

Full Length Research Paper

Study of double breakpoints during chlorination of river Yamuna water, Delhi, India

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A study on chlorination of raw Yamuna River water is reported in this study. Samples were chlorinated with increasing doses of standard chlorine water and residual chlorine (Cl_2) was measured by Starch-iodide method. For each sample, the chlorination curve (chlorine residual versus chlorine dose) was obtained. Curves showed the typical irregularity attributed to the formation and destruction of chloramines and transformation of toxic cyanobacteria (blue-green algae) by chlorine. It was observed that, after reactions with strong reductants and chloramines forming compounds, the remaining organic matter exerted a certain demand of chlorine. The evolutions of chlorination curves were studied. Till date, study on breakpoint chlorination revealed only single breakpoint but, in present study single breakpoints during chlorination of raw waters were not established in many cases. Double breakpoints have been reported in this study. The evolutions of different breakpoint curves might be attributed to formation and destruction of numerous chemical disinfection by-products (DBPs) and biological bacteria/alga, due to variant pollution conditions of raw water.

Key words: Ammonia, breakpoint chlorination, cyanobacteria, chlorine, pollution, nitrite.

INTRODUCTION

There has been limited research done on the breakpoint chlorination phenomenon. Initial research occurred in the last 60 years, when breakpoint was a hot topic and drew the attention of researchers. The latter half of this century has seen little done in the way of research into breakpoint chlorination. With the exception of a few papers (March and Gual, 2007), mostly plant specific studies have been performed. No study on double breakpoint during chlorination of water has been observed/reported in any research paper. There has however, been a great deal of research done in the field of chlorine with cyanobacterial blooms and chlorine-ammonia chemistry, as well as advances in the fields of chlorine and ammonia analysis. While this study certainly challenges all obtainable research on breakpoint chlorination, it also focuses on research done in the field of chlorine-ammonia chemistry, as it pertains to the breakpoint reaction. Establishment of

double breakpoints during chlorination of water has been reported in this study. Chlorine and other disinfectants react with natural organic matter (NOM) and/or inorganic substances occurring in water to form various disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs) and other compounds (Rook, 1974; Singer, 1994). Cyanobacterial blooms are also a great challenge for drinking water production, for their occurrence in drinking water resource often causes several process disturbances in treatment plant, such as faster filter clogging and reactant (chlorine demand) consumption increase.

REVIEW OF LITERATURE

Initial research efforts into the mechanism of the breakpoint

reaction are attributed to Calvert (1940), and later studies by Griffin and Chamberlin (1941), and Rossum (1943). Ensuing research by others (Palin, 1950; Wei and Morris, 1974; Weil and Morris, 1949) has led to an understanding of the stoichiometry and kinetics associated with the breakpoint process. A comprehensive study of the kinetics of breakpoint chlorination was performed by Saunier and Selleck (1976). The goal of their work was to develop 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" (Saunier and Selleck, 1976). Unfortunately, past research yielded little or no insight into the problem of successfully controlling the breakpoint process in a full-scale water treatment plant. Although Saunier and Selleck (1976) performed comprehensive pilot study work, the results were never incorporated into a full-scale plant application. Pressley et al. (1973) 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. (1973) performed an extensive pre-design pilot study to provide information for full-scale breakpoint operations at the Owosso wastewater treatment plant in Michigan. The engineering firm of Camp, (Dresser and McKee, 1983) also performed bench scale. Figure 5 shows what happens when chlorine (either chlorine gas or a hypochlorite) is added to water. First (between points 1 and 2), the water reacts with reducing compounds in the water, such as hydrogen sulfide. These compounds use up the chlorine, producing no chlorine residual. Next (between points 2 and 3), the chlorine reacts with organics and ammonia naturally found in the water. Some combined chlorine residual is formed (chloramines). Note that if chloramines were to be used as the disinfecting agent, more ammonia would be added to the water to react with the chlorine. The process would be stopped at point 3. Using chloramines as the disinfecting agent results in little THMs production but causes taste and odor problems since chloramines typically give a "swimming pool" odor to water. In contrast, if hypochlorous acid is to be used as the chlorine residual, then chlorine will be added past point 3. Between points 3 and 4, the chlorine will break down most of the chloramines in the water, actually lowering the chlorine residual.

Finally, the water reaches the breakpoint, shown at point 4. The breakpoint is the point at which the chlorine demand has been totally satisfied; the chlorine has reacted with all reducing agents, organics, and ammonia in the water. When more chlorine is added past the breakpoint, the chlorine reacts with water and forms hypochlorous acid in direct proportion to the amount of chlorine added. This process, known as breakpoint chlorination, is the most common form of chlorination, in which enough chlorine is added to the water to bring it

past the breakpoint and to create some free chlorine residual (White, 1992). Sodium hypochlorite or chlorine is used to oxidize the ammonia in raw, secondary and lime clarified municipal wastewaters. In systems with only ammonia as the chlorine demand, the breakpoint exhibits a minimum chlorine dose at approximately an 8:1 weight ratio of Cl:NH₃-N in the pH range of 6 to 7. End products at the breakpoint are N₂, NCl₃, and NO₃⁻.

Kinetic analysis of the oxidation of toxins in natural water revealed significant differences in their susceptibility to chlorine, saxitoxins being the easiest to oxidize, followed by cylindrospermopsin and microcystin-LR. Furthermore, concentrations of THMs and HAAs (<40 µg/L) and N-nitrosodimethylamine (<10 ng/L) as chlorination by-products were lower than the guideline values even at the highest chlorine exposure (CT) value (220 mg min/L). However, the DBP concentrations in environmental bloom conditions with very high cell numbers were over the guideline values (Arash et al., 2012).

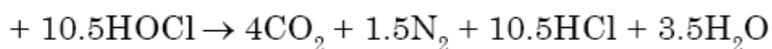
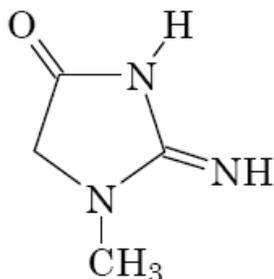
Thus, there are numbers of intermediate chlorination by-products which are still unidentified and contribute to double breakpoint during chlorine demand of water.

Oxidations of chemical pollutants

More than 500 DBPs in drinking water have been detected and divided into several groups of compounds (Richardson, 1998; Richardson et al., 2000): halogenated organic by-products (e.g., THMs, HAAs), inorganic by-products (e.g., chlorate, chlorite, bromated and iodate ions, ammonia) and organic oxidation by-products (e.g., aldehydes, carboxylic acids, assimilable organic carbon). Several DBPs result from chlorine disinfection (that is, CBPs) such as THMs, HAAs, haloacetonitriles (HANs) and other halonitriles (that is, cyanogen chloride), halo ketones (HKs), halophenols (that is, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol), halonitromethanes (that is, chloropicrin), haloaldehydes (that is, chloral hydrate) and MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) (US.EPA, 1999; Richardson et al., 2000). These compounds are formed under different conditions of pH and temperature, nature and amount of NOM and/or inorganic substances in raw and treated water, contact time between water and the disinfecting agent and biological degradation for some compounds (Singer, 1994; Chen and Weisel, 1998; Williams et al., 1998; Rodriguez and Serodes, 2001; Liang and Singer, 2003; Baribeau et al., 2005). This variability of conditions related to the formation of these CBPs in drinking water makes it difficult to study their occurrence in drinking water distribution systems (Rodriguez et al., 2004).

Oxidation of creatinine and creatine

Creatinine is a cyclic compound containing two reactive nitrogen atoms. It forms relatively stable chlorinated



Reaction 1. Creatinine.

derivatives (Lomas, 1967) that are decomposed by excess available chlorine (Alouini and Seux, 1988). Under swimming pool conditions, chlorocreatinines decompose very slowly and can persist beyond the breakpoint in oxidation of ammonia and have been characterized as nuisance residuals. Creatinine and creatine (a linear compound $\text{H}_2\text{NC}(\text{N}=\text{H})\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$), are closely related compounds. Dehydration of creatine yields creatinine (creatine \rightarrow creatinine + H_2O). Oxidation of creatinine and creatine by excess available chlorine yields carbon dioxide, water, hydrochloric acid, and ammonia chloramines that are then oxidized to nitrogen. The overall reaction for creatinine is shown in Reaction 1.

In the absence of free chlorine, chlorocreatinines can decompose to intermediate products such as: creatinine, creatine, chlorocreatines, and 1-methylhydantoin.

Oxidation of uric acid

Uric acid can form mono-, di-, tri-, and tetrachloro derivatives. With excess chlorine, uric acid is oxidized to carbon dioxide, nitrogen, hydrochloric acid, and water. Meso-oxalic acid may form as an intermediate product that can be oxidized to carbon dioxide and water (Reaction 2).

Oxidation of biological pollutants

Cyanobacteria also known as blue-green bacteria, blue-green algae, and cyanophyta, are a phylum of bacteria that obtain their energy through photosynthesis. Some cyanobacteria produce toxins, called cyanotoxins. These include anatoxin-a, anatoxin-as, and some cyanobacteria produce toxins, called cyanotoxins. These include anatoxin-a, anatoxin-as, aplysiatoxin, cylindrospermopsin, domoic acid, microcystin LR, nodularin R (from *Nodularia*), or saxitoxin. Cyanobacteria reproduce explosively under certain conditions. These results in algal blooms, can become harmful to other species if the cyanobacteria involved produce toxins. Microcystins are cyclic nonribosomal peptides produced by cyanobacteria

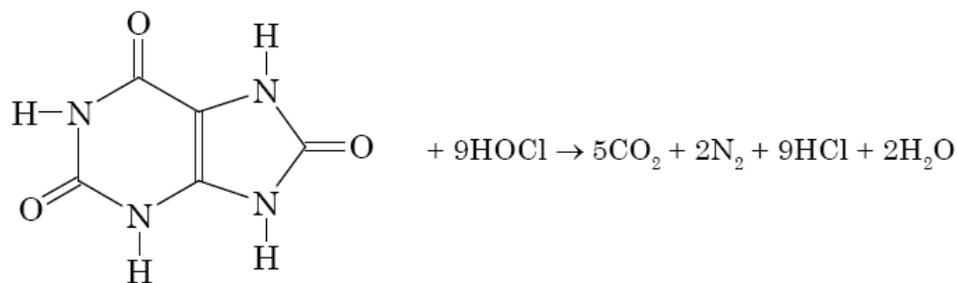
(e.g. *Microcystis aeruginosa* and *Planktothrix*). They are cyanotoxins and can be very toxic for plants and animals including humans. Their hepatotoxicity may cause serious damage to the liver. Sufficient chlorine doses are required to react with *Microcystins* and to satisfy chlorine demand of NOM which compete with toxins and potentially reduce chlorination efficiency (Kull et al., 2006) (Reaction 3).

Chlorination of microcystin

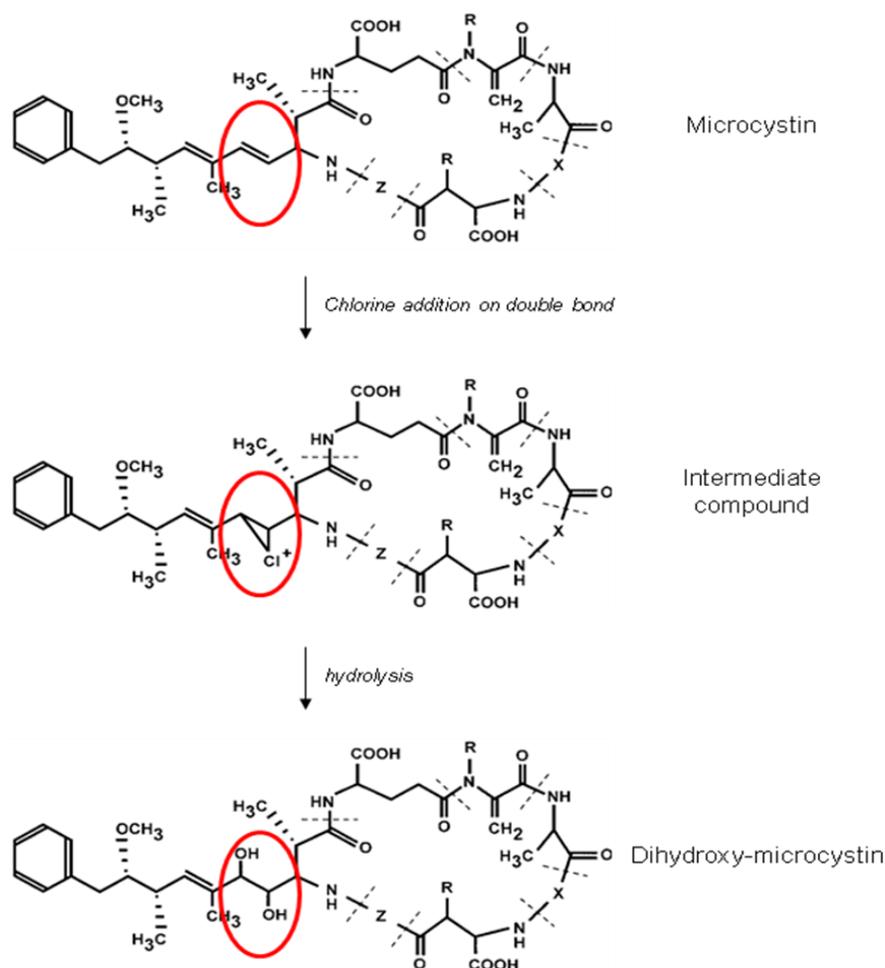
Cylindrospermopsin (abbreviated to CYN or CYL) is a cyanotoxin produced by a variety of freshwater cyanobacteria. CYN is a polycyclic uracil derivative containing guanidino and sulfate groups. It is also zwitterionic, making it highly water soluble. CYN is toxic to liver and kidney tissue and is thought to inhibit protein synthesis and to covalently modify DNA and/or RNA. CYN was shown to be vulnerable to chlorine (Senogles et al., 2000; Banker et al., 2001; Newcombe and Nicholson, 2004; Rodríguez et al., 2007a; Rodríguez et al., 2007b) (Reaction 4).

Chlorination of CYN

The bulk of the research on chlorine demand has been related to chlorination of potable waters. Feben and Taras (1950, 1951) 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. (1973) 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 $\text{Cl}:\text{NH}_3\text{-N}$ dosages to reach the breakpoint, while all other factors were constant. The end products of the breakpoint reaction were found to be primarily nitrogen gas (N_2) and secondarily nitrate (NO_3^-) (Palin, 1950; Pressley et al., 1973; Saunier and Selleck, 1976). The introduction to above literature is cited to interpret formation of multi-chlorination by-products which are potentially responsible



Reaction 2. Uric acid.



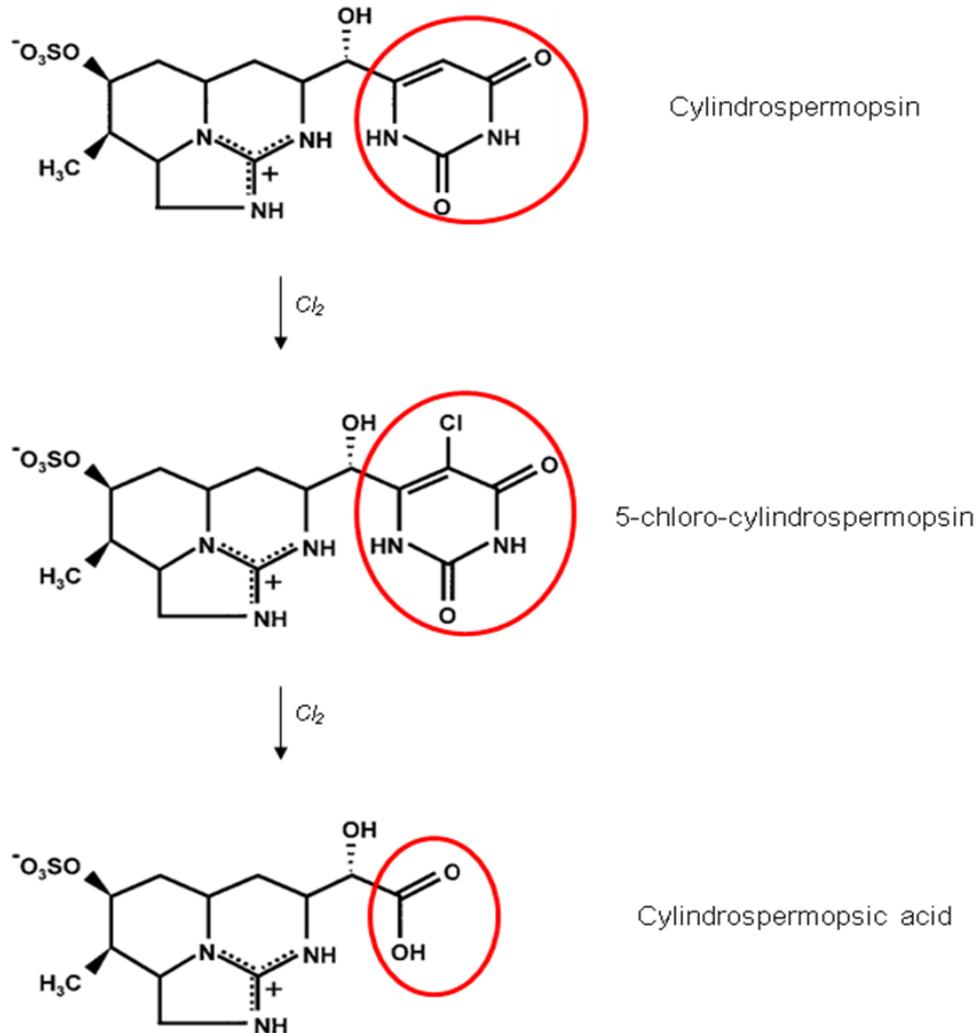
Reaction 3. Chlorination of microcystin.

for the cause of double breakpoint during chlorine demand of raw Yamuna River water.

MATERIALS AND METHODS

The physical-chemical process of ammonia oxidation with chlorine has been practiced in the water treatment field for over 60 years. As early as the 1920s, super chlorination 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 (1939) 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



Reaction 4. Chlorination of CYN

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. Figure 5 shows a hypothetical breakpoint curve for water with a dose requirement of 9:1 Cl:NH₃ (Jensen and Johnson, 1989).

Sample

The Wazirabad Water Works located in Delhi, India is one of the ancient water treatment plants running since 1966, which claims River Yamuna water for use in a potable water supply. The Yamuna River water is a reliable source of good quality water for a system serving over 50, 00000 (5 million) people in central and allied South Delhi of India National Capital territory. The Wazirabad Water Treatment plant is designed for operational reliability and redundancy in order to maintain high quality water under all circumstances. To this end, breakpoint chlorination process has been provided for nitrogen management. Nitrification involves the conversion of ammonia to nitrate. Breakpoint chlorination involves the use of chlorine (in the form of gas or sodium hypochlorite

solution) to chemically oxidize ammonia and convert it to nitrogen gas. The water quality of River Yamuna kept deteriorating frequently exceeding its ammonia contents sometime 1.0 mg/L from 0.00 mg/L and nitrite contents to 0.10 mg/L from 0.006 mg/L. The results of this study are not likely to be repeatable with raw water that has not been polluted/deteriorated to the same degree as Yamuna River receiving at Wazirabad Barrage.

Data collection

Samples of River Yamuna water were collected and analyzed as per the guidelines laid in the book "Standard Methods" (1992) For Examination of Water and Wastewater prepared and published jointly by APHA, AWWA and WEF Washington, DC 20005. Tests were conducted during the year 2011 at 120 MGD Water Treatment Plant, Water Works Wazirabad, Delhi (India). The samples were tested in plant laboratory of water works as per "Standard Methods" book by Electrometric Method (4500-H⁺ B) for pH, Argentometric Method (4500-Cl⁻ B) for chloride, Nesslerization Method (4500-NH₃ C) for Ammonia, Colorimetric Method (4500-NO₂⁻ B) for Nitrite, Chlorine Demand/Requirement Method (2350 B) for determining

breakpoint, and Iodometric Method I (4500-Cl B) for residual chlorine. The raw water pH fluctuation of all the samples was in the range of 7.6 to 8.8 and chloride fluctuated in the range of 6.0 to 500 mg/L. Parametric values of pH, chloride, ammonia and nitrite were determined before performing detection of breakpoint in chlorine demand test. All tests were performed at normal room temperatures, fluctuated from 10 to 35°C in accordance with climate and season change from January, 2011 to December, 2011.

Breakpoint determination in chlorine demand test by Starch-iodide method

Chlorine demand test were made daily on river water samples entering to Water Works Wazirabad, Delhi, India from January, 2011 to December, 2011. Standard chlorine water solution of 200 mg/L strength was added in general to a series of portions of the samples using increment of 1 to 2 ppm (part per million) chlorine. After 30 min contact, the residual chlorine was determined by the starch-iodide method according to "Standard Methods". Potassium iodide and starch were added to the sample and the liberated iodine was titrated with 0.0056338 sodium thiosulphate. The pH of the raw water samples was usually between 7.6 and 8.8. A stock solution of chlorine was prepared by mixing liquefied chlorine gas into 1 L distilled water. Chlorine dosage in increments of 0.1 mg/L for determining low chlorine demand/requirement and up to 1.0 mg/L or more for higher demands was used keeping in view ammonia and nitrite contaminations. Sample portions were dosed according to a staggered schedule that would permit determining the residual after predetermined contact time of half an hour. At the end of contact period of half an hour, residual chlorine of each of the bottle measured and noted. For determination of residual chlorine, 2 ml acetic acid was added followed by 2 ml KI solution (5% solution prepared freshly each time) to each of the bottle. Instantly each of the bottle was titrated with standard solution of sodium thiosulphate of 0.0056338 normality strength using starch solution as an indicator.

RESULTS AND DISCUSSION

Special investigations were performed to determine the specific chlorine demand of River Yamuna water (raw water) receiving at Wazirabad Barrage in Delhi, India. Two hundred (200) raw water samples were tested for studying breakpoint curves. Theoretical Chlorine Demand curve shows a sharp breakpoint as shown in Figure 5.

The plotting of applied chlorine dose versus residual chlorine gives a curve that can be depicted under four distinct areas or product formation as shown in Figure 5. The first area represents the oxidation of more reactive compounds than NH_3 by chlorine where residual chlorine found nil and is an inorganic demand phase. The second area represents an increase in combined chlorine residual (chloramines). The residual begins to drop because of destruction of the combined chloramines. At this point the nitrogen is given off as a gas and is lost to the atmosphere. Phase three continues until breakpoint. After breakpoint, all NH_3 products have been fully oxidized and free chlorine residual begins to form. But, in this present study, it was found that the theoretical

chlorine demand curve as shown in Figure 5 did not always match but, differs at many times depending on the pollution condition of raw waters. It is widely held that N_2 and NO_3^- are the two main products of breakpoint and combined residue chlorination. Leao (1981) measured the amount of ammonia oxidized per chlorine reduced in the combined chlorine dose region after several days over considerable ranges of initial pH and Cl/N conditions and found no correlation to either of these parameters. Indeed, others have shown that at least one as yet unidentified product (Valentine et al., 1986; Hand et al., 1983; Leung, 1989; Valentine et al., 1990) and nitrate can be formed in the combined region. The unidentified product is relatively stable and contains chlorine, which is released as chloride ion upon reaction with sodium sulfite, indicating that it can act as an oxidant (Leung, 1989). During chlorine demand test of water, double breakpoints were found in the process of breakpoint chlorination as shown in Figures 1 and 2.

Here, water was heavily polluted with ammonia containing pollutants ($\text{NH}_3 - \text{N} > 0.40$ mg/L), while nitrite containing pollutants are in smaller magnitude ($\text{NO}_2^- - \text{N} < 0.1$ mg/L). The hypothetical reason for double breakpoints might be attributed to the formation of multi unidentified chlorine reaction products with ammoniacal contaminations and cyanobacterial bloom. The occurrence of cyanobacterial blooms is drastically increasing in temperate countries and drinking water resources are threatened. As a result, cyanotoxins should be considered in water treatment to protect human health. Chlorination efficiency on cyanotoxins alteration depends on pH, chlorine dose and oxidant nature. Microcystins and cylindrospermopsin are efficiently transformed by chlorine, with respectively 6 and 2 by-products identified. In addition, chlorination of microcystins and cylindrospermopsin is associated with a loss hump and dip of acute toxicity. Even though they have been less investigated, saxitoxins and nodularins are also altered by chlorine. For these toxins, no by-products have been identified, but the chlorinated mixture does not show acute toxicity. On the contrary, the fact that anatoxin-a has a very slow reaction kinetics suggests that this toxin resists chlorination. The typical profile of breakpoint curves can be attributed to the formation and destruction of chloramines and transformation of toxic cyanobacteria (blue-green algae) by chlorine that may have breakpoint earlier than disruption of ammonia compounds. Formation of unidentified products was estimated to account for up to 10 to 20% of the total observed reduction in chloramines oxidizing capacity under some conditions (Leung, 1989; Valentine et al., 1990). Nitrate formation, equivalent to approximately 15% of the loss in chloramines oxidizing capacity has also been observed in conjunction with the formation of unidentified product (Chad and Richard, 1992).

It is found that when raw water contaminated with nitrite containing pollutant heavily ($\text{NO}_2^- - \text{N} > 0.10$ mg/L) and

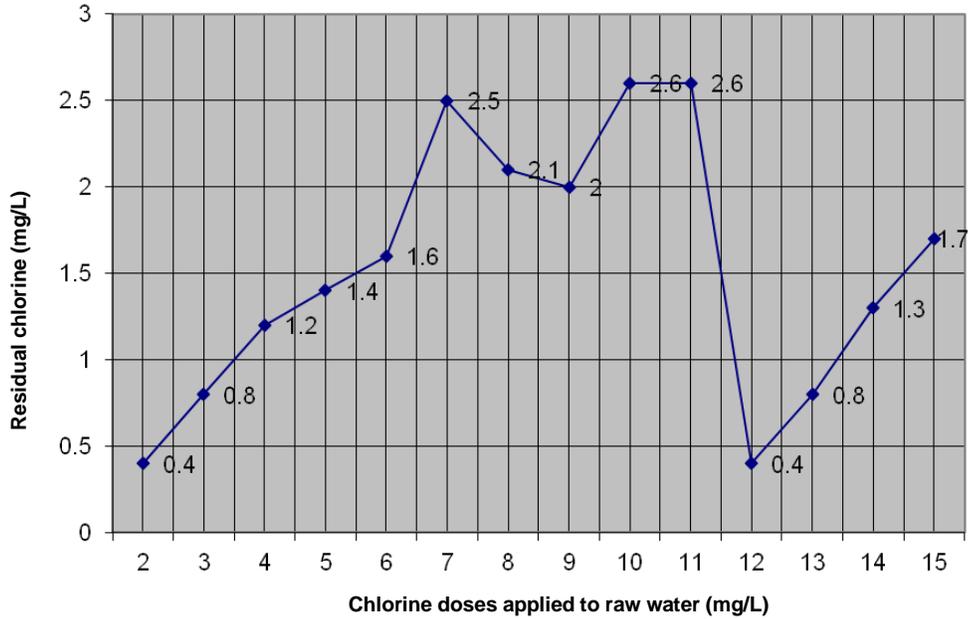


Figure 1. Chlorine residuals versus chlorine dose (Double breakpoints when ammonia is >0.4 mg/L and nitrate >0.1 mg/L).

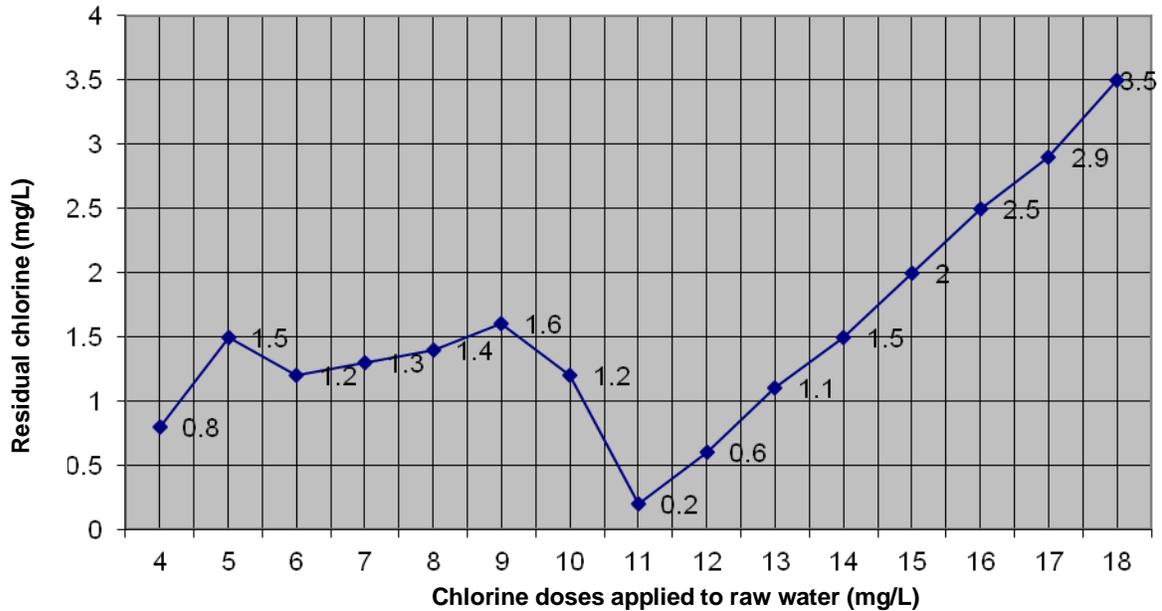


Figure 2. Chlorine residuals versus chlorine dose (Double breakpoints when ammonia is >0.4 mg/L and nitrate >0.1 mg/L).

ammonia containing pollutants are present to a lesser extent ($\text{NH}_3 - \text{N} < 0.10$ mg/L), a chlorine demand test curve does not have a breakpoint in it but, the graph is a straight line. The chlorine dose applied initially in Figure 3 is taken as 1.0 mg/L as minimum dose because applied chlorine below this amount does not show any residual

and got consumed because of contaminants other than ammonia. The water samples under test might be contaminated by many others unidentified reducing compounds other than ammonia and nitrite.

This might be attributed to conversion of nitrite ion into nitrate, where no destruction of chloramines and other

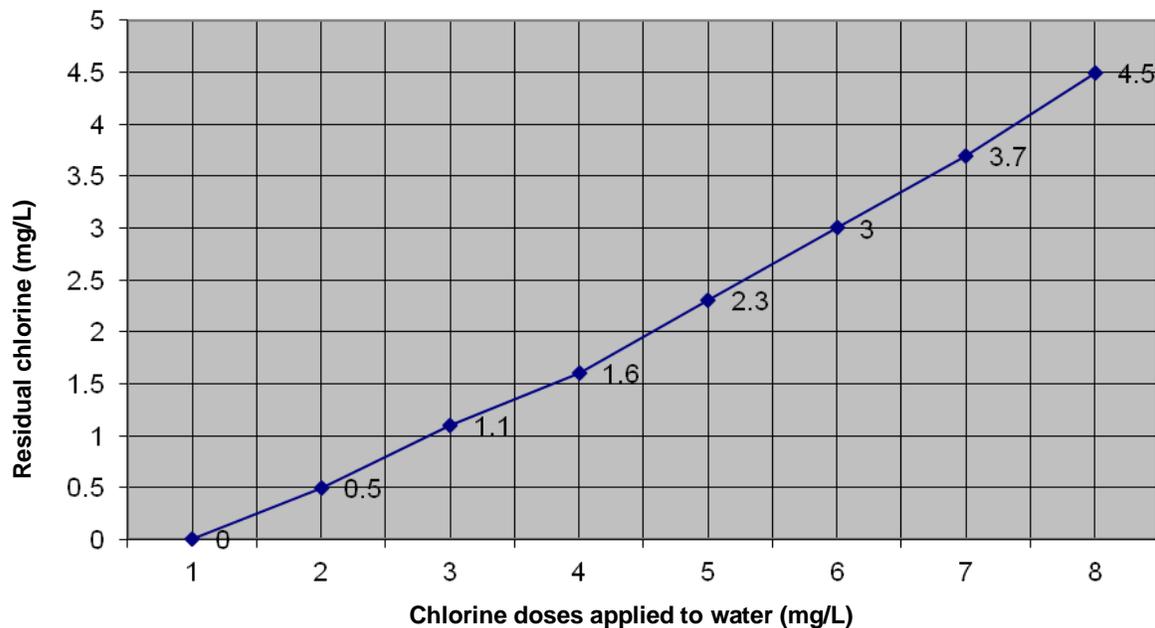


Figure 3. Chlorine residuals versus chlorine dose (No breakpoints when ammonia is <0.4 mg/L and nitrate >0.1 mg/L).

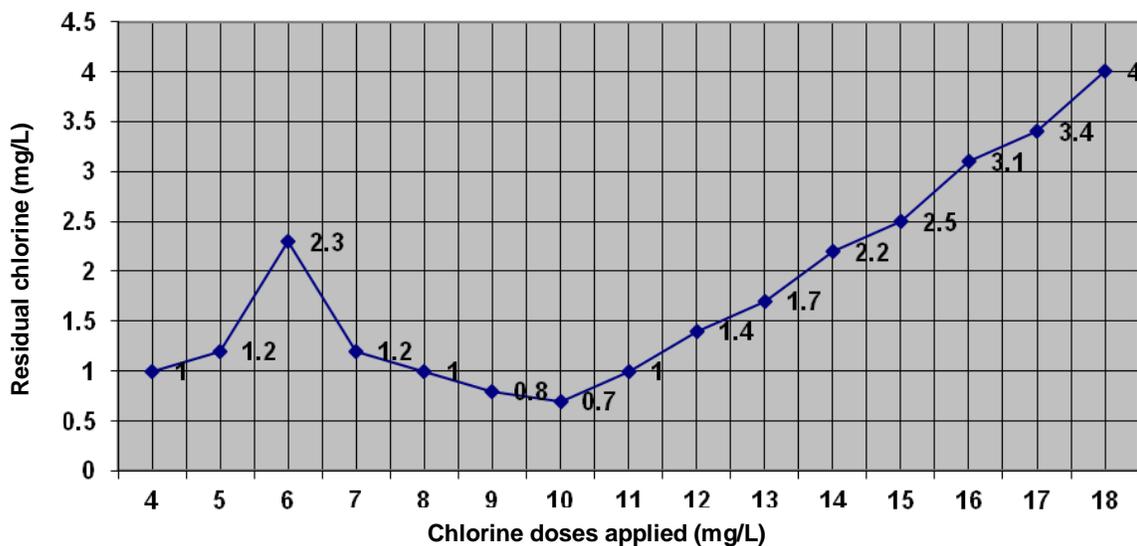


Figure 4. Chlorine residuals versus chlorine dose (Single breakpoint when ammonia is >0.4 mg/L and nitrate <0.1 mg/L).

organic- inorganic pollutants are required. No breakpoint has been observed with nitrite polluted water.

When raw water of River Yamuna was polluted with ammonia containing pollutants discharged from industries and non-functional/partially functional sewage treatment plants a graph similar to theoretical graph having single breakpoint was obtained.

Water samples collected and tested for ammonia and

nitrite pollutants were found heavily polluted with ammonia ($\text{NH}_3 - \text{N} > 0.40$ mg/L) and nitrite ($\text{NO}_2^- - \text{N} > 0.10$ mg/L). Here, a single breakpoint is observed with increasing doses of chlorine (Figure 4). Earlier results on breakpoint chlorination curves had shown only a single breakpoint during chlorination of water. However, any more specialized study especially on breakpoint chlorination curves has not been found in any journal.

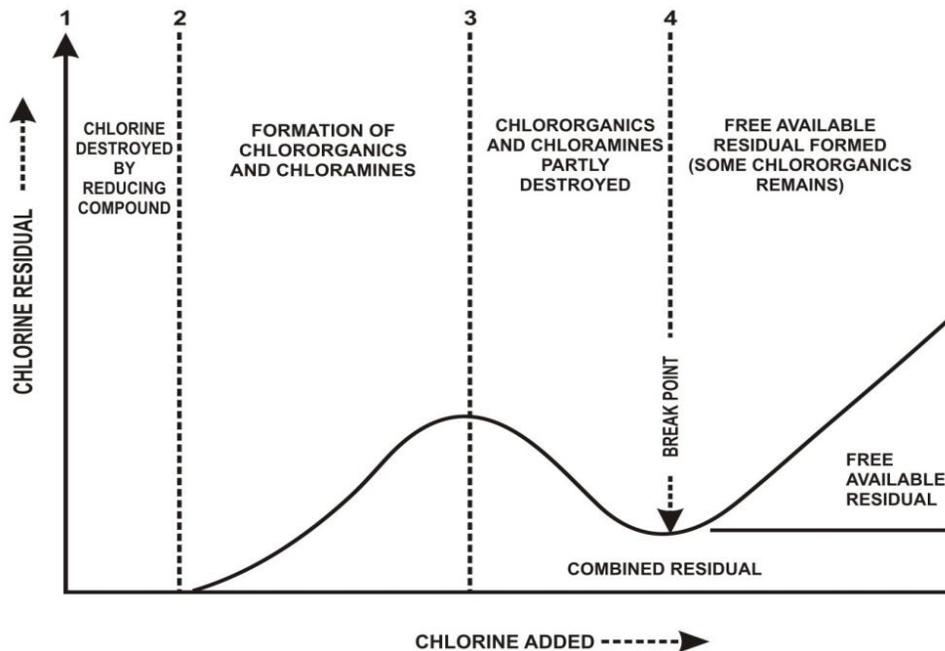


Figure 5. A breakpoint chlorination graph.

Conclusion

It has been observed that “double breakpoints” also exists during chlorination of water which supersedes all studies indicating establishment of a single breakpoint during super chlorination of water. A single breakpoint was observed during chlorine demand test of water, when raw water was polluted/ contaminated with ammonia pollution. Double breakpoints were observed during chlorine demand test of water, when water was severely polluted with ammonia (>0.4 mg/L as N), nitrite (<0.01 mg/L as N), chloride and other suspected cyanobacterial blooms. A straight line/linear graph was observed during chlorine demand test between chlorine doses added versus residual chlorine for a contact period of half an hour when water was polluted severely with nitrite contents (>0.01 mg/L) and low ammonia containing pollutants (<0.1 mg/L). Ammonia and chlorine were both found co-existing in raw water. Despite what is known about reaction schemes between chlorine and ammoniacal pollutants in water, there is a considerable amount of critical information lacking, particularly information regarding reaction products. Double breakpoints in chlorination of River Yamuna water might be attributed to the oxidation of slower reacting organic chloramines, e.g., chlorinated derivatives of amino acids, creatinine, other organic nitrogen compounds and cyanobacterial blooms.

An extensive need of detailed study of kinetics of reaction between chlorine and different water pollutants are required to interpret causes of double breakpoints

during chlorine demand of River Yamuna water. Additional research is necessary to identify all products over wide range of reaction conditions.

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