{ml. sample taken for titration}}$$

2.11 DETERMINATION OF PH, CONDUCTIVITY, AND TOTAL DISSOLVED SOLIDS

The Instrument model Hach HQ 440 d Multi Ion Analyser, made in Lovel, Colorado, United States, measured the pH values, total dissolved solids, and electrical conductivity. The Hach instrument is shown in Figure 20.

Figure 20:Hach HQ 440 d Multi Ion Analyser

2.12 SPECTRUM AND CHEMICAL ANALYSIS OF ZEOLITES BY XRD AND XRF

The zeolite materials were analyzed before (virgin) after Use (treatment) on the X-Ray Diffraction (XRD) X-Ray Fluorescence (XRF) instruments. The X-Ray Diffraction was performed on a Rigaku X-ray diffractometer (XRD), model Ultima IV, made in the USA (Figures 21 and 22). XRF was performed on the Malvern Panalytical Energy Dispersive X-ray fluorescence (EDXRF) spectrophotometer model Epsilon 4, made in the United Kingdom (Figures 23 and 24). The tests were performed at Central Revenue Customs Laboratory (CRCL), New Delhi, India.

Figure 21: Rigaku X-ray diffractometer (XRD) Ultima IV made in the USA

Figure 22: Rigaku X-ray diffractometer (XRD) Ultima IV made in the USA

Figure 23: Malvern Panalytical Energy Dispersive X-ray fluorescence (EDXRF) spectrophotometer model Epsilon 4, made in the United Kingdom

Figure 24: Malvern Panalytical Energy Dispersive X-ray fluorescence (EDXRF) spectrophotometer model Epsilon 4, made in the United Kingdom

CHAPTER 3

Performance of Cow-Dung Sludge in Water Treatment for Mitigation and Conversion of Ammonia Nitrogen into Nitrate

CHAPTER 3: PERFORMANCE OF COW-DUNG SLUDGE IN WATER TREATMENT FOR MITIGATION AND CONVERSION OF AMMONIA-NITROGEN INTO NITRATE

3. COW-DUNG AND COMPOSTED COW-DUNG

Bovine animals, which are herbivores, excrete dung. Cow dung is made up of partially digested food particles that have gone through the cow's digestive tract (Gupta et al., 2016; Munshi et al., 2018). Cow dung is a cheap and readily available rich microflora source (Randhawaand Kullar, 2011). The government of India, Department of Animal Husbandry Dairying, Ministry of Fisheries, Animal Husbandry Dairying (FAHD) has mentioned several cow-dung uses as a bio-resource. Cow dung refers to the fresh excreta, whereas composted cow dung refers to the cow dung sludge which has been composted on being laid down in a large heap under anaerobic conditions.

3.1 USES FOR COW-DUNG(Secretary, 2019)

1) Fuel – cow-dung patties are used as fuel in Indian houses for cooking purposes.
2) Fertilizer – composted sludge is used as fertilizer in fields for crop production.
3) Mud dwellings use floor coating, which is mud and water combined together. It enhances the mud's capacity to absorb water.
4) Mudbrick additive: enhances disintegration resistance
5) Skin tonic that has been blended with crushed neem leaves and applied topically works well for boils and heat rashes.
6) Smoke producer: burning cow pies keep insects at bay.
7) Ash from burgers is used to clean cooking pots. When used dry, it absorbs oil and fat; when used wet, it serves as a general cleaner.
8) Tamarind reduces oxidation; wet ashes polish; brass polisher
9) Alkaline fertilizer is made from cow dung ash, which contains lime and a few other minerals.
10) Mud additive: dries up muddy puddles that are slick. Mudbrick additive: When combined with lime (cow dung ashes), mud becomes cement-like.
11) Pond pH balancer: neutralizes the pond's pH when added.

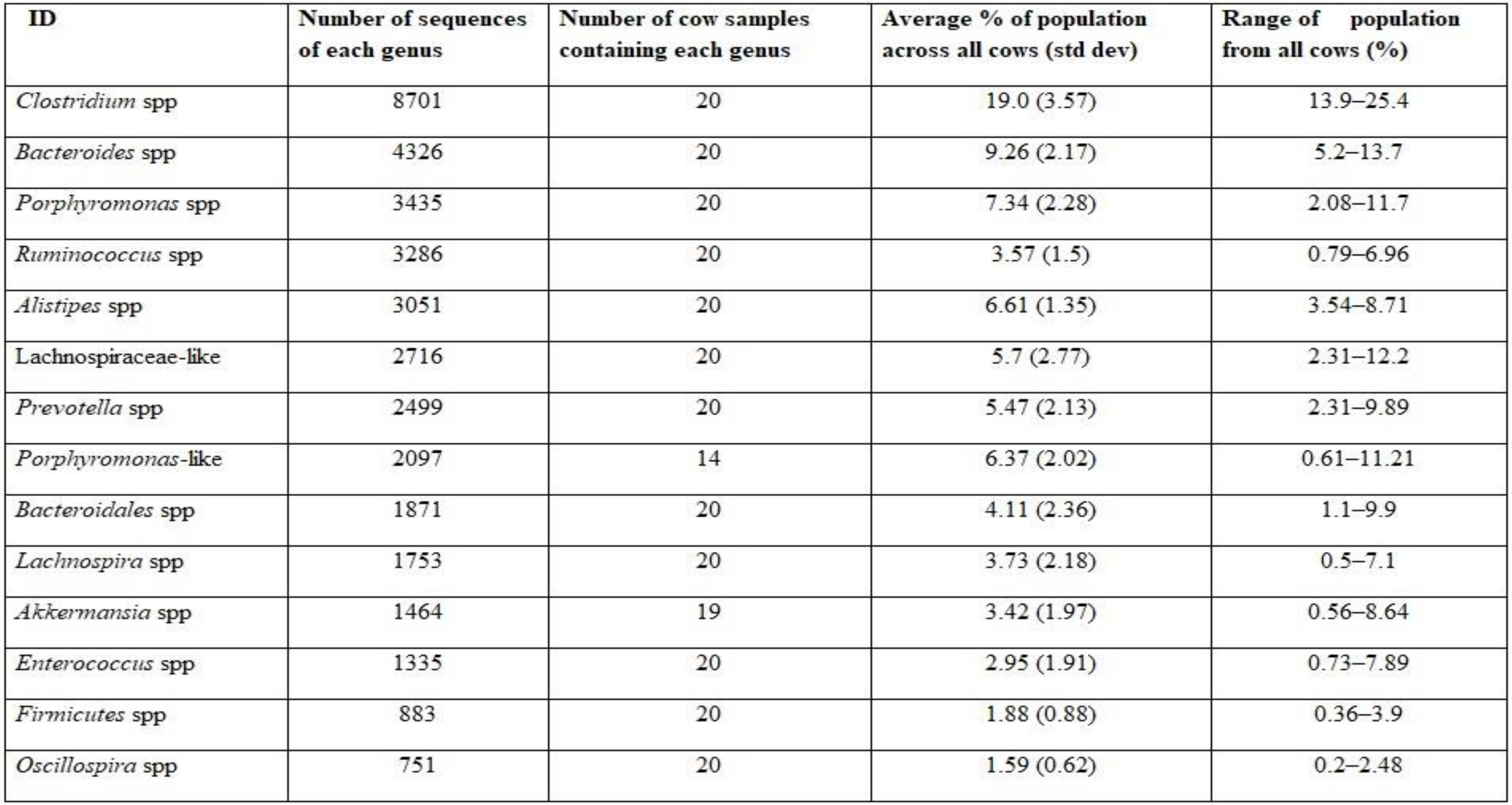
12) Ash from cow dung is used to polish teeth.
13) Deity worship is a component of pancha-gavya.
14) Seed protector: Before planting, coating seeds with dung can help prevent pest infestations.
15) To treat skin conditions, make a paste out of cow pies (camel dung) and freshwater. It appears to be effective in reducing psoriasis itching.
16) Cow urine is a natural remedy for athletes' feet. Soak your feet in it.
17) The traditional Indian village technique ensures that flies won't congregate there by cleaning the floor each day with a solution of water and fresh cow dung.
18) Cow dung slurry, which is the residue after making biogas from it, still contains great liquid compost that may be used in gardens.

The bioremediation of metals, pesticides, pharmaceuticals, petrochemicals, and biomedical waste uses the microbial consortia of cow dung (Lalitha, Ch. and Krishna, 2019). The nitrogenous molecules expelled in the fecal matter include a portion of metabolic nitrogen and a portion of undigested or unabsorbed dietary nitrogen. The metabolic fraction consists of chemicals that come from within the body, such as bile and other digestive juice residues, intestinal epithelial cells, and bacterial residues. Fecal residues are essentially undigested fiber, remnants of the intestinal epithelium that has shed, some expelled bile products (such pigments), intestinal bacteria, and mucus. The rumen of a cow contains more than 100 types of protozoa and over 60 species of bacteria. Fermenters of cellulose, hemicellulose, and pectin make up the majority of the microorganisms. For cow manure, the total number of aerobic heterotrophic bacteria ranged from 55 x 105 c.f.u. from g-1 to 94 x 105 c.f.u. g-1. Cow dung, which has the rakshoghna, bitter, and ogaru taste of Kapha disorders and is generally used to cure them, is also effective in managing skin conditions. Cow dung with urine has antiseptic and preventative effects, is a good medium for biocontrol agents, and is advantageous to Rhizobium Azobacter. It is also rich in bacteria that compete with pathogens (Akinde & Obire, 2008; Balasubramanian, 2006; Lalitha, Ch. and Krishna, 2019; Randhawa & Kullar, 2011).

3.2 THE BIOLOGICAL CONSORTIUM OF COW-DUNG

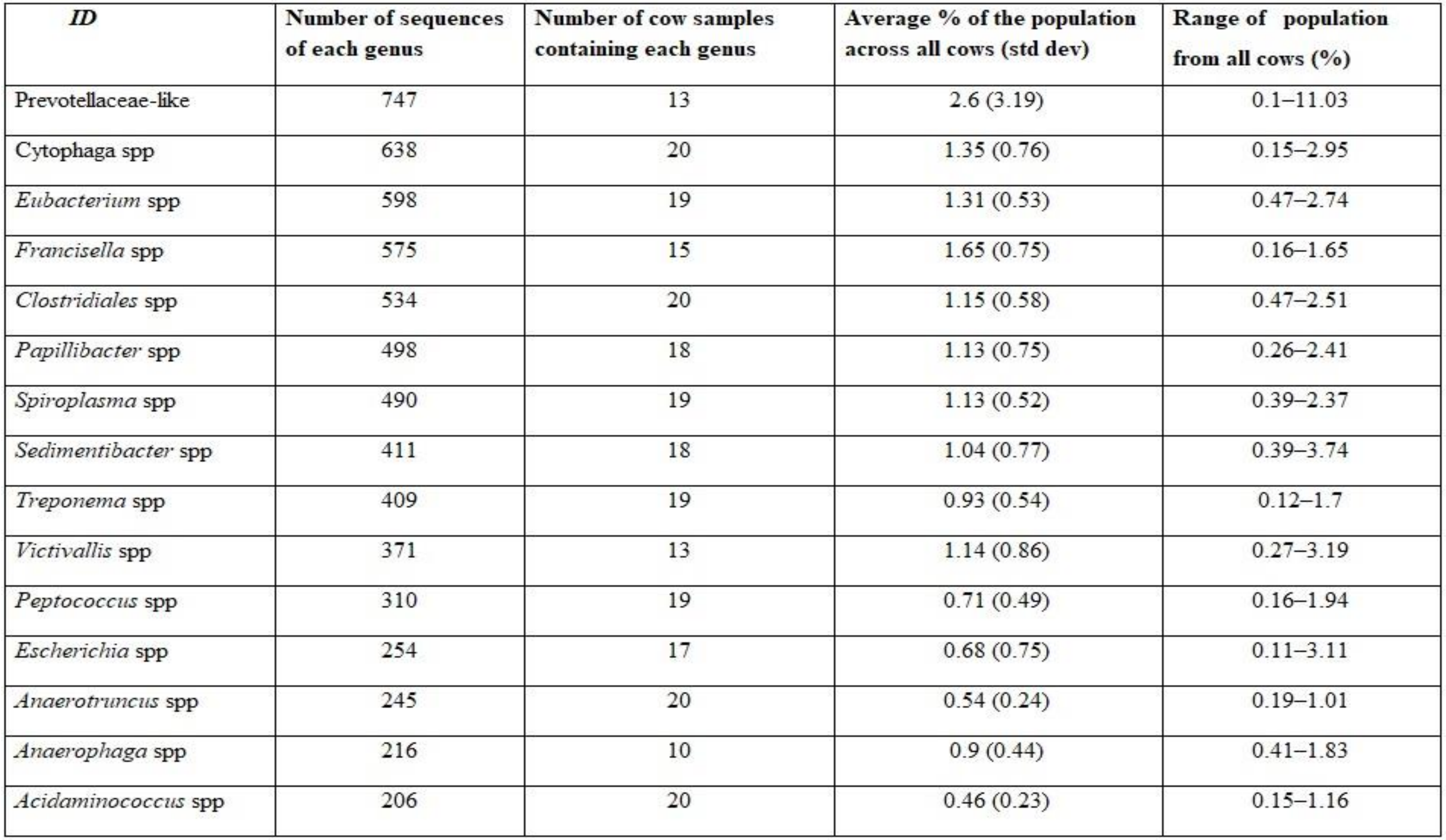
The bacteria, fungi, and actinomycetes discovered in cow dung slurry include Fecal Streptococcus, Streptococcus, Pseudomonas Sp, Sarcina, Nocardia, Mucor Sp, Rhizopus Sp, Aspergillus, E. coli sp, and Penicillium Sp (Lalitha, Ch. and Krishna, 2019). Axylan-degrading sporulated bacterium was isolated and identified as a member of a novel species of the genus Paenibacillusfrom recent old cow dung rectal samples, based on 16S rRNA gene sequences. According to Velázquez et al. (2004), it was discovered that the new species in cow dung produce a wide range of hydrolytic enzymes, including urease, gelatinase, amylases, cellulases, xylanases, and b-galactosidase. Aerobic heterotrophic bacteria, including Acinetobacter spp., Alcaligenes spp., Bacillus sp., Pseudomonas spp., and Serratia sp., were identified from cow dung for their potential ability to degrade gasoline (Akinde & Obire, 2008). The microbiome of 20 commercial nursing dairy cows was examined by Dowd et al. (2008) for the common bacterial consortia. Prevotella, Enterococcus, Clostridium, Bacteroides, Oscillospira, Cytophage, Lachnospira, Ruminococcus, Lachnospiraceae, Porpyhyromonas, Alistipes, Anaerotruncus, and Acidaminococcussp were among the microbiomes found in the cattle feces. Also found in some of the livestock were food-borne harmful microorganisms. Six cows tested positive for Campylobacter, whereas four cows tested positive for Salmonella spp. (tentative enterica). During their investigation, Dowd et al. (2008) found a total of 37 distinct species of Clostridium spp. The most frequent Clostridium species were (tentatively) straminisolvens, hathewayi, leptum, fimetarium, orbiscindens, and lactatifermentans were found by collecting fecal samples from twenty different cows to be the most prevalent varied genus. The 20 samples of cow feces in Tables 8(a), 8(b), and 8(c) show the most common genera found there (Dowd et al., 2008).

Table 8 (a): Most ubiquitous genera identified from the cow fecal samples



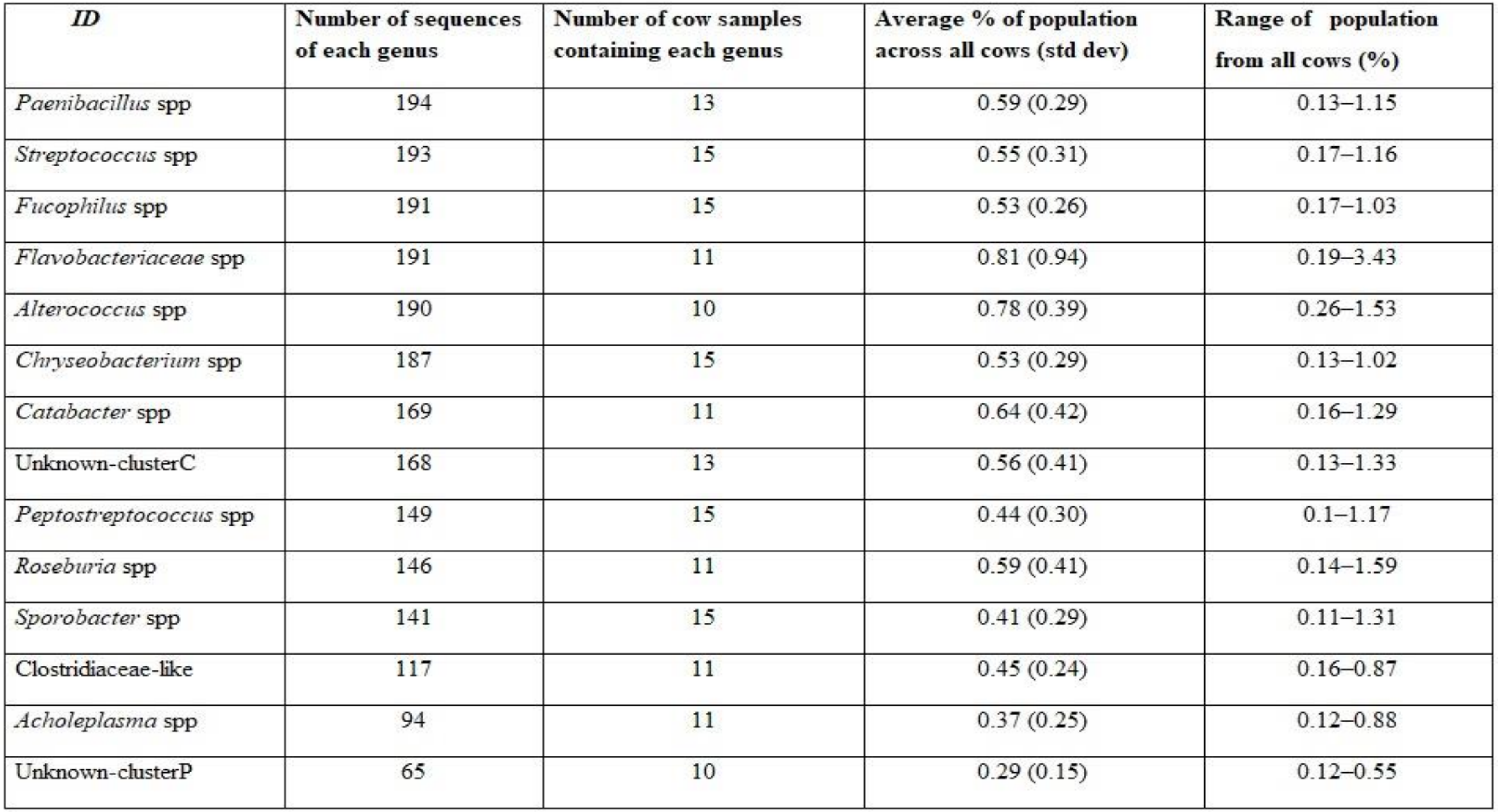
ID	Number of sequences of each genus	Number of cow samples containing each genus	Average % of population across all cows (std dev)	Range of population from all cows (%)
Clostridium spp	8701	20	19.0 (3.57)	13.9–25.4
Bacteroides spp	4326	20	9.26 (2.17)	5.2–13.7
Porphyromonas spp	3435	20	7.34 (2.28)	2.08–11.7
Ruminococcus spp	3286	20	3.57 (1.5)	0.79–6.96
Alistipes spp	3051	20	6.61 (1.35)	3.54–8.71
Lachnospiraceae-like	2716	20	5.7 (2.77)	2.31–12.2
Prevotella spp	2499	20	5.47 (2.13)	2.31–9.89
Porphyromonas-like	2097	14	6.37 (2.02)	0.61–11.21
Bacteroidales spp	1871	20	4.11 (2.36)	1.1–9.9
Lachnospira spp	1753	20	3.73 (2.18)	0.5–7.1
Akkermansia spp	1464	19	3.42 (1.97)	0.56–8.64
Enterococcus spp	1335	20	2.95 (1.91)	0.73–7.89
Firmicutes spp	883	20	1.88 (0.88)	0.36–3.9
Oscillospira spp	751	20	1.59 (0.62)	0.2–2.48

Table 8 (b): Most ubiquitous genera identified from the cow fecal samples



ID	**Number of sequences of each genus**	**Number of cow samples containing each genus**	**Average % of the population across all cows (std dev)**	**Range of population from all cows (%)**
Prevotellaceae-like	747	13	2.6 (3.19)	0.1–11.03
Cytophaga spp	638	20	1.35 (0.76)	0.15–2.95
Eubacterium spp	598	19	1.31 (0.53)	0.47–2.74
Francisella spp	575	15	1.65 (0.75)	0.16–1.65
Clostridiales spp	534	20	1.15 (0.58)	0.47–2.51
Papillibacter spp	498	18	1.13 (0.75)	0.26–2.41
Spiroplasma spp	490	19	1.13 (0.52)	0.39–2.37
Sedimentibacter spp	411	18	1.04 (0.77)	0.39–3.74
Treponema spp	409	19	0.93 (0.54)	0.12–1.7
Victivallis spp	371	13	1.14 (0.86)	0.27–3.19
Peptococcus spp	310	19	0.71 (0.49)	0.16–1.94
Escherichia spp	254	17	0.68 (0.75)	0.11–3.11
Anaerotruncus spp	245	20	0.54 (0.24)	0.19–1.01
Anaerophaga spp	216	10	0.9 (0.44)	0.41–1.83
Acidaminococcus spp	206	20	0.46 (0.23)	0.15–1.16

Table 8 (c): Most ubiquitous genera identified from the cow fecal samples



ID	Number of sequences of each genus	Number of cow samples containing each genus	Average % of population across all cows (std dev)	Range of population from all cows (%)
Paenibacillus spp	194	13	0.59 (0.29)	0.13–1.15
Streptococcus spp	193	15	0.55 (0.31)	0.17–1.16
Fucophilus spp	191	15	0.53 (0.26)	0.17–1.03
Flavobacteriaceae spp	191	11	0.81 (0.94)	0.19–3.43
Alterococcus spp	190	10	0.78 (0.39)	0.26–1.53
Chryseobacterium spp	187	15	0.53 (0.29)	0.13–1.02
Catabacter spp	169	11	0.64 (0.42)	0.16–1.29
Unknown-clusterC	168	13	0.56 (0.41)	0.13–1.33
Peptostreptococcus spp	149	15	0.44 (0.30)	0.1–1.17
Roseburia spp	146	11	0.59 (0.41)	0.14–1.59
Sporobacter spp	141	15	0.41 (0.29)	0.11–1.31
Clostridiaceae-like	117	11	0.45 (0.24)	0.16–0.87
Acholeplasma spp	94	11	0.37 (0.25)	0.12–0.88
Unknown-clusterP	65	10	0.29 (0.15)	0.12–0.55

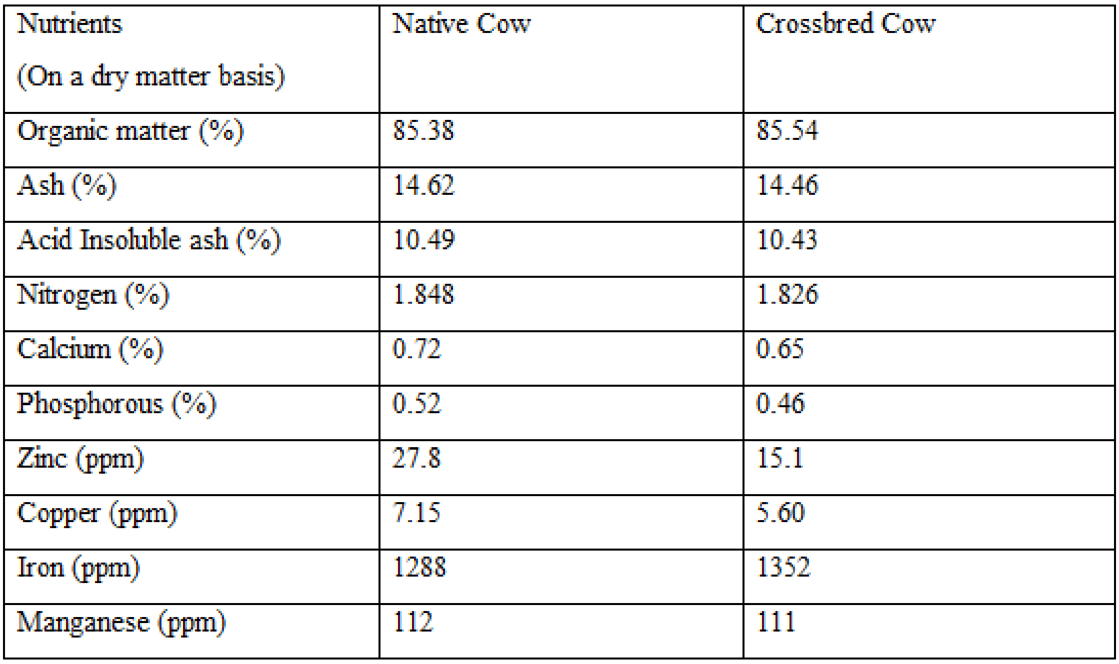
Geetha Fulekar (2008) analyzed (Table 9) various microbiological consortiums in cow dung to study the bioremediation of pesticides in surface soil treatment units using microbial consortia.

Table 9: Microbial Characteristics in Cow-Dung

Parameters	Quantified Value (In Cow-dung)
Total viable count/g	65×10^9
Total coliform count /g	189×10^7
Total Yeast Mould count/g	59×10^3
Pseudomonas count/g	72×10^3
Actinomycetes count/g E.coli count/g	83×10^4 23,600
Anaerobic bacterial count	<30
Thermophilic bacterial count	790
Anaerobic spore count	Nil
Thermophilic spore count	Nil
Anaerobic thermophilic spore count	Nil
Salmonella	Absent
S.aureus	Absent
Shigella	Absent
Fecal streptococcus	Present
Flavobacterium	Absent
Alcaligen	Absent
Bacillus	Present
Streptococcus	Present
Sarcina	Absent
Serratia	Absent
Nocardia	Present
Mucor spp.	Present
Rhizopus stolonifera	Present
Aspergillus	Present
Penicillium	Present

Cow dung has been found to contain about total solids, 454 g/kg; pH (1:10 ratio) 7.64; total organic carbon (TOC), 421 g/kg; total Kjeldahl nitrogen(TKN), 6.1 g/kg; total phosphorus (TP), 6.8 g/kg C:N ratio, 69.0(Kaushik & Garg, 2004). The chemical composition of the cow-dung of Indian native (desi) crossbred cows has been presented in Table 10 (Garg, 2007).

Table 10: Chemical composition of native (Indian) crossbred cow-dung



Nutrients (On a dry matter basis)	Native Cow	Crossbred Cow
Organic matter (%)	85.38	85.54
Ash (%)	14.62	14.46
Acid Insoluble ash (%)	10.49	10.43
Nitrogen (%)	1.848	1.826
Calcium (%)	0.72	0.65
Phosphorous (%)	0.52	0.46
Zinc (ppm)	27.8	15.1
Copper (ppm)	7.15	5.60
Iron (ppm)	1288	1352
Manganese (ppm)	112	111

3.3 PREVIOUS STUDIES ON COW DUNG IN WATER TREATMENT

In Indian culture, cow dung in various forms (raw, composted, ash, dried cakes) is used for several medical, environmental, and religious activities(Geetha Fulekar, 2008; Lalitha, Ch. Krishna, 2019; Notermans, 2019; Ojedokun Bello, 2016; Teo Teoh, 2011; Quraishi, T. et al., 2018). Though, no study has been performed on its potential usefulness in water treatment for combating ammonia nitrogen. In a study to look into petroleum-using bacteria in a bioremediation process of oil-polluted soil, the aerobic heterotrophic bacteria isolated from cow dung revealed potential utility for crude oil breakdown. Acinetobacter spp., Alcaligenes spp., Bacillus sp., Pseudomonas spp., and Serratia spp. were the organisms that were discovered to be helpful (Akinde & Obire, 2008). A novel ammonia-oxidizing bacterium belonging to the genus *Nitrosomonas* was isolated from a cattle manure pile's surface layer during the composting process's final step.(Nakagawa & Takahashi, 2015). In a different trial, the soil was separately treated with an acetone-based solvent that contained insecticides (chlorpyrifos, cypermethrin, fenvalerate, TBEE). The presence of nutrients and microorganisms in cow dung has significantly influenced the bioremediation of pesticides(Geetha & Fulekar, 2008). The maximum organic matter mineralization rate was seen with exhausted grape and cow dung in a study on carbon-nitrogen transformations in the evaluation of compost stability when distillery wastes were combined with animal manures (Bustamante et al., 2008). Bacteria, fungi, and actinomycetes from cow dung could decompose phenol concentrations between 100 and 1000 mg/L. (Singh & Fulekar, 2007).Cow-dung ash can remove Chemical Oxygen Dem (COD) from Landfill Leachate. The results demonstrate that activated cow-dung ash (ACA) may remove up to 79 percent of COD at an ideal temperature of 30 °C at pH 6.0 using a 20 g/L dose in 120 minutes, whereas cow dung ash can remove 66 percent of COD at pH 8.0 using a 20 g/L amount in 120 minutes (Kaur et al., 2016).*Periconiella*Sp. of fungus isolated from fungus extracted from cow-dung acts as a degrader of biomedical waste (Pey*et al.*, 2008). Vermicompost containing earthworm *E.foetida*has been found to reduce metals Cr Cu(Srivastava *et al.*, 2005). Cow-dung sludge has been found helpful in the COD removal of industrial effluents. Initial amounts of three industrial wastewater samples containing COD as 1650, 3646, and 8743 mg/L were found to be reduced to 897, 622, 263mg/L; 2848, 1674, 1260mg/L, 7836, 5120, 4332mg/L on the 5th, 10th, 15th day of the experiment(Quraishi, T. et al., 2018). For the slow-growing, poorly flocculating population of nitrifying bacteria to have a chance to flourish, a relatively high MCRT (>8 days) is needed in the aeration tank of municipal industrial activated sludge processes (Michael H. Gerardi, 2002).

3.4 THE PRESENT STUDY ON COW DUNG IN WATER TREATMENT FOR COMBATING AMMONIA

Treated sewage effluent water samples were collected from a municipal sewage treatment plant after the secondary treatment unit. The municipally treated sewage effluent (MTSE) samples were experimented with to combat ammonia nitrogen using composted cow dung. A jar test apparatus was used to observe the biomass's effectiveness with an agitating speed of 35 RPM. The experiments were carried out in triplicate for more precise results (Appendix 3). Because the jar test apparatus had six arrangement units, triplicate samples were treated and noted separately. Initially, cow dung was used with varying concentrations in the presence-absence of lights. We measured initial levels for ammonia nitrogen and other parameters of MTSE, and the experiments were performed at room temperature with the pristine state of the samples. Experiments were conducted using the excreta of bovine animals like Blue-buck, Buffalo, and Cow as a potential bioresource to combat ammonia nitrogen from wastewater. Among all these, cow dung was the most effective for mitigating ammonia nitrogen.

3.5 AN EXPERIMENTAL STUDY WITH COW DUNG SLUDGE

The reported results are the final valid values extracted after performing several experiments under varying experimental conditions. The collected MTSE were taken into the six one-liter beakers. The concerned initial parameters of ammonia nitrogen, nitrite, nitrate, pH, electrical conductivity, total dissolved solids, color, odor, and temperature were determined immediately after collecting samples. The first and second beakers were kept in series for reference or control samples. Beaker 1 served as a control to measure the amount of water evaporated during the experiment. Beaker 2 served as a control to measure the change of parameters naturally. We added 1.00 5.00 grams of cow dung into beakers 3, 4, 5, and 6 (in duplicate). Four 15-watt tungsten bulbs were hung over the Jar Test apparatus to illuminate the system round the clock. The stirrers of the equipment are set at 35 RPM. Every 48 hours, a 100 ml sample was taken from the jars numbered 2 to 6 and was tested for the change in parameters. The content of beaker one was used for measuring the quantity of water evaporated during the processing period of 48 (2 days), 96(4 days), 144 (6 days), and 192 hours (8 days), respectively. Wastewater samples setup in a pristine state with cow dung dosing is shown in Figures 25, 26, 27, and 28, respectively.

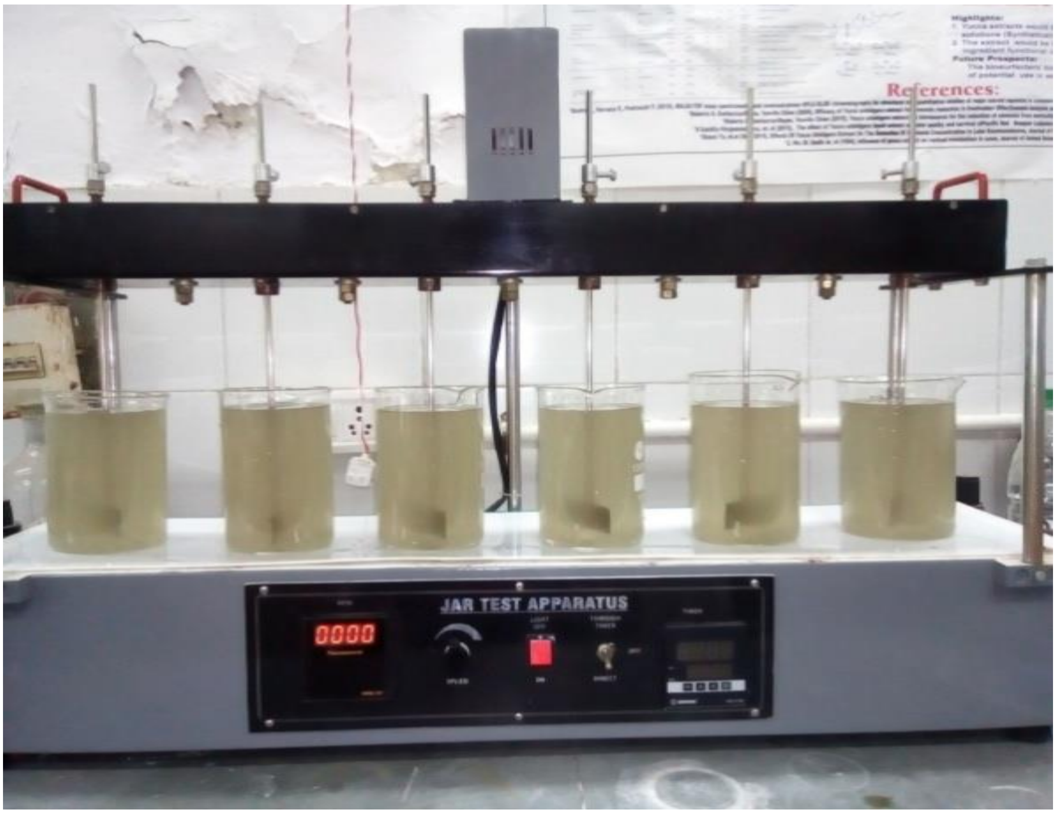


Figure 25: Experimental Setup with MTSE samples in the pristine state

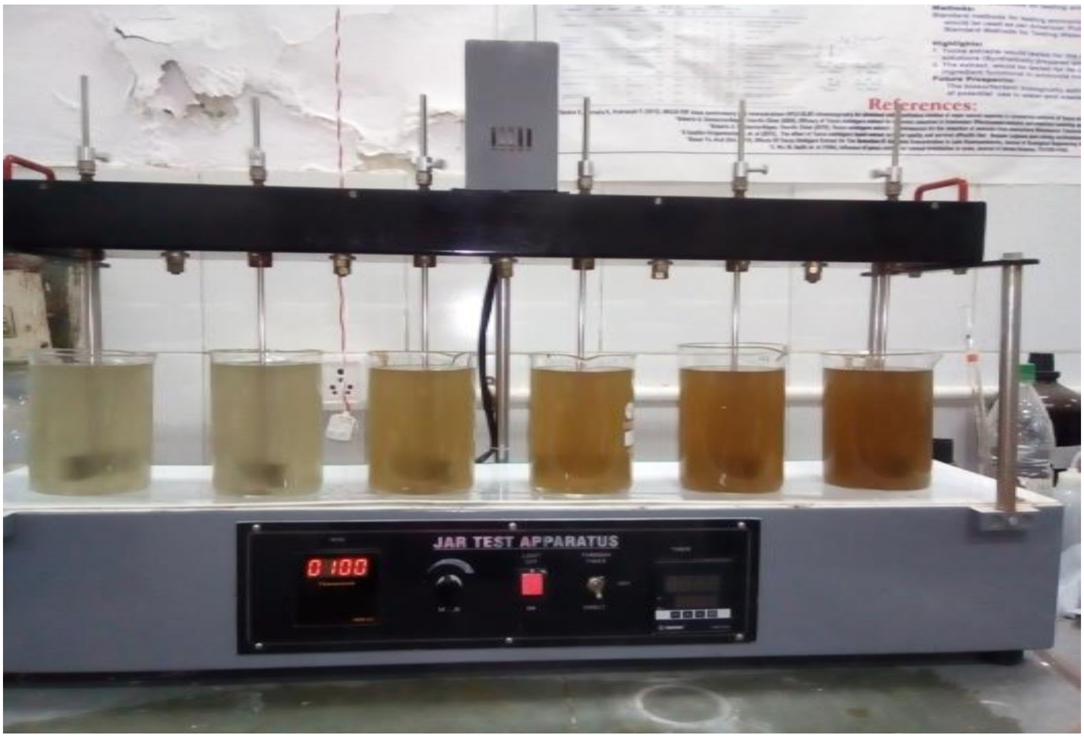


Figure 26: Experimental Setup with added cow dung in increasing amount

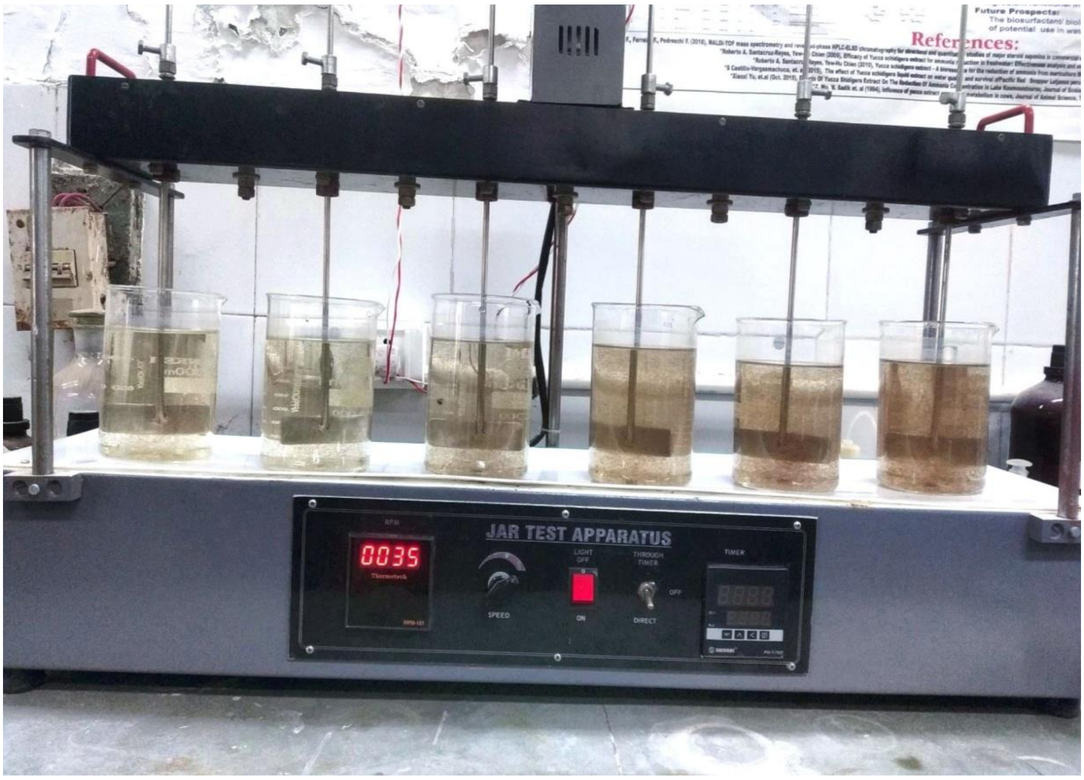


Figure 27: Experimental setup after the flocculation process of wastewater using composted cow dung

Figure 28: Clarification of wastewater ammonia removal status

3.6 REDUCTION OF AMMONIA-NITROGEN USING COW DUNG SLUDGE

Multiple experimental studies with digested cow dung found that catalytic enzymes nitrifying bacteria in cow dung reduced ammonia significantly. Composted cow dung mitigated ammonia nitrogen significantly and was helpful in oxidizing ammonia nitrogen into a stable form of nitrogen, i.e., nitrate. The results of the present study, as depicted in Figure 29 wherein, from an initial amount of 34.780 mg/L ammonia nitrogen (as NH_3) in municipally treated sewage effluent (MTSE) was reduced to 23.210 (In control sample), 22.590 (with one g/L cow-dung), 18.390 mg/L (with five g/L cow-dung) in 48 h or 2nd day of process at 32°C temperature 35 RPM. In 96 h, or the 4th day of the experimental set-up, ammonia nitrogen was reduced to 2.040 mg/L, 0.960 mg/L, and 1.390 mg/L, respectively. On 144 h or the 6th day, ammonia-nitrogen was decreased to 0.032 mg/L, 0.00 mg/L, and 0.00 mg/L. In 192 h or the 8th day, ammonia nitrogen had been reduced to 0.00 mg/L, 0.00 mg/L, and 0.00 mg/L, respectively.

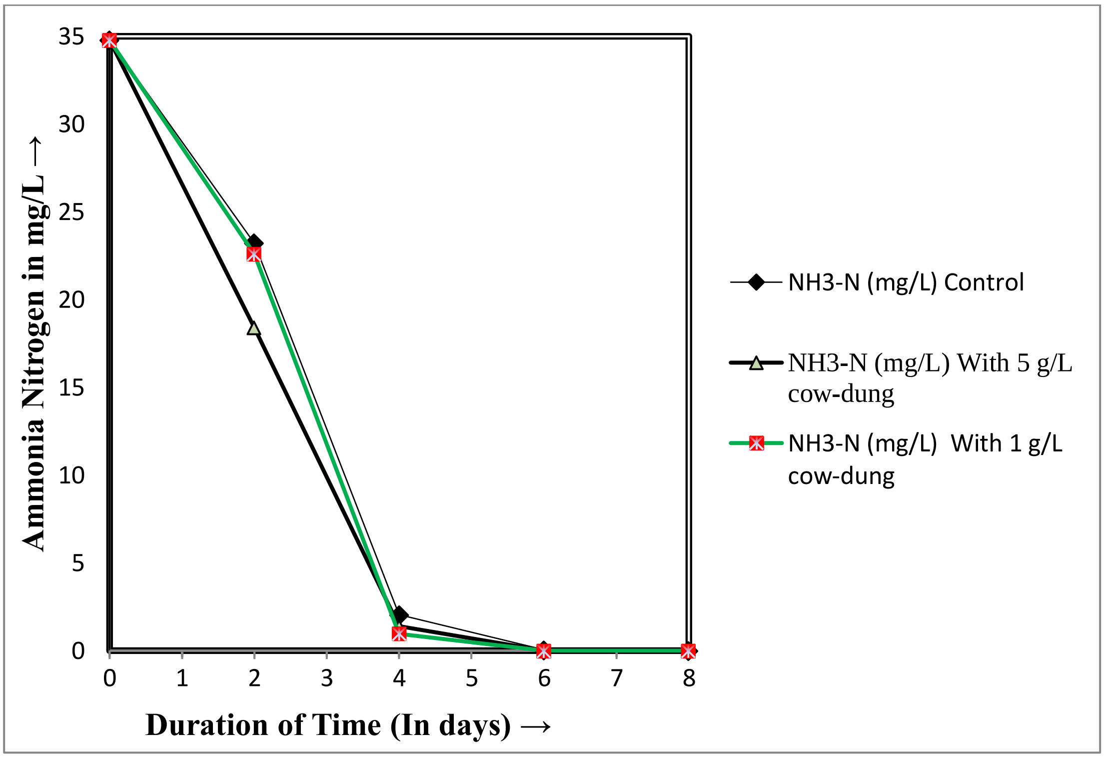


Figure 29:Biological Oxidation of Ammonia Nitrogen

3.7 BIOLOGICAL OXIDATION OF AMMONIA INTO NITRITE

Figure 30 shows the oxidation of Nitrite(NO_2) into Nitrate (NO_3). The initial content of ammonia nitrogen in municipally treated sewage effluent (MTSE) gets converted to nitrite and nitrate simultaneously. The conversion of ammonia into nitrite and nitrate in biological oxidation is a continuous process. An experimental study explored that the effluent having an initial amount of 34.789 mg/L ammonia nitrogen and 0.150 mg/L nitrite nitrogen has converted or oxidized to 0.210 mg/L (In blank), 2.880 mg/L (with one g/L cow-dung), 3.265 mg/L (with five g/L cow-dung into nitrite (NO_2)in 48 h or 2nd day of process at 32°C temperature 35 RPM. In 96 h or the 4th day of the experimental set-up, ammonia nitrogen oxidized to 11.70 mg/L, 16.15 mg/L, and 11.45 mg/L nitrite (NO_2), respectively. In 144 h or the 6th day, ammonia nitrogen gets converted to nitrite (which further kept oxidizing to nitrate) to 14.70 mg/L, 8.80 mg/L, and 0.30 mg/L. After 192 h or 8th-day, ammonia-nitrogen oxidized to 17.80 mg/L, 0.18 mg/L, and 0.09 mg/L nitrite (NO_2), respectively.

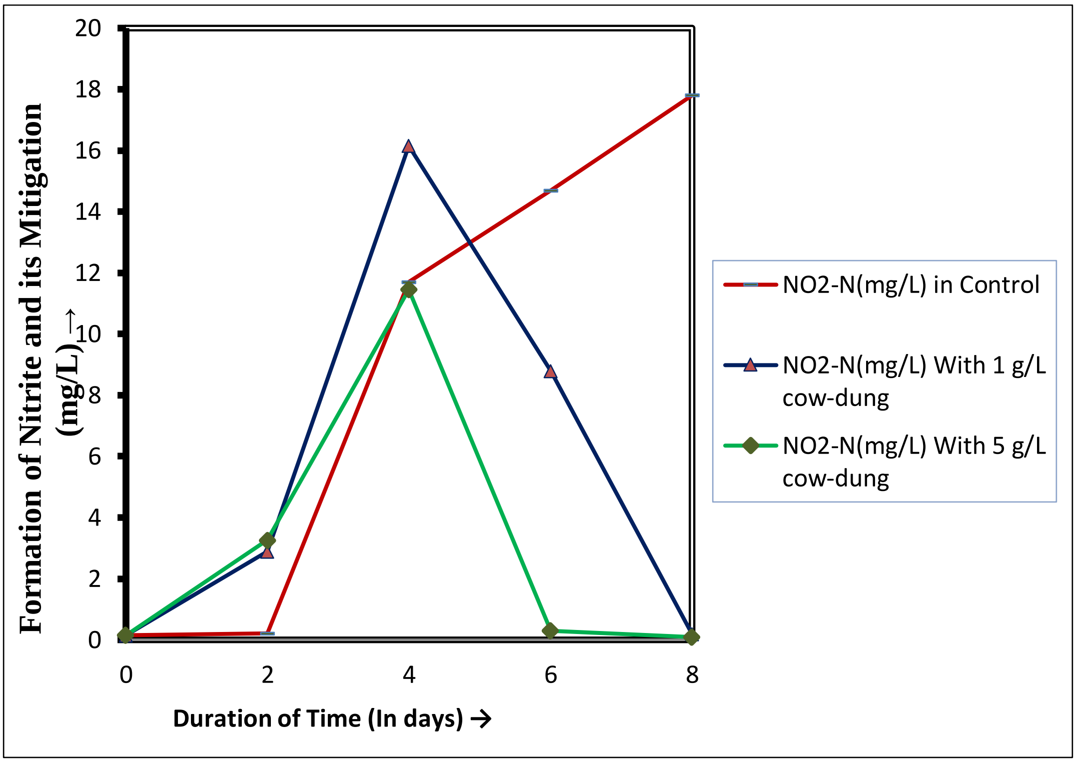


Figure 30:Formation of Nitrite nitrogen during oxidation of ammonia nitrogen

3.8 OXIDATION OF NITRITE (NO_2) INTO NITRATE (NO_3)

Ammonia nitrogen readily gets converted to nitrite biologically, but its further oxidation to nitrate (a stable form) is typical. It has been observed that the oxidation of nitrite into nitrate is recalcitrant. Cow-dung accelerated the process of nitrification. Figure 31 shows that the initial amount of 34.789 mg/L ammonia nitrogen 0.45 mg/L nitrate as NO_3 converted or oxidized to 2.25 mg/L (In blank), 3.80 mg/L (with 1-g/L cow-dung), 11.70 mg/L (with 5-g/L cow-dung) into nitrate (NO_3)in 48 h or 2nd day of process at 32°C temperature 35 RPM. In 96 h or the 4th day of the experimental set-up, ammonia-nitrogen oxidized to 12.90 mg/L, 22.25 mg/L, and 59.30 mg/L nitrates(NO_3). In 144 h or the 6th day, ammonia-nitrogen converts to nitrate as 16.60 mg/L, 67.30 mg/L, and 109.0 mg/L. In 192 h or 8th day, ammonia nitrogen oxidized to 21.80 mg/L, 110.10 mg/L, 133.5 mg/L nitrate(NO_3), respectively.

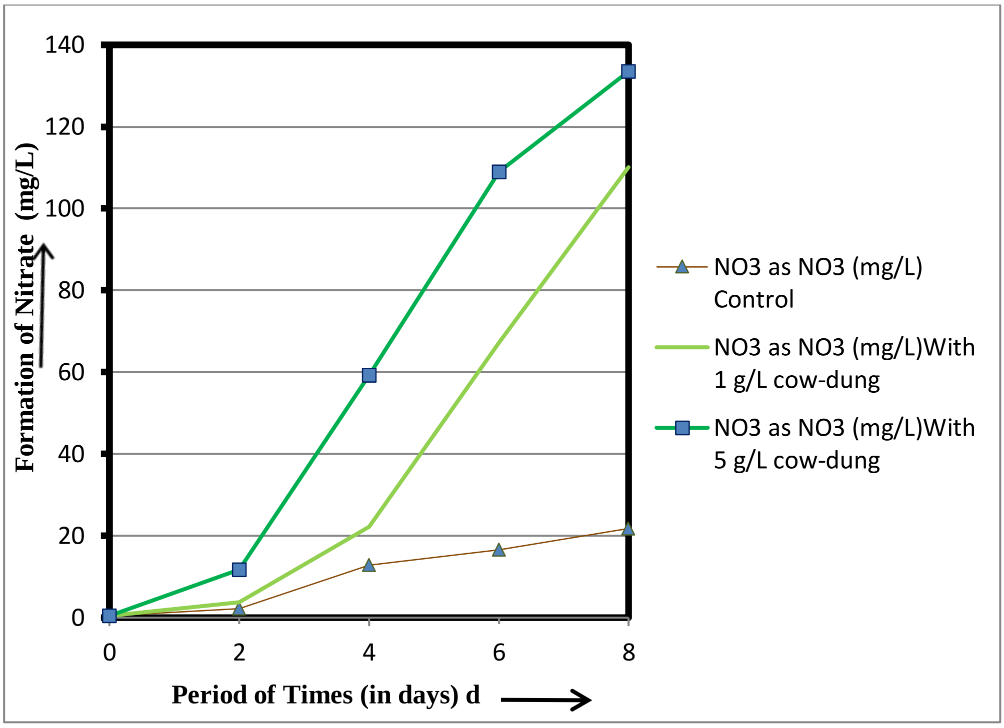


Figure 31: Conversion of Ammonia nitrogen into nitrate

The ammonia nitrogen has been completely converted to its final stable product nitrate in 6 to 8 days, depending on the amount of cow-dung dosed. However, the samples' total dissolved solids have been found to increase due to water evaporation during ammonia nitrogen oxidation. Because of evaporation, there was 5.7 %, 10.2 %, 15.7 %, and 21.9 % water loss on the experimental process's 2nd, 4th, 6th, and 8th days.

3.9 RESULTS DISCUSSIONS - SEWAGE TREATMENT WITH COW DUNG SLUDGE

Experimental studies were carried out with Municipally Treated Sewage Effluent (MTSE) for combating ammonia nitrogen. In the MTSE control sample, an initial amount of 34.780 mg/L ammonia nitrogen (as NH_3) reduced to 23.210 mg/L in 48 h, 2.040 mg/L in 96 h, 0.032 mg/L in 144 h, 0.00 mg/L in196 h. Nitrite concentration increased to 0.210 mg/L, 11.7 mg/L, 14.7 mg/L, and 17.8 mg/L, respectively, after 48, 96, 144,196 hours. Simultaneously, nitrate formation was found to be 2.25 mg/L, 12.90 mg/L, 16.60 mg/L, and 21.8 mg/L after 48, 96, 144, and 196 hours of the period (Table 11).

Table 11: Reduction of ammonia-nitrogen conversion to nitrite, nitrate in MTSE Control Sample

Duration of Treatment	Ammonia (as N)		Conversion to Nitrite (as NO_2)/ Formation		Formation of Nitrate (as NO_3)	
	Remained	Reduced				
	In mg/L	In percent	In mg/L	In percent	In mg/L	In percent
48 Hours	23.21	33.26	0.210	1.17	2.25	1.68
96 Hours	2.040	94.13	11.7	65.73	12.90	9.66
144 Hours	0.032	99.90	14.7	82.58	16.60	12.43
196 Hours	Nil	100	17.8	100	21.8	16.32

An initial amount of 34.780 mg/L ammonia nitrogen (as NH_3) in MTSE (with 1g/L cow-dung) reduced to 22.59 mg/L, 0.96 mg/L, 0.00 mg/L, 0.00 mg/L in 48 h, 96 h, 144 h an 196 h respectively. Nitrite concentration was found to increase/decrease at 2.88 mg/L, 16.15 mg/L, 8.8 mg/L, and 0.18 mg/L, respectively. Nitrate content rose consistently in the order of 3.80 mg/L, 22.25 mg/L, 67.3 mg/L, and 110.1 mg/L after 48, 96, 144, and 196 hours of the time period (Table 12).

Table 12: Reduction of ammonia-nitrogen conversion to nitrite nitrate in MTSE with one g/l cow-dung

Duration of Treatment	Ammonia (as N)		Nitrite (as NO_2) Formed (F)/ Reduced ®		Formation of Nitrate (as NO_3)	
	Remained	Reduced				
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
48 Hours	22.59	35.04	2.88 (F)	16.18 (F)	3.80	2.84
			--------	--------		
96 Hours	0.96	97.23	16.15 (F)	90.73 (F)	22.25	16.66
			---------	---------		
144 Hours	Nil	100 %	8.8(F)	49.43(F)	67.3	50.41
			9.0 ®	50.56 ®		
196 Hours	Nil	100 %	0.18(F)	1.01(F)	110.1	82.47
			17.62 ®	98.98®		

Ammonia nitrogen is reduced substantially with an increased amount of cow dung (5g/L). An initial concentration of 34.780 mg/L ammonia nitrogen (as NH_3) in MTSE (with 5g/L cow-dung) reduced to 18.39 mg/L, 1.39 mg/L, 0.00 mg/L, 0.00 mg/L in 48 h, 96 h, 144 h and196 h. Nitrite conversion was found as 3.265 mg/L, 11.45 mg/L, 0.30 mg/L, and 0.09 mg/L, respectively. Nitrate content was increased in the order of 11.70 mg/L, 59.30 mg/L, 109.0 mg/L, 133.5 mg/L after 48, 96, 144, and 196 hours of the period (Table 13).

Table 13: Reduction of ammonia-nitrogen conversion to nitrite and nitrate in MTSE with five g/l cow-dung

Duration of Treatment	Ammonia (as N)		Nitrite (as NO_2) Formed (F)/ Reduced ®		Formation of Nitrate (as NO_3)	
	Remained	Reduced				
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
48 Hours	18.39	52.87	3.265 (F)	18.34 (F)	11.70	8.76
			----------	-----------		
96 Hours	1.39	96.00	11.45 (F)	64.32(F)	59.30	44.41
			6.35®	35.67®		
144 Hours	Nil	100	0.30(F)	1.68 (F)	109.0	81.64
			17.5®	98.31®		
196 Hours	Nil	100	0.09 (F)	0.50 (F)	133.5	100
			17.71®	99.49®		

So, based on the above experimental results, cow dung was found to be highly efficient in neutralizing and converting ammonia-nitrogen into stable forms of nitrate-nitrogen.

CHAPTER 4

POTENTIAL USE OF *YUCCA SCHIDEGRA*, A PLANT EXTRACT IN WATER TREATMENT FOR COMBATING AMMONIA NITROGEN

CHAPTER 4: POTENTIAL USE OF *YUCCA SCHIDEGRA,* A PLANT EXTRACT IN WATER TREATMENT FOR COMBATING AMMONIA NITROGEN

4. INTRODUCTION: YUCCA SCHIDIGERA, A DESERT PLANT

Yucca schidigera (Agavaceae) is a plant that is indigenous to Mexico and the southwest United States. It grows in the desert of Baja California. In order to prevent ammonia buildup in animal holding facilities and lower the ammonia concentration in animal excrement, its extract has been employed as an ingredient in the cosmetic, soft drink, and livestock sectors. It is fed to livestock fowl in poultry farms to increase growth productivity and reduce ammonia odors in chicken excrement (Cheeke, 2000; Gaber, 2006). Yucca extract contains a substantial amount of saponins, the high concentration of which is thought to be the cause of its beneficial mode of action (10 percent of dry weight). Natural detergents (surfactants) called saponins are present in a wide range of plants. *Yucca schidigera* from Mexico and Quillaja Saponaria from Chile are the two main desert plants used as sources of saponins for the pharmaceutical industry.

4.1 YUCCA AND ITS CHARACTERISTICS

Quillaja saponins are triterpenoid structures, whereas yucca saponins have steroid nuclei. The surfactant action of saponins is produced by the presence of both fats- and water-soluble moieties in a single molecule. Saponins have a lipophilic core (steroid or triterpenoid) and one or more water-soluble carbohydrate side chains. Saponins interact with cholesterol in protozoal cell membranes to create complexes that contain antiprotozoal, surfactant, and membrane-lysing characteristics that lead to cell lysis. They reduce ruminal protozoa and affect ruminal fermentation by having antibacterial activity and by specifically inhibiting certain bacteria (Wu et al., 1994; Yu et al., 2015). Ammonia levels in the rumen are decreased. Yucca extract is used to prevent and treat arthritis in horses, despite the lack of solid proof of its effectiveness. Through the production of micelles in the intestine with bile salts and cholesterol, saponins have an impact on the absorption of lipids. Vaccines delivered orally and by injection both benefit from the use of quillaja saponins as adjuvants because of their effects on cell membranes. According to available data, oral saponin treatment may boost the immune system and increase resistance to a disease challenge. Thus, dietary saponin sources have a number of advantageous characteristics in the development of animals(Budan, 2012; Cheeke, 2000).

4.2 YUCCA EXTRACT AND WATER TREATMENT

Several researchers looked into the extract from *Yucca schidigera's* ability to reduce ammonia levels in seawater (Castillo-Vargasmachuca et al., 2015; Santacruz-reyes & Chien, 2010; Yu et al., 2015). There have been a few studies on its application in aquaculture. The addition of yucca extract to fish feed improved nitrogen/protein metabolism and decreased ammonia excretion. Additionally, it was utilized to show that yucca extract might lower ammonia levels in the water. However, its efficiency could not be specifically identified or measured. The majority of investigations were conducted in open systems, like in the study done by Sarkar (1999), where the total ammonia nitrogen (TAN) input from cultured animals might fluctuate between treatments for the entirety of culture trials (Sarkar, 1999). The microbial conversion of ammonia to nitrite, then to nitrate, could also interfere with the TAN output.

4.3 PREPARATION OF *YUCCA* EXTRACT SOLUTION

Yuccaschidigera, a desert plant, was collected from the Forest Research Institute, Dehradun, Uttrakh State, India. The Yucca plant's stem (about 250 grams) was chopped with a knife into small pieces. Then, the chopped pieces were grounded in a grinder mixture, dried in the open sun for three days, and again ground to make a fine powder. This Yucca powder was sieved through a 150-mesh sieve and stored in an airtight container. In the present study, *Yucca* extract was used as a solution. *Yucca* solution was prepared by mixing and dissolving 50 grams of *Yucca* powder in 700 ml distilled water in a 1-liter beaker. It was stirred on Jar Apparatus for seven days (about 250 ml of water evaporated in the air) so that its contents could dissolve well, filtered through ordinary filter paper, and made up to 500 ml with distilled water in a volumetric flask. Thus, 1 ml of *Yucca* extract produces 100 mg of solution.

4.4 WATER TREATMENT USING *YUCCA* EXTRACT

Municipally treated sewage effluent (MTSE) samples were treated to combat ammonia nitrogen by using *yucca* extract. The jar test apparatus was used to observe the biomass's effectiveness (*Yucca* extract) with an agitating speed of 35 RPM. Initially, *Yucca* schidigera extract was used with varying concentrations in the presence or absence of lights. We measured initial levels for ammonia nitrogen and other parameters of MTSE, and the experiments were performed at room temperature with the pristine state of the samples. It was observed that, even with multiple experimental studies using the different dosages of *Yucca* extract, there was no significant difference in the concentration of ammonia nitrogen, nitrite, and nitrate in the control sample. Instead, the ammonia nitrogen was found to increase in the *Yucca* extract dosed samples after the 8th day. An increase in ammonia content indicated that the *Yucca* extract itself started fermenting after the 6th day. The *Yucca* extract was not found helpful for combating ammonia nitrogen in municipal sewage water.

The results are the final valid values extracted after several experiments under varying conditions. The collected MTSE were taken into the six one-liter beakers. The initial parameters of ammonia nitrogen, nitrite, nitrate, pH, electrical conductivity, total dissolved solids, color, odor, and temperature were determined immediately after collecting samples. The first and second beakers were kept in series for reference or control samples. Beaker 1 served as a control to measure the amount of water evaporated during the experiment. Beaker 2 served as a control to measure the change of parameters naturally. 100mg and 500 mg of *Yucca* extract were added to beakers 3, 4. 5, and 6 in duplicate. Four 15-watt tungsten bulbs were hung over the Jar Test apparatus to illuminate the system round the clock. The stirrers of the equipment are set at 35 RPM. Every 48 hours, a 100 ml sample was taken from the jars numbered from 2 to 6 and tested for the change in parameters. The authors used the content of the beaker one for measuring the quantity of water evaporated during the processing period of 48 (2 days), 96(4 days), 144 (6 days), and 192 (8 days)hours, respectively.

4.5 REDUCTION OF AMMONIA-NITROGEN WITH *YUCCA* EXTRACT

The *yucca* extract could not degrade ammonia nitrogen to a significant amount. The results of the present study, as depicted in Figure 32 wherein, from an initial amount of 34.780 mg/L ammonia nitrogen (as NH_3) in municipally treated sewage effluent (MTSE) was reduced to 23.210 (In the control sample), 23.580 mg/L (with 100 mg/L *Yucca* extract) 24.705 mg/L (with 500 mg/L *Yucca* extract) in 48 h or 2nd day of process at 32°C temperature 35 RPM. In 96 h, or the 4th day of the experimental set-up, ammonia nitrogen was reduced to 2.040 mg/L, 2.735 mg/L, and 7.135 mg/L, respectively. In 144 h or the 6th day, ammonia-nitrogen was reduced to 0.032 mg/L, 0.036 mg/L 0.154 mg/L. In 192 h or the 8th day, ammonia nitrogen had been reduced to 0.00 mg/L, 0.00 mg/L, and 0.88 mg/L, respectively.

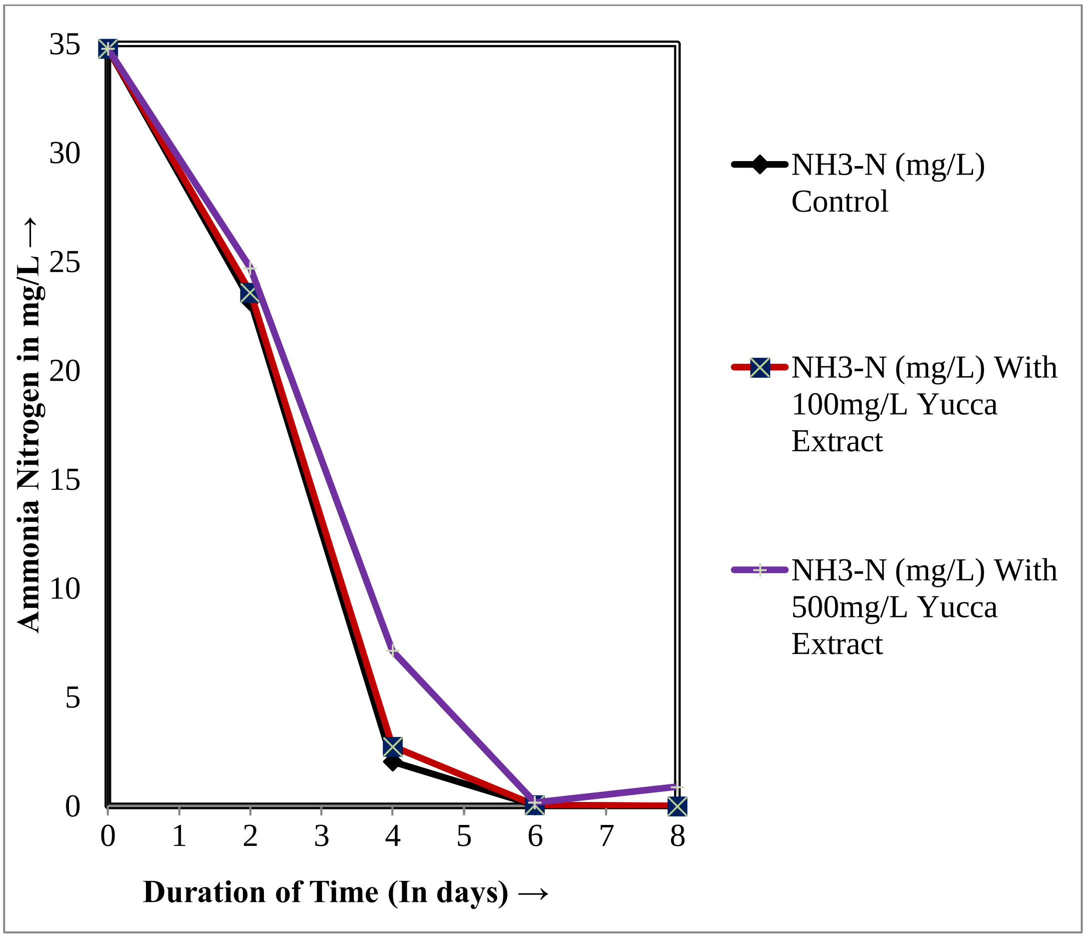


Figure 32:Biological oxidation of ammonia-nitrogen with Yucca extract

4.6 OXIDATION OF AMMONIA INTO NITRITE USING *YUCCA* EXTRACT

Figure 33 shows the oxidation of Nitrite (NO_2) into Nitrate (NO_3). The initial content of ammonia nitrogen in municipally treated sewage effluent (MTSE) gets converted to nitrite and nitrate simultaneously. The conversion of ammonia into nitrite and nitrate in biological oxidation is a continuous process. An experimental study explored that the effluent having an initial amount of 34.789 mg/L ammonia nitrogen and 0.150 mg/L nitrite nitrogen has converted or oxidized to 0.210 mg/L (In blank), 0.545 mg/L (with 100 mg/L *Yucca* extract) 0.575 mg/L (with 500 mg/L *Yucca* extract) into nitrite (NO_2)in 48 h or 2nd day of process at 32°C temperature 35 RPM. In 96 h or the 4th day of the experimental set-up, ammonia nitrogen oxidized to 11.70 mg/L, 13.525 mg/L, and 9.60 mg/L nitrites(NO_2), respectively. In

144 h or the 6th day, ammonia nitrogen gets converted to nitrite (which further kept oxidizing to nitrate) as 14.70 mg/L, 15.525 mg/L, and 14.375 mg/L. In 192 h or 8th-day, ammonia nitrogen oxidized to 17.80 mg/L, 18.65 mg/L, 18.85 mg/L nitrites(NO_2).

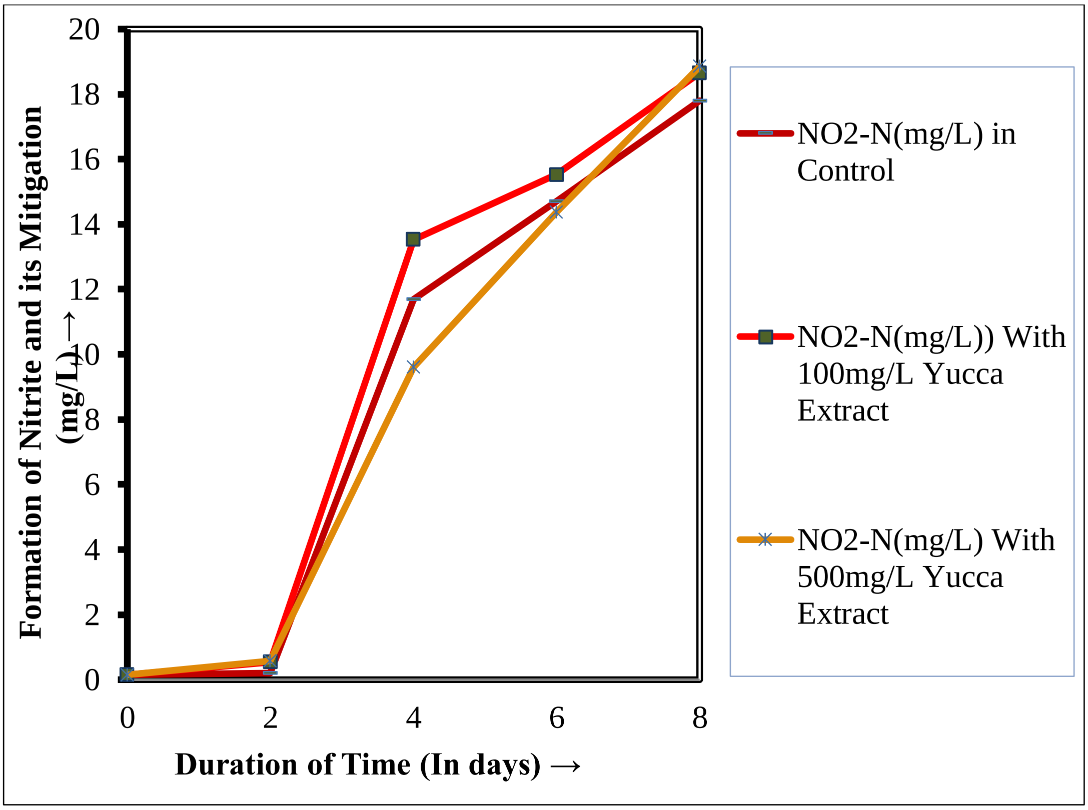


Figure 33: Formation of Nitrite nitrogen during oxidation of ammonia nitrogen with *Yucca* extract

4.7 OXIDATION OF NITRITE (NO_2) INTO NITRATE (NO_3) WITH *YUCCA* EXTRACT

Figure 34 shows that the initial amount of 34.789 mg/L ammonia nitrogen 0.45 mg/L nitrate as NO_3 converted or oxidized to 2.25 mg/L (In blank), 1.60 mg/L (with 100 mg/L *Yucca* extract), 2.35 mg/L (with 500 mg/L *Yucca* extract) into nitrate (NO_3)in 48 h or 2nd day of process at 32°C temperature 35 RPM. In 96 h or the 4th day of the experimental set-up, ammonia nitrogen oxidized to 12.90 mg/L, 11.75 mg/L, and 8.05 mg/L nitrate (NO_3), respectively. In 144 h or the 6th day, ammonia nitrogen converts to nitrate at 16.60 mg/L, 17.80 mg/L, and 17.0 mg/L. In 192 h or 8th day, ammonia nitrogen oxidized to 21.80 mg/L, 20.50 mg/L, 20.80 mg/L nitrates(NO_3).

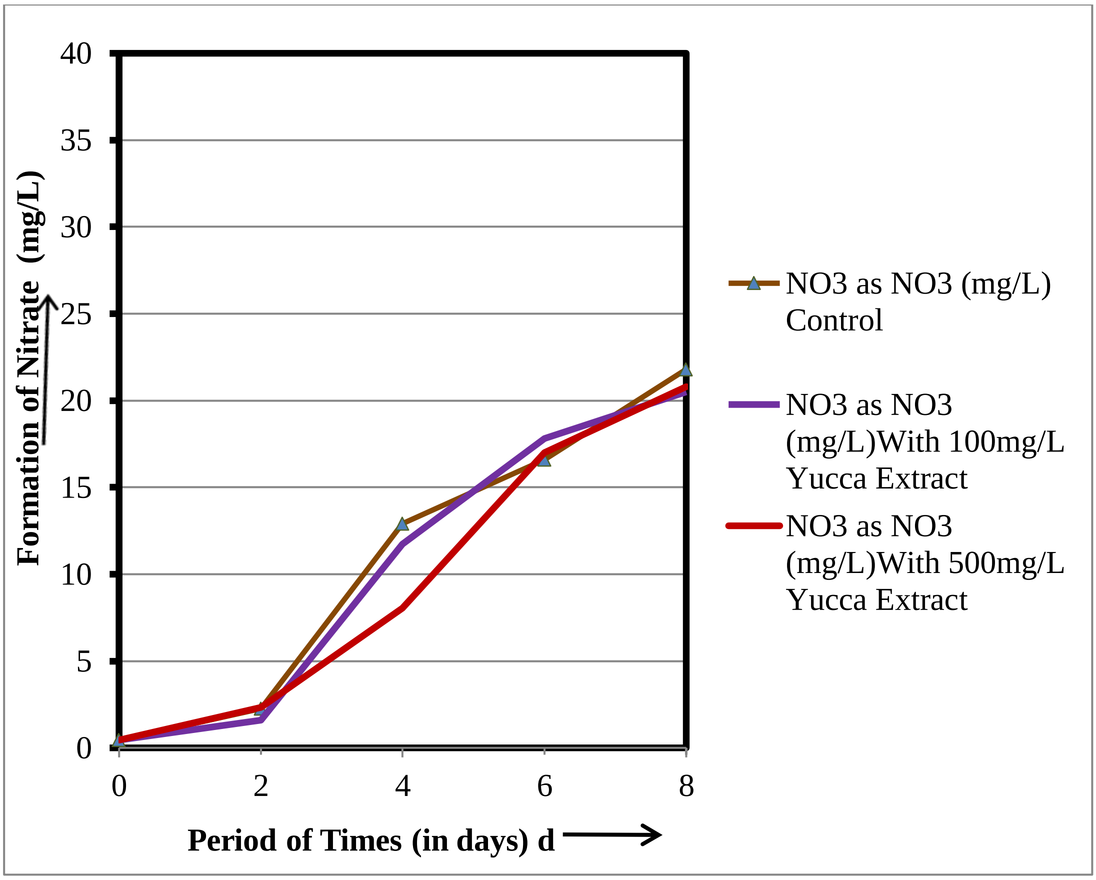


Figure 34: Oxidation of Ammonia nitrogen into nitrate with Yucca extract

4.8 RESULTS DISCUSSIONS - WASTEWATER TREATMENT WITH *YUCCA* EXTRACT

Ammonia nitrogen reduction with *Yucca* extract was found not of any substantial importance. When MTSE samples were treated with *Yucca* extract(100 mg/L 500 mg/L), the results obtained are tabulated below (Tables 14 and 15, respectively).

Table 14: Reduction of ammonia-nitrogen conversion to nitrite nitrate in MTSE with 100mg/L *Yucca* extract

Duration of Treatment	Ammonia (as N)		Nitrite (as NO_2) Formation		Formation of Nitrate (as NO_3)	
	Remained (mg/L)	Reduced (%)	(mg/L)	(%)	(mg/L)	(%)
48 Hours	23.585	32.18	0.545	3.06	1.60	1.19
96 Hours	2.735	92.13	13.525	75.98	11.75	8.80
144 Hours	0.036	99.89	15.525	87.22	17.80	13.33
196 Hours	Nil	100	18.65	104.77	20.50	15.35

Table 15: Reduction of ammonia-nitrogen conversion to nitrite nitrate in MTSE with 500 mg/L *Yucca* extract

Duration of Treatment	Ammonia (as N)		Nitrite (as NO_2) Formation		Formation of Nitrate (as NO_3)	
	Remained	Reduced				
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
48 Hours	24.71	28.96	0.575	3.23	2.35	1.76
96 Hours	7.135	20.51	9.60	53.93	8.05	6.02
144 Hours	0.154	99.55	14.375	80.75	17.0	12.73
196 Hours	0.88	97.46	18.85	105.89	20.8	15.58

The above results show that *yucca* extract is not of any help in reducing ammonia-nitrogen and also of no use in oxidizing it into nitrite or nitrate. Moreover, it undergoes self-fermentation when put in water for an extended period beyond six days. During its self-fermentation period, ammonia-nitrogen increases in the water. This leads to the deterioration of water quality at the end of the process.

CHAPTER 5

EVALUATION OF AMMONIA ADSORPTION CAPACITY OF ZEOLITES IN SYNTHETIC WATER

CHAPTER 5: EVALUATION OF AMMONIA ADSORPTION CAPACITY OF ZEOLITES IN SYNTHETIC WATER

5. OCCURRENCE OF ZEOLITES IN NATURE

In reference to how particular silicate minerals behaved when heated, Swedish mineralogist Alex Fredrik Cronstedt gave them the term "zeolite" in 1756 (zeo = boil, lithos = stone) (Coombs, 2001). He discovered that heating the mineral, called stilbite, caused it to produce a lot of steam from the water it had absorbed. Zeolites can foam at a temperature of around 200˚C. Zeolites that are found in nature are rarely pure and frequently contain different amounts of other minerals, metals, quartz, etc. (Ramesh & Reddy, 2011). Zeolites are crystalline aluminium silicates with a very well-ordered arrangement of Silicon Aluminium tetrahedra. Zeolite is described as a crystalline mineral material having a structure characterized by a framework of connected tetrahedral, each consisting of four O-atoms encircling the cation. This definition comes from the International Mineralogical Association of 1993. In other terms, zeolites are inorganic substances made of hydrated aluminium silicates, also referred to as aluminosilicates. Zeolites are three-dimensional structures composed of the tetrahedral oxides SiO_4 and AlO_4, which are connected by oxygen bridges to create microporous structures that can accommodate cations such as sodium, calcium, and magnesium (Donald W. Breck, 1974). In order to balance out the negative charge on the structure brought on by the substitution of aluminium, the cations are often present in the pore voids. Water molecules are also present as solvent or guest molecules in the pores' spaces. Zeolites' structural formula is written as $Mx/n[(AlO_2)x(SiO_2)y).wH_2O$.

Where:
[ ] = the framework composition
w = the number of water molecules per unit cell
x + y = the total number of tetrahedral per unit cell
n = the valence of the cation
M = an alkali or alkaline earth cation

Zeolites can be produced chemically or naturally (Scott, 1980). Clinoptilolite, chabazite, and mordenite are three common natural zeolites. Zeolites A, X, and Y are examples of manmade zeolites, in contrast. After various natural processes, such as the formation of volcanic deposits, natural zeolites are produced from the uncontrolled environment. On the other hand, synthetic zeolites are made in a controlled setting in a laboratory. As a result, natural zeolites frequently have impurities and structural defects that may restrict their applicability, whereas synthesized zeolites typically have high levels of purity and consistent crystallinity. A synthetic zeolite's structural characteristics can also be modified depending on the application (Sherman, 1999).

5.1 FORMS OF ZEOLITES

Zeolites are classified based on their framework silicon and aluminium constitution. This classification is mainly based on the silicon to aluminium ratio. More than eighty distinct zeolite species are available based on nomenclature for zeolite minerals. Of all naturally occurring zeolites studied by researchers, the most well-known ones are heulandites, clinoptilolite, erionite, chabazite, stilbite, mordenite, and phillipsite. Zeolites are comprehensively classified based on(D. L. Bish, 2001; Margeta et al., 2013):

1. Crystal structure
2. Chemical composition
3. Morphology
4. Effective pore diameter

The SiO_4 and AlO_4 tetrahedra are the primary building blocks (PBU) of zeolites. They join up with the three-dimensional crystalline structure of the zeolite's secondary building units (SBU) through oxygen ions (Figure 35). Alkaline earth alkaline metal cations balance out the negative charge of the zeolite structure, which is defined by the substitution of Si with Al. As a result of having a negative surface charge, natural zeolites act as cation exchangers. Si-Al substitution is not the only type of substitution possible in the zeolite lattice. Additionally, silicon may be replaced with atoms of chromium, iron, germanium, boron, and titanium. Large cavities with vacancies may contain water molecules that are connected to the exchangeable framework ions by aqueous bridges. (Margeta et al., 2013; McCusker et al.,2007; DW, 1974; Bish and Ming, 2001).

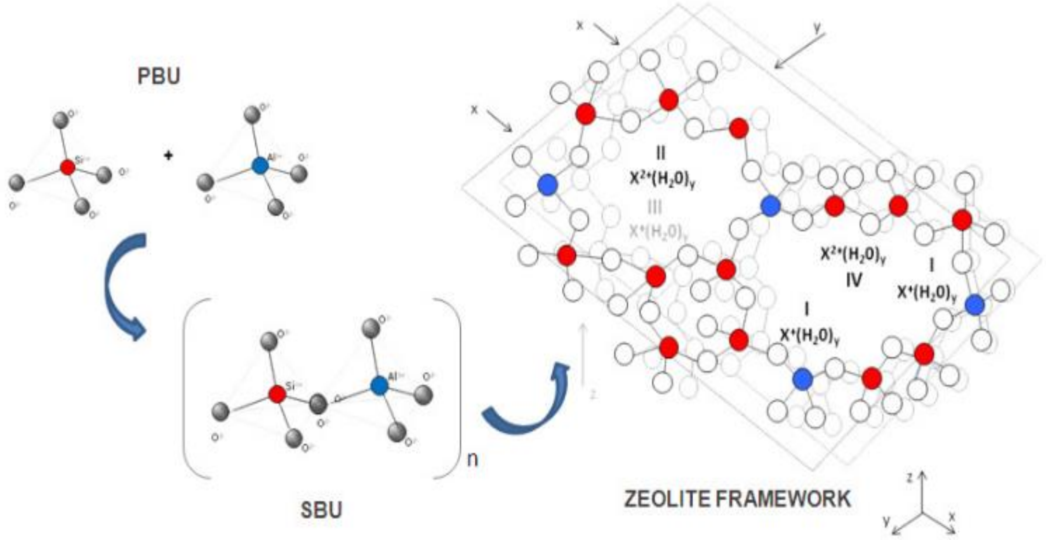


Figure 35: Three-dimensional structure of zeolite- clinoptilolite, Binding of Primary Building Unit (PBU), Secondary Building Unit (SBU)

5.1.1 CLINOPTILOITE, A NATURAL ZEOLITES

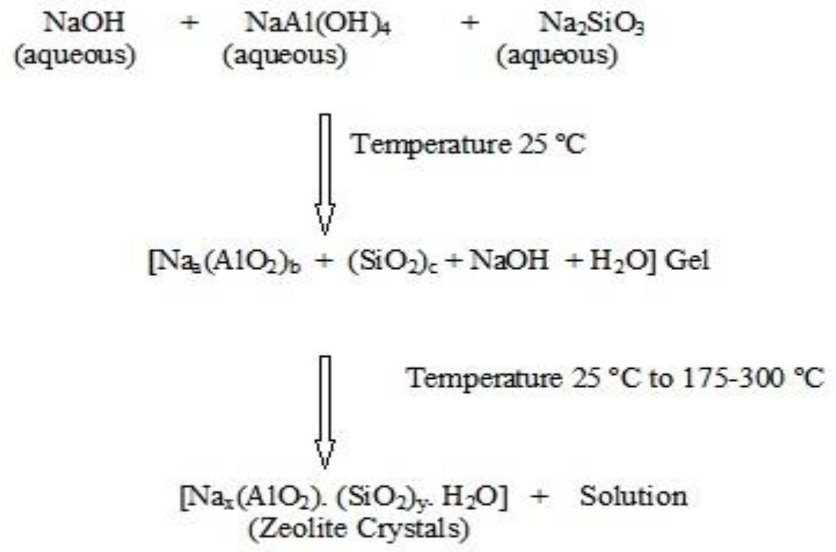
Clinoptilolite (CLI), $(Na,K)_6[Al_6Si_{30}O_{72}].20H_2O$, has an Al/Si ratio of 4.0 and a monoclinic tetrahedral structure. High-silica zeolites typically have Si:(Al + $Fe^{3+)}$ ratios between 4.0 and 5.6 and are found in silicic volcaniclastic deposits. Clinoptilolite minerals are more prevalent in the Atlantic and Indian Ocean sediments than in the Pacific Ocean. Si/Al ratios for deep-sea clinoptilolite range from 4.2 to 5.2, while 80 percent of it has values between 4.5 and 5.0. Si:Al ratios of clinoptilolites that are higher than 5.7 have not been discovered. Clinoptilolite has been the subject of numerous ion-exchange experiments, mainly due to its capacity to remove NH4+ from municipal wastewater streams and 137Cs from radioactive waste solutions. Column experiments were used to undertake the first thorough studies on the selectivity of clinoptilolite for inorganic ions. Because clinoptilolite also demonstrates comparatively high selectivity for NH4+, some researchers have looked at its application in the treatment of sewage in populated areas. Numerous tonnes of clinoptilolite is used in the 27,000 M3/d wastewater treatment facility in Lake Tahoe in, California. Some studies have mentioned much larger plants with capacities of 45,000 to 245,000 M3/d in Virginia. Zeolite-rich materials are successful at removing NH_4^+ and other pollutants from municipal wastewater, according to numerous additional research (Bish & Ming, 2001). The clinoptilolite structure has channels with widths ranging from 2.5 to 5.0 angstroms on average. The exceptional selectivity for NH4+ ions in clinoptilolite is due to structurally similar ion sieve characteristics that are present in many zeolites to varying degrees (Liu, 2000).

5.1.2 MORDENITE, A NATURAL ZEOLITE

How(Breck, 2005; McCusker et al., 2007) initially gave the silica-rich mineral mordenite its name in 1864, naming it for the Nova Scotian town of Morden, where samples were found. Orthorhombic Mordenite (MOR), $(Na_3,K,Ca_2)_4[Al_8Si_{40}O_{96}]\bullet28H_2O$. Si:Al ratios in clinoptilolite mordenite are comparable. Additionally, it has been discovered in sedimentary rocks containing quartz, clinoptilolite, and mordenite. Mordenite is linked with clinoptilolite, chabazite, opal, K-feldspar, ferrierite, analcime, tridymite, erionite, phillipsite, cristobalite, and smectite in diagenetically altered volcanic deposits. X-Ray Absorption Spectroscopy, X-Ray Photoelectron Spectroscopy, Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy, X-Ray Absorption Spectroscopy, and Mössbauer X-Ray analysis of a sample from Cuba that contained clinoptilolite and mordenite showed that the Fe was present as an additional framework cation (octahedral coordination). Mordenite zeolites in silicic volcaniclastic deposits have Si: $(Al + Fe^{3+})$ in the range of 4.1 – 5.7(Breck, 1974).

5.1.3 ZEOLITE 4A (SYNTHETIC ZEOLITES)

The chemical formula for zeolite 4A is $Na_{12}[(AlO_2)(SiO_2)_{12}].27H_2O$. Its structure contains two types of polyhedra. The octahedron (α-cages) connects 24-hedron (β- cages), creating thus a three-dimensional layout of pores size 4.2 Å(Ian D. Wilson, 2000; Rahman et al., 2018). Under hydrothermal circumstances, the gel containing silica-alumina as a source of cations in water is converted into synthetic zeolites. Reactive starting materials, such as freshly prepared gel or amorphous solids, relatively high pH introduced in the form of an alkali metal hydroxide, low-temperature hydrothermal conditions with concurrent low autogenous pressure at saturated water vapor pressure, and a high degree of supersaturation of the constituents that will lead to the nucleation of the desired crystals are the general prerequisites for the synthesis of zeolites. Alumina and silica sources are dissolved in a strongly basic aqueous solution to produce the bulk of zeolites (Figure 36). (Maesen &Marcus,2001).



The above systems can be presented in simplified form of equation as follows:

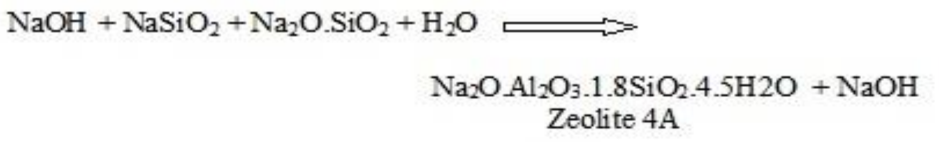


Figure 36: Illustration of a general procedure for the synthesis of a zeolite

The preparation of zeolite 4A starts with gel formation. The gel, hydrous metal aluminosilicate, is prepared from aqueous solutions of alkali metal silicate and aluminate. Analysis of many aluminosilicate gel samples showed that Si/A1 ratio consistently exceeds one, whereas Na/Al ratio is close to one. Aluminium in the gel skeleton is coordinated 4-fold within the common (Si, Al)) framework, whereas alkaline cations compensate for excess negative charges of aluminium oxygen tetrahedra. The gel is subjected to crystallization in the ambient temperature range of 175 degrees C or sometimes up to 300 degrees C. The growth of Zeolite first requires the formation of a nucleus. The smallest structural secondary building units are the single four or 6-membered rings, which, after sufficient induct on period, exceed critical size to form a nucleus. Zeolite 4A is used as an ion exchange in detergents. Ion exchange agents are chemicals that enhance the cleaning efficiency of surfactants.

5.2 ADSORPTION PROPERTIES OF ZEOLITES

Zeolites are used for the two main adsorption processes that take place during wastewater treatment. Physical adsorption is the initial procedure. Ion exchange-based chemical adsorption is the second procedure. Physical adsorption took place when dissolved pollutants in the water clung to and immobilized on the surface of the zeolite particle without causing the zeolite's atomic structure to be disturbed. The degree of aluminium substitution for silicon in the framework structure primarily determines the ion-exchange capacity (Liu, 2000). The cation species' nature (size, charge, etc.), concentration in solution, the presence of competing ions, and the structural properties of the zeolite are all factors that affect a material's ability to exchange ions. Selective ion exchange utilizing natural zeolite is one of the various high-rate ammonia removal technologies that offer a number of specific benefits:

1. The natural zeolite clinoptilolite is very selective for ammonium ions, in contrast to the vast majority of other cations often present in sewage.
2. The zeolite's ability to exchange ions is mostly temperature-independent.
3. Ion exchange does not result in an increase in dissolved or suspended particles when ammonia is removed.

Ion exchange adsorption takes place when zeolite comes into contact with NH_4^+-containing solutions. Jorgensen et al. (1976) have performed experimental studies to determine whether zeolites have ion-exchange properties and adsorption properties or both. They discovered that when natural zeolites were used, the conductivity of the NH_4Cl solution remained unchanged. The findings show that the ions at the active sites of the natural sorbents initially display electrochemical characteristics akin to those of the NH_4^+ ions (S. E. Jorgensen et al., 1976). The NH_4^+occupied sorbents were heated to 400 ˚C to cause the ammonium ions to escape and the zeolites to change into the H+ zeolite. An NH_4Cl solution is used to treat the sorbent. H+ ions had to have been present on the active sites of the sorbents following the activation process, as evidenced by the significantly increasing specific conductivities, significantly reducing electrode potential, and significantly decreasing electrode pH. Second, it was discovered that the conductivity of HCl solutions in contact with the sorbents decreased after the sorbents were treated with the solution. Ions were attracted to the surface of the sorbents by the solutions they were in. Because the sorbents contained the same cations as counter ions in the solution, this refers to adsorption (S. E. Jorgensen et al., 1976).

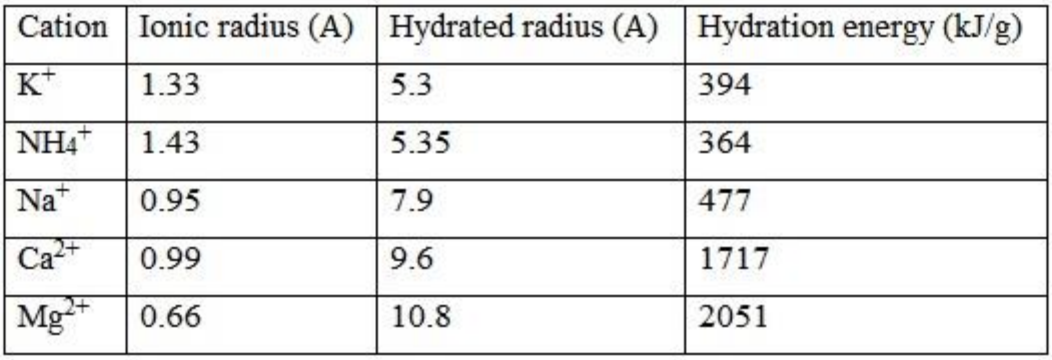
5.3 SPECIFIC ZEOLITES WATER TREATMENT

Clinoptilolite is one of the zeolites that has been the subject of the most fundamental applied study. These materials are highly porous, with channel cavities in the structure that have particular pore sizes and shapes as a result of the peculiar way in which PBUs are linked to the creation of discrete structural units. There are three different types of channels in the clinoptilolite structure: two parallel channels comprised of ten Si/AlO_4 rings with eight members each and a vertical channel defined by eight-membered rings. The following list summarises several potential cation selectivity-influencing factors:

1. Cation charge, first
2. Cation diameter, with or without hydration water
3. Hydration energy from cations
4. The species concentration in the liquid phase, particularly that of the electrolytes
5. Temperature
6. The resin's structure number of sites

The diameter of the cations is a crucial factor in selectivity. Another critical factor is the hydration energy of the water molecules around the cation. Based on the similar number of exchangeable cations, clinoptilolite and mordenite have the same cation exchange capacity or 2.2 mEq/g.The synthetic zeolite 4A, on the other hand, has a cation exchange capacity of 5.6 mEq/g. Table 16 shows the ionic radius, hydrated radius, and hydration energy of some of the particular cations (K^+, NH_4^+, Na^+, Ca^{2+}, and Mg^{2+}). When exchanging ions with zeolites, these cations are particular.

Table 16: Cation Size hydration energy(Dryden, 1984)



Cation	Ionic radius (A)	Hydrated radius (A)	Hydration energy (kJ/g)
K^+	1.33	5.3	394
NH_4^+	1.43	5.35	364
Na^+	0.95	7.9	477
Ca^{2+}	0.99	9.6	1717
Mg^{2+}	0.66	10.8	2051

It is clear that the favored ions have a smaller hydrated ionic radius and lower hydration energy when the cations are arranged in order of selectivity from top to bottom. Molecular sieve effects are less common with smaller ions. The zeolitic forces more easily defeat the hydration forces due to the decreased hydration energy.

The majority of water filtration technologies rely on the distinctive cation-exchange behavior of natural zeolites, which allows dissolved cations to be removed from water by trading with cations on the zeolite's exchange sites. NH_4^+ is the most prevalent cation in waters that are harmful to human and animal health. It can be eliminated by trading with biologically appropriate cations present on the zeolite's exchange sites, such as Na^+, K^+, H^+, Mg^{2+}, and Ca^{2+}. Fortunately, several naturally occurring zeolites, such as chabazite, clinoptilolite, phillipsite, and mordenite, are selective for NH_4^+, which enables them to exchange NH_4^+ even in the presence of higher concentrations of rival cations. Transition metals, such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Cr^{3+}, Mo^{2+}, and $Ni^{2+,}$ are frequently present in industrial streams and can be highly poisonous even at concentrations as low as several mg/L, is another element that clinoptilolite and mordenite are selective for. Both clinoptilolite and mordenite exhibit extremely high selectivities for Cs^+ Sr^{2+}, as was stressed in talks on radioactive waste treatments. As a result, they can be utilized to remove trace levels of radioactive ^{137}Cs and ^{90}Sr from wastewater generated during the nuclear process. Many different contaminants, including NH4+, heavy metals, As, H2S, and humic acids, are frequently found in natural waters. Even though NH4+ is a frequent pollutant in natural water, its concentration in a solution might be lower than what is advised for drinking water. The quantity of ring-forming zeolite framework components determines a zeolite's pore size. Thus, tiny, medium, comprehensive, and large pore diameters are present in eight-member rings, ten-member rings, twelve to fourteen-member rings, and eighteen to twenty-member rings. Micropores of entry in zeolites range in size from 3 to 12 Angstrom(Å).

5.4 INTERPRETATION OF SORPTION AND UP-TAKE CAPACITY OF ZEOLITES

The degree of ammonia removal (%) from the investigated solutions was calculated from the following formula(Zabochnicka-Świątek & Malińska, 2010):

$$\text{Uptake}(\%) = \frac{C_0 - C_k}{C_0} 100$$

Whereas: C_0 and C_k are the initial final concentration (mg/L)

The sorption capacity was calculated from the following equation:

$$A = \frac{C_0 - C_k}{m} V$$

whereas: A: the adsorption capacity (mg/g); C_0 C_k: the initial final concentration (mg/ L); V: the sample volume (L); m: the zeolites weight (g).

The amount of ammonia-nitrogen in the synthetically prepared water and the sorption capacity of three different zeolites are graphically depicted in Figure 37. Herein, it is clear from the graphical representation that the sorption capacity of zeolites increases with the increased amount of ammonia-nitrogen in the water. Sorption capacity is also highest in synthetic water because of the absence of other interfering ions.

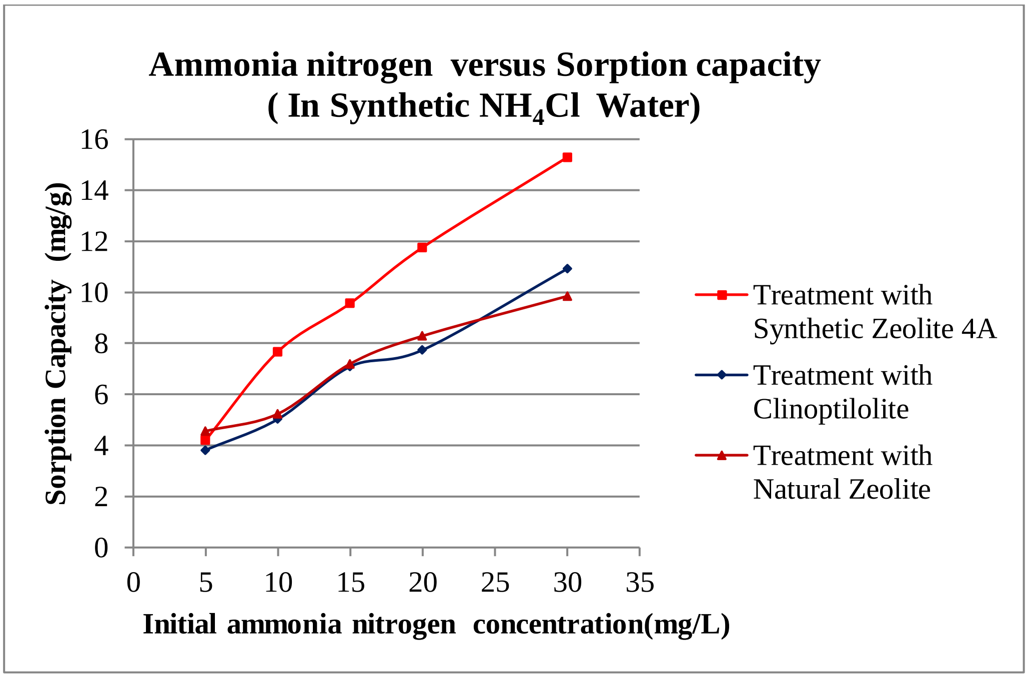


Figure 37: Increasing Ammonia Sorption Capacity With Increased Ammonia Concentration

The present experimental study explored that most ammonium uptake was achieved within 5 to 30 minutes (Figures 49, 50, 51). Researchers are consistent that the uptake of ammonium ions is maximum in 5 to 15 minutes and negligible after 4 hours(Bish & Ming, 2001; T. C. Jorgensen, 2002; Kazemian et al., 2012; Nguyen & Tanner, 1998; Prajapati et al., 2014; Schoeman, 1986; Shakoor, 2016; Zhang et al., 2016). In Figures 38, 39, and 40, uptakes of ammonia nitrogen (Appendix 2)are depicted with synthetic water when treated with Synthetic zeolites 4A, Clinoptilolite, and mordenite in the form of residual ammonia-nitrogen(mg/L).

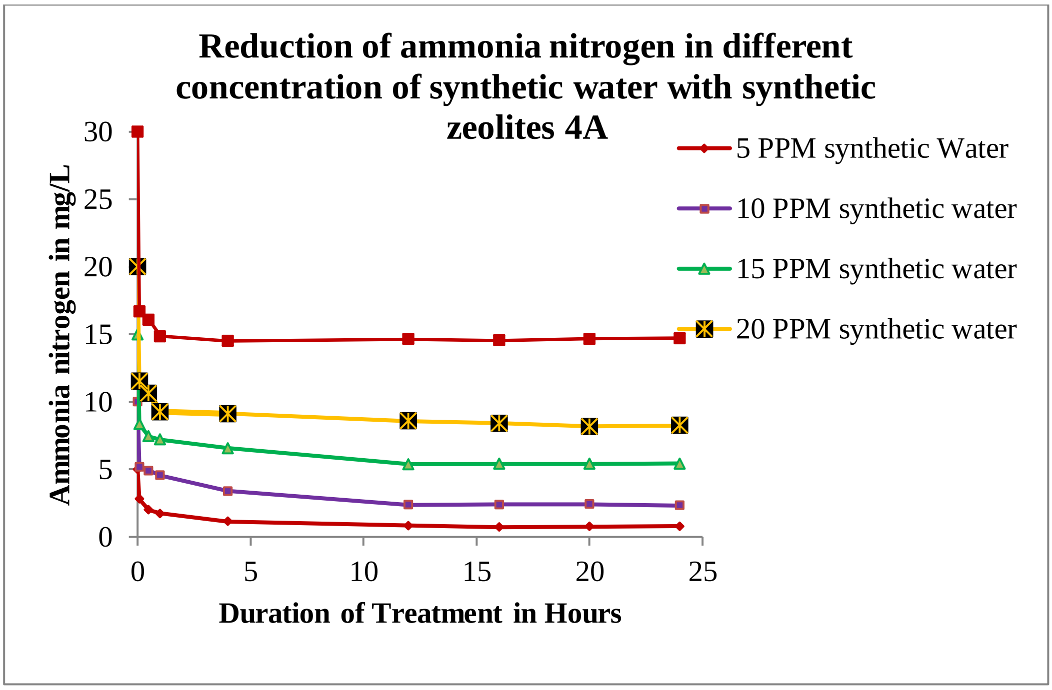


Figure 38: Ammonium Uptake in Synthetic Zeolites

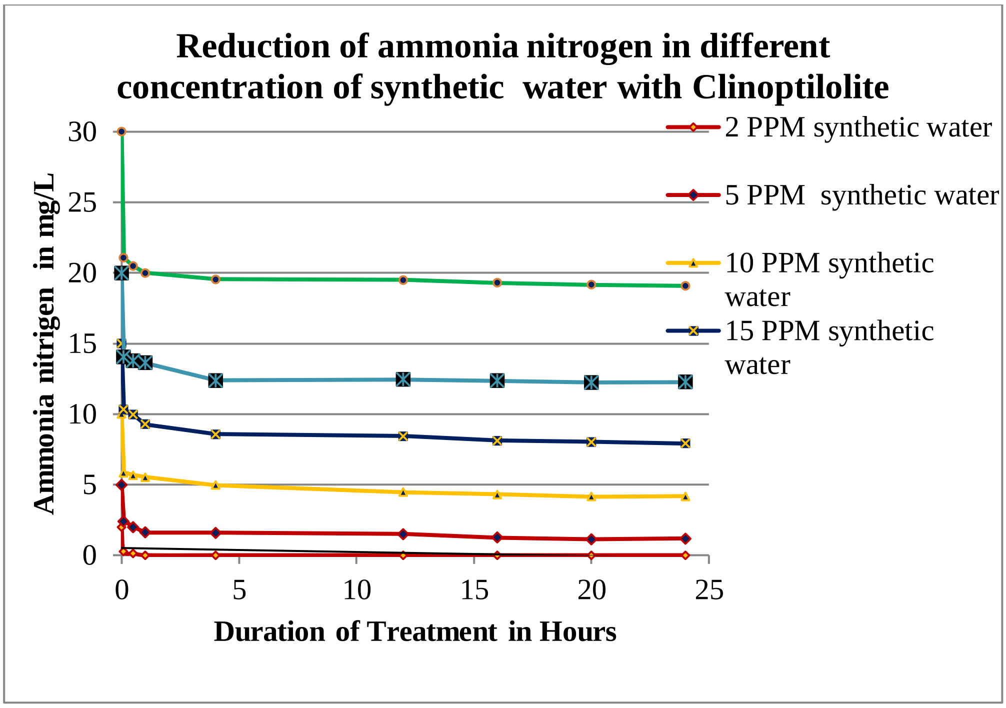


Figure 39: Ammonium Uptake in Clinoptilolite

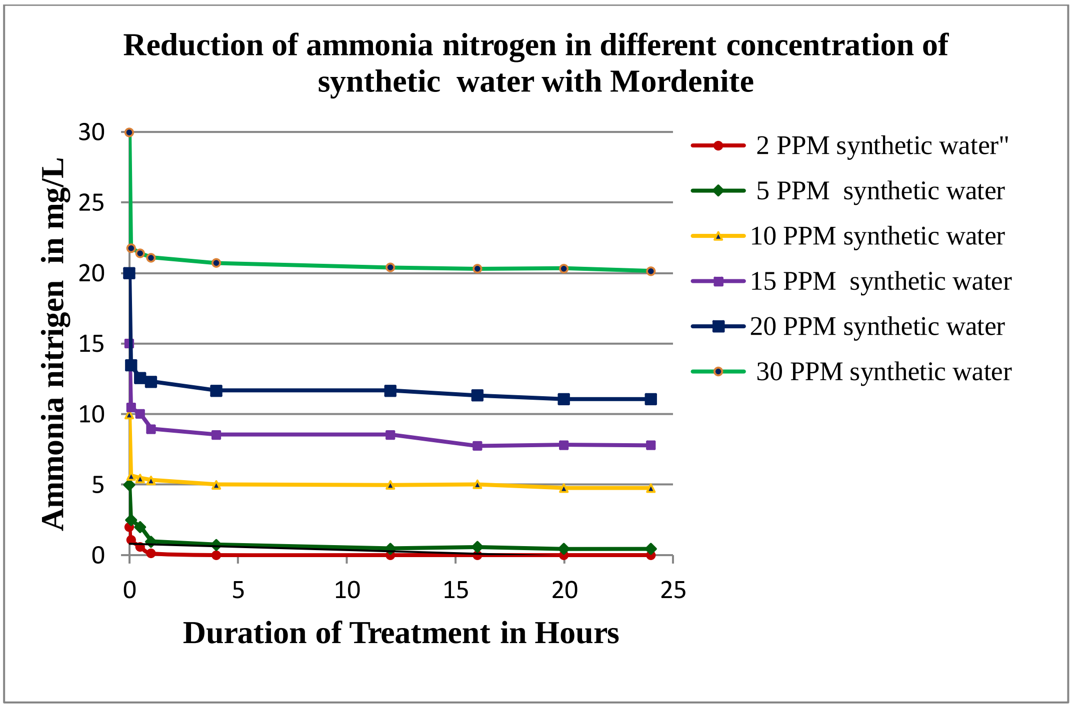


Figure 40: Ammonium Uptake in Mordenite

5.5 RESULTS DISCUSSIONS - TREATMENT OF AMMONIA IN SYNTHETIC WATER

The synthetic and natural zeolites understudy effectively combated ammonia nitrogen when synthetically prepared ammonium chloride solution/ water was used for treatment. The sorption capacity of synthetic zeolite 4A was observed as 4.21, 7.68, 9.67, and 11.76 mg/g with 5.0, 10.0, 15.0, 20.0, and 30.0 mg/L ammonia nitrogen synthetic water. The ammonia nitrogen sorption with Clinoptilolite was observed as 3.82, 5.03, 7.09, 7.74, 10.92 with 5.0, 10.0, 15.0, 20.0, 30.0 mg/L ammonia nitrogen synthetic water. The removal capacity of Mordenite was found as 4.56, 5.24, 7.20, 8.29, and 9.85 mg/g with 5.0, 10.0, 15.0, 20.0, and 30.0 mg/L ammonia nitrogen synthetic water. The sorption capacity of zeolites increased with increased ammonia nitrogen concentration in water (Figure 48). A higher concentration of ammonia nitrogen in water provides the necessary driving force for ammonium ions to diffuse through the interface (film) into the pores of the zeolites and replace cations on the surface of the internal micropores within a given contact time(DU et al., 2005; Margeta et al., 2013b; Mazloomi & Jalali, 2016). Therefore, ammonia-nitrogen removal is higher in the case of synthetic water with a higher concentration of a specific solute (ammonium ion).

CHAPTER 6

THE EFFICIENCY OF ZEOLITES IN WATER TREATMENT FOR COMBATING AMMONIA ON TREATED SEWAGE EFFLUENT

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6. AMMONIA REMOVAL AT SEWAGE TREATMENT PLANTS

Most sewage treatment plants are limited to secondary treatment units, wherein activated sewage treatment processes are used. The Water (Prevention Control of Pollution) Act, passed in 1974, has a provision for the Ministry of Environment, Government of India, to address the prevention and control of water pollution as well as the maintenance or restoration of the country's water wholesomeness. The ammonia-nitrogen limit under the Environment (Protection) Rules of 1986 used to be 50 mg/L, but as of the notice date of April 8, 2015, the norm is 5.0 mg/L. An activated sewage treatment plant is not concerned with ammonia-nitrogen treatment up to secondary treatment units. So, presently, no specific treatment is given for ammonia removal in old-designed conventional sewage treatment plants. Thus, a particular requirement is to treat ammonia-nitrogen pollution from sewage effluents at all sewage treatment plants.

6.1 AMMONIA NITROGEN ITS HAZARDOUS EFFECTS ON AQUATIC ANIMALS AND PLANTS

Most of the ammonia nitrogen in the natural water exists in the form of ammonium ions. This ammonia nitrogen is dangerous to humans, aquatic animals, and plants, depending on the concentration for individual tolerance. Water having unionized NH_3 less than 0.02 mg/L is considered safe for fish reproduction (Holden, 1981). The Canadian Council of Ministers of the Environment 2010 (Canadian Council of Ministers of the Environment, 2010) has prescribed the water quality guidelines for unionized ammonia to protect marine life as 0.019 mg/L. The ammonia toxicity to the fish depends on the length of the exposure, pH, temperature, and fish species. The ammonia nitrogen content in the river waters beyond the tolerance limit results in hazardous conditions to aquatic lives. Excessive ammonia nitrogen affects the fish's central nervous system, thus leading to convulsion, hyper-excitability, breathing problems, cardiac attack, oxygen uptake, coma, death. The lower content of ammonia nitrogen in water resources causes a hatching reduction in fish morphological changes in gills, liver, kidney, and growth retardation(Wicks et al., 2002). Aquatic plants are less sensitive than animals, so ammonia nitrogen is less hazardous for plants than animals. The reason for the higher tolerance of the phytoplankton in vascular plants to ammonia is a readily available energy-efficient nitrogen source for plants. However, it can be toxic when present at high concentrations. Biologically, ammonia nitrogen (NH_3 + NH_4^+) gets converted to nitrite (NO_2^-), with the help of several genera of bacteria, like *NitrosospiraNitrosomonas,* to Nitrate (NO_3^-), with the use of bacteria, including *NitrospiraNitrobacter*. The intermediate product nitrite is toxic to the fish, even at a low concentration of 0.10 mg/L. The end product nitrate is considered harmless to fish up to a limit of 250 mg/L in water resources. It is used as fertilizer by aquatic plants, including phytoplankton (Francis-Floyd et al., 2012).

6.2 PREVIOUS STUDIES ON ZEOLITES WASTEWATER TREATMENT

According to several studies (Allen, 1978; Chmielewska-Horváthová, 1996; Investigation, 2005; Smith et al., 1979), the natural zeolite clinoptilolite, which was utilized in a sewage treatment process at the Tahoe-Truckee (Truckee, CA, USA), successfully eliminates >97% of the NH4+ from tertiary effluent. Several nations have reported on pilot-scale research that used clinoptilolite-rich tuff to remove NH4+ from municipal wastewater. Ammonia was removed from the solution following the zeolite exchange and subsequent regeneration with NaCl/KCl solutions, and an ammonium and phosphate fertilizer was created (Armbruster, 2001; Cejka et al., 2007). The Tahoe-Truckee Sanitation Agency (CA, USA) treated about 8.107 m3 of wastewater between 1978 and 1993 by using a clinoptilolite tuff for ammonia exchange.The system was built to handle 26,100 m3/day of sewage flow in order to extract 19.5 mg NH4/liter (507 kg) from feed water around 25 mg/Liter (Investigation, 2005). Before aeration, adding natural zeolites to sewage (such as powdered clinoptilolite) may boost oxygen consumption and sedimentation yield, producing a sludge that is easier to dewater and utilize as fertilizer (Szekely & Szekely, 2000). Sludge nitrification is accelerated with the use of natural clinoptilolite. Clinoptilolite selectively absorbs NH4+ from sewage and offers nitrifying bacteria the perfect habitat for growth, converting NH4+ to nitrate (Armbruster, 2001; Cejka et al., 2007; Sims & Little, 1973; Wojciech Franus, 2018). Numerous tonnes of clinoptilolite-rich tuff were also used for the same purposes, primarily in the United States. For example, in Upper Occoquan, Virginia (57,000 m3/day), Alexia, Virginia (245 000 m3/day), Denver, Colorado (3800 m3/day), Rosemont, Minnesota (2250 m3/day), and a few other tiny plants in Toba, Japan.(Colella, 1999; Kalló, 2001; Pansini, 1996; Wojciech Franus, 2018).

Tuffs from the Tokaj Hills in Hungary, which are rich in clinoptilolite, have been applied in two stages of municipal wastewater treatment in a pilot-scale study (Kalló, 2001). When 30-100 g of powdered tuff with a grain size of 40-160 m were added to 1-M^3 of raw sewage before the aeration tank.

It was discovered that:

1. The oxygen consumption rate increased (increasing the biological activity of the living sludge by at least 25%).
2. The sedimentation rate increased because the amount of suspended solids in the effluent after the secondary settling tank decreased (for example, from 35 to 18 mg/Liter or (i.e. similar amounts of phosphate were removed using less of an excess of these salts).
3. The resulting sludge could be utilized as fertilizer and was easier to dewater. Instead of 30–35 days, anaerobic digestion takes 20–24 days.

6.3 CHEMICAL COMPOSITION OF ZEOLITES AND WASTEWATER TREATMENT (XRF ANALYSIS)

Chemical treatment of water for combating ammonia nitrogen was done by using three different zeolites. Municipally treated sewage effluent (MTSE) was treated with alum using the coagulant alum with the help of a Jar Test Apparatus. MTSE water samples were further treated with different zeolites (5g/L) using the Jar Test apparatus for one hour, agitated at 100 RPM. The effluents were filtered through ordinary filter papers, and the filtrates collected on the filter papers were dried in a hot air oven at 100 °C. The zeolites were cooled in a desiccator and collected/stored in 10-gm capacity glass bottles for XRD and XRF analysis. All three zeolites were tested for X-Ray Fluorescent (XRF). X-Ray Diffraction (XRD) analysis in a virgin and used state. The XRF analyzed the chemical composition of zeolites. These compositions are depicted in tables 17, 18, 19, 20,21, and 22, respectively.

Table 17: Chemical Composition of Synthetic Zeolite 4A before use analyzed by XRF

COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT
SiO_2	47.20%	Fe_2O_3	912.5ppm	Rb	4.2ppm
Al_2O_3	32.52%	Cl	693.2ppm	Br	2.2ppm
Na_2O	16.45%	Tl	124.2ppm	Re	1.6ppm
MgO	2.53%	Sn	70.1 ppm	Ir	0.8ppm
P_2O_5	0.50%	Ga	27.4 ppm	Tl	0.0ppm
SO_3	0.11%	Zn	9.8 ppm	Eu	0.0ppm
CaO	0.38%	Mn	5.6ppm	V	0.0ppm
K_2O	0.14%	Cr	3.7 ppm		

Table 18: Chemical Composition of Synthetic Zeolite 4A after use analyzed by XRF

COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT
SiO_2	45.51%	Cl	0.126 %	Cr	12.6ppm
Al_2O_3	35.24%	Fe_2O_3	753.5ppm	Rb	4.4ppm
Na_2O	14.99 %	Tl	124.2ppm	Br	2.2ppm
MgO	0.33 %	Sn	83.3 ppm	As	1.8ppm
P_2O_5	0.46 %	Ga	30.2 ppm	Re	1.6ppm
SO_3	0.13 %	Zn	56.1 ppm	Tl	1.5ppm
CaO	2.69 %	Mn	32.1 ppm	Ir	1.1ppm
K_2O	0.41 %	Zr	15.6 ppm	Pt	0.5ppm

Table 19: Chemical Composition of Clinoptilolite before Use analyzed by XRF

COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT
SiO_2	73.71%	SO_3	916.7ppm	Th	53.5ppm
Al_2O_3	13.16%	Mn	514.0ppm	As	39.9ppm
CaO	5.37%	Ce	290.6ppm	Ga	26.4ppm
K_2O	3.30%	Zr	204.8ppm	Nb	22.8ppm
Fe_2O_3	2.61%	Pb	140.4ppm	Cu	11.1ppm
MgO	0.88%	Eu	98.8 ppm	Yb	9.5 ppm
P_2O_5	0.45%	Sn	97.9 ppm	Ni	5.2 ppm
Cl	0.11%	Zn	85.6 ppm	Ir	4.0 ppm

Table 20: Chemical Composition of Clinoptilolite after Use analyzed by XRF

COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT
SiO_2	73.51%	Mn	555.0ppm	Te	39.7ppm
Al_2O_3	12.60%	Ce	327.3ppm	As	30.8ppm
CaO	6.54%	Zr	211.0ppm	Ga	26.1ppm
K_2O	3.27%	Eu	112.0ppm	Yb	8.7 ppm
Fe_2O_3	2.74%	Zn	111.2ppm	Ni	4.5 ppm
MgO	0.97%	Sn	98.2 ppm	Ir	0.5 ppm
Tl	0.15%	Pb	54.0 ppm	Nd	0.0 ppm
Cl	672.2ppm	Th	53.0 ppm		

Table 21: Chemical Composition of Mordenite before Use analyzed by XRF

COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT
SiO_2	73.79%	Mn	733.3ppm	As	33.8ppm
Al_2O_3	14.09%	Cl	294.9ppm	Th	33.4ppm
K_2O	5.27%	Ce	987.9ppm	Yb	17.8ppm
Fe_2O_3	3.59%	Zn	252.8ppm	Cu	15.2ppm
CaO	2.09%	Eu	170.2ppm	Nb	6.7 ppm
P_2O_5	0.46%	Sn	107.8ppm	Mo	1.7 ppm
MgO	0.28%	Pb	53.4 ppm	Ir	0.1 ppm
Tl	0.23%	Ga	26.3 ppm	Nd	0.0 ppm

Table 22: Chemical Composition of Mordenite after Use analyzed by XRF

COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT	COMPOUND/ ELEMENT	CONTENT
SiO_2	73.89%	Cl	978.9ppm	Pb	28.5ppm
Al_2O_3	13.73%	Mn	565.3ppm	Yb	25.5ppm
K_2O	5.12%	Ce	377.2ppm	Cu	18.1ppm
Fe_2O_3	3.67%	Zn	182.5ppm	Te	6.4 ppm
CaO	2.39%	Eu	160.9ppm	Tl	1.3 ppm
P_2O_5	0.48%	Sn	114.4ppm	Ir	0.3 ppm
MgO	0.24%	Th	36.7 ppm	Nd	0.0 ppm
Tl	0.22%	As	29.4 ppm		

6.4 XRD SPECTRUM ANALYSIS OF ZEOLITES

XRD spectrum analysis of Zeolites has been carried out. Different peaks are clearly observed while analyzing the XRD spectra of zeolites in virgin and exhausted (used) states (Figures 41, 42, 43, 44, 45, and 46, respectively).

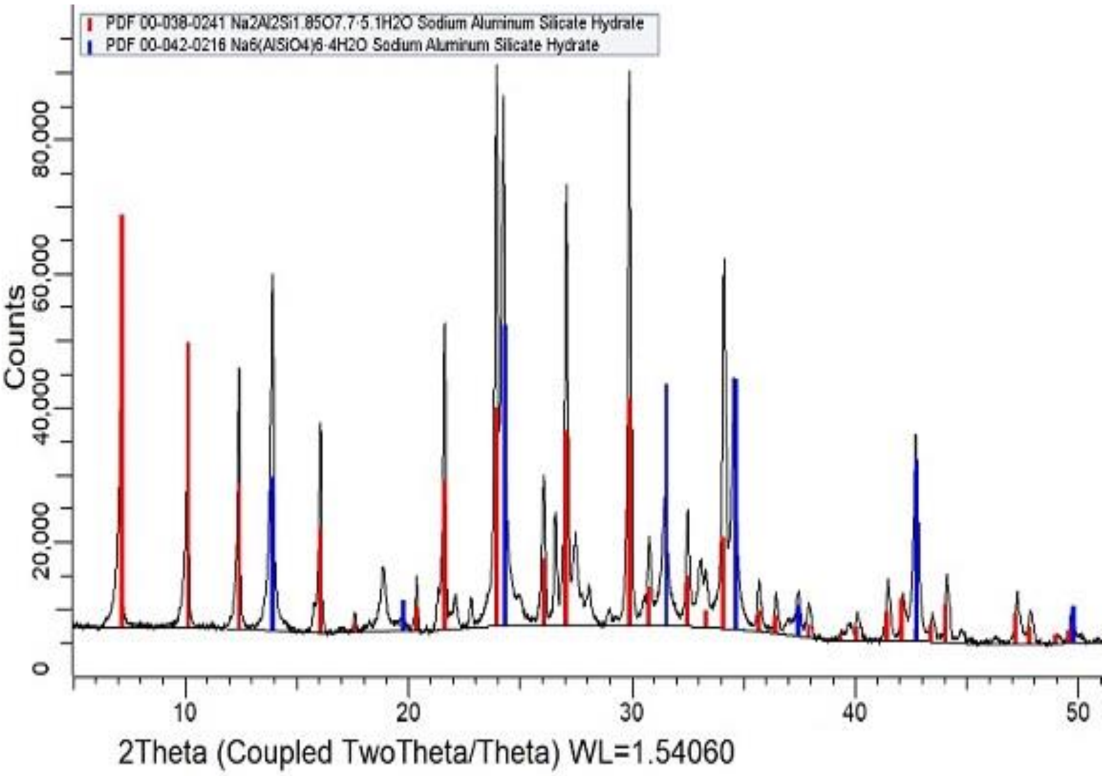


Figure 41: XRD Spectra of Synthetic Zeolites 4A before Use

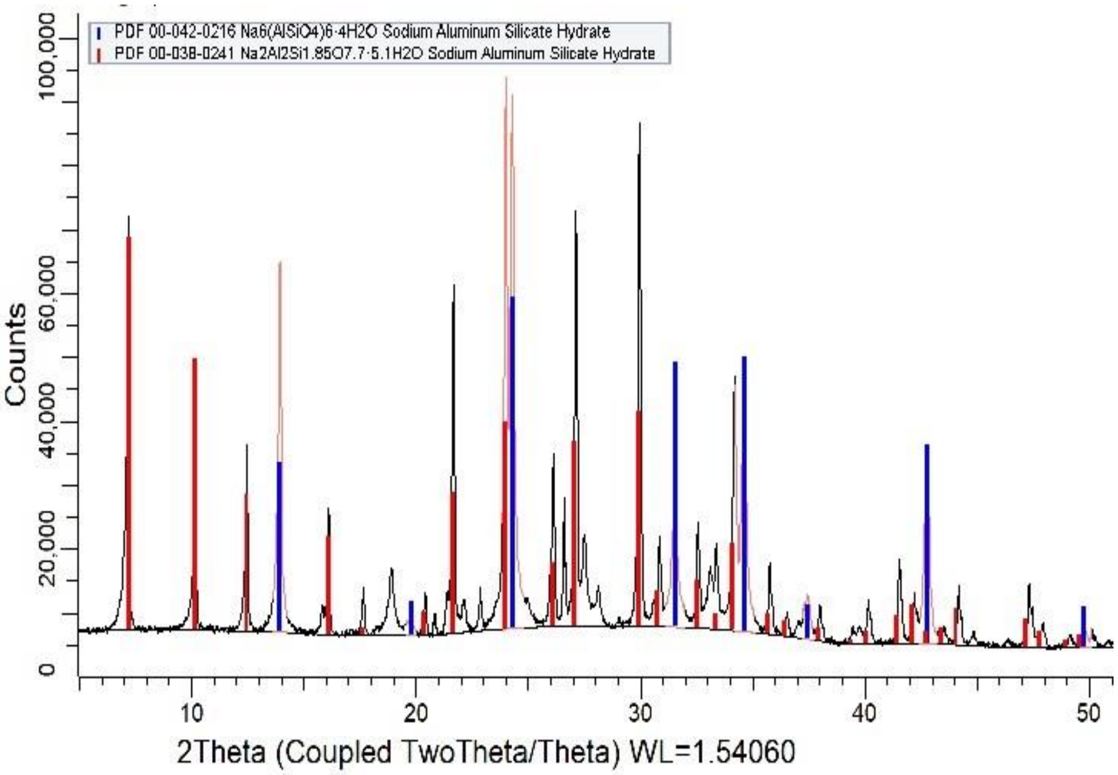


Figure 42: XRD Spectra of Synthetic Zeolites 4A after Use

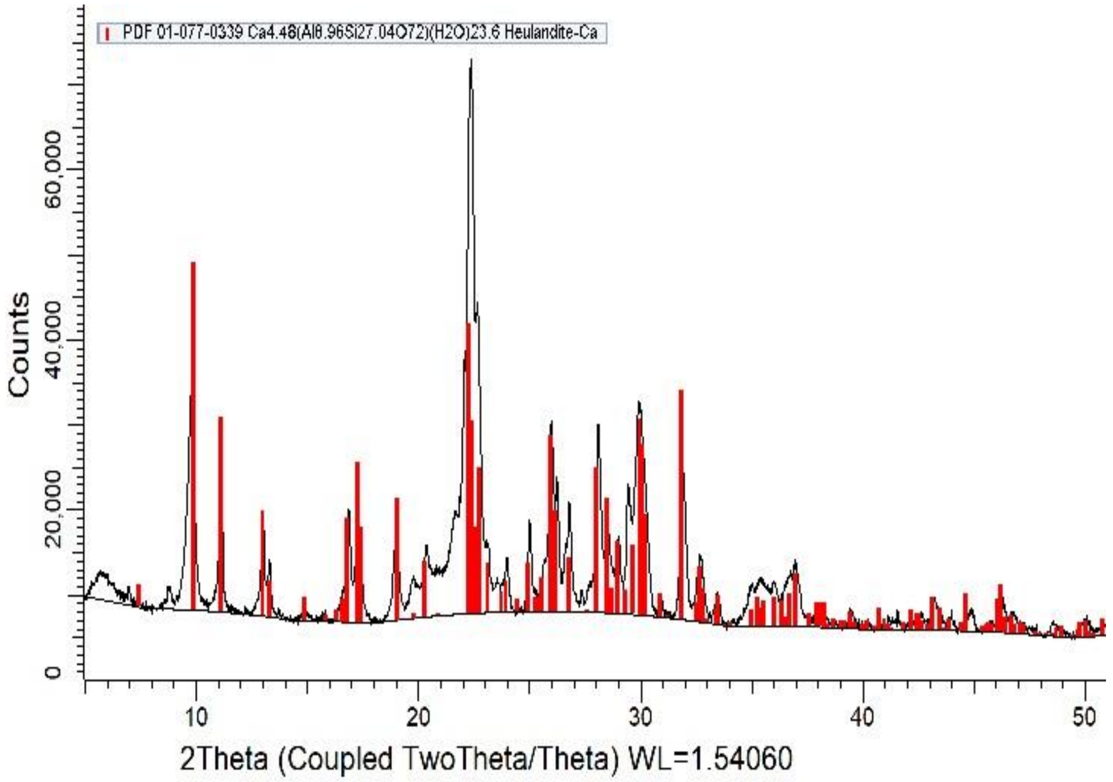


Figure 43: XRD Spectra of Clinoptilolite before Use

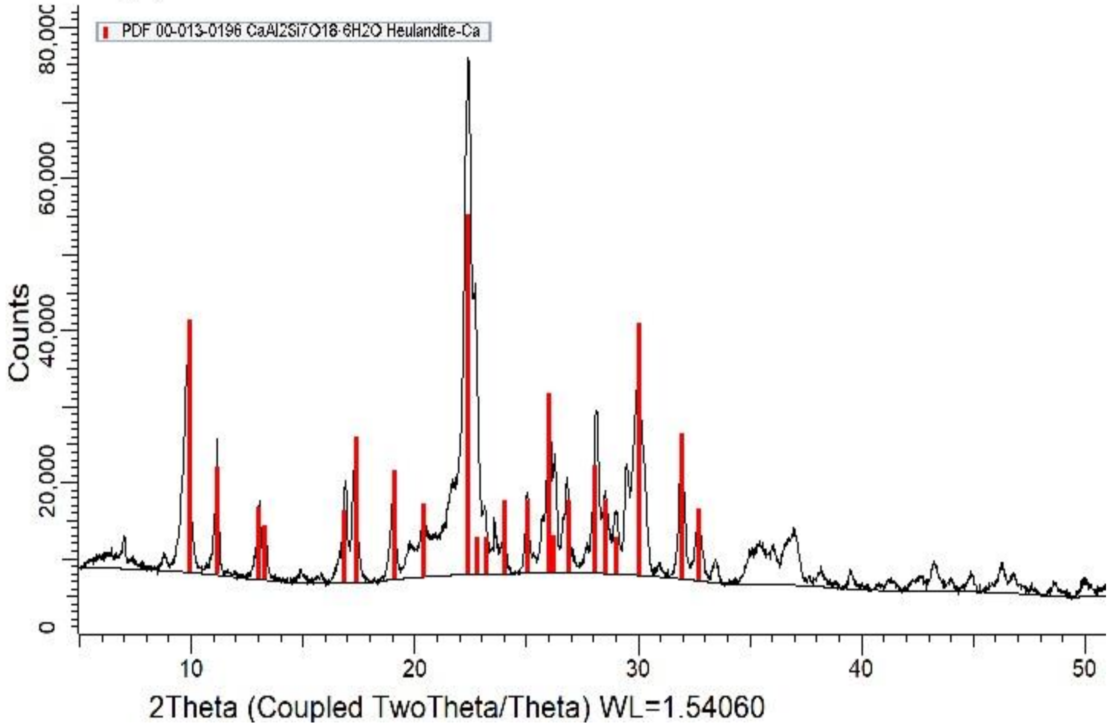


Figure 44: XRD Spectra of Clinoptilolite after Use

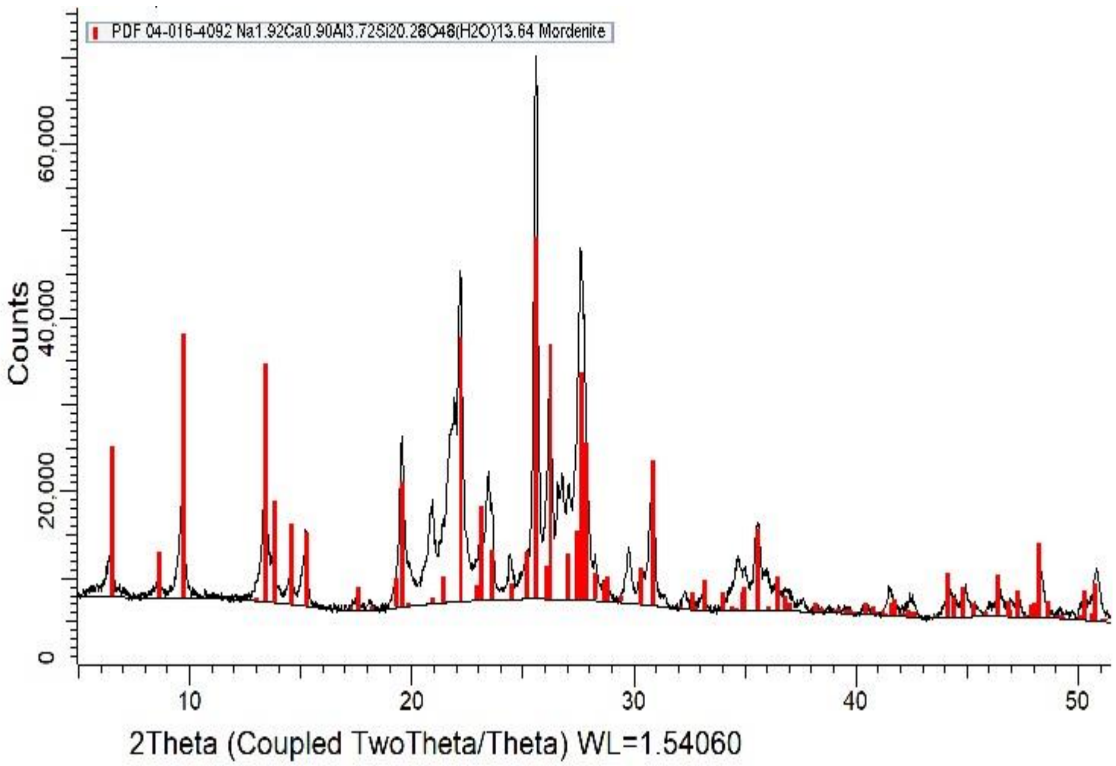


Figure 45: XRD Spectra of Mordenite before Use

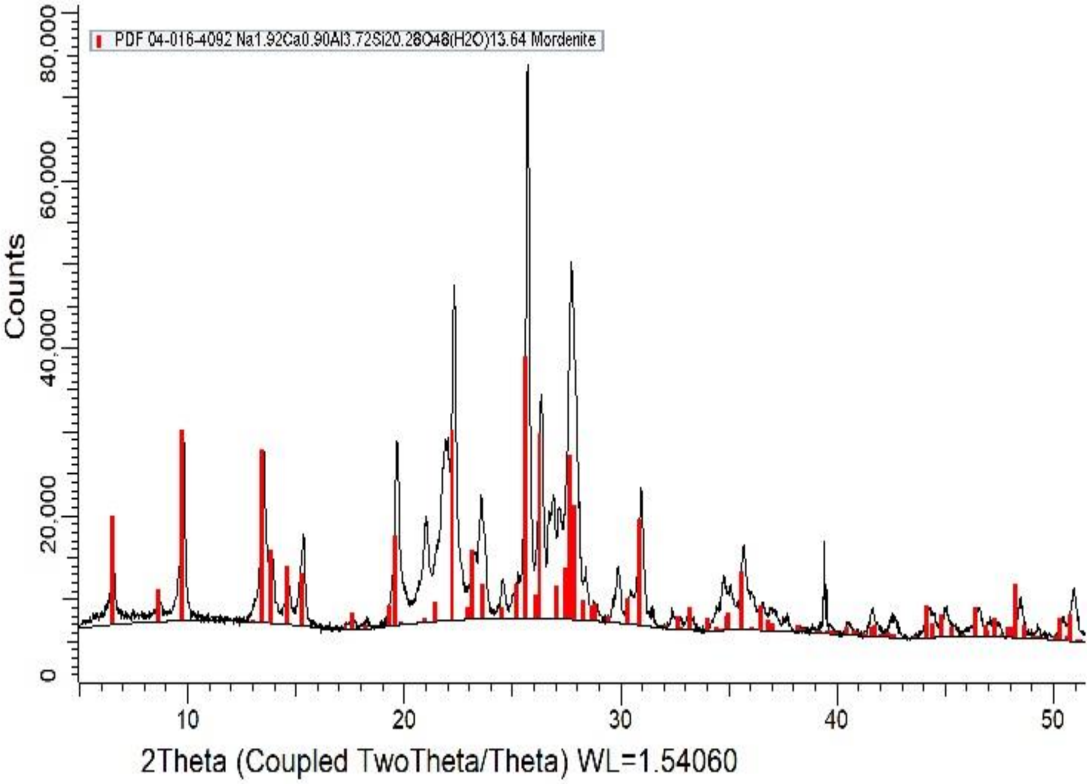


Figure 46: XRD Spectra of Mordenite after Use

6.5 WATER TREATMENT WITH ZEOLITES USING JAR TEST APPARATUS

Municipally treated sewage effluent (MTSE) treated with synthetic and natural zeolites removed a significant amount of ammonia-nitrogen (Figures 47, 48, and 49. respectively).

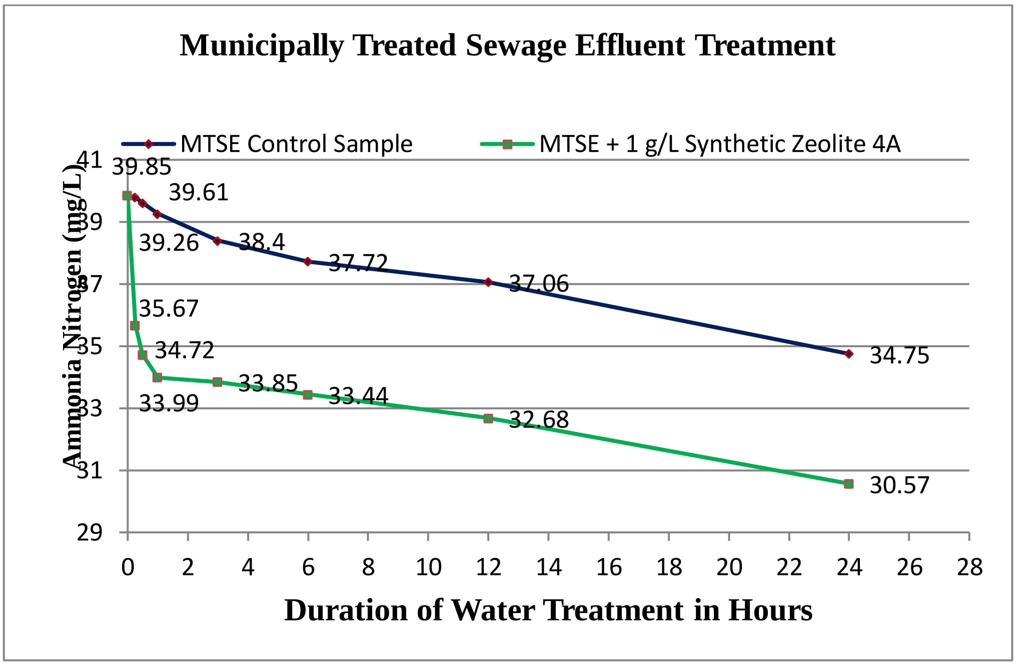


Figure 47: Ammonium Sorption with Synthetic Zeolites 4A in MTSE

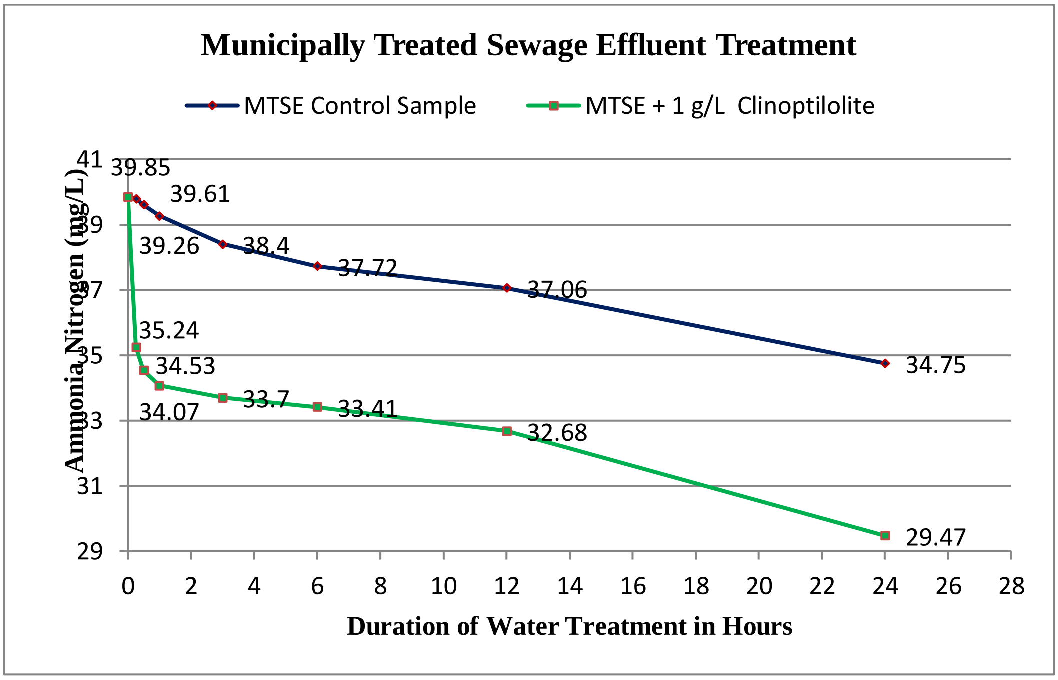


Figure 48: Ammonium Sorption with Clinoptilolite in MTSE

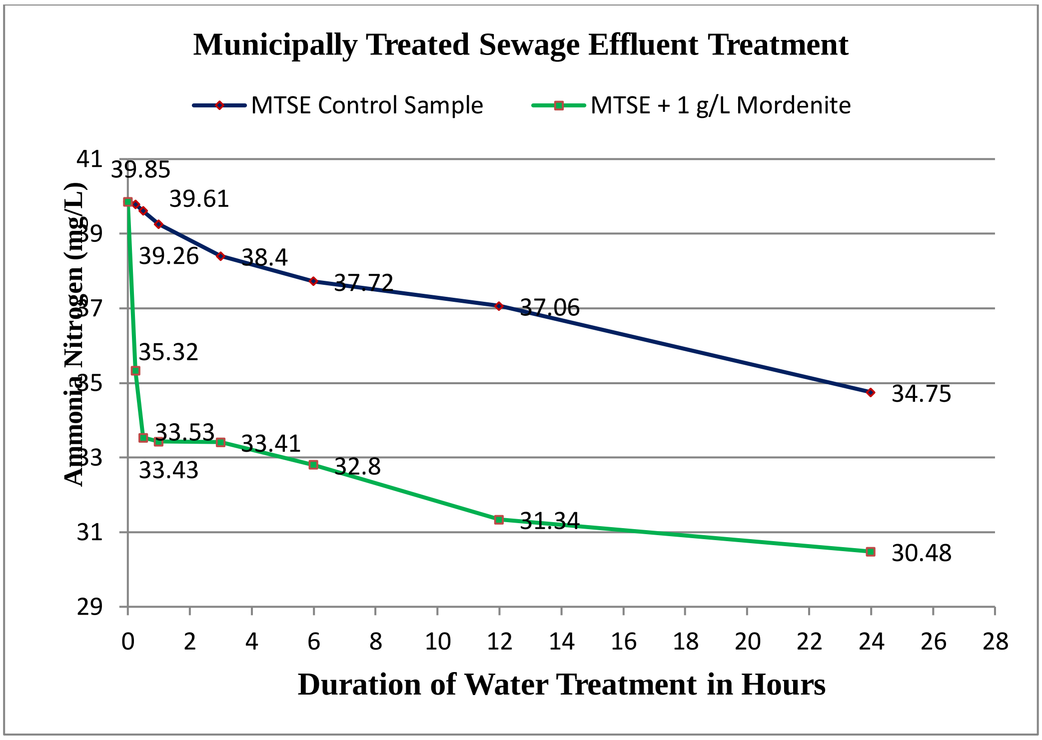


Figure 49: Ammonium Sorption with Mordenite in MTSE

Water quality parameters of control (MTSE) sample with synthetic zeolites 4A, Clinoptilolite, and Mordenite zeolites treatment are shown in tabular forms in Tables 23, 24, 25, and 26, respectively.

Table 23: Quality Parameters of Control (MTSE) Sample Sample with Synthetic Zeolites 4A Treatment

Particulars	Initial Values: NH_3=39.85, pH=7.31, EC=1462, TDS=737, T. Alkalinity=320, T. Hardness=280; Control (MTSE) Sample						MTSE + 1gm/L Synthetic Zeolite 4A						%age Loss of Water	NH_3 (mg/L) Reduction
Parameters Timing	NH_3 (mg/L)	pH	EC (μS/cm)	TDS (mg/L)	Total Alkalinity	Total Hardness	NH_3 (mg/L)	pH	EC (μS/cm)	TDS (mg/L)	Total Alkalinity	Total Hardness		
15 minutes	39.26	7.46	1451	728	320	280	33.85	7.84	1444	724	332	216	0.05	5.41
30 minutes	40.34	7.43	1450	723	316	284	35.67	7.87	1483	743	340	216	0.10	4.67
60 minutes	39.61	7.46	1440	715	316	280	34.72	7.84	1463	732	336	200	0.17	4.89
180 minute	37.06	7.72	1441	721	316	284	33.44	7.87	1430	711	340	188	0.32	3.62
360 minutes	37.72	7.95	1433	705	320	280	33.99	8.11	1474	730	352	188	0.42	3.73
720 minutes	38.40	8.08	1439	714	320	288	33.81	8.23	1478	736	352	188	0.67	4.59
1440minutes	34.75	8.15	1416	707	316	288	30.57	8.19	1462	730	336	184	1.22	4.18

Table 24: Quality Parameters of Control (MTSE) Sample Sample with Clinoptilolite (natural zeolites) Treatment

Particulars	Initial Values: NH_3=39.85, pH=7.31, EC=1462, TDS=737, T. Alkalinity=320, T. Hardness=280; Control (MTSE) Sample						MTSE + 1gm/L Natural Zeolite Clinoptilolite						%age Loss of Water	NH_3 (mg/L) Reduction
Parameters Timing	NH_3 (mg/L)	pH	EC (μS/cm)	TDS (mg/L)	Total Alkalinity	Total Hardness	NH_3 (mg/L)	pH	EC (μS/cm)	TDS (mg/L)	Total Alkalinity	Total Hardness		
15 minutes	39.26	7.46	1451	728	320	280	34.07	7.74	1386	696	316	276	0.05	5.19
30 minutes	40.34	7.43	1450	723	316	284	35.24	7.67	1442	723	320	284	0.10	5.10
60 minutes	39.61	7.46	1440	715	316	280	34.53	7.61	1396	692	308	276	0.17	5.08
180minutes	37.06	7.72	1441	721	316	284	32.68	7.79	1413	707	316	280	0.32	4.38
360minutes	37.72	7.95	1433	705	320	280	33.41	8.02	1420	703	320	288	0.42	4.31
720minutes	38.40	8.08	1439	714	320	288	33.70	8.15	1427	711	316	300	0.67	4.70
1440minutes	34.75	8.15	1416	707	316	288	29.47	8.12	1422	710	316	312	1.22	5.28

Table 25: Quality Parameters of Control (MTSE) Sample Sample with Mordenite (natural zeolites) Treatment

Particulars	Initial Values: NH_3=39.85, pH=7.31, EC=1462, TDS=737, Total Alkalinity=320, T. Hardness=280; Control (MTSE)						MTSE + 1gm/L Natural Zeolite Mordenite						%age Loss of Water	NH_3 (mg/L) Reduction
Parameters Timing	NH_3 (mg/L)	pH	EC (µS/cm)	TDS (mg/L)	Total Alkalinity	Total Hardness	NH_3 (mg/L)	pH	EC (µS/cm)	TDS (mg/L)	Total Alkalinity	Total Hardness		
15 minutes	39.26	7.46	1451	728	320	280	32.80	7.65	1413	710	316	276	0.05	6.46
30 minutes	40.34	7.43	1450	723	316	284	35.32	7.64	1440	720	320	282	0.10	5.02
60 minutes	39.61	7.46	1440	715	316	280	33.53	7.64	1435	714	308	276	0.17	6.08
180minutes	37.06	7.72	1441	721	316	284	33.43	8.05	1479	739	316	280	0.32	3.63
360minutes	37.72	7.95	1433	705	320	280	33.41	8.03	1423	704	320	288	0.42	4.31
720minutes	38.40	8.08	1439	714	320	288	31.34	8.16	1436	709	316	300	0.67	7.06
1440minutes	34.75	8.15	1416	707	316	288	30.48	8.14	1409	704	316	312	1.22	4.27

Table 26: Combined Comparative Treatment of MTSE Samples with All the three Zeolites

Particulars	MTSE + 1gm/L Synthetic Zeolite 4A						MTSE + 1gm/L Clinoptilolite o						MTSE + 1gm/L Mordenite					
Parameters → Timing ↓	NH_3 (mg/L)	pH	EC (µS/cm)	TDS (mg/L)	Total Alkalinity (mg/L)	Total Hard-ness	NH_3 (mg/L)	pH	EC (µS/cm)	TDS (mg/L)	Total Alkalinity (mg/L)	Total Hard-ness	NH_3 (mg/L)	pH	EC (µS/cm)	TDS (mg/L)	Total Alkalinity (mg/L)	Total Hard-ness
15 minutes	35.67	7.84	1444	724	332	216	35.24	7.74	1386	696	316	276	35.32	7.65	1413	710	316	276
30 minutes	34.72	7.87	1483	743	340	216	34.53	7.67	1442	723	320	284	33.53	7.64	1440	720	320	282
60 minutes	33.99	7.84	1463	732	336	200	34.07	7.61	1396	692	316	276	33.43	7.64	1435	714	312	276
180minutes	33.85	7.87	1430	711	340	188	33.70	7.79	1413	707	316	280	33.41	8.05	1479	739	316	280
360minutes	33.44	8.11	1474	730	352	188	33.41	8.02	1420	703	320	288	32.80	8.03	1423	704	320	288
720minutes	33.81	8.23	1478	736	352	188	32.68	8.15	1427	711	316	300	31.34	8.16	1436	709	316	300
1440minutes	30.57	8.19	1462	730	336	184	29.47	8.12	1422	710	316	312	30.48	8.14	1409	704	316	312

6.6 RESULTS AND DISCUSSIONS - WASTEWATER TREATMENT WITH ZEOLITES

Zeolites were found effective in wastewater treatment for combating ammonia-nitrogen. However, it is clear from the experimental results that the extent of ammonia nitrogen removal could not be achieved as in the case of synthetic water prepared with ammonium chloride in distilled water. Experimental results show that all three types of zeolites, namely Zeolites 4A, Clinoptilolite, and Mordenite, removed ammonia-nitrogen to its maximum extent within 30 minutes of agitation/ contact period. With an initial amount of 39.26 mg/L ammonia-nitrogen in municipally treated sewage effluent (MTSE), the ammonia removal results in the form of sorption capacity are in the order of Mordenite > Clinoptilolite > Zeolites 4A.

The respective values of sorptions are 5.73, 4.73, and 4.54 mg/g. Uptake capacity is maximum in the case of mordenite zeolite, i.e., 14.59 %. Thus, the above results indicate that mordenite zeolites have a maximum sorption capacity of 5.73 mg/g. The synthetic zeolite 4A also decreases the total hardness of the water in addition to ammonium ion removal. The natural zeolites clinoptilolite and mordenite do not affect the hardness of water but are effective in removing ammonia-nitrogen. Because of organically bound ammonia-nitrogen in water and wastewater, 100 % removal of ammonia-nitrogen is not feasible with zeolites. However, zeolite treatment can be beneficial in conjunction with other biological-chemical water and wastewater treatments.

CHAPTER 7

THE EFFICIENCY OF ZEOLITES IN WATER TREATMENT FOR COMBATING AMMONIA IN THE YAMUNA RIVER WATER

CHAPTER 7: THE EFFICIENCY OF ZEOLITES IN WATER TREATMENT FOR COMBATING AMMONIA IN THE YAMUNA RIVER WATER

7. THE YAMUNA RIVER AND WATER POLLUTION

With a length of over 1,370 kilometers, the Yamuna is the Ganga's biggest tributary in northern India. North of Haridwar in the Himalayan Mountains, in Yamunotri (38°59'N, 78°27'E), in the Uttrakhand Himalaya, is where it originates. Before joining the Ganges at Allahabad, it travels through Delhi, Haryana, and Uttar Pradesh states.(Bhardwaj et al., 2018). The Yamuna river is divided into two segments from the origin to the Wazirabad Barrage (Water Treatment Plant of the Delhi Government). The Himalayan Segment runs 172 kilometers from the source to Tajewalan Barrage, and the Upper Segment runs 224 kilometers from Tajewala Barrage to Wazirabad Barrage (Sharma et al., 2009). The catchment area of the Yamuna River includes the states of Himachal Pradesh, Uttaranchal, Uttar Pradesh, Rajasthan, Haryana, Madhya Pradesh, and the entire state of Delhi. The Yamuna river is not highly polluted upstream. Its water is used for drinking purposes after treatment at Waterworks Wazirabad. However, it becomes polluted downstream because of the dirty drains of Delhi. The Yamuna river's leading causes of pollution include untreated/ partially treated sewage, septic tanks discharge, and leachates of municipal solid waste disposal sites dumped into the drains of Delhi. These drains are not dredged/cleaned and maintained by the respective governing authorities, thus leading to water pollution of the Yamuna river.

7.1 WATER TREATMENT PLANTS AND POLLUTION LOAD

One of the older water treatment facilities still in operation today, Wazirabad Waterworks in Delhi, India, uses Yamuna River water for its potable water supply. It has been operating since 1966.Wazirabad is located in the Delhi region (28^{o} 42' 15.5" N; 77^{o} 14' 03.9" E) near Yamuna River(Dubey et al., 2013). The Yamuna river is a dependable source of high-quality water for a system providing water to over five million people in central and southern Delhi in India's National Capital Territory. In addition to the Wazirabad Yamuna river, water is supplied as raw water to ChandrawalWaterworks and Okhla Waterworks. The Wazirabad

Water Treatment plant is designed for operational reliability and redundancy to maintain high-quality water under all circumstances. At most water treatment utilities, breakpoint chlorination technology is used for nitrogen management. Nitrification involves the conversion of ammonia to Nitrate. In the breakpoint chlorination process, chlorine is added as a chlorine gas into the water to oxidize ammonia-nitrogen. This process converts ammonical-nitrogenous pollutants into simpler compounds. The Yamuna River's water quality continued to deteriorate often, occasionally reaching 1.0 mg/L of ammonia from 0.00 mg/L and 0.10 mg/L of nitrite from 0.006 mg/L. With raw water that has not been contaminated or degraded to the same extent as the Yamuna river received at Wazirabad Barrage, the findings of this study are unlikely to be reproducible (Kumar, 2013). Pollution loads in the upstream Yamuna before entering the waterworks of Delhi are depicted in the graphical forms in Figures 50, 51, and 52, respectively. These pictorial elaborations show the ammonia-nitrogen pollution, chloride pollution, and chlorine demand requirement from January 2004 to December 2008(Kumar, 2009).

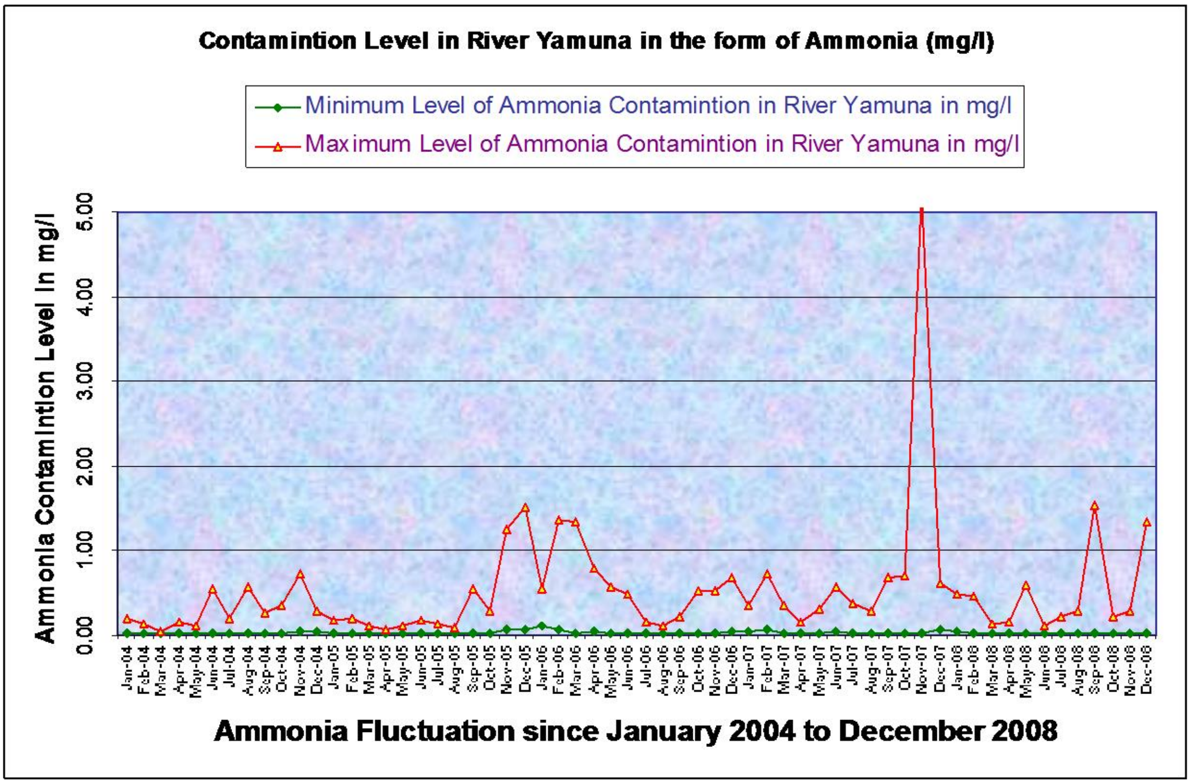


Figure 50: Minimum-Maximum Pollution of Ammonia-Nitrogen in the Yamuna River Water

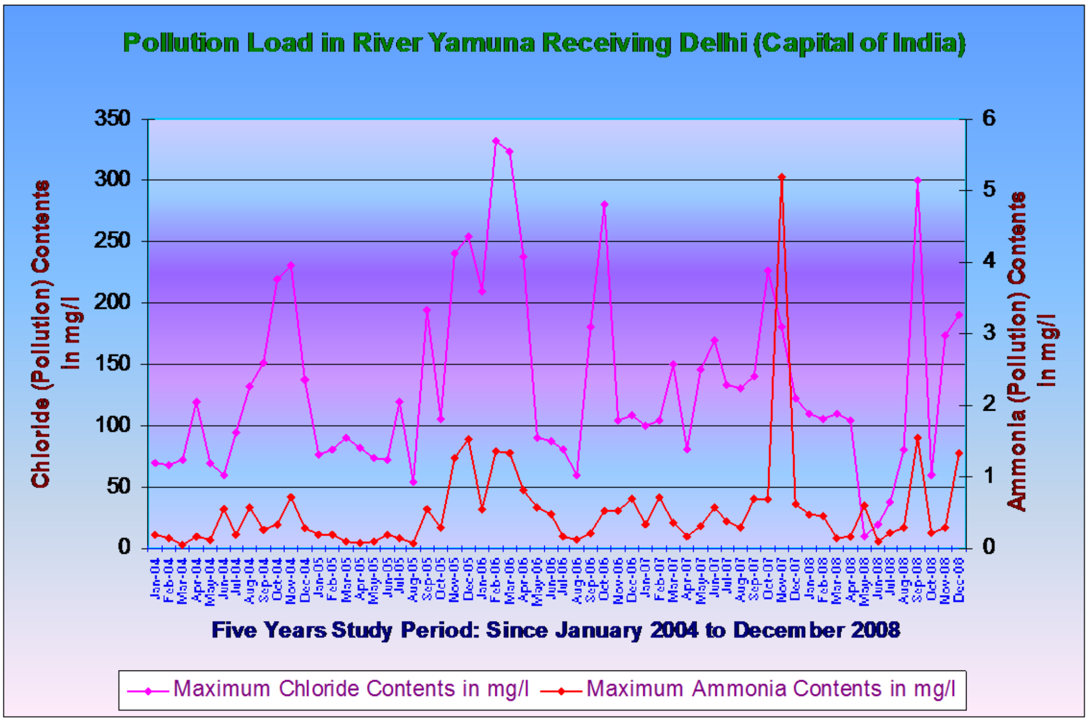


Figure 51: Graphical Comparison of Ammonia and Chloride Pollution in the Yamuna River Water

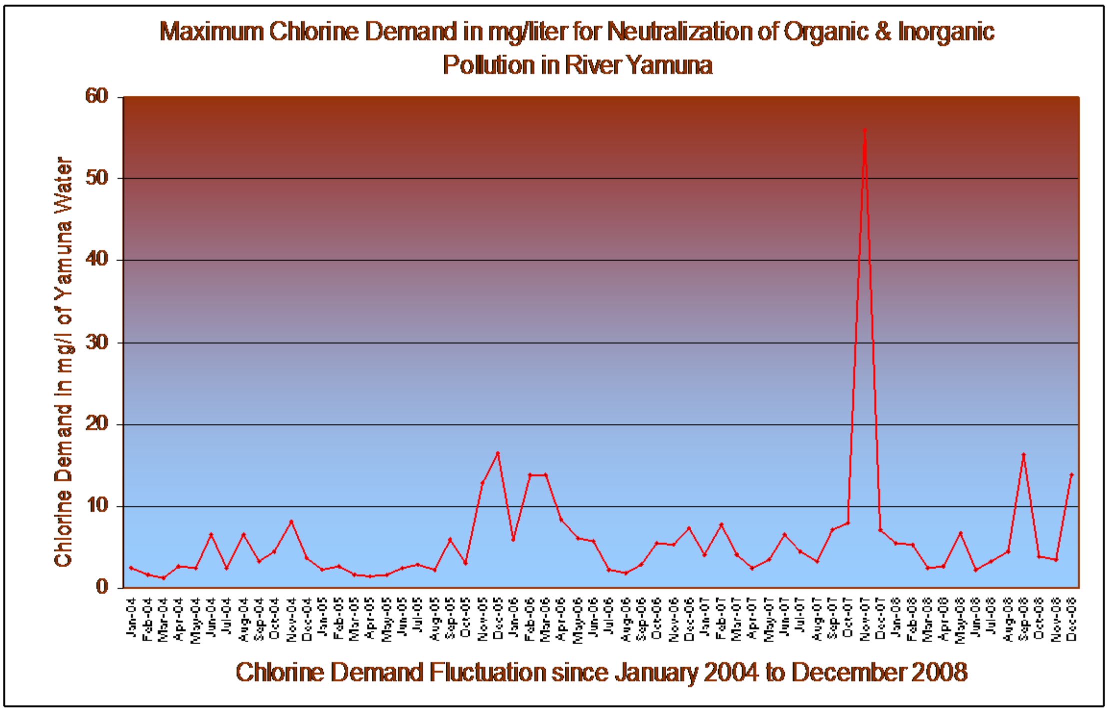


Figure 52: Chlorine Demand Requirement of the Yamuna River Water

7.2 RIVER WATER TREATMENT WITH CHLORINE

River water containing a high amount of ammonia, nitrogen, and other organic-inorganic pollutants produces many disinfection by-products when treated with chlorine gas for disinfection. When chlorine gas reacts with water containing ammonia nitrogen, it makes three types of chloramines:monochloramine, dichloramine, and trichloramine depending on the concentration of the chlorine-ammonium contamination. The treatment of secondary sewage effluents produces the potent carcinogen NDMA, also known as Dimethylnitrous amide ($C_2H_6N_2O$) (Mitch & Sedlak, 2002). The World Health Organization has also identified NDMA as a disinfection by-product of chlorination. Monochloramine and dimethylamine reaction is a frequent elements of waterways damaged by wastewater discharges (Sayato, 1989). A nitroso (N=O) group is attached to an amine in the chemical structure of NDMA, which is a kind of nitrosamine with the formula R1N(-R_2)-N=O. Nitrosamines are created in sewage effluents when nitrites and amines are present; these substances frequently take the form of proteins.Nitrosamines are a class of compounds, many of which are carcinogenic, mutagenic, and teratogenic, as stated by Choi Valentine (Choi & Valentine, 2002). Sewage effluents contain Dimethylamine (DMA,$(CH_3)_2NH$)and other related compounds, as it is found abundantly in human urine (Tsikas et al., 2007). Choi Valentine has proposed an NDMA formation mechanism in chlorinated water containing DMA Ammonia (Figure 53).

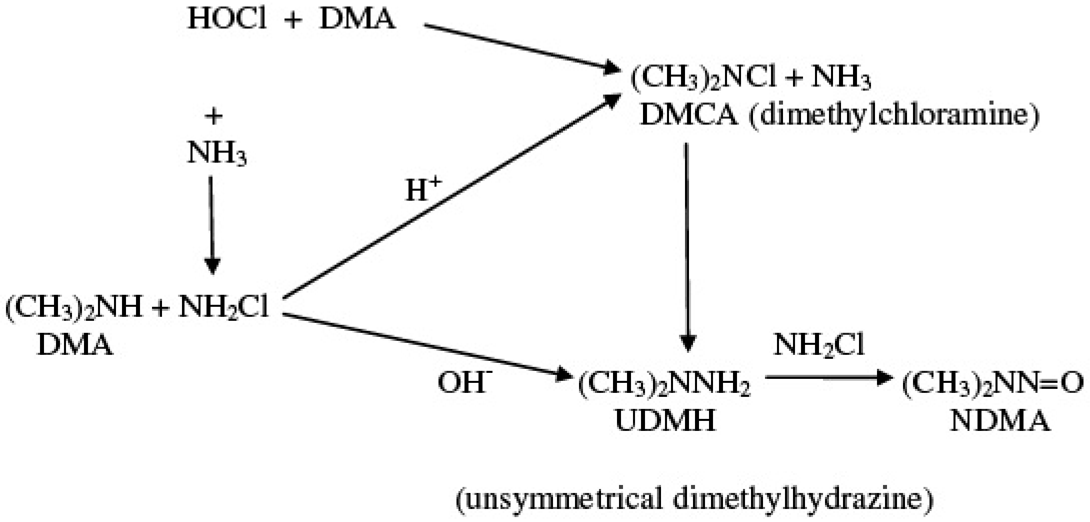
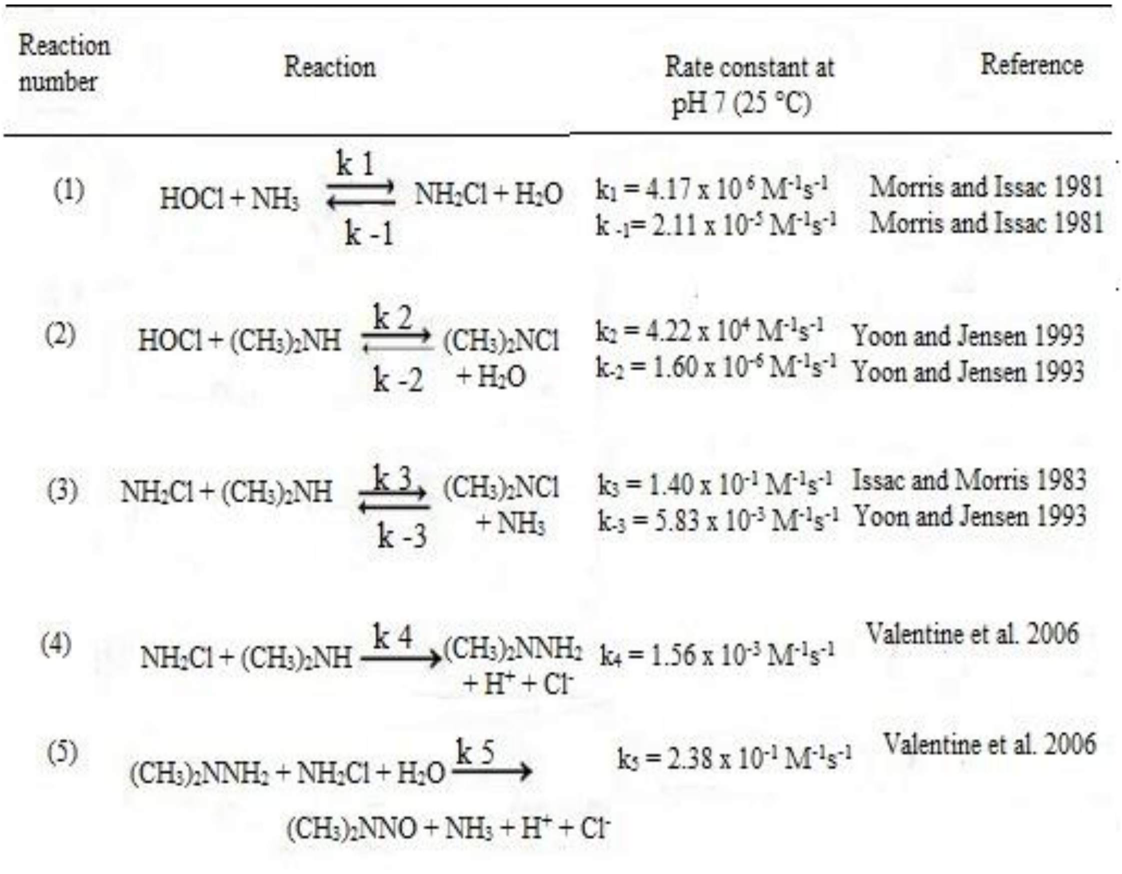


Figure 53: Formation of N-Nitrosodimethylamine (NDMA)

When DMA reacts with the monochloramine, it produces unsymmetrical dimethylhydrazine (UDMH), an intermediate product, which finally gets oxidized by monochloramine (NH_2Cl) to NDMA. From the first addition of HOCl, the earliest reactions involve the production of monochloramine (reaction 1). DMA and HOCl combine to generate DMCA, or dimethylchloramine (reaction2). Its rate of formation is, however, approximately 100 times slower than that of monochloramine. The slow depletion of monochloramine is explained by the transfer of chlorine from monochloramine to DMA to create DMCA (reaction 3). The reaction between DMA and monochloramine (reaction 4) produces UDMH, which serves as the catalyst for the synthesis of NDMA. UDMH is then oxidized by monochloramine to make NDMA (reaction 5). The mechanisms of NDMA formation in chlorinated water containing DMAAmmonia have been depicted in Table 27 and Figure 54, respectively(Valentine & Barrett, 2006)(Reproduced with permission: Appendix 1).

Table 27: Mechanism of NDMA formation in chlorinated water containing DMA Ammonia (monochloramine-UDMH pathway



Reaction number	Reaction	Rate constant at pH 7 (25 °C)	Reference
(1)	$HOCl + NH_3 \xrightleftharpoons[k\ -1]{k\ 1} NH_2Cl + H_2O$	$k_1 = 4.17 \times 10^6\ M^{-1}s^{-1}$ $k_{-1} = 2.11 \times 10^{-5}\ M^{-1}s^{-1}$	Morris and Issac 1981 Morris and Issac 1981
(2)	$HOCl + (CH_3)_2NH \xrightleftharpoons[k\ -2]{k\ 2} (CH_3)_2NCl + H_2O$	$k_2 = 4.22 \times 10^4\ M^{-1}s^{-1}$ $k_{-2} = 1.60 \times 10^{-6}\ M^{-1}s^{-1}$	Yoon and Jensen 1993 Yoon and Jensen 1993
(3)	$NH_2Cl + (CH_3)_2NH \xrightleftharpoons[k\ -3]{k\ 3} (CH_3)_2NCl + NH_3$	$k_3 = 1.40 \times 10^{-1}\ M^{-1}s^{-1}$ $k_{-3} = 5.83 \times 10^{-3}\ M^{-1}s^{-1}$	Issac and Morris 1983 Yoon and Jensen 1993
(4)	$NH_2Cl + (CH_3)_2NH \xrightarrow{k\ 4} (CH_3)_2NNH_2 + H^+ + Cl^-$	$k_4 = 1.56 \times 10^{-3}\ M^{-1}s^{-1}$	Valentine et al. 2006
(5)	$(CH_3)_2NNH_2 + NH_2Cl + H_2O \xrightarrow{k\ 5} (CH_3)_2NNO + NH_3 + H^+ + Cl^-$	$k_5 = 2.38 \times 10^{-1}\ M^{-1}s^{-1}$	Valentine et al. 2006

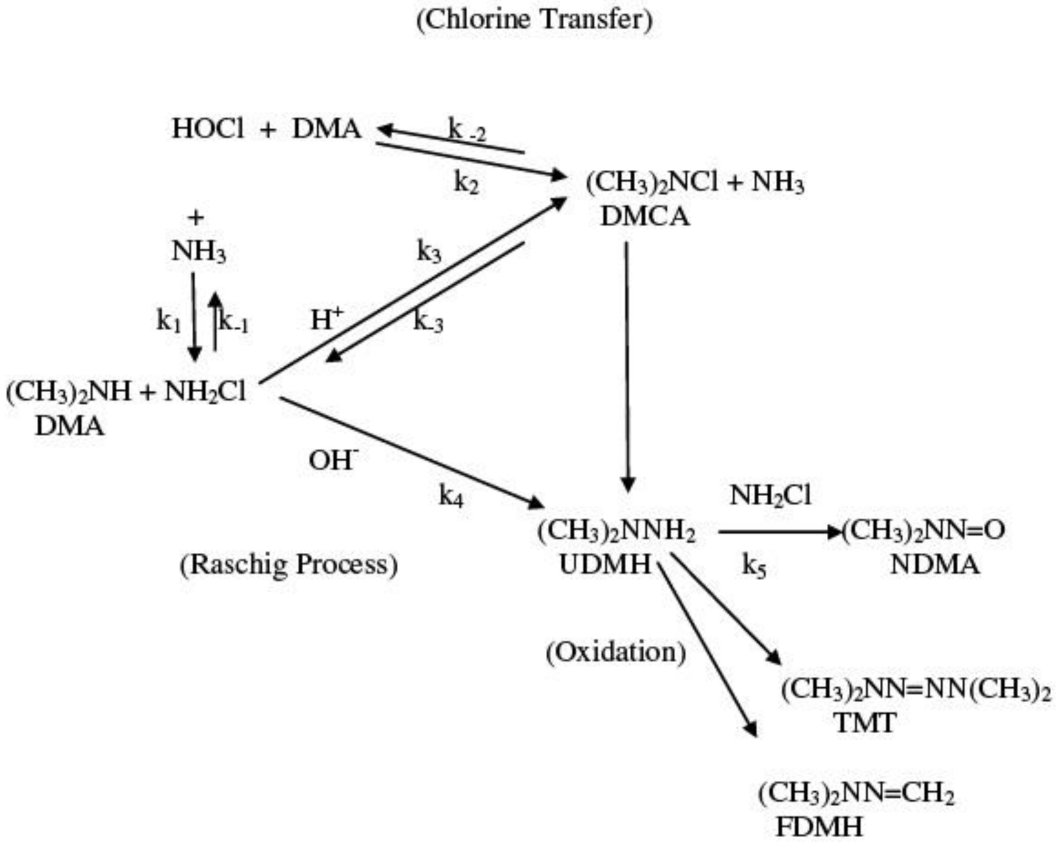


Figure 54: Proposed mechanism of NDMA formation

Source: Valentine et al., 2006. Reprinted with permission. © AwwaRF

7.2.1 DISINFECTION BY-PRODUCTS PRECURSORS

In water treatment plants, chlorinating ammonia-rich water produces disinfection by-products (DBPs). The DBPs are one of the significant challenges in water treatment distribution system operations in addition to regulated DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs), bromates, and chloride. In recent years, unregulated compounds such as nitrosamines, iodinated DBPs, and haloacetamides (HAMs) have attracted much attention. Free chlorine, organic chloramines, and inorganic chloramines are all chemically linked and easily transform into one another. These chemicals can never be found alone. Chloramines in the inorganic matter are not persistent. These substances, however, have a higher persistence than chlorine compounds that are easily accessible. According to studies, the half-lives of inorganic chloramines might vary depending on the situation from one minute to 23 days ("Health Canada," 2020b"). Chloramines can also exist in water as organic chloramines in addition to their inorganic counterparts. Any halogenated organic substances that are assessed as a percentage of combined chlorine may be referred to as "organic chloramines" (the difference between the measured free total chlorine concentrations). When free chlorine or inorganic chloramines react with either dissolved organic nitrogen or dissolved organic carbon, organic chloramines can result. They could be dangerous to people and serve as a precursor to other disinfection byproducts. According to research, organic chloramines' half-lives can range from 0.002 hours to more than 240 hours (How et al., 2017).

According to a 1999 survey, the following disinfection procedures are used in larger water treatment facilities in the United States (the vast majority of smaller water treatment facilities typically employ a form of chlorine):

UV	< 1
Ozone	5.6
Sodium hypochlorite (onsite)	2
Chlorine dioxide	8.1
Sodium hypochlorite	18.3
Chloramines	29.4
Chlorine gas	83.3 percent*

*Given that some utilities employ multiple disinfection techniques, the overall proportion is more significant than 100 percent. However, chlorination is the most popular form of disinfection (AWWA, 2006). More than 600 disinfection by-products (DBPs) are identified when raw water containing ammonia-nitrogen and other organic compounds is treated with chlorine and other oxidizing agents (How et al., 2017). DBPs can be grouped into three categories (Galvin R.M. and Mellado J.M.R., 2016):

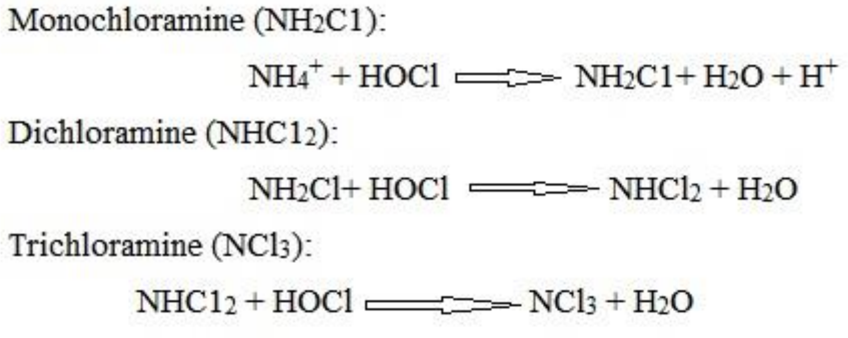
1) Halogenated Compounds: Halonitromethanes, haloaldehydes, halo ketones, haloacetamides, haloacetonitriles, haloacetic acids, haloalcohols, trihalomethanes (THMs).
2) Non-halogenated compounds: Carboxylic acids, ketonic acids, nitriles, nitrosamines, aldehydes, low molecular weight ketones.

3) Inorganic by-products: Chlorites, chlorates, cyanogen chlorides, bromates.

7.2.2 INORGANIC CHLORAMINES AND DISINFECTION BY-PRODUCTS

Inorganic nitrogen in the water in the form of free ammonia, ammonium chloride, ammonium sulfate, or ammonium nitrate readily reacts with oxidizing agents (chlorine, etc.) used for disinfection of water producing inorganic chloramines. Amines that include at least one chlorine atom directly linked to a nitrogen atom are known as chloramines (N). Three distinct inorganic chloramines, monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine, are produced during this reaction (NCl_3). The amount type of Chloramine formation depends on the water's pH value, temperature, contact time, chlorine ammonia ratio, and mixing(Lenntech, 2022). In general, the optimal pH for the formation of monochloramine lies in the range of 7.5–9.0. Cl_2:NH_3-N ratios of ≤5:1 by weight are optimum for monochloramine formation. Dichloramine has a maximum formation at pH 4–6. In idealized conditions, ratios between 5:1 and 7.6:1 favor dichloramine production. A pH <4.4 higher Cl_2:NH_3-N ratios favor trichloramine formation (Griffin et al., 1941.; Toft Malaiyi, 1984).

The generalized inorganic chloramine formation reactions are depicted as follows(Distribution, 2006):



Monochloramine (NH_2C1):

$$NH_4^+ + HOCl \Longrightarrow NH_2C1 + H_2O + H^+$$

Dichloramine ($NHC1_2$):

$$NH_2Cl + HOCl \Longrightarrow NHCl_2 + H_2O$$

Trichloramine (NCl_3):

$$NHC1_2 + HOCl \Longrightarrow NCl_3 + H_2O$$

The initial ratio of chlorine to ammonia (Cl:NH_3), pH, temperature, and time all affect how quickly monochloramine (NH2Cl) and dichloramine ($NHCl_2$) are formed. In general, high pH and low Cl:NH_3 ratios prefer monochloramine. Monochloramine is classified as the least detectable chlorinous taste and odor of all the chlorine residuals and is widely employed as a lasting residual that will develop lower amounts of disinfection by-products (DBPs). The breakpoint reaction occurs best when the pH is between 7.0 and 7.5, but it can also proceed more slowly from a pH of 6.5 to 8.5. The reaction needs enough chlorine, which was empirically determined to be around 8.5 mg/L chlorine per mg/L NH_3-N. Additionally, additional chlorine may be needed to satisfy a number of side reactions, such as the production of minor products such as nitrogen trichloride and other chlorine requirements (caused by organic and other compounds). Time is the only additional reaction needed. The breakpoint reaction is not immediate and could take up to 30 minutes to complete. In this process, a variety of reaction steps occur; the following are summaries of two of the most common reaction sequences (AWWA, 2006):

$$\underset{\text{ammonia}}{2NH_4^+} + \underset{\substack{\text{hypochlorous}\\ \text{acid}}}{3HOCl} \rightarrow \underset{\text{nitrogen}}{N_2} + \underset{\text{hydrogen}}{5H^+} + \underset{\substack{\text{chloride}\\ \text{ion}}}{3Cl^-} + 3\,H_2O$$

$$\underset{\text{ammonia}}{NH_4^+} + \underset{\substack{\text{hypochlorous}\\ \text{acid}}}{4HOCl} \rightarrow \underset{\text{nitrate}}{NO_3^-} + H_2O + \underset{\substack{\text{hydrogen}\\ \text{ion}}}{6H^+} + \underset{\text{chloride}}{4Cl^-}$$

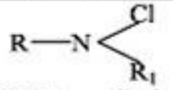
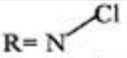
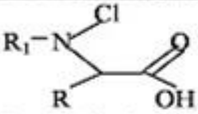
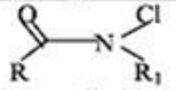
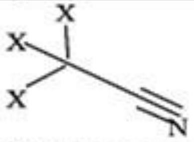
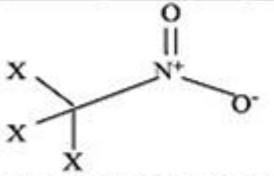
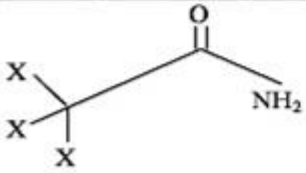
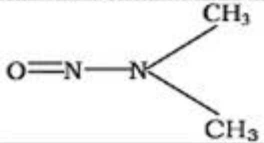
Cyanogen chloride, chlorites, chlorates, and bromates are the other inorganic disinfection by-products produced during the disinfection process of water and wastewater.

7.2.3 ORGANIC CHLORAMINES AND DISINFECTION BY-PRODUCTS

When free chlorine or organic chloramines are combined with either dissolved organic nitrogen (DON) or dissolved organic carbon (DOC), organic chloramines are created(Hunter, 1967; Snyder Margerum, 1982; Isaac Morris, 1985).

Cytotoxicity increased drastically when nitrogen atoms entered the structure of DBPs. The haloacetomides, halonitromethanes, haloacetonitriles are more cytotoxic as compared to non-nitrogenous DBPs (Plewa et al., 2008a). Effects of DBPs in regard to cytotoxicity (cell death) genotoxicity (DNA damage) on mammals have been studied by Professor Michael Plebba at the University of Illinois (Yang et al., 2014). Nitrogenous DBPs (Table 28) are required essential to be regulated.

Table 28: Structures of different organic chloramines species (Nitrogenous DBPs)

Name	Structure	Precursors	Reference
N-Chloramines	 R,R$_1$: alkyl, aromatic, halogen or hydrogen	Amines	(How et al., 2017)
N-Chloraldimines	 R: Alkyl or hydrogen	Imines and amino acids	(How et al., 2017)
N-Chloramino acids	 R$_1$: Alkyl, halogen or hydrogen	Amino carboxylic acids and amino sulfonic acids	(How et al., 2017)
N-Chloramides	 R,R$_1$:Alkyl,halogen or hydrogen	Amides and imides	(How et al., 2017)
Haloacetonitriles (HANs)	 X: Halogen or hydrogen	-----------------	(Cuthbertson et al., 2020)
Halonitromethanes (HNMs)	 X: Halogen or hydrogen	------------------	(Cuthbertson et al., 2020)
Haloacetamides (HAMs)	 X: Halogen or hydrogen	-----------------	(Cuthbertson et al., 2020)
N-nitrosodimethylamine (NDMA)		Secondary and tertiary amines	(Krasner et al., 2013)

7.3 THE FATE OF NITROGENOUS DISINFECTION BY-PRODUCTS BY HAZARDS

The DBPs include halogenated furanones, haloacids, haloketones, halonitromethanes, haloacetaldehydes, haloacetonitriles, and haloacetamides are largely formed on priority by chlorine or chloramine disinfection. Chinese hamster ovary (CHO) cells, a consistent analytical, biological platform endpoint, have been used to conduct systematic, quantitative, and comparative assessments on the induction of cytotoxicity and genotoxicity for more than 100 DBPs, including these key DBPs (Plewa et al., 2008a; Wagner & Plewa, 2017).

According to their ranking from most potent to least potent, the top 10 most cytotoxic DBPs in the CHO essay are as follows: least to most potent: Bromoiodoacetamide <Tribromoacetaldehyde <Chloroacetaldehyde <Bromoacetonitrile <Tribromoacetamide <Iodoacetic acid <Dibromoacetonitrile <Bromoacetamide <Iodoacetamide <Diiodoacetamide. Dibromochloronitromethane <Dibromoa-acetonitrile <Bromoacetonitrile<<Bromoacetamide <Iodoacetamide <Diiodoacetamide < Tribromoacetamide<Dibromonitromethane<Bromoacetic acid<Iodoacetic acid are the top 10 most genotoxic DBPs in the CHO comet assay (Dong et al., 2019; Plewa et al., 2004; Wagner & Plewa, 2017).

This thorough investigation revealed several toxicity trends, such that iodinated DBPs (I-DBPs) are more toxic than brominated DBPs (Br-DBPs), which are much more dangerous than chlorinated analogs (I > Br "Cl), and that nitrogenous DBPs (N-DBPs) tend to be more hazardous than DBPs lacking nitrogen (Plewa et al., 2008b, 2017; Richardson et al., 2008; Wagner & Plewa, 2017).

7.4 SIGNIFICANT FINDINGS: WATER TREATMENT AND CHANGE IN QUALITY PARAMETERS

The water quality parameters of the Yamuna river water treatment for combating ammonia nitrogen using synthetic and natural zeolites are shown in tabular forms in Tables 29, 30, and 31, respectively. It is evident from the tables that an increasing amount of zeolites certainly affects the quality parameters.

Table 29: Treatment of Natural Water (of the Yamuna River) with synthetic zeolites 4A agitated in Jar Test Apparatus at 100 RPM for 1 Hour

Particulars→ Parameters↓	Control	NW + 200 mg/L SZ-4A	NW + 400 mg/L SZ-4A	NW + 600 mg/L SZ-4A	NW + 800 mg/L SZ-4A	NW + 1000 mg/L SZ-4A
Ammonia NH_3-N (mg/L)	0.942	0.865	0.791	0.741	0.674	0.628
pH	8.30	8.40	8.49	8.66	8.70	8.77
Electrical Conductivity,(µMho/cm)	557	560	563	567	574	580
Total Alkalinity as $CaCO_3$ (mg/L)	136	136	140	142	144	148
Total Hardness as $CaCO_3$ (mg/L)	196	172	148	136	116	100

Table 30: Treatment of Natural Water (of the Yamuna River) with natural Clinoptilolite agitated in Jar Test Apparatus at 100 RPM for 1 Hour

Particulars→ Parameters↓	Control	NW + 200 mg/L Clinoptilolite	NW + 400 mg/L Clinoptilolite	NW + 600 mg/L Clinoptilolite	NW + 800 mg/L Clinoptilolite	NW + 1000 mg/L Clinoptilolite
Ammonia NH_3-N (mg/L)	0.912	0.890	0.840	0.798	0.740	0.700
pH	8.11	8.18	8.20	8.18	8.18	8.16
Electrical Conductivity, (µMho/cm)	533	531	537	539	534	541
Total Alkalinity as $CaCO_3$(mg/L)	136	136	136	140	140	144
Total Hardness as $CaCO_3$ (mg/L)	196	196	196	196	196	196

Table 31: Treatment of Natural Water (of the Yamuna River) with natural Mordenite agitated in Jar Test Apparatus at 100 RPM for 1 Hour

Particulars→ Parameters↓	Control	NW + 200 mg/L Mordenite	NW + 400 mg/L Mordenite	NW + 600 mg/L Mordenite	NW + 800 mg/L Mordenite	NW + 1000 mg/L Mordenite
Ammonia NH_3-N (mg/L)	1.12	1.00	0.94	0.88	0.79	0.70
pH	8.15	8.22	8.23	8.25	8.25	8.25
Electrical Conductivity, EC (µMho/cm)	532	531	531	529	530	529
Total Alkalinity (mg/L)	132	132	132	132	132	132
Total Hardness (mg/L)	192	192	192	192	192	192

7.5 RESULT AND DISCUSSIONS: RIVER WATER TREATMENT WITH ZEOLITES

All three zeolites were used to treat natural water collected from the Yamuna River in Delhi. It was found the sorption capacity and uptake (%) of synthetic zeolites 4A to be 0.314 mg/g 34.13 %, with an initial concentration of 0.942 mg/L ammonia nitrogen. Total alkalinity increased from 136 mg/L to 148 mg/L; electrical conductivity from 557 to 580 (µMho/cm); pH from 8.30 to 8.77. However, a reduction in total hardness to 96 mg/L from an initial concentration of 196 mg/L has also been noticed. Thus, synthetic zeolites effectively remove the hardness of water compared to ammonia nitrogen in natural water. However, sorption capacity and uptake (%) with clinoptilolite were found to be 0.212 mg/g 23.24 %, with an initial amount of 0.912 mg/L NH_3-N, last with mordenite zeolites 0.42 mg/g 37.5 % with an initial amount of 1.12 mg/L NH_3-N(Figure 55). However, there was noticed o significant change in total hardness, electrical conductivity, pH, and total alkalinity in the case of Clinoptilolite Mordenite.

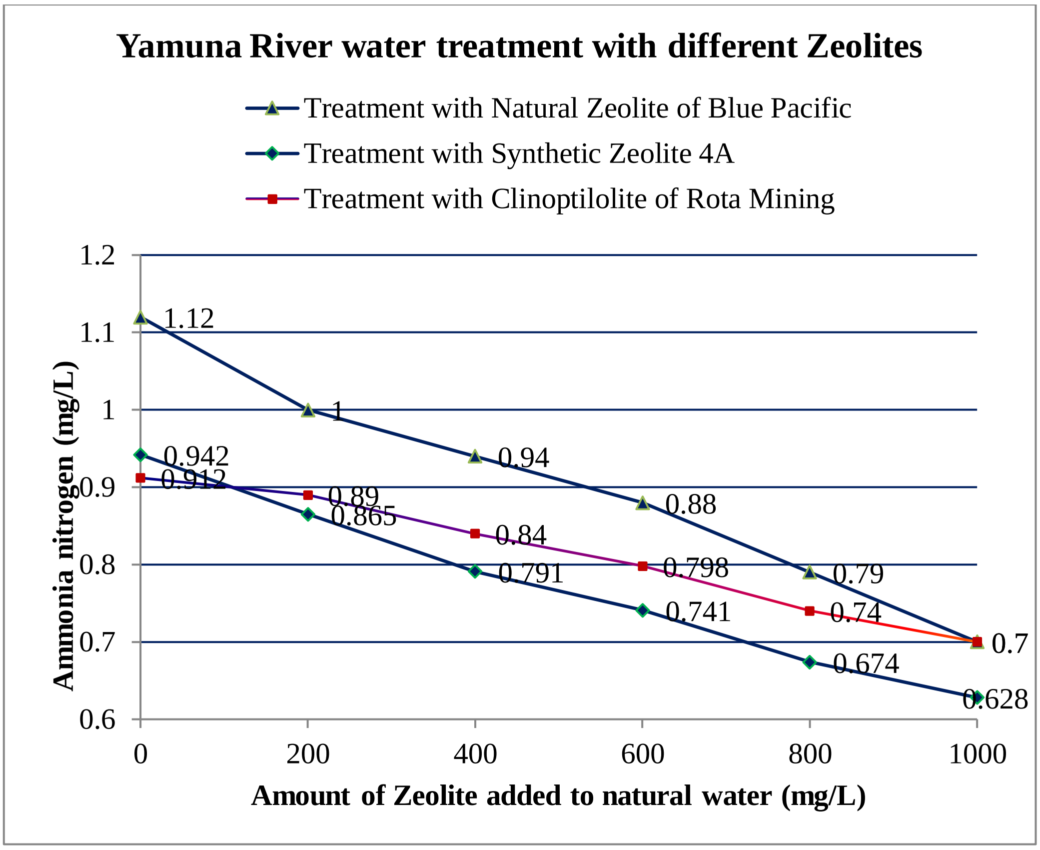


Figure 55: Ammonium Sorption of Zeolites in the Yamuna River Water

It is clear from the experimental results that the extent of ammonia nitrogen removal could not be achieved as compared to that of synthetic water prepared with ammonium chloride in distilled water. The reason for inadequate ammonia removal by zeolites in natural water may be attributed to competing ions in natural water, such as K^+, Na^+, $Ca^{2+,}$ Mg^{2+}, etc., which approach the ion-exchange sites of the zeolites to inhibit the adsorption of ammonia. It compared ammonia removal efficiencies by different zeolites in untreated Yamuna river water (with an ammonia concentration of 0.942 mg/L, 0.912 mg/L, and 1.12 mg/L). The ammonia removal efficiency was as follows: Natural zeolites > Synthetic zeolites > Clinoptilolite with Yamuna River water. It has also been observed that Clinoptolite is more effective in removing ammonia nitrogen than Natural zeolites and synthetic zeolites in a long course of contact time.

Mordenite proved quick in removing ammonia nitrogen as per its removal capacity. Additional experiments were performed to evaluate coagulation-flocculation feasibility tests. These results are not reported in the present research study. Coagulation-flocculation tests were not feasible with powdered zeolites because of the high demand for coagulant and residual coagulant risk in filtered water. Commercially available poly-aluminum Chloride (PACl), Ferric Alum, and Tanfloc were used as coagulants. A high dose of 80 ppm Alum, 60 ppm PAClindividually, and 40 ppm tanfloc was found inadequate for complete clarification. The turbidity removal efficiency was found with coagulant (Alum) aid in the order of mordenite> Clinoptilolite > Synthetic zeolites. Mordenite powder was found to be the most supportive in the coagulation process.

Because of natural zeolites' relatively high exchange capacity for ammonia and other metallic cations, Mordenite Clinoptilolite can be replaced for s media beds used at municipal waterworks utilities. As the pore size of Mordenite Clinoptilolite is between 6 - 8 Angstrom, the filter media would be able to filter out particles down to the size of 1–2 μm without any chemical additives. Zeolite filter media beds remove pathogens such as Giardia, Cryptosporidium, and other bacteria from their spores because most of these organisms are 0.5 – 10 microns(HUGHES, 1998; Kellam et al., 2018). Zeolite filters can triple the filtration rate without harmful effects. Natural zeolites have about 100 times the surface area of s. The combination of the physico-chemical durability of zeolite's fine particles and the capability for molecular sieving of contaminants makes zeolites a superb water filtration media, producing superior water quality to conventional s filters(Kazemian et al., 2012; McNair et al., 1987). The water samples treated with three zeolites were further processed for coagulation-flocculation using coagulants Alum, PACl, and Tanfloc through Jar test Apparatus. The addition of fine zeolite powders to water in the batch study increased water turbidity from about 50 NTU to 4000 NTU, depending on the amount of zeolites added. Thus, a high coagulant dem was required to clarify the water. The addition of high coagulants in the water led the water to increase total dissolved solids (TDS) residual coagulants. Therefore, natural Mordenite Clinoptilolite is excellent for removing ammonia from drinking water.

CHAPTER 8

CONCLUSIONS AND FUTURE SCOPE OF WORK

CHAPTER 8: CONCLUSIONs AND FUTURE SCOPE OF WORK

8.1 IMPORTANCE OF COW DUNG SLUDGE IN WATER TREATMENT TO COMBAT AMMONIA-NITROGEN

In this Thesis, the effects of cow-dung *Yucca* extract dosing on different parameters such as Ammonia, Nitrite, Nitrate, pH, Electrical Conductivity, and Total Dissolved Solids (TDS) have been studied. It is observed that both light temperatures have a significant role in the biological treatment of ammonia nitrogen. During the initial experimental studies, it was seen that, in the absence of light at low temperatures, the nitrite (intermediate product) could not be converted to nitrate substantially. In some cases, intense white light illuminated by LED bulbs resulted in algal growth. The development of algae in the samples hindered the conversion of nitrite into nitrate and increased the high pH to about ten; algae grew out into large masses. However, the total dissolved solids decreased substantially. The tungsten bulbs were found fit for illuminations, as they did not support the algal formation in the samples. The conversion of ammonia nitrogen into the stable nitrate form is a very typical mechanism. In general practice, the treated effluent's mechanical stirring oxidizes the ammonia nitrogen to nitrite in the presence of nitrifying bacteria and natural oxidation. But nitrite is also as harmful as ammonia in the production of disinfection by-products. In the present experimental study, the conversion of ammonia nitrogen into nitrite and nitrite into nitrate is simultaneous. However, the cow dung (digested) adds an insignificant amount of ammonia-nitrogen to the samples. This negligible amount has not been counted for the sake of convenience. The exact maximum amount of nitrite and nitrate formation has been analyzed.

8.2 PROPOSAL FOR BIOLOGICAL TERTIARY TREATMENT UNIT

Based on the current experimental studies, adding cow dung sludge and making a few additional modifications to the existing conventional sewage treatment plants' infrastructure can give better final effluent quality, free from ammonia-nitrogen and nitrite pollution. The proposed design of a modified sewage treatment plant working on the activated sludge process has been suggested in Figure 56, including tertiary treatment units. Here, Hydraulic Retention Time (HRT) in the Flocculator chamber with RPM 35 is eight days for the biological oxidation of ammonia nitrogen (NH_3-N into Nitrate (NO_3). Cowdung is abundantly available in India. Using cow dung as a bio-resource in wastewater treatment plants is safe and environmentally friendly because cow-dung cow-urine is used to treat several human diseases in Indian herbal natural treatment systems. Activated sludge from the final settling tank has to be taken to feed into the aeration tank. In addition, a temperature of 32 °C to 38 °C in the mesophilic range is optimum, as microbiological activities are more prominent at this range of temperatures. Cowdung has successfully proved to play an important role in wastewater treatment. Even cow-dung ash has been found to be active in water disinfection. The dried powder form of cow dung is also helpful as a green adsorbent material to remove carcinogenic heavy metal water pollutants. Cowdung and cow urine possess complex degrading substances.

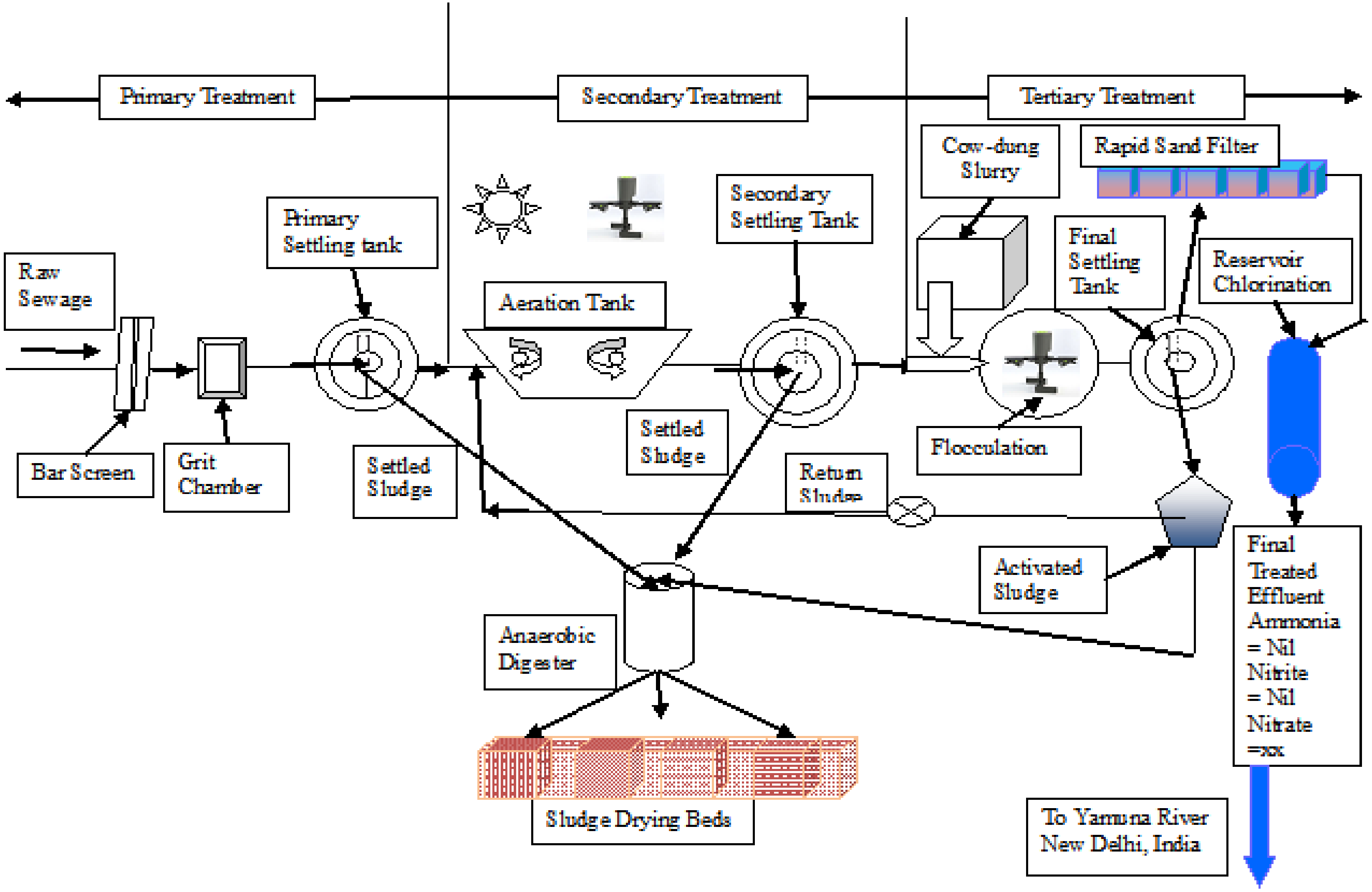


Figure 56:Proposed sewage treatment design for Activated Sludge Process with Tertiary Treatment Units

8.3 POTENTIAL USE OF ZEOLITES MEDIA IN WATER TREATMENT TO COMBAT AMMONIA-NITROGEN

The study of ammonia removal efficiencies using different zeolites, including Synthetic zeolites 4A, Clinoptilolite, and Mordenite, was investigated with low to high ammonia water. Mordenite and clinoptilolite were demonstrated to be the most efficient adsorbent for ammonia removal. The removal of ammonia by mordenite was faster than clinoptilolite and reached equilibrium in about 5 minutes at a pH lower than the pKa value of ammonia at room temperature. However, clinoptilolite was more efficient in ammonia removal in the long course of the contact period. Synthetic zeolites 4A also reduced the ammonia content, but it can not be helpful as it is not in the granular form that increased dissolved solids during treatment processes.

Chemical composition analyzed by X-Ray Fluorescence (XRF) for Synthetic zeolites 4A, Clinoptilolite zeolites, and Mordenite zeolites before and after the exhaust (use)indicates that the action of adsorption and desorption are highly active in the case of synthetic zeolite 4A. Experimental results with natural water (MTSE) showed that in treating wastewater with synthetic zeolites, 4A increases water's electrical conductivity, which means a fraction of zeolites get dissolved in the water. Synthetic zeolite has a high proportion of aluminium in its composition.

The analytical results report SiO_2 and Al_2O_3 contents as 47.20 % and 32.52 %, respectively. A high ratio of aluminium leads to its high electronegative nature. Thus, synthetic zeolite 4A is highly susceptible to pollutant removal in water because of its highly electronegative nature. This zeolite has been meant for the removal of hardness in water. It has reduced calcium and magnesium hardness significantly. In the pristine state, the initial amount of CaO (0.38 %) has increased substantially in an exhausted zeolite (CaO 2.69 %). Sodium content (Na_2O) from an initial 16.45 % has drastically decreased to 14.99 % in the depleted state, which means that counter-ions have replaced sodium ions. The analytical results of composition analysis prove that synthetic zeolite has a good affinity for the adsorption of other pollutants, too, in addition to hardness and ammonium ions (NH_4^+). The used synthetic zeolite has adsorbed a significant amount of chromium (from 3.7 ppm to 12.6 ppm), arsenic (0.0 ppm to 1.8 ppm), thallium (from 0.0 ppm to 1.5 ppm), iridium (from 0.8 ppm to 1.1 ppm), platinum (0.0 ppm to 0.5 ppm).

In the cases of natural zeolites, their structural bindings are more rigid compared to synthetic zeolites. Natural zeolites clinoptilolite and mordenite do not significantly change their composition concerning SiO_2 contents before or after use. However, Al_2O_3 content decreases slightly in the natural zeolites after being used in water treatment. The Al_2O_3 changed from 13.16% to 12.60% in the case of clinoptilolite and 14.09% to 13.73% in the case of mordenite. CaO content increased in used zeolites from 5.37% to 6.54% in the case of clinoptilolite but not in any significant reduction in the case of mordenite.

Phosphate (P_2O_5) copper (Cu) elements have been missed from the used clinoptilolite, indicating that phosphate copper ions have been released from the clinoptilolite structure into the water treated. In comparison, phosphate ions are rigid in the case of mordenite. An element, tellurium, is additionally observed in the analytical composition report of used mordenite zeolite, indicating that tellurium has been taken up from water onto the mordenite. Other elements like chloride and cesium have also changed their composition in a pristine and used state of zeolites. Overall, it is concluded that some compositional change in some aspects of zeolite composition occurs when they are used in water treatment.

8.4 PROPOSED WATER FILTERS USING NATURAL ZEOLITES

In this thesis, based on the experimental research studies, filter media of rapid and slow filter beds at waterworks sewage disposal works of public utilities are proposed to be replaced by natural zeolites media. A schematic Figure of the proposed slow/ rapid zeolites(clinoptilolite and mordenite) media filter bed is shown in Figure 57. Microbiological contamination can pass through a sand filter media when the coagulation-flocculation processes are not appropriately undertaken. But, natural zeolites have micro-pores in addition to sieve properties. This property of zeolites would help trap micro-organisms and micro-algae, inhibiting passing them through the filter media.

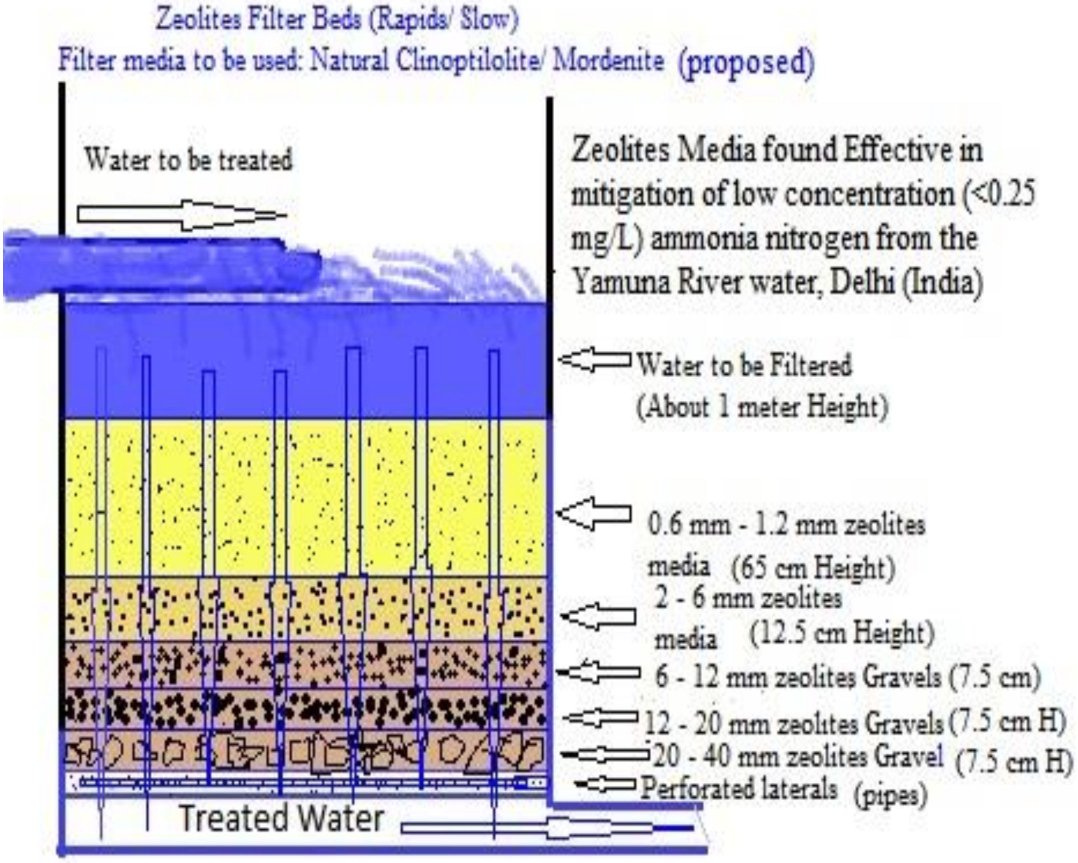


Figure 57: Proposed Water Filter Bed for Combating Ammonia-Nitrogen

Natural zeolite-based filters have a more significant surface area than synthetic ones, making it possible to remove particles as small as 2 to 3 microns, which results in apparent water. Zeolite filters are ten times more effective than sand filters and may capture particles as small as 30 microns. A zeolite-based filter has a larger loading capacity and can cut backwash time by up to 50%. When the annual filter beds are being cleaned, the upper removed zeolites might improve the agricultural soil quality. The Water (Prevention Control of Pollution) Act of 1974's sewage discharge standards has been modified by the Central Pollution Control Board (CPCB), a statutory agency of the Indian Government. A-10014/43/06-MON/709, dated April 21, 2015, contains further information about the 199th Board meeting on September 8, 2015. (Appendix 5).

The new standard for ammonia nitrogen in treated sewage has stipulated that it should be not more than five mg/L and that total nitrogen is not more than ten mg/L. Previously the standard values for ammonia nitrogen were limited to 50 mg/L of total nitrogen or Kjeldahl nitrogen to 100 mg/L. Based on the present research, cow-dung sludge is recommended to treat wastewater and sewage to combat ammonia-nitrogen and other hazardous pollutants. On the other side, in case of low ammonia nitrogen contamination in raw water, natural zeolites Clinoptilite Mordenite media filter beds are recommended to replace s media in rapid s filters for water treatment plants.

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LIST OF PUBLICATIONS AND PRESENTATIONS ARISING FROM THIS THESIS

(1) Lokesh Kumar, Raminder Kaur and Jai Gopal Sharma (**2018**), Water treatment for combating ammonia using Clinoptilolite Zeolite, proceeding of XII World Aqua Congress International Conference, Aqua Foundation, New Delhi, In Theme: Enhancing Water Use Efficiency, pp179-186

(2) Lokesh Kumar, Jai Gopal Sharma, Raminder Kaur (**2020**), "Water Scarcity, Trans-Boundary Water Unabated Water Pollution" proceedings of 'National Conference on Water Sustainability: Conservation, Policy, Ethics Science,' New Delhi, organized by Department of Environmental Studies and Srishti: Nature Environment Society Zakir Husain Delhi College (University of Delhi), pp 14-15

(3) Lokesh Kumar, Raminder Kaur, Jaigopal Sharma (**2021**), The efficiency of zeolites in water treatment for combating ammonia – An experimental study on Yamuna River water and treated sewage effluents, Journal of Inorganic ChemistryCommunications,www.elsevier.com/locate/inoche https://doi.org/10.1016/j.inoche.2021.108978

(4) Lokesh Kumar, JaigopalSharma, Raminder Kaur(2022), Catalytic Performance of Cow-Dung Sludge in WaterTreatment Mitigation Conversion of Ammonia Nitrogen into Nitrate, *Sustainability* **2022**, *14*, 2183. https://doi.org/10.3390/su14042183

Oral Presentations

- Lokesh Kumar, Raminder Kaur, Jai Gopal Sharma (**2018**). "Water treatment for combating ammonia using *Yucca schidigera* extract" at International Conference on Water from Pollution to Purification, MahatamaGhi University, Kottayam, Kerala, India.

- Lokesh Kumar, Jai Gopal Sharma, Raminder Kaur (**2019**), Water Scarcity, Trans-Boundary Water Unabated Water Pollution" at 1st WASAG International Forum on Water Scarcity in Agriculture Celebrating World Water Day, 19-22 March 2019, Praia, Cape Verde, West Africa.

- Lokesh Kumar, Jai Gopal Sharma, Raminder Kaur(**2020**), Water Scarcity, Trans-Boundary Water Unabated Water Pollution" at National conference on Water Sustainability: Conservation, Policy, Ethics Science, 21st – 22nd January 2020, New Delhi, India.

- Lokesh Kumar, Raminder Kaur, Jai Gopal Sharma (**2020**), Ammonia Nitrogen Removal from Wastewater at Technical Education Quality Improvement Programme on Green Chemistry, 25-29 February 2020, MahatamaJyotiba Phule Rohilkh University, Bareilly, U.P., India.

- Lokesh Kumar, Raminder Kaur, Jai Gopal Sharma (**2021**). Presented innovative work in the 15th I.H.E. Ph.D. Symposium 2021 hosted online by IHE Delft Institute for Water Education in partnership with UNESCO, held from 14th to 15th of October 2021.

Poster Presentations

- Lokesh Kumar, Raminder Kaur, Jai Gopal Sharma (**2018**), Potential Applications of Cow-Dung in Biological Treatment of Wastewater for Combating Ammonia Nitrogen, at National Workshop on Thieme Chemistry: Science of Synthesis", September 28, 2018, University of Delhi, India.

- Lokesh Kumar, Raminder Kaur, Jai Gopal Sharma (**2019**), Sewage Treatment by Clinoptilolite zeolites its Applications, in Agriculture, at XIV AGRICULTURAL SCIENCE CONGRESS on 'Innovations for Agricultural Transformation, 20-23rd February 2019, National Agricultural Science Complex, New Delhi, India

APPENDIXES

Appendix 1

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To: Lokesh Kumar, Delhi Technological University

From: Alyse Greenberg

Date: October 11, 2019

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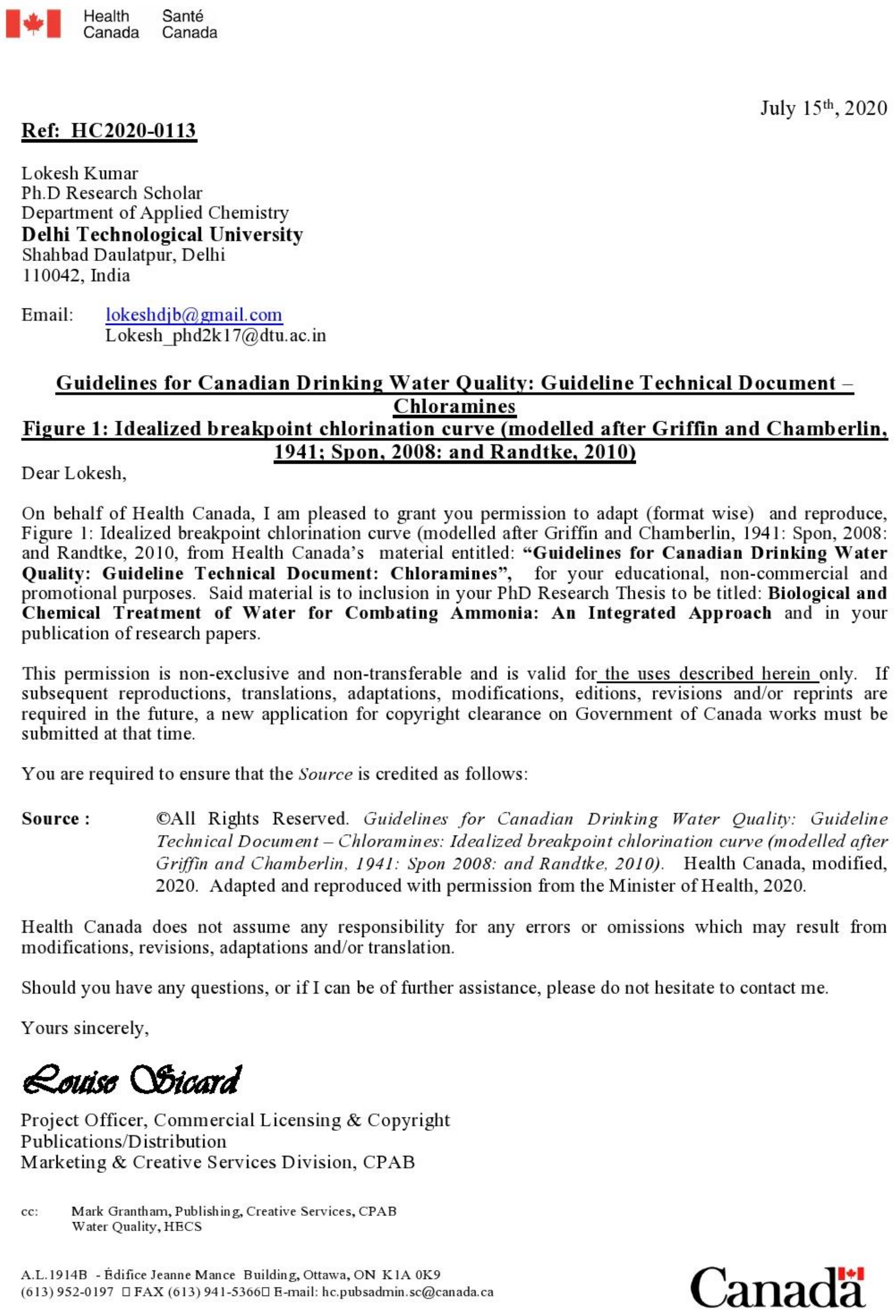
Appendix 2



Health Canada Santé Canada

July 15th, 2020

Ref: HC2020-0113

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Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Chloramines
Figure 1: Idealized breakpoint chlorination curve (modelled after Griffin and Chamberlin, 1941; Spon, 2008: and Randtke, 2010)

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Appendix 3

Mean, Standard Deviation, and Standard Error of Mean of Ammonia, Nitrite, and Nitrate Values determined with triplicate samples using cow-dung

Time in Hours	Ammonia (R1)	Ammonia (R2)	Ammonia (R3)	Mean Value	S.D.	SEM Control
48	23.21	24.09	22.08	23.1266667	1.0076	0.58
96	2.04	3.09	1.98	2.37	0.6243	0.36
144	0.032	0.028	0.029	0.02966667	0.0021	0.0012
192	0	0	0	0	0	0

Time in Hours	Ammonia (R1)	Ammonia (R2)	Ammonia (R3)	Mean Value	S.D.	SEM with 1g CD
48	22.59	21.98	23	22.5233333	0.5133	0.296
96	0.96	1.02	0.9	0.93	0.0424	0.024
144	0	0	0	0	0	0
192	0	0	0	0	0	0

Time in Hours	Ammonia (R1)	Ammonia (R2)	Ammonia (R3)	Mean Value	S.D.	SEM with 5g CD
48	18.59	19.09	18.98	18.8866667	0.2627	0.151
96	1.39	1.29	1.42	1.36666667	0.0681	0.039
144	0	0	0	0	0	0
192	0	0	0	0	0	0

Time in Hours	Ammonia (R1)	Ammonia (R2)	Ammonia (R3)	Mean Value	S.D.	SEM with 10 mg YE
48	23.585	24	23.98	23.855	0.234	0.135
96	2.735	2.9	2.53	2.72166667	0.1854	0.107
144	0.036	0.029	0.039	0.03466667	0.0051	0.0029
192	0	0	0	0	0	0

Time in Hours	Ammonia (R1)	Ammonia (R2)	Ammonia (R3)	Mean Value	S.D.	SEM with 50 mg YE
48	24.705	23.09	24.92	24.2383333	1.0003	0.579
96	7.135	7.298	7.0921	7.17503333	0.1086	0.062
144	0.154	0.168	0.148	0.15666667	0.0103	.0059
192	0.88	1.02	0.7	0.86666667	0.1604	0.092

Time in Hours	Nitrite (R1)	Nitrite (R2)	Nitrite (R3)	Mean Value	S.D.	SEM Control
48	0.21	0.198	0.226	0.21133333	0.014	.008
96	11.7	10.98	11.5	11.5	0.3717	0.214
144	14.7	15.03	14.09	14.6066667	0.4769	0.275
192	17.8	17.09	18.098	18.098	0.5178	0.298

Time in Hours	Nitrite (R1)	Nitrite (R2)	Nitrite (R3)	Mean Value	S.D.	SEM with 1g CD
48	2.88	3	2.69	2.85666667	0.1563	0.09
96	16.15	16.35	15.98	16.16	0.1852	0.107
144	8.8	8.93	8.74	8.82333333	0.0971	0.056
192	0.18	0.2	0.16	0.18	0.02	0.011

Time in Hours	Nitrite (R1)	Nitrite (R2)	Nitrite (R3)	Mean Value	S.D.	SEM with 5g CD
48	3.265	3.198	3.2	3.221	0.0381	0.021
96	11.45	11.98	11.02	11.4833333	0.4809	0.277
144	0.3	0.32	0.29	0.30333333	0.0153	0.009
192	0.09	0.12	0.082	0.09733333	0.02	0.011

Time in Hours	Nitrite (R1)	Nitrite (R2)	Nitrite (R3)	Mean Value	S.D.	SEM with 10 mg YE
48	0.545	0.0575	0.49	0.36416667	0.267	0.154
96	13.525	13.038	13.45	13.3376667	0.2622	0.15
144	15.525	15.45	14.98	15.3183333	0.2954	0.17

192	18.65	18.23	17.98	18.2866667	0.3386	0.195

Time in Hours	Nitrite (R1)	Nitrite (R2)	Nitrite (R3)	Mean Value	S.D.	SEM with 50 mg YE
48	0.575	0.548	0.509	0.544	0.0332	0.019
96	9.6	9.8	9.42	9.60666667	0.1901	0.109
144	14.375	14.298	14.56	14.411	0.1347	0.078
192	18.85	18.65	18.98	18.8266667	0.1662	0.095

Time in Hours	Nitrate (R1)	Nitrate (R2)	Nitrate (R3)	Mean Value	S.D.	SEM Control
48	2.25	2.09	2.35	2.23	0.1311488	0.075
96	12.9	13.45	12.73	13.0266667	0.376342	0.217
144	16.6	16.09	17.75	16.8133333	0.8503137	0.49
192	17.8	17.02	18.23	17.6833333	0.6133786	0.354

Time in Hours	Nitrate (R1)	Nitrate (R2)	Nitrate (R3)	Mean Value	S.D.	SEM with 1g CD
48	3.8	3.89	3.72	3.80333333	0.085049	0.05
96	22.25	22.84	22.09	22.3933333	0.3950105	0.23
144	67.3	66.98	67.44	67.24	0.2357965	0.136
192	0.18	0.17	0.178	0.176	0.0052915	0.003

Time in Hours	Nitrate (R1)	Nitrate (R2)	Nitrate (R3)	Mean Value	S.D.	SEM with 5g CD
48	11.7	11.29	11.89	11.6266667	0.3066486	0.177
96	59.3	60.32	58.95	59.5233333	0.7117818	0.411
144	109	109.9	108.8	109.233333	0.5859465	0.338
192	0.09	0.096	0.088	0.09133333	0.0041633	0.0023

Time in Hours	Nitrate (R1)	Nitrate (R2)	Nitrate (R3)	Mean Value	S.D.	SEM with 10 mg YE

48	1.6	1.69	1.58	1.62333333	0.0585947	0.034
96	11.75	11.62	11.9	11.7566667	0.140119	0.080
144	17.8	17.79	17.95	17.8466667	0.0896289	0.051
192	18.65	18.23	18.98	18.62	0.3758989	0.217

Time in Hours	Nitrate (R1)	Nitrate (R2)	Nitrate (R3)	Mean Value	S.D.	SEM with 50 mg YE
48	2.35	2.42	2.29	2.35333333	0.0650641	0.037
96	8.05	8.13	7.95	8.04333333	0.090185	0.052
144	17	17.24	16.95	17.0633333	0.1550269	0.089
192	18.85	17.98	18.25	18.36	0.4453089	0.257

Appendix 4

Uptake and Sorption of Ammonia Nitrogen with Zeolites

Experiment performed on synthetically prepared Ammonium Chloride water in Distilled Water RPM of Jar Test Apparatus: 100; Room Temperature: 3 - 15 °C; Zeolites Used: Synthetic Zeolite 4A

Particulars Synthetically prepared Ammonia Water In Distilled Water	Ammonia Nitrogen After 05 Min				Ammonia Nitrogen After 30Min				Ammonia Nitrogen After 01 Hour				Ammonia Nitrogen After 4 Hours			
	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)
SW1 (5 PPM) +1g/L SZ 4A	**2.74**	**2.81**	**43.8**	**2.09**	**1.99**	**2.00**	**60**	**3.0**	**1.65**	**1.74**	**65.2**	**3.26**	**1.08**	**1.14**	**77.2**	**3.86**
	2.90				**1.98**				**1.85**				**1.22**			
	2.80				**2.05**				**1.72**				**1.13**			
SW2 (10PPM) +1g/L SZ 4A	**5.20**	**5.2**	**48.1**	**4.8**	**4.80**	**4.92**	**50.8**	**5.08**	**4.70**	**4.56**	**54.4**	**5.44**	**3.40**	**3.40**	**66**	**6.6**
	5.30				**5.00**				**4.48**				**3.27**			
	5.10				**4.90**				**4.50**				**3.45**			
SW3 (15 PPM) +1g/L SZ 4A	**8.53**	**8.35**	**44.33**	**6.65**	**7.42**	**7.44**	**50.4**	**7.56**	**7.31**	**7.21**	**51.93**	**7.79**	**6.57**	**6.58**	**56.13**	**8.42**
	8.13				**7.35**				**7.22**				**6.68**			
	8.40				**7.56**				**7.10**				**6.50**			
SW4 (20PPM) +1g/L SZ 4A	**11.53**	**11.51**	**42.45**	**8.49**	**10.66**	**10.63**	**46.85**	**7.37**	**9.28**	**9.27**	**53.65**	**10.73**	**9.16**	**9.12**	**54.4**	**10.88**
	11.62				**10.50**				**9.36**				**9.00**			
	11.40				**10.75**				**9.18**				**9.20**			
SW5 (30PPM) +1g/L SZ 4A	**16.56**	**16.68**	**44.4**	**13.32**	**16.52**	**16.58**	**44.73**	**13.42**	**14.50**	**14.40**	**52.0**	**15.6**	**14.70**	**14.51**	**51.63**	**15.49**
	16.70				**16.67**				**14.32**				**14.34**			
	16.80				**16.56**				**14.40**				**14.50**			

Particulars Synthetically prepared Ammonia Water In Distilled Water	Ammonia Nitrogen After 12 Hour				Ammonia Nitrogen After 16 Hour				Ammonia Nitrogen After 20 Hour				Ammonia Nitrogen After 24 Hours			
	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)
SW1 (5 PPM) +1g/L SZ 4A	**0.86**	**0.85**	**83.0**	**4.15**	**0.71**	**0.72**	**85.6**	**4.28**	**0.79**	**0.77**	**84.6**	**4.23**	**0.84**	**0.79**	**84.2**	**4.21**
	0.89				**0.75**				**0.80**				**0.75**			
	0.82				**0.70**				**0.72**				**0.80**			
SW2 (10PPM) +1g/L SZ 4A	**2.29**	**2.39**	**76.1**	**7.61**	**2.48**	**2.4**	**76.0**	**7.6**	**2.52**	**2.42**	**75.8**	**7.58**	**2.20**	**2.32**	**76.8**	**7.68**
	2.50				**2.46**				**2.40**				**2.40**			
	2.38				**2.26**				**2.35**				**2.36**			
SW3 (15 PPM) +1g/L SZ 4A	**5.54**	**5.39**	**64.54**	**9.61**	**5.52**	**5.40**	**64.0**	**9.6**	**5.42**	**5.42**	**63.86**	**9.58**	**5.38**	**5.43**	**63.8**	**9.57**
	5.28				**5.40**				**5.47**				**5.52**			
	5.35				**5.30**				**5.38**				**5.40**			
SW4 (20PPM) +1g/L SZ 4A	**8.72**	**8.58**	**57.1**	**11.42**	**8.47**	**8.41**	**57.95**	**11.59**	**8.23**	**8.19**	**59.05**	**11.81**	**8.30**	**8.24**	**58.8**	**11.76**
	8.44				**8.36**				**8.14**				**8.24**			
	8.60				**8.40**				**8.20**				**8.19**			
SW5 (30PPM) +1g/L SZ 4A	**14.57**	**14.65**	**51.16**	**15.35**	**14.38**	**14.56**	**51.46**	**15.44**	**14.57**	**14.66**	**51.13**	**15.34**	**14.60**	**14.71**	**50.96**	**15.29**
	14.80				**14.80**				**14.92**				**14.80**			
	14.60				**14.50**				**14.50**				**14.75**			

Abbreviations:

Min = Minutes ; Red.= Reduction; Res.= Residual Ammonia; Mg/L= Milligram per Liter; %age= Percentage Reduction; SW= Synthetic Water of Ammonium Chloride Prepared with Distilled Water; SZ 4A= Synthetic Zeolite 4A

Experiment performed on synthetically prepared Ammonium Chloride water in Distilled Water RPM of Jar Test Apparatus: 100; Room Temperature: 3 - 15 °C; Zeolites Used: Natural Zeolites Clinoptilolite of Rota Mining

Particulars Synthetically prepared Ammonia Water In Distilled Water	Ammonia Nitrogen After 05 Min				Ammonia Nitrogen After 30 Min				Ammonia Nitrogen After 01 Hour				Ammonia Nitrogen After 04 Hours			
	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)
SW1 (2 PPM) +1g/L NZ-RM	0.29	0.27	86.5	1.73	0.10	0.120	94.0	1.88	ND	0.00	100.0	2.0	ND	0.00	100.0	2.0
	0.23				0.15				ND				ND			
	0.30				0.12				ND				ND			
SW1 (5 PPM) +1g/L NZ-RM	2.29	2.40	52.0	2.6	2.00	2.0	60.0	3.0	1.60	1.61	67.8	3.39	1.50	1.58	68.4	3.42
	2.42				1.90				1.64				1.56			
	2.50				2.10				1.59				1.68			
SW2 (10PPM) +1g/L NZ-RM	4.45	4.48	55.2	5.52	4.18	4.32	56.8	5.56	4.15	4.14	58.6	5.86	4.18	4.18	58.2	5.82
	4.50				4.50				4.18				4.20			
	4.50				4.28				4.10				4.16			
SW3 (15 PPM) +1g/L NZ-RM	10.40	10.32	31.2	4.68	10.30	10.33	31.13	4.67	9.21	9.28	38.13	5.72	8.53	8.57	42.86	6.43
	10.26				10.40				9.34				8.58			
	10.31				10.30				9.30				8.62			
SW4 (20PPM) +1g/L NZ-RM	13.93	14.05	29.75	5.95	13.75	13.79	31.05	6.21	13.62	13.63	31.55	6.31	12.53	12.38	38.1	7.62
	14.03				13.75				13.59				12.28			
	14.20				13.89				13.70				12.34			
SW5 (30PPM) +1g/L NZ-RM	21.00	21.06	29.8	8.94	20.35	20.48	31.73	9.52	19.90	19.99	33.36	10.01	19.45	19.55	34.73	10.42
	21.08				20.50				20.00				19.60			
	21.12				20.60				20.09				19.60			

Particulars Synthetically prepared Ammonia Water In Distilled Water	Ammonia Nitrogen After 12 Hours				Ammonia Nitrogen After 16 Hours				Ammonia Nitrogen After 20 Hour				Ammonia Nitrogen After 24 Hours			
	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)
SW1 (2 PPM) +1g/L NZ-RM	**ND**	**0.00**	**100.0**	**2.0**	**ND**	**0.00**	**100.0**	**2.0**	**ND**	**0.00**	**100.0**	**2.0**	**ND**	**0.00**	100.0	2.0
	ND				**ND**				**ND**				**ND**			
	ND				**ND**				**ND**				**ND**			
SW1 (5 PPM) +1g/L NZ-RM	**1.49**	**1.49**	**70.2**	**3.51**	**1.35**	**1.40**	**72.0**	**3.6**	**1.12**	**1.13**	**77.4**	**3.8**	**1.20**	**1.18**	**76.4**	**3.82**
	1.51				**1.40**				**1.15**				**1.16**			
	1.48				**1.45**				**1.14**				**1.18**			
SW2 (10PPM) +1g/L NZ-RM	**5.92**	**5.86**	**41.4**	**4.14**	**5.79**	**5.66**	**43.4**	**4.34**	**5.40**	**5.31**	**46.9**	**4.69**	**4.90**	**4.97**	**50.3**	**5.03**
	5.08				**5.65**				**5.25**				**4.98**			
	6.00				**5.55**				**5.30**				**5.03**			
SW3 (15 PPM) +1g/L NZ-RM	**8.52**	**8.43**	**43.8**	**6.57**	**8.09**	**8.13**	**45.8**	**6.87**	**8.00**	**8.03**	**46.46**	**6.97**	**7.90**	**7.91**	**47.26**	**7.09**
	8.31				**8.18**				**8.08**				**8.00**			
	8.48				**8.12**				**8.03**				**7.84**			
SW4 (20PPM) +1g/L NZ-RM	**12.54**	**12.46**	**37.7**	**7.54**	**12.40**	**12.35**	**38.25**	**7.65**	**12.24**	**12.24**	**38.8**	**7.76**	**12.20**	**12.26**	**38.7**	**7.74**
	12.26				**12.30**				**12.29**				**12.29**			
	12.60				**12.35**				**12.20**				**12.30**			
SW5 (30PPM) +1g/L NZ-RM	**19.46**	**19.50**	**35.0**	**10.5**	**19.30**	**19.29**	**35.7**	**10.71**	**19.08**	**19.16**	**36.13**	**10.84**	**19.00**	**19.08**	**36.4**	**10.92**
	19.46				**19.28**				**19.20**				**19.08**			
	19.58				**19.29**				**19.20**				**19.18**			

Abbreviatios:
Min = Minutes ; Red.= Reduction; Res.= Residual Ammonia; Mg/L= Milligram per Liter; %age= Percentage Reduction; SW= Synthetic Water of Ammonium Chloride Prepared with Distilled Water

Experiment performed on synthetically prepared Ammonium Chloride water in Distilled Water RPM of Jar Test Apparatus: 100; Room Temperature: 3 - 15 °C; Zeolites Used: Natural Zeolites (Mordenite) of Blue Pacific

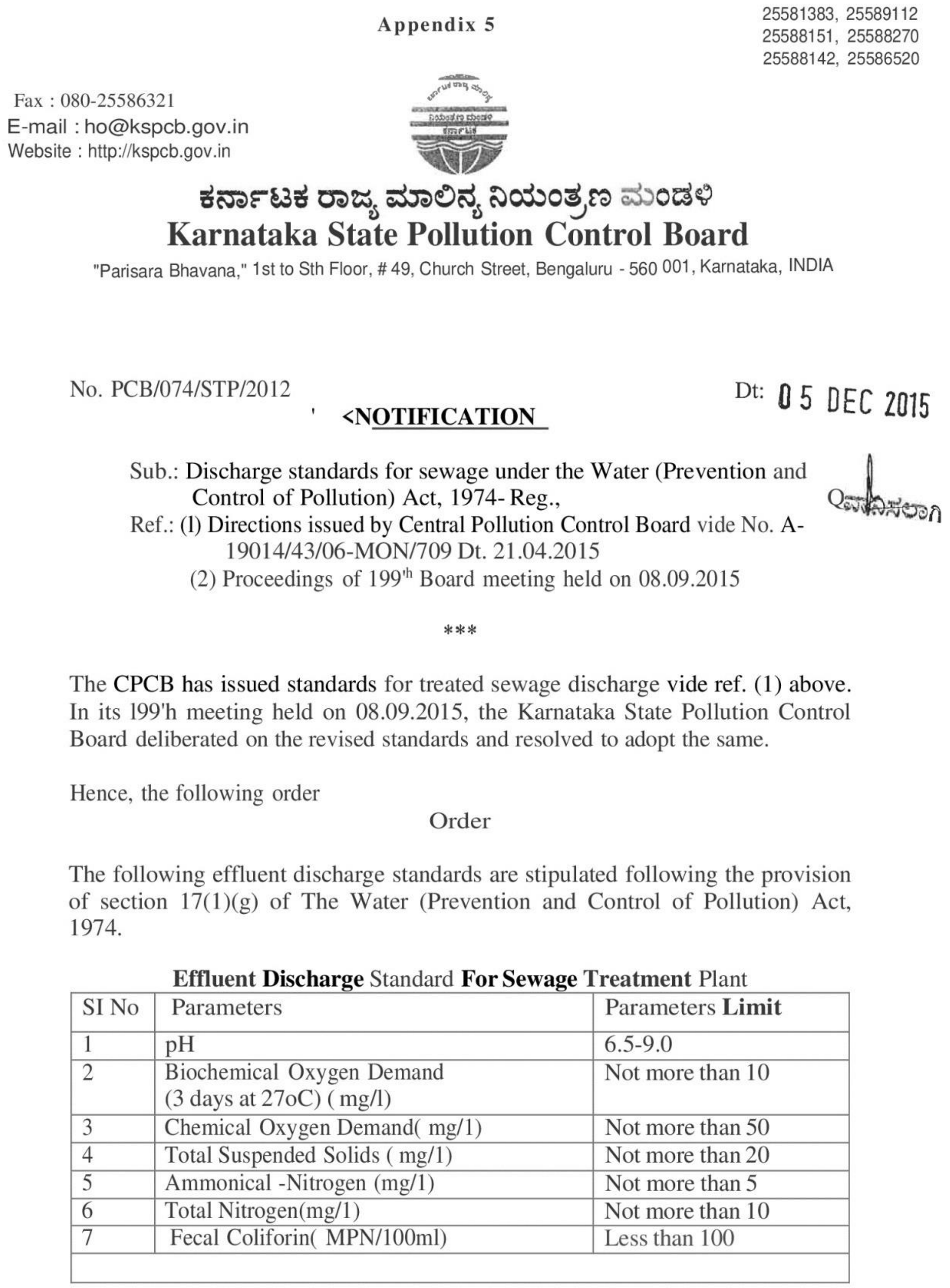
Particulars Synthetically prepared Ammonia Water In Distilled Water	Ammonia Nitrogen After 05 Min				Ammonia Nitrogen After 30Min				Ammonia Nitrogen After 01 Hour				Ammonia Nitrogen After 4 Hours			
	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)
SW1 (2 PPM) +1g/L NZ-BP	**1.05**	**1.07**	**46.5**	**0.93**	**0.70**	**0.60**	**70.0**	**1.40**	**0.15**	**0.12**	**94.0**	**1.88**	**ND**	**0.00**	100.0	2.0
	1.08				**0.50**				**0.10**				**ND**			
	1.10				**0.60**				**0.12**				**ND**			
SW1 (5 PPM) +1g/L NZ-BP	**2.45**	**2.48**	**50.4**	**2.52**	**1098**	**2.02**	**59.6**	**2.98**	**0.86**	**0.96**	**80.8**	**4.04**	**0.68**	**0.73**	**85.4**	**4.27**
	2.50				**2.00**				**0.98**				**0.72**			
	2.51				**2.08**				**1.05**				**0.80**			
SW2 (10PPM) +1g/L NZ-BP	**5.52**	**5.63**	**43.7**	**4.37**	**5.60**	**5.46**	**45.4**	**4.54**	**5.25**	**5.31**	**46.9**	**4.69**	**4.84**	**5.01**	**49.9**	**4.99**
	5.60				**5.40**				**5.35**				**5.00**			
	5.78				**5.38**				**5.35**				**5.19**			
SW3 (15 PPM) +1g/L NZ-BP	**10.5**	**10.46**	**30.27**	**4.54**	**10.2**	**10.56**	**29.6**	**4.44**	**9.00**	**8.94**	**40.4**	**6.06**	**8.5**	**8.53**	**43.13**	**6.47**
	10.5				**10.5**				**9.03**				**8.5**			
	10.4				**11.0**				**8.80**				**8.6**			
SW4 (20PPM) +1g/L NZ-BP	**13.10**	**13.47**	**32.65**	**6.53**	**12.50**	**12.56**	**37.2**	**7.44**	**12.00**	**12.30**	**38.5**	**7.7**	**11.98**	**11.66**	**41.7**	**8.34**
	13.52				**12.60**				**12.40**				**11.60**			
	13.81				**12.60**				**12.50**				**11.40**			
SW5 (30PPM) +1g/L NZ-BP	**21.60**	**21.78**	**27.4**	**8.22**	**21.60**	**22.00**	**26.67**	**8.00**	**21.50**	**21.56**	**28.13**	**8.44**	**21.25**	**20.71**	**30.96**	**9.29**
	21.74				**22.00**				**21.60**				**20.20**			

Particulars Synthetically prepared Ammonia Water In Distilled Water	Ammonia Nitrogen After 12 Hours				Ammonia Nitrogen After 16Hours				Ammonia Nitrogen After 20 Hour				Ammonia Nitrogen After 24 Hours			
	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)	Residual Ammonia (mg/L)	Average (mg/L)	Uptake (%)	Sorption (mg/g)
SW1 (2 PPM) +1g/L NZ-BP	**ND**	**0.00**	**100.0**	**2.0**	**ND**	**0.00**	**100.0**	**2.0**	**ND**	**0.00**	**100.0**	**2.0**	**ND**	**0.00**	**100.0**	**2.0**
	ND				**ND**				**ND**				**ND**			
	ND				**ND**				**ND**				**ND**			
SW1 (5 PPM) +1g/L NZ-BP	**0.42**	**0.46**	**90.8**	**4.54**	**0.52**	**0.59**	**88.2**	**4.41**	**0.42**	**0.45**	**91.0**	**4.55**	**0.39**	**0.44**	**91.2**	**4.56**
	0.48				**0.56**				**0.49**				**0.46**			
	0.50				**0.60**				**0.46**				**0.47**			
SW2 (10PPM) +1g/L NZ-BP	**4.80**	**4.99**	**50.1**	**5.01**	**4.9**	**5.03**	**49.7**	**7.97**	**4.60**	**4.76**	**52.4**	**5.24**	**4.8**	**4.76**	**52.4**	**5.24**
	5.00				**5.0**				**4.80**				**4.6**			
	5.19				**5.2**				**4.90**				**4.9**			
SW3 (15 PPM) +1g/L NZ-BP	**8.49**	**8.55**	**43.0**	**6.45**	**7.88**	**7.74**	**48.4**	**7.26**	**7.61**	**7.81**	**47.93**	**7.19**	**7.52**	**7.8**	**48.0**	**7.2**
	8.52				**7.65**				**7.94**				**7.88**			
	8.66				**7.69**				**7.88**				**8.00**			
SW4 (20PPM) +1g/L NZ-BP	**11.20**	**11.66**	**41.7**	**8.34**	**11.0**	**11.33**	**43.35**	**8.67**	**10.98**	**11.06**	**44.7**	**8.94**	**11.89**	**11.71**	**41.45**	**8.29**
	11.80				**11.50**				**11.20**				**11.50**			
	11.98				**11.50**				**11.00**				**11.75**			
SW5 (30PPM) +1g/L NZ-BP	**20.81**	**20.41**	**31.96**	**9.59**	**20.13**	**20.31**	**32.3**	**9.69**	**20.00**	**20.34**	**32.2**	**9.66**	**19.91**	**20.15**	**32.83**	**9.85**
	20.20				**20.40**				**20.35**				**20.05**			
	20.24				**20.00**				**20.19**				**20.50**			

Abbreviations:

Min = Minutes ; Red.= Reduction; Res.= Residual Ammonia; Mg/L= Milligram per Liter; %age= Percentage Reduction; SW= Synthetic Water of Ammonium Chloride Prepared with Distilled Water

Appendix 5



Appendix 5

25581383, 25589112
25588151, 25588270
25588142, 25586520

Fax : 080-25586321
E-mail : ho@kspcb.gov.in
Website : http://kspcb.gov.in

ಕರ್ನಾಟಕ ರಾಜ್ಯ ಮಾಲಿನ್ಯ ನಿಯಂತ್ರಣ ಮಂಡಳಿ
Karnataka State Pollution Control Board
"Parisara Bhavana," 1st to 5th Floor, # 49, Church Street, Bengaluru - 560 001, Karnataka, INDIA

No. PCB/074/STP/2012 Dt: 05 DEC 2015

<NOTIFICATION

Sub.: Discharge standards for sewage under the Water (Prevention and Control of Pollution) Act, 1974- Reg.,

Ref.: (1) Directions issued by Central Pollution Control Board vide No. A-19014/43/06-MON/709 Dt. 21.04.2015
(2) Proceedings of 199th Board meeting held on 08.09.2015

***

The CPCB has issued standards for treated sewage discharge vide ref. (1) above. In its 199'h meeting held on 08.09.2015, the Karnataka State Pollution Control Board deliberated on the revised standards and resolved to adopt the same.

Hence, the following order

Order

The following effluent discharge standards are stipulated following the provision of section 17(1)(g) of The Water (Prevention and Control of Pollution) Act, 1974.

Effluent Discharge Standard **For Sewage Treatment** Plant

SI No	Parameters	Parameters **Limit**
1	pH	6.5-9.0
2	Biochemical Oxygen Demand (3 days at 27oC) (mg/l)	Not more than 10
3	Chemical Oxygen Demand(mg/1)	Not more than 50
4	Total Suspended Solids (mg/1)	Not more than 20
5	Ammonical -Nitrogen (mg/1)	Not more than 5
6	Total Nitrogen(mg/1)	Not more than 10
7	Fecal Coliforin(MPN/100ml)	Less than 100

Note:

(i) The above standards are applicable for the new STPs to be established / proposed with immediate effect. For existing STPs, to the above standard shall be achieved by necessary up-gradation of the system within two years from the date of issue of directions by CPCB.

(ii)These standards are applicable for the Sewage treated for the STPs established by local bodies, industries, commercial establishments, apartments, residential layout, townships, CETPs treating only sewage

(iii) Secondary treated sewage should be mandatorily sold for use for non-potable purpose such as industrial process, railway & bus cleaning, flushing of toilets through dual piping, horticulture and irrigation. No potable water to be allowed for such activities.

(iv) The STP owners will also digest methane for captive power generation to further improve viability of STPs and to reduce green house gas emissions.

(v) Dual piping system should be followed in new housing constructions for use of treated sewage for flushing purpose and washing.

This notification supersedes the earlier notices concerning sewagedischarge standards

sd/-
MEMBER SECRETARY

To,

(1) Secretary to Government,
Urban Development Department,
Room No.434, Vikasa Soudha, Bengaluru - 560001.

(2) Director,
Directorate of Municipal Administration,
9th floor & 10th floor, VIshveshwariah Tower,
Dr. B.R. Ambedkar Veedhi, Bengaluru - 560001.

(3) Managing Director
Karnataka Water Supply and Drainage Board
#6, Jalabhavan 1st Stage,
1st Phase, BTM Layout,
Bannerghatta Road,
Bangalore - 560 029.

(4) Managing Director
Karnataka Urban Infrastructure Development Finance Corporation
2nd Floor, Unity Building, Silver Jubilee Park Road,
3rd Cross, Mission Road, Bangalore- 560027

(5) Chairman
Bengaluru Water Supply and Sewerage Board
Cauvery Bhavan, K.G. Road
Bengaluru

Copy Submitted to :

Secretary Department of Ecology and Environment, Bengaluru for information with a request to call for the meeting of concerned departments about this matter.

Copy to :

(1) CEO 1, CEO2, CEO3 KSPCB
(2)All RSEOs for information and necessary action
(3)All ROs for information and issue new standards to all local bodies

SENIOR ENVIRONMENTAL OFFICER (WMC)

CURRICULUM VITAE

Name: LOKESH KUMAR

Date of Birth: 9th May 1970

Residence: Delhi, India

Job Profile: I have been working in Municipal Water Supply and Sewage Disposal Undertaking, Delhi, since 1997. I am a Laboratory Chemist presently posted at a Sewage Disposal Works. I have been entrusted the job of water, wastewater, and sewage effluents analytical testing and treating water and wastewaters with biological and chemical methods.

ACADEMIC QUALIFICATIONS:

S. No.	Degree	Division	Subjects	University/Institute	Year
1.	M.Sc. Chemistry (AIC)	56 %	Analysis of Water & Sewage; Analysis of Oils, Fats & Soaps	Institution of Chemists (India)	2002
2.	B.Sc. (General)	43 %	Physics, Chemistry, & Mathematics	University of Delhi	1991
3.	Senior Secondary (10+2)	65 %	Physics, Chemistry, & Mathematics	Central Board of Secondary Education, Delhi	1987
4.	Secondary School (10th)	46 %	General Sciences, English, Hindi, Social Sciences	Central Board of Secondary Education, Delhi	1985

Membership in scientific organizations:

1. Fellow, Indian Water Works Association, Head Office: Mumbai, India (#.LF 1173)
2. Fellow, Institution of Chemists (India), Kolkata (#LF267(4)/5207)
3. Member, Royal Society of Chemistry, Cambridge, U.K. (#515940)
4. Member, Indian Science Congress Association, Head Office: Kolkata, India [#.L18289]
5. Member, World Water Council, New Delhi Centre (# 078/11/2013/Life Member)
6. Awarded status of 'Chartered Chemist' by Institution of Chemists (India) on 5th Feb. 2016
7. Member, International Water Association, London, United Kingdom(#1612505)
8. Member, American Water Works Association, Denver, CO 80235 USA (#00924035)
9. Member, Water Environment Federation, Alexandria, VA, United States; (#18028966)
10. Member, Federal Water Quality Association, Washington, DC; (#18028966)