Use of Ozone in Water Treatment

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Abstract—In most water treatment plants across the globe, Chlorine is used as primary disinfectant to treat water at water treatment plants. However, recent study suggests that, when chlorine reacts with any kind of organic matter present in the water, it forms by-products which include trihalomethanes (THMs) such as chloroform. When THMs enters the body, they increase the production of free radicals in the body which are highly carcinogenic. According to the U.S. Council of Environmental Quality, "Cancer risk among people using chlorinated water is as much as 93 percent higher than among those whose water does not contain chlorine." Chlorine and THMS can potentially cause various types of cancer, kidney and liver damage, immune system dysfunction, disorders of the nervous system, hardening of the arteries, and birth defects. Hence, United States have incorporated ozone in more than 280 major water treatment plants as disinfectant. In water treatment, ozone is more than twice as powerful as chlorine and acts 3000 times faster. Ozone can be used as a disinfectant deodorizer, detoxifier and a coagulant. Any pathogen or contaminant that can be disinfected, altered or removed via an oxidation process, will be affected by ozone. Hence, this paper summarizes the applications of ozone as alternative disinfectant to chlorine in water treatment.

Keywords—Chlorine, trihalomethane, carcinogenic, ozone, alternative disinfectant.

I. INTRODUCTION

Ozone has been applied for many years to the treatment of drinking water, however due to lack of research about its by-products; it was not used in many countries for water treatment. After detection of trihalomethanes in chlorinated water, applications of ozone in drinking water once again started gaining popularity. Drinking water treated with ozone kills or inactivates any pathogenic microorganisms including viruses, bacteria, and parasites and removes inorganic trace contaminants found in water systems due to pollution. Also, chlorine and chloramines cannot be used to deactivate protozoa like Cryptosporidium. The Ct-value for deactivation of Cryptosporidium by chlorine varies between 3000 and 4000 mg min/L for 1-log deactivation. The Ct- value for disinfection rate of the Giardia cyst is also much lower for ozone in comparison with chlorine. The use of ozone for pre-treatment of sewage by filtration and oxidation of organics by granular activated carbon has been shown to provide significant benefits, which include extension of the useful life of the GAC adsorbers before regeneration is required. Ozone treatment also reduces naturally occurring organic compounds such as humic acid and algal metabolites. Pre-ozonation can eliminate taste, colour, odour and various mineral compounds. It can also be utilized for natural organic matter degradation and micro-organism inactivation, Camel V. and Bermond. The mechanism of bacterial inactivation by ozone is thought to occur by general inactivation of the whole cell. Thus, ozone causes damage to the cell membrane, to the nucleic acids, and to certain enzymes. Ozone is particularly effective against viruses, where its use can achieve the highest standards (Tyrrell et al., 1995). The mechanism of viral inactivation involves coagulation of the protein and oxidation of the nucleobases forming the nucleic acid, Panagiota Paraskeva, Nigel J. D. Graham. Ozone is also used to remove inorganic species using pre-oxidation (Rice and Gomez-Taylor, 1986). However, pre-ozonation must be followed by a filtration or a coagulation-floculation-decantation step.

Table no 1. Case Studies of Bladder Cancer caused by drinking Chlorinated Water

Case studies	Location	Study population	Exposure measurement
Cantor et al 1998	Iowa (USA)	732 cases 914 population controls	Chlorinated surface water
Koivusalo et al 1998	Finland	1123 cases 1983 population controls	Substantially mutagenic drinking water
King et al 1996	Ontario (Canada)	696 cases 1545 population controls	Chlorinated surface water
McGeehin et al 1993	Colorado (USA)	327 cases 261 other cancer sites controls	Chlorinated water

A comparison by Hoff (1986) illustrates the greater effectiveness of ozone as compared to other water treatment disinfectants.

Table no. 2: CT values (mg.min/l) are for 99 % (2 log) inactivation of micro-organisms at 5°C.

Micro-organisms	Ozone: pH: 6 to 7	Chlorine: pH: 6 to 7	Chloramine pH: 8 to 9	Chlorine dioxide pH 6 to 7
E. coli	0.02	0.034-0.05	95-180	0.4-0.75
Poliovirus 1	0.1-0.2	1.1-2.5	770-3740	0.2-6.7
Rotavirus	0.006-0.06	0.01-0.05	3806-6480	0.2-2.1
Giardia lamblia cysts	0.5-0.6	47->150	-	-
Giardia muris cysts	1.8-2.0	30-630	-	7.2-18.5

II. USE OF OZONE

A. Removal of colour:

Ozone is an effective oxidizer of color due to dissolved organic compounds and unlike chlorine won't create chlorinated organic compounds. For fulvic and humic substances ozone doses of 1-3 mg ozone/mg of carbon can affect nearly complete removal of color, (Watts, C.D. 1985 & Killops, S. D. 1986). Also, studies have shown that 1 mg ozone/liter can remove 10 color units, (Flogstad,H. & Odegaard, H.O. 1985).(R. Tosik) has shown that about 1 mg ozone/mg dye is required to achieve 95% color removal, although this ratio varies by dye type. The ratio increases to about 1.5 for 100% removal. Reaction times were on the order of 10 minutes. In the textile industry a typical dosage might be 15 mg/l post biological treatment, but the levels could easily reach 25 mg/l. It is important to note that the ozone dose only needs to make the dye compound uncolored and not necessarily completely mineralize the material. At any dose there appears to be a threshold limit to the amount of color that can be removed using ozone. If additional treatment is required the combination of ozone with activated carbon has been shown to provide overall removal of color, Klimkina, N.V. 1987.

B. Removal of odour

Odor and taste production in drinking water can have several causes. Odor and taste forming compounds can be present in raw water, but they can also be formed during water treatment. These compounds may derive from the decomposition of plant matter, but normally they are a result of the activity of living organisms present in the water. Using hypochlorite as a wet chemical in scrubbing systems can cause emission of chlorinated compounds and particulate from the scrubber exhaust stack, as well as a potential for emission of a bleach odor if chemical feed is not properly controlled. The use of ozone as the oxidant can minimize these problems. Wet chemical scrubbing using ozone are a good solution for odor control in situations where there is high intensity odor, high air volumes, or limited space to site an odor control system, (Dr. Giancarlo Riva). Ozone is more effective for the oxidation of unsaturated compounds. As was the case for the oxidation of pesticides, ozone combined with hydrogen peroxide (AOP process) is more effective than ozone alone. Geosmin and 2-methylisoborneol (MIB) are examples of resistant odorous compounds, which are often present in the water. These are produced by algae and have a low odor and taste threshold. Nevertheless, ozone is still very affectively removes these compounds. Generally, the most effective way to remove taste and odor components appears to be a combination of pre-oxidation and filtration. Table 3 shows Ozone with sand filtration and GAC filtration is the most efficient combination (82% removal).

Table no. 3: effect of ozone and subsequent treatment on odor threshold and odor reduction at Saint-Maur pilot treatment (France)

Treatment	Average Taste Threshold	Flavor Reduction (%)
Raw Water	10	-
Settled Water	7	30
Filtered Water	5.3	47
Filtered Water with Ozone	3.3	67
Sand without Ozone	3	70
Sand with Ozone	3	70
Sand and Activated Carbon without Ozone	2.8	72
Sand and Activate Carbon with Ozone	1.8	82
Activated Carbon without Ozone	2.3	77
Activated Carbon with Ozone	2.8	72

C. Micro Flocculation

It has been observed for more than 30 years that "Preozonation" ahead of particle removal units can improve the efficiency significantly, can induce a lower coagulant demand or allow higher flow rates, e.g. in deep-bed filtration. Ozone gas is added either before or together with the coagulant (ferric or aluminum salts or cationic polymers) at rather low dosages of 0.5-2mgL-1. The terms "micro- flocculation" or "ozone-induced particle destabilization" are used in practice. The cause of the improved effluent turbidities is not fully understood, but several explanations have been suggested:

- Ozone forms organic compounds with functional groups such as carboxylic acid. These groups can complex with aluminum oxide to aid in the association of the aluminum with the organic material. Carboxylic functional groups can also complex calcium which may improve adsorption of organics to metal oxide surfaces.
- Ozonation of NOM may create organic polymers that either enhance coagulation or are more easily coagulated.
- Ozone can breakdown Fe and Mn complexes which might be tied up with NOM. The release of the oxidized metals creates a source of coagulant.

Though, ozone is known to increase micro-flocculation, studies have also shown that, if ozonation is conducted under conditions which promote the formation of oxalic acid (high ozone dosages, high pH, high Fe(II) concentrations), higher coagulant dosages may be required and decreased TOC removal may result. A postulated microflocculation mechanism is that increased concentrations of oxygenated functional groups (especially carboxylic acids) following ozonation may lead to the formation of organic matter-aluminum hydroxide complexes. The results indicate that the presence of oxalic acid adversely affects coagulation. An increase in the optimum alum dose or a decrease in the amount of turbidity or total organic carbon (TOC) removal occurred in the waters containing oxalic acid, William C. Becker, O'Brien and Gere Engineers, Charles R. O'Melia.

D. Disinfection

When ozone decomposes in water, the free radicals hydrogen peroxy (HO_2) and hydroxyl (OH) that are formed have great oxidizing capacity and play an active role in the disinfection process. It is generally believed that the bacteria are destroyed because of protoplasmic oxidation resulting in cell wall disintegration (cell lysis). The effectiveness of disinfection depends on the susceptibility of the target organisms, the contact time, and the concentration of the ozone. A study found that within a pH range of 6 to 10, at 3 to 10 EC, and with ozone residuals between 0.3 to 2.0 mg/L, bacteriophage MS-2 (a surrogate test organism) and Hepatitis A virus were completely inactivated. Inactivations ranged from >3.9-log to >6-log, and occurred within very short contact periods (i.e., 5 seconds). A 1992 research report describes treatment studies conducted on MS-2, poliovirus, and Giardia cysts. It found that MS-2 in natural waters are very sensitive to ozone in comparison to poliovirus type 3. In addition, Giardia muris and enteric viruses may be inactivated by ozone (as the primary disinfectant) with 5 minutes contact time and ozone residuals of 0.5 to 0.6 mg/L to 3-log and 4-log removals, respectively. The report concludes that design of ozone as a primary treatment should be based on simple criteria including ozone residual, competing ozone demands, and a minimum contact time to meet the required cyst and viral inactivation requirements, in combination with USEPA guidance recommendations.

E. Reduction in Bod and Cod

According to a study by ESCO International, The chemical oxygen demand (COD) removal rate for industrial wastewater is higher than 95 percent, when using high ozone (oxidants) dosages. The results indicate that the primary control parameters for COD and BOD removal using ozone based advanced oxidation process are dosage, contact time and pH, the company says. As the ozone (oxidants) dose is increased, carbon-carbon single bonds are attacked and broken, resulting in a loss of COD, BOD and TOC. At stoichiometric ozone (oxidants) dosages, COD removal rate is higher than 95 percent. According to the review made by Panagiota Paraskeva and Ningel J. D. Graham, table no. 4 and 5 shows the effects of ozone in reducing COD and BOD of secondary effluents.

Table no. 4: Summary of COD reduction by ozone treatment of secondary effluents

Source	Ozone Dose (mg/L)	Initial COD (mg/L)	Final COD (mg/L)	Reduction (%)
Gardiner and Montgomery, 1968	5-41	26-56	Reduction of approximately 50% ozone dose	n/a*
Nebel et al., 1973	12-16	20-40	n/a	23
Fressonnet-Chambarlhac et al., 1983	6-9	20-35	15-30	n/a
Legube et al., 1987	6-12	33-75	n/a	25
Absi et al., 1993 14	14	40-170	n/a	5
Toffani and Richard, 1995	20	120-200	n/a	30-50
Sasai et al., 1997	15	20	13	33

Table no. 5: Summary of BOD changes after ozone treatment of secondary effluents

Source	Ozone Dose (mg/L)	Initial BOD_5 (mg/L)	Final BOD_5	Reduction (%)
Gardiner and Montgomery, 1968	6-21	4	5-6	n/a*
Nebel et al., 1973	12-16	10-25	n/a	15
Legube et al., 1987	6-12	5-23	n/a	50
Absi et al., 1993	18	26-48	n/a	-4

III. CASE STUDY :

In order to check the feasibility of using ozone as primary disinfectant, we conducted case study at Dhayafule Spinning Mills Pvt. Ltd, Tandulwadi Madha, Solapur where A. M. Ozonics have installed Septic-Ozone system to treat industrial sewage. In this system, effluent of septic tank after treating it with ozone is reused for industrial purposes and not drained off in the drainfield. Here's the plan layout, cost comparison of treating industrial sewage from Septic-Ozone system with conventional sewage treatment plant and quality of effluent.

PLAN LAYOUT

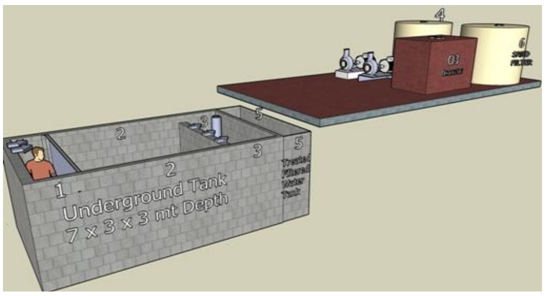

Fig. no. 1: Overview of entire project

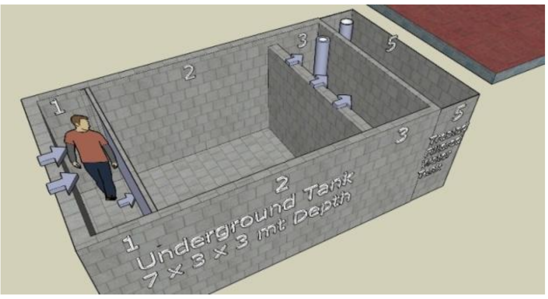

Fig no. 2 : Close view of septic tank and inspection chamber

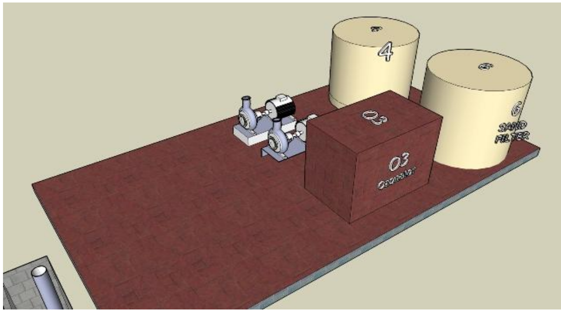

Fig no. 3: Close view of ozonator, pumps, and sand filter

1- Inspection chamber
2- Treated water tank
3- Final filtration and supply
4- Carbon filter
5- Septic tank and sand filter
6- Ozonator

COST COMPARISON:

System was designed for STP flow of 10,000 lit/day

Cost of Septic-Ozone System:

For 10 years:

Table no. 6 Cost of entire system

Unit	Cost
Septic Tank	3,00,000
2 Sand Filter	1,30,000
1 Carbon Filter	70,000
3 Pumps (1hp)	50,000
Ozone Mixer	50,000
Ozone Generator	1,50,000*2
Total	9,00,000

Considering 10% electricity charges and 5% maintenance charges,

Grand Total = 10,35,000

Note: Ozone generator rates are added twice as it has to be changed after every 5 years.

Cost of treating and supplying water by Government:

For 10 years:

Table no. 7 Cost of treating and supplying water by government

Description	Rates (Rs.)
Current water charges per 1000 lit for industries	46.66
Water charges for 10,000 lit/day	46.66*10= 466.6
Water charges per year	466.6*300= 1,39,980
Water charges for 10 year	1,39,980*10= 13,99,800

Note: Only 300 days are taken into consideration, as it is expected that mill will be closed for 65 days in a year.

We also haven't calculated tax levied by government in building new sewage treatment plants, which can considerably increase the cost of treatment.

Quality of effluent:

Description	Inlet	Outlet
COD (mg/L)	350-450	<70
BOD (mg/L)	150-200	<20
TSS (mg/L)	50	<10
pH	6-8	6-8

Table no. 8 Quality of sewage at inlet and outlet

IV. ACKNOWLEDGEMENT

We gratefully acknowledge A. M. Ozonics Pvt. Ltd. for assisting us in case studies and providing necessary data for calculating cost of septic-ozone system. We are also thankful to Dr. S. B. Patil for guiding us in the project.

V. SUMMARY AND CONCLUSION:

From the results presented following broad conclusions were deduced:

- Septic tank in conjuction with ozone is cost effective when sewage is to be treated for industrial purposes.
- Ozone effectively removes colour, odour, bacteria, COD, BOD and organic matter.
- Instead of using land for drainfield, it can now be used for other important purposes which can save the cost of land.
- Load on treatment plants can be reduced as considerable amount of sewage will be treated on-site.
- CT value of ozone for deactivation of Cryptosporidium and Giardia cyst is also much lower than that of chlorine.
- Ozone does not produce any harmful by-products like Trihalomethanes and haloacetic acid.

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