EFFECT OF CHLORINATION ON WASTE WATER QUALITY PARAMETERS AND FORMATION OF TRIHALOMETHANES

A DISSERTATION

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in
ADVANCED CHEMICAL ANALYSIS

By

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CERTIFICATE

It is certified that the Dissertation report entitled "**EFFECT OF CHLORINATION ON WASTEWATER QUALITY PARAMETERS AND FORMATION OF TRIHALOMETHANES**" is the result of work carried out during the period of July, 2011 to June, 2012, by Bhanu Pratap Singh Gangwar, Department of Chemistry, Indian Institute of Technology Roorkee, under my supervision. His work neither in part nor in whole has been submitted for any other degree.

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the project entitled "**EFFECT OF CHLORINATION ON WASTEWATER QUALITY PARAMETERS AND FORMATION OF TRIHALOMETHANES**" in partial fulfillment of the requirements for the award of the degree of Masters of Technology submitted in the Department of Chemistry, IIT Roorkee is an authentic record of my own work carried out during the period from July, 2011 to June, 2012 under the supervision and guidance of Dr. Naseem Ahmed.

The matter embodied in this project work has not been submitted for the award of any other degree.

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Abstract

The behavior of COD, BOD, TOC and ammonical nitrogen of secondary effluents under varied concentration of chlorine was investigated. The three parameters (mainly) were measured in final effluents treated with different chlorine dosages in the range of 1-50 mg/L and 30 min contact time. Chlorine dosages above 10 mg/L resulted in increased BOD and COD level of the effluent, with chlorine dosages above 40 mg/L resulted in almost double the original BOD and COD values. TOC measurements showed obvious stability against chlorine impact, which makes TOC a better indicator for the organic contents of wastewater. Almost all the observed increase in BOD measurements could be attributed to modification of dissolved part of the organic matter by chlorine .The results also show that the response of BOD and COD to chlorination is a function of chlorine dosage and the organic content of wastewater. But chlorination of raw samples did not show the same degree of influence on BOD, COD and TOC when compared to secondary effluents because the effect of chlorination on BOD and COD diminishes with increasing the organic content of the wastewater. After chlorination of treated water at different chlorine dosages (1-6 mg/L) and at 30 min contact time, the level of chloroform are found above the regulated WHO guide line value of 200 μg/L, and dichlorobromomethane, chlorodibromomethane, bromoform found under WHO guideline.

1.1. Introduction

Chlorine is a strong oxidizing agent and it is the most widely used wastewater disinfectant and it kills most bacteria, viruses and other micro-organisms that cause disease.

Wastewater disinfection is generally considered an important stage of wastewater treatment as it is the last barrier for protection of receiving water and effluent users from pathogenic organism. Chlorine is introduced to wastewater in the form of gas, hypochlorite and other compounds. Its application for waste water disinfection is likely to modify the chemical and biological nature of waste water, most notably its organic characteristics by the formation of disinfection by-products (DBPs), as a result of the oxidative breakdown of numerous organic substances present in treated effluents. The formations of DBPs are as follows.

$$HOCl + Organics \Longrightarrow DBPs$$

$$HOCl + Br^{-} \Longrightarrow HOBr + Cl^{-}$$

$$\mathrm{HOBr + Organics} \Longrightarrow \mathrm{DBPs}$$

The organic content of wastewater is measured using lumped parameters such as BOD, COD and TOC. The effect of chlorination on bulk organic content of waste water, measured as BOD, COD or TOC, is reduces the parameters and provides some treatment advantage. Similarly, Ammonia also plays an important role in determining chlorine demand of waste water effluents by the formation of numerous chloramines. The formations of chloroamines during chlorination are as follows.

$$\mathrm{NH_3 + HOCl} \Longrightarrow \mathrm{NH_2Cl\ (monochloramine) + H_2O}$$

$$\mathrm{NH_2Cl + HOC} \Longrightarrow \mathrm{NHCl_2\ (dichloramine) + H_2O}$$

$$\mathrm{NHCl_2 + HOCl} \Longrightarrow \mathrm{NCl_3\ (trichloramine) + H_2O}$$

During chlorination many disinfection by-products are formed like heloacetic acids, heloacetonitriles, chlorophenols, heloketones, chloropicrin, chloramines, THMs but Trihalomethanes (THMs) constitute a major class of DBPs, including Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Chlorodibromomethane ($CHClBr_2$), and bromoform ($CHBr_3$). Trihalomethanes (THMs) are most commonly occurring and toxic disinfection by-product generated during chlorination process. More recently, THM were classified as possible human carcinogens (Category 2B) by the International Agency for Research on Cancer [1]. Therefore, the use of chlorinated reclaimed water for agricultural applications, with the subsequent human consumption of crop foods irrigated with reclaimed water, could be a route of exposure to DBPs [2]. Furthermore, it has been shown that skin absorption and lung inhalations are potentially significant routes of exposure to some DBPs in water [3-5]. Suspected THM toxicity has led to adoption of specific regulations for the control of total THM (TTHM) in wastewater. World Health Organization[6] have regulated the health related guideline value (GV) for such compounds in drinking water, and there values are 200 µg/L, 60 µg/L, 100 µg/L and100 µg/L for Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Chlorodibromomethane ($CHClBr_2$), and Bromoform ($CHBr_3$) respectively, The occurrence of THMs in chlorinated waters in India has been reported earlier [7-9]. Several water quality parameters, such as pH, ammonia nitrogen, bromide, electrical conductivity, COD, and turbidity were also studied to determine their possible correlation with TTHM formation. However, limited informations are available of effects on water quality parameters such as COD, BOD, TOC, ammonical nitrogen and the formation of THMs during chlorination of treated effluents in full-scale waste water treatment plants. Therefore, study is needed to evaluate the effects on water quality parameters and formation of THMs during chlorination.

1.2. Literature Review

1.3. Wastewater Chlorination

In ancient times, people began collecting rain and storm water to support the growing cities. It was not until the mid 1800s, however, that the collection of wastewater became common in Europe. The practice of systematic treatment of wastewater began in the late 1800s early 1900s, brought about in part by the limited size of the receiving bodies of water accessible to Europeans. The relationship of untreated wastewater to disease was beginning to be understood. Originally, disease was thought to spread through odors and therefore the control of odors would prevent disease. To control the odors, chlorine was used as a deodorant without the understanding of its germicidal capabilities [10]. The earliest use of chlorine as a deodorant was documented in 1854 when the Royal Sewage Commission used chloride of lime to deodorize London sewage [10]. The major disease relationship breakthrough of Koch and Pasteur's germ theory in the late 1800s created a new age of sanitation practices. It was now understood that certain pathogens caused certain diseases. Chlorine was first used as a disinfectant in 1879, when William Soper of England treated the faces of typhoid patients with chlorinated lime before disposal in the sewage system [11]. Here in the United States, wastewater treatment and disposal was not of great concern until the late 1800s. Previous to this time, our discharges had not caused a noticeable aesthetic change in our waters due to the large volume of the receiving bodies. More advanced methods of treatment were developed as nuisance and health conditions worsened [11]. To counter a waterborne typhoid epidemic in 1894, chlorine was used on a plant wide basis to disinfect the New York City water supply coming from the Brewster, New York, water plant [10]. Since the development of metering and supply systems for chlorine gas, the use of chlorine to disinfect wastewater has grown tremendously.

1.4. Types of Disinfectants

The following sections provide historical background and chemical information for several disinfectants used in the U.S. Chlorine, chloramines; chlorine dioxide ozone and ultraviolet disinfection are discussed. Each different type of disinfectant has both advantages and disadvantages in wastewater/drinking water treatment. Free chlorine is very effective at inactivating pathogens but it produces some of the highest concentrations of DBPs. Chloramination is a weaker disinfectant compared to free chlorine but very few DBPs are formed when water treatment plants use chloramination. Ozone is an effective disinfectant and doesn't produce many DBPs of concern but ozone is not capable of providing a residual through the distribution system. Ultraviolet light has been shown to be effective at inactivating pathogens and it doesn't produce any DBPs that are yet regulated by the U.S. EPA but like ozone it does not produce a residual.

1.4.1. Chlorine Disinfection

In 1881, a German named Koch showed the role bacteria play in waterborne diseases. Koch demonstrated that minute quantities of chlorine could inactivate harmful waterborne pathogens. The introduction of chlorination resulted in significant decreases in worldwide waterborne diseases, such as typhoid [12]. The use of chlorination for the disinfection of drinking water first occurred in the United States in Louisville, Kentucky in 1896. The first time a continuous supply of chlorine was used as a disinfectant for drinking water was in 1902, in Middlekerke, Belgium. In 1905, chlorination was used in London, England to disinfect the drinking water supply. The first continuous practice of chlorination in drinking water in the U.S. began in 1908 and was used on the Boonton Reservoir, the water supply for Jersey City, New Jersey. By World War II, disinfection with chlorine had become a treatment that was standard worldwide [13].

1.4.2. Chloramine Disinfection

Chloramines are an alternative disinfectant to chlorine. Chloramination does not cause the taste and odor problems often experienced when disinfecting with chlorine.The main disadvantage to chloramination is that it requires a very large CT (concentration * time) value to provide effective disinfection. A water treatment plant in Denver, Colorado was the first in the United States to use chloramination in 1908 (although it did not provide continuous use of chloramination). The first continuous use of chloramination in the United States occurred at the Greenville, Tennessee water treatment plant in 1926. Disinfection by chloramines was used often between 1929 and 1939; however, during World War II there was a lack of ammonia so treatment plants stopped disinfecting with chloramines. In the first half of the 20th century, chloramines were used to prevent unpleasant tastes and odors when disinfecting. By the mid 1930s, chloramines were discovered to be more stable that free chlorine in the distribution system. As a result of this discovery, chloramines were often used to limit bacterial regrowth. Chloramines have grown in popularity since the 1980s because chloramines do not produce as high concentrations of DBPs as free chlorine.

Monochloramine is the best chemical for disinfecting water because unpleasant taste and odors can arise when dichloramines or trichloramines are formed. A chlorine to ammonia ratio of 3:1 to 5:1 is commonly used to limit the amount of dichloramines and trichloramines formed and promote the formation of monochloramines. In addition, these ratios limit nitrification and biofilm growth, which can occur when higher levels of ammonia are used [14]. Chloramines are not strong disinfectants compared to free chlorine. In order to meet the Surface Water Treatment Rule (SWTR) regulations for primary disinfection of such organisms as *Giardia* and viruses, extremely long detention times or high chloramine concentrations would be needed. However, since chloramines are capable of producing a stable disinfectant residual, chloramination is a possible secondary disinfectant to control bacterial growth in distribution systems.

1.4.3. Chlorine Dioxide Disinfection

Chlorine dioxide was first used as a water disinfectant in the United States in 1944, at the Niagara Falls, New York water treatment plant. A survey of United States water treatment facilities in 1977 showed that 84 water treatment plants used chlorine dioxide. As of 1977, 495 water treatment plants in Europe used chlorine dioxide in some part of their treatment processes, most often as a disinfectant residual for the distribution system[15]. The main disadvantages of using chlorine dioxide as a water disinfectant compared to chlorine are higher operating costs, health risks caused by residual oxidants and the creation of harmful by-products. Although not commonly used in the United States, chlorine dioxide is effective at inactivating waterborne pathogens. Chlorine dioxide does not react with organic material in water supplies to form trihalomethanes, however, some halogenated by-products are created when chlorine dioxide is used as a disinfectant [13]. Another disadvantage of chlorine dioxide is that it is a very unstable chemical and it rapidly dissociates into chlorite and chlorate. High concentrations of chlorite and chlorate can cause an increase in methemoglobanemia [15].

1.4.4. Ozone Disinfection

Ozone is created when oxygen (O_2) is separated by an energy source into oxygen atoms. The oxygen atoms collide with each other to form a more stable configuration (O2), which later forms ozone (O_3) gas. Ozone is a very strong purifier when used for primary disinfection in water and wastewater treatment plants. Because ozone gas does not have a stable chemical residual, it is not used as a secondary disinfectant [16]. Ozone gas was first used in Europe in 1893. Ozone treatment for drinking water is still more common in Europe than in the United States. Recent changes in the cost of ozone equipment have led more communities in the United States to use ozone disinfection in their drinking water treatment plants. In addition, ozone is becoming more widely used today because very few, if any, TTHMs and HAAs are formed from this disinfectant.

Ozone is more effective at inactivating organisms than chlorine. The other advantages to using ozone treatment include taste and odor control, oxidation of humic organic substances in water, and the destabilization of particles. There have been concerns about the safety of ozone with regard to DBP formation (other than TTHMs and HAAs). Bromate and formaldehyde can be formed in water after ozone disinfection, if the water has a high bromide ion concentration. Halopropanones and chloral hydrates are some other DBPs that are formed from disinfection with ozone. All of these DBPs are toxic.

1.4.5. Ultraviolet Disinfection

Ultraviolet light was first discovered in 1835 and was first used wastewater as a disinfectant in 1901 in Europe. At that time, ultraviolet light was unpredictable and difficult to control, so chlorine became the disinfectant of choice. Ultraviolet disinfection is the transmission of electromagnetic energy from a mercury arc lamp. As UV radiation enters the cell wall of a microorganism, the UV light damages the deoxyribonucleic acid (DNA) or ribonucleic acid (RNA), thus preventing the organism from reproducing. Pathogens are successfully killed at wavelengths ranging from 245 to 285 nm. Either low-pressure (254 nm) or medium pressure (180–1370 nm) mercury arc lamps, set at low or high intensities, can be used as the source of UV radiation [17]. UV disinfection is very effective at inactivating pathogens at low dosages [17]. Very small concentrations of DBPs are formed when UV disinfection is used. However, high concentrations of turbidity and certain minerals can decrease the effectiveness of UV [17]. In addition, this type of disinfection does not produce a disinfectant residual; therefore it can only be used as a primary disinfectant. A secondary disinfectant, such as chlorine gas, in combination with UV radiation has to be used when treating drinking water with UV disinfection.

1.5. Factors Affecting the Formation of DBPs

There are several factors affecting the formation potential of DBPs. Previous research studies have shown that the major variables that affect DBP formation are: residence time, temperature, pH, disinfectant type and concentration, total organic carbon concentration and chlorine to nitrogen levels.

1.5.1 Disinfectant Concentration

Scientists have been studying how the disinfectant concentration affects DBP formation. The studies have shown that as the disinfectant concentration increases, DBP formation also increases. For example, Singer *et al.* (1995) conducted a study in North Carolina on eight conventional water treatment plants that practiced chlorine disinfection [18]. The treatment plant that used the largest chlorine dose had average TTHM and HAA levels of 52 µg/L and 80 µg/L, respectively. The plant which used the smallest chlorine dose had mean TTHM and HAA levels of 19 µg/L and 39 µg/L, respectively.

1.5.2. Residence Time

Several research studies have been conducted to examine how residence time affects DBP formation. The studies have shown that as residence time increases, the concentration of TTHMs increases and the concentration of HAAs decreases. Chen and Weisel (1998) conducted experiments examining the concentrations of DBPs in a conventional treatment plant that used chlorine to disinfect the water supply [19]. Over 100 samples were collected in four groups, each group representing an increasing residence time from the point of disinfection. The average concentrations for TTHMs at days zero, one, two and three or more were 25±14 µg/L, 30±16 µg/L, 29±15 µg/L, and 30±14 µg/L, respectively. The average levels for HAA at days zero, one, two and three or more were 24±6 µg/L, 23±7 µg/L, 21±8 µg/L, and 14±6 µg/L, respectively. These findings showed that as residence time increases, TTHMs increase (up to day one) and HAAs decrease. Similar results were found by Le Bel *et al.* (1997), who performed an experiment on a conventional water treatment system that used chlorine for its primary and secondary disinfectant [20]. Four sampling points were used at an increasing distance from the treatment plant. At the first, second, third, and fourth points, TTHM levels were analyzed and the results were 24.8 μg/L, 37.5 μg/L, 48.4 μg/L, and 61.4 μg/L, respectively. HAAs concentrations were also determined at the four sites and the results were 31.2 μg/L, 34.4 μg/L, 33.1 μg/L, and 8.8 μg/L, respectively. The results showed that TTHM levels increased and HAAs levels decreased as the distance from the treatment plant increased.

1.5.3. Temperature

Many studies have been conducted to evaluate how temperature affects the rate of DBP formation and the concentration of DBPs that are formed. Some studies have shown that as the temperature increases, the concentration of TTHMs also increases. However, the results are not conclusive because conflicting results have been found from different research studies. Nieminski *et al.* (1993) examined TTHM and HAA concentrations (during all four seasons) in 14 conventional water treatment plants which disinfect with chlorine [21]. In this study, the mean TTHM levels for summer, fall, winter, and spring were 32.1 μg/L, 28.7 μg/L, 17.6 μg/L, and 16.5 μg/L, respectively. This study showed that the highest TTHM concentrations were found in the summer and fall seasons, and the lowest TTHM concentrations were present in the winter and spring. Chen and Weisel (1998) collected 144 water samples from the Elizabethtown, N.J. water system, which uses chlorine disinfection and conventional treatment, between November 1991 and October 1993 [19]. The samples were collected in all seasons. As the water exited the treatment plant, the TTHM level in the winter was 14±4 μg/L and the TTHM level in the summer was 33±13 μg/L. The HAA concentrations in the winter and summer were 24±6 μg/L and 26±8 μg/L, respectively. Chen and Weisel's research showed that TTHM levels increased significantly in the summer and the HAA levels remained the same throughout the year [19]. An addition study was conduct by Doijlido *et al.* (1999), on water disinfected with chlorine and treated by conventional treatment [22]. The smallest concentrations of HAAs were formed in January, February, and March (total HAA concentration of less than 1μg/L). The highest concentrations of HAAs occurred in May and June, when the levels reached 120 μg/L. The results of Dojilido *et al.* [22] are in contradiction with the results of the Chen and Weisel [19] study. Therefore, the impact of temperature on HAA levels is unclear.

1.5.4. P^H effect

Several studies have been done to analyze concentrations of DBPs and how they relate to pH levels of the water supply. The studies have shown that as the pH increases, the concentration of TTHMs also increases. HAA concentrations were not as dependent on pH. Diehl *et al.* (2000) conducted a series of experiments to determine the effect of pH on DBP formation in water supplies treated with chloramines [23]. TTHMs were measured at pH conditions of 6, 8 and 10 and the results were 161 µg/L, 259 µg/L, and 295 µg/L, respectively. HAAs were also examined at these pH conditions and the concentrations were 74.5 µg/L, 74.3 µg/L, and 55.5 µg/L, respectively. These results lead Diehl *et al.* (2000) to state that as pH increases, TTHM levels increase and HAA levels decrease [23]. Nieminski *et al.* (1993) evaluated water treatment systems in Utah which used chlorine disinfection [21]. TTHMs and HAAs were first analyzed at a pH of 5.5 and the results were 39.9 µg/L and 35.3 µg/L, respectively. TTHM and HAA levels were again tested at a pH of 8.46 and the results were 49.8 µg/L (TTHMs) and 14.6 µg/L (HAAs). The findings support the conclusion that higher pH conditions cause HAA concentrations to decrease and TTHM concentrations to increase.

1.5.5. Total Organic Carbon Concentrations

Several researchers have studied the impact of total organic carbon concentration on DBP formation. These experiments have found that as the total organic carbon level increased, the DBP formation also increased. Two studies which looked at the total organic carbon levels with respect to TTHMs and HAAs are discussed. Singer *et al.* (1995) conducted a study on eight North Carolina water supply systems [18]. At a TOC concentration of 5.4 mg/L, an average of 82 µg/L of TTHMs was produced and an average of 106 µg/L of HAAs was formed. At a TOC level of 2.4 mg/L, a mean of 39 µg/L of TTHMs were created and a mean of 36 µg/L of HAAs were produced. These results showed that as TOC concentrations increased so did TTHM and HAAs levels. Dojilido *et al.* (1999) also found HAAs formation was dependent on the organic matter present in the sample, higher concentrations of HAAs were formed at higher TOC concentrations [22].

1.5.6. Bromide Concentrations

Recent studies have been completed which examined the relationship between bromide concentration in wastewater/ drinking water supply and DBP formation. These studies have shown that as the concentration of bromide is increased, the concentration of TTHMs and HAAs also increases. When there are high bromide concentrations in a raw water source and chlorine is added to the water supply, more brominated THMs will be formed because there is more bromide present in the water source for the organics to react with. In typical raw water supplies when chlorine is added, chloroform is the major compound of TTHMs found in the water supply. Diehl *et al.* (2000) performed experiments on three different water sources and tested the effect of bromide levels on DBP formation [23]. Results showed that as the bromide concentration increased, the TTHM concentration also increased. For example, at one treatment plant using chloramines at a Cl_2: N ratio of 5:1 and pH of 6, the TTHM concentration without bromide addition was 14.8 μg/L and with bromide addition was 40.2 μg/L. Pourmoghaddas *et al.* (1993) also conducted experiments to study the relationship of bromide concentrations to HAA formation in drinking water [24]. The study used ultra pure water with humic acid added. The study included differing residence time and pH values to give a better representation of a true water source. Pourmoghaddas *et al.* (1993) found the highest HAA values were observed when the largest amount of bromide was added to the water [24]. For monobromoacetic acid (MBAA), the highest concentration (15 μg/L) of this HAA was observed when 4.5 mg/L of bromide was added. When no bromide was added, almost no MBAA was found.

1.6. Use of Chlorine for Effluent Disinfection

Chlorine is added to the hydrosphere in vast amounts through many different anthropogenic processes. Ten percent of the world's chlorine production is by one company, Dow Chemical, at a rate of approximately five million tons yearly. Over 10,000 different chlorine compounds are produced to manufacture the goods we use daily [25]. As of 1958, 30% of all WWTPs in the US, over 2200 plants, were equipped with chlorination equipment [10]. As a result of the 1970 Water Pollution Control Act, almost all treatment plants are now subject to some form of disinfection. The majority of WWTPs requiring disinfection currently use some form of chlorination. Based on the health hazards and environmental concerns of chlorination, many of the plants are installing alternative disinfection processes such as UV irradiation or Ozonation. Over 400 facilities have been designed for chlorination/dechlorination with approximately 50% of those facilities in use as of 1986 [26].

1.6.1. Wastewater Treatment Process.

Disinfection is only a part of the wastewater treatment process. Current practice includes the use of physical and chemical methods to remove contaminants from the influent. Those processes which involve physical removal methods are known as unit operations. Those methods which involve a chemical process to change the wastewater characteristics are known as unit processes. These two types of removal strategies are combined together to provide what is known as primary, secondary, and tertiary treatment. Primary treatment usually consists of screening and sedimentation to remove floating and settleable solids from the wastewater. In secondary treatment, chemical and biological processes are used to remove organic matter from the wastewater. Tertiary treatment is needed if the effluent contains other constituents such as nitrogen or phosphorous that has not been sufficiently reduced through secondary treatment. A combination of chemical and physical operations could also be used during this phase to reduce the amount of heavy metals or other pollutants from the effluent. Lastly, the effluent is disinfected to reduce the amount of pathogenic organisms discharged to receiving waters [11].

1.6.2. Chlorination Chemistry

To understand how the chlorinated DBPs (THMs, HAAs etc) and the DBPs formation ofter chlorination are formed, the basics of chlorine chemistry must first be understood. Chlorine is an element of the halogen family. The halogens are strong oxidants and are highly reactive [27]. Chlorine is never found uncombined in nature, it exists only as the negative chloride ion (valence -1) combined with other elements in the form of soluble chlorides. Chlorine's properties differ greatly depending upon its physical state. Chlorine gas is a pungent-smelling, greenish-yellow gas that is extremely irritating to mucous membranes. In the gaseous state, it is about two and one-half times as heavy as air and readily sinks to the ground when released. Chlorine gas is soluble in water and has a bleaching effect on many forms of natural fibres. Liquid chlorine is formed by compressing chlorine gas, one volume of liquid yielding approximately 450 volumes of gas. The yellowish amber liquid volatilizes violently when depressurized [10], one of the many hazards to WWTP workers.

1.6.3. Chemistry of Free Chlorine

Chlorine's high reactivity and oxidizing capacity are caused by the fundamental properties of chlorine. Chlorine's high electron affinity tends to draw electrons towards it, resulting in high reactivity with other atoms. It is an electron acceptor. Chlorine's oxidizing capacity is based on fundamental oxidation-reduction reactivity. Oxidation-reduction reactions are those involving a change of oxidation state of the reactants. These reactions can be visualized as the Transfer of electrons from one species to another. For example, chlorine may be added to water in three common ways: as chlorine gas (Cl_2), as sodium hypochlorite (NaOC1), and as calcium hypochlorite [($Ca(OCI)_2$]. When added to water as gas, it rapidly hydrolyzes to produce hypochlorous acid (HOCI) according to the following reaction

$$Cl_2\,(gas) + H_20 \Longrightarrow HC1 + H^+ + Cl^-$$

The hydrogen is oxidized and the chlorine gas is reduced [27]. At a typical 18°C, hydrolysis occurs in a few tenths of a second. Only a few seconds are needed for complete hydrolysis if the temperature decreases to 0^0C. The weak hypochlorous acid then easily dissociates into hypochlorite ions (OCI^-) and hydrogen ions (H^+):

$$HOCI \Longrightarrow OCI^- + H^+$$

Hypochlorous acid is the most effective germicide of all the chlorine compounds except possibly chlorine dioxide [10]. Singer [28] reported in 1988 that Snoeyink and Jenkins found "HOCI to be 80 to 100 times more effective than OCI^- at killing *E. coli"*. This effectiveness is a result of HOCI's strong oxidative capacity. When chlorine exists as either hypochlorous acid or as the hypochlorite ion, it is referred to as free chlorine or free available chlorine [28]. Free available chlorine not only acts as a germicide but combines with other organic and inorganic compounds present in water and wastewater. The compounds compete for free available chlorine and sometimes lead to lessened germicidal effectiveness. One of the main competing reactions, when chlorine enters wastewater, is its reaction with ammonia.

1.6.4. Ammonia Chemistry

The presence of ammonia in wastewater is due in most part to the hydrolysis of urea to the ammonium ion at the pH values (7.0-7.5) typically found in raw domestic wastewater. The ionization reaction for the ammonium ion is:

$$NH_3 + H^+ \Longrightarrow NH_4^+$$

Dissociation constants for ammonia published by Bates and Pinching [29] are summarized below:

Table 1. Temperature Dependency of pK_b for Ammonia (NH_3)

Temperature °C	0	5	10	15	20	25	30
pK_b	10.08	9.90	9.73	9.56	9.40	9.25	9.09

Data from the above table show that one is very unlikely to find significant NH_3 at the pH values encountered during normal breakpoint chlorination operations (pH<9.0).

1.6.5. Chlorine-Ammonia Chemistry

Numerous studies and reviews have been done in the field of chlorine-ammonia chemistry [30-33] from these studies; the following generalized reaction scheme is accepted for chloramines formation:

$$NH_3+HOCl \Longrightarrow NH_2Cl \text{ (monochloramine)}$$

$$NH_2Cl+HOCl \Longrightarrow NHCl_2 \text{ (dichloramine)}$$

$$NHCl_2+HOCl \Longrightarrow NH_3 \text{ (trichloramine)}$$

The chloramine composition in solution has been shown to be pH dependent [34- 36]. Morris [37] gives the following information on the chloramine formation pH dependency:

- at pH > 7.5, monochloramine is the dominant chloramine species
- as pH decreases from 7.5, dichloramine becomes the dominant chloramine species
- increases in the chlorine to nitrogen dose ratio results in corresponding increases of nitrogen trichloride, but only when the pH is < 7.4.

Monochloramine

Monochloramine is very soluble in water and is prone to decomposition when exposed to light and heat [38].

NH_2Cl Chemistry

Polarity of the N-Cl bond in chloramine is very low [38]. It has been shown that the N-Cl bond is polarized differently by various reactants [39], hence the more negative end may be the nitrogen in one case and the chlorine in another. The formation reaction is:

$$NH_3 + HOCl \Longrightarrow NH_2Cl + H_2O$$

Numerous studies of this reaction rate have been performed [40-41, 31]. As recently as 1983, Morris and Isaac [41] concluded (based on research from all previous studies) that this reaction is elementary and has a rate constant of $6.6x10^8 \exp(-1510/T)\ M^{-1}sec^{-1}$.

It has been determined that the monochloramine reaction does achieve equilibrium [42]. Numerous researchers [42-44] have reported dissociation constants for monochloramine, none of which are in very good agreement.

Dichloramine

Dichloramine occurs in solution only. The nitrogen-chlorine bond in dichloramine should be even less polar than in the case of monochloramine due to the additional chlorine atom bound to the nitrogen, thereby increasing the electronegativity of the latter [38]. This theory is substantiated by data that show the solubility of dichloramine is greater in nonpolar organic solvents [45].

$NHCl_2$ Chemistry

Research by Chapin [46] concluded that production of dichloramine was a direct result of excess chlorination of ammonia in the pH range of 4.4 to 8.5, and that at pH 4.5 to 5.0 dichloramine was the sole product. The formation reaction is:

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

Several researchers [40-41, 37], have determined estimates of the rate constant for dichloramine. Based on the analysis of past research, as well as their own, Morris and Isaac [41] derived a composite forward rate constant of $3.0x10^5 \exp(-2010/T)\ M^{-1}sec^{-1}$.

Stating the equilibrium constant as:

$$K= \frac{[NHCl_2]}{[NH_2Cl]\ [HOCl]}$$

The reciprocal of K (from above) was estimated to be about 25 times larger than that found for the corresponding monochloramine equilibrium [43]. Many other researchers have estimated this constant, the most recent being Morris and Isaac [41] who (based on all available research at the time) estimated the reciprocal of K for dichloramine to be

2.2×10^{-9} M in fresh water at 25°C. Conflicting estimates of the acid dissociation constant of dichloramine have been presented in the literature:

pKa ≅7 (Jolly, 49), pKa ≅8 (Morris, 47) and pKa ≅13 (Hand *et al.*, 48)

Although the equilibrium constant estimated by Morris was confirmed by the theoretical calculations of Jolly, dichloramine could not be detected even at very high pH values in research done by Hand. This absence of dichloramine led Morris to postulate that dichloramine must dissociate rapidly [47].

Nitrogen Trichloride

Nitrogen Trichloride was first discovered in 1811 from the action of chlorine on a solution of ammonium chloride by Dulong, who lost an eye and three fingers as a result of an explosion. Dulong [50] determined the formula NCl_3 for the yellow explosive oil. Further early research [51] showed that the thick oily NCl_3 would explode violently when heated to 93 °C, when exposed to strong light, or brought into contact with a number of other substances. Nitrogen trichloride is sparingly soluble in water and is known to exert a high vapor pressure. These factors together result in NCl_3 being easily stripped from water [51].

NCl_3 Chemistry

The formation reaction for nitrogen trichloride is:

$$NHCl_2 + HOCl \Longrightarrow NCl_3 + H2O$$

Several researchers have presented rate constants for the above reaction [41, 52-53]. Morris and Isaac [41] based their rate constant on all research available at the time of publication and recommended a rate constant of $3.0 \times 10^5 \exp(-3420/T)\ M^{-1}S^{-1}$ ($3.2 < pH < 4.5$) for fresh water. The decomposition reaction for nitrogen trichloride is:

$$NCl_3 + H2O \Longrightarrow NHCl_2 + HOCl$$

The rate of nitrogen trichloride decomposition has been shown to be first order as a function of time [53]. Kumar [54] demonstrated that NCl3, in the presence of excess hypochlorous acid, decomposed to either HOCl or was otherwise lost through oxidation/reduction.

1.6.6. Breakpoint Chlorination

The physical-chemical process of ammonia oxidation with chlorine has been practiced in the water treatment field for over 50 years. As early as the 1920s superchlorination was used as a successful means of controlling taste and odors in water treatment plants. In the 1930s an unexplained phenomenon was being observed at water treatment plants using higher than normal chlorine dosages. These events prompted research into the chlorination reactions occurring at water treatment plants. Among the first researchers to explain these chlorine reactions Griffin [55] used the term breakpoint to describe the point where chlorine and ammonia concentrations were simultaneously minimized. The breakpoint reaction is defined as the chlorination of a water containing ammonia resulting in an initial increase in combined chlorine residual, followed by a decrease in the combined chlorine residual along with ammonia concentrations, followed by an increase in free chlorine residual and near complete removal of ammonia as nitrogen gas. Fig. 1 shows a hypothetical breakpoint curve for a water with a dose requirement of 9:1 Cl_2: N [56]. Initial research efforts into the mechanism of the breakpoint reaction are attributed to Calvert [57], and later studies by Griffin and Chamberl [58], and Rossum [59]. Ensuing research by others [52, 60, 31] has led to an understanding of the stoichiometry and kinetics associated with the breakpoint process. More recently, a comprehensive study of the kinetics of breakpoint chlorination was performed by Saunier and Selleck [61]. The goal of their work was to develope a mathematical model, derived from laboratory observations, which would provide “a rational basis for the design and operation of the breakpoint process in order to achieve predictable ammonia removal"[61]. Unfortunately, past research yielded little or no insight into the problem of successfully controlling the breakpoint process in a full-scale wastewater treatment plant. Although Saunier and.Selleck [61] performed comprehensive pilot study work, the results were never incorporated into a full-scale plant application. Pressley *et al.* [62] performed extensive pilot study research in order to provide design criteria for a full scale breakpoint operation at the Blue Plains wastewater treatment plant in Washington, D.C. Atkins *et al.* [63] performed an extensive pre-design pilot study to provide information for full- scale breakpoint operations at the Owosso wastewater treatment plant in Michigan.

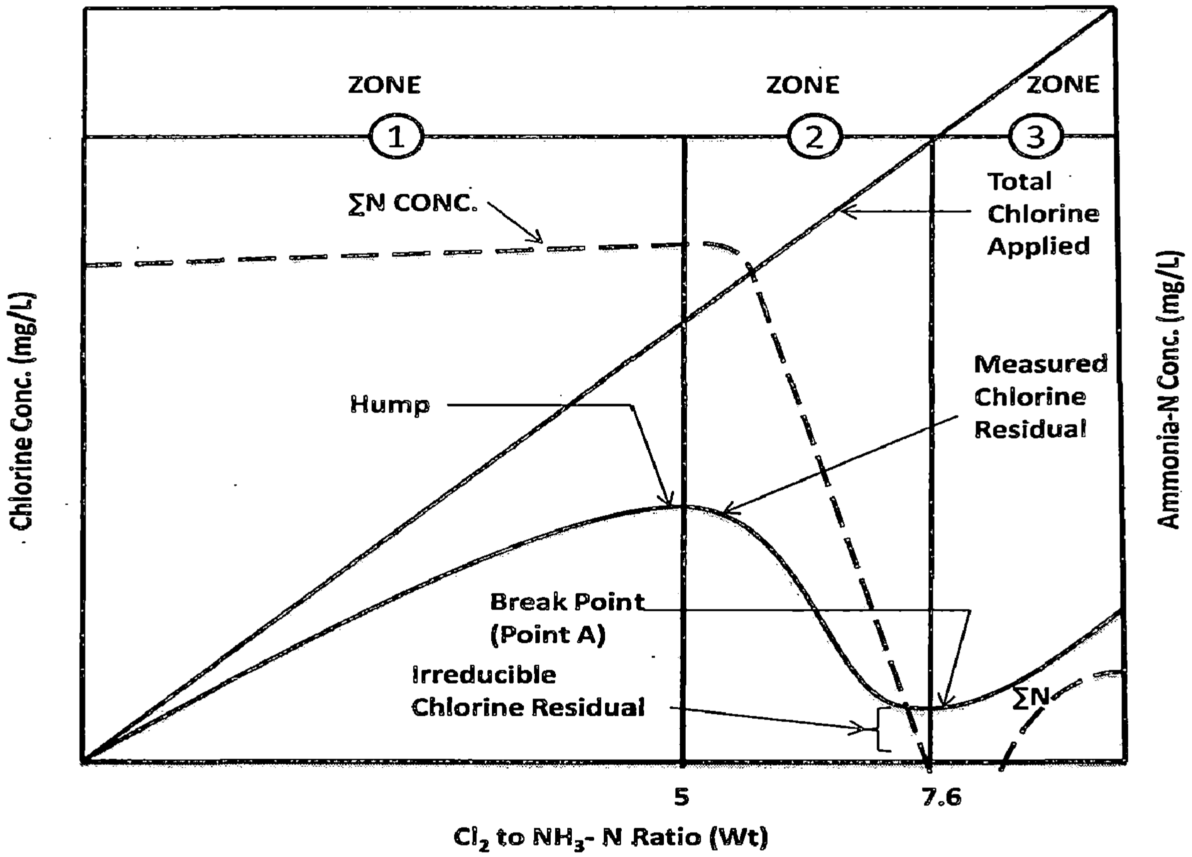

Fig.1. Theoretical breakpoint curve

Zone 1 is associated with the reactions of chlorine and ammonia to form Monochloramine; Zone 2 is associated with an increase in dichloramine and the disappearance of NH_3;

Zone 3 is associated with the appearance of free chlorine after the breakpoint [32].

End Product of breakpoint chlorination

The end products of the breakpoint reaction were found to be primarily nitrogen gas (N_2) and secondarily nitrate (NO_3^-) [52, 61-62]. Attempts were made by Pressley *et al.* [62] to isolate N_2O, NO, and NO_2 but these proved unsuccessful. The following reaction scheme is given for the formation of N_2 and NO_3^- [32]:

$$NH_4^+ + 1.5HOCl \Longrightarrow 0.5N_2 + 1.5H_2O + 2.5H^+ + 1.5Cl^-$$

$$NH_4^+ + 4HOCl \Longrightarrow NO_3^- + H_2O + 6H^+ + 4Cl^-$$

Stoichiometry

The weight ratio of chlorine to ammonia required to reach the breakpoint, assuming N_2 is the major end product, is 7.6:1 or, on a molar basis, 1.5:1. Research by Wei and Morris [60] indicated that the stoichiometric ratio of the breakpoint reaction was not affected by pH in the 6.7-7.2 range. This was in agreement with earlier studies [55, 58]. In more recent studies by Saunier and Selleck [61] the ratio of moles of chlorine reduced : moles of ammonia N oxidized increased with increasing contact time, and with increasing chlorine to-ammonia dose ratio. The data agreed with previous studies by Wei and Morris [60]. Pressley [62] showed that chlorine-to-ammonia dose ratios varied from approximately 8:1 to 10:1 for the waters tested in his studies. The dose ratio required was attributed directly to the extent of pretreatment the water received, with the more highly treated water requiring a lower dose ratio of 8:1. Saunier and Selleck [61] conducted studies with both tap water and tertiary effluent. They found higher chlorine-to-ammonia ratios were required to reach the breakpoint in the tertiary effluent than in tap water, and attributed this result to the oxidation of organics present in the tertiary treated water.

Kinetics

The rate at which the overall breakpoint reaction proceeds to completion can be measured by combined chlorine concentration disappearance over time. The breakpoint reaction rate may be affected by temperature, pH, and initial ammonia nitrogen concentration. Studies by Wei and Morris [60] showed a significant temperature effect on the breakpoint reaction with activation energies ranging from 7.8 kcal/mole to 12.85 kcal/mole. Data from these studies also showed a direct relationship between reaction stream temperature and persistence of combined chlorine residuals. Decreasing temperatures caused longer reaction times. Data from Saunier and Selleck [61] showed faster reaction rates as pH increased. The optimum reaction rates occurred between pH 7.0 and 8.0. Wei and Morris [60] noted that the most important effect of pH on breakpoint was how it affected the transient state of $NHCl_2$. As the pH dropped, they noted a decrease in the rate of decomposition of $NHCl_2$ and hence slower overall breakpoint reaction rates. According to the proposed mechanism by Wei and Morris [60], the formation of $NHCl_2$ is a second order reaction while its decomposition is first order. Based on this proposal they concluded that the maximum $NHCl_2$ concentration should occur sooner and have a larger magnitude when the initial reactant (NH_3-N) concentration is increased. As a consequence, the rate of decrease of $NHCl_2$ and total chlorine would also be expected to increase with increased reactant concentration. The experimental data collected of Wei and Morris confirmed an increase in the breakpoint reaction rates with increases of initial ammonia concentration [60]. Saunier and Selleck [61] observed a reaction rate increase by an order of magnitude when operating breakpoint at higher initial ammonia concentrations.

1.7. Disinfection By-Products (DBPs)

At the time of this research there had been no known research to determine the which if any disinfection by-products were being created during breakpoint chlorination. While not the main focus of this research due to time and funding limitations, DBP formation potential from breakpoint reactions will be addressed.

1.7.1.Organochloramines

Wastewaters containing organic nitrogen, in addition to ammonia nitrogen, can create a variety of problems for breakpoint chlorination operations. Taras [64-65] categorized the source of chlorine consuming nitrogenous compounds as: ammonia, amino acids, and proteins. The formation of organochloramines in water during chlorination is well documented, [52, 64-66, 33]. Griffin [58] found that waters containing both ammonia and organic nitrogen did not display a large dip in the breakpoint curve as compared to waters containing only ammonia. Organochloramines have also been identified as interfering compounds in chlorine residual determinations [32].

1.7.2. Reactions with Organic Compounds.

The reactions of chlorine with organic compounds in water are varied and complex, depending upon the water characteristics, the chlorine dose, and the physical state of the added chlorine [67]. Reactions with organic compounds can be divided up into two groups based on whether the reaction mechanism is oxidation or substitution [68]. Oxidation reactions are the most prevalent reactions. These reactions occur when free available chlorine oxidizes organic compounds. The oxidative capacity of chlorine is lost and any chlorine added past the equilibrium point is found as the unreactive non-toxic chloride ion [28]. In saline water, bromide is instantaneously oxidized into bromine, which gives rise to bromamines. This first group of reactions is responsible for the efficiency of chlorine disinfection as well as for toxicity towards non-targeted organisms.

Toxicity eventually disappears as the oxidizing capacity is lost or transformed from one chemical entity to another [67]. The second reaction results in the formation of halogenated organic derivatives which are of interest in this study. The reaction occurs when chlorine atoms are substituted for some other atom present in the organic compound [69]. These substitutive reactions are significant because: (a) End products of these reactions may be numerous, (b) They persist in the environment longer than the first group of compounds [67], (c) They may present carcinogenic risk. This research will focus on modeling the formation of THMs, one group of these halogenated organic derivatives.

1.7.3. Formation of Chlorinated Organic Compounds during Wastewater Chlorination

Halogenated organic compounds, including the THMs, are formed during wastewater chlorination and also by the reaction of free chlorine residual in chlorinated wastewater with organics in the receiving surface waters. THMs were first identified as a potential pollution problem by Rook in 1974 [70]. In the investigation, halogenated organic compounds (also known as haloforms) were found at significant levels immediately following chlorination of a natural water source. Principal among the haloforms found were the THMs, especially chloroform. Haloforms have the general formula CHX3, where X denotes a halogen (fluorine, chlorine, bromine, iodine).

Table 1.2. THM Precursors [68]

Source	Examples of precursors
Plants	Fulvic and humic acid degradation products (resorcinal, vanillic acids, syringic acids,3,5-dihydroxybenjoic acids), plants pigments (chlorophyll, phloroacetophenone)
Algae	Algal biomass, Amino Acids and pyrimidines (tryptophan, proline, uracil)
Industry	Effluents (phenols)

The currently regulated THMs are chloroform ($CHCl_3$), bromodichloromethane ($BrCHCl_2$), dibromochloromethane (Br_2CHCl), and bromoform ($CHBr_3$) [71]. THMs are formed through alternate hydrolysis and halogenation steps, with the first ionization steps being rate determining [72]. The precursors needed for this reaction are generally classed as aquatic humic materials [68]. Table 2 summarizes the sources of these precursors THMs can be easily determined using gas chromatography and a sensitive detector such as a flame-ionization detector. Standard Methods for the Examination of Water and Wastewater, 18th Ed. gives several methods which are accepted under regulatory scrutiny. Liquid-liquid extraction gas chromatograph is highly sensitive and very precise; purge and trap gas chromatograph/mass spectrometric can detect THMs along with a wide range of other compounds; purge and trap GC methods with similar target compounds are also as effective to detect THMs [73]. Method choice depends on equipment availability and operator choice. These methods need to be followed and documented to ensure data from different investigations are valid.THM formation is ubiquitous in part due to the amount of readily available precursor compounds, humics that are almost always naturally present in water (See Table 2). Factors which affect the THM formation kinetics include: pH, temperature, level of precursor organics, and level of chlorine dose. THM formation increases with increased temperature and pH, increased level of precursors, and increased chlorine dose [68]. Average concentrations of regulated THMs found in municipal wastewater following secondary biological treatment ranged from 1.5 ug/L to 13.3 ug/L [74]. Treatment plants studied were Washington DC, Orange County, Phoenix, Denver, and Palo Alto. The presence of the THMs prior to the chlorination process at these plants indicates that they are formed by a variety of industrial and commercial activities as well as the chlorination of drinking water/wastewater. The additional chlorination of the wastewater then adds to the amount of THMs discharged to surface waters. The amount of THM production is not the only factor which causes concern. Once the THMs are produced, they are persistent in aqueous environments. The half-life of the halomethanes in the aqueous environment depends upon the rate of aeration and on the stability of the haloform. As the halogen bond energies decrease with descending order from chlorine to iodine, the stability of the halomethanes with similar number of halogens can be expected to decrease also [75] .Therefore, chloroform is expected to be the most stable of the tri-halogenated haloforms. Chloroform was found to have a half-life of 15 months in a sealed aqueous system at 25^0 C [75]. It was concluded that hydrolysis was the likely degradation mechanism. The THMs quickly volatilize if exposed to the atmosphere, so in most receiving bodies of water, the rate of aeration will determine how quickly the THMs are degraded if they are not removed through treatment. Air stripping combined with activated carbon treatment is currently the most effective means of removing THMs from a water source [74]. It can be seen that using chlorine to disinfect wastewater forms additional toxic compounds which are released into the hydrosphere. The disadvantages of using chlorine as a wastewater disinfectant include: demonstrated toxicity to organisms and the formation of chlorinated organic compounds. A chloroform concentration of 12.1 μg/L was found as an average for purified chlorinated wastewater by Belier in 1974 [67]. Compounds such as chloroform may be carcinogenic and can seriously impact downstream public water supplies [76]. If viable alternatives are available, is it important to stop using chlorine as a disinfectant thereby minimizing the amount of disinfection by-products formed and the risk to the environment and to human health.

1.8. Chlorine Demand

The bulk of the research on chlorine demand has been related to chlorination of potable waters. Feben and Taras [77-78] found a definite relationship between chlorine demand and the complexity of the organic nitrogen compounds found in the city of Detroit water supply. Pilot study work by Pressley *et al.* [62] correlated the level of pretreatment of the wastewater to the chlorine-to- ammonia ratio required to reach breakpoint. In their studies, water receiving high levels of treatment, e.g. waters with lower concentrations of organics present required lower Cl_2:N dosages to reach the breakpoint, while all other factors were constant [62].

1.9. Toxicity of Chlorine Residuals and Halogenated Organic Compounds

Early investigations into the toxicity of chlorine and its derivatives focused on free available and combined chlorine with little concern for the possible toxicity of disinfection by-products (DBPs). It was reported by Singer (1988:13) [28] that Wolfe surmised in 1984 that a measure of total residual chlorine present after a chlorination process would be sufficient to express the relative toxicity of water. This method of measuring toxicity may not be sufficient to account for the toxicity of DBPs. The toxicity of an effluent is caused in part by the oxidizing capacity of any free available chlorine residual. The free chlorine acts as a biocide by altering the permeability of a cell, damaging cellular nucleic acids and inactivating viruses by damaging the viral protein coating or causing nucleic acid mutations [76]. Many studies have been done since the early 1980s to establish that not only are residual chlorine compounds toxic, but the halogenated organic compounds formed during chlorination are also toxic. The following two sections briefly describe selected studies.

1.9.1. Laboratory Investigations

The use of toxicological indicies for regulatory and management purposes became widespread in the late 1940's when these methods appeared in publications by the American Society for Testing and Materials [79]. Most of the first indicies used were single species laboratory toxicity tests using fish. Findings were then used to make assumptions as to the toxicity of the compound to humans. In recent years the toxicity of compounds towards plant life has gained precedence as more and more pollution is released to the environment. This section covers both plant and animal studies.

1.9.2. Field Investigations

The use of field investigations is not as prevalent as the use of laboratory experiments. Controls are harder to maintain, conditions are always changing, and results are difficult to interpret. The investigations discussed here are attempts to use the natural environment to monitor changes. They are not simply lab experiments which have been adapted to a field environment. In this way, researchers are beginning to understand more about the dynamics of aquatic environments and the effects of pollution on them.

2.9.3. Ecotoxicological Studies

Ecological risk can be defined as the probability of observing a specified effect as the result of toxic chemical exposure [80]. An ecological risk can affect the processes, diversity, reproduction rates, and quality of populations of an ecosystem. A disruption of ecosystem parameters can have many effects including reduced biomass, reduced species diversity, species extinction, and propagation of less desirable species. Reduced diversity is caused by avoidance behavior, by mobile species leaving the effected area, and/or by the death of sensitive species. Avoidance responses eventually lead to the loss of habitat in the case of continuous discharges such as chlorinated cooling tower waters or chlorinated effluents [67]. An ecosystem can range from a single microbial community, to an entire watershed, or more. The ecological risk assessment process involves the selection of an indicator species and biological monitoring of that species to determine the "health" of the ecosystem. Cumulative effects of other risk elements and uncertainties complicate the assessment. For purposes of this research, the risk assessment process need not be explained. (The most recent ecological risk assessment practices are explained in Cothern (1993, [81]). One example of an ecosystem toxicity experiment is the outdoor enclosure tests performed by Cairns *et al* in 1988 [82]. The researchers brought their efforts on the toxicity of chlorine residuals and DBPs to a field investigation through the use of outdoor enclosure tests. Knowing the toxicity of chlorine, the tests were meant to measure precise levels of residual which cause ecosystem harm. The tests were performed in 130 L polyethylene bags floated in Douglas Lake, Michigan in July 1986. Five nominal chlorine concentrations and a control were tested in triplicate [82]. The bags were kept afloat, open at the top to expose contents to light, wave action, rain, and air, and the nominal concentrations of chlorine were added daily to the benthic sediment and alga communities which were established in the bags. Initial concentrations that were tested were 10, 30, 100, 300, and 1000 µg/L. Rainfall and exposure diluted the chlorine residual in all enclosures. At only a concentration of 24 µg/L, protozoan colonization rate was significantly reduced [82]. In the enclosures with the two highest concentrations, 79 and 261 µg/L, algal biomass and species numbers were significantly reduced when compared to controls [82]. Measurements of DBPs were not taken. Although test results as exact as laboratory measurements could not be obtained through this field experiment, results indicate that exposure to very low levels of residual chlorine can have significant effects on aquatic life.

1.9.4. Biological Effects.

The biological effects produced by water chlorination on marine organisms has been researched in many countries. Many investigations of WWTP effluents in this country have been prompted by major fish kills. White [10] reports that a major kill on the Sacramento River prompted an investigation using an in situ static bioassay. All the King

Salmon fry below the waste plume died within a captive (kept within a cage type enclosure) 14 hour period of exposure. All fry held upstream survived. Total chlorine residuals were measured from 0.2 mg/L to 0.3 mg/L during the test period. It was assumed that the fish kill was caused by the effluent toxicity, mainly the chlorine residual [10]. Sub-lethal effects include decrease in reproductive potential, growth reduction, irritation of tissues, and disruption of cellular structure among many others. Abarnou and Miosser [67] provide a comprehensive summary of sublethal toxicity tests performed from 1973 to 1983. Overall, growth reduction was observed regardless of the species of animal or plant. Eggs displayed development impairment. A loss of sperm mobility and viability decreased reproductive potential. Photosynthesis and respiration deteriorated in plant species. Gill tissues deteriorated causing an imbalance of gaseous exchanges in fish. The resulting liver hyperactivity leads to degeneration of the liver tissue. Behavioral responses such as avoidance were also observed [67].

1.10. Research Objective

1. To study the effect on water quality parameters such as COD, BOD, TOC and NH^{+}_{4}-N during chlorination of raw Sewage.

2. To study the effect on water quality parameters such as COD, BOD, TOC and NH^{+}_{4}-N during chlorination of secondary effluent collected from different full-scale waste water treatment plants.

3. To study the formation of THMs during chlorination of secondary effluent collected from different full-scale waste water treatment plants.

References

1. IARC, 1999. hhttp://monographs.iarc.fr/htdocs/indexes/vol52index.htmli, accessed at, 2006.

2. Levine, A., Asano, T. Recovering sustainable water from wastewater. *Environ. Sci. Technol.* **2004**, *38*, 201A–208A.
3. Gordon, S. M., Wallace, L. A., Callahan, P. J., Kenny, D. V., Brinkman, M. C. Effect of water temperature on dermal exposure to chloroform. *Environ. Health Persp.* **1998**, *106*, 337–345.
4. Fantuzzi, G., Righi, E., Predieri, G., Ceppelli, G., Gobba, F., Aggazzotti, G. Occupational exposure to trihalomethanes in indoor swimming pools. *Sci. Total Environ.* **2001**, *264*, 257–265.
5. Xu, X., Weisel, C. P. Dermal uptake of chloroform and haloketones during bathing. *J. Expos. Anal. Environ. Epidemiol.* **2005**, *15*, 289–296.
6. World Health Organization, Developing human health related chemical guidelines for reclaimed water and sewage sludge applications in agriculture, **1996**.
7. Satyanarayana, M., Chandrasekhar, M. 'Occurrence and control of trihalomethanes in drinking water supplies'. *Indian J. Environ. Prot.* **1996**, *16*, 423–426.
8. Thacker, N. P., Vaidya, M. V., Sipani, M., Kaur, P., Rudra, A. Water Systems and Organohalide Contaminants, 22nd Wat. Eng. and Dev. Center, Conference held at New Delhi, September 9–13, **1996**, *2*, 361–362.
9. Thacker, N. P., Kaur, P., Rudra, A. 'Halogenated compounds in and around Nagpur City water resources, India'. *Environ. Educ. Inf.* **1997**, *16*, 367–376.
10. White, G. C. Handbook of Chlorination and Alternative Disinfectants. New York: Van Nostrand Reinhold, **1992**.
11. Tchobanoglous, G., Burton, F. L. Wastewater engineering: treatment, disposal, and reuse / Metcalf & Eddy, Inc. 3rd edition. New York: McGraw-Hill, Inc., **1991**.

12. Haas, C. N., Aturaliye, D. N. Kinetics of electroporation-assisted chlorination of Giardia muris. *Water Research*, **1999**, *8*, 1761-1766.

13. Jacangelo, J. G., Trussell, R. R. Internation report:water and wastewater disinfection – trends, issues and practices. *Water Science and Technology*, Water Supply. **2002**, *3*, 147- 157.

14. American Water Works Association. Water Quality & Treatment, A Handbook of Community Water Supplies. 5th edition. McGraw Hill. Technical editor: Letterman, R. D., (**1999**).

15. Korn, E. L., Graubard, B. I. Analysis of health surveys. *Journal of Statistical Planning and Inference*. **2002**, *100*, 1-89.

16. U.S. Environmental Protection Agency, Office of Water, Washington, D. C., EPA 832-F-99-063, *Wastewater Technology Fact sheet, Ozone disinfection* (online), **1999a**.

17. U.S. Environmental Protection Agency, Office of Water, Washington, D. C., EPA 832-F-99-064, *Wastewater Technology Fact sheet, Ultraviolet disinfection* (online), **1999b**.

18. Singer, P. C., Obolensky, A., Greiner, A. DBPs in chlorinated North Carolina drinking waters. *J. Am. Water Works Assoc.* **1995**, *87*, 83-92.

19. Chen, W. J., Weisel, C. P. Halogenated DBP concentrations in a distribution system. *J. Am. Water Works Assoc.* **1998**, *90*, 151-163.

20. Le Bel, G. L., Benoit, F. M., Williams, D. T. A one-year survey of halogenated disinfection by-products in the distribution system of treatment plants using three different disinfection processes. *Chemosphere*. **1997**, *34*, 2301-2317.

21. Nieminski, E.C., Chaudhuri, S., Lamoreaux, T. The occurrence of DBPS in Utah drinking waters. *J. Am. Water Works Assoc.* **1993**, *85*, 98-105.

22. Dojlido, J., Zbiec, E., Swietlik, R. Formation of the haloacetic acids during ozonation and chlorination of water in Warsaw waterworks (Poland). *Water Resource*. **1999**, *33*, 3111 -3118.

23. Diehl, A. C., Speitel, G. E., Symons, J. M., Krasner, S.W., Hwang, C. J., Barrett, S. E. DBP formation during chloramination. *J. Am. Water Works Assoc*. **2000**, *92*, 76-90.

24. Pourmoghaddas, H., Stevens, A. A., Kinman, R. N., Dressman, R. C., Moore, L. A., Ireland, J. C. Effect of bromide ion on formation of HAAs during chlorination. *J. Am. Water Works Assoc*. **1993**, *85*, 82-87.

25. Amato, Ivan. "The Crusade Against Chlorine". *Science*. **1994**, *261*, 152-154.

26. US Environmental Protection Agency (USEPA). Design Manual: Municipal Wastewater Disinfection. *Water Engineering Research Laboratory, Cincinnati*, OH, **1986**.

27. Manahan, Stanley E., Environmental Chemistry. Chelsea, Michigan: Lewis Publishers, Inc., **1991**.

28. Singer, P. C., Brown, R. A., Wiseman, J. F. J. "Formation of Halogenated Organics during Wastewater Disinfection". *Report for the Water Resources Research Institute of the University of North Carolina* Chapel Hill, North Carolina, **1988**.

29. Bates, R. G., Pinching, G. D. "Dissociation Constants of Aqueous Ammonia at 0 to 50^0 from E. m. f. Studies of the Ammonium Salt of a Weak Acid". *J. Am. Chem. Soc*. **1950**, *72*, 1393-1396.

30. Wei, I. W. "Chlorine-Ammonia Breakpoint Reactions: Kinetics and Mechanisms". Ph. D Thesis, Harvard University, Cambridge, Mass., **1972**.

31. Weil, I., Morris, J. C. "Kinetic studies on Chloramines". *J. Am. Chem. Soc.* **1949**, *71*, 1664-1671.

32. White, G. C. Handbook of Chlorination. 3rd edition: Van Nostrand Reinhold Co., New York, **1992**.

33. Yoon, J., Jensen, J. N. "Distribution of Aqueous Chlorine with Nitrogen Compounds: Chlorine Transfer from Organic Chloramines to Ammonia". *Environ. Sci. and Technol.* **1993**, *27*, 403.

34. Dods, Thomas, Personal Communication, Tahoe Truckee WWT Plant C.A., **1993**.

35. Palin, A. T. "The Determination of Free and Combined Chlorine in Water by the use of Diethyl-pphenylene Diamine". *Journal AWWA*, **1957**, *49*, 873-880.

36. Standard Methods for the Examination of Water and Wastewater, 18th ed. APHA, AWWA, WEF: Amer. Public Health Assoc., Washington D.C., **1992**.

37. Morris, J. C. "The formation of chloramine and dichloramine in water chlorination". 117th Meeting, Am. Chem. Soc., Detroit, Mich., April 16-20, **1950**.

38. Selleck, R. E. A Literature Review of Chlorine - Ammonia Reaction Chemistry, Private Paper, April, **1991**.

39. Jander, J., Engelhardt, U. "Nitrogen compounds of Chlorine, Bromine, and Iodine" from Developments in Inorganic Nitrogen Chemistry. Vol. 2, p. 70, Colburn & Elsevier Scientific Publishing Co., **1973**.

40. Margerum, D. W. "Chlorination and the formation of N-chloro compounds in water treatment". Organometals & organometalloids : occurance and fate in the environment. *J. Am. Chem. Soc.* **1978**, *82*, 278-281.

41. Morris, J. C., Issac, R. A. "A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system". Water chlorination –

chemistry: environmental impact & health effects, Vol. 5, Jolley, R.L., Ann Arbor science, Seven Oaks, Kent, England, **1983**.

42. Corbett, R. E. "Studies of N-halogeno-compounds". *J. Am. Chem. Soc.* **1953**, *22*, 1927-1929.
43. Granstrom, M. L. "The disproportionation of monochloramine" PhD Thesis, Harvard University, Cambridge, Mass., 1954. Quoted from Selleck, **1991**.
44. Gray, E. T. "Chloramine equilibria and the kinetics of disproportionation in aqueous solution". *Journal ACS.* **1978**, *82*, 264-268.
45. Morris, J. C. "The Acid Ionization Constant of HOCl from 5 to 35^{0}". *J. Phys. Chem.* **1966**, *70*, 3798-3805.
46. Chapin, R. M. "Dichloro-Amine". *J. Am. Chem. Soc.* **1929**, *51*, 2112-2117.
47. Morris, J. C. "Kinetics of reactions between aqueous chlorine and nitrogen compounds". Principles and applications of water chemistry. Faust, S. D., John Wiley & Sons, Inc. New York, **1965**.
48. Hand, V. C., Margerum. R. W. " Kinetics and mechanisms of the decomposition of dichloramine in aqueous solutions". *Inorg. Chem.* **1983**, *22*, 1449-1456.
49. Jolly, W. L. "The thermodynamics properties of chloramine, dichloramine, and nitrogen trichloride". *J. Phys. Chem.* **1956**, *60*, 507-508.
50. Dulong, P. L., Schweigger's J. Chem. Pharm. **1812**, *8*, 32. Quoted from paper "Chemistry of Nitrogen Trichloride" by Carl Vogler.
51. Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VIII, p.598.
52. Palin, A. T. "A Study of the Chloro Derivatives of Ammonia". *Water and Water Engineering,* **1950**, *54*, 151-153.

53. Saguinzin, J. L., Morris, J. C. " The chemistry of aqueous nitrogen trichloride". In Disinfection of Water and Wastewater, Johnson, J. D., ed. Ann Arbor Science Publishers, Inc. **1975**, p.277.
54. Kumar, K., Shinness, R. W., Margerum, D. W. "Kinetics and mechanisms of the base decomposition of nitrogen trichloride in aqueous solutions". Inorg. Chem. **1987**, *26*, 3430-3434.
55. Griffin, A. E. "Reaction of Heavy Doses of Chlorine in Various waters". *J. Am. Water Works Assoc.* **1939**, *31*, 2121-2129.
56. Jensen, J. N., Johnson, J. D. "Specificity of the DPD and Amperometric Titration Methods for Free Available Chlorine: A Review". *J. Am. Water Works Assoc.* **1989**, *81*, 59-64.
57. Calvert, C. K. "Treatment with Copper Sulfate, Chlorine, and Ammonia". *J. Am. Water Works Assoc.* **1940**, *32*, 1155-1164.
58. Griffin, A. E., Chamberlin, N. S. "Some Chemical Aspects of Breakpoint Chlorination". *J. New England Water Works Assoc.* **1941**, *55*, 371.
59. Rossum, J. R. "A Proposed Mechanism for Break-point Chlorination". *J. Am. Water Works Assoc.* **1943**, *35*, 1446.
60. Wei, I., Morris, J. C. Dynamics of Breakpoint Chlorination, in Chemistry of Water Supply Treatment and Distribution, Rubin, A. J., ed. Ann Arbor, Mich. : Ann Arbor Science, **1974**.
61. Saunier, B. M., Selleck, R. E. "Kinetics of Breakpoint Chlorination and of disinfection". SERL Report No. 76-2, University of California, Berkeley, C.A., **1976**.
62. Pressley, T. A., Bishop, D. F., Pinto, A. P., Cassel A. F. "Ammonia-Nitrogen Removal by Breakpoint Chlorination". EPA report - 670/2-73-058, **1973**.

63. Atkins, P. F., Scherger, D. A., Barnes, R. A., Evans III, F. L. "Ammonia Removal by Physical-Chemical Treatment". *Journal WPCF*, **1973**, *45*, 2372-2388.

64. Taras, M. J. "Effect of Free residual Chlorine on Nitrogen Compounds in Water". *J. Am. Water Works Assoc.* **1953**, *45*, 47-61.

65. Taras, M. J. "Chlorine Demand Studies". *J. Am. Water Works Assoc.* **1950**, *42*, 462-474.

66. Baker, R. J. "Types and Significance of Chlorine Residuals". *J. Am. Water Works Assoc.* **1959**, *51*, 1185-1190.

67. Abarnou, A., Miossec, L. "Chlorinated Waters Discharged tr' the Marine Environment: Chemistry and Environmental Impact. An Overview". *The Science of the Total Environment, 11 September* **1992**, *126*, 173-197.

68. Johnson, J. D., Jensen, J. N. "THM and TOX Formation: Routes, Rates, and Precursors". *J. Am. Water Works Assoc.* April. **1986**, *22*, 156-162.

69. Morrison, R. T., Boyd, R. N. Organic Chemistry. Englewood Cliffs, New Jersey: Prentice Hall, **1992**.

70. Rook, J. J. "Formation of Haloforms during Chlorination of Natural Waters". *Water Treatment & Examination*, **1974**, *23*, 234-243.

71. Gilbert, Charles, E. and Calabrese, Edward J. (editors). Regulating Drinking Water Quality. Chelsea, Michigan: Lewis Publishers, Inc., **1992**.

72. Trussell, R. R., Umphres, M. D. "The Formation of Trihalomethanes". *J. Am. Water Works Assoc. November.* **1978**, *70*, 604-612.

73. Franson, Mary Ann H. (editor). *Standard Methods for the Examination of Water and Wastewater, 18th Edition.* Washington, DC: American Public Health Association, 1992.
74. Ram, N. M., Christman, R. F., Cantor, K. P. *Significance and Treatment of Volatile Organic Compounds in Water Supplies.* Chelsea, Michigan: Lewis Publishers, Inc., 1990.
75. National Research Council (NRC). *Chloroform, Carbon Tetrachloride, and other Halomethanes: An Environmental Assessment.* Washington, D. C: National Academy of Sciences, 1978.
76. Longley, Karl E. (editor). Wastewater Disinfection: Manual of Practice No. FD-1O. Alexandria, Virginia: *Water Pollution Control Federation,* 1986.
77. Feben, D., Taras, M. J. "Chlorine Demand in Detroit Water". *J. Am. Water Works Assoc.* 1950, *42*, 453-461.
78. Feben, D., Taras, M. J., "Chlorine Demand Constants". *J. Am. Water Works Assoc.* 1951, *43*, 922-932.
79. Cairns, J. J., Pratt, J. R. "Ecotoxicological Effect Indices: A rapidly evolving system". *Water Science Technology,* 1987, *19,* 1-12.
80. Bartell, Steven M., Gardner, Robert H., O'Neill, Robert V. (editors). *Ecological Risk Estimation.* Chelsea, Michigan: Lewis Publishers, 1992.
81. Cothern, C. Richard (editor). Comparative Environmental Risk Assessment. Boca Raton, Florida: Lewis Publishers, 1993.
82. Cairns, J. J., Pratt, J. R., Niederlehner, B. R., Bowers, N. J. "Structural and Functional Responses in Aquatic Ecosystems". Final Technical Report to the Air Force Office of Scientific Research. Blacksburg, Virginia, 1988.

Table 3.4.8b. Effect of chlorination on chlorine residuals and chlorine demands observed at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	Residual chlorine (mg/L)		Chlorine demand (mg/L)	
	Average	S.D (±)	Average	S.D (±)
0	0.00	0.00	0.00	0.00
5	3.91	0.18	1.09	0.18
10	8.88	0.19	1.12	0.17
20	18.83	0.17	1.17	0.20
30	28.78	0.20	1.22	0.23
50	47.73	0.21	2.27	0.21

Table 3.4.9a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	16.5 ± 1
pH	7.3 ± 0.1
NH_4^+-N (mg/L)	4 ± 0.1
COD (mg/L)	28 ± 1.5
BOD_5 (mg/L)	16 ± 1
TOC(mg/L)	8 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.9b. Effect of chlorination on NH_4^+-N at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	NH_4^+-N (mg/L)	
	Average	S.D (±)
0	4.0	0.10
1	3.7	0.11
2	3.3	0.12
3	3.0	0.12
4	2.7	0.11
5	2.5	0.13

Table 3.4.7a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	16 ± 1
pH	7.1 ± 0.1
NH_4^+-N (mg/L)	15 ± 1
COD (mg/L)	50 ± 1.5
BOD_5 (mg/L)	20 ± 1
TOC (mg/L)	17 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 5.7b. Effect of chlorination on chlorine residuals and chlorine demands observed at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	Residual chlorine (mg/L)		Chlorine demand (mg/L)	
	Average	S.D (±)	Average	S.D (±)
0	0.0	0.000	0.0	0.000
1	0.2	0.023	0.8	0.018
3	1.6	0.027	1.4	0.027
5	3.2	0.029	1.8	0.023
7	5.1	0.023	1.9	0.017
9	6.4	0.028	2.6	0.025
10	7.1	0.023	2.9	0.019

Table 3.4.8a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	22 ± 1
pH	7.33 ± 0.05
NH_4^+-N (mg/L)	15.4 ± 1
COD (mg/L)	37 ± 2
BOD_5 (mg/L)	22 ± 2
TOC (mg/L)	11 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.5b. Effect of chlorination on chlorine residuals and chlorine demands observed at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	Residual chlorine (mg/L)		Chlorine demand (mg/L)	
	Average	S.D (±)	Average	S.D (±)
0	0.00	0.000	0.00	0.000
1	0.54	0.015	0.46	0.019
2	1.49	0.029	0.51	0.028
3	2.37	0.028	0.63	0.022
4	3.29	0.028	0.71	0.019
5	4.21	0.019	0.79	0.025

Table 3.4.6a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^0C)	16 ± 1
pH	7.1 ± 0.05
NH_4^+-N (mg/L)	9.2 ± 0.5
COD (mg/L)	34 ± 10.5
BOD_5 (mg/L)	16 ± 1
TOC (mg/L)	12 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.6b. Effect of chlorination on chlorine residuals and chlorine demands observed at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	Residual chlorine (mg/L)		Chlorine demand (mg/L)	
	Average	S.D (±)	Average	S.D (±)
0	0.00	0.000	0.00	0.000
1	0.37	0.014	0.63	0.018
2	1.25	0.027	0.75	0.027
3	2.14	0.029	0.86	0.021
4	3.07	0.023	0.93	0.017
5	4.00	0.018	1.00	0.024
7	5.64	0.023	1.36	0.019

Table 3.4.4a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	20 ± 1
pH	7.3 ± 0.1
NH_4^+-N (mg/L)	9 ± 1
COD (mg/L)	55 ± 1.09
BOD_5 (mg/L)	25 ± 1.12
TOC (mg/L)	13 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.4b. Effect of chlorination on COD, BOD_5 and TOC during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	**COD (mg/L)**		**BOD_5 (mg/L)**		**TOC (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	55	1.09	25	1.12	13	1.00
3	45	2.53	23	0.53	12	0.52
5	37	1.00	21	1.01	13	1.03
10	45	1.07	26	1.07	13	1.31
20	57	1.79	34	0.92	12	0.99
30	69	2.59	45	1.80	12	0.98
40	105	3.93	50	2.90	10	1.29

Table 3.4.5a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	16.5 ± 1.5
pH	7.3 ± 0.1
NH_4^+-N (mg/L)	9 ± 1
COD (mg/L)	26 ± 1
BOD_5 (mg/L)	17 ± 1
TOC (mg/L)	11 ± 0.5
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.2b. Effects of chlorination on COD, BOD$_5$ and TOC for Rishikesh (SBR) effluent during 30 min

Chlorine dosage (mg/L)	COD (mg/L)		BOD$_5$ (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	40	1.09	17	1.01	12	1.00
1	35	0.56	16	0.55	10	0.56
2	24	1.00	14	1.00	11	1.02
3	21	1.12	13	1.06	11	1.31
4	20	0.56	12	0.51	13	0.53
5	26	0.51	16	0.64	10	0.78
7	34	0.62	19	0.61	12	0.62

Table 3.4.3a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	19 ± 1
pH	7.2 ± 0.1
NH$_4^+$-N (mg/L)	6.5 ± 0.7
COD (mg/L)	60 ± 1.09
BOD$_5$ (mg/L)	33 ± 1.01
TOC (mg/L)	18 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.3b. Effect of chlorination on COD, BOD$_5$ and TOC during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	COD (mg/L)		BOD$_5$ (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	60	1.09	33	1.01	18	1.00
3	55	2.56	28	0.57	17	0.52
5	48	1.00	25	1.01	16	1.02
10	55	1.01	32	1.04	16	1.31
20	77	1.79	43	0.92	14	0.92
30	89	2.53	46	1.89	17	0.97
40	110	3.91	60	2.98	18	1.20

Appendix C

Table 3.4.1a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	17 ± 1
pH	7.2 ± 0.1
NH_4^+-N (mg/L)	7 ± 0.5
COD (mg/L)	38 ± 1
BOD_5 (mg/L)	19 ± 1
TOC (mg/L)	12 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.1b. Effect of chlorination on COD, BOD_5 and TOC for Rishikesh (SBR) effluent during 30 min

Chlorine dosage (mg/L)	**COD (mg/L)**		**BOD_5 (mg/L)**		**TOC (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	38	1.00	19	1.00	12	1.00
1	23	0.57	16	0.59	9	0.57
2	20	1.00	13	1.00	11	1.00
3	18	1.00	11	1.09	13	1.31
4	17	0.57	12	0.58	12	0.53
5	21	0.59	14	0.62	9	0.91
7	27	0.61	17	0.71	11	0.73

S.D = Standard Deviation

Table 3.4.2a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	18 ± 1
pH	7.29 ± 0.1
NH_4^+-N (mg/L)	6 ± 0.5
COD (mg/L)	40 ± 1.09
BOD_5 (mg/L)	17 ± 1.01
TOC (mg/L)	12 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.13a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	16 ± 1
pH	7.1 ± 0.05
NH_4^+-N (mg/L)	6.9 ± 0.28
COD (mg/L)	32.42 ± 1
BOD_5 (mg/L)	19.61 ± 1.5
TOC (mg/L)	10 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.13b. Effect of chlorination on COD, NH_4^+-N, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	COD (mg/L)		NH_4^+-N(mg/L)		Residual chlorine (mg/L)		Chlorine demand (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	32	1.00	6.9	0.28	0.000	0.000	0.000	0.000
1	30	0.73	5.1	0.27	0.355	0.070	0.645	0.040
2	28	1.22	4.6	0.29	1.243	0.076	0.758	0.043
3	26	1.15	3.4	0.23	2.130	0.079	0.870	0.047
4	24	0.91	2.9	0.24	3.018	0.076	0.983	0.047
5	21	1.38	2.6	0.29	3.994	0.076	1.006	0.045
7	20	0.92	2.1	0.22	5.680	0.069	1.320	0.055

Table 3.3.14a. Trihalomethane formation

Chlorine dosage (mg/L)	$CHCl_3$ (µg/L)		$CHCl_2Br$ (µg/L)		$CHBr_2Cl$ (µg/L)		$CHBr_3$ (µg/L)
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)	
0	ND	0.0	ND	0.0	ND	0.0	ND
1	100.3	2.5	27.4	2.1	13.2	2.2	ND
2	125.3	2.6	30.4	2.3	15.4	1.8	ND
3	150.4	2.4	40.3	1.9	16.9	2.0	ND
4	175.5	2.3	45.4	1.8	18.3	2.1	ND
5	200.4	2.6	52.9	2.6	40.6	2.3	ND

ND = Not Detected

Table 3.3.11b. Effect of chlorination on COD, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	**COD (mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	36	1.00	0.00	0.00	0.00	0.00
5	30	0.73	3.90	0.20	1.09	0.10
10	33	1.21	8.52	0.26	1.48	0.13
20	45	1.13	18.81	0.25	1.19	0.17
30	59	0.92	28.76	0.26	1.25	0.17
50	68	1.37	47.75	0.26	2.25	0.15

Table 3.3.12a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	16.5 ± 1
pH	7.3 ± 0.04
NH_4^+-N (mg/L)	4 ± 0.18
COD (mg/L)	26 ± 1
BOD_5 (mg/L)	15.7 ± 1.5
TOC (mg/L)	8.9 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.12b. Effect of chlorination on COD, NH_4^+-N, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	**COD (mg/L)**		**NH_4^+-N(mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	26	1.00	4.0	0.18	0.00	0.000	0.000	0.000
1	24	0.73	3.6	0.17	0.53	0.050	0.468	0.040
2	22	1.22	3.2	0.19	1.42	0.046	0.580	0.043
3	20	1.15	3.0	0.13	2.30	0.059	0.693	0.047
4	18	0.91	2.8	0.14	3.19	0.056	0.805	0.047
5	17	1.38	2.6	0.13	4.08	0.046	0.975	0.045

Table 3.3.10a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	16 ± 1
pH	7.1 ± 0.05
NH_4^+-N (mg/L)	28.5 ± 1.4
COD (mg/L)	47 ± 1
BOD_5 (mg/L)	29 ± 1.5
TOC (mg/L)	16 ± 0.5
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.10b. Effect of chlorination on COD, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	**COD (mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	47	1.00	0.0	0.000	0.0	0.000
1	41	0.73	0.0	0.000	1.0	0.057
3	38	1.21	1.6	0.056	1.4	0.059
5	36	1.13	3.2	0.059	1.8	0.063
7	31	0.92	5.3	0.068	1.7	0.067
9	35	0.87	6.4	0.066	2.6	0.058
10	40	1.03	7.2	0.073	2.8	0.062

Table 3.3.11a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	22 ± 1
pH	7.33 ± 0.06
NH_4^+-N (mg/L)	15.4 ± 1.2
COD (mg/L)	37 ± 1
BOD_5 (mg/L)	23 ± 1.2
TOC (mg/L)	12 ± 0.9
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.8b. Effect of chlorination on COD, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	**COD (mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	26	1.00	0.00	0.000	0.00	0.000
1	24	0.73	0.53	0.053	0.47	0.059
2	22	1.26	1.42	0.058	0.58	0.058
3	20	1.15	2.31	0.059	0.69	0.065
4	19	0.91	3.19	0.066	0.81	0.068
5	21	0.88	4.08	0.069	0.98	0.057

Table 3.3.9a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	16 ± 1
pH	7.1 ± 0.05
NH_4^+-N (mg/L)	6.9 ± 1.2
COD (mg/L)	32.42 ± 1
BOD_5 (mg/L)	21.02 ± 1
TOC (mg/L)	13 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.9b. Effect of chlorination on COD, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	**COD (mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	32	1.00	0.00	0.000	0.00	0.000
1	30	0.72	0.36	0.053	0.65	0.059
2	28	1.24	1.24	0.057	0.76	0.058
3	26	1.15	2.13	0.059	0.87	0.064
4	24	0.92	3.02	0.065	0.98	0.068
5	22	0.88	3.99	0.068	1.01	0.059
7	21	1.02	5.68	0.070	1.32	0.060

Table 3.3.7a. The average initial characteristics of waste water are given below (average result of table 3.3.5a and 3.3.6a)

parameters	Range (± S.D)
Temperature (^{0}C)	(19-20) ± 1
pH	(7.2-7.3) ± 0.05
NH_4^+-N (mg/L)	(4.0-5.1) ± 0.5
COD (mg/L)	(52-42) ± 5.77
BOD_5 (mg/L)	(31-25) ± 3.44
TOC (mg/L)	(11-13) ± 2.41
Available residual chlorine (mg/L)	(0.0-0.0) ± 0.0

Table 3.3.7b. Variation of, COD, BOD_5 and TOC with different chlorine dosages during 30 min for Haridwar (SBR) effluent (Average result of table 3.3.5b and 3.3.6b)

Chlorine dosage (mg/L)	Number of tests	COD (mg/L)			BOD_5 (mg/L)			TOC (mg/L)		
		Range	Average	S.D (±)	Range	Average	S.D (±)	Range	Average	S.D (±)
0	2	42-52	47	5.77	25-31	28	3.44	13-17	15	2.41
3	2	39-49	44	5.76	23-28	25	3.45	12-16	14	2.13
5	2	37-43	40	3.44	20-26	23	2.98	14-15	14	0.51
10	2	45-55	50	5.67	27-32	29	2.88	13-16	14	1.24
20	2	57-67	62	5.76	34-43	38	4.51	11-14	12	1.25
30	2	69-70	69	0.57	44-46	45	1.21	12-17	14	2.72
40	2	79-79	79	0.56	50-54	52	2.41	10-16	13	3.74

Table 3.3.8a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	16.5 ± 1
pH	7.3 ± 0.05
NH_4^+-N (mg/L)	4.0 ± 0.5
COD (mg/L)	26 ± 1
BOD_5 (mg/L)	17 ± 1.2
TOC (mg/L)	11 ± 1.5
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.5b. Effect of chlorination on COD, BOD_5 and TOC during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	COD (mg/L)		BOD_5 (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	52	1.00	31	1.00	17	1.00
3	49	0.73	28	0.59	16	0.87
5	43	1.20	26	1.00	15	1.00
10	55	1.09	32	1.09	16	1.32
20	67	0.97	43	0.88	14	0.93
30	70	0.89	46	0.91	17	0.92
40	79	0.92	54	0.92	16	0.84

Table 3.3.6a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^0C)	20 ± 1
pH	7.3 ± 0.05
NH_4^+-N (mg/L)	5.1 ± 0.5
COD (mg/L)	42 ± 1
BOD_5 (mg/L)	25 ± 1
TOC (mg/L)	13 ± 1.09
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.6b. Effect of chlorination on COD, BOD_5 and TOC during 30 min for Haridwar (SBR) effluent

Chlorine dosage (mg/L)	COD (mg/L)		BOD_5 (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	42	1.00	25	1.00	13	1.09
3	39	0.72	23	0.59	12	0.87
5	37	1.24	20	1.00	14	1.12
10	45	1.10	27	1.09	13	1.32
20	57	0.91	34	0.88	11	0.91
30	69	0.89	44	0.91	12	0.92
40	79	0.92	50	0.92	10	0.83

Table 3.3.4a. The average initial characteristics of waste water are given below (average result of table 3.3.1a, 3.3.2a and 3.3.3a)

Parameters	Range (± S.D)
Temperature (^{0}C)	(17-18) ± 1
pH	(7.2-7.4) ± 0.05
NH_4^+-N (mg/L)	(3.4-5) ± 0.5
COD (mg/L)	(30-39) ± 1
BOD_5 (mg/L)	(18-24) ± 1.08
TOC (mg/L)	(11-13) ± 1
Available residual chlorine (mg/L)	(0.0-0.0) ± 0.0

Table 3.3.4b. Overall Variation of COD, BOD_5 and TOC during chlorination for Haridwar (SBR) effluent during 30 min (Average result of table 3.3.1b, 3.3.2b and 3.3. 3b)

Chlorine dosage (mg/L)	Number of tests	COD (mg/L)			BOD_5 (mg/L)			TOC (mg/L)		
		Range	Average	S.D (±)	Range	Average	S.D (±)	Range	Average	S.D (±)
0	3	30-39	34	1.00	18-24	21	1.08	11-13	12	1.00
1	3	24-36	30	0.52	15-21	18	0.53	10-12	11	0.54
2	3	21-31	26	1.23	12-19	15	1.21	11-13	12	1.02
3	3	19-30	24	1.04	10-17	13	1.02	10-12	11	1.31
4	3	18-28	23	0.53	11-19	14	0.51	12-13	13	0.54
5	3	20-32	26	0.56	13-21	17	0.63	9-12	10	0.57
7	3	25-35	30	0.49	15-24	20	0.52	11-15	13	0.82

Table 3.3.5a The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	19 ± 1.5
pH	7.2 ± 0.04
NH_4^+-N (mg/L)	4 ± 0.5
COD (mg/L)	52 ± 1
BOD_5 (mg/L)	31 ± 1
TOC (mg/L)	17 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.2b. Effects of chlorination on COD, BOD_5 and TOC for Haridwar (SBR) effluent during 30 minutes

Chlorine dosage (mg/L)	COD (mg/L)		BOD_5 (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	35	1.00	20	1.00	12	1.00
1	26	0.53	17	0.58	11	0.57
2	24	1.20	13	1.00	12	1.00
3	21	1.09	12	1.02	11	1.32
4	20	0.57	13	0.54	13	0.54
5	25	0.59	16	0.61	10	0.92
7	29	0.52	19	0.53	13	0.86

Table 3.3.3a. The initial characteristics of waste water are given below

Parameters	Values (± S.D)
Temperature (^{0}C)	18 ± 1
pH	7.4 ± 0.05
NH_4^+-N (mg/L)	5 ± 1
COD(mg/L)	39 ± 1
BOD_5 (mg/L)	24 ± 1
TOC (mg/L)	13 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.3b. Effect of chlorination on COD, BOD_5 and TOC for Haridwar (SBR) effluent during 30 min

Chlorine dosage (mg/L)	COD (mg/L)		BOD_5 (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	39	1.00	24	1.00	13	1.00
1	36	0.53	21	0.53	12	0.57
2	31	1.20	19	1.20	13	1.03
3	30	1.06	17	1.02	12	1.34
4	28	0.57	19	0.54	13	0.54
5	32	0.52	21	0.61	12	0.58
7	35	0.51	24	0.53	15	0.86

Appendix B

Table 3.3.1a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	17 ± 1
pH	7.2 ± 0.05
NH_4^+-N (mg/L)	3.5 ± 0.5
COD (mg/L)	30 ± 1
BOD_5 (mg/L)	18 ± 1
TOC (mg/L)	11 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.3.1b. Effect of chlorination on COD, BOD_5 and TOC for Haridwar (SBR) effluent during 30 min

Chlorine dosage (mg/L)	**COD (mg/L)**		**BOD_5 (mg/L)**		**TOC (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	30	1.00	18	1.00	11	1.00
1	24	0.53	15	0.59	10	0.57
2	21	1.20	12	1.00	11	1.00
3	19	1.09	10	1.09	10	1.32
4	18	0.57	11	0.58	12	0.53
5	20	0.59	13	0.61	9	0.92
7	25	0.62	15	0.62	11	0.64

S.D = Standard Deviation

Table 3.3.2a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	18 ± 1
pH	7.29 ± 0.05
NH_4^+-N (mg/L)	4.2 ± 0.7
COD (mg/L)	35 ± 1
BOD_5 (mg/L)	20 ± 1
TOC (mg/L)	12 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.2.7b. Effect of chlorination on COD, Residual chlorine and Chlorine demand for Khanjarpur, Roorkee raw sewage during 30 min

Chlorine dosage (mg/L)	COD (mg/L)		Residual chlorine (mg/L)		Chlorine demand (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	450	3.30	0.0	0.000	0.0	0.000
2.4	410	3.53	0.0	0.000	2.4	0.340
12.0	385	3.40	2.0	0.000	10.0	0.353
24.2	310	3.39	6.9	0.533	17.3	0.367
36.2	325	3.67	12.7	0.521	23.5	0.359
48.3	458	3.59	17.2	0.494	31.11	0.368

Table 3.2.6a. The initial characteristics of waste water are given below

Parameters (^0C)	**Values (± S.D)**
Temperature	20 ± 1
pH	7.3 ± 0.05
NH_4^+-N (mg/L)	59 ± 2
COD (mg/L)	425 ± 3
TOC (mg/L)	140 ± 2
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.2.6b. Effect of chlorination on COD, Residual chlorine and Chlorine demand for Khanjarpur, Roorkee raw sewage during 30 min

Chlorine dosage (mg/L)	**COD (mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	425	3.00	0.0	0.000	0.0	0.000
2.4	394	3.33	0.0	0.000	2.4	0.370
12.0	372	3.20	0.0	0.000	12.0	0.373
24.2	416	3.19	6.7	0.723	17.4	0.377
36.2	383	3.47	11.7	0.741	24.5	0.369
48.3	429	3.59	15.75	0.734	32.55	0.368

Table 3.2.7a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	20 ± 1
pH	7.3 ± 0.05
NH_4^+-N (mg/L)	80 ± 2
COD (mg/L)	450 ± 3.30
TOC (mg/L)	140 ± 2
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.2.4a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	18 ± 1
pH	7.4 ± 0.1
NH_4^+-N (mg/L)	75 ± 1.5
COD (mg/L)	300 ± 2
BOD_5 (mg/L)	150 ± 2.10
TOC (mg/L)	100 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.2.4b. Effect of chlorination on COD, BOD_5 and TOC during 30 min for Khanjarpur, Roorkee raw sewage

Chlorine dosage (mg/L)	**COD (mg/L)**		**BOD_5 (mg/L)**		**TOC (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	***S.D (±)***
0	300	2.00	150	2.10	100	1.00
3	285	2.03	147	2.19	97	1.17
5	280	2.10	140	2.00	92	1.05
10	274	2.09	138	2.08	98	1.12
20	284	2.14	144	2.27	95	1.24
30	290	2.37	148	2.21	102	1.12
50	305	2.53	154	2.23	91	1.13

Table 3.2.5b. Effect of chlorination on COD, NH_4^+-N, Residual chlorine and Chlorine demand observed at different chlorine dosages during 30 min for Khanjarpur, Roorkee raw sewage

Chlorine dosage (mg/L)	**COD (mg/L)**		**NH_4^+-N (mg/L)**		**Residual chlorine (mg/L)**		**Chlorine demand (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	452	2.00	53.5	0.98	0.0	0.000	0.0	0.000
2.4	409	2.33	33.25	0.97	0.0	0.000	2.4	0.070
12.0	383	2.20	12.2	0.99	2.1	0.086	9.9	0.073
24.2	308	2.19	10.1	0.93	6.7	0.089	17.5	0.077
36.2	323	2.47	7.0	0.94	11.9	0.086	24.4	0.069
48.3	459	2.59	5.9	0.93	16.2	0.086	32.1	0.068

Table 3.2.2b. Effects of chlorination on COD, BOD_5 and TOC for Khanjarpur, Roorkee raw sewage during 30 min

Chlorine dosage (mg/L)	COD (mg/L)		BOD_5 (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	420	2.00	215	2.10	145	1.00
1	418	2.33	213	2.49	140	1.27
2	418	2.20	212	2.00	137	1.00
3	415	2.19	210	2.09	138	1.32
4	412	2.47	207	2.48	136	1.43
5	400	2.59	209	2.61	139	1.32
7	395	2.72	198	2.52	137	1.54

Table 3.2.3a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	18 ± 1
pH	7.4 ± 0.1
NH_4^+-N (mg/L)	58 ± 2
COD (mg/L)	332 ± 2
BOD_5 (mg/L)	150 ± 2.10
TOC (mg/L)	117 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.2.3b. Effects of chlorination on COD, BOD_5 and TOC for Khanjarpur, Roorkee raw sewage during 30 min

Chlorine dosage (mg/L)	COD (mg/L)		BOD_5 (mg/L)		TOC (mg/L)	
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)
0	332	2.00	150	2.10	117	1.00
1	315	2.03	142	2.19	114	1.17
2	290	2.10	135	2.00	116	1.00
3	295	2.09	138	2.09	110	1.12
4	305	2.17	142	2.28	115	1.23
5	315	2.39	148	2.21	112	1.12
7	327	2.52	152	2.22	116	1.14

Appendix A

Table 3.2.1a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	17 ± 1
pH	7.3 ± 0.05
NH_4^+-N	60 ± 2
COD (mg/L)	400 ± 2
BOD_5 (mg/L)	210 ± 2
TOC (mg/L)	148 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.2.1b. Effect of chlorination on COD, BOD_5 and TOC for Khanjarpur, Roorkee raw sewage during 30 min

Chlorine dosage (mg/L)	**COD (mg/L)**		**BOD_5 (mg/L)**		**TOC (mg/L)**	
	Average	**S.D (±)**	**Average**	**S.D (±)**	**Average**	**S.D (±)**
0	400	2.00	210	2.00	148	1.00
1	395	2.53	206	2.59	143	1.27
2	390	2.20	208	2.00	145	1.00
3	386	2.09	200	2.09	147	1.32
4	385	2.57	198	2.58	140	1.53
5	382	2.59	193	2.61	138	1.22
7	378	2.62	192	2.62	146	1.64

S.D = Standard Deviation

Table 3.2.2a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	18 ± 1
pH	7.4 ± 0.1
NH_4^+-N (mg/L)	65 ± 2
COD (mg/L)	420 ± 2
BOD_5 (mg/L)	215 ± 2.10
TOC (mg/L)	145 ± 1
Available residual chlorine (mg/L)	0.0 ± 0.0

Conclusions

The findings of this study clearly show that high dosage chlorination of secondary effluents influences both COD and BOD measurements. A chlorine dosage above 40 mg/L could result in nearly doubling the BOD and COD measurements of secondary treatment effluents. Such observations may have serious implications on attainability of the BOD or COD standard of some plants when the effluents are chlorinated with high chlorine dosage.

TOC measurements showed more stability after chlorination, with minor increase or decrease depending on Chlorine dosage and wastewater conditions. This makes TOC a better measure of the organic content of waste water. On the other hand, BOD remains the best indicator for dissolved oxygen consuming ability of final effluents

The effect of chlorination on BOD and COD diminishes with increasing the organic contents of the wastewater. This was clearly observed when raw sewage was chlorinated with same dosages (1-50 mg/L). After chlorination of treated water at different chlorine dosages (1-6 mg/L) and at 30 min contact time, the level of chloroform are found above the regulated WHO guideline value of 200 µg/L at 6mg/L and dichlorobromomethane, chlorodibromomethane, bromoform are found under WHO guideline.

During chlorination in this set of experiment the formation of THMs namely chloroform, dichlorobromethane and dibromochloromethane was found and the concentration of THMs increased from 110-250, 26-50 and 12-30 μg/L respectively by the increasing the chlorine dosage from 1-6 mg/L. in this experiment the concentration of chloroform was found four time greater than the dichlorobromethane due to readily available chlorine to organic matter. Bromoform as mentioned above not detected again due to might be less concentration of bromide ions in waste water sample.

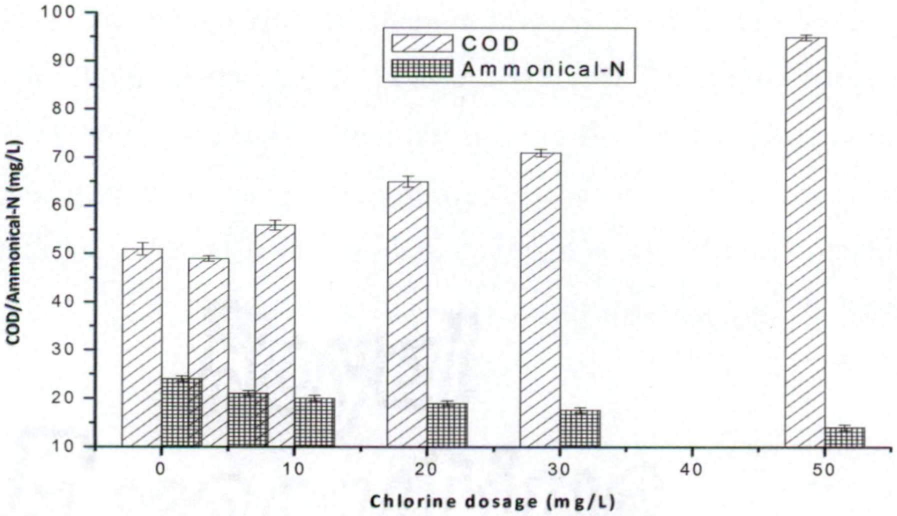

Fig 3.4.11c. Effect of chlorination on COD and ammonical nitrogen

THMs formation during chlorination of secondary effluent of Rishikesh SBR plant at different dosage of chlorine

Fig 3.4.12b and Table 3.4.12a (ref. in Appendix C) shows the THMs variations during chlorination of secondary effluent sample of Rishikesh SBR plant. The concentration of COD, BOD, TOC and NH_4-N was found 37.45, 18.32, 15.32 and 3.5 mg/L respectively. The temperature and pH of treated effluent sample was found to 20 °C and 7.4 respectively.

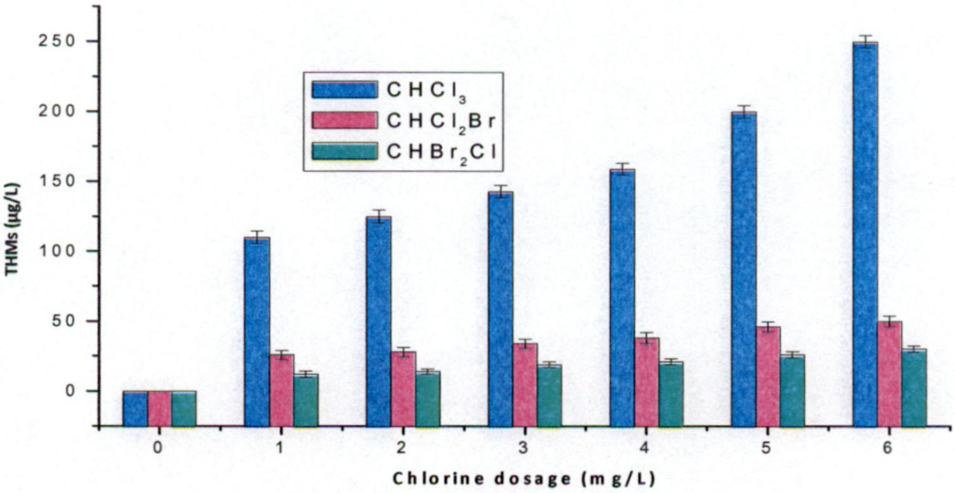

Fig 3.4.12b. THMs formation during chlorination.

3.4.10c) ammonical nitrogen continuously decreases from 6.2-2.1 mg/L. when applying chlorine dosages from 0-50 mg/L (Fig 3.4.11c) ammonical nitrogen continuously decreases from 24.05-14.03 mg/L. During chlorination, chlorine initially react fastly with ammonical nitrogen and form chloramines, as increases the Cl_2/NH_4-N weight ratio first monochloramines are formed then dichloramine and in the last trichloramines formed. Hence increasing the chlorine dosages more ammonia is react with chlorine hence decreasing the ammonia concentration continuously.

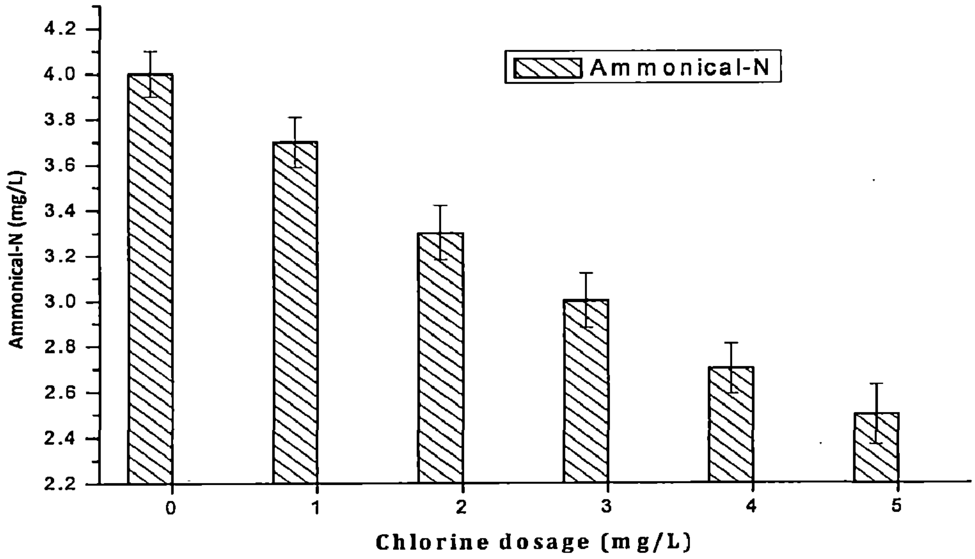

Fig 3.4.9c. Effect of chlorination on ammonical nitrogen

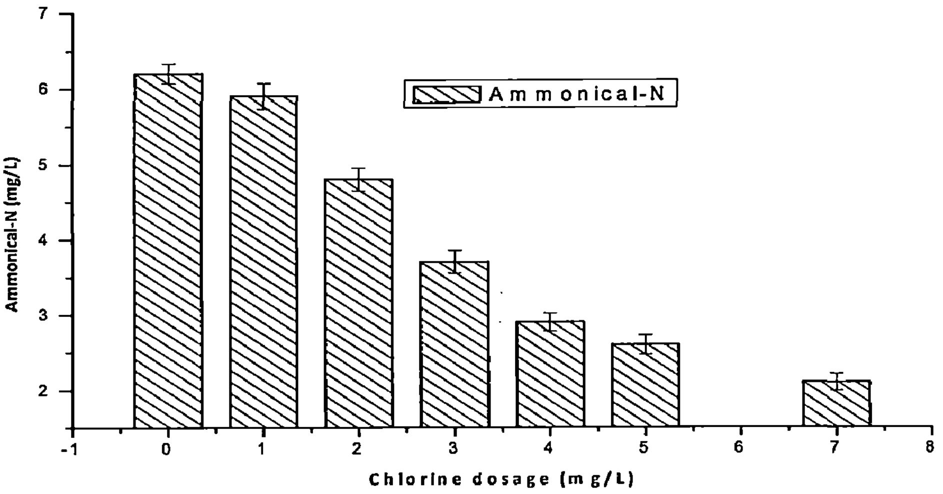

Fig 3.4.10c. Effect of chlorination on ammonical nitrogen

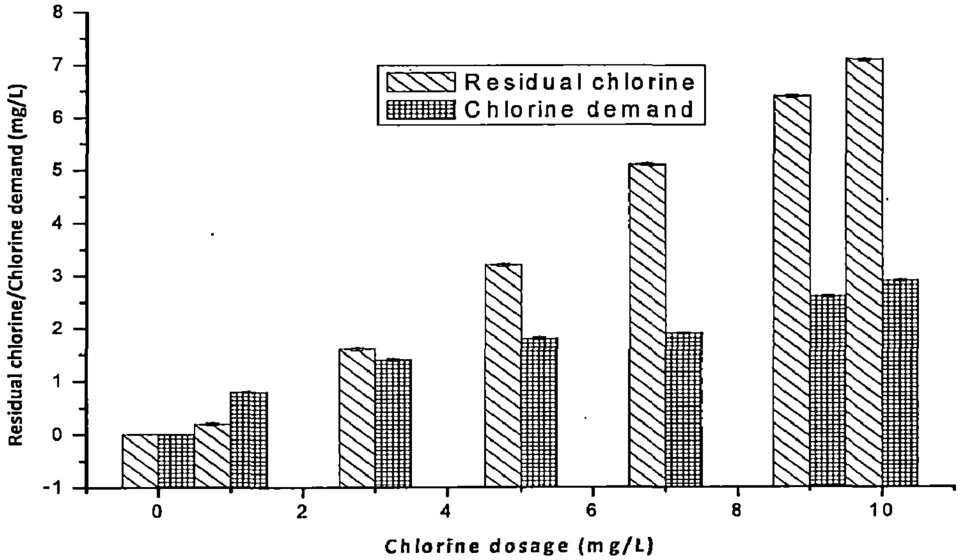

Fig 3.4.7c. Residual chlorine and Chlorine demand variation during chlorination.

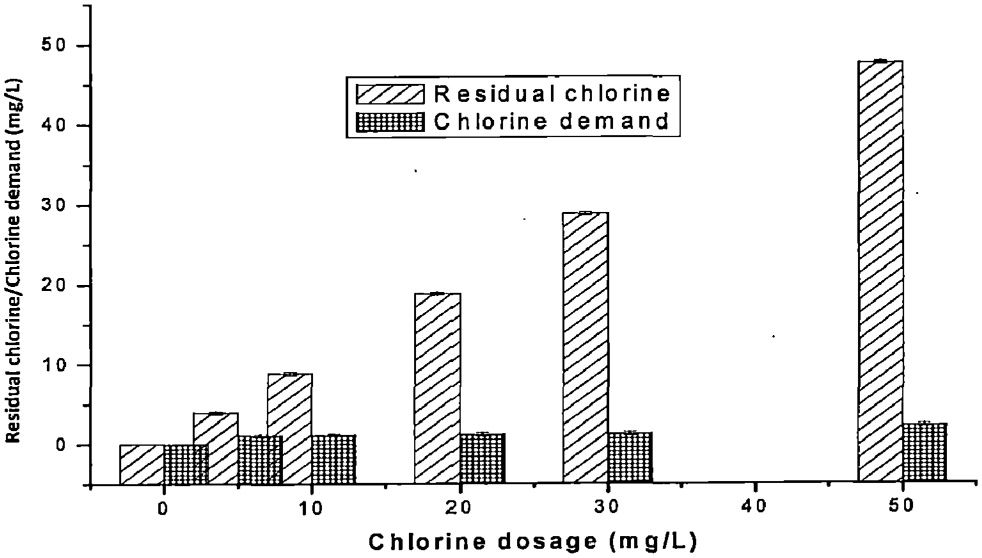

Fig 3.4.8c. Residual chlorine and chlorine demand variation during chlorination.

- **Effect of chlorination on ammonical Nitrogen**

Individual initial characteristics of raw sewage are given in tables 3.4.9a, 3.4.10a, and 3.4.11a (ref. in Appendix C). Fig 3.4.9c, 3.4.10c, and 3.4.11c and Table 3.4.9b, 3.4.10b, and 3.4.11b (ref. in Appendix C) shows the variations of NH_4-N during chlorination. On applying chlorine dosages 0-5 mg/L (Fig.3.4.9c) ammonical nitrogen continuously decreases from 4.0-2.5 mg/L. When applying chlorine dosages from 0-7 mg/L (Fig

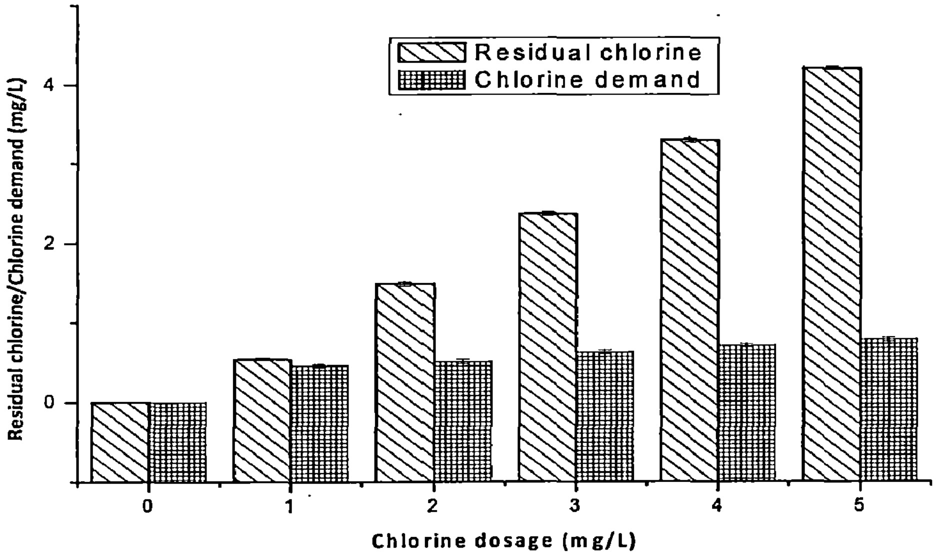

Fig 3.4.5c. Residual chlorine and Chlorine demand variation during chlorination

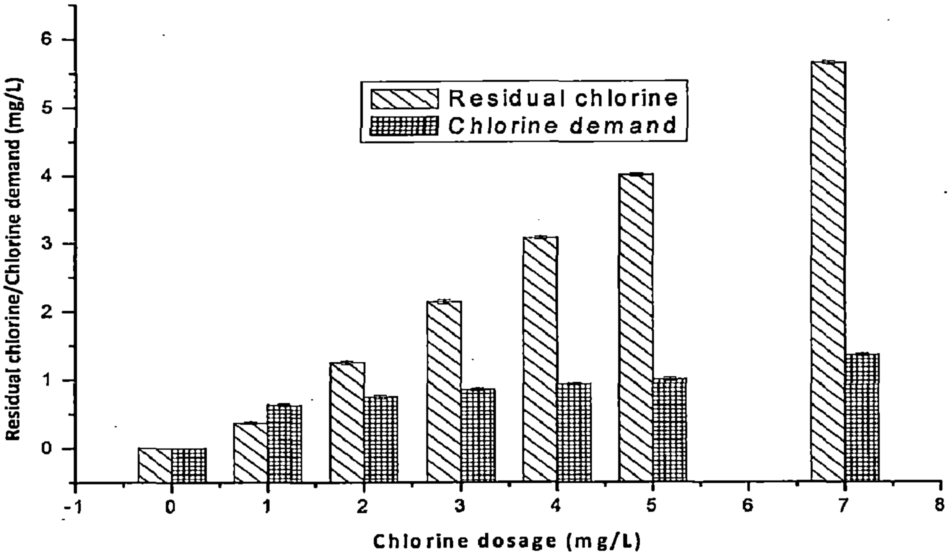

Fig 3.4.6c. Residual chlorine and Chlorine demand variation during chlorination

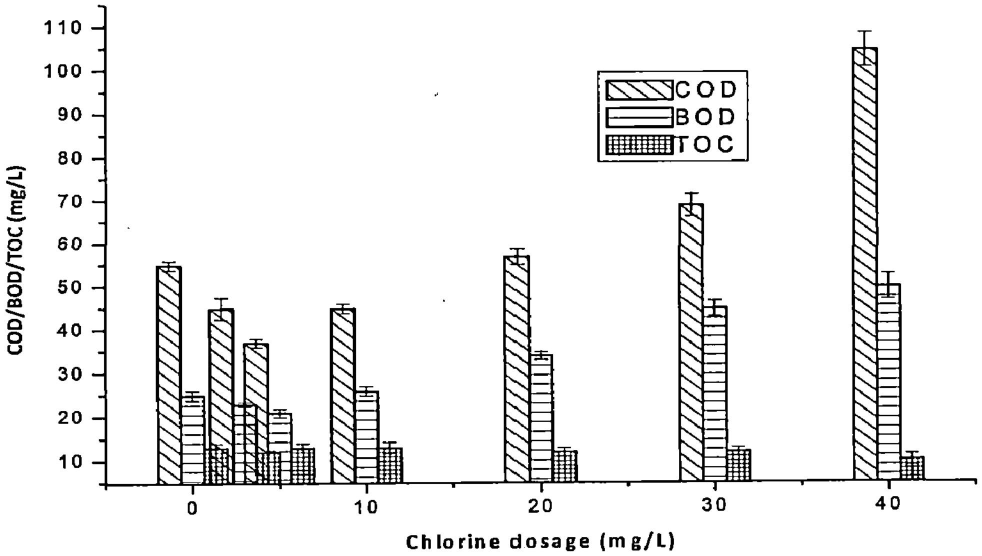

Fig 3.4.4c. COD, BOD and TOC variation during chlorination

- **Effect on Residual chlorine and Chlorine demand during chlorination**

Individual initial characteristics of raw sewage are given in Tables 3.4.5a, 3.4.6a, 3.4.7a and 3.4.8a (ref. in Appendix C). Fig 3.4.5c, 3.4.6c, 3.4.7c and 3.4.8c and Table 3.4.5b, 3.4.6b, 3.4.7b and 3.4.8b (ref. in Appendix C) shows variation in Residual chlorine and chlorine demand. On applying chlorine dosages 0-5 mg/L (Fig 3.4.5c) then found that residual chlorine increases from 0.0-4.2 mg/L and chlorine demand increases from 0.0-0.7mg/L. when applying chlorine dosages 0-7 mg/L (Fig 3.4.6c) then found that residual chlorine increases from 0.0-5.64 mg/L and chlorine demand increases from 0.0-1.36 mg/L. when applying chlorine dosages 0-10 mg/L (Fig 3.4.7c) then found that residual chlorine increases from 0.0-7.1 mg/L and chlorine demand increases from 0.0-2.9 mg/L. when applying chlorine dosages 0-50 mg/L (Fig 3.4.8c) then found that residual chlorine increases from 0.0-47.73 mg/L and chlorine demand increases from 0.0-2.27 mg/L.These result shows that when we increases the concentration of chlorine dosages the residual chlorine and chlorine demand increases, because ammonia present in sewage continuously react with free chlorine and formed chloramines (residual chlorine)and higher concentration of chlorine dosages increases the oxidation rate hence more free chlorine is required (so increases the chlorine demand).

chlorine dosage) and BOD decreases from 33-25 mg/L (0-5 mg/L chlorine dosages) then increases from 25-60 mg/L (5-40 mg/L chlorine dosages) but TOC change was insignificant. When applying chlorine dosages 0-40 mg/L (Fig 3.4.4c) then found that COD decreases from 55-37mg/L (0-5 mg/L) then increases 37-105 mg/L (5-40 mg/L chlorine dosages) and BOD decreases from 25-21 mg/L (0-5 mg/L chlorine dosages) then increases from 21-50 mg/L (5-50 mg/L chlorine dosages) but TOC insignificantly changes. This decreasement and increasement in COD and BOD is due to the modification in organic contents after chlorination. As we increases the chlorine dosages (higher chlorine dosages) modification in organic matter occure and increases the biodegradability of organic matter and increases the COD and BOD of sewage water, therefore at the higher dosages (40 mg/L chlorine dosages) the COD and BOD value becomes nearly double the unchlorinated sample.

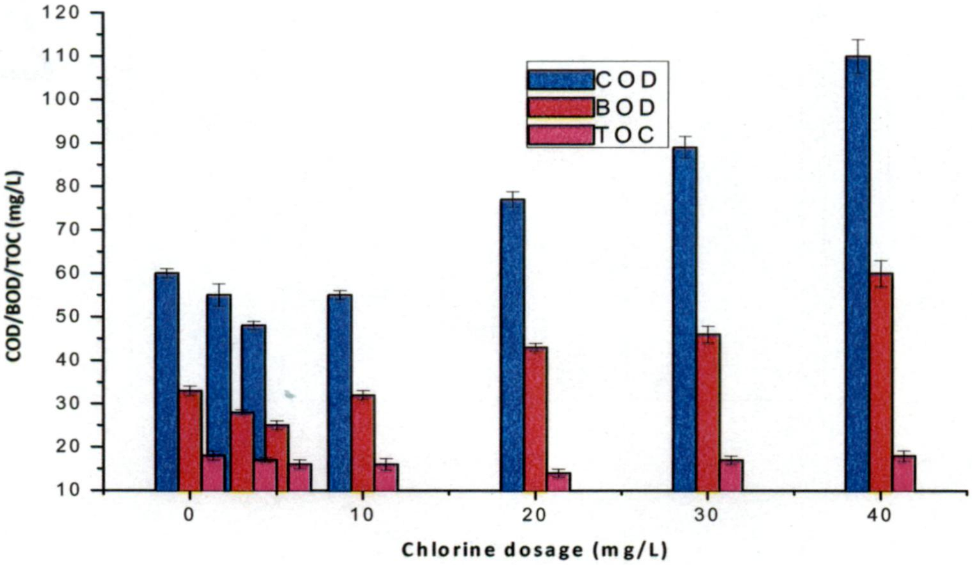

Fig 3.4.3c. COD, BOD and TOC variation during chlorination

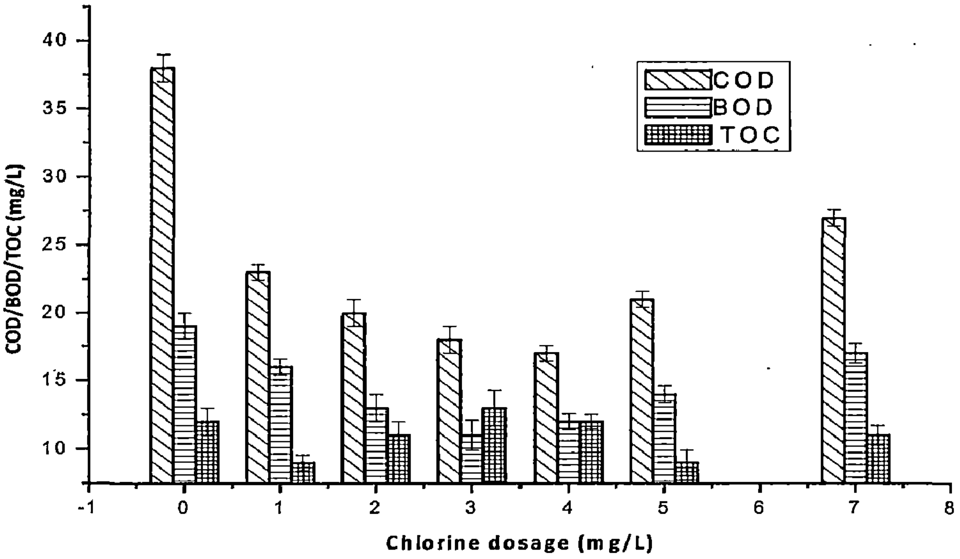

Fig 3.4.1c. COD, BOD and TOC variation during chlorination

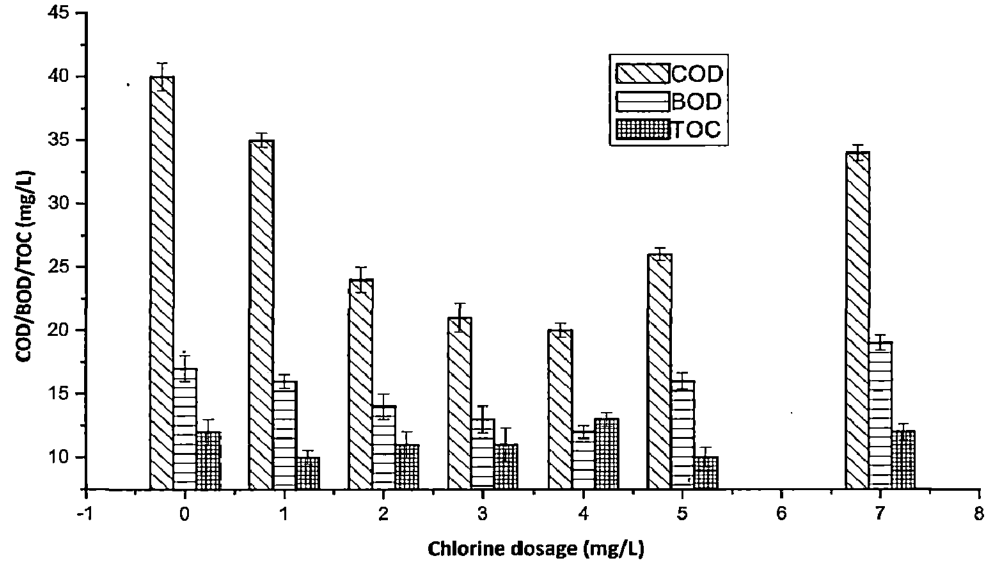

Fig 3.4.2c. COD, BOD and TOC variation during chlorination

- **Effect of chlorination on COD, BOD and TOC at higher dosage of chlorine**

Fig 3.4.3c, and 3.4.4c, Table 3.4.3b, 3.4.4b (Tables ref. in appendix C) shows the variations of COD, BOD and TOC with different dosages of chlorine namely 0-40 mg/L. On applying chlorine dosages 0-40 mg/L (Fig 3.4.3c) then found that COD decreases from 60-48 mg/L (0-5 mg/L chlorine dosages) then increases 48-110 mg/L (5-40 mg/L

3.4. Chlorination of secondary effluent from Rishikesh SBR plant

- **Effect of chlorination on COD, BOD and TOC at low dosage of chlorine**

Several chlorination experiments performed in secondary effluent of Rishikesh sewage treatment plant (SBR) at different dosages of chlorine during two month. The chlorine dosages were varied between 0.0 and 7.0 mg/L. Sewage samples for chlorination were obtained from the Rishikesh sewage SBR plant. The sewage samples temperature was ranges 17-21 °C and pH ranges 7.1-7.6. The initial characteristics (average) of all collected sewage samples are given in table 5. The individual initial characteristics of raw sewage are given in Tables 3.4.1a and 3.4.2a (appendix C).

Table 3.4. The initial characteristics (range) of waste water are given below

Parameters	**range (± S.D)**
Temperature (^{0}C)	(17-21) ± 1
pH	(7.1-7.6) ± 0.05
NH_4^+-N (mg/L)	(4-26) ± 0.5
COD (mg/L)	(30-70) ± 1.5
BOD_5 (mg/L)	(17-35) ± 1.2
TOC (mg/L)	(11-15) ± 1
Available residual chlorine (mg/L)	(0.0-0.0) ± 0.0

Fig 3.4.1c, and 3.4.2c, Table 3.4.1b, 3.4.2b (Tables ref. in Appendix C) shows the variations of COD, BOD and TOC with different dosages of chlorine namely 1-7 mg/L. On applying chlorine dosages 1-7 mg/L (Fig 3.4.1c) then found that COD decreases from 38-17 mg/L (0-4 mg/L chlorine dosages) then increases 17-27 mg/L (4-7 mg/L chlorine dosage) and BOD decreases from 19-11 mg/L (0-3 mg/L chlorine dosages) then increases from11-17 mg/L (4-7 mg/L chlorine dosages), and TOC insignificantly changes. When applying chlorine dosages 1-7 mg/L (Fig 3.4.2c) then found that COD decreases from 40-20 mg/L (0-4 mg/L chlorine dosages) then increases 20-34 mg/L (4-7 mg/L chlorine dosages) and BOD decreases from 20-12 mg/L (0-4 mg/L chlorine dosages) then increases from 12-19 mg/L (4-7 mg/L chlorine dosages), the TOC insignificantly changes. This decreasement and increasement in COD and BOD is due to the modification in organic contents after chlorination.

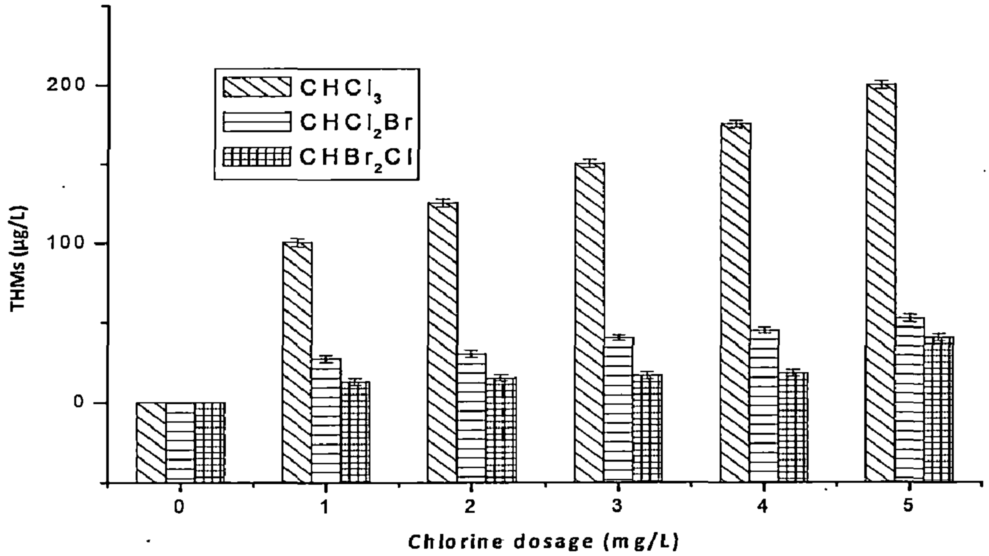

Fig 3.3.14b. THMs formation during chlorination

The chlorine was allowed to react for half an hour because that is the average residence time of the water from the point of chlorination in the treatment plant through the clear wells. After the water had been chlorinated for half an hour, ammonia was react with chlorine and formed different chloroamines which also serves as their secondary disinfectant. The average concentration of COD, BOD, TOC and NH_4-N was found 35.32, 17.34, 13.45 and 3.2 mg/L respectively. The pH and temperature of secondary effluent sample was found 7.2 and 18 °C respectively.

The chloroform, Bromodichloromethane, dibromochloromethane and bromoform were not detected in sample at zero chlorine. When the chlorination started with 1mg/L chlorine dosage the formation of THMs also started and the chloroform concentration was found 100.3 µg/L, the bromodichloromethane concentration was 27.4 µg/L and the dibromochloromethane concentration was 13.2 µg/L. Chloroform was the most prevalent trihalomethane formed: its concentration was approximately 4 times greater than bromodichloromethane in every case of chlorination (1-5 mg/L). when we increase the dosage of chlorine the concentration of chloroform in every case increases but the concentration of bromodichloromethane and dibromochloromethane was almost same except case 5 mg/L. Bromofom was not detected in every case of chlorine dosage due to might be less concentration of bromide ions in sewage sample.

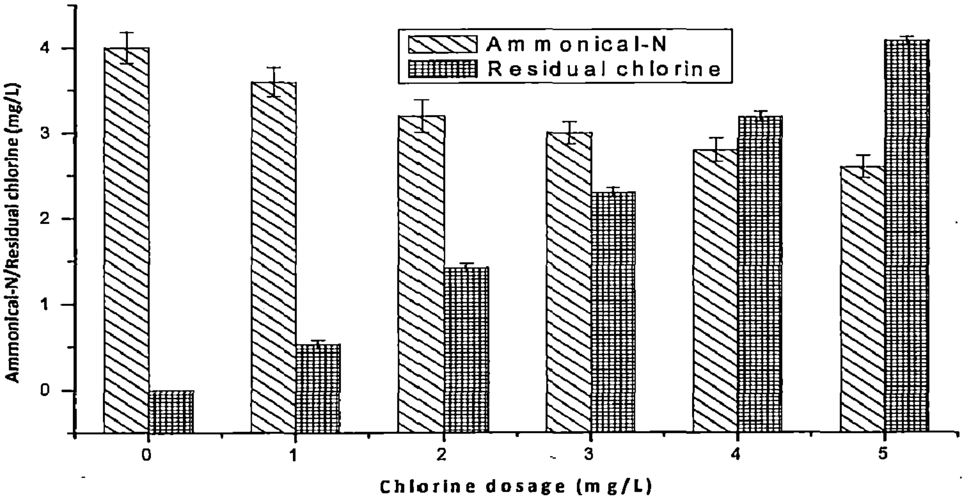

Fig 3.3.12c. Effect of chlorination on ammonical nitrogen and residual chlorine.

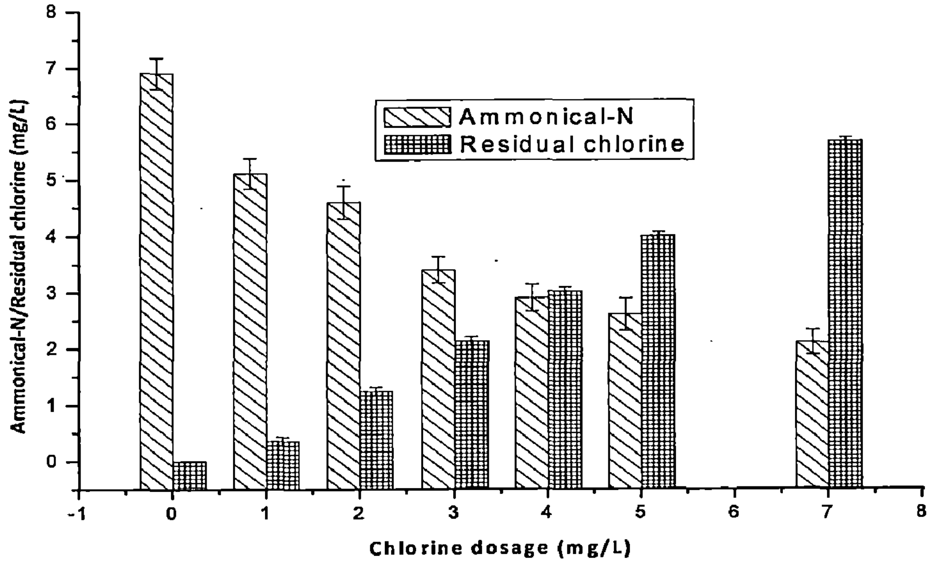

Fig 3.3.13c. Effect of chlorination on ammonical nitrogen and residual chlorine.

THMs formation during chlorination of secondary effluent of Haridwar SBR plant at different dosage of chlorine

Fig 3.3.14b and Table 3.3.14a (ref. in Appendix B) presents the different THMs like $CHCl_3$, $CHCl_2Br$ and $CHBr_2Cl$ variations at different dosages of chlorine (0-5 mg/L).

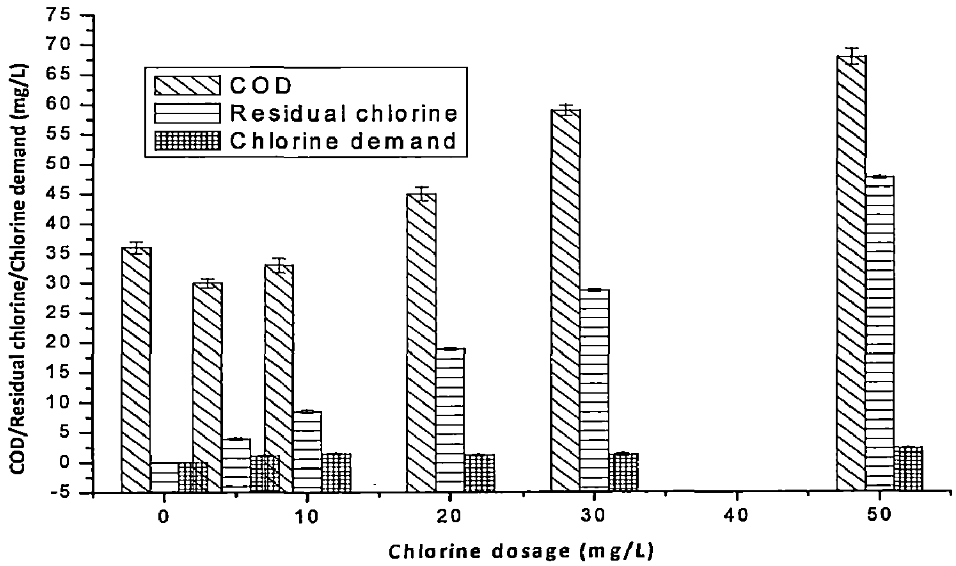

Fig 3.3.11c. COD, Residual chlorine and Chlorine demand variation during chlorination

- **Effect of chlorination on ammonical nitrogen**

Fig 3.3.12c, 3.3.13c and Table 3.3.12a, 4.13a (Initial characterization of waste water) and Table 3.3.12b, 3.3.13b (ref. in Appendix B) shows the variations of NH_4-N during chlorination. On applying chlorine dosages 1-5 mg/L (Fig 3.3.12c) ammonical nitrogen continuously decreases from 4.0-2.6 mg/L. When applying chlorine dosages 1-7 mg/L (Fig 3.3.13c) ammonical nitrogen continuously decreases from 6.9-2.1 mg/L. During chlorination, chlorine initially react fastly with ammonical nitrogen and form chloramines, as increases the Cl_2 /NH_4-N weight ratio first monochloramines are formed then dichloramine and in the last trichloramines formed .Hence increasing the chlorine dosages more ammonia is react with chlorine hence decreasing the ammonia concentration continuously (when applying dosages 1-7 mg/L).

increase the chlorine concentration the chlorine demand also increases because chlorine present in wastewater oxidised organic, inorganic metal ions present in wastewater, when chlorine concentration increases the oxidation rate of matter increases hence more chlorine is consumed when chlorine dosages increases.

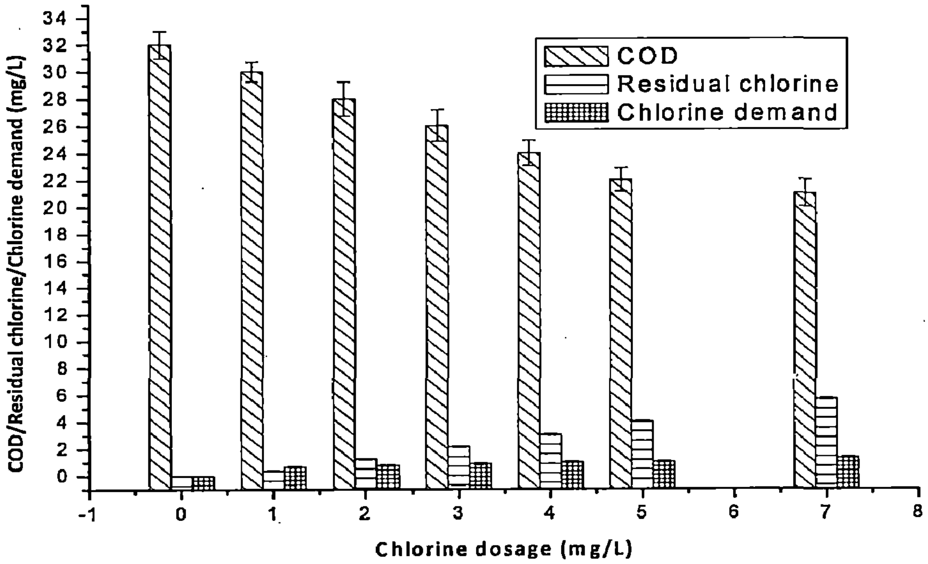

Fig 3.3.9c. COD, Residual chlorine and Chlorine demand variation during chlorination

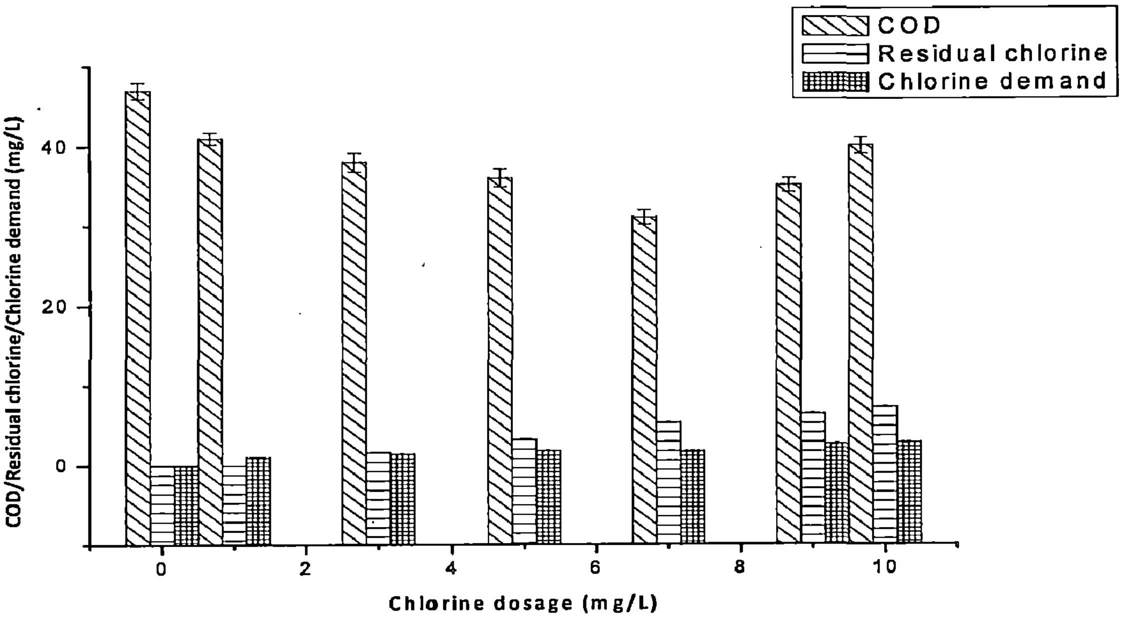

Fig 3.3.10c. COD, Residual chlorine and Chlorine demand variation during chlorination

demand is 0.98 mg/L. These result shows that residual chlorine and chlorine demand continuously increases.

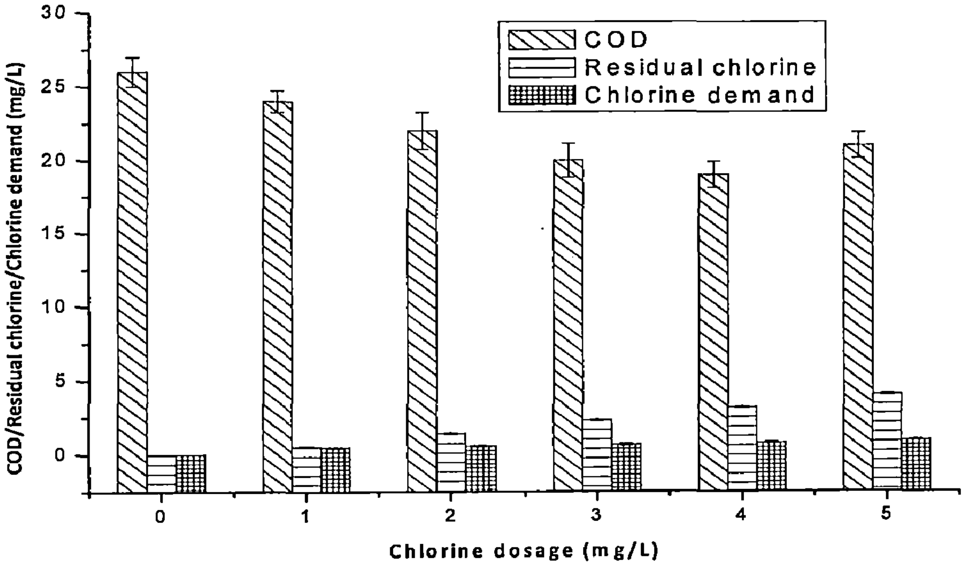

Fig 3.3.8c. COD, Residual chlorine and chlorine demand variation during chlorination

Fig 3.3.9c, 3.3.10c and 3.3.11c and Table 3.3.9b, 3.3.10b, and 3.3.11b (ref. in Appendix B) shows variation in COD, Residual chlorine, and chlorine demand and Table 3.3.9a, 3.3.10a, 3.3.11a present the initial characteristics of wastewater (ref. in appendix B). On applying chlorine dasages 1-7 mg/L (Fig 3.3.9c) the chlorine residual increases continuosly from 0.36 -5.68 mg/L and chlorine demand increases continuously from 0.6-1.32 mg/L. On applying chlorine dasages from 1-10 mg/L (Fig 3.3.10c), the chlorine residual is 0.0 mg/L at 1.0 mg/L chlorine dosages because total chlorine (1.0 mg/L) consumed in oxidation of organic matter and inorganic metal ions (called chlorine demand) then increases continuously upto 7.2 mg/L and chlorine demand increases continuously from 1-2.8 mg/L. On applying chlorine dasages 5-50 mg/L (Fig 3.3.11c) the chlorine residual increases continuously from 3.9-47.75 mg/L and chlorine demand increases continuously from 1.09-2.25 mg/L. From these result we find that when increases the chlorine dosages, the chlorine residual and chlorine demand both are increase because ammonia present in wastewater react with chlorine and formation of chloramines (residual chlorine) occure as we increase the chlorine dosages the more chloramines formation occure and more chlorine residual concentration found. As we

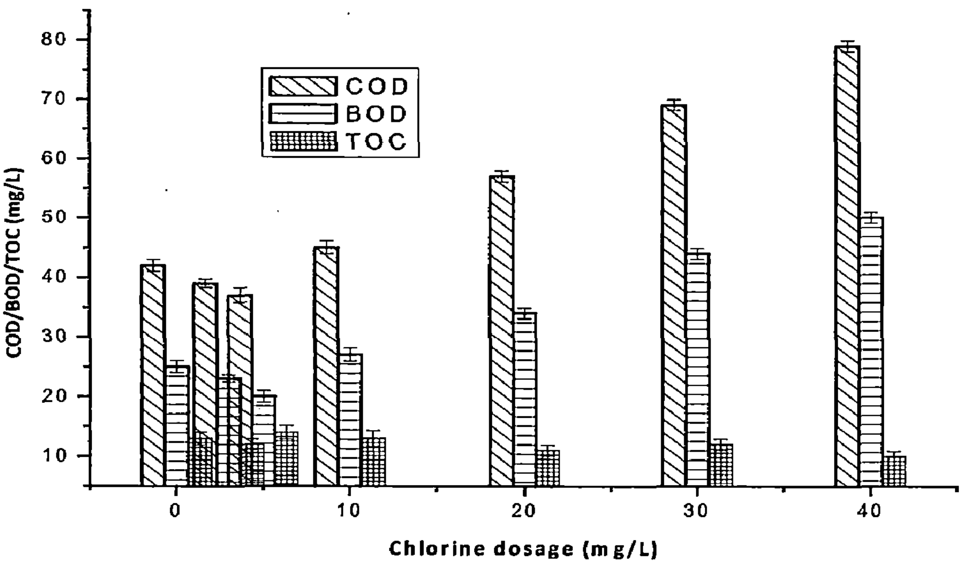

Fig 3.3.6c. COD, BOD and TOC variation during chlorination

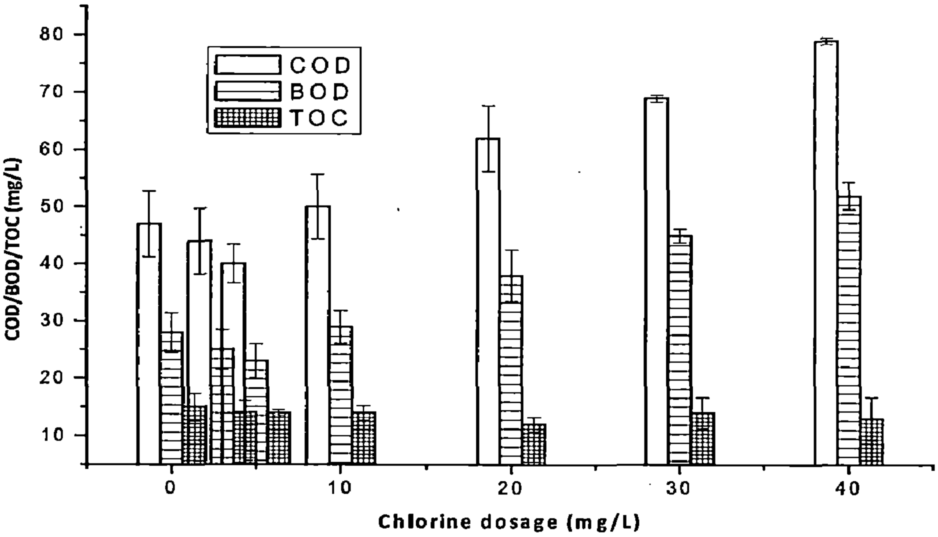

Fig 3.3.7c. COD, BOD and TOC variation during chlorination.

- **Effect of chlorination on Residual Chlorine and Chlorine demand**

Fig 3.3.8c and Table 3.3.8b (ref. in Appendix B) shows variation in COD, Residual chlorine, and Chlorine demand and table 3.3.8a present the initial characteristics of wastewater (ref. in Appendix B). On applying chlorine dosages 1-5 mg/L. Then At 1.0 mg/L chlorine dosages the residual chlorine is 0.53 mg/L and chlorine demand is 0.47 mg/L. At chlorine dosages 5 mg/L the residual chlorine is 4.08 mg/L and chlorine and BOD decreases from 28-23 mg/L (0-5 mg/L chlorine dosages) then increases from 23-52 mg/L (5-40 mg/L chlorine dosages) but TOC was insignificantly change. These result shows that at lower concentration (0-5 mg/L chlorine dosages) the value of COD and BOD decrease but at higher concentration (5-40 mg/L chlorine dosages) the value of COD and BOD increases continuously and at the concentration of 40 mg/L chlorine dosage the value of COD and BOD becomes double the unchlorinated sample. But result of COD shows that COD is insgnificantly changes. These COD and BOD increasement occure due to the modification in organic contents in sewagewater.

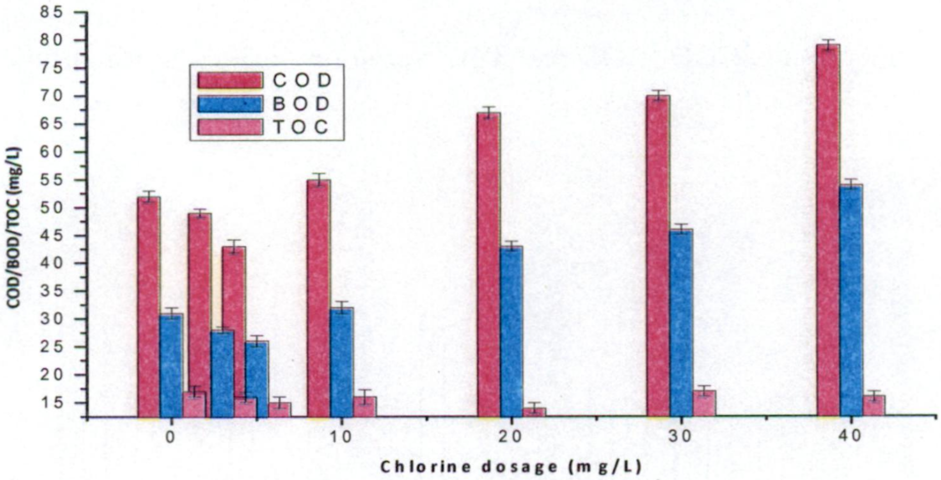

Fig 3.3.5c. COD, BOD and TOC variation during chlorination.

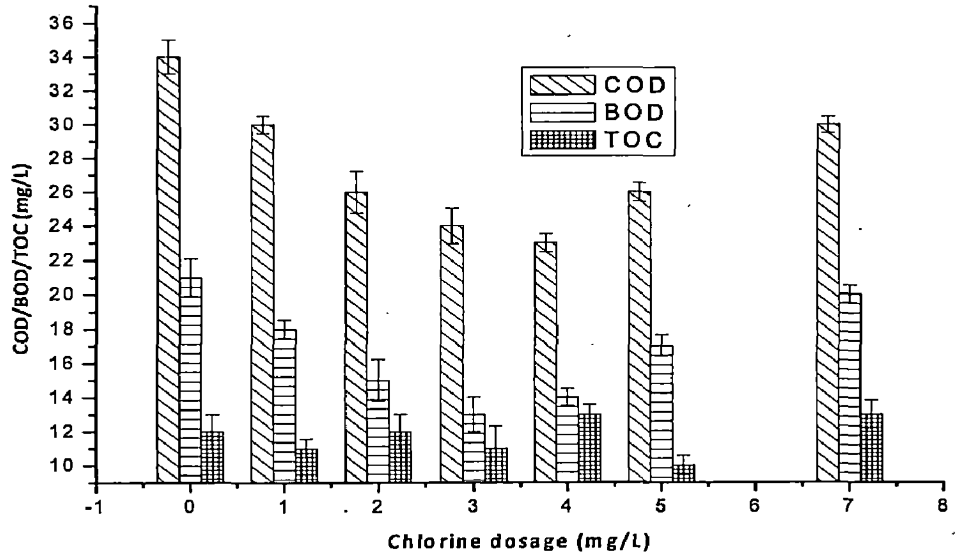

Fig 3.3.4c. COD, BOD and TOC variation during chlorination.

- **Effect of chlorination on COD, BOD and TOC at higher dosage of chlorine**

The chlorine dosages were varied between 0-50 mg/L. The individual initial characteristics of raw sewage are given in Tables 3.3.5a and 3.3.6a (appendix B). Fig 3.3.5c, 3.3.6c, and Table 3.3.5b, 3.3.6b (Tables ref. in appendix B) shows the variations of COD, BOD and TOC with different dosages of chlorine namely 0.0-40 mg/L. On applying chlorine dosages 0-40 mg/L (Fig 3.3.5c) then found that COD decreases 52-43 mg/L (0-5 mg/L chlorine dosages) then increases 43-79 mg/L (5-40 mg/L chlorine dosage) and BOD decreases from 31-26 mg/L (0-5mg/L chlorine dosages) then increases from 26-54 mg/L (5-40 mg/L), TOC insignificantly changes . On applying chlorine dosages 0-40 mg/L (Fig 3.3.6c) then found that COD decreases from 42-37 mg/L (0-5 mg/L) then increases 37-79 mg/L (5-40 mg/L chlorine dosages) and BOD decreases from 25-20 mg/L (0-5 mg/L chlorine dosages) then increases from 20-50 mg/L (5-40 mg/L chlorine dosages) but TOC insignificantly change. This decreasement and increasement in COD and BOD is due to the modification in organic contents after chlorination. The Table 3.3.7a shows (average result of Table 3.3.5a, 3.3.6a, in Appendix B), Table 3.3.7b shows (average result of Table 3.3.5b, 3.3.6b in Appendix B) and table 3.3.4c shows (average result of Table 3.3.5c, 3.3.6c), and these result represent that COD decreases from 47-40 mg/L (0-5 mg/L) then increases 40-79 mg/L (5-40 mg/L chlorine dosages)

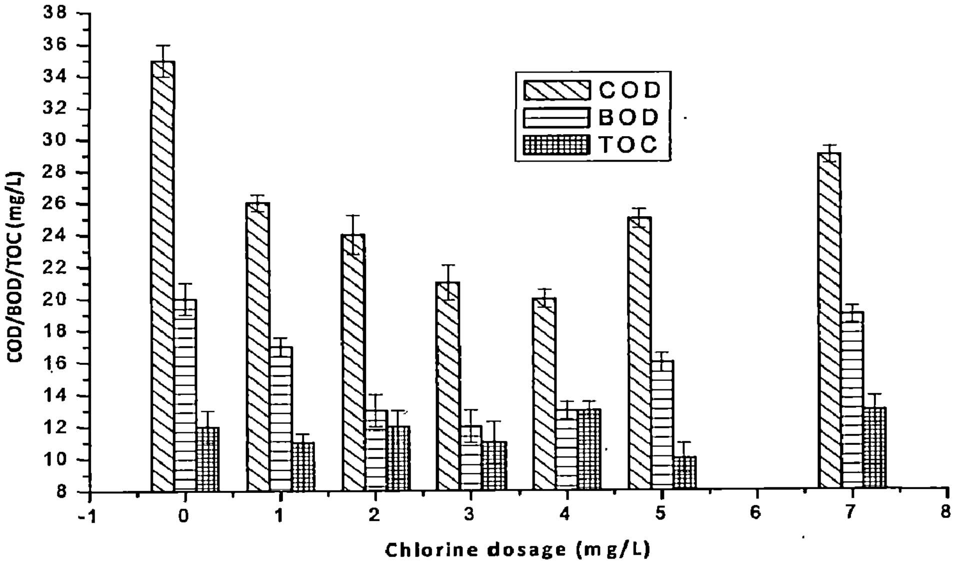

Fig 3.3.2c. COD, BOD and TOC variation during chlorination

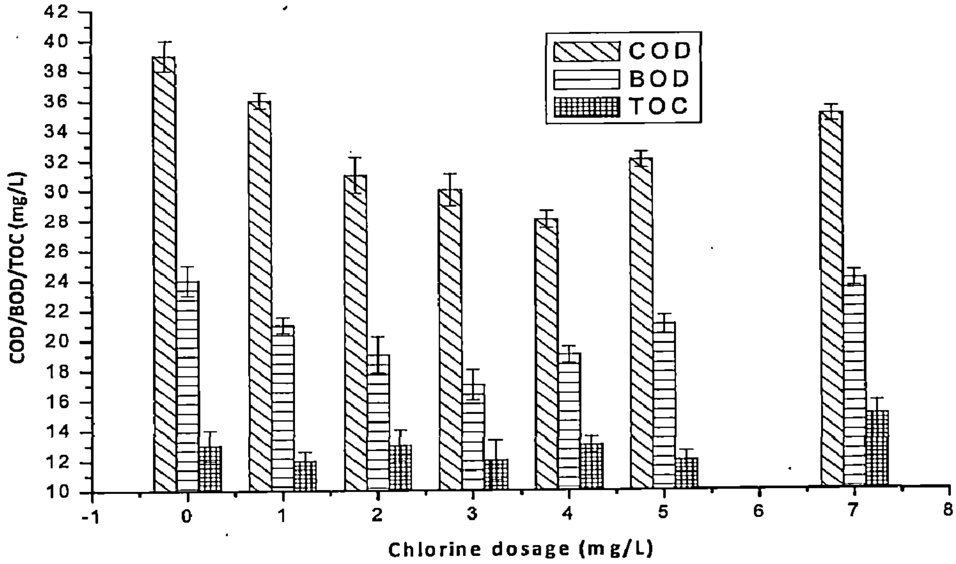

Fig 3.3.3c. COD, BOD and TOC variation during chlorination

Fig 3.3.1c, 3.3.2c and 3.3.3c, Table 3.3.1b, 3.3.2b and 3.3.3b (Tables ref. in Appendix B) shows the variations of COD, BOD and TOC with different dosages of chlorine 1-7 mg/L. On applying chlorine dosages 1-7 mg/L (Fig 3.3.1c) then found that COD decreases from 30-18 mg/L (0-4 mg/L chlorine dosages) then increases 18-25 mg/L (4-7 mg/L chlorine dosage) and BOD decreases from 18-10mg/L (0-3 mg/L chlorine dosages) then increases from10-15 mg/L (4-7 mg/L chlorine dosages) but TOC insignificantly changes. On applying chlorine dosages 1-7 mg/L (Fig 3.3.2c) in new sample then found that COD decreases from 35-20 mg/L (0-4 mg/L chlorine dosages) then increases 20-29 mg/L (4-7 mg/L chlorine dosages) and BOD decreases from 20-12 mg/L (0-3 mg/L chlorine dosages) then increases from12-19 mg/L (4-7 mg/L chlorine dosages), TOC show insignificantly change. On applying chlorine dosages 1-7 mg/L (Fig 3.3.3c) then found that COD decreases from 39-28 mg/L (0-4 mg/L) then increases 28-35 mg/L (4-7 mg/L chlorine dosages) and BOD decreases from 24-17 mg/L (0-3 mg/L chlorine dosages) then increases from 17-24 mg/L (4-7 mg/L chlorine dosages), TOC insignificantly change. This decreasement and increasement in COD and BOD is due to the modification in organic contents after chlorination. The Table 3.3.4a shows (average result of Table 3.3.1a, 3.3.2a and 3.3.3a, in Appendix B), Table 3.3.4b shows (average result of Table 3.3.1b, 3.3.2b and 3.3.3b, in Appendix B) and Fig 3.3.4c shows (average result of Table 3.3.1c, 3.3.2c, 3.3.3c).

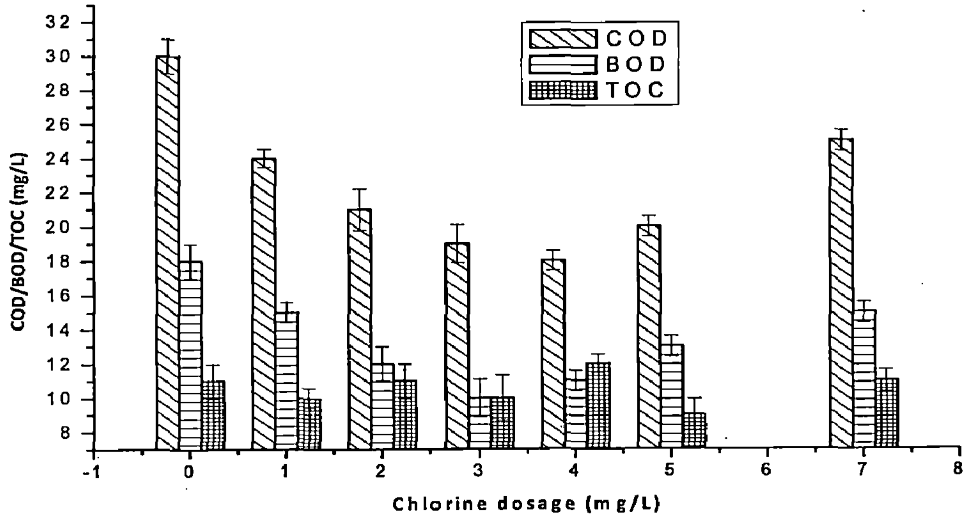

Fig 3.3.1c. COD, BOD and TOC variation during chlorination

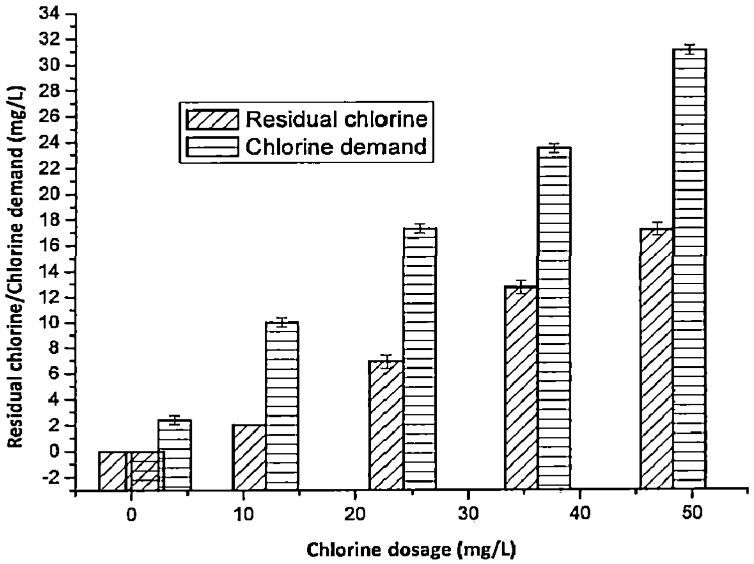

Fig 3.2.7c. Variations of Residual chlorine and Chlorine demand duing chlorination

3.3.Chlorination of secondary effluent from Haridwar SBR plant

- **Effect of chlorination on COD, BOD and TOC at low dosage of chlorine**

Several chlorination experiments performed in secondary effluent of haridwar sewage treatment plant (SBR) at different dosages of chlorine for a period of one month. The chlorine dosages were varied between 0.0 and 7 mg/L. Sewage samples for chlorination were obtained from the haridwar sewage SBR plant. The sewage samples temperature was ranges 17-21 °C and pH ranges 7.1-7.6. The initial characteristics (average) of all collected sewage samples are given in table 4. The individual initial characteristics of raw sewage are given in tables 3.3.1a, 3.3.2a and 3.3.3a (Appendix B).

Table 3.3. The initial characteristics (range) of waste water are given below

Parameters	**Range (± S.D)**
Temperature (^{0}C)	(17-21) ± 1
pH	(7.1-7.6) ± 0.05
NH_4^+-N (mg/L)	(3.5-28.5) ± 0.5
COD (mg/L)	(30-52) ± 1
BOD_5 (mg/L)	(17-30) ± 1
TOC (mg/L)	(11-17) ± 0.9
Available residual chlorine (mg/L)	(0.0 - 0.0) ± 0.0

Fig 3.2.6c, 3.2.7c and Table 3.2.6a, 3.2.7a (initial charecterization) and Table 3.2.6b, 3.2.7b (ref. in Appendix A) presentes variations in COD, Residual chlorine and Chlorine demand. As mentioned above (in section COD, BOD and TOC variations) the COD concentration decreased initially during low chlorination and increased with increasing chlorine dosages (due to the modification in dissolved organic content). Morever, by the increasing chorine dosages 0 mg/L to 48.3 mg/L, increases their residual chorine (0.00-15.75 mg/L, 88%) with increasing chlorine demand (0.00-32.55 mg/L, 92.2%). This confirmed that by increasing chlorine dosage more than 2.4 mg/L minimise the ammonia concentration and increase the probability of chlorine reaction with organic and inorganic matter present in waste water and form toxic organic compounds like chloroamine and THMs.

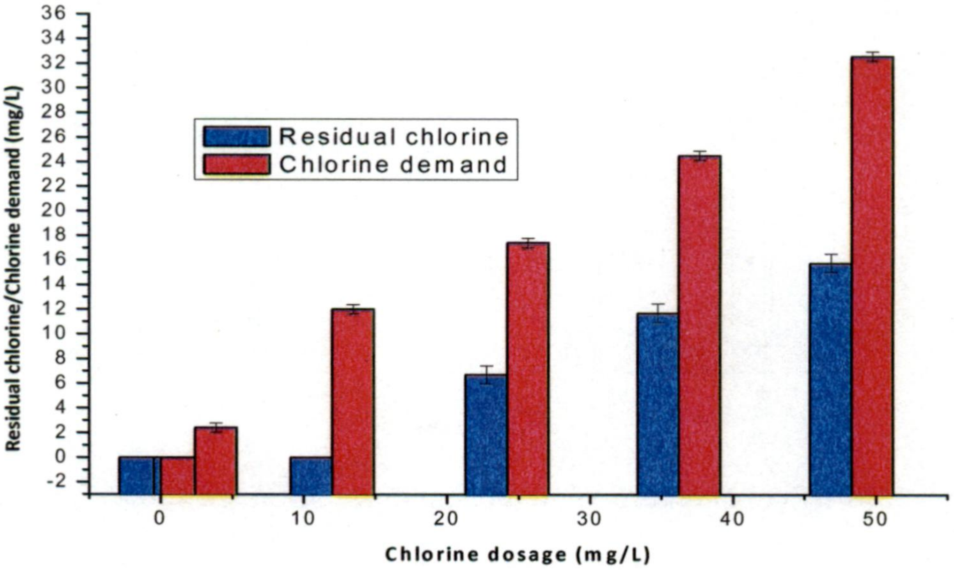

Fig 3.2.6c. Variations of Residual chlorine and Chlorine demand duing chlorination

react with ammonia very fast within 1-5 min) subsequently, increasing chlorine dose 2-48.3 mg/L ammonical nitrogen reduced shlowly from 12.2 mg/L to 5.9 mg/L due to consumption of major fraction of chlorine initially and formation di and trichloroamines.

Table 3.2.5a The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^{0}C)	16 ± 1
pH	7.4 ± 0.05
NH_4^+-N (mg/L)	53.5 ± 0.5
COD (mg/L)	452 ± 3
TOC (mg/L)	150 ± 2.5
Available residual chlorine (mg/L)	0.0 ± 0.0

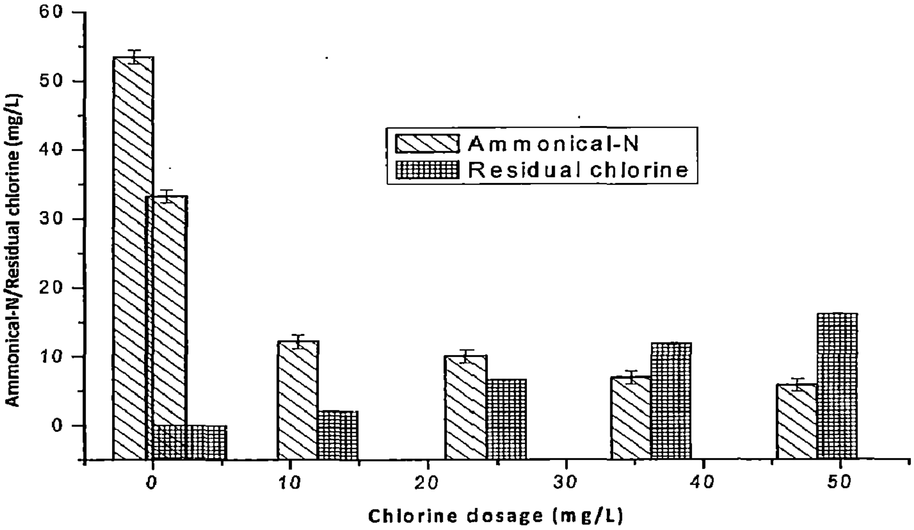

Fig 3.2.5c. Effect of chlorination on ammonical nitrogen and residual chlorine

However, residual chlorine (free chlorine, mono, di and trichloroamines) increases from 0-2.1 mg/L when chlorine was 0-12 mg/L. After that residual increases with constant rate from 2.1-16.2 mg/L when the chlorine dosage increases from 12-48.3 mg/L due to the high consumption of ammonical nitrogen (formation of mono, di and trichloroamines and nitrogenous organic compounds) in later stage of chlorination.

- **Effect on COD, Residual Chlorine and Chlorine demand during chlorination**

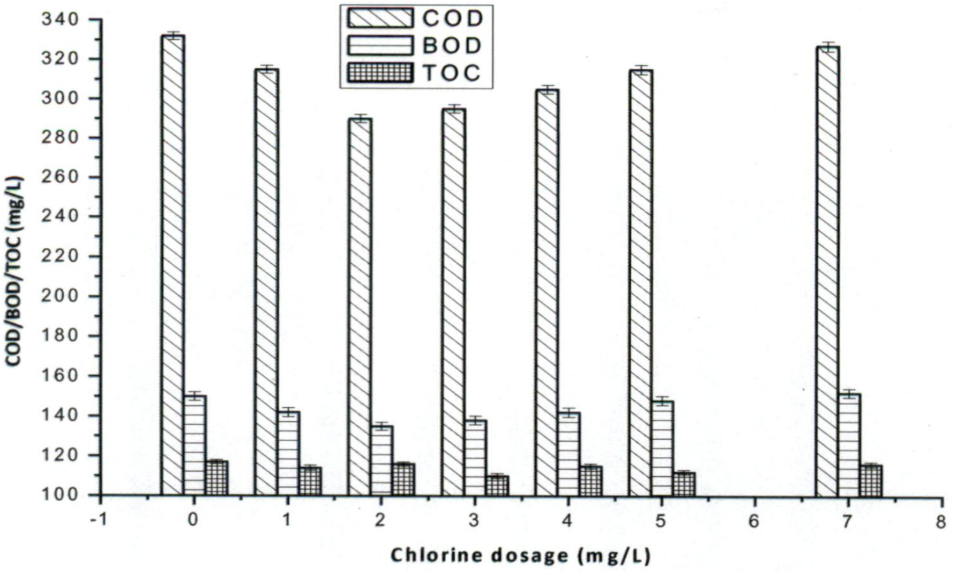

Fig 3.2.3c. COD, BOD and TOC variations during chlorination

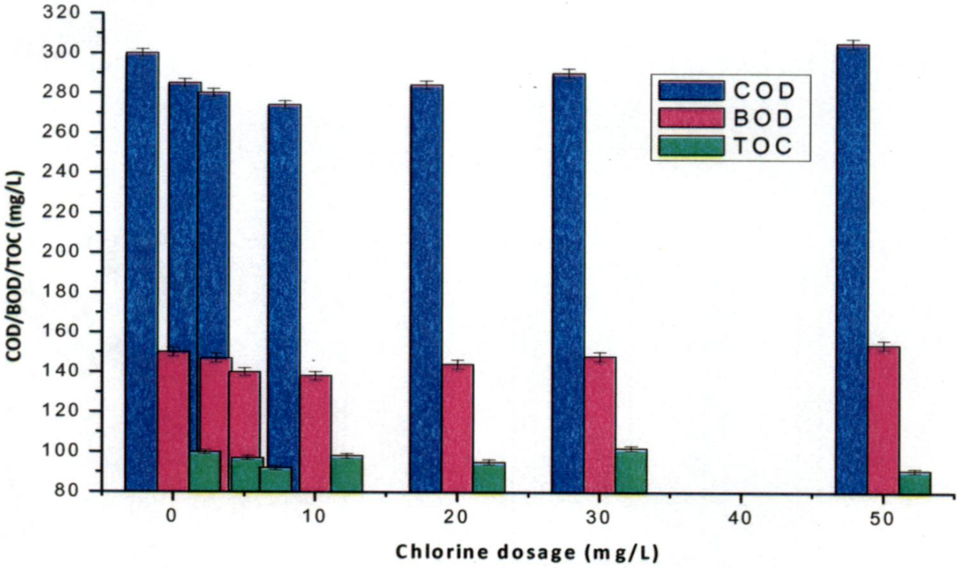

Fig 3.2.4c. COD, BOD and TOC variations during chlorination

- **Effect of chlorination on ammonical Nitrogen**

Fig 3.2.5c, Table 3.2.5a (initial charecterization) and 3.2.5b (Tables ref. in Appendix A) shows the variations of NH_4-N and chlorine dosages (0-48.3 mg/L) . Ammonical nitrogen suddenly during chlorination reduced from 53.50 mg/L to 33.25 mg/L when chlorine dosage was 0-2 mg/L due to formation of mono, di and trichloroamine (chlorine chlorination. These observations may also indicate that TOC parameter is the best measurement for total organic content of waste water during chlorination.

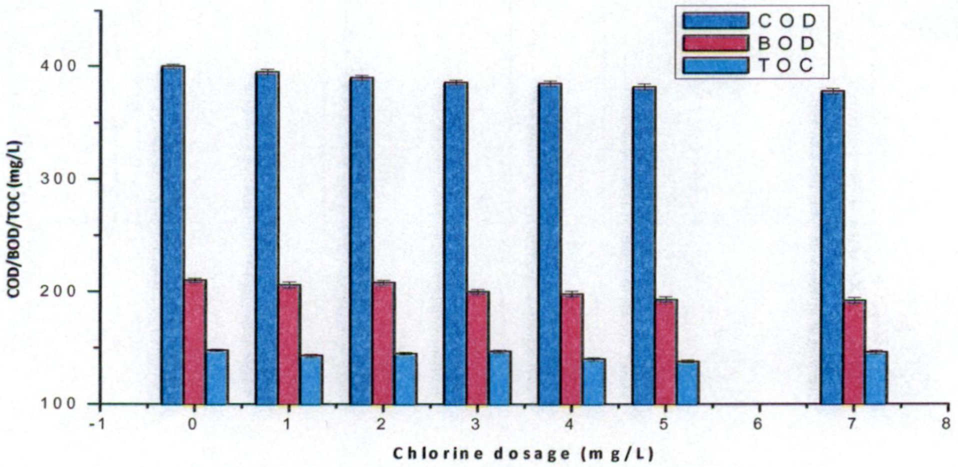

Fig 3.2.1c. COD, BOD and TOC variations during chlorination.

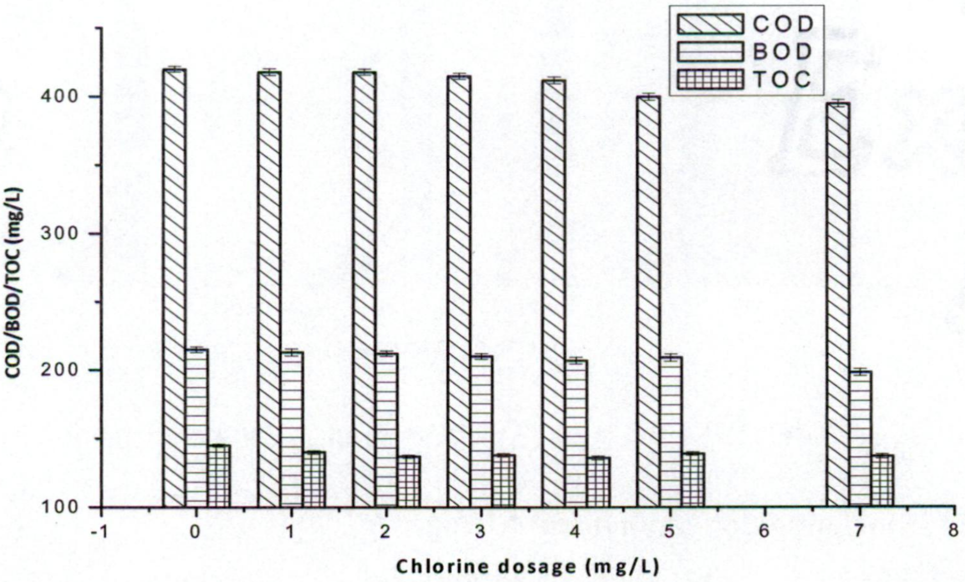

Fig 3.2.2c. COD, BOD and TOC variations during chlorination

Table 3.2. The initial characteristics (range) of waste water are given below

Parameters	**Range (± S.D)**
Temperature (^{0}C)	(17-19) ± 1
pH	(7.3-7.5) ± 0.05
NH_4^+-N (mg/L)	(58-75) ± 0.5
COD (mg/L)	(300-452) ± 3
BOD_5 (mg/L)	(140-215) ± 2
TOC (mg/L)	(100-148) ± 2
Available residual chlorine (mg/L)	(0.0 - 0.0) ± 0.0

Fig 3.2.1c, 3.2.2c, 3.2.3c and 3.2.4c, Table 3.2.1b, 3.2.2b, 3.2.3b and 3.2.4b (Tables ref. in Appendix A) shows the variations of COD, BOD and TOC with different dosages of chlorine 1-7 mg/L (Fig 3.2.1c & 3.2.2c), 1-30 mg/L (Fig 3.2.3c) and 1-50 mg/L (Fig 3.2.4c). On applying 1-7 mg/L chlorine dosages (Fig 3.2.1c), COD decreases from 400-378 mg/L (5.5 % decrease) and BOD decreases from 210-192 mg/L (8.5 % decreasement) continuously but TOC changes insignificantly. Similarly, on applying chlorine dosages 1-7 mg/L (Fig 3.2.2c) in new sample, COD decreases from 420-395 mg/L (5.9 % decreasement) and BOD decreases from 215-198 mg/L (7.9 % decreasement) continuously and TOC show insignificant change. On applying chlorine dosages 0-30 mg/L (Fig 3.2.3c), the COD concentrations decreases initially from 332-295 mg/L (11.1% decreasement, chlorine dosages 0-15 mg/L) and then increases from 295-327 mg/L (1.5% decreasement, chlorine 20-30 mg/L) and BOD concentrations decreases initially from 150-135 mg/L (10 % decreasement, chlorine dosage 0-10 mg/L) and then increases from 135-152 mg/L (1.3% increasement, chlorine10-30 mg/L) but TOC change was insignificant. Similar result were found in new sample on applying chlorine dosages from 0-50mg/L (Fig 3.2.4c) first decrease COD from 300-274 mg/L (0-10 mg/L chlorine dosages), then increase from 274-305 mg/L (20-50 mg/L) and BOD first decreases from150-138 mg/L (0-10 mg/L) then increases from 138-154 mg/L (20-50 mg/L chlorine dosages) but TOC change remains insignificant. From the above result we see that initially COD decreases then increases reach to the slightly higher value of unchlorinated samples (this is due to the reaction of organic matter with chlorine and some modification of the organic matter rendering it more biodegradable and more amenable in COD test). There were no significant changes in TOC concentration during

3.1. Results and Discussion

The major goal of this research was to determine the effect of chlorination on water quality parameters such as BOD, COD, TOC and Ammonical-N (NH_4-N) and the formation of trihalomethanes at raw sewage and two different sequencing batch rector (SBR) sewage treatment plants. This chapter shows the data obtained from this study. After chlorination with different dosages, it was found that several conditions affect the level of COD, BOD, TOC, NH_4-N and TTHMs. Each test was carried out in triplicate. The experiments tested at temperature ranged 17-25 °C, pH values ranging from approximately 6 to 8 and residence times of chlorination was 30 min. The experiments were conducted at raw sewage (Kanjarpur, Roorkee) and two different SBR plants (Haridwar and Rishikesh). For the study, 8 raw sewage samples were collected weekly for a period of two months. Subsequently, four sample per month were collected from each SBR plant for a period of four months. Trihalomethanes were measured by gas chromatography mass spectrometry (GC-MS).

3.2. Chlorination of Raw sewage (Khanjarpur, Roorkee)

- **Effect of chlorination on COD, BOD and TOC**

Several chlorination experiment performed in raw sewage of khanjarpur with different dosages of chlorine during two months (Aug 2011-September 2011). The chlorine dosages were varied between 0.0 and 50 mg/L. Sewage samples for chlorination were obtained from the Khanjarpur pumping station, Roorkee. The temperature and pH range of sewage samples were 15-23 °C and 7.2-8 respectively. The initial charecterstics (range) of all collected sewage samples are given in Table 3.2. The individual initial characteristics of raw sewage are given in Tables 3.2.1a, 3.2.2a, 3.2.3a and 3.2.4a (Appendix A)

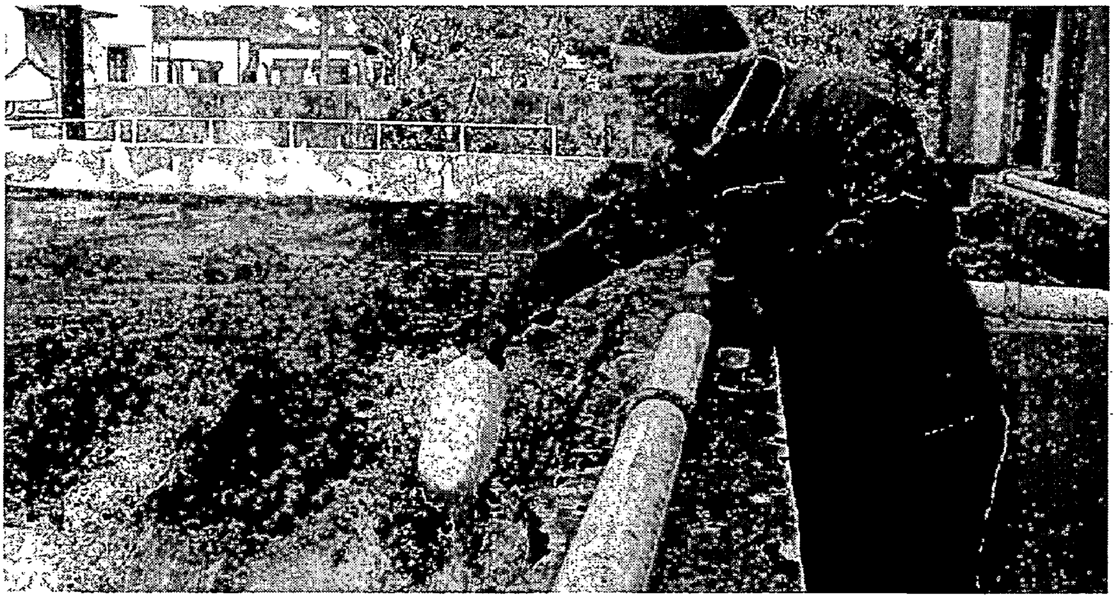

Fig 2.11. Haridwar sewage plant.

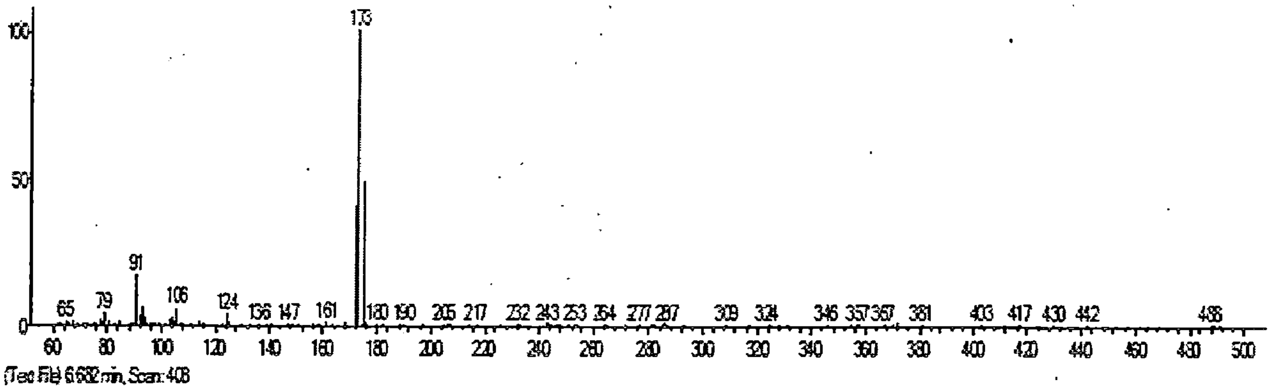

Fig.2.8. Mass spectra of Bromoform ($CHBr_3$).

Sewage was collected from Khanjarpur Sewage Pumping Station Roorkee, Haridwar , Rishikesh, and location shown below:

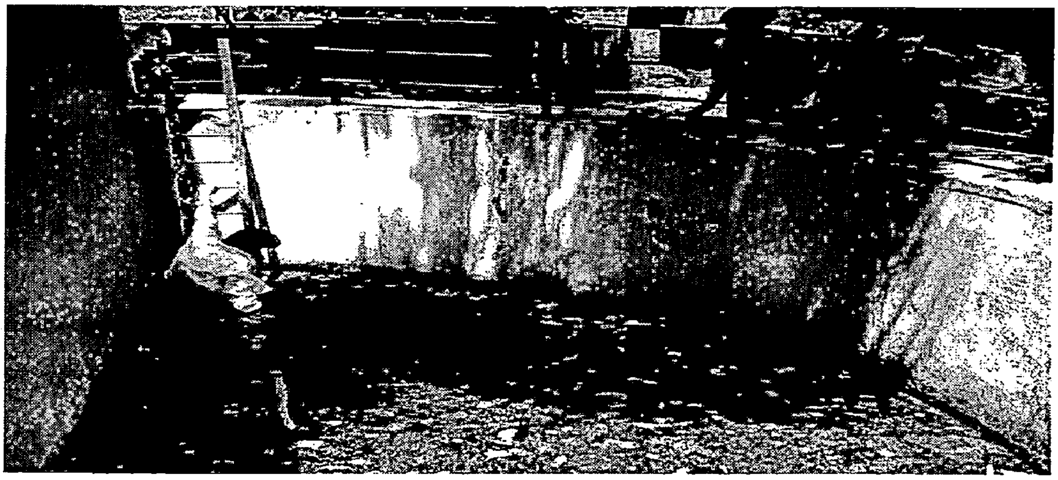

Fig.2.9. Khanjarpur Sewage Pumping Station, Roorkee.

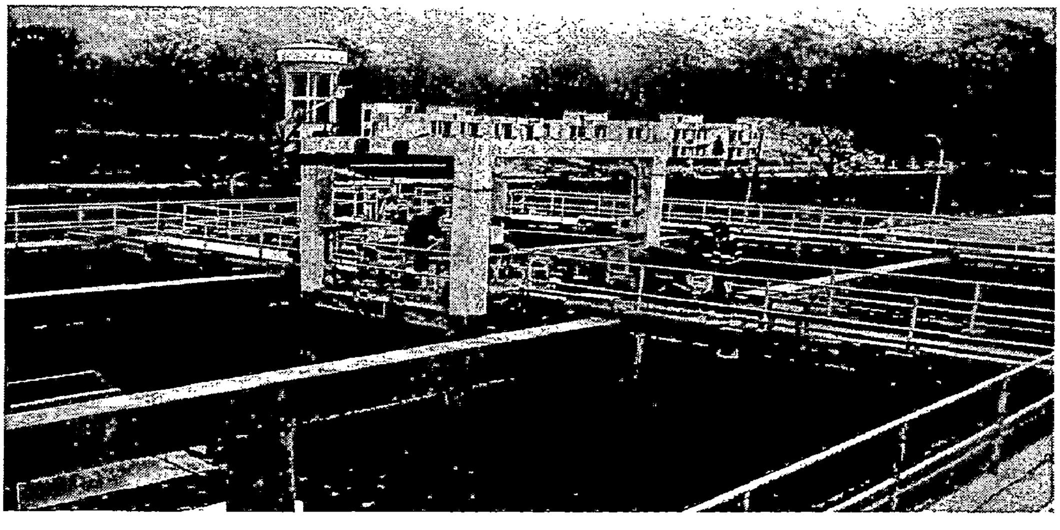

Fig 2.10. Rishikesh sewage plant.

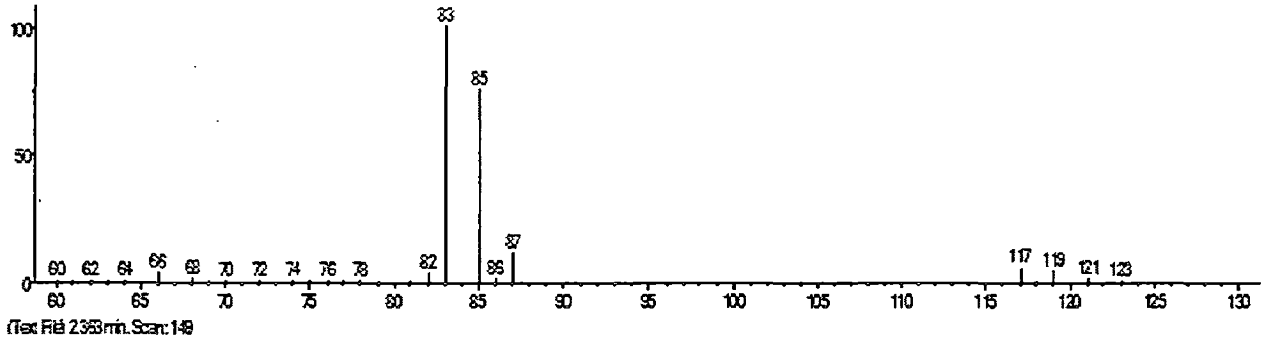

Fig.2.5. Mass Spectra of Chloroform ($CHCl_3$).

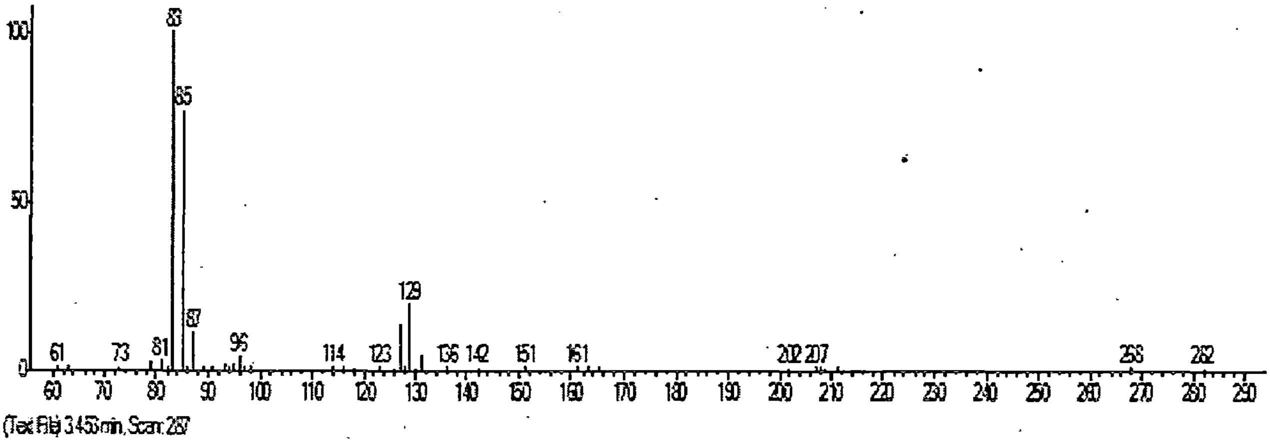

Fig.2.6. Mass Spectra of Bromodichloromethane ($CHBrCl_2$).

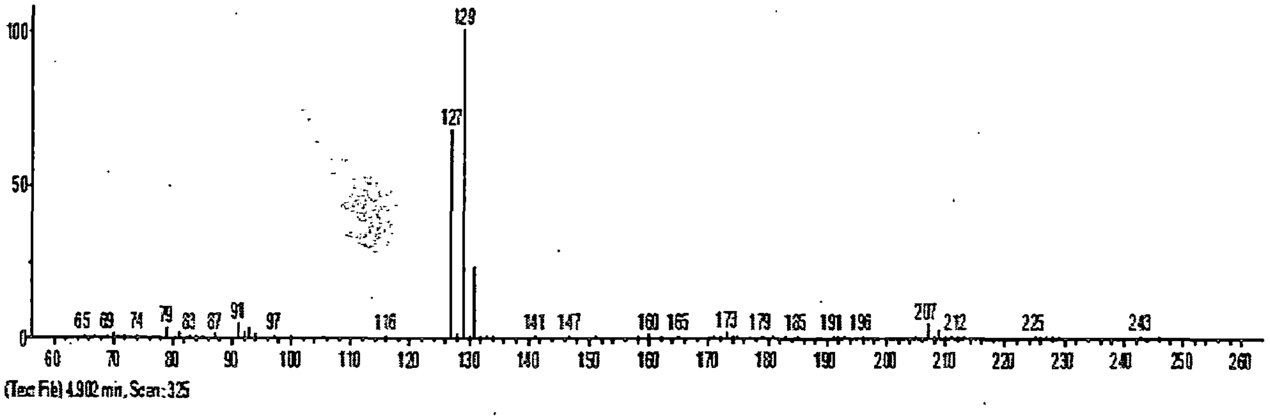

Fig.2.7. Mass spectra of Chlorodibromomethane ($CHBr_2Cl$).

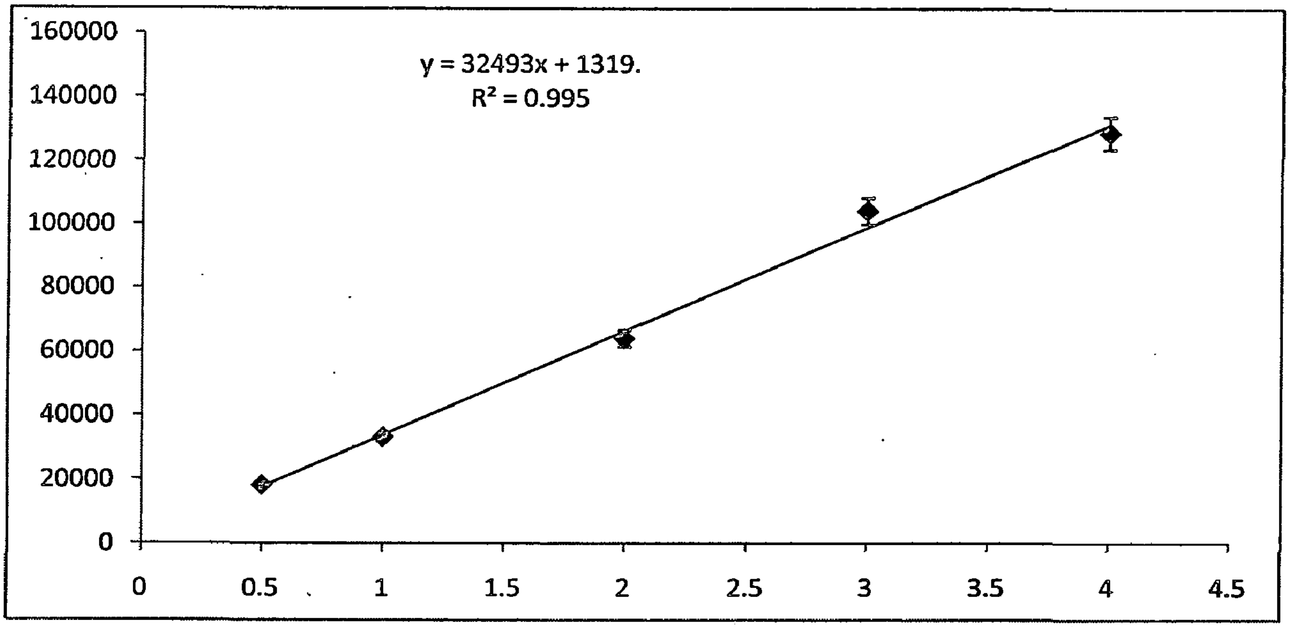

Fig.2.3. Calibration curve of Chlorodibromomethane ($CHBr_2Cl$).

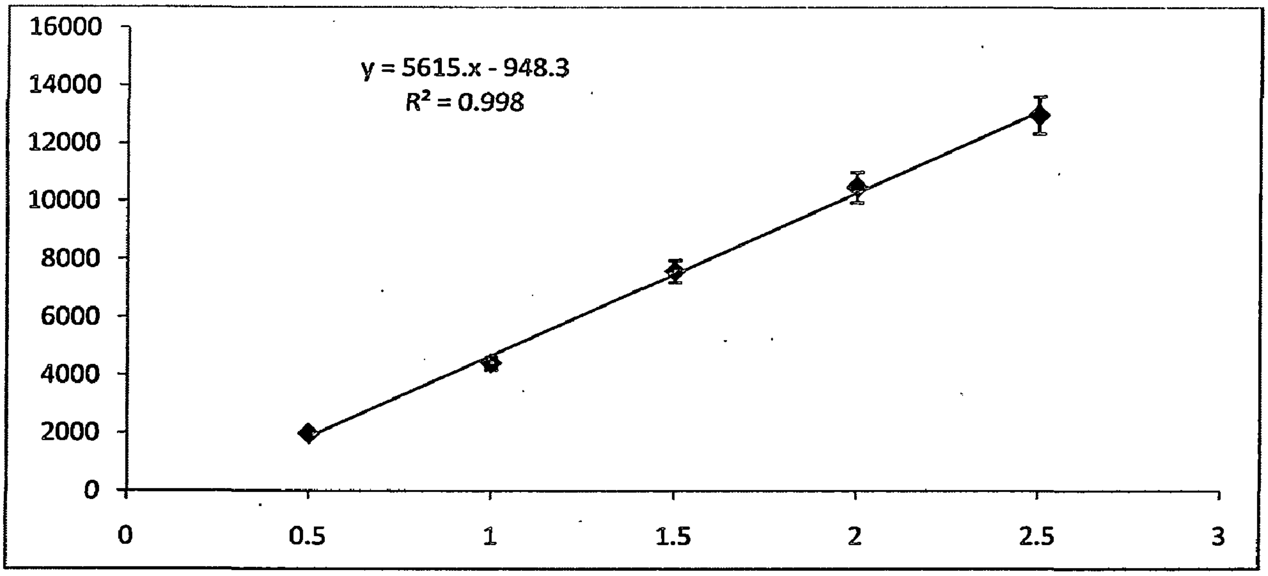

Fig.2.4. Calibration curve of Bromoform ($CHBr_3$).

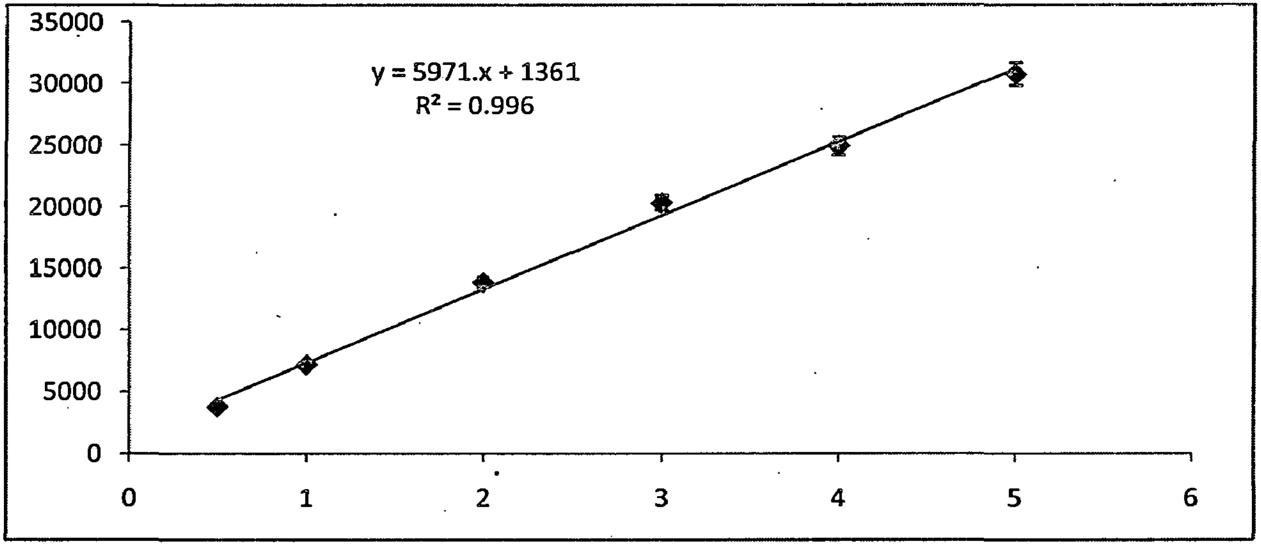

Fig.2.1. Calibration curve of chloroform ($CHCl_3$).

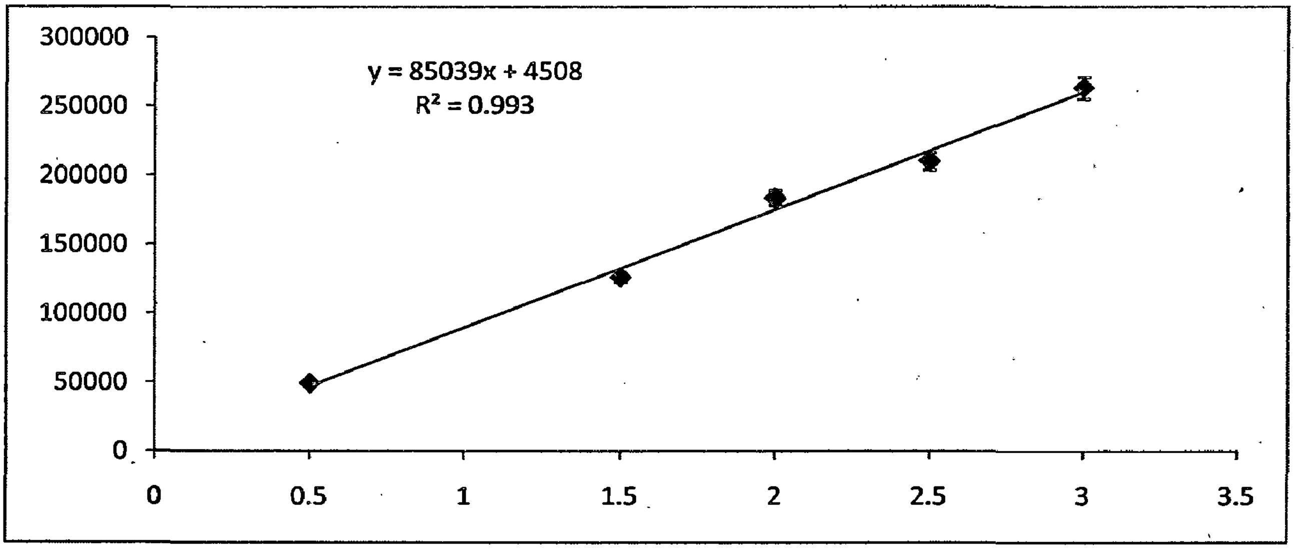

Fig.2.2. Calibration curve of Bromodichloromethane ($CHBrCl_2$).

vigourously for 1 min and separate with separating funnel. Analysed sample by injecting 1 µL of upper (organic) phase into GC-MS.

GC–MS conditions

Mass spectrometric analyses were carried out with a Varian GC-MS instrument (Germany) equipped with a VF-5MS fused-silica capillary column (30 m x 0.25mm, I.D. film thickness 0.25 µm). Helium was used as the carrier gas at a flow rate of 1.0 ml/min. A 1µL sample was introduced by split mode injection (split ratio 10:1). Both the GC injection port and the MS system were held at 280 °C. After sample injection, the oven temperature was held at 80 °C for 1 minute, raised to 240 °C at 20 °C/min and held for 5 min, raised to 280 °C at 5 °C /min, and held for 5 min.

Calibration curve

For each pesticides determination by CG-MS, the range of concentration was appropriated to the level usually found in wastewater. In standard solutions used, for the range of 0.4, 1, 2, 3, 4, 5 ppm respective compounds. The calibration technique is the external standard multipoint calibration using six concentration levels.

Table 2.4. Analytical parameters for THMs in water samples.

THMs	Calibration Curve Equation	R^2	Retention time
Chloroform ($CHCl_3$)	Y = 5971.7x + 1361	0.9963	3.064
Dichlorobromomethane ($CHCl_2Br$)	Y = 85039x + 5408	0.9933	3.459
Dibromochloromethane ($CHBr_2Cl$)	y = 32493x + 1319.5	0.9952	4.902
Bromoform ($CHBr_3$)	y = 5615.4x - 948.3	0.9981	6.682

$1.00\ mL = 1.00\ mg\ N = 1.22\ mg\ NH_3$

2.4. THMs analysis

Chemicals

Grade calcium hypochlorite with ultrapure water and they were standardized with FAS titration analyser before chlorine disinfection. Stock solutions of ammonia were prepared with analytical grade NH_4Cl and ultrapure water. Standard solutions of THMs were prepared in n-hexane at a different concentrations namely (0.5 ,1, 2, 3, 4, 5ppm for chloroform, 0.5, 1.5 All trihalomethanes (THMs) standards, Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Dibromochloromethane($CHClBr_2$) and Bromoform ($CHBr_3$) were purchased from Sigma Aldrich (USA). Stock solutions of chlorine (1079.2 mg/L) were prepared by anylytical, 2.0, 2.5, 3 ppm for dichlorobromomethane, 0.4, 0.5, 1, 2, 3, 4ppm for dibromochloromethane and 0.5, 1, 1.5, 2, 2.5 ppm for bromoform)and diluted with n-hexane when necessary. Organic solvents (n-hexane, acetone, methanol, and acetonitrile) were of HPLC grade and supplied by J.T. Baker (USA). Anhydrous sodium sulfate obtained from Sigma Aldrich (USA) and sodium sulfate used after baking at 400 ^{0}C for 12 hours. All glassware was cleaned with laboratory detergents, sequentially rinsed with distilled water of milli-Q system.

Chlorine disinfection

The chlorine disinfection experiment was conducted in 500 ml conical flask and covered with aluminium foil. The stock chlorine solution was added to conical flasks at different dosages (as available chlorine) for the wastewater samples. Then the flasks were sealed, mixed well in dark. after a contact time of 30 minute, the DBPs were analysed immediately.

Extraction and analysis of THMs

For extraction of Trihalomethanes (THMs), liquid-liquid extraction method followed by qualitative and quantitave estimation by GC-MS equipped with FID detector has been used for the determination of THMs. Standards along with samples were placed in sample sorage vials and identical procedures followed for preservation and transfer to the extraction vessel. Carefully pour 10 ml sample in to sample vial, add 2.0and shake

Also calculate the BOD of dilution water blank by above giving formula and subtract the sample BOD to blank BOD to get the final value of sample BOD in mg/L.

- **Total Organic Carbon (TOC):** About 5-10 mL water sample was used for the determination of TOC by Shimadzu (TOC-V_{CSN}) Liquid Sample Module (LSM-5000A).
- **Available Chlorine:** For bleaching powder. Take 5 g of fresh bleaching powder. Add small quantity of water to prepare fine paste. Add some more water stir and allow settling for a few min. Filter and dilute upto 1L with distilled water. Take 25 mL of bleaching powder solution. Add a pinch of KI add 100 mL of distilled water and 10 mL acetic acid, Titrate with standard 0.1N Sodium thiosulphate solution until the yellow color is almost faded out, add 1ml starch solution and titrate until blue color disappears. For blank sample, take 125 mL distilled water, add a pinch of KI add 10 mL acetic acid and titrate with 0.1N Sodium thiosulphate solution.

Calculations:

Available Chlorine (mg/L) = (A-B) xN x35500/mL of sample

Where,

N = Normality of Sodium thiosulphate,

A & B = mL of sodium thiosulphate required for sample and blank,

- **Residual Chlorine:**

  Take 200 mL of tap water in a reagent bottle or conical flask, add a pinch of KI and 2 mL acetic acid, add 1mL starch solution. If colorless, no residual chlorine. If blue in color, titrate with N/100 $Na_2S_2O_3$ until blue colour disappears.

  Calculation:

  Residual chlorine (mg/L) = (0.01xVx35500)/200

- **Ammonical Nitrogen (NH_4^+-N):** Take 50 mL sample add 1 drop 0.01N EDTA solution and 2 mL Nessler's reagent. Finally take absorbance at 640 nm.
- **Stock ammonium chloride solution:** Dissolve 3.819 g anhydrous NH_4Cl (dried at 100 ^{0}C) in water, and dilute to1000 mL,

Table 2.3 Performance Evaluation Parameters adopted from APHA.

S.No.	Parameters	Principle	Instruments/ Technique used
1.	**Temperature**	-	Temperature meter
2.	**pH**	Electrochemical	pH meter
3.	**NH_3-N**	Colorimetric Method	Spectrophotometer
4.	**BOD**	Volumetric	Winkler's method. Incubation for 5 days at 27 ^{0} C
5.	**COD**	Closed Reflux, Colorimetric	Spectrophotometer
6.	**TOC**	-	TOC Analyzer
7.	**Residual Chlorine**	Redox reaction	Iodometric method
8.	**Available chlorine in calciumhypochlorite**	Redox reaction	Iodometric method

- **Temperature:** Thermometer.
- **Chemical Oxygen Demand (COD):** Take 1.5 mL $K_2Cr_2O_7$ (Digestion solution) + 2.5 mL sample + 3.5 mL Sulfuric acid reagent in COD vial. Digest it for 2 h digester at 150 °C. Cool down at room temperature. Measure absorption of each sample, blank and standards at a wavelength of 600nm.
- **Biochemical Oxygen Demand (BOD):** Take two set of BOD bottles fill the sample of dilution. One set should be placed in BOD incubator at 20°C for 5 days and fix the DO of other set (by adding 1 mL $MnSO_4$ + 1 mL KI) and then add 1 mL H_2SO_4. Take volume of sample for titration according to total volume of bottle i.e. for 300 mL bottle volume = (300x200) /(300-2) = 201.34 mL. Add 1 mL starch indicator (Color change-blue). Titrate it with N/40 Sodium thiosulphate titrant till it becomes color less. Check the DO of incubated samples after 5 days.

Calculate the BOD_5 of sample

$$\mathbf{BOD_5\ mg/L = (DOi_1 - DOf_5) x DF}$$

Where,

DF = dilution factor

DOi_1 = Dissolve Oxygen initial

DOf_5 = Dissolve Oxygen final in three days

2.1. Materials and Methods

2.2. Description of STPs and monitoring plan

All STPs monitored in this study adopted the sequence of units as screens-grit chambers-SBR reactors followed by Polishing Unit for disinfection chlorination. The different STPs configuration and operational conditions studied are presented in Table 2.1. The monitoring schedule and type of sampling are mentioned in Table 2.2.

Table 2.1 Monitoring schedule of STPs.

STPs	**Monitoring schedule**	**Sampling type**	**Frequency of sampling (n)**
Rishikesh (3MLD)	2011-2012	Grab	12
Haridwar (27 MLD)	2011-2012	Grab	19
Khanjarpur (25MLD)	2011-2012	Grab	10

The Sewage and final treated effluent were brought from different location of the treatment plants to laboratory. Different chlorine dosed was applied in order to evaluate the different reaction and concentration of ammonia and COD. All samples were investigated extensively through the following parameters summarized in table 1 with given methodologies (APHA, 21ed. 2005).

Table 2.2 Summary of treatment performance of SBR reactors.

STPs Location	Capacity (MLD)	Range and Mean effluent concentration (mg/L)		
		pH	COD	NH_4-N
khanjarpur	25	7-7.6	300-500	45-90
Rishikesh	3	7-7.4	30-60	5-9
Haridwar	27	7-7.5	22-55	3-16

2.3. Analysis methodology

Grab samples of sewage from inlet chamber and final effluent from post treatment systems like chlorination. Samples were collected in five litre plastic bottles and kept in an air tight ice box and transported to the Environmental Engineering Laboratory, Department of Civil Engineering, IIT Roorkee, India.

Analysis of all water quality parameters (physico-chemical parameters), available and residual chlorine were made following the standard methods (APHA, 2005) (Table2.3). The detailed methodology of water quality parameters are as follows.

Table 3.4.10a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	16 ± 1
pH	7.1 ± 0.05
NH_4^+-N (mg/L)	7.2 ± 0.13
COD (mg/L)	32.42 ± 1.5
BOD_5 (mg/L)	19.6 ± 1.5
TOC (mg/L)	10 ± 1.2
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.10b. Effect of chlorination on NH_4^+-N observed at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	**NH_4^+-N (mg/L)**	
	Average	**S.D (±)**
0	6.2	0.13
1	5.9	0.17
2	4.8	0.15
3	3.7	0.15
4	2.9	0.12
5	2.6	0.13
7	2.1	0.11

Table 3.4.11a. The initial characteristics of waste water are given below

Parameters	**Values (± S.D)**
Temperature (^0C)	22 ± 1
pH	7.33 ± 0.05
NH_4^+-N (mg/L)	24.05 ± 1.5
COD (mg/L)	51 ± 1.29
TOC (mg/L)	10 ± 1.5
Available residual chlorine (mg/L)	0.0 ± 0.0

Table 3.4.11b. Effect of chlorination on COD, NH_4^+-N observed at different chlorine dosages during 30 min for Rishikesh (SBR) effluent

Chlorine dosage (mg/L)	COD (mg/L)		NH_4^+-N (mg/L)	
	Average	S.D (±)	Average	S.D (±)
0	51	1.29	24.05	0.55
5	49	0.56	21.09	0.51
10	56	1.00	20.05	0.58
20	65	1.12	19.01	0.54
30	71	0.76	17.62	0.57
50	95	0.61	14.03	0.58

Table 3.4.12a. Trihalomethane formation

Chlorine dosage (mg/L)	$CHCl_3$ (µg/L)		$CHCl_2Br$ (µg/L)		$CHBr_2Cl$ (µg/L)		$CHBr_3$ (µg/L)
	Average	S.D (±)	Average	S.D (±)	Average	S.D (±)	
0	ND	0.0	ND	0.0	ND	0.0	ND
1	110	4.5	26	3.1	12	2.2	ND
2	125	4.6	28	3.3	14	1.8	ND
3	143	4.4	34	3.2	19	2.0	ND
4	159	4.3	38	3.8	21	2.1	ND
5	200	4.6	46	3.6	26	2.3	ND
6	250	4.4	50	3.7	30	2.2	ND

ND = Not detected