Chemical Oxidation with CHLORINE

In the field of Waste Water treatment, chemical oxidants such as chlorine, ozone & hydrogen peroxide are widely used for disinfections, removing organic materials that are resistance to biological & other treatment processes & conversion of Cyanides to innocouos products. Use of chlorine as a disinfectant destroys or inactivates bacteria present in waste water before it is discharged into receiving streams. Chlorine rapidly penetrates bacterial cells & kills the bacteria. However, the effectiveness of chlorine is influenced greatly by the physical & chemical characteristics of waste water.

Initially when chlorine is added to water, it forms by chlorous acid HOCl

$$Cl_2 + H_2O \longrightarrow HOC + H^+ + Cl^-$$

Hypochlorous acid is the disinfecting agent & is referred to us free residual or free available chlorine. If any reducing agents such as ferrous ions or hydrogen sulphide are present in waste water, chlorine reacts with them & the concentration of chlorine available to destroy pathogenic bacteria is reduced. The reduction reaction with hydrogen sulphide may be represented as :

$$H_2S + 4Cl_2 + H_2O \longrightarrow H_2SO_4 + 8\ HCl$$

Waste water usually contain ammonia. In the presence of ammonia, HOCl reacts to form sequentially, monochloroamine (NH_2Cl) dichloramine ($NHCl_2$) & Trichloramine according to the following :

$$NH_3 + HOCl \longrightarrow H_2O + NH_2Cl$$
$$HOCl + NH_2Cl \longrightarrow H_2O + NHCl_2$$
$$HOCl + NHCl_2 \longrightarrow H_2O + NCl_3$$

Monochloramine & Dichloramine are referred to as combined residuals & are more stable then free residual but less effective as disinfectants. Once all ammonia has reacted, further addition of chlorine converts the combined residuals into a free residual, the conversion being proportional to the dose at the "break point". This is the limit beyond which all the residual chlorine is available as free chlorine.

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Chlorination is used to oxidize cyanide in industrial waste water to harmless carbon & nitrogen compounds. This is done in alkaline media at pH greater than 8.5 to prevent the generation of poisonous hydrogen cyanide gas.

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

The residual cyanide concentration after a reasonable reaction time, is very small.

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Method of Testing of CHLORIDE

Method :- Argentometric Method

For Chloride as ppm :- Method of calculation of Chloride as ppm. Method given in Alfloc.

Our previous calculation for chloride method is given below :

Calculation :-

$$\text{Chloride [Cl-]} = \frac{\{\text{ml of N/50 (0.02N) } AgNO_3 \text{ / B.R. in ml}\} * 1000}{\text{sample taken for titration in ml}} \text{ Mg /L (ppm)}$$

Or

$$\text{Cl- mg /L (in ppm)} = \frac{1000 \times \text{B.R.}}{\text{Sample taken for titration}}$$

Note :-

1) In this method the calculation for chloride is expressed in ppm as $CaCO_3$.
2) In this calculation Normality of $AgNO_3$ solution considered as Std 0.02N

Conclusion :- ppm of Chloride in this calculation consider Equivalent weight of calcium chloride [E.W.- 50]. SO ppm of Chloride is expressed in ppm as $CaCO_3$.

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Modified calculation method consider Eq.Wt of Chloride (Cl^-) and in this method Normality is not considered as 0.02N, but we standardize $AgNO_3$ solution & take the Normality whatever it is in the modified calculation method.

Calculation of this method is given below :

$$\text{Cl- mg/L In ppm} = \frac{\text{B.R. x N x Eq.wt (35.45) x } 10^6}{\text{ml sample taken x 1000}}$$

$$= \frac{\text{B.R. x N x Eq.wt (35.45) x } 10^3}{\text{ml sample taken x 1000}}$$

$$= \frac{\text{B.R. x N x Eq.wt 35.450}}{\text{ml sample taken x 1000}}$$

Where,

B.R. = titration reading in ml
N = Normality of $AgNO_3$ solution
Eq.wt = equivalent weight of chloride (Cl^-) = 35.450

One example for both calculation method

Ex :- Sample taken for titration is 10 ml

B.R. {Titration reading} is 5.0 ml
Normality of $AgNO_3$ solution = 0.02N and observed chloride in ppm from both method

PREVIOUS METHOD :-

$$Cl^- \text{ in ppm} = \frac{1000 \times B.R.}{\text{Sample taken}}$$

$$= \frac{1000 \times 5.0}{10.0}$$

= 500 ppm

Where,

B.R. = 5.0 ml
Sample taken :- 10.0 ml

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MODIFIED METHOD

Cl^- in ppm = $\frac{B.R. \times N \times 35450}{\text{Sample taken}}$

$= \frac{5.0 \times 0.02 \times 35450}{10.0}$

$= \frac{354.5}{10}$

= 35.45 ppm

The chloride difference from both method is :

Difference = previous chloride method - modified chloride method
= 500 – 354.5
= 145.5 ppm
Difference in % is 29.1

Conclusion :-

In this calculation, consider equivalent weight of chloride [E.W. – 35.45]

Difference between both the method :-

Previous method gives 29.1% more ppm chloride because it is expressed as Calcium Carbonate. Hence we determine chloride as per modified method.

Ref :-1. This calculation method is based on "ALFLOC" Water Treatment Service.
2. Amended method of calculation for Chloride as ppm is given in American Std.

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