APPENDIX-1: Most Frequently Asked Questions about Chlorination (FAQs)

1. What are the functions of Chlorinations?

Functions and purposes of chlorinations are $(1-5, 16-22)$.

- 1. Elimination or reduction of colors and odors: Color and odor-producing substances present in wastewaters are oxidized by chlorine. The oxidizing ability of chlorine is employed for odor control and color removal in treatment of many industrial effluents (beet sugar, cannery, dairy, pulp and paper, textiles).
- 2. Disinfection: Owing to its strong oxidizing capacity, chlorine destroys or inhibits growth of bacteria and alage.
- 3. BOD reduction: Chlorine accomplishes BOD reduction by oxidation of organic compounds present in wastewaters.
- 4. Oxidation of metal ions: Metal ions which are in reduced state are oxidized by chlorine (e.g., ferrous to ferric ion and manganous to manganic ions).
- 5. Destruction of cyanides, phenols and detergents.
- 6. Control of foams and flies.
- 7. Aiding scum and grease removal.

Chlorination of wastewater for BOD reduction was practised as long as 1859 in England⁽⁴⁾. A number of studies of BOD reduction by effluent chlorination where it was recognised as such were conducted the 1920s and 1930s (5). In the USA in the 1920s and 1930s and thereafter the chlorination of Sewage was in use for purposes of protecting water supplies, bathing beaches and shellfish layings situated at the sewer outfalls. Chlorination was reported to reduce Biochemical Oxygen Demand of sewage as well as to control odors⁽⁴⁾. Applications of chlorine in wastewater collection, treatment and disposal are reported in several publications $(5, 6)$.

In spite of the use of chlorine as disinfacting chemical today, renewed interests have been shown in using chlorine for treating textile dyeing-finishing wastewaters through in-situ generation of chlorine by electrolysis of a chlorine bearing salt in the wastewater $(7-15)$. Major achivements reported are: color destruction and significant reduction of COD and BOD. Creative Environmental Consultants have offered technology to treat dyebath effluents with chlorine gas (18) .

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2. Is chlorine capable of reducing BOD and COD while treating wastewater?

Yes. Chlorine is a well-known oxidant and has long been used to purify water, destroy organisms in wastewater and swimming pools and oxidize chemicals in wastewater. The destruction of cyanide and phenols by chlorine oxidation is well-known in waste-treatment technology (1) .

US Patent No. 3,910,999 describes the stepwise chlorine oxidation of mixture of compounds present in industrial wastes, such as glycols, chloroalcohols, organic acids and ketenes by controlling the pH in the alkaline range initially to oxidize those most favorably destroyed by hypochlorite ion, then allowing the pH to drop to the acid range to destroy those oxidized more rapidly at low pH $^{(12)}$.

Chlorine generally reacts in a prescribed order, first with inorganic reducing compounds. If enough chlorine is added to react with these substances, then the addition of more chlorine will result in reactions of chlorine with the organic matter that is present. These chlororgano compounds have little or no disinfecting action. Again, if enough chlorine is added to react with all the reducing compounds and all the organic matter, then the addition of little more chlorine will react with ammonia or other nitrogenous compounds to produce chloramines or other combined forms of chlorine. The continued addition will result in the destruction of the chloramines and organic compounds and the formation of free chlorine (11) .

Though all three species, Cl₂, HOCl and OCl, will readily oxidize organic compounds, HOCl is the most reactive for its higher redox potential (3) . The reactivity of HOCl is based on the electrophollic nature of the molecule at either the oxygen or chlorine atom. Reactions occurring at the oxygen atom produce a chloride ion by displacement in reactions with organic compounds, the chlorine atom may become electrophillic and may combine with an electron pair in the substrate. This behaviour accounts for the reactions of HOCl with ammonia and amines, with phenols and other aromatic substances and in the formation of chloroform from organic substrate (3).

Chemical Oxidation of BOD and $\text{COD}^{(2)}$:

The overall reaction for oxidation of organic molecules comprising BOD, for example, with chlorine, ozone and hydrogen peroxide, can be represented as follows:

Multiple arrows in the direction of the reaction are used to signify that a number of steps are involved in the overall reaction sequences. The overall reaction rates are reported to be slow. Typical dosages of chlorine for the oxidation of organic in wastewater are reported in the range 1.75 to 2.0 kg/kg BOD destroyed.

Chlorine oxidation can be used to oxidize nonbiodegrable organic compounds also. Chlorination of wastewater for BOD reduction was practiced as long as 1859 in England with wastewater putrefaction reported to be delayed by the addition of chlorinated lime (4) . This in effect was chlorination for BOD reduction (10) . A number of studies of BOD reduction by effluent chlorination where it was recognized as such were conducted in the 1920's and 1930's. These studies indicated that chlorination effects a reduction in the 5-day BOD value that increases with increasing chlorine dose, with the optimum dose being that produces a slight residual chlorine after ten minute contact time $(4,5,6,7,8)$.

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- 12. Oxidation of mixtures of organic compounds with hypochlorite ion source materials, US patent 3910999 (The Dow Chemical Company)

3. How does chlorine perform decolorization; react with hydrogen sulfide, salts, alkalies, cyanides, phenols; and reduce BOD/COD and TDS?

The reactions with chlorine mentioned hereabove are well known and can be found in books and journal publications $(1-8)$.

Decolorization (Bleaching) step involves the following reaction with hypochlorous acid:

 $\text{dye (colored)} + \text{HOCI} \rightarrow \text{HCl} + (\text{dye colorless} + \text{O}) \dots \dots (1)$

Reaction of chlorine with hydrogen sulfide:

H2S (g) + Cl2 (g) → 2 HCl (g) + S (s) (2)

Many metals salts and alkalies react with chlorine; with alkali solution, hypochlorite and chloride of the metal are formed for example:

 $Cl_2(g) + 2NaOH (aq) \rightarrow NaOCl (aq) + NaCl (aq) + H_2O (l)$ (3)

 $Zn(s) + Cl₂(g) \rightarrow ZnCl₂(s)$ (4)

 $2FeCl₂(aq) + Cl₂(g) \rightarrow 2FeCl₃(aq)$ (5)

Reaction with cyanides $(1,2,3)$:

 $2CN^- + 8OH^- + 5Cl_2 \longrightarrow 2CO_2(g) + N_2(g) + 10Cl^- + 4H_2O$ (6)

Reaction with phenols $(1, 4, 5)$

C6H5 + Cl² → C6H5Cl+ HCl (7)

Chemical Oxidation of BOD and COD⁽⁶⁾:

The overall reaction for oxidation of organic molecules comprising BOD, for example, with chlorine, ozone and hydrogen peroxide, can be represented as follows:

Organic molecule (e.g. BOD) $Cl₂$ Intermediate oxygenated molecules Simple end products $(e.g. CO₂, H₂O, etc)$ (8)

Multiple arrows in the direction of the reaction are used to signify that a number of steps are involved in the overall reaction sequences. The overall reaction rates are reported to be slow. The reaction for CoD reduction is same as reaction (8).

From reactions (1), (2), (6) and (8), it is evident that the TDS of the effluent are likely to decrease.

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4. Will the use of chlorine gas lead to Occupational Health and Safety Issues?

No, as long as the handling procedures are strictly followed.

Chlorine gas is slightly soluble in water (8). The solubility of chlorine in water at different temperatures is given in Table 1 and Figure $1^{(2)}$.

Figure 1: Solubility of Chlorine Gas in water

When dissolved in water, chlorine gas reacts reversibly to form hypochlorous (HOCL) and hydrochloric (HCl) acids $(3, 4)$.

 $Cl_2(g) + H_2O(l) \longrightarrow HCl(l) + HOCl(l)$ (1)

This is a hydrolysis reaction. The hypochlorous acid dissociates to form a hydrogen ion $(H⁺)$ and hypochlorite ion (OCI) as follows $(3, 4)$.

HOCl H⁺ + OCl- (2)

For all practical purpose, the reaction (1) is irreversible and very fast. The reaction (2) is an ionization reaction.

All three species, Cl₂, HOCl and OCl⁻, are present in aqueous chlorine solution and their relative concentrations are pH dependent. Chlorine gas is present only in minute amounts ⁽³⁾.

The ETPs based on chlorine system will not generate chlorine from the treated effluent as a product or by-product at concentration level jeopardizing health and safety of the plant personnel. Aeration and sunlight reduce the presence of chlorine in the effluent.

The handling and maintenance of chlorine cylinders at the ETP site shall be in accordance with the guidelines provided (8). Several publications outline handling precautions, recommendation and safety practices and these include ⁽⁶⁾: (a) "The Chlorine Manual and "Chlorine Safety for Water and Wastewater Operation" by the Chlorine Institute, (b) "Safety Practices for Water Utilities" by American Water Works Association and (c) MSDS of Chlorine (7) .

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5. How is dechlorination of residual chlorine in the treated effluent carried out and at what costs?

Residual chlorine from the treated effluents can be removed by treating with Sulfur Dioxide gas or by reacting with sodium sulfite (Na₂SO₃), sodium bisulfite (NaHSO₃), sodium metabisulfite $(Na₂S₂O₅)$, sodium thiosulfate $(Na₂S₂O₃)$ or by passing over a bed of activated carbon, Iron turnings or by aeration or by sun light $(1, 2, 3, 4, 5, 6)$. The reactions involved include:

With $SO₂$ gas

 SO_2 + Cl_2 + $2H_2O \rightarrow H_2SO_4$ + $2HCl$

With sodium sulfite

 $Na₂ SO₃ + Cl₂ + H₂O \rightarrow Na₂SO₄+2HCl$

With sodium bisulfite

 $NaHSO₃ + Cl₂ + H₂O \rightarrow NaHSO₄ + 2HCl.$

With activated carbon

 $C + 2Cl_2 + 2H_2O \rightarrow 4HCl + CO_2$

With iron turnings

2Fe (s) + $3Cl_2(g) \rightarrow 2FeCl_3(s)$

With aeration the effluent is stripped of chlorine. Typical quantity of dechlorinating compounds or material required for each mg/l of residual chlorine is listed in Table 1.

Table 1: Consumption of Dechlorinating Compounds

If the residual chlorine is equivalent to 2 mg/l, dechlorination of a cubic meter (1000 l) effluent would cost: for $\text{Na}_2\text{SO}_3 = \text{Tk } 0.32$ (Tk 80/kg Na_2SO_3) and for Iron Turnings = Tk 0.06 (Tk 30/kg Iron turnings)

Dechlorination will add little to the treatment cost.

References:

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6. What is the historical development of the use of chlorine gas in wastewater treatment application?

The use of chlorine for the treatment of water and wastewater is widely practiced worldwide. More than 5% of the the total chlorine production in the United States is used for the treatment of water and wastewater and this 5% represents more than one million ton of chlorine.

The following paragraphs are quoted from G.C. White's **Handbook of Chlorination and** Alternative Disinfectants (4th edn., Wilely Interscience, 1999) to give some background of chlorination and its applications.

"Until the development of a suitable gas chlorinator in 1913, the adoption of chlorination for disinfection and odor control of sewage was very slow because the chlorinated lime was found to deteriorate in storage and was relatively expensive, messy to handle, and awkward to apply.

The use of chlorinatioin in wastewater processes has grown tremendously over the years since the development of suitable equipment. In 1958, it was reported that over 2200 plants serving a population of almost 38 million were equipped with chlorination facilities.⁽¹⁾ This represented about 30 percent of all treatment plants in the United States and about 50 percent of the population served by treatment facilities.

Chlorination is now established as an integral part of wastewater treatment practice in the United States and Canada. Several hundred technical articles have been written on the subject. It is the consensus that the primary use of chlorine is for disinfection.

Acitve interest in wastewater disinfection began in the United States about 1945. Up to that time the primary use of chlorine in sewage disposal systems was for odor control, hydrogen sulfide destruction, and prevention of septicity. Most of the sewage treatment plants practicing disinfection during that time belonged to the U.S. Armed Forces. It was military policy during World War II that sewage effluents at all Army bases in the United State, had to be chlorinated. Today, as a result of the 1970 Federal Water Pollution Control Act, almost all wastewater treatment plants are subjected to some disinfection requirement.

In 1961 the first chlorine residual controlled disinfection system for wastewater was installed at Napa, California. In 1975 chlorine was first used on a plant scale for nitrogen removal from wastewater. Both of these applications proved successful.

The uses of chlorine in wastewater treatment practice may be summarized as follows: disinfection; controlling odor and preventing septicity; improving grease and scum removal; controlling odor in the sludge-thikening process; controlling waste-activated suldge disposal; controlling foaming; destroying cyanides; destroying phenols; and foul air scrubbing."

References:

 1. Thomes, J.R and Jenkins, K.H., Statistical summary of sewage chlorination practice in the US, Sew. and Ind. Wastes, 30, 1461 (1958).

7. Since Chlorine is toxic; is it too dangerous to handle and use it?

No. The worldwide annual production capacity of chlorine is today 68.2 million tons. In the USA during the period 1979 through 2008, the annual production of chlorine ranged from 16 to 20 tons and of which more than one million ton chlorine gas was used in water and wastewater treatment. Other major used of chlorine in USA are: PVC production (20%), solvent manufacture (24%), organic chemicals (20%), inorganic (12%) and pulp and paper (12%). ⁽¹⁾

The daily production capacity of chlorine gas in Bangladesh is about 100 tons. More than 80% of it is used in the treatment of water in hundreds of location all over Bangladesh by WASA, and the industries. Bangladesh also imports and exports chlorine gas in cylinders from time to time.

The safe handling of chlorine gas in cylinder is well established. The handling and maintenance of chlorine cylinders at the ETP site shall be in accordance with the guidelines provided $⁽²⁾$.</sup> Several publications outline handling precautions; recommendation and safety practices and these include (3) : (a) "The Chlorine Manual" and " Chlorine Safety for Water and Wastewater Operation by the Chlorine Industries; (b) "Safety Practices for Water Utilities" by American Water Works Associations and (c) MSDS of Chlorine^{(4)}.

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8. What about production of Organo-chloro compounds and THMs during Chlorination of Textile Wastewater?

The organics present in the water or wastewater can react with dissolved chlorine forming chloro-organo compounds. The reaction depends on the type of organics (alkanes, alkenes etc), pH and availability of chlorine. Any process that uses chlorine gas directly or chlorine liberating chemicals or where chlorine is produced in the process, formation of chloro-organo compounds is a real possibility if alkanes etc are available.

Any water or wastewater that contains Fulvic or Humic acids can produce THMs when these acids react with chlorine if available. The origin of textile wastewater being different from the sewage it is unlikely for these waters to contain Humic and Fulvic acids; so the possibility of THM formation is remote.

The following paragraphs quoted from G.C White's Hanbook of Chlorination and Alternative Disinfectants $(4th$ edn., Wiley Interscience, 1999) tell the story of the Beginning of the Water Quality Scare from the use of chlorination in water treatment.

"About 1970 the U.S Public Health Service became concerned over an increase in waterborne disease outbreaks and possible surface water contamination by herbicides, pesticides, and other petrochemical products. In 1970, a community water supply survey discovered that the levels of dissolved organics in many water supplies exceeded the Public Health Service's recommended limit of 0.02 mg/L .⁽¹⁾ About the same time other government agencies began to examine various parts of the environment, making that a magic word. The focus changed from ensuring potable water quality to protect consumers' health to protection of the environment from pollution of all kinds, beginning with the protection of aquatic life by regulations issued by the Fish and Game Commission, another federal bureau."

In 1974, articles began to appear in the various technical journals blaming all types of human cancer on pollution of the environment.⁽²⁾ Since then cancer researchers have found these conclusions to be flawed because a simplistic casual relationship was drawn between the development of tumors in rats and mice and the introduction of nearly lethal dosages of carcinogens.⁽³⁾ One group of scientists tried very hard to prove that Americans were facing several natural disasters due to pollution of the environment. This group, from Oak Ridge Tennessee, was involved in a variety of projects relating to nuclear reactors, air and water pollution, and the possible environmental health effects of countless synthetic chemicals found in a variety of source waters; and it was headed by a great organizer and capable Ph.D. scientist, Robert Jolley.⁽⁴⁾ These scientists focused on the detrimental effects of disinfection of potable water and wastewater by the use of chlorine, in spite of the fact that chlorine is the planet's nearuniversal water disinfectant. They concentrated their efforts on the examination of chloroorganics that entered surface waters from industrial discharges, sewage treatment plant effluents, agricultural area runoffs, and urban area runoffs.

In a 1977 publication, $\overset{(4)}{ }$ Jolley's group emphasized that: "surface water pollutants identified thus far had ppb concentrations of highly chlorinated pesticides and hydrocarbons that represented a more serious problem with respect to water treatment, than does the presence of monochlorinated reaction products from sewage and cooling water treatment. Chlorinated pesticides and hydrocarbons have been found in some municipal drinking waters."

In 1972, the EPA reported that 46 organic chemicals were present in trace amounts in both the raw and finished water supplies at three locations along the Lower Mississippi,⁽⁵⁾ and a 1974 EPA study identified 66 organic compounds in the New Orleans drinking water.⁽⁶⁾ These were known as the Harris reports, and were most attractive to the EPA regulators, who focused on the dangers of the cancer causing carcinogens in the chlorinated Mississippi River water serving the people in New Orleans and the surrounding area. These cancer data were based upon a primitive method of dosing rats and mice with trihalomethanes (THMs) in concentrations a mere fraction less than lethal to the rats and mice. This approach to cancer research is now outdated by at least 20 years. The aforementioned doses did cause tumors in the rats and mice, which caused the EPA to conclude that disinfection by chlorine, caused cancer in humans. In this writer's opinion, the EPA could not have been "wronger." (2)

To assess the general situation across the United States, a National Organics Reconnaissance Survey was conducted in 1975 by Professor James Symons and 10 coauthors.^{$(7, 8)$} This survey revealed trace amounts of four trihalomethanes (THMs): chloroform (trichloromethance, CHCl₃) bromodichloromethane (CHCl₂Br), dibromonochloromethane (CHClBr₂), and bromoform (tribromomethance, CHBr3) in the drinking water of 27 large cities in the United States. The average amounts in mg/L were as follows: CHCI₃ = 0.39, CHCl₂Br = 0.0377, CHBr₃ = 0.0030. Carbon tetrachloride, CCl4, was not identified in 27 city water supplies; one had 0.002 mg/L and two had less than 0.002 mg/L CCl₄.

We now know, owing to new and more reliable information, gathered in the last decade by experienced and reliable epidemiologists, $(9,10,11,12)$ that chlorinated water was not and never could be a carcinogen.

The current (1997) EPA regulations are based upon outmoded information, created some two decades ago.^{$(5, 13-16)$} A far better procedure would be for the EPA to forget the THMs and establish an acceptable chlorine demand for the finished water. In addition to this, owing to the increasing variety of pathogenic organisms, it would be more protective to choose a "consensus organism" instead of total coliforms for proof of disinfection."

"Now, more than 20 years later, there is an entirely different story. In the passing years, cancer researchers have found without any doubt that the "rodent carcinogen" kill method used for evaluating the health risks of potable water consumers at that time was flawed. In effect, current researchers have found that the haloform compounds (THMs) are trivia, and the miniscule amounts in the NORS report are not a health risk. Actually, there are so many carcinogens in the fruits and vegetables we eat, that a dinner vegetable salad has more carcinogens in it than 200 gal of chlorinated drinking water."

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9. Will chlorination of Textile Wastewater produce Dioxins?

No. Dioxin has been in the atmosphere before the industrialization and people are concerned with dioxin because it has been found in food chain from various sources. Chlorinated plastics, mainly PVC (polyvinyl chloride) are a major source of chlorine which is necessary for dioxin generation in incinerators. Formation of dioxin needs chlorine, carbon and oxygen simultaneously. Dioxins are formed in incinerators while burning chlorinated plastics such PVC at temperatures in the range 400-600[°]C. 2,3,7,8, TCDD (2,3,7,8 tetrachlorodibenzo (p) dioxin), is an example of much talked about non-genotoxic carcinogen.

The textile wastewaters that contain very low dissolved oxygen lack a major component, that is, abundance of oxygen to support dioxin formation. Chlorination of textile wastewater will not produce dioxin.

10. Why do you want to use chlorination for the treatment of textile wastewater?

By using chlorination all the objectives of textile wastewater treatment listed hereunder are achieved. The main objectives of textile wastewater treatment technologies are:

- color and odor removal
- reduction of BOD
- reduction of TDS and TSS
- maintaining pH of the treated effluent in the range $6.5 9.0$

And the treated effluent shall meet the limits set in Schedule 12-B of ECR 1997 issued by DoE, Bangladesh.

This is a practical technological option for Bangladesh because of low cost of chlorine gas here, Tk. 7.50/kg (10.8 US Cents). The price of one kg of chlorine gas in the USA is 42 US Cents (Tk. 29.00).

11. Why do you want to use an "old outdated technology" like chlorination in Bangladesh?

A technology is based on laws of physical sciences and scientific principles which never get old or outdated. On the other hand, an effluent treatment plant (ETP) is basically a chemical process plant consisting of a number of unit operations and unit processes whose performances are governed by underlying principles of thermodynamics, transport processes, reaction kinetics, separation processes etc. These underlying principles do not get old or outdated. The very idea that the ETP of an industry is a chemical process plant is unfamiliar with those who always compare it with a sewage treatment plant.

While planning and designing an ETP for textile wastewater with chlorine gas, advantages of the different functions of chlorination have been employed based on underlying fundamental principles. The resultant ETPs are simple to construct and operate. The so-called and perceived disadvantages of chlorine-based ETPs outweigh the benefits of operating such ETPs with chlorine gas.

Moreover, process engineering assembles technologies of different ages and unrelated areas as long as the designed process plant performs satisfactorily and remains economically viable in a competitive market. It is important to appreciate the sequence in which the various steps in process proceed to completion chemically or physically yielding the desired result. This is how a conscious process engineer can give a simple solution for the so-called difficult problems and the solution may appear to be a common-sense solution.

12. What is the set standard for the effluents from the Composite Textile Mills in Bangladesh?

The Environment Conservation Rules of 1997 (ECR – 1997) have laid down the standards for the effluents from the Integrated Textile Plants and Large Processing Units (with investment more than Taka three crores) as per Schedule 12-B as mentioned below:

Standards for Textile Effluents as per ECR-1997 (Schedule 12-B)

* BOD limit of 150 mg/l implies only with physico-chemical processing

* * Special parameters based on type of dye used

The Standards for Industrial or Project Effluent set in Schedule-10 of ECR-1997 shall not be applicable for the industries for which separate specific standards have been set (Schedule-12). Please refer to Clause 13 of ECR-1997.

13. How do you measure the different parameters of the effluent mentioned in Schedule 12-B?

After the gazette notification of ECR-1997 (August 27, 1997), the Department of Environment has not to-date worked out the procedures and methods to be used to measure these parameters. In absence of these procedures which are to be issued through a separate gazette notification by DoE one should use procedures laid down by the US EPA as per CFR-40 or the relevant Indian Standards. Samples are to be analyzed by the accredited Laboratories or Laboratories recognized by the Department of Environment, Bangladesh.

14. Should Bangladesh make the standards for the effluents such as Schedule-12B more stringent than India?

The answer is simply "No".

When the effluent standards were worked out for ECR-1997, the relevant standards of India were examined. As India deals with more countries than Bangladesh for exporting their products, in terms of volume and value, if the importing countries accept the environmental standards in force for the industries in India, there is no reason why Bangladesh should need more stringlent effluent standards for its industries. Bangladesh should only closely follow how the standards in India are revised from time to time and should revise its standards accordingly.