STUDY OF
PHARMACEUTICAL LIQUID WASTE

A Project Report
By
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ABSTRACT

Pharmaceutical industries are now increasing in Bangladesh along with other industries. The liquid wastes of those industries are discharged to nearby natural stream, surface drain, lowland or ditch. The effluents contain some pollution parameters such as pH, ammonia nitrogen, suspended solids, total solids, colour etc. But there is no proper treatment method for safe disposal. As a result this causes death of aquatic life and pollution effect on plants, animals and human.

Beximco Pharma, one of the largest Pharmaceutical industries in Bangladesh produces various type of products from different plants. Among them Basic Raw Materials Plant discharges the liquid waste which contain severe pollution load, such as low pH, high ammonia nitrogen content, higher amount of total solids and colour. Plant authority follow a complicated, lengthy and costly treatment method which controls only pH. Concentration of ammonia nitrogen in the existing treated sewage is very high. Total solids and colour are also increased after existing treatment system.

All possible methods to reduce ammonia nitrogen are applied in laboratory. The methods are aeration, sedimentation with coagulation, chlorination and biological nitrification (dropping waterhyacinth and adding domestic sewage).But obtained no fruitful result. Because there may be some chemicals (which is used in production process) in waste which are not known to us may bound ammonia or nitrogen in

complicated form. Beximco Pharma did not leak out the name of chemical due to their business secret. Overall it is found that 1000 times dilution of waste would be the safe disposal of waste for aquatic life.

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TERMINOLOGY AND SYMBOLS

BOD = Biochemical Oxygen Demand, mg/l

COD = Chemical Oxygen Demand, mg/l

DO = Dissolved Oxygen, mg/l

EC = Electrical Conductivity, micro mho/cm

SS = Suspended Solid, mg/l

WHO = World Health Organisation

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Like many other industrial waste pharmaceutical waste contains pollution parameters such as low or high pH, high colour, high turbidity, high ammonia nitrogen, high total solids, low dissolve oxygen, heavy metals. Total number of industries in Bangladesh is now increasing. And Pharmaceutical industries are also increasing. In these industries wastes are discharged on the low land or into the natural stream. Discharging the waste into the stream may cause the damage of aquatic life and microorganism and affect the biological treatment. Dumping into a ditch or on land may cause objectionable odour. The sludge removed on land may decrease the fertility of land. So a careful study of pharmaceutical liquid waste regarding characterization, treatment and effects should be needed.

Beximco Pharma is one of the largest pharmaceutical industries in Bangladesh. In this study attempts have been taken to analyze and treat effluent of Beximco Pharma and also compare with some other pharmaceutical wastes.

1.2 OBJECTIVE OF THE STUDY

1. To analyse the pollution constituents and potential of a pharmaceutical liquid waste generated in Beximco Pharma of Bangladesh.

2. To develop suitable treatment process (mostly physical and chemical) in order to reduce impurities of the waste.

3. To observe effects on aquatic life.

1.3 SCOPE AND METHOD

Samples of raw and treated effluent of Beximco Pharma were collected. The pollution characteristic parameters were measured in the laboratory. Experiments were conducted in the laboratory to reduce some polluting parameters. Pollution effects on aquatic life were also observed by dropping fish in the samples with different concentration of waste.

Different types of liquid waste in Beximco Pharma are discussed. The existing treatment facilities are studied. The effects of the waste on surrounding are also discussed in this study.

1.4 LAYOUT OF THE REPORT

Pollution potential, types and source of pharmaceutical waste, their characterstic parameters (definition and effects), pollution effects and previous study of pharmaceutical wastes are discussed in Chapter 2. Various treatment process to remove or reduce the pollution parametrs are described in chapter 3. Collection of pharmaceutical waste and their reuse and disposal are also discussed in this chapter. Contents of Chapter 2 and 3 provide a general discussion on pharmaceutical waste. Detail study of a pharmaceutical liquid waste of Beximco Pharma in Bangladesh are described in Chapter 4. In this chapter the location of the industry, different types of liquid waste, their pollution parameters, existing treatment facilities, various attempts to remove pollution parametrs, pollution effects on surroundings are discussed. Conclusions and recommendation for further study have been made in the final chapter.

CHAPTER 2

PHARMACEUTICAL EFFLUENT
(LITERATURE REVIEW)

2.1 POLLUTION POTENTIAL

There are about 3801 manufacturing industries in Bangladesh. All these manufacturing industry are more or less creating environmental pollution. The nature and composition of the effluents will differ from industry to industry according to their nature of production and raw material used. The volume of effluent will depend on the size and capacity of production of the industry. The pollution effects on environmental by the industrial effluent depend mainly upon these nature, composition, and volume of effluent discharged. Considering this pollution effect by the effluent discharged, the manufacturing industries are categorized in three divisions. These are-

i) Major polluting industry
ii) Moderate polluting industry
iii) Minor polluting industry

Pharmaceutical Industry falls into the Major polluting industry. A list of major polluting industries in Bangladesh has been tabulated in Table 2-1. Pharmaceutical industries like other industries are also increasing which is shown in Table 2-2.

Table 2-1: Major Polluting Industries in Bangladesh (Haq, 1989)

Category number	Name of Industries	Number of Industries Recorded	 Existing
3114	Fish and Seafood	22	88
3123	Sugar mill	15	16
3201	Cotton Textile	99	99
3202	Woolen Textile	1	1
3203	Jute Textile	86	86
3204	Silk and Synthetic Textile	154	154
3207	Dying and Bleaching	42	42
3231	Tanning and Finishing	115	250
3411	Pulp and Paper	4	7
3412	Paper and Hardboard	2	2
3501	Allopathic and Medicine	143	143
3514	Fertilizer manufacturing	3	6
3530	Petroleum refinery	1	1

Table 2-2 Licentiate business units in drugs by categories, 1988 (Statistical Year book, 1991)

Category	Number		
	1988	1989	1990
Licensed pharmaceutical (Aliphatic) manufacturing Units	196	198	198
Licensed Uninani drug manufacturing Units	231	234	235
Licensed Ayurvedie drug manufacturing Units	166	167	170
Licensed Homeopathic drug manufacturing Units	55	55	58
Whole Sale trading fitm for drugs	1175	1188	1204
Retail trading firms for drugs	17475	17475	17475

These industries have major pollutional effect on water, air and soil. These are generally big industries which discharge huge amount of wastes. These wastes may contain toxic substances. The liquid wastes generated by these industries are generally discharged directly or indirectly into the nearby natural stream. As a result the water of receiving stream is heavily polluted and around the discharge point where aquatic life is greatly endangered. Also air is polluted by these industries due to the emission of huge amount of smoke and ashes. The ashes ultimately fall onto the ground in vicinity of industrial area. Some industries cause serious odour problem in the surrounding. Soil is also polluted due to the leaching of chemicals from the wastes generally dumped on the open ground in the industrial area. The leaching of chemicals from the wastes sometimes causes pollution of the groundwater.

2.2 TYPES AND SOURCE OF WASTES

2.2.1 GENERAL

The wastes from industries consist of sanitary sewage, process waste, and cooling waters. These wastes are not like domestic sewage and pose special problems of their own. The strength and composition of industrial wastes may vary considerably from domestic sewage and even from industry to industry or with the same type of plant within a single industry. This variably in industrial wastes has been used to relative uniformly of domestic sewage.

2.2.2 SANITARY SEWAGE

The sanitary sewage from an industry is different from the domestic sewage. In a light office building 90 percent of the domestic sewage will come from toilets and wash basins, while the remaining 10 percent will come from water foundation and weakly floor washing, if necessary. This sewage comes within the normal 8 - 10 hr working period. The average sanitary sewage volume for a light office building will be 20 gallon per person per shift, with about 0.05 pound 5-day BOD per person per shift. (McKinney, 1962).

With light manufacturing the sewage flow will go up to 25 gallon per person per shift, with 0.06 pound 5-day BOD per person per shift. As the manufacturing operation becomes more complex, there is a need for regular shower facilities and considerably more clean up. This can run the domestic sewage contribution to 40 gallon per person per shift, with 0.1 pound of BOD per person per shift. Extreme care must be used in estimating the strength and volume of sanitary sewage from industry. It is amazing how few sanitary engineers can make a reasonable estimate of sanitary sewage from an industry. The altitude is basically one of the estimating the sewage quantity and then doubling it to be safe.

2.2.3 PROCESS WASTES

Each industry products its own characteristic process wastes. These wastes result from washing operations: washing of the raw materials, the intermediate product and the final product, as well as washing the product containers. The wash waters usually contain a small quantity of the process materials, which imparts the characterstics to the process wastes. For the sake of convenience the process wastes will be divided into two sections, inorganic and organic.

2.2.3.1 INORGANIC PROCESS WASTES

The processing of inorganic chemicals from raw materials result is discharge of wash waters containing untreated materials. The contaminant concentration is often so great as to make disposal by dilution almost impossible. To prevent damage to the biological life in water courses, it is necessary to lagoon wash waters and allow solar energy to evaporate the water, leaving the untreated materials in the solid state.

For the most part, the inorganic wastes do not pose many biological problems other than toxicity. When combined with organic wastes, they can accentuate the problems of disposal of organic wastes. A high sulfate reduce bacteria and creat a hydrogen sulfide problem.

2.2.3.2 ORGANIC PROCESS WASTES

It is impossible to discuss all the different types of wastes product in the chemical industry. These wastes reflect the raw materials used, the intermediate products, and final product. Most of organic compounds produced by the organic chemical industry can be metabolized biologically, but many of them require adaptation before degradation rapid. Some few compounds appear to be inert or highly resistant to degradation. Actually it is the resistance to biological degradation that is posing some of the major problems in the chemical industry. Instead of being destroyed by biological action the resistant compound resist for long periods of time in the water course and can creat problems if the water is reused. A good example of this is with tetrapropylene-based synthetic detergents. They are not degraded biologically to completion and persist with the production of foam. Nitro-substituted aromatics are another group of compounds not readily degraded, but not completely resistant.

2.2.4 COOLING WATER

The third type of waste discharged from industries is cooling water. While it might seem that the relatively clean cooling waters would not be a waste problem, in many instances they are. The reason for this lies in the fact that cooling waters often creat thermal pollution when discharged into receiving waters. Industries using large volume of cooling water actually can raise the temperature of the receiving water quite materially. The biological effect on the receiving water is twofold: (1) decreasing the solubility of oxygen and (2) stimulating the biological activity.

2.2.5 ANTIBIOTIC WASTE

Antibiotic and vitamins are produced by the fermentation of fairly complex nutrient solutions of organic matter and inorganic salts, by fungi or bacteria.

In the production of penicillin, molds of "Penicillium notatum-chrysegenum group" are cultured under submerged aerobic conditions on a medium consisting of corn steep liquor (nitrogen source), peanut meal, mineral salts, and lactose. After fermentation the mold mycelium is separated by filtration. The filtrate is then acidified to a suitable pH using phosphoric acid, and the penicillin is removed by extracted with a buffered solution of sodium chloride. The isolated penicillin is finally purified by extraction with an organic solvent.

Streptomycin is produced in similar way, using a "streptomyces griseus" culture on a medium consisting of glucose, corn steep liquor etc. The fermentation broth is filtered, and the filtrate is adsorbed on charcoal or a resin. The Streptomycein is eluted from the charcoal or a resin with dilute acids. The elute is then neutralised and concentrated. The crude Streptomycein is then precipitated by addition of acetone, and further purified.

Yields from the above processes, in terms of weight, are small, and out of the raw materials used in the fermentation more than 90% appear as wastes. This waste mycelium may either be solid as manure or stock feed, or may be disposed off in any other way.

The liquid wastes from any antibiotic plant may be divided into following groups:

(i) spent liquor of the fermentation process,

(ii) wash waters used for cleaning of floors and equipments,

(iii) wastes containing acids, bases, and, solvents used for extraction and purification of the product, of the product,

(iv) "Filter Aids" used in the filtration, such as, "Diatomaceous Earth",

(v) Condensate from barometric condensers in evaporation and drying under reduced pressure. (Rao, 1987))

(2.3 WASTEWATER CHARACTERSTICS

2.3.1 GENERAL

While a huge amount of water is required for different industrial process only a small portion is incorporated in their products and lost by evaporation, the rest finds its way into the water course as wastewater called industrial waste. The industrial waste either join the stream or other natural water bodies directly or indirectly when the wastes are emptied into the municipal sewers which ultimately are connected with the streams or other natural bodies, thus contributing to the "pollution" of natural waters. Almost any substance can get into wastewater and therefore the effects on receiving water are varied and occasionally disastrous. Streams can assimilate certain amount of waste before they are polluted. Unlike the domestic waste, the industrial wastes are very difficult to generalize. The characterstics of the industrial waste not only vary with type of end products due to difference in manufacturing process and to a lesser degree the quality of original raw water used. Different types of liquid waste originate from the raw materials, process chemicals, final products, process intermediates, process byproducts and impurities in raw materials.)

Broadly the pollutants of industrial waste can be classified as follows:

1) Organic substances e.g., starch, sugar, protein, polysaccharides, fats etc., cause oxygen depletion in streams and estuaries and improve a great load on the biological units of the treatment plant.

2) Inorganic substances e.g., nitrogen, phosphorous, carbonates chlorides etc. render the water unfit for further use and sometime enhance eutrophication in water.

3) Acids and alkalies affect biological treatment, natural degradation of wastes and prevent growth of fish and aquatic life.

4) Toxic substances like cyanide, sulfides, acetylene, alcohol, phenol etc. cause damage to the flora and fauna of the receiving streams and affect the municipal treatment processes.

5) Heavy metal ions like Cu, Zn, Hg, Cr etc. cause toxic effect and for which rigid standards and discharge limit are imposed.

6) Colour and turbidity are aesthetically undesirable and impose load on water treatment plants.

7) Odour compounds like sulfides cause load small and atmospheric pollution.

8) Oil and floaty materials are aesthetically undesirable and interfere the self purification process of the stream, lakes and seas.

9) Refractory materials (e.g. ABS) may result is downstream foaming.

10) Suspended solids (organic or inorganic) cause leenthal deposits and effect stream life.

11) Temperature results in depletion stream dissolved oxygen and condition unfavorable for aquatic life.

2.3.2 CHARACTERISTIC PARAMETERS

The increased emphasis on water qualities for multipurpose use has defined a number of parameters of special significance in industrial wastewater. The physical properties and the chemical and biological constituents of wastewater, and their sources, are listed in Table 2-3.

Table 2-3 Physical, chemical, and biological characterstics of wastewater and their sources (Metcaff & Eddy, 1979)

Characteristic	Sources
Physical properties:	
Colour	Domestic and industrial wastes, natural decay of organic materials
Odour	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes, soil erosion,inflow-infiltration
Temperature	Domestic and industrial wastes
Chemical constituents:	
Organic:	
Carbohydrates	Domestic, commercial, and industrial wastes
Fats, oils, and grease	Domestic, commercial, and industrial wastes
Pesticides	Agriculture wastes
Phenols	Industrial wastes
Surfactants	Domestic and commercial wastes
Others	Natural decay of organic materials
Inorganic:	
Alkalinity	Domestic wastes, domestic water supply, groundwater infiltration
Chlorides	Domestic water supply, domestic waters, groundwater infiltration
Heavy metals	Industrial wastes
Nitrogen	Domestic and agricultural wastes
pH	Industrial wastes
Phosphorus	Domestic and industrial wastes, natural runoff
Sulfur	Domestic water supply, domestic and industrial wastes
Toxic compounds	Industrial wastes
Gases:	
Hydrogen sulfide	Decomposition of domestic wastes
Methane	Decomposition of domestic wastes
Oxygen	Domestic water supply, surface water-water infiltration
Biological constituents:	
Animals	Open watercourses and treatment plants
Plants	Open watercourses, and treatment plants
Protista	Domestic wastes, treatment plants
Viruses	Domestic wastes

2.3.2.1 pH

The determination of pH of an industrial waste might supply needed information concerning its nature. pH is a measure of hydrogen ion concentration. The acidity or alkalinity of wastes are frequently expressed in terms of their pH value. Many industrial wastes are either acidic or alkaline. pH is a parameter having direct effect on the treatability of a waste by biological means particularly in the control of anaerobic digestion of organic matter. For example, if the pH approaches 5.0, the acidic stage of digestion is becoming predominant and digestion will be unsatisfactory. Remedies must be taken to raise the pH value varying between 6.5 to 8.0 is required for a proper biological treatment.

2.3.2.2 ODOUR

Industrial wastewater may contain either odours compounds or compound that produce odours during the process of wastewater treatment.

The importance of odours in human terms is related primarily to the psychological stress they produce rather than to the harm they do the body. Offensive odours can cause poor appetite for food, lowered water consumption, impaired respiration, nausea and vomiting returbation. In extreme situations, offensive odours can lead to the deterioration of personal and community pride, interfere with human relations, discourage capital investment, lower socioeconomic status, and deter growth. These

These problems can result in a decline in market and rental property values, tax revenues, payrolls, and sales.

2.3.2.3 TOTAL SOLIDS

Analytically, the total solids content of a wastewater is defined as all the matter that remains as residue upon evaporation at 103 to 105 ^{0}C. Matter that has a significant vopour pressure at this temperature is lost during evaporation and is not defined as a solid. Total solids, or residue upon evaporation, can be classified as either suspended solids or filterable solids by passing a known volume of liquid through a filter. The filter is commonly chosen so that the minimum diameter of the suspended solid is about 1 micron (μ). The suspended solids fraction includes the settleable solids that will settle to the bottom of a cone-shaped container (called an Inhoff cone) in a 60-minute period. Settleable solids are an approximate measure of the quantity of sludge that will be removed by sedimentation.

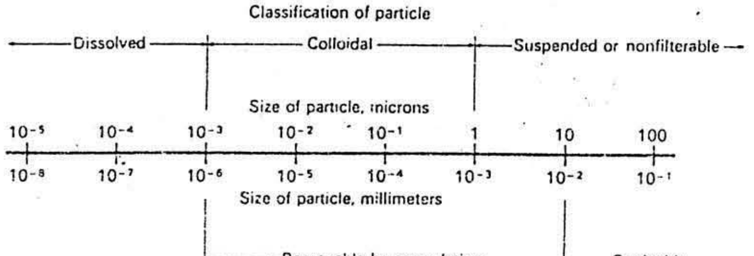

Figure 2-1 Classification and Size Range of Particles found in Wastewater.

The filterable-solids fraction consists of colloidal and dissolved solids. The colloidal fraction consists of the particulate matter with an approximate diameter range of from 1 millimicron (mμ) to 1 μ (see Figure 2-1). The dissolved solids consist of both organic and inorganic molecules and ions that are present in true solution in water. The colloidal fraction can not be removed by settling. Generally to remove these particles from suspension.

2.3.2.4 SUSPENDED SOLIDS

It is important to measure the concentration of suspended solids in an effluent since such solids can cause pollution of surface waters and add to the sludge problem at the treatment works. Organic suspended and dissolved solids undergo biodegradation and their pollution potentials are usually expressed in terms of BOD. The fixed or inorganic solids and heavier organic solids settle quickly and form a sludge blanket near the point of discharge. Colour may be partially imparted by the suspended solids but turbidity is almost wholly caused by the suspended solids.

2.3.2.5 TOXICITY

Wastewater specially those originating from industrial source, contain elements like Arsenic, Boron, Copper, Cyanide, Chromium, Lead, Mercury etc. which are toxic to microorganisms responsible for biological treatment. Toxic threshold limit for Copper, Zinc, Cad.

2.3.2.6 DO, BOD, COD

The polluting strength of an effluent is best defined in terms of the organic substances which will effect the Dissolve Oxygen (DO) content of the receiving water. It is not usual to analyse for individual organic compound but to measure the overall oxygen demand of these substances. This demand may be assumed in a number of ways like BOD, COD.

2.3.2.6.1 Biochemical Oxygen Demand (BOD)

It is usually defined as the amount of oxygen required to stabilize organic matter under aerobic condition. It is used to determine the biodegradable organic content of the waste in terms of Oxygen which will be required if discharged into natural water course in which aerobic condition prevails

Almost all oxidizable compounds can be oxidized, by biochemical oxidation. Basically this reaction is written as:

Oxidizable compounds+Bacteria+Nutrient Oxygen = Oxidized inorganic+CO_2+ H_2O

Since all natural waterways will contain bacteria and nutrient almost any waste compound introduced into a natural waterway will initiate biochemical reacts which will consume part of the dissolved oxygen in the water. These biochemical reactions creat what is measured in laboratory as the Biochemical Oxygen demand (BOD). The most widely and acceptable measure of biodegradable organic content of a wastewater is the 5 day 20 ^{0}C Biochemical Oxygen Demand (BOD_5) value. BOD data is used to design biological treatment units to control the quality of effluents discharged into receiving water and to fix charges made by the local authorities for the reception of industrial waste.

2.3.2.6.2 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is widely used to do determine the organic strength of wastewater and pollutions of natural waters. The best measures the amount of Oxygen required for chemical oxidation of organic matters in the sample of wastewater to Carbon dioxide and water. It is an attempt to carryout a wet chemical combustion of all carbonaceous materials of a wastewater sample. There are however some carbonaceous materials will not be completely oxidized, also there may be oxidation of nitrogenous material under certain circumstances. These is no definite relationship between the carbonaceous content of a sample and its COD value. The COD value however, is important in testing industrial waste for it gives a reasonable close approximation of the total chemically oxidizable carbonaceous content of a sample. The Chemical Oxygen Demand measured as either 4-hour Permanganate test, measures the Oxygen absorbed from acid potassium permanganate in 4 hours at 27 ^{0}C. And the dichromate test measures the Oxygen consumed from boiling acid potassium dichromate. Moore and Reuchhopt (5) have concluded that "where a given industrial waste is fairly constant in composition and contains no toxic materials, a satisfactory COD to BOD ratio may be determined."

2.3.3 PREVIOUS STUDY

M. Narayana Rao and Amal K. Datta studied on Pharmaceutical plants waste in India which characterstics are shown in Table 2-4.

Table 2-4 Characterstics of Antibiotic Wastes. (Rao & Datta, 1987).

Item	Penicillin plant	Streptomycein plant
Colour	Colourless	Pale yellow
Odour	Fruity smell	Septic
BOD, mg/l (5 day, 37^0 C)	650 - 5500	500 - 2800
Free ammonia nitrogen, mg/l	0 - 5.6	0.3 - 18.2
Nitrate Nitrogen mg/l	1.1 - 0.5	0 - 0.8
Phosphate, mg/l	18 - 700	9 - 700
Total solid mg/l	480 - 26200	960 - 4950
Suspended solid, mg/l	70 - 1080	80 - 1800
Total volatile solid, mg/l	200 - 12180	480 - 3070
pH	3.9 - 7.8	2.9 - 8.7

The above table is based on the analysis of the grab samples taken the plant effluents. The wide variations is observed due to the fact that the batch processes are adopted for the production in the plant.

Syed Azizul Hoq studied on wastewater of I.C.I. Pharmaceutical Industry. He took sample from main drain of industry and measured different pollution parameters from March 1979 to December 1979 which are tabulated in the Table 2-5.

Table 2-5 Analysis of wastewater of I.C.I. Pharmaceutical Industry (sample taken from main drain) (Haq, 1989).

tem	March 1979	April 1979	June 1979	July 1979	August 1979	Sept. 1979	Nov. 1979	Dec. 1979
Temperature ^{0} F	84	83	86	86	79	82	80	89
pH	6.8	6.7	6.8	6.0	7.1	5.7	6.7	7.2
E.C.,micro.mho/cm	350	225	350	150	260	240	650	250
Chloride, mg/l	8	12	12	10	7	10	15.5	5.3
T.Alkalinity, mg/l	120	88	120	49	44	52	94	92
SS, mg/l	19	8	105	6	13	15	40	17
DO, mg/	6.0	3.5	1.5	1.6	3.8	6.5	--	--
BOD, mg/l	2.7	1.2	1.3	1.4	2.5	1.5	6.2	4.8
COD mg/l	--	--	--	--	--	--	--	--
Ammonia, mg/l	1.0	1.4	1.8	1.0	1.0	1.0	0	0
Nitrate, mg/l	0	0.1	0.1	0	0	0	1.4	0.1
Turbidity, mg/l	25	5	25	25	25	25	0	0

2.4 TOXIC AND POLLUTION EFFECT OF WASTES

(2.4.1 EFFECTS OF ANTIBIOTIC WASTES

If a crude waste from an antibiotic waste discharged into a stream, it not only imparts an objectionable odour to the stream, but also adversely affects the biological population in it. This waste should not be allowed to discharge into a municipal sewer, unless the sewage treatment plant is properly designed to handle a widely varying and concentrated waste from such a plant. Penicillin waste is found to have a disturbing effect on the process occurring within the sludge digestion tank.)

2.4.2 EFFECTS OF SYNTHETIC DRUG WASTES

(Wastes containing toxic elements like cyanides and heavy metals, if discharged without any treatment are harmful to the aquatic life in streams. These toxic elements interfere with the biological sewage treatment units very badly. Similar effects are observed with raw acidic wastes; these wastes corrode structures in the sewerage system. Due to their high BOD content, a raw waste when discharged into stream rapidly depletes the dissolved oxygen of the stream and renders the water unsuitable for further use.)

2.4.3 EFFECT ON RECEIVING STREAM

Industrialization is a prerequisition for economic development of any country. But it is paradoxical that such development is always accompanied with potential pollution for the environment.

The problem of environment pollution has already reached a serious level in the industrial developed countries in Europe, North America and Japan. It is also spreading to the less developed countries like Bangladesh, where the problem is not yet very serious on a national scale but several reports of river pollution, poisoned fish, pesticides induced deaths or devil have been reported.

Water is the ultimate dumping depot of all physical, chemical and biological pollutants. In one sense river system is the natural drainage channel for receiving all the pollutions from land surface. Every substance is a potential pollutant to water depending on its concentration and toxicity.

The concentration of pollutants in water depends primarily on (i) the amount and concentration of polluting substances and (ii) the volume of diluting water. These are the two basic guide lines for water pollution abatement.

In Bangladesh industrial waste is one of the major pollutional wastes that causes water pollution. There is little problem of water pollution during monsoon. The real problem of water pollution may rise only three to four months in a year during dry season when the river flow becomes sluggish. And this may aggravate with saline intrusion and other ecological and limnological changes due to diversion of river waters upstream in the neighboring countries.

All the big districts like Dhaka, Chittagong, Khulna, Rajshahi are situated on the banks of river. Not only these districts, but almost all the districts in Bangladesh have a river or its tributaries passing through it. Along the banks of these rivers, generally maximum numbers of industrial zones built-up because of the ease of transportation of the raw materials and also the finished product by the water way. The another reason of settling an industry by the side of river banks is for easier disposal of its waste into the river.

In Dhaka city there are two major rivers passing through it. These are Buriganga and Balu river. All the industrial wastes of Dhaka ultimately are disposed off into the river Buriganga and the wastes from Tongi industrial zone ultimate fall into the Balu river.

Balu river is flowing by the side of Tongi industrial zone in Dhaka district. Various type of industrial like pulp and paper mill, textile mills, rubber industry, detergent factory, pharmaceutical industries etc. have been developed in this industrial zone. The effluent discharge from those industries ultimately find its way into the Balu river. An analysis of Balu river water near Tongi bridge is shown in Table 2-6.

Table 2-6 Analysis of Balu River near Tongi Bridge (Haq, 1989).

Item	Maximum	Minimum	Average
Temperature, ^{0}F	90	75	80
pH	7.6	6.3	6.9
E.C., micro.mho/cm	520	90	265
Chloride, mg/l	50	5.0	15
T.Alkalinity	200	26	93
S.S., mg/l	131	9	21
DO, mg/l	7.0	5.5	6.3
BOD, mg/l	5.3	0.2	2.3
COD, mg/l	--	--	--
Ammonia, mg/l	1.3	0	0.8
Chromium, mg/l	0	0	0
Nitrate, mg/l	0	0	0
Turbidity	50	25	30

From the analysis of pollution of Balu river water, it reveals that pH range remains within desirable limit with little exception in same times. Alkali limit is beyond the maximum allowable WHO limit, which is 100 ppm. The alkalinity increases due to the poor discharge of river water during December to April.

2.5 EFFLUENT STANDARDS

In the Table 2-7 the allowable limits of some organic and inorganic parameters in the natural water the propagation of aquatic lives are given. In the cases of various uses of this water, obviously these limiting values will differ.

Table 2-7: Allowable limit of waste parameters in the water body for survival of aquatic life(Haq, 1989).

Parameters	Allowable limit	Remarks
Temperature	85 ^{0}F	
Alkalinity/ Acidity	75 % of natural level	Addition of acid unacceptable
pH	6 - 9	
DO	Minimum 4 ppm	
BOD	Maximum 5 ppm	
S.S.	80 ppm	
Free ammonia	0.02 ppm	
Chromium	0.03 to 0.05 ppm	
Ammonia, N	0.5 ppm	
Chloride	250 ppm	
Conductance	500 - 100 micro.mho/cm	
Nitrate	50 ppm	Suggested by W.H.O.

In Bangladesh like other countries, some industrial effluent quality standards have been formulated. In Bangladesh the only organization for the controlling and monitoring the environmental pollution is the Department of Environmental pollution Control (EPC), Bangladesh. This organization has formed a committee in 1977, naming the National Committee on Industrial Effluent Standards, which was formulated some quantitative standards for some selected categories of industries in keeping with laboratory test results which decisively indicated that these industrial categories are the principal polluting agencies in Bangladesh.

CHAPTER 3

WASTE TREATMENT AND DISPOSAL
(LITERATURE REVIEW)

3.1 WASTE TREATMENT

3.1.1 INTRODUCTION

The economy of industrial water use can be improved by reducing wastewater volume, recovering water or byproducts from wastewaters and reusing wastewaters.

Recycling with treatment for prevention of excessive buildup of dissolved or suspended matter, scale deposition, and organic growths is often less expensive than once-through used of water. established reuse, generally after intermediate or partial purification may be used in any stage of production cycle.

The recovery of otherwise wastes components, too, is not uncommon. Some can be returned to the manufacturing process itself. Also worth salvage are the waters from the washing of chemical crystal and precipitates.

Some wastewater contaminants that are not salvageable for reused may be recovered instead as marketable byproducts. However, the valuable market for possible byproducts is often limited or unsuitable. Furthermore, the marketing of the

byproduct is often quit different production, sales, and management organization. Also to be recognized is that the output of a single manufacturing company may be large enough to saturate the market for a specialized byproduct. Nevertheless, byproduct recovery remains a laudable concept and a worthy challenge.
Hand in hand, good housekeeping and good engineering design and practice can prevent or contain spills, overflows, splashes, drips, and the avoidable losses. The dry cleaning or spilled solids and dusts from equipment and flocs may be less satisfactory than their hosing, but it does keep large amounts of pollutional solids out of the plant drains. At least one dry cleaning should normally precede washing. Good house keeping is more than an exercise of common sense. Yet the results can be surprisingly beneficial. (Fair, Gorden, Maskew & others, 1967)

Treatment of the liquid wastes formed during the production of antibiotics starts from the plant itself. For economic reasons, most of the organic solvents used in the process, like Amyl acetate in penicillin production and Butyl alcohol in Aureomycin production, are recovered in the plant. The recovery reduces the BOD of the wastes by a great extent.

Industrial wastewaters may be discharged into municipal wastewater systems at conventional points, provided they do not overload them or damage the collecting and treatment works. Pretreatment before discharge to the municipal sewer is also a matter of decision.

Within manufacturing plants themselves there may be rigid separation of different process waters and other wastewaters than can be isolated.

Not all lines need be laid as underground gravity-flow conduits. Relatively small volume of wastewaters may be collected in sumps and plumed through overhead lines instead.

When there is good promise of reasonable recovery of water or waste matters or of treatment simplification. Spent waters may be segregated even if collecting lines must be duplicated. Examples are: (1) pretreatment of strong wastewaters before-admixture with similar double wastewaters and (2) the separation of Cyanide wastewaters for destruction by Chlorine before mixing them with wastewaters containing reaction-inhibiting Nickel. However, it may also pay to blend wastewaters in order to (1) dilute strong wastes, (2) equalize wastewater flows and composition, (3) permit self-neutralization to take place, (4) faster other beneficial reactions, and (5) improve the overall economy. As a rule, it pays to separate wastewaters while significant benefits can still accure. After that they may well be blended to advantage into single waste stream.

Wash water may require special collection and treatment when they differ from process waters. Thus wastewaters from Pharmaceutical plant contains nutrients that are amenable as such to biological treatment. However, they may no longer be so after strong alkalis, soaps or synthetic detergents, sanitizer, and germicides have been added to them together with the washwaters of the industry. Difficulties of this small in volume when they can be collected during nonprocessing hours - the night shift, for instance.

The treatment of industrial wastewaters is generally accomplished in part or as a whole while either process commonly employed in municipal wastewater works or by process uniquely applicable to the removal or destruction of specific chemical constituents of industrial origin. Sedimentation is normally a first treatment step in the removal of suspended matter and in the simplification of soluble contaminants. Grit chambers can remove finer mineral and organic suspensions.

Because industrial wastewater are more varied than domestic wastewaters, their treatment also varied. Because industrial wastewaters are often more concentrated than municipal wastewaters, treatment techniques too costly for municipal wastewaters are often practical. Examples are centrifugation, air flotation, heat treatment, and evaporation.

The following is a summary of combinations of treatment process commonly used in treating industrial wastes:

1. Remove settleable and suspended solids by screening and/ or settling.

2. Remove fats, oils and greasy solids by floatation and skimming procedures aided in some cases by chemical treatment.

3. Remove colloidal solids by flocculation with chemical coagulants and electrolytes, followed by settling and possible filtration.

4. Neutralize excessive acidity or alkalinity by addition of chemicals.

5. Remove or stabilize dissolved solids by chemical precipitation, ion exchange or biological processes or a combination of these.

6. Decolourize by chemical treatment, with settling or filtration, singly or in combination.

7. Re-oxygenate the wastes by suitable aeration methods.

8. Lower the temperature of excessively hot wastes by a suitable cooling process.

It should be understood that the treatment concept may be used either singly or in combination either as pretreatment or complete treatment or may not be used at all depending on the treatment need before discharge to a sewer system or to the receiving waters.

3.1.2 FLOW EQUALIZATION

In consideration of process fundamentals, it was assumed, for the purpose of simplifying the analysis, that the flow rate was constant. If instead a variable flow rate is substituted for the assumed constant value, it can often be shown that because of variation involved, there may be deterioration in performance from the optimum value that can be achieved,. Flow equalization is used to overcome the operational problems caused by these variations and to improve the performance of the downstream process.

Flow equalization simply is dumping of flow rate variations so that a constant or nearly constant flow rate is achieved. This technique can be applied in a number of different situations, depending on the characteristics of the collection system. The principal applications are for the equalization of:

1. Dry-weather flows
2. Wet-weather flows from separate sanitary sewers
3. Combined storm water and sanitary waste water flows.

The principal benefits that are cited as diverting from the application of flow equalization are as follows: (1) wastewater treatability is reportedly is enhanced after equalization (this remains to be demonstrated conclusively); (2) biological treatment is enhanced, because shock loadings are eliminated or can be minimized, inhibiting substances can be diluted, and pH can be stabilized; (3) the effluent quality and thickening performance of secondary sedimentation tanks following biological treatment is improved through constant solids loading; (4) effluent-filtration surface-area requirements are reduced, filter performance is improved, and more uniform filter-backwash cycles are possible; and (5) in chemical treatment, damping of mass loading improves chemical feed control and process reliability. Apart from improving the performance of most treatment operation and process, flow equalization is an attractive option for upgrading the performance of overloaded treatment plants because of the relatively low costs involved. (Metcalf & Eddy, 1979)

3.1.3 SEDIMENTATION

Sedimentation is the separation from water, by gravitational settling, of suspended particles that are heavier than water. It is one of the most widely used unit operation in wastewater treatment. The terms sedimentation and settling are used interchangeably. A sedimentation basin may also be refereed to as a sedimentation tank, settling basin, or settling basin, or settling tank.

Sedimentation is used for grit removal, particulate-matter removal in the primary settling basin, biological-floc removal, particulate-matter removal in the activated-sludge settling basin, and chemical-floc removal when the chemical coagulation process is used. It is also used for solids concentration in sludge thickness. In most cases, the primary purpose is to produce a clarified effluent, but it is also necessary to produce sludge with a solids concentration that can be easily handled and treated. In the design of sedimentation basin, consideration must be given to production of both a clarified effluent and a concentrated sludge. (Metcalf & Eddy, 1979)

3.1.4 CHEMICAL PRECIPITATION

Chemical precipitation in wastewater treatment involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation. In some cases the alteration is slight, and removal is effected by entrapment within a voluminous precipitate consisting primarily of the coagulant itself. Another result of chemical addition is net increase in the dissolved constituents in wastewater.

In the past, chemical precipitation was used to enhance the degree of suspended solids and BOD removal (1) where there were seasonal variations in the concentration of the wastewater , (2) where an intermediate degree of treatment was required, and (3) as an aid to the sedimentation process.

Since about 1970, the need to provide more complete removal of the organic compounds and nutrients (nitrogen and phosphorus) contained in wastewater has brought about renewed interest in chemical precipitation. Chemical process, in conjunction with various physical operations, have been developed for the complete secondary treatment of untreated wastewater, including the removal of either nitrogen or phosphorus or both. (Metcalf & Eddy, 1979)

Over the years a number of different substances have been used as precipitants. The most common ones are listed in Table 3-1. The degree of clarification obtained depends on the quantity of chemicals used and the care with which the process is controlled. It is possible by chemicals used and the care with which the process is controlled. It is possible by chemical precipitation to obtain a clear effluent, substantially free from matter in suspension or in the colloidal state. From 80 to 90 percent of the total suspended matter, 40 to 70 percent of the BOD_5, 30 to 60 percent of the COD, and 80 90 percent of the bacteria can be removed by chemical precipitation. In comparison, when plain sedimentation is used, only 50 to 70 percent of the total suspended matter and 30 to 40 percent of organic matter settles out.

Table 3-1 Chemicals Used in Wastewater Treatment (Metcaff & Eddy, 1979)

Chemical	Formula	Molecular Weight
Alum	$Al_2(SO_4)_3\ 18H_2O^a$	666.7
Ferrous Sulfate (Copperas)	$FeSO_4\ 7H_2O$	278.0
Lime	$Ca(OH)_2$	56 as CaO
Ferric Chloride	$FeCl_3$	162.1
Ferric Sulfate	$Fe_2(SO_4)_3$	400

[a] Number of bound water molecules will vary from 13 to 18

The chemicals added to wastewater interact with substances that are either normally present in wastewater or added for this purpose,

3.1.5 ADVANCED WASTEWATER TREATMENT

Primary and secondary treatment remove the majority of BOD and suspended solids found in wastewaters. However, in an increasing number of cases this level of treatment has provided to be insufficient to protect the receiving waters or to provide reusable water for industrial and/or domestic recycle. Thus, additional treatment steps have been added to wastewater treatment plants to provide for further organic and solids removals or to provide for removal of nutrients and/ or toxic materials.

Advanced waste treatment may be defined as:(6) any process designed to produce an effluent of higher quality than normally achieved by secondary treatment process or containing unit operations not normally found in secondary treatment.

Advanced wastewater treatment may be broken into three major categories by the type of process flow scheme utilized:

1. Tertiary treatment
2. Physical-Chemical treatment
3. Combined Biological-Physical treatment

Tertiary treatment may be defined as any treatment process in which unit operations are added to the flow scheme following conventional secondary treatment. Additional to conventional secondary treatment could be as similar as the addition of a filter for suspended solids, nitrogen and Phosphorous removal.

Physical-Chemical treatment is defined as a treatment process in which biological and physical-chemical process are intermixed to achieve the desired effluent. Combined biological-physical-chemical treatment is differentiated from tertiary treatment in that in tertiary treatment any unit processes are added after conventional biological treatment are mixed.

Another way to classify advanced wastewater treatment is to differentiate on the basis of desired treatment goals. Advanced wastewater treatment is used for;

1. Additional organic and suspended solid removal
2. Nutrient removal
3. Removal of toxic materials.

Various unit process may be used to achieve are or more of the above treatment goals. Table 3-2 lists each of the goals and the unit processes which may be used to achieve the chosen levels of treatment.

Additional organic and suspended solids removal by advanced treatment is necessary for followings:

1. Advanced wastewater treatment plant effluents may be recycled directly or indirectly to increase the available domestic water supply.

2. Advanced wastewater treatment effluents may be used for industrial process or cooling water supplies.

3. Some receiving waters are not capable of withstanding the pollutional loads from the discharge of secondary effluents.

4. Secondary treatment does not remove as much of the organic pollution in wastewater as may be assumed.

Table 3-2 Advance Wastewater Treatment (Mekinney, 1962)

Goal Process	Organic and SS Removal	Removal of Nitrogenous Oxygen Demand	Nutrient Removal	Toxic Removal
Biological Nitrification	X	X		
Denitrification			X	
Ammonia stripping		X	X	
Break point Chlorination		X	X	
Ion Exchange		X	X	
Chemical Precipitation	X		X	X
Granular Media Filtration	X			
Activated Carbon adsorption	X			X

The first three reasons for additional organic removal through advanced wastewater treatment are simple. The forth requires some explanation. The performance of secondary treatment plant is almost always measured in terms of BOD and SS removals. A well designed and operated secondary plant will remove from 85 to 95 percent of the influent BOD and SS. However, the BOD test does not measure all of the organic material present in the wastewater. An average secondary effluent may have a BOD of 20 mg/l and a COD of 60 to 100 mg/l. The average secondary plant removes approximately 65 percent of the influent COD. Thus, when high quality effluents are required additional organic removals must be accomplished.

In addition to the organic materials remaining in most secondary effluents, there is an additional Oxygen demand resulting the nitrogen present in the wastewater.

In wastewater, much of nitrogen is found in that of ammonia. When secondary treatment is used, a great deal of this ammonia is discharged in the effluent, Bacteria can utilized this ammonia as an energy source and convert ammonia to nitrite and nitrate.

$$NH_3 + O_2 \xrightarrow{\text{Bacteria}} NO_2 + O_2 + \xrightarrow{\text{Bacteria}} NO_3 \qquad (3\text{-}1)$$

In the simplified equation presented above it may be seen that it requires Oxygen to convert the ammonia to nitrate. Approximately 4.5 mg/l of dissolved Oxygen is needed to convert 1 mg/l of ammonia to nitrate. Unless this conversion takes place in the treatment plant or the ammonia is removed during treatment, the Nitrogenous Oxygen Demand (NOD) will often greatly exceeded the effluent BOD. For example, an effluent containing 20 mg/l BOD_5 and 25 mg/l ammonia nitrogen would require approximately 20 mg/l DO to satisfy the ultimate BOD and about 112 mg/l of DO to satisfy the NOD.

Another reason for advanced wastewater treatment may be to remove nutrients contained in discharges from secondary treatment plants. The effluents from secondary treatment plants contain both nitrogen and phosphorous. Nitrogen and phosphorus are ingredients in all fertilizers. When excess amounts of nitrogen and phosphorous are discharged, plant growth in the receiving waters may be accelerated. Algae growth may be stimulated causing blooms which are toxic to fish life as well as aesthetically unpleasing. Fixed plant growth may also be speeded up. Therefore, it has become necessary to remove nitrogen and phosphorous prior to discharge in some cases.

Toxic materials, both organic and inorganic are discharged into sewage collection systems. When these materials are present in sufficient quantities to be toxic to bacteria, it will be necessary to remove them prior to biological treatment. In other cases, it is necessary to remove even small amounts of these materials prior to discharge to protect receiving waters or drinking water supplies. Thus, advanced wastewater treatment process have been used in cases where conventional secondary treatment was not possible due to materials toxic to bacteria entering the plant as well as in cases where even trace amounts of toxic materials were unacceptable in plant effluents. (McKinney, 1962)

3.1.5.1 NITRIFICATION AND NITROGEN REMOVAL

Common forms of Nitrogen or organic nitrogen, ammonia, nitrate, nitrite, and gaseous nitrogen. Decomposition of nitrogenous organic matter releases ammonia to solution, Equation 3-2. Under aerobic conditions, bacteria perform Equation 3-3, oxidizing ammonia to nitrite and subsequently to nitrate. Nitrifying bacteria are autropic, using energy from ammonia oxidation and carbon from carbon dioxide for synthesis. Bacterial decomposition, Equation 3-4, occurs under anaerobic conditions when organic matter (AH_2) is oxidized and nitrate is used as hydrogen acceptor releasing nitrogen gas.

$$\text{Organic nitrogen compounds} \xrightarrow[\text{decomposition}]{\text{bacterial}} NH_3 \text{ (ammonia)} \qquad (3\text{-}2)$$

$$NH_3 + O_2 \xrightarrow[\text{nitrification}]{\text{bacterial}} NO_3^- \text{ (nitrate)} \qquad (3\text{-}3)$$

$$NH_3 + AH_2 \xrightarrow[\text{nitrification}]{\text{anaerobic}} A\,H_2O + N_2 \qquad (3\text{-}4)$$

Pollution problems related to nitrogen are decrease of dissolved oxygen in streams and lakes resulting from oxidation of ammonia nitrogen, toxic effect of ammonia on fishes, limitation of nitrate nitrogen in drinking water to protect public health, and nitrogen as a plant nutrient in eutrophication of lakes and estuaries. (Hammer, 1977)

Biological nitrification may be used to prevent oxygen depletion from NOD in the receiving waters. Nitrification is simply the conversion of ammonia to nitrate in the treatment plant rather than in the receiving water. Nitrification may be carried out in the same tank as BOD removal or in a separate stage. Nitrification may be carried either in activated sludge floc or in fixed films.

Regardless of the particular scheme, the same basic requirements for nitrification must be maintained:

1. Oxygen level
2. Loading rates
3. Solids retention time
4. Alkalinity
5. pH
6. Freedom from toxic materials
7. Temperature

Sufficient oxygen must be available for nitrification to occur. Approximately 4.5 pounds of DO are required for the conversion of 1 pound of ammonia to nitrate. DO sufficient to satisfy the remain BOD is also required. In activated sludge plants the mixing requirements of the basis must also be considered. Generally, DO levels of Approximately 2-3 mg/l are recommended for nitrification.

Loading rates to nitrification systems are considerably lower than those for BOD removal. Loading ratio vary widely with temperature and MLVSS. For example, with 2000 mg/l MLVSS a plant loaded at 10 pounds ammonia nitrogen per 100 cu.ft per day at 10 ^{0}C could be loaded at 25 pounds ammonia nitrogen per 1000 cu.ft per day at 20 ^{0}C.

The bacteria responsible for nitrification reproduce at a much slower rate than those responsible for BOD removal. Thus, the danger always exists for the "washout" of the nitrifying organisms. That is, unless the nitrifying bacteria reproduce at the same or greater rate than they removed from the system (by waste sludge) then the population of bacterial will insufficient to carry out nitrification. For the reason, nitrification systems are operated at higher return sludge rates than conventional secondary treatment. The amount of sludge to be wasted is significantly less than from a conventional activated sludge system.

Nitrification systems are sensitive to pH variation. Optimum pH has been found to be approximately 7.8 to 9.8. Reductions in nitrification have been found outside this range. Alkalinity is also destroyed during nitrification. Theoretically, 7.3 pounds of alkalinity are destroyed in converting 1 pound of ammonia to nitrate. In low alkalinity wastewaters, lime (CaO) or $Ca(OH)_2$ is often used to provide alkalinity and pH control.

Generally the influent BOD to nitrification systems has not been found to effect performance. However, sufficient oxygen must be provided for the oxygen demand

and organic shock loads must be avoided. (Manual of Instruction for Waste water Treatment Plant of Operators)

3.1.5.2 BIOLOGICAL NITRIFICATION-DENITRIFICATION

This process involves oxidation of ammonia to nitrate followed by reduction of nitrogen gas (Figure 3-1). The important parameters in bacterial nitrification kinetics are temperature, pH , and dissolve oxygen concentration. reaction rate is decreased markedly at reduced temperatures with about 8 ^{0}C being the minimum reasonable value. Optimum pH is near 8.4 and the dissolve oxygen level should be greater than 1.0 mg/l. Continuous flow aeration systems required a long sludge retention time to prevent excessive loss of viable nitrifying bacteria. In other words, the growth rate of nitrifying microorganisms must be rapid enough to replace bacteria lost through sludge washing and washout in the plant effluent. Although it may be possible to perform nitrification along with organic matter removal in a single-stage extended aeration unit in southern climates, two-step treatment is necessary at reduced operating temperatures. The first-stage is for removing BOD, without oxidation of ammonia nitrogen, to produce a suitable effluent for second-stage nitrification. A high ammonia nitrogen to BOD ratio provides greater growth potential to the nitrifiers, relative to the hetarotrophs, allowing operation at an increased sludge age in the nitrification step to compensate for lower operating temperatures. Because the rate of oxidation of ammonia is nearly linear, the tank configuration destroys alkalinity, lime may be needed to raise the pH to the optimum level in the nitrification tank.

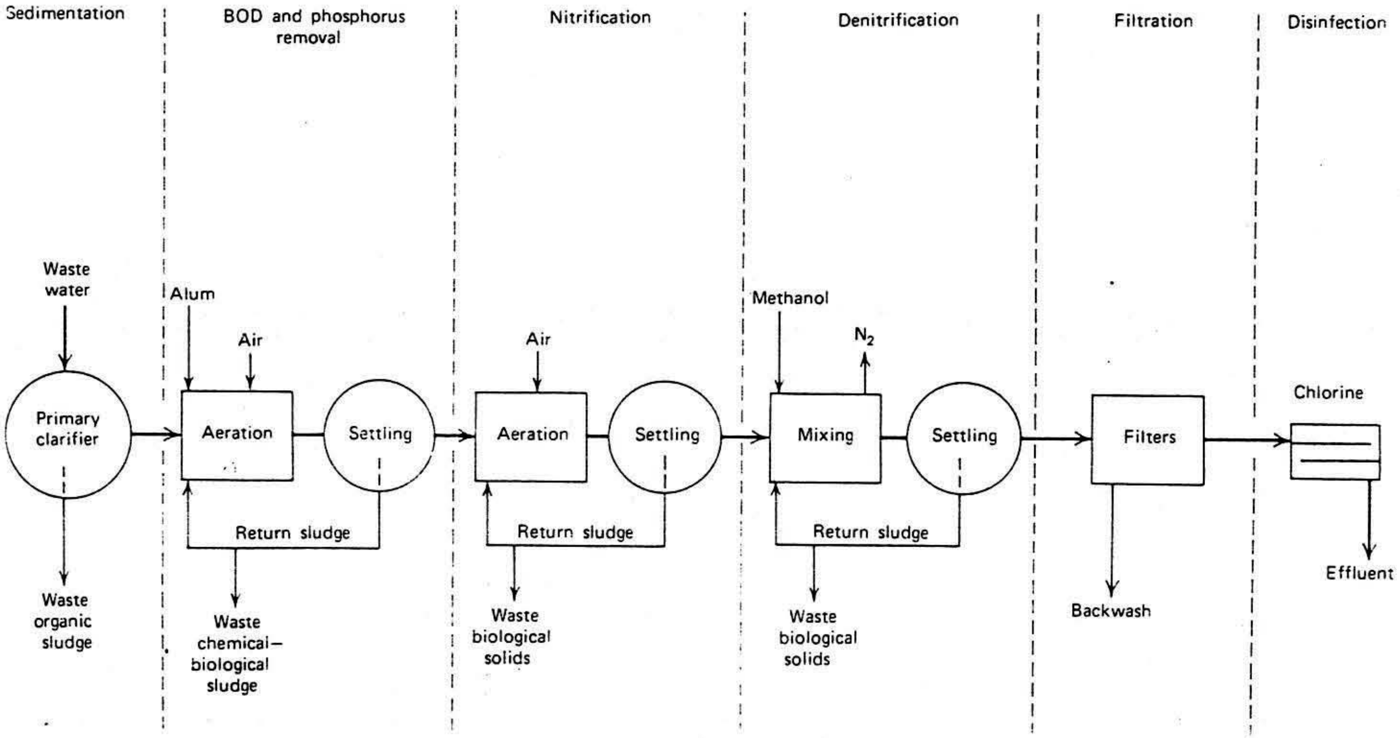

Figure 3-1 Three-sludge system schematic incorporating nutrient removal and final filtration. Organic matter is removed by primary settling and secondary activated sludge. Phosphorus is precipitated in the aeration secondary using a metal coagulant. Second-stage aeration converts ammonia to nitrate, and denitrification liberates nitrogen gas. Filtration removes nonsettleable solids and chlorination disinfects the plant effluent.

Nitrate is reduced to nitrogen gas by a variety of facultative bacteria in an anaerobic environment. An organic carbon source (AH_2 in Equation 3-4) is needed to act as a hydrogen donor, and to supply carbon for biological synthesis. Numerous reduced organic substances have been successfully tested as a carbon source, including acetic acid, acetone, ethanol. methanol, and sugar. Methanol has been preferred in most applications because it is the best expensive synthetic compound available that can be applied without leaving a residual BOD in the process effluent. However, this is not to imply that methanol treatment is cheap; it is estimated to contribute about one-half of the total costs of denitrifications. The recommended denitrification system consists of plug-flow basin with underwater mixers followed by a clarifier for sludge separation and returns. The level of agitation must keep the microbial floc in suspensions, but controlled to prevent undue aeration. Denitrification can also be accomplished in a submerged (anaerobic) filter; however, there are few data on field-scale studies as basis for design.

Nitrification-denitrification in a two stage system, proceeded by secondary biological treatment, should achieve 90 percent inorganic nitrogen reduction and 80 to 95 percent total nitrogen removal at design flows. Advantages of biological nitrogen removal are that the nitrification process can be built to meet a current requirement for ammonia removal, adding denitrification in the future if required. also system is adaptable as an addition to existing secondary treatment. (Hammer, 1977)

Biological nitrification satisfies the nitrogenous oxygen demand by converting NH_3 to nitrate. In some applications, such as discharge into enclosed bodies of eater or recycle to water supplies, nitrification may not be sufficient. When N_2 removal is required, one of the available methods is to follow biological nitrification with biological denitrification.

Denitrification is accomplished under anaerobic or near anaerobic conditions by bacterial commonly found in wastewater. Nitrates are removal by two mechanisms: (1) Conversion of nitrate to nitrogen gas by bacterial metabolism and (2) conversion of nitrate to nitrogen contained in cell mass which may be removed by settling.

In order to denitrification to occur, a carbon source must be added in sufficient quantity to provide for cell growth and to consume any DO which may be carried into the denitrification reactor.

Usually 3 to 4 pounds of methanol per pound of nitrate are required. A careful control of methanol feed is necessary to prevent waste of chemicals. In addition, if excess methanol is fed to the system, unused methanol will be carried out in the effect causing excessive BOD.

Denitrification may be carried out in either a mixed slurry reaction or in fixed load reactors. Denitrification filters carryout both denitrification and filtration in the same unit. Mixed slurry systems consist of a denitrification reactor, reaeration basin and clarifiers. Reaeration prior to clarification is required to free the sludge from trapped bubbles of nitrogen gas.

Denitrifying bacteria grow very slowly and are extremely sensitive to temperature. Denitrification rates have been shown to increase five-fold when the temperature is increased from 10 ^0C to 20 ^0C . Thus operating parameters such as sludge age and retention time must be varied with temperature.

The pH in denitrification systems must be carefully controlled. The optimum pH is from 6.0 to 8.0.

Denitrification is a very sensitive and difficult process to operate. Little full scale operational experience is available. Constant monitoring of pH methanol feed and temperature is essential to successful operation. (Manual of Instruction for Waste water Treatment Plant of Operators)

3.1.5.3 AMMONIA STRIPPING

Nitrogen removal from wastewaters may be accomplished by ammonia stripping. Ammonia stripping consists of:

1. Converting ammonia ion (NH_4^{+1}) To ammonia gas by raising the pH above 10.8.
2. Forming and reforming droplet of water.
3. Circulating large quantities of air to provide air water.

Ammonia stripping may be accomplished in a tower similar to a cooling tower. Stripping ponds utilizing sprays of water into the air may also be used.

The efficiency of ammonia removal in stripping towers is a function of:

1. Hydraulic flow rate
2. Air flow rate
3. pH
4. Temperature

The higher the air to water ratio, the better the ammonia removal. However, the higher the air to water ratio, the higher the capital and operating cost. Thus, stripping tower design consists of balancing two competing goals: good ammonia removal and economics. Stripping towers are generally operated at a hydraulic loading rate of 1 to 3 gpm/ ft^2 and air to water ratio of 300 to 500 cfm air per gpm water. Generally the towers are from 20 to 25 feet high.

Ammonia stripping is most effective at high temperatures. Efficiency is reduced as the temperature is lowered until freezing occurs and the tower no danger functions. For this reason ammonia stripping is most common in warm climates. (Manual of Instruction for Waste water Treatment Plant of Operators)

Ammonia can be air stripped from at an alkali pH of about 11, Equation 3-5. After lime treatment for precipitation of Phosphorus a waste water can be pumped to the top of a cooling tower and distribution over the column peaking (Figure 3-2). Forced air is drawn through the media to extract ammonia from the water droplets. The simplicity of the process makes it the least expensive method of denitrification where

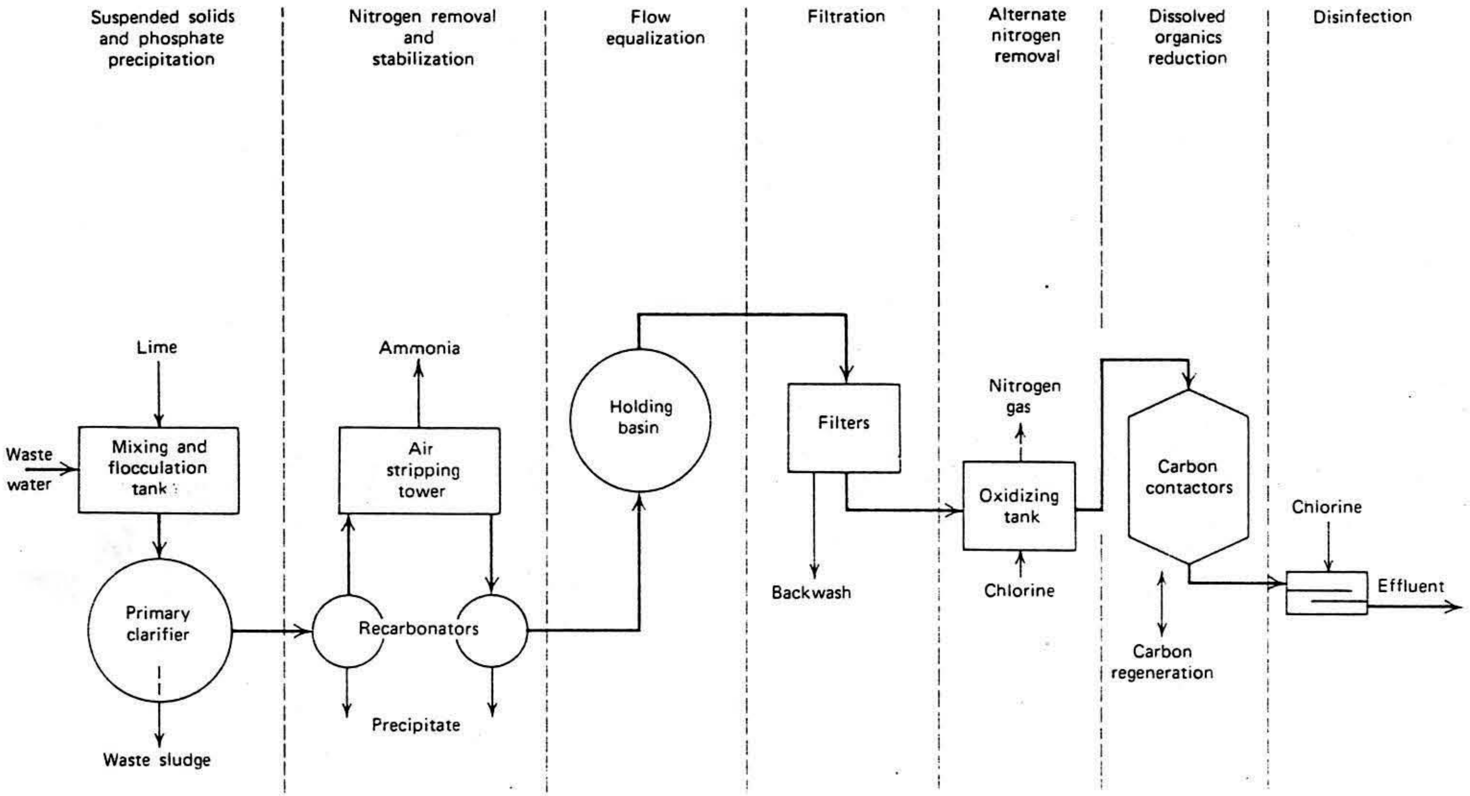

Figure 3-2 Schematic of physical-chemical treatment including various unit operations for different degrees of treatment. Primary lime application precipitates phosphorus and removes the majority of suspended solids and BOD. Air stripping, with backup breakpoint chlorination, extracts nitrogen. Flow equalization allows uniform operation of filters and contactors. Filtration removes nonsettleable suspended solids, and activated carbon columns reduces dissolved organics. Chlorination provides final disinfection.

pretreatment with lime is employed for phosphorus removal. At Lake Tahoe during warm weather, air stripping can achieve 95 percent removal of ammonia nitrogen at a pH of about 11.5 by using 3000 liters of air per liter of waste water.

$$NH_4^+ + OH^- \xrightarrow[\text{acidic}]{\text{basic}} NH_4OH \xrightarrow[\text{stripping}]{\text{air}} H_2O + NH_3 \qquad (3\text{-}5)$$

Several technical problems must be resolved, however, before air stripping of ammonia can receive wide application. Experience with packed cooling towers has revealed the following operational problems: scale formation on the tower packing that must be removed frequently by acid washing or mechanical scrubbing; ice formation in tower during the winter season; reduced removal efficiency because of increased ammonia solubility at low temperatures, possibly requiring tower heating during the winter; and the fact that nitrate nitrogen in adverantly produced in the biological pretreatment is not removed by air stripping. Attempts are being made to resolve the scaling problem by experimenting with media less susceptible to fine water spray to eliminate tower packing entirely. Inability to operate at ambient air temperatures below 0 ^{0}C may be solved during short periods of time by providing an alternate method, for example, break point chlorination, where weather is not serve, high pH holding ponds with long detention times and surface agitation are being studied. Climate may also limit the application of air stripping, since ammonia released to the atmosphere can be returned by rainfall. (Hammer, 1977)

3.1.5.4 BREAK-POINT CHLORINATION

When chlorine is added to water containing ammonia the following reactions occur:

$NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+$ (3-6)

$NH_2Cl + HOCl \longrightarrow NH_2Cl_2 + H_2O$ (3-7)

$NH_2Cl + HOCl \longrightarrow N_2 + 3HCl + H_2$ (3-8)
(under slightly alkaline conditions)

Large amount of chlorine is required. Experience shows that for a secondary effluent about 91 pounds of chlorine are required to remove 110 pounds ammonia.

The process is affected by pH, temperature, alkalinity and other chlorine demanding substances in the wastewater. Sufficient alkalinity is required to insure that highly odourous NCl_3 is not formed rather than nitrogen gas. Violent mixing is required to prevent formation of NCl_3 in local areas of low pH.

Hypochlorite is favoured are chlorine gas since the alkalinity consumed and the total dissolved solids produced are much lower for hypochlorite. (Manual of Instruction for Waste water Treatment Plant of Operators)

The chemistry of breakpoint reacts between ammonia and chlorine are not particularly well defined. Equation 3-8 is an unbalanced chemical reaction to illustrate the possible products formed in the oxidation of ammonia; in order of importance, these are nitrogen gas, nitrous oxide, and nitrite-nitrate nitrogen.

$$NH_3 + HOCl \longrightarrow N_2 + N_2O + NO_2^- + NO_3^- + Cl^- \qquad (3\text{-}8)$$

Weight ratio of chlorine to ammonia required for breakpoint chlorination of wastewaters have been reported as ranging from 8 to 1 to 10 to 1 as Cl_2 to N; the lower value being applicable for the most highly pretreated waste water. Tests have been shown that breakpoint chlorination in the pH range of 6.5 to 7.5 can yield 95 percent ammonia removal, and for initial ammonia nitrogen concentration of 8 to 15 mg/l, the nitrate and nitrogen trichloride residuals have never exceed 0.5 mg/l chlorinate is adaptable to physical chemical treatment, and the process is relatively inexpensive and easy to operate and control. One disadvantage to heavy chlorination is that essentially all of the chlorine added is reduced to chloride ions, thus contributing to dissolves solids unconcentration in the treated water. For example, at an 8 to 1 weight ratio, the oxidation of 20 mg/l of ammonia nitrogen contributes 160 mg/l of chloride ion. In many instances, something less than complete ammonia removal may be sufficient to meet the water quality objectives. However, at subbreakpoint levels the problems if they are discharged directly to receiving waters. Activated carbon in effective in destroying both free and combined residual of chlorine; therefore, one solution is to pass the treated water through carbon column. (Hammer, 1977)

3.1.5.5 ION EXCHANGE

Ammonia and nitrate ions are present in low concentrations relative to other ions in wastewater, and their behavior does not differ significantly. Consequently they are difficult to selectively extract by in exchange. In order for denitrogenation by ion exchange to be an economical process, materials of relatively high specification for the inorganic nitrogen are required. Since the cost of removal of all ions by demineralization is not feasible for municipal treatment. Currently, a specific ion exchange resin for the nitrate ion is not available, but for the ammonium ion, clinoptilolite has unusual selectives. It is a natural inorganic zeolite material currently available is small quantities. Research is underway in an attempt to develop a synthetic material.

Pretreatment prior to cation exchange involves clarification by chemical coagulation and filtration. Adjustment to pH 6.5 is necessary to convert ammonia to ammonium ion, since free ammonia does spent exchange material is regenerated with a lime slurry, which is subsequently air stripped discharging ammonia to atmosphere. Nevertheless this process of ammonium ion exchange is still experimental, and it is difficult to speculate as to its future applicable in removal of nitrogen from wastewater. (Hammer, 1977)

The use of anion exchange resin known as clinoptiolite for ammonia removal has been investigated. Removals upto 95 percent of the influent ammonia have been achieved. The resin is generated with a lime slurry containing some sodium chloride, operational problems consist of spent regenerate disposal and organic fouling of the resin. Considerable research is going on in this area and ion exchange is being designed into a small number of advanced treatment plants. (Manual of Instruction for Waste water Treatment Plant of Operators)

3.1.6 TREATABILITY OF WASTES

Often it is desired to know if an industrial waste is biologically treatable and know the ultimate BOD instead of the five day BOD. The procedure for obtaining an acclimated seed for the BOD test will usually be sufficient to determine if a waste will appear which will not yield an activated sludge. In order to determine the treatability of such a waste, the following procedure has been used successfully.

An activated sludge is built up on a readily degradable organic compound of similar chemical structure to the compounds in the waste. Sodium benzoate or Sodium acetate is used when the wastes contain simple hydrocarbons.

The activated sludge unit is operated on a once 9-day feed, fill-and-draw basis with no sludge wasting at an organic loading of 1,000 mg/liter. When the suspended solids reach 2,000 mg/liter the easily degradable organic is replaced with the waste. By the use of the dichromate chemical oxygen demand test (COD) it is possible to determine if the organic matter is being defrauded. If the COD does not decrease after a week's operation, the unit is restarted on the easily degradable organics. When the suspended solids have built back up to 2,000 mg/liter, 10 percent of the easily degradable organics are removed from the feed and substituted by 10 percent of the industrial wastes. The second day the ratio is changed to 30 : 70. In ten days the units should be converted the full waste load. While this procedure seems long it is often the only way to obtain an acclimated seed or unusual industrial wastes. A good example of this was in degradation of sulfanilic acid, Sulfanilic acid is not easily degraded biologically but it is possible to slow adapt a seed to metabolize this compound. A small laboratory activated sludge pilot unit is shown in Figure 3-3. (McKinney, 1962)

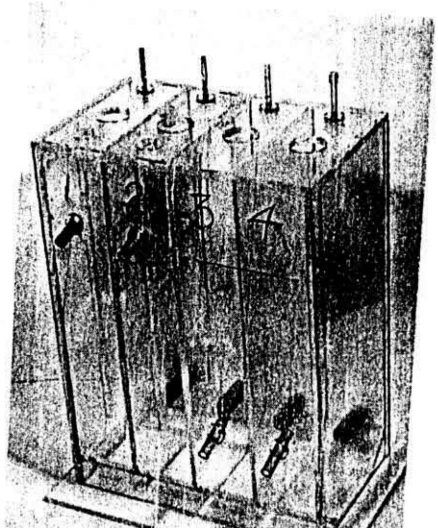

Figure 3-3 Small Plastic Laboratory Activated Sludge Pilot Unit for Use in Studying Treatability of Industrial Wastes.

3.2 WASTE DISPOSAL

3.2.1 DISPOSAL OF WASTEWATER

Municipal collecting and treatment systems must be protected against harmful substances in industrial wastewaters, among them (1) flammable or toxic wastewaters, (2) corrosive acids and other chemicals, (3) hot fluids that weaken pipe joints and accelerate undesirable chemical reaction, (4) flow-reducing heavy sludges and greases, (5) high hydraulic or organic loads, (6) toxic substances interfering with biological treatment, and (7) in relation to receiving waters, residues of these and other substances not removed in the treatment works. Communities regulate, by ordinance, what waste matters are allowed to be emptied into wastewater conduits. High flows or excessive loads of suspended solids, organic contaminants measured as BOD, or Chlorine-consuming chemical are accepted by some municipalities at a surcharge over the normal system-use fee.

Most industries like to be connected to municipal wastewater systems: pretreatment, simple or elaborate, can often make their wastewaters acceptable. It is a simple matter to neutralize acids, skimoff oils, strainout coarse solids or settle finer ones, and cool hot liquids. Even when more complicated techniques are necessary, the cost of purification is generally less than for direct discharge to natural water courses.

Industrial plants situated in rural areas or in small towns with treatment plants that can not handle the hydraulic or pollutional loads of the manufactories must be prepared to collect, treat, and dispose of their wastewaters themselves. Long cities, too may require separate treatment for technical and political reasons. Wastewater releases to receiving waters then become subject to regulation by responsible government agencies. Industries near to dewater may be able to discharge their wastewaters to ocean under less stringent rules than normally apply to inland waters.

Underground disposal of wastewater is costly. Geological formations must be able to disperse the wastewaters yet protect higher-lying fresh-water sources against contamination. The wastewater must be clean enough to along the underground formations, be relatively free from unneutralized acids and their chemicals that might attack well equipment or the minerals composing the geological formations, and be unable to supply nutrients to biological growths. Wastewaters disposal of in this way include brines and other strong inorganic liquors from chemical plants and strong organic and toxic fluids from pharmaceutical industry.

Strong industrial wastewaters can be held long enough in large earth basins or lagoons diked off from receiving waters to be emptied into the receiving waters only when they are flood stage. In arid regions wastes may be ponded for natural evaporation of liquids and consolidation of solids. (Fair, Gordon, Mskew & Others, 1967)

3.3.2 DISPOSAL OF WASTEWATER SOLIDS

Waste slurries and sludges are normally deposited on land or discharged into the sea. Only a rarely and under unusual circumstances are they introduced into following streams or standing bodies of fresh water. Stable industrial slurries can be mounted or close-by cheap land. Putriscible or other noxious wastes must be buried or covered with earth, as in sanitary land fills. The danger of soluble components leaching from them into surface streams or underground aquifers must not be overlooked.

For more convenient handling and conservation of space, waste solids may be dewatered. Combustion destroys putriscible solids and further simplifies disposal. Whether incineration can change the leaching properties of solids depends on their nature. Objectionable features of disposal on land are odourous and dusty dumps, quagmires of men drying sludge, and potential harm to persons or to animals by corrosive contact or toxicity.

CHAPTER 4

STUDY ON BEXIMCO PHARMA

4.1 LOCATION

The factory of Beximco Pharmaceutical Ltd. is situated at 109, Auspara, Mouza - 128, Kathalia, Police station - Tongi, Dist.- Gajipur, Bangladesh. The location of factory is shown in Figure 4-1. Surface drain lies adjacent to the front i.e. east side of the factory and main road from Dhaka - Mymensingh highway named Squib road is on its south side. There is a canal on south side of the road which carry pharmaceutical waste to the river. A branch road from squib road move around the east side to half of the north side of the factory. There is residential area on south sides of the factory and there is a pond on west side of the factory. There are three Pharmaceutical industry including above beside the Squib road lying very close with each other. Squib (now closed) is on the South-West side of Beximco Pharmaceutical, and Ciba-Geigy is on the West side of the Squib. Among them pollution load is maximum from Beximco Pharmaceutical Plants in production of basic raw materials. Others produce only formulated medicine which cause less pollution load.

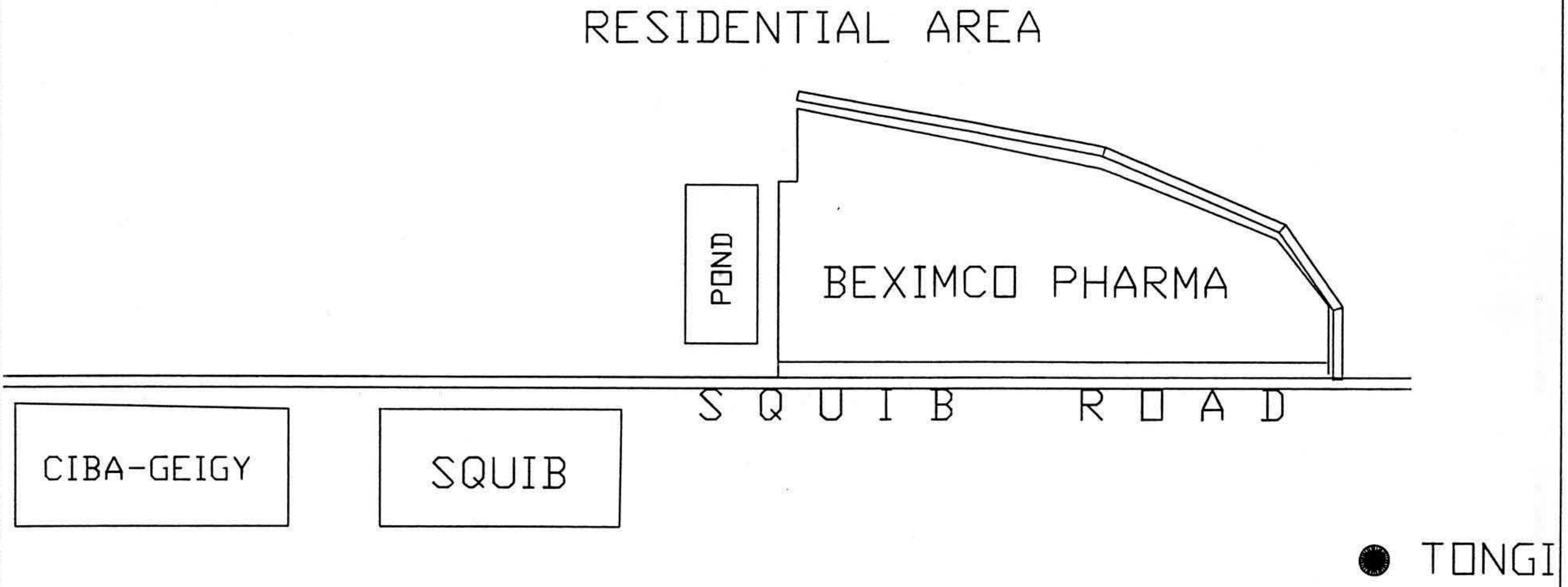

Figure 4-1 Location Map of Beximco Pharma

4.2 (TYPES OF LIQUID WASTE

There are mainly three types of liquid waste discharged by Beximco Pharmaceuticals from the following three plants.

1) I.V. Solution Plant - Intervainous solution is produced from this plant. The liquid waste from the plant is factory washing water and process water containing salt and discharge.

2) Paracetamol Plant - Raw materials for Paracetamol are produced from this plant. The liquid waste from this is washing water and process water of low pH.

3) Basic Raw Materials plant - Bulk raw materials e.g. Amoxyline, Ampicillin e produced from this plant. The liquid waste discharged from this plant is highly pollutant such as high in colour, odour, ammonia nitrogen, total solids; low pH and dissolve oxygen.

Other liquid waste discharged are mainly domestic and washing water from other plants which produce only formulated medicine.)

4.3(EXISTING TREATMENT FACILITIES

All the waste except from Paracetamol plant and Basic raw materials plant are discharged to the surface drain without any treatment. The waste from Paracetamol plant is of low pH. So they add lime to neutralize it and discharged to the surface drain. The waste from Raw materials plant is treated as following process.

After closing the discharge valve of the reactor the reactor is filled by using a pump. After filling the reactor inlet valve is kept close and mixing is started. Temperature of the reactor is raised to 90 ^{0}C with steam and kept for one hour.

Caustic soda solution (2 kg caustic soda is dissolved in 50 liter) is added to the reactor and heating is continued for 24 hours at 90 ^{0}C. Then 50 gm of $CuSO_4$, $5H_2O$ is added in the reactor. Valve for air entrainment is opened and pressure is adjusted at 2 kg/ cm^2 by operating a valve through opening. After adding $CuSO_4$, $5H_2O$ the temperature is maintained at 90 ^{0}C and pressure of 2 kg/ cm^2 for 2 hours.

Then pressure is released slowly and liquid in the reactor is discharged in tank-2. The following steps of treatment is given in Figure 4-2.

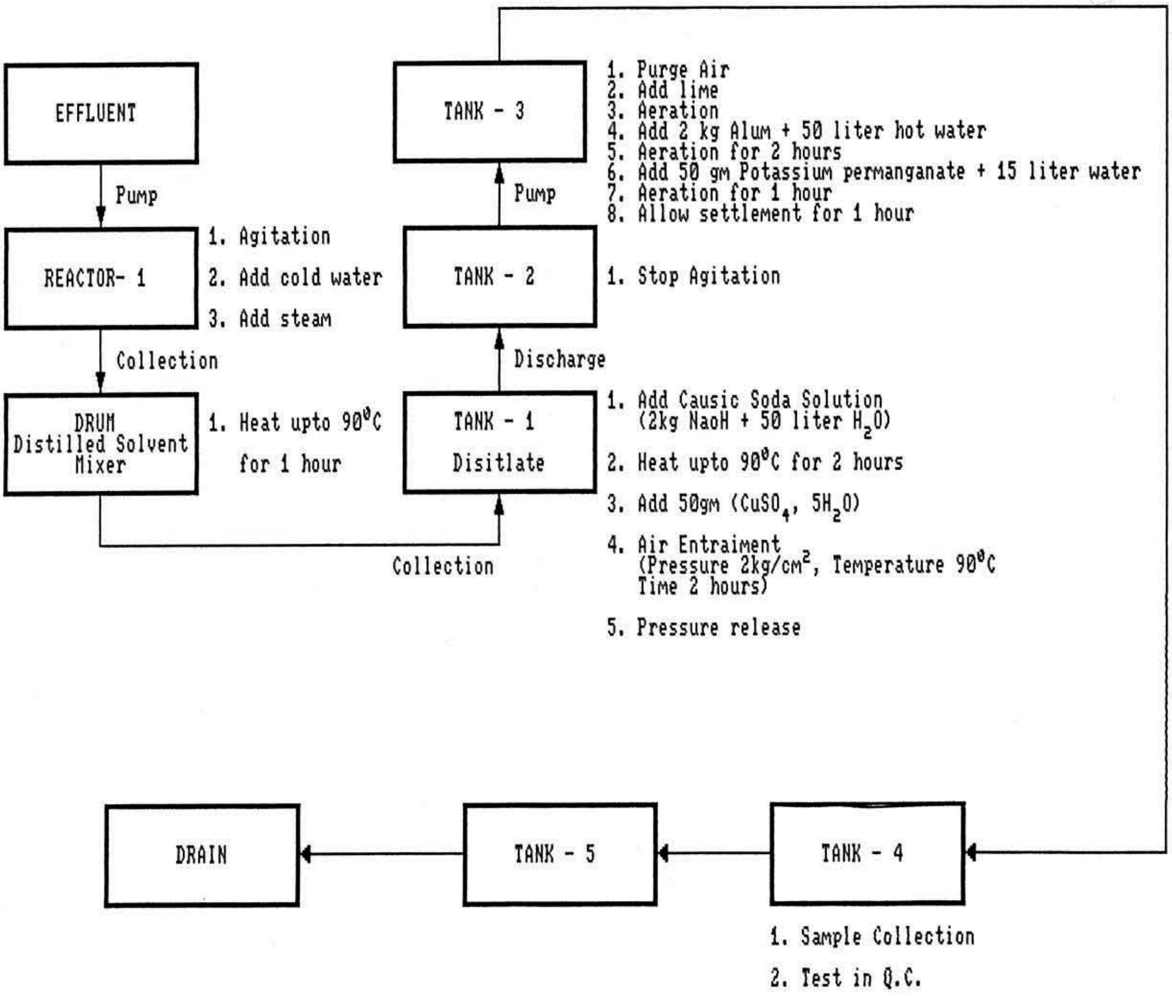

Figure 4-2 Treatment layout of liquid waste from basic raw materials of Beximco Pharma.

So it is found that the existing treatment method is lengthy, complicated and costly. In this treatment they adjust pH only. Other pollution parameters are neglected. In treated effluent there are ammonia nitrogen, suspended solid total solids and colour in high amount.)

4.4 DISPOSAL OF LIQUID WASTES

All the treated waste from Basic raw materials and Paracetamol plant and other untreated waste are discharged to the surface drain (Figure 4-4) which carry the waste to the canal situated of the South side of the factory. The canal carry the waste to the river Turag.

The wastes from three pharmaceutical industries (Beximco, Squib, Ciba-Geigy) are discharged to the canal nearby which is shown in Figure 4-5. In dry season there is no water in the canal. So the waste water is leached to the ground water which may pollute the groundwater. The solids left on the surface make the soil unsuitable for cultivation. In monsoon heavy rainfall may cause harmful effect on the aquatic life of ponds(Figure 4-6) nearby due to overflooding the surface drain. The water containing the pharmaceutical wastes discharged to the Turag river which may produce pollution load in the river water. Objectionable odour from liquid waste may cause nuisance. The photographs of Main gate of Beximco Pharma and its surroundings are given below.

4.5 ANALYSIS OF LIQUID WASTE

As mentioned earlier liquid waste from I.V. Solution plant contain salt and dextrose and from Paracetamol plant is acidic. The waste from Basic raw materials is highly pollutant. So it is given preference to analyze liquid waste from Basic Raw materials.

4.5.1 SAMPLE COLLECTION

Raw effluent of Beximco Pharma is accumulated in a masonry tank. After treating the effluent is collected to another masonry tank from this tank the effluent is discharged to the surface drain. Raw and treated effluents of the above two tanks were collected for the analysis of Beximco Pharma liquid waste. Samples were collected on several times. In each time two 20 litre plastic jars were used.

4.5.2 CHARACTERISTIC MEASURE

In order to ascertain the treatability pollution effect of the pharmaceutical liquid waste the characterstic parameters should be measured. The important characterstics of the sample are pH, colour, turbidity, total solids, suspended solids, ammonia nitrogen, BOD, COD.

With open eye it was found that the colour of raw sample was yellow and colour of treated sample was straw. After opening the cap of the container there was a odour of ammonia in both sample. pH and colour were measured eloctrometrically. Turbidity was measured by Turbidimeter. Ammonia nitrogen was measured by Nessler method. But BOD and COD could not be measured due to high colour and ammonia content. After testing the samples in the laboratory following charecterstics are found:

Table 4-1 Charecterstics of liquid waste from Basic raw materials plant of Beximco Pharma.

Charecterstics	Raw Effluent	Treated Effluent
pH	4.75	7.55
Turbidity, NTU	5.8	7.0
Ammonia, nitrogen, mg/l	1820	1400
Colour, mg/l	55	500+
Odour	odour of ammonia	odour of ammonia
TS, mg/l	1414	1848
SS, mg/l	--	1678
*BOD	--	--
*COD	--	--

* Due to high colour and ammonia content it is not possible to measure BOD and COD.

From Table 4-1 it is found that the pH of raw sample is very low. From Figure 4-1 it is found that addition of lime and caustic soda raised pH but addition of $CuSO_4$ makes pH low. However pH is increased from 4.75 to 7.55. Turbidity of raw sample is 5.8 but turbidity of treated sample is 7. Turbidity is increased due to addition of chemicals in their treatment process. The amount of ammonia nitrogen of raw sample is 1820 mg/l and that of treated sample is 1400 mg/l. The allowable limit for survival of aquatic life in water body is 0.5 mg/l (Hoq, 1989). The treated sewage is also harmful to aquatic life. The colour is increased in treated effluent. Total solids and suspended solids are also increased due to different chemicals used in treatment process. BOD and COD could not be measured due to high colour and ammonia nitrogen. The comparison with other pharmaceutical wastes are given in the following section.

4.5.3 COMPARISON OF CHARACTERSTICS

The comparison of characterstics of liquid waste of Beximco Pharma with a pharmaceutical industry in India and I.C.I. Pharmaceutical Industry in Bangladesh is shown in Figure 4-7 to 4-9.

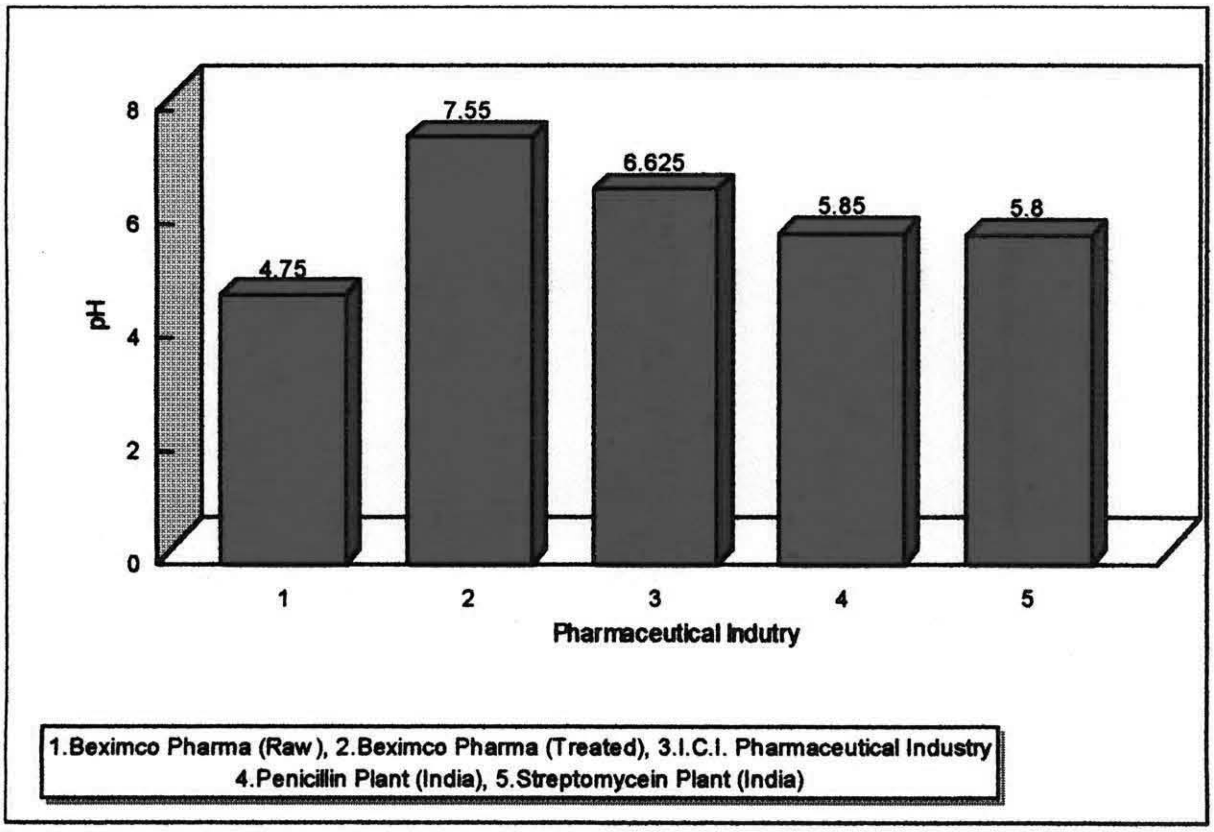

Figure 4-7 Comparison of pH of Waste Water from Different Pharmaceutical Industries.

From Figure 4-7 it is found that pH of raw sample in Beximco Pharma is the lowest. But pH of treated sample is almost neutral.

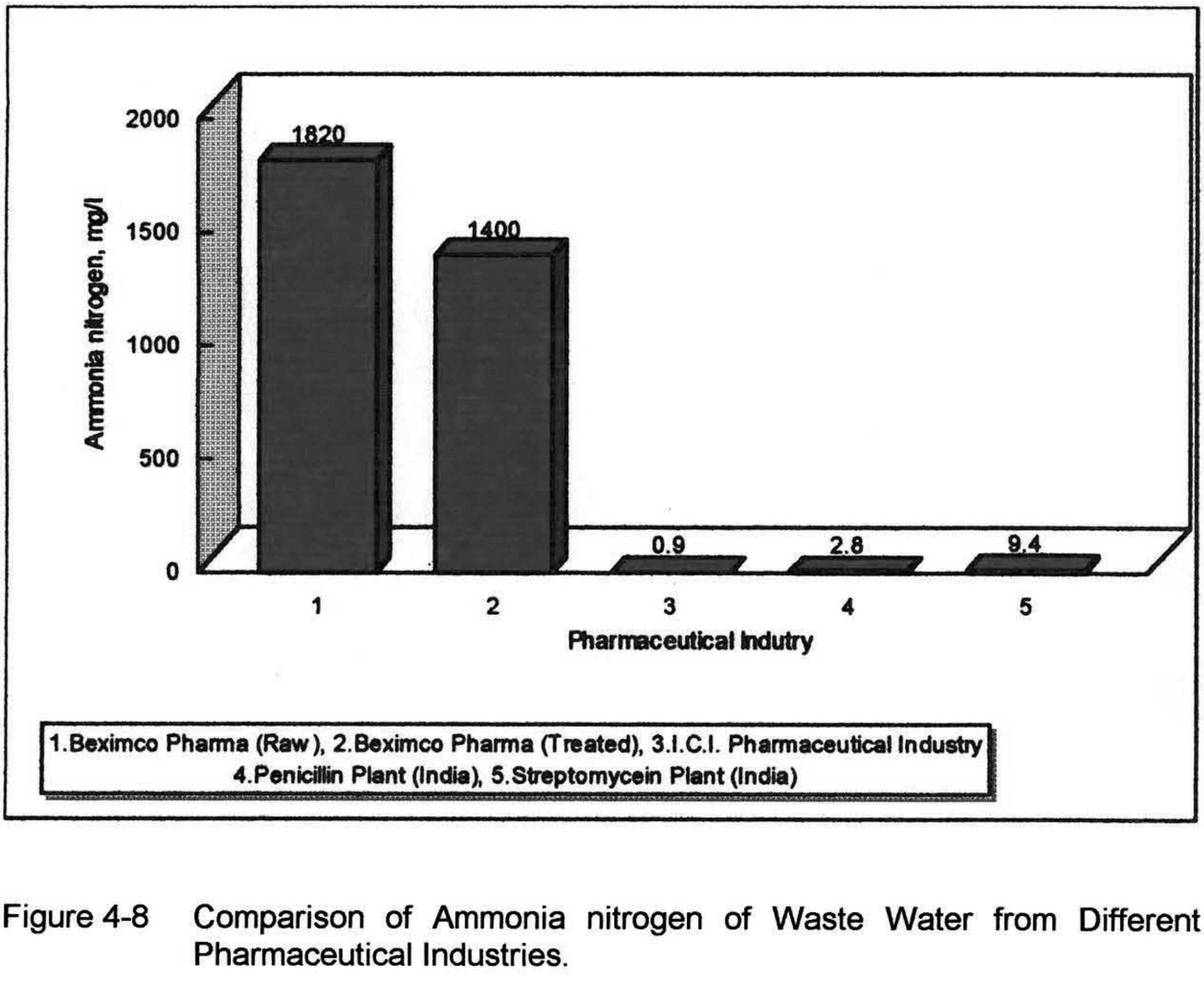

Figure 4-8 Comparison of Ammonia nitrogen of Waste Water from Different Pharmaceutical Industries.

From Figure 4-8 it is found that the amount of ammonia nitrogen in both raw and treated samples of Beximco Pharma is much more than the others and also much more than the allowable limit (0.5 mg/l) for survival of aquatic life (Haq, 1979).

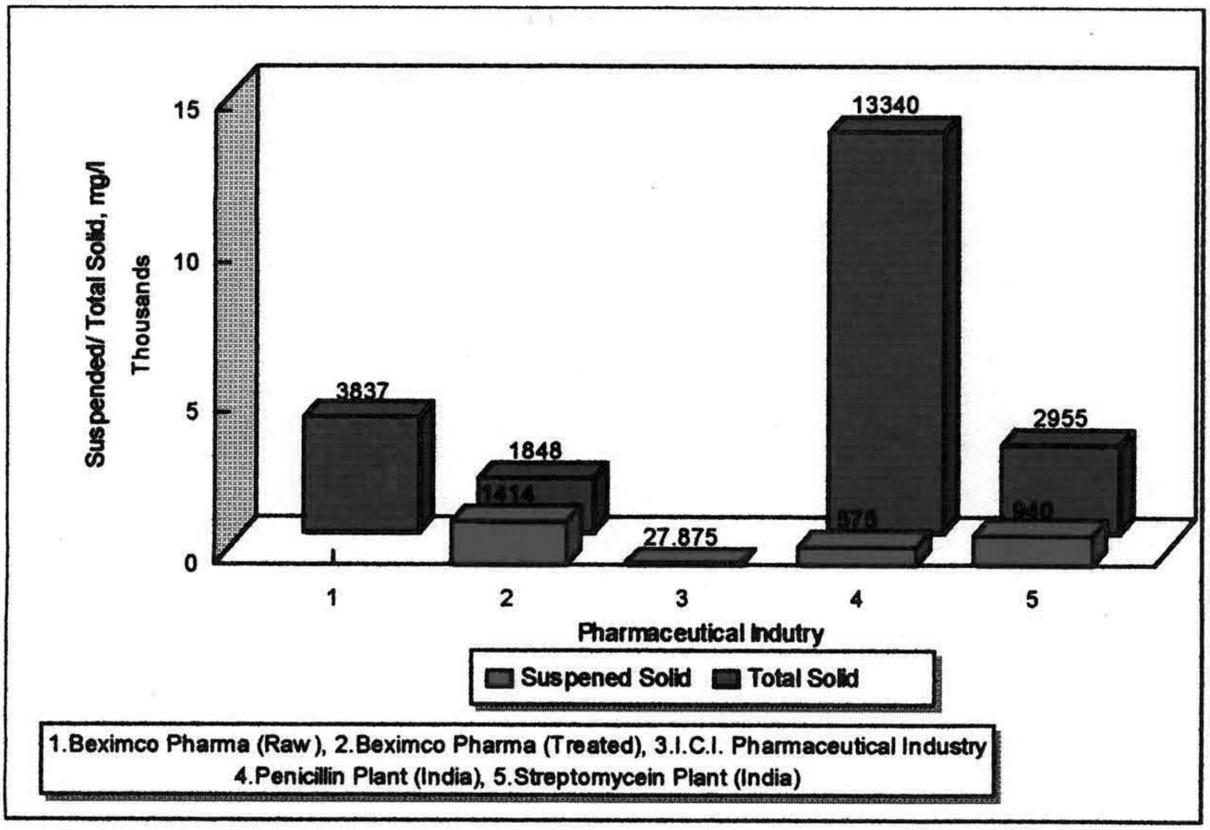

Figure 4-9 Comparison of Suspended and Total Solids of Waste Water from Different Pharmaceutical Industries.

From Figure 4-9 it is found that the amount of suspended and total solids of Beximco Pharma are maximum from other industries.

4.5.4 TREATMENT OF LIQUID WASTE

4.5.4.1 GENERAL

Attempts have been taken to adjust pH of raw sample and to reduce ammonia nitrogen level of the Beximco Pharma. The treatment methods are Alkali Treatment, Aeration, Boiling, Sedimentation with Coagulation, Chlorination, Biological Treatment by adding domestic sewage and dropping waterhyacinth.

4.5.4.2 ALKALI TREATMENT

200 ml of raw sample is taken in a flask. 0.1(N) NaOH solution from burette was added to the flask and pH was measured and amount of NaOH used was recorded. This was repeated until pH is reached beyond 7. 50 ml 0.1 (N) NaOH solution was required to make PH 7.

Again 200 ml of raw sample was taken in a flask. $Ca(OH)_2$ solution (10 mg/l) from burette was added to the flask and pH was measured and amount of $Ca(OH)_2$ used was recorded. This was repeated until pH is reached beyond 7.

Comparison of pH adjustment of pharmaceutical raw samples by using NaOH and $Ca(OH)_2$ solution is shown in Figure 4-10.

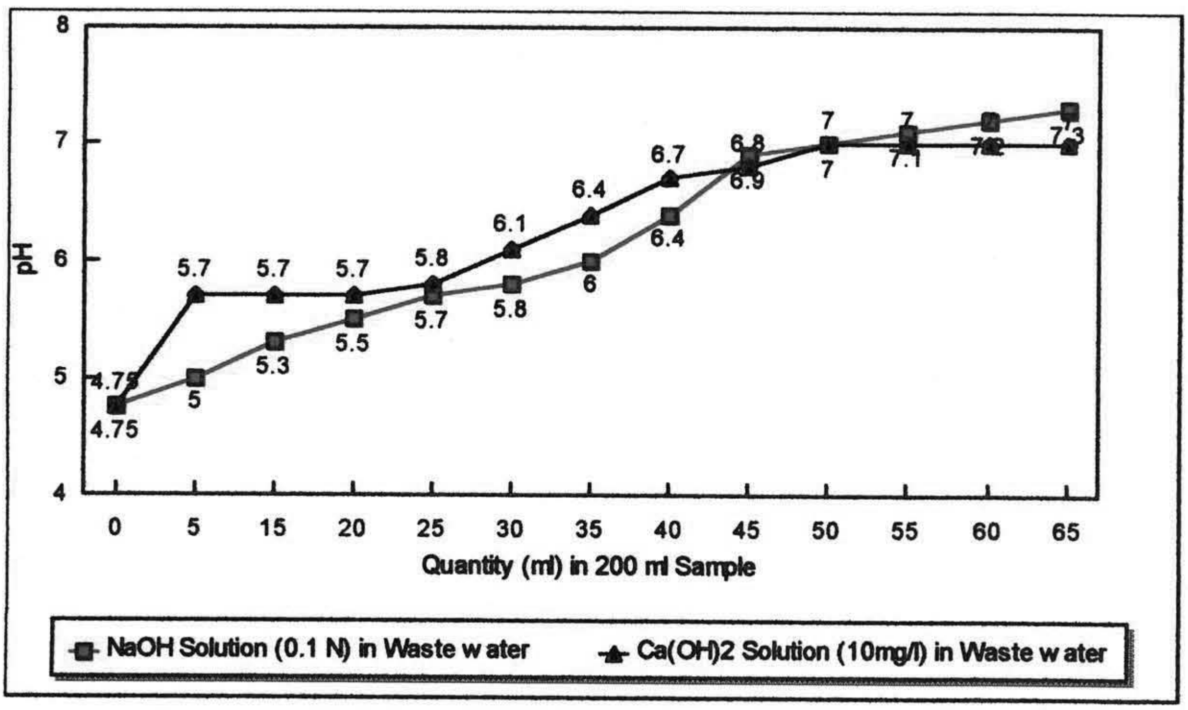

Figure 4-10 Comparison of pH Adjustment of Pharmaceutical Raw Samples by using NaOH and $Ca(OH)_2$ Solution.

4.5.4.3 AERATION

From Table 4-1 it is found that ammonia nitrogen is much more in both raw and treated samples. In order to reduce ammonia nitrogen according to the section 3.2.6.3 500 ml raw sample was taken in a jar and air is introduced in the sample by air compressor through a pipe of 6 mm diameter opening for 1 hour. Then the ammonia nitrogen was measured. It was found 1810 mg/l. So reduction is 0.54 % only. This may be due to low pH (4.75).

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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (4\text{-}1)$$

At pH levels above 7, the equilibrium is displaced to left; at levels below pH 7, the ammonium ion is predominant.

Again,

$$NH_4OH \xrightarrow[\text{at basic pH}]{\text{air stripping}} NH_3 \qquad (4\text{-}2)$$

In order to follow the equation (4-2) 200 ml sample was taken in a beaker and 0.1 (N) NaOH was added until pH reach beyond 7. Then air was introduced in the sample by air compressor through a pipe of 6 mm diameter opening for 1 hour. Then the ammonia nitrogen was measured. It is found 1610 mg/l. So reduction is 11.54 % only. There are many reasons for less ammonia reduction. Ammonia stripping may be accomplished in a tower similar to a cooling tower. The higher the air to water ratio, the better the ammonia removal. Ammonia stripping is most effective at higher temperature (Mannual of Instruction for Wastewater Treatment Plant of Operators). Besides this some compounds are used by Beximco Pharma which is unknown to us as their business secret. And these compounds may bound ammonia nitrogen which is not released by aeration.

4.5.4.4 BOILING

200 ml raw sample was taken and $Ca(OH)_2$ solution (10 mg/l) was added until pH reach beyond 7. Then sample wasbeing boiled. But tremendous odour was emitted during boiling. So after 10 minutes boiling waas stopped and ammonia nitrogen was measured and it was found as 1810 mg/l.

According to Equation 4-2 ammonia is in gaseous state at basic pH and ammonia is released to air when boiling. But ammonia nitrogen reduction is 0.54 % only. The reason may be the presence of some compound which may bound the ammonia nitrogen or nitrogen in the sample may exist in complicated form.

4.5.4.5 SEDIMENTATION WITH COAGULATION

In order to treat the raw effluent as per section 3.1.4, six samples of raw effluent each containing 500 ml were taken in six beaker. Alum solution (5 gm/ liter) was added to six samples in different doses such as 6 ml, 8 ml, 10 ml, 12 ml, 14 ml, 16 ml and pH was maintained at 7.1 in all cases. Then flocculation was applied by 1 minute rapid mixing (25rpm) and 15 minutes slow mixing (45rpm) with slow mixing paddles. Then the samples were kept rest for sedimentation. Next day turbidity of each sample was measured by turbidimeter. The results are shown in Figure 4-11.

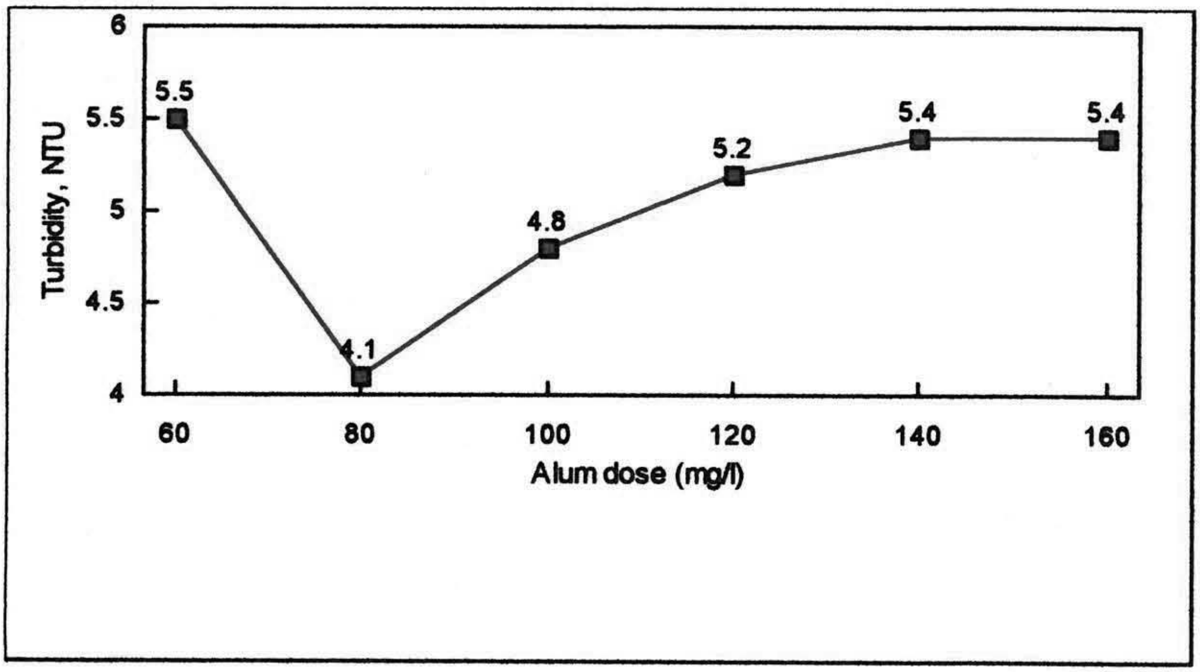

Figure 4-11 Optimum Alum Dose in Pharmaceutical Waste

From Figure 4-11 it is found that optimum alum dose to reduce turbidity is 80.0 mg/l and turbidity is reduced 29.31%. After coagulation and sedimentation for 1 hour the supernants were filtered. The results of residual turbidity and colour are given in Figure 4-12 and 413.

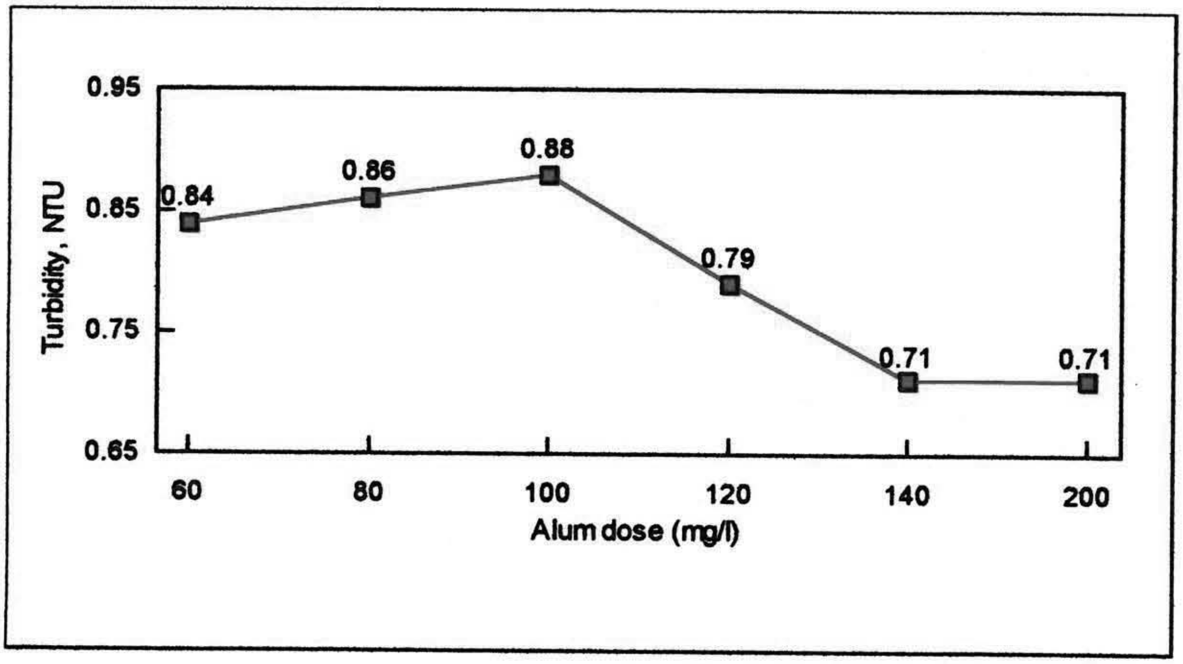

Figure 4-12 Optimum Alum Dose after Coagulation and Filtration at pH 7.1 (on the basis of Residual Turbidity)

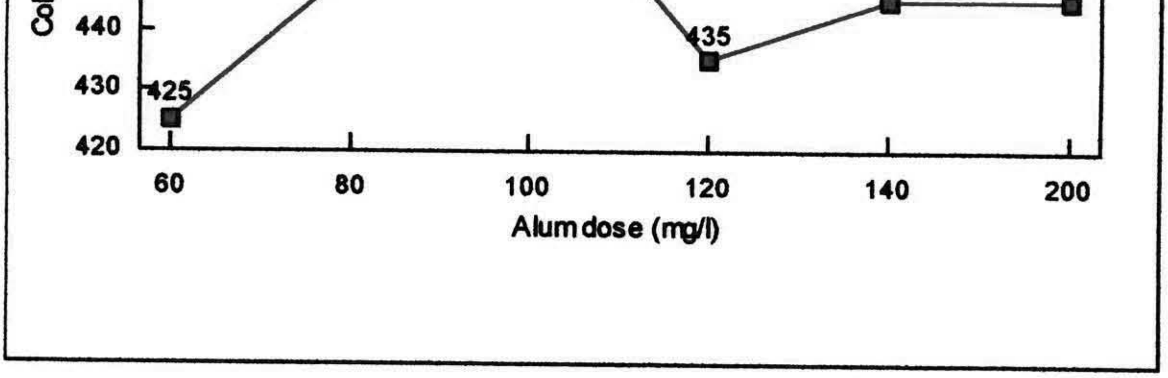

Figure 4-13 Optimum Alum Dose after Coagulation and Filtration at pH 7.1 (on the basis of Colour)

From Figure 4-12 it is found that the turbidity is reduced from 5.8 to 0.71. So reduction is 87.76 percent and optimum dose of alum is 140.0 mg/l .But the colour of sample were varied with different dose of alum. Ammonia nitrogen were measured and obtained 1810 mg/l in all cases.

4.5.4.6 CHLORINATION

Raw sample was diluted to 100 times. 1.0 mg/l of bleaching powder was added to diluted sample and stirred for 30 minutes. Then ammonia nitrogen of the mixed sample was measured and obtained as 1810 mg/l. Though chlorination is effective in removing ammonia (as described in section 3.1.5.4), in this case it did not work.

4.5.4.7 BIOLOGICAL TREATMENT

4.5.4.7.1 Adding Domestic Sewage and Aeration

The sample was diluted 10 times and pH was adjusted to 7.0. 100 ml domestic sewage was added to 5000 ml diluted sample and air was introduced in the solution by a compressor for 13 hours. Ammonia nitrogen were measured after 6 hours and 13 hours aeration and found 177 in both cases , i.e. reduction in this case is 2.75 %.

4.5.4.7.2 Dropping Waterhyacinth

Five samples each containing 2 liter with different dilution as 1, 2, 10, 100, 1000 times were taken in five jars and waterhyacinths were dropped in each jar. The effect on waterhyacinths were observed during 25 days. On several days samples were collected from the jar and ammonia nitrogen was measured. The observations and measure of ammonia nitrogen are shown in Table 4-2.

Table 4-2 Ammonia Nitrogen Reduction by Dropping Waterhyacinth

Sample	Dilution (times)	Day	Ammonia (mg/l)	Observation on Waterhyacinth
1	1	1st	1820	Leaves start bend down after 4 hrs
		2nd		Completely dead
		3rd	1740	
2	2	1st	910	Leaves start bend down after 4 hrs
		3rd	910	Completely dead
3	10	1st	182	Leaves start bend down after 5.25hr
		3rd	182	
		5th	185	
		8th		Completely dead
		9th	198	
4	100	1st	18.2	
		3rd	18.2	
		4th	18.2	
		22nd		Completely dead
5	1000	1st	1.82	
		3rd	1.70	
		5th	2.00+	
		25th		No change

From above Table it is found that on 3rd day ammonia nitrogen is reduced. After 3rd day ammonia nitrogen is increased. This is due to water reduction by vaporization and photosynthesis by waterhyacinth. Waterhyacinth can not live in upto 100 times dilution (ammonia nitrogen content is 1.82 mg/l). The survivality of waterhyacinth against ammonia content is shown in Figure 4-14.

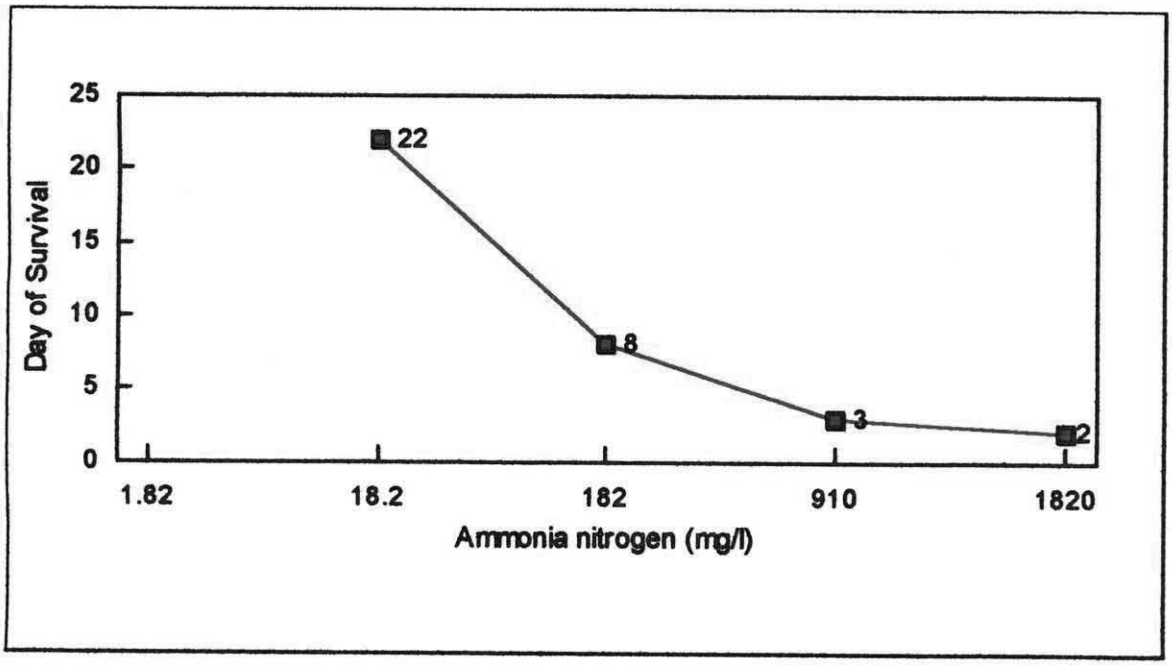

Figure 4-14 Survivality of Waterhyacinth Against Ammonia nitrogen

4.5.5 EXPERIMENT ON FISH

Alive fishes were dropped in five jars as describe in section 4.3.4.2.7 and observation on fishes were taken. The observations are listed in Table 4-3.

Table 4-3 Effect of Pharmaceutical Effluent on Fish

Sample	Dilution (times)	Ammonia nitrogen (mg/l)	Day	Observation on fish
1	1	1820	1st	Can not survive
2	2	910	1st	Can not survive
3	10	182	1st	Can not survive
4	100	18.2	1st	Can not survive
5	1000	1.82	1st	Survive
			20th	Survive

From the above Table it is found that fish can survive in the water containing ammonia nitrogen 1 ppm. The allowable limit of ammonia in waste water for survival of aquatic life is 0.5 ppm (Haq, 1979).

4.6 SUMMARY OF DISCUSSIONS

After laboratory analysis it is found that ammonia nitrogen is the leading pollution potential of the liquid waste of Beximco Pharma. Different methods as per section 4.3.2.2 to 4.3.2.7 are applied to reduce ammonia nitrogen. The Comparative results are shown in Figure 4-15.

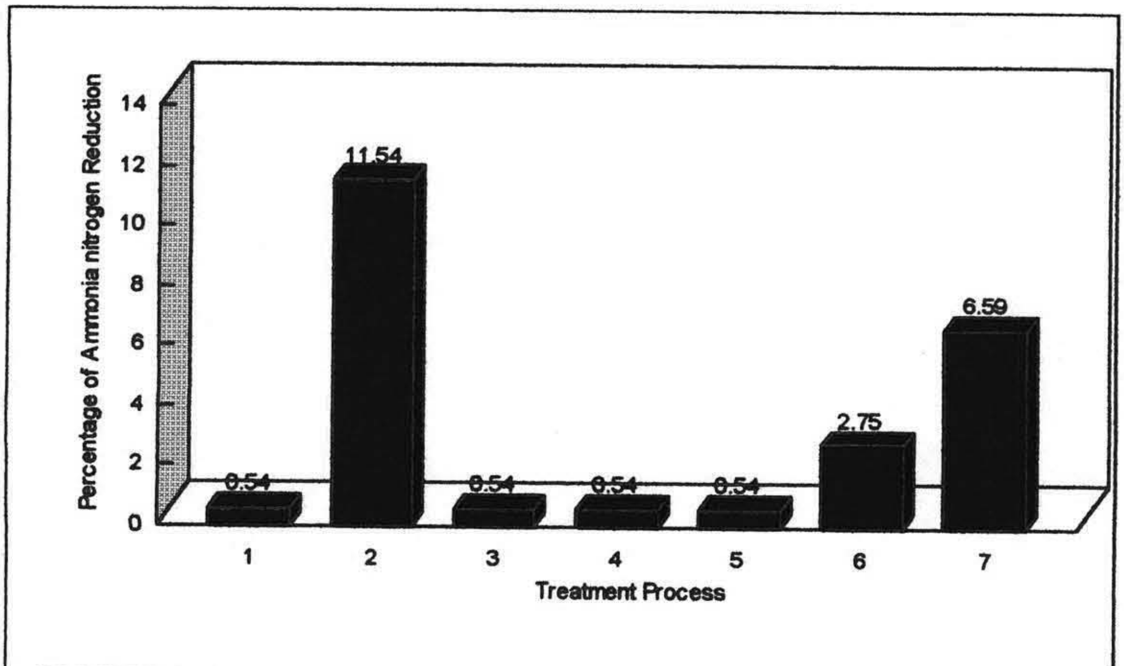

Figure 4-15 Comparison of Ammonia Nitrogen Reduction in Various Process.

The existing treatment procedure is lengthy, complicated and costly. Also from Table 4-1 it is found that after treatment turbidity, colour , total solid and dissolve solid are increased and amount of ammonia nitrogen is slightly reduced but concentration is very high. From Figure 4-9 it is found that aeration at basic pH is the most effective method for ammonia nitrogen reduction. Ammonia nitrogen reduction may be increased by using cooling tower and raising pH more. Second effective method is dropping waterhyacinth (considering raw sample). It may be applied by discharging wastewater to a pond filled with waterhyacinth and which is not used by households or there is no fish in it. Third effective method is adding domestic sewage and aeration. This method may be applied by mixing pharmaceutical liquid waste with domestic sewage and then discharged. Other methods are not suitable for ammonia nitrogen reduction. The existing treatment process followed by Beximco Pharma is complicated, lengthy and costly. Also the treated wastewater contains ammonia nitrogen in high amount which is harmful to aquatic life of natural stream. After experiment we found that 1000 times dilution of the waste is not harmful effect to fish. However extensive analysis should be needed. Beximco Pharma did not leak out the name of the chemicals used due to their business secrecy. So after knowing the name of chemicals and extensive chemical analysis it is possible to determine the nitrogen in various form and which compound inhibit to release ammonia nitrogen. And it will be possible to reduce ammonia nitrogen more effectively

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

On the basis of discussion mentioned above the following conclusions may be drawn from the study:

1. Amount of ammonia nitrogen is much more in both raw and treated liquid waste of Beximco Pharma.

2. Fishes can not survive up to 100 times diluted liquid waste (ammonia nitrogen 18.2 mg/ l) of Beximco Pharma. Fish can survive in 1000 times diluted liquid waste (ammonia nitrogen 1.82 mg/l) for more than 20 days.

3. Waterhyacinth can not survive in raw or existing treated liquid waste of Beximco Pharma. In 1000 times diluted liquid waste (ammonia nitrogen 1.82 mg/l) water hyacinth can survive for more than 20 days.

4. General methods such as aeration, sedimentation witrh coagulation, boiling, chlorination, adding domestic sewage and dropping waterhyacinth are not effective to remove the ammonia nitrogen of liquid waste of Beximco Pharma.

5.2 RECOMMENDATION FOR FUTURE WORK

Following recommendation are made for further study in this fields.

1. Extensive chemical analysis of the pharmaceutical liquid waste should be needed. Different chemicals used in production process should be identified and accordingly suitable treatment process should be followed.

2. Similar Study will be needed for other Pharmaceutical Industries in Bangladesh.

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