



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

# IJIRSET

International Journal of Innovative Research in  
**SCIENCE | ENGINEERING | TECHNOLOGY**



# INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 10, Issue 9, September 2021

**ISSN** INTERNATIONAL  
STANDARD  
SERIAL  
NUMBER  
INDIA

Impact Factor: 7.569



# Advance Wastewater Treatment at Tertiary Level

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**ABSTRACT:** It is tertiary treatment of wastewater involves RO, MEE & many other treatment being used in industry which are expensive & energy intensive. In this study are propose breakpoint chlorination as a single remedy the issue of wastewater at tertiary level. The focus will be to reduce refractive COD, ammonical nitrogen, & other parameters through breakpoint chlorination techniques.

**KEYWORDS:** Calcium Hypochlorite (CH), Breakpoint Chlorination, Ammonical nitrogen, pH, Wastewater treatment, Color.

## I. INTRODUCTION

The use Chlorine for water or wastewater disinfection as a public health measure reduces the spread of diseases. Various disinfection technologies can be used to meet the pathogen inactivation demand in water. Many of these chemical disinfectants if overdosed or used inappropriately can react with organic and inorganic precursors and bring the formation of disinfection by-products (DBPs) with adverse health effects. The disinfection technologies applied in drinking water treatment plants (DWTPs) and in wastewater treatment plants (WWTPs). This work consists of three parts. The first section reports the conventional processes applied on full scale; while the second one presents the advanced processes. In the third section the natural disinfection technologies are exposed. For conventional technologies, the following are examined: the action mechanisms; the possible formation of DBPs; the operative conditions, and; advantages and disadvantages. For advanced and natural processes the action mechanisms are reported. (Marin Cristins Collivignarelli et al, 2017). The three most common chlorine-containing substances used in water treatment are chlorine gas, sodium hypochlorite, and calcium hypochlorite. Chlorine gas (liquid chlorine) is greenish yellow in color and heavier than air. Its high toxicity makes it an excellent disinfectant for water but also a hazard to human health who handles it, Calcium hypochlorite (CH) is manufactured from chlorine gas. It is best known as chlorine pellets and granules in residential water treatment and it contains 70% available chlorine, Sodium hypochlorite is a chlorine-containing compound most easily recognized as household bleach, it is a light yellow liquid, it contains 15% available chlorine. (Hydro instrument).

Removing ammonia from wastewater lagoons has become a hot topic over the past few years. State Environmental Protection Agencies have been introducing new ammonia limits for aerated wastewater lagoons. This is a problem because most wastewater lagoon systems were not originally designed for ammonia treatment. As a result, most lagoon systems will require some kind of upgrade. Lagoon ammonia removal via nitrification is not an easy process to master, and with new lagoon ammonia effluent requirements, it's a problem that won't go away any time soon. By investing in the right infrastructure and treatment system, as well as monitoring the right constituents, you can stay ahead of the curve in terms of wastewater lagoon ammonia treatment (Gy. Kollar and L. Ribar, 1999).

The ammonia stripping process has been successfully employed for many types of high-strength ammonia wastewater. The method refers to one that is controlled and unaltered by toxic compounds. Nevertheless, the ammonia stripping process has several drawbacks. Among the issues involving the implementation of ammonia stripper to remove ammonia nitrogen in wastewater are fouling problems, sludge production, and release of ammonia gas (Hideki Kawanishi et al, 2018).

Calcium Hypochlorite (CH) is a strong oxidizer and an effective anti-microbial compound. It Serves as a multi-functional sanitizer in drinking water, wastewater treatment, irrigation, swimming pools and spas, fruit washing, beverage plants, cooling towers and abattoirs. In municipal and wastewater treatment CH is used at all stages from Surface Raw Water, Finished Water, Booster Stations, Reservoirs, Remote Well Sites, Reclaimed Water and

Overflows. It is used as backup chlorination on chlorine gas treatment plants and in emergency potable and wastewater treatment situations across the world. CH has been an approved chemical for disinfection and oxidation of wastewater in, CH is part of the chlorine based oxidizing family sodium hypochlorite, chlorine gas, and related chlorine dioxide and chloramines. Oxidation by chlorine can remove ammonia from wastewater. This process, known as breakpoint chlorination, is practical only as an effluent polishing technique, not for removing high levels of influent nitrogen. (Chris Smith, 2011).

Type	Form	avCl is use (%)	pH
Chlorine	gas	100	1.0
Sodium hypochlorite	liquid	7.5-15	13
Calcium hypochlorite	Solid	65-70	8-11

Table 1: Physical forms and chemistry of common chlorine sources



Figure 1: Calcium hypochlorite in typical moulded forms

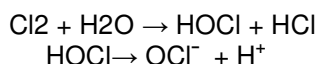
Industrial wastewaters are played one of the most important roles in environmental pollutions, but discharge these wastewater to environment has always with irreparable damages. Today, for the treatment of these pollutants and its control, various methods have been developed. Textile industrials are among industrials that are highly contaminated effluent and need special consideration in their treatment. The biggest problems these effluents are include remaining dyes, high temperature, low pH, non-biodegradation resistant chemical that usually completed through various chemical treatments on fabrics are imported. With respect to current standards for effluent discharge into acceptor waters and regarding the problems of conventional methods exists for color separation, it seems necessary Select the proper a method to remove paint that has high performance, and have few problems than other methods. In addition, so far methods of various physical, chemical and biological have been used for wastewater color removal from various textile industries. Calcium hypochlorite was explore the removal efficiency of COD and color of Textile industries. (Mohamadreza Massoudinejad at al, 2015).

Human activities (e.g. communities, industrial plants, intensive livestock and farming, uncontrolled waste disposal) discharge many pollutants in water, including nitrogen. Nitrogen is one of the causes of eutrophication, while some N-compounds (e.g., ammonia, ammonium, nitrite, nitrate, chloramines) can be harmful for human health. Nitrogen removal from wastewater can be achieved by biological or physico-chemical processes. a broad spectrum of physico-chemical technologies for the removal of nitrogen from wastewater is available ammonia air and steam stripping; ammonia vacuum distillation; ammonia precipitation as struvite; ammonia and nitrate removal by selected ion exchange; breakpoint chlorination; chloramines removal by selected activated carbon; ammonia adsorption on charcoal; chemical reduction of nitrate; advanced oxidation processes to convert ammonia and organic-N into nitrogen

gas or nitrate. (Mohamadreza Massoudinejad et al., 2015). Application of chlorine dioxide, chlorine mediated electrochemical oxidation, and aqueous oxidants like Hydrogen peroxide, Sodium Hypochlorite and Calcium Hypochlorite at different temperatures & reaction durations reduces COD effectively (Vaezi F.2004; Rajkumar D., 2006; Ali Awan M, 2004). The study presents the application of Sodium hypochlorite ( $\text{NaOCl}$ ), Calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and their Combination for polishing a secondary effluent at Common Effluent treatment plant. (Abhishek Jain and Mrs. Anjal khambete, 2013)

## II. BREAKPOINT CHLORINATION OF WASTEWATER

Breakpoint chlorination has been practical at wastewater plants as a physical- chemical process for removing ammoniacal nitrogen (ammonia) on both a polishing dynamics of a full scale breakpoint operation are poorly understood. When chlorine gas is dissolved in water, it also reacts with the water to form hypochlorous acid and hydrochloric acid:



The two chemical species formed by chlorine in water, hypochlorous acid ( $\text{HOCl}$ ) and hypochlorite ion ( $\text{OCl}^-$ ) are commonly referred to as “free” or “available”. The pH of the water is important relative to the varying proportions of the hypochlorous acid and hypochlorite ions. In a solution with pH rising over 6.0 the proportion of hypochlorous acid declines from virtually 100% down to almost 0 at pH 9.0. The activity of hypochlorous acid as a bactericide is greatly superior to that of the hypochlorite, being almost 80 times more powerful. It may be concluded that in free residual chlorination, the higher the pH value the less active is the residual because of its lower proportion of hypochlorous acid. The graph below shows how the equilibrium changes with pH. (Fig. 2)

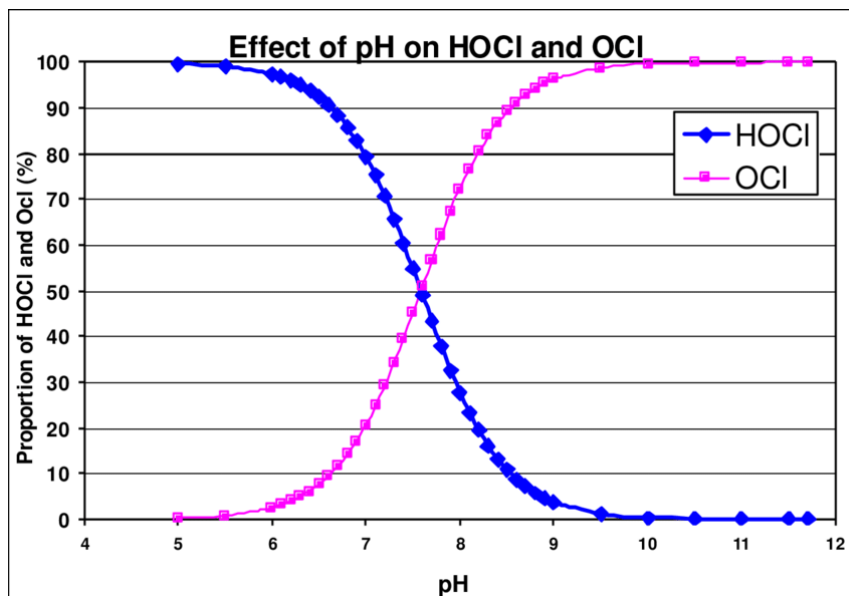
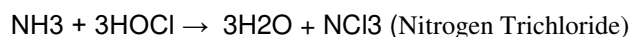
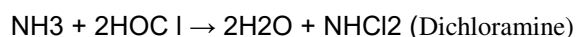
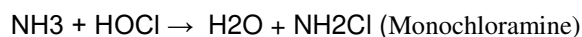
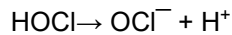


Figure 1: Relationship between  $\text{HOCl}$  and  $\text{OCl}^-$  at various pH values (researchgate.net)

All wastewater contains ammonia ( $\text{NH}_3$ ) and some potable waters do too. Breakpoint chlorination, as practiced for many years in the water treatment industry, providing a physical-chemical means for removing ammonia from wastewater. The possible reactions between  $\text{HOCl}$  and ammonia are as follows:







These reactions occur essentially instantaneously and are pH dependant. At pH levels above 8.5 only monochloramine is formed; below this, mixtures of mono and dichloramine result; and below pH 4.2 only nitrogen trichloride exists. For wastewater and drinking water that has been treated with both ammonia and chlorine, the predominant species is monochloramine. The chloramines, together with some other compounds that can occur are totaled and considered combined available chlorine. These forms of chlorine, although much weaker than hypochlorous acid, are very useful in some applications. When sufficiently high chlorine dosages are applied to waters containing ammonia different reactions will occur resulting in the destruction of the ammonia and the formation of free chlorine residual. (Hydro Instruments).

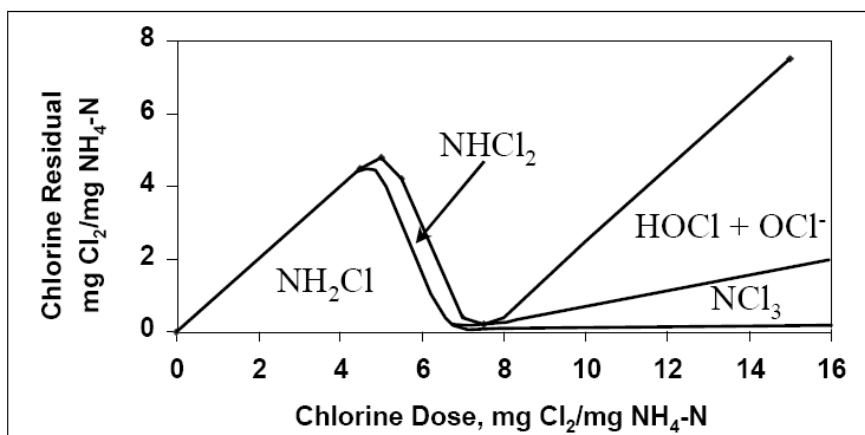
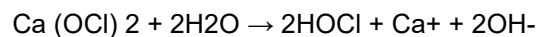


Figure 3: Chloramine formation with chlorine dosage

Commercial grades of NaOCl contain about 10% available chlorine generally. Many consumers are replacing chlorine gas with sodium hypochlorite as the oxidizing or disinfecting agent because of safe handling measures (John, 2001). The reaction between sodium hypochlorite and water is shown in following reaction.



Calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ) is essentially a solid that is used in place of Chlorine gas. Commercial grades of  $\text{Ca}(\text{OCl})_2$  generally contain about 70% available chlorine. It is appropriate for wastewater applications (Leslie, 1998). The reaction between calcium hypochlorite and water is shown in following reaction.



The application of calcium hypochlorite to water also produces Hypochlorous acid, similar to sodium hypochlorite as shown in above reaction Hypochlorous acid is a weak acid it dissociates slightly into hydrogen and hypochlorite ions. The Hypochlorous acid is the prime disinfecting agent in wastewater treatment. The sum of the  $\text{OCl}^-$  and  $\text{HOCl}$  concentration is called the free available chlorine (EPA 1999). From analysis it was observed that 1000 ppm concentration can reduced the COD from 519 mg/L to 234 mg/L but increases TSS from 196 mg/L to 1186 mg/L and free  $\text{Cl}_2$  from 0 mg/L to 443.13 mg/L while comparing the results at different concentration it was found out that 200 ppm concentration reduces COD from 519 mg/L to 337 mg/L with a little increase in TSS from 196 mg/L to 252 mg/L and free  $\text{Cl}_2$  from 0 mg/L to 44.31 mg/L which can be easily dechlorinated. From analysis it was observed that 1000 ppm concentration can reduced the COD from 524 mg/L to 247 mg/L but increases TSS from 196 mg/L to 1192 mg/L and free  $\text{Cl}_2$  from 0 mg/L to 472.23 mg/L while comparing the results at different concentration it was observed that 200 ppm concentration reduces COD from 524 mg/L to 356 mg/L with a little increase in TSS from 196 mg/L to 320 mg/L and free  $\text{Cl}_2$  from 0 mg/L to 44.31 mg/L which can be easily dechlorinated. (Abhishek Jain and Mrs. Anjal khambete, 2013).



### III. ADVANTAGES

1. As a mixture with lime and calcium chloride, Calcium Hypochlorite is marketed as chlorine powder or bleach powder for water treatment and as a bleaching agent.
2. In addition to water treatment, Calcium hypochlorite is used in kitchens to disinfect surfaces and equipment. Other common uses include bathroom cleansers, household disinfectant sprays, algacides, herbicides, and laundry detergents.
3. This compound is relatively stable, is similar to sodium hypochlorite in disinfection properties and has greater available chlorine than sodium hypochlorite (liquid bleach).
4. It has excellent stability when kept in dry storage, maintaining its potency over time. Commercial grades of Ca (OCl)<sub>2</sub> generally contain about 70% available chlorine making it appropriate for both drinking water and wastewater applications.
5. Calcium Hypochlorite is appropriate for both drinking water and wastewater applications.
4. Chlorine is commercially available.
5. Chlorine is very economical.
6. The chlorine residual that remains in the wastewater effluent can prolong disinfection even after initial treatment and can be measured to evaluate the effectiveness.

### IV. DISADVANTAGES

1. Because the chemistry is so similar to chlorine gas and NaOCl ("liquid chlorine"), this method offers no disinfection efficiency advantages (i.e., Giardia and Cryptosporidium kill rates) or disinfection by-product advantages.
2. Although solid Ca (OCl)<sub>2</sub> is more stable and safer to handle than its liquid counterpart NaOCl, it is corrosive and hygroscopic (i.e., readily absorbs moisture), reacting slowly with moisture in the air to form chlorine gas if not stored in air-tight containers. Therefore, containers of Ca (OCl)<sub>2</sub> must be completely sealed or emptied entirely. As with chlorine gas and NaOCl, wastewater systems using Ca(OCl)<sub>2</sub> generally require dechlorination after disinfection to reduce chlorine discharges to receiving waters.
3. On small scale, dissolving calcium hypochlorite in water forming chlorinated water with some precipitate of undissolved calcium so you have to discard the precipitate otherwise it would cause problems e.g. hardness.

### V. CONCLUSION

1. Calcium hypochlorite contains 70% available chlorine and Sodium hypochlorite contains 15% available chlorine then the Calcium hypochlorite is more effective than the Sodium hypochlorite for the removal of ammoniacal nitrogen from wastewater.
2. Calcium hypochlorite is a versatile source of chlorine suitable for a range of dosing methods, many of which are simple, low maintenance, very economical/cheaper, do not require power and can cope with variable demand and suitable for all sizes of municipal and wastewater treatment.

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