Jr. of Industrial Pollution Control 21 (2)(2005) pp 235 - 245

APPLICATION OF OZONE IN THE TREATMENT OF INDSTRIAL AND MUNICIPAL WASTEWATER

K. UPADHYAY AND J.K. SRIVASTAVA

Chemical Engineering Department, Ujjain Engineering College
Ujjain, M.P. India

Key words : Disinfection, Micro-flocculation, Biological activated carbon, Biofiltration

ABSTRACT

Ozone can be effectively used for the treatment of municipal and industrial waste water. Extensive research in application of ozone investigating the stoichiometry of reaction, reaction kinetics, reaction regime, mechanism of reaction has made possible to apply ozone safely in different fields of waste water treatment. The application may be pre ozonation, post ozonation or solely Ozonation. Ozone is a powerful oxidant, leaves no residual harmful product, no sludge disposal problem and increases the DO content of wastewater which helps further in the degradation of residual pollutant. Therefore ozone finds use in treatment of all types of waste such as municipal waste water, industrial waste water, contaminated ground water, treatment of swimming pool water, treatment of paper industry waste water, dye industry waste water, removal of colour, treatment of gaseous effluent, treatment of cyanide waste water, treatment of heavy metals, elimination of phenolic compounds etc. and specially as strong disinfectant. All these properties have made ozone as an ultimate treatment for all types of waste water treatment. The objective of the paper is to provide a detailed study on the use of ozone in different fields of waste water and drinking water.

INTRODUCTION

In the last decade the application of ozone became more and more popular. The development in technology of producing ozone and reaction kinetics has made the process reliable in producing low cost ozone and applying them to

wastewater treatment problems. The application may be solely ozonation, pre ozonation and post ozonation depending on the type of wastewater and its physico-chemical properties. The field of application increases tremendously because of its high oxidizing character and no sludge problem. Most of the applications are more viable and feasible. Ozone is powerful oxidant and is capable of oxidative degradation of many organic and inorganic compounds. It is soluble in water easily monitored; it readily decomposes to oxygen and leaves no byproduct or residual toxic compounds. It is powerful disinfectant. Ozone does not produce any secondary pollutants as compared to chlorine which produces THM, chloramines and other toxic compounds that are carcinogenic in nature. Many ozone reactions are rapid in nature. A faster reaction means shorter contact time required and large volume can be easily handled. The reactions with viruses are so rapid that they are difficult to study analytically. It leaves behind oxygen residual in wastewater that helps in further degradation. There is no risk and toxicity and odour problem. Ozone is effective 25 times more than hypochlorous acid, 2500 times more than hypochlorite and 5,000 times more than chloramines. All these excellent properties have made ozonation more and more applicative in different fields of wastewater and drinking water treatment. Ozone is widely used for treatment of drinking water to improve taste, odour, colour, as disinfection and biodegradability of impurities. Tertiary treatment of ozone reduces BOD/COD, turbidity, colour TS and increases the DO level. **Table 1** shows the application of ozone in various fields of wastewater treatment.

Ozone

Discovered in 19th century generally produced during lighting storm, ozone is tri atomic allotrope of oxygen having molecular weight 48. It is blue gas with pungent odour with a concentration of approximately 0.01 ppm is easily detectable in air by most people. It is 1.5 times dense than 02 and 12.5 times more soluble in water. The structure of ozone molecule is that of an obtuse angle in which a central oxygen atom is attached to the two equidistant oxygen atom. The included angle about 160°49′ and bond length is 1.278 °A. Ozone has strong absorption band in infrared visible and ultraviolet radiation. The absorption maximum at 2537 °A is particularly strong and affords a convenient means of measurement. The oxidation potential and reactivity of ozone

Table - 1
Applications of Ozone

Application	Concentration Os (ppm)	Contact Time (minute)
Reverse osmosis water	0.3-0.5	4-5
Drinking Water	1.0-2.0	5-10
Pool	0.3-0.7	1
Seafood Wash	0.1-0.15	1-2
Fruit & Vegetable Wash	0.2-0.4	1-5
Hydroponics	0.1-0.2	2-5
Cooling Tower	0.2-0.5	2
Pre-surgical wash	3-5	3-5

is exceeded only by fluorine. The application of ozone includes sterilization of all form of bacteria and virus in potable water, removal of taste odor and colour, oxidation of humic and fulvic acid, removal of tri halomethane precursors, removal of lignin content of pulp and paper industry, decolonization of synthetic colour bodies-organic dyes, removal of soluble refractory organics, viable alternative to either chlorination or hypo chlorination, oxidation of compounds resistant to biological degradation, disinfections of swimming pool water, bacterial disinfection's, viral inactivation, oxidation of soluble iron/ or manganese, colour removal, taste and odor removal and algae removal, oxidation of phenols, detergents, pesticides and micro flocculation of dissolved organics. Some of the applications are discussed in details.

MUNICIPAL AND DRINKING WATER TREATMENT

Ozone as disinfectant

Ozone has been used for the disinfections of water. Since the beginning of the century when it was applied to the treatment of water for the city of Paris, and France. There are about 38 sewage treatment plants in US using ozone mostly for disinfection's. Two French plants are working at Atlantic resort town. These plants have different objectives, one uses ozone for removal of SS other uses for floatation removal and third oxidizes organics. Not only ozone is a disinfectant but also an integral part of other treatment processes. The investigation on ozone shows that ozone is a quicker and more efficient disinfectant than chlorine and when properly used, it can reduce SS, BOD, COD and other pollutant. 5mg/L of ozone applied for 2 minutes yielded a significant reduction in total plate count and fecal coliform level. When ozone treatment is given to advanced wastewater a 2.5 mg/L. concentration applied for the same contact time reduced bacteria level by 1,000 times. Otis sprout university of Maine noted that there are more than 100 different strains of viruses capable of spreading diseases in water; only one or two virus may be required to produce sickness. Ozone application for disinfection's is essential for medical health and future of any nation. It is a potent virucide. Recent work shows that ozone kills viruses more thoroughly and rapidly than it does bacteria.

Dewatering of sludge

In the late 1960 detrimental effects of disinfecting municipal wastewater with chlorine were noted and studies of alternate disinfectants were initiated. Ozone causes the destruction of the filamentous bacterial growth that makes sludge so difficult to dewater. Small dosages of ozone applied selectively could destroy the cellular structure that holds water so tightly. Ozone for odor control is an established process and cities such as Cedar Rapids, Iowa and Winston-Salem, N.C. have been using it successfully in their wastewater treatment plants.

Flotation

Ozone is effective in destructing the cellular structure and floating particles. In mid 1980 a new 1,25,000 gal/day sewage treatment plant went on-line in Marion, New York. Secondary treatment is provided by 3 aerated lagoons, which remove about 90 % of the BOD. The remaining BOD is treated by ozone floatation prior to discharge, in addition to lowering the BOD content in the effluent to 5 mg/L. Ozonation also destroys algae, causes coagulation, removal of SS, destroy bacteria and inactivates viruses as well as provides protection against toxic substances that might enter the plant. Requirement of ozone are of the order of 10 mg/L.

Water reuse in Japan

The Japanese install attractive gardens throughout their country, all of these containing small rivulets of water. Use of ozone to treat sewage in the complexes to such a degree that the effluents can discharge into these gardens, to be acceptable for this purpose, the effluents must be crystal clear and odorless.

Sludge conditioning

At the 10 mgd sewage treatment plant in West New York, New Jersey, a unique free radical process has been installed for converting primary sludge to a dry, free flowing cardboard like material that is acceptable for landfill. The process is called oxyozosynthesis and cost about half the price for conventional sludge treatment process.

Ozone in drinking water treatment

Ozone is highly effective in the treatment of drinking water. Since 1906 the city of Nice, France has been ozonizing mountain stream water for potable purposes. Today more than 600 other French water treatment plants are using ozone for number of purposes. Throughout the world more than 1,300 drinking water treatment plants employs ozone for one or other purposes, 20 plants are being operated in U.S. using ozone technology. Most tastes and odor in water supplies come from naturally occurring or man made organic material contamination. Bacterial decomposition of humic material imparts taste to surface water, also the action of algae and actinomycetes give rise to objectionable tastes. Most of these odors are removed by treatment with ozone.

Improvement in GAC performance

Ozone is successfully used to improve the performance of GAC, once Ozonation was installed prior to GAC adsorption, however sulfide odor disappeared and the useful life of GAC, which before reactivation would have been required, was extended to over 21 months. The full-scale 50 mgd westerly plant is in fully operation with ozone, sand filtration, then GAC adsorption and chlorine disinfection's. Schalekamp has found that pretreatment with ozone has extended the useful lifetime of GAC absorber. Triple stage Ozonation has become popular in Europe in 1970. It has been observed that 80% of organics are removed and the product contains no trihalomethane. The ozone doses require is 3.5 mg/L and in triple stage the requirement of ozone is 4.5 mg/L.

Promotion of biological activity

When GAC adsorption follows Ozonation/sand filtration, biological oxidation of dissolved organics provides an extension of the useful life of the GAC. Today there are at least two dozens European water works utilizing the ozone/filtration/GAC adsorption process, which has been called biological activated carbon. The French recently have incorporated Ozonation into several drinking water treatment plants for promotion of biological activities. The first plant to incorporate the process is at Rouen in which high-quality water is produced. In the Rouen process, which incorporates pre ozonation for oxidation of iron, manganese and organics early in the process. The two-stage process shows economics in the use of ozone. Multiple stage ozonation can be cost effective over a single stage Ozonation. In the multiple treatments process the ozone requirement is 4.5 mg/L. ozone for all applications.

Ozone treatment of contaminated ground water

The treatment of ground water by ozone is an effective method having the advantage of high level of dissolved oxygen; the dissolved organics have been partially oxidized by the ozone and thus are now more biodegradable. DO level has risen from 1 mg/L to between 6-8 mg/L with the installation of ozone system. In Germany successful treatment of polluted ground water by ozone has been achieved and all the contaminated ground water has been successfully treated into high quality drinking water.

Removal of suspended solids

At chino basin, California a 5-mgd secondary treatment plant has been using ozone to micro flocculate and removes suspended solids without adding chemicals since 1978. Effluent from this plant is recharged to ground water. Ozonation reduces levels of suspended solids without adding any total dissolved solids to the effluent, provides effective virus removal and is cost effective, over alternative treatment processes. Dosages of ozone required in the process are 10 mg/L. In California a 5 mgd secondary treatment plant has been using ozone to micro flocculate and removes SS.

Ozone and removal of turbidity

Ozone is highly effective in reducing turbidity, converting the SS and DS into the respective stabilized form. There is a drinking water treatment plant in city of loss Angeles California based on ozone technology and having capacity of 580 mgd drinking water to lower turbidity to 0.3 turbidity units.

The largest drinking water treatment plant was designed in 1986 in the city of loss Angels based on ozone technology. About 7,300 Ib/day of ozone is generated from oxygen to treat 580 mgd of the city drinking water to lower turbidity to less than 0,3 turbidity units. The high filtration rate is made possible by employing ozone as a micro flocculant's. Without Ozonation filtration rates of the coagulated and flocculated water could not exceed 9 gal/min/ft^2.

Ozone and swimming pool water treatment

The use of ozone for treatment of swimming pool water has been developed in Europe since 1950. There are 3,000 swimming pool using Ozonation processes. Since the pink eye reaction are caused by chloramines therefore ozone based treatment plant are getting more popularity.

In recent years German swimming pool technologists have developed an innovative water treatment process that takes advantage of the oxidative power of ozone and that substitutes bromine for chlorine. It has been shown that pink eye reactions are caused by chloramines and that bromamines do not produce this effect.

In the new treatment process bromide is added to the pool water, which then is ozonized. During ozonization bromide ion is oxidized to bromine, which is biocide/ disinfectant. The ozonized water is passed through GAC to destroy the ozone. Water containing bromine and no ozone enter the pool.

INDUSTRIAL APPLICATIONS

Ozone in paper industry effluent treatment

Long back research started to eliminate pollution caused by effluents of pulp and paper industry, Ozonation has been widely investigated method. The effluent of paper industry contains many types of Hgnocellulose's structure. The wastewater produced by this industry tends to be heavily contaminated and highly coloured, especially when the industrial process makes use of artificial colouring agents. Here conventional wastewater treatment often proves to be of limited efficiency, Ozonation effectively removes colour from paper industry effluent containing humic material. It is difficult to determine the exact chemical effect that Ozonation had upon the humic structure. Ozone reacts with the molecules responsible for colouration, breaking down those functional groups that have high electron densities. These include the humic acids, tannins, and lignin commonly found in vegetable matter. Ozone close to 10-15 mg/lit. is required to reduce the pollution load to significant level for industrial wastewater.

Ozone in dyeing industry effluent treatment

The wastewater produced by the dyeing industry contains many artificial colouring agents. We can classify the effluent based on different parameters. Physical properties includes colour, turbidity (dissolved and suspended impurities) etc. whereas chemical properties includes the constituents of acidic dyes, basic dyes, sulphides dyes, azo dyes, metallic complex dyes etc.

Generally speaking, biological treatments are only capable of bringing about, slight improvements in wastewater colour. This is because the molecules responsible for colouration are not biodegradable. Effluent colour can however be improved by aeration or oxygenation. One-way of decolourization might be through destruction of the double nitrogen-nitrogen bonds, this is confirmed by the appearance of NO and NOz radicals following ozone treatment.

Ozone in removal of colour

Surface water are generally coloured by natural organic materials such as humic, fulvic and tannic acids. These compounds results from the decay of vegetative materials and are generally related to condensation products of phenol like compounds, they have conjugated carbon/carbon double bond. Ozone rapidly break organic double bond. As more of this double bond is eliminated, the colour disappears. Surface water can usually be decolourized when treated with 2-4 ppm of ozone.

Ozone in treatment of toxic waste

The detoxification of industrial wastewater is an issue that has taken a marked importance in recent times. The chemical industry, in particular, discharges many substances of high immediate toxicity. For this type of waste, mere dilution is not a sufficient anti-pollution measure. The concentration levels are crucial factor when considering toxicity. Ozone is increasingly used in tertiary treatment for eliminating all traces of harmful substances. The advantage here is that ozone treatment does not require the use of additives, which may prove toxic than the compound removed.

In mixtures containing toxic compounds, ozone will not always react specifically with the compound that we wish to eliminate. For this reasons it is advisable, wherever possible to apply conventional purification techniques first and follow up with Ozonation as a second or third stage. Concentration levels are a crucial factor when considering toxicity.
Thus ozone is increasingly used as final treatment stage for eliminating all traces of harmful substances.

Ozone in treatment of cyanide waste

Chemically speaking, cyanide pollutants can be categorized in three main groups :

a) Hydro cyanic acid,
b) Simple alkaline cyanides (sodium cyanide, potassium cyanide)
c) Soluble complex cyanide (potassium copper cyanide, sodium, iron cyanide, potassium iron cyanide, etc).

Cyanides are a prime example of highly toxic wastewater; the substances are toxic to fish at concentration as low as 25 ppb. They are powerful enzyme inhibitors and continue to find widespread use in many industries e.g. froth floatation for mineral extraction, cyaniding of precious metal ores, gas purification in coking plants, synthesis of organic compounds (plastic, textiles), manufacture of pharmaceutical products etc.

The largest quantities of cyanide are discharged from the degreasing tanks, electroplating vats and rinsing baths found in surface treatment plant. The cyanide concentration in wastewater from these sources can vary from 20-100 mg/L.

Cyanide and cyanide complexes can be destroyed by ozone treatment, in test performed for U.S. air force industrial wastes containing up to 10,000

mg/L of cyanide were treated with ozone and ultraviolet light. The treatment reduces the cyanide concentration to below detectable level.

Ozone in elimination of heavy metals from wastewater

Industrial effluent often contains heavy metals, the toxicity of which is widely known. Like the cyanides, heavy metals may be present in the water in both free form and in complex compounds. Ozone oxidizes the transition metal to their higher oxidation state in which they usually form less soluble oxides; easy to separates by filtration. Other metals like cadmium, chromium, cobalt, copper, lead, manganese, nickel, zinc etc. can be treated in a similar way.

Broadly speaking, ozone oxidizes these heavy metals to form metallic oxides or hydroxides, which precipitate off and can easily be removed from water. Ozone is used for eliminating heavy metals from the effluent produced by many types of industries, a typical case being that of mineral extraction plant.

Ozone in elimination of phenols

Many types of industrial plant discharge phenolated wastewater such as coking plant, oil refineries, petrochemical plant, mines, chemical and pharmaceutical process lines, foodstuff, canning plant, paint stripping shops, hi aeronautical industry etc.

A number of purification methods exist for eliminating these toxic compound from wastewater. One such method is oxidation of ozone. Several highly detailed studies have been conducted into the way ozone reacts with phenols. Basically, ozone breaks down phenols to form oxalic acids and oxygen. Studies into the kinetics of Ozonation reactions show that many factors can affect the efficiency of the purification process. Predominant among these factors are the temperature and above all the pH. Thus increasing the pH from 8.0-11.0 doubles the rate at which phenols are broken down. At the higher pH value, ozone attacks phenolated compounds in preference to the other oxidizable matter, and this substantially reduces reaction times. Generally five parts of ozone are required to break down one part of phenol in wastewater.

Ozone in deodorization and treatment of gaseous effluent

In the last several years scientific evidence has indicated what are breathing in homes and other buildings can be more polluted than outside in the latest and most industrialized cities.

Ozone reacts with many organic substances responsible for causing unpleasant odors; among these are olefms, short- chain fatty acids, ketones, nitrites, esters, amines and sulphur bearing compounds such as mercaptains. Owing to the very low concentrations of pollutant, it is not usually possible to carry out economical treatment using conventional methods such as thermal or catalytic oxidation, absorption, washing or biofiltration. Ozone treatment is the only way to ensure rapid economical deodorization

There are ozone generators that run on 110-220 V AC or 12 V DC for cars, boat, truck or home. Purifiers help in the disinfections and oxidation

of undesirables in our living environment. Ozone oxidizes many inorganic and organic impurities as well as inactivates bacteria, virus and cysts. Ozone oxidizes organic chemicals into safer elements. During the Ozonation process, some compounds like ammonia and cyanide is broken down into nitrogen and water.

Ozone application in air food and water

Ozone applications for disinfection's and purification of air, food and water supplies are essential for the medical health and future of any strong and healthy nation. Ozone, if injected into the waste holding ponds will break down contaminates while oxygenating it at the same time. The waste material is more biodegradable after oxidation and safer for the environment. Ozone neither changes the pH nor does it react with the remaining organ ics to from carcinogenic trihalomethanes. Ozone can be safely applied as seen in **Table 2.**

Table - 2
Application of ozone in differnet fields

Air conditioning	Fabric stores	Pharmaceuticals
Apartments	Factories	photo labs
Aquariums	farms and dairy	poultry farms
Aquatic plants	fire restoration	printing companies
Automobiles	Fish markets	produce markets
Bars/taverns	florist's shops	paper mills
Banks	food processors	pulp mills
Barbershops	furniture stores	realtors
Barns	green houses	rendering plants
Basements	grocery stores	restaurants
Beauty salons	Gymnasium	rest rooms
Bingo halls	Homes	Retail sales
Bottled water	Hospitals/clinics	Retirement homes
Bowling centers	Hotels and motels	salad bars
Carpet cleaners	Kennels	schools
Casinos	locker rooms	senior centers
Catering halls	lumber mills	smoking areas
Chemical distributors	meat markets	spas/pools
Compactors	medical labs	Taxidermy shops
Cooling towers	Meeting rooms	Textile industry
Country clubs	Morgues/mortuaries	trash bins
Day care centers	nursing homes	storage facilities
Dental labs	nurseries	warehouses
Dry cleaners	office	wastewater
Electronic industry	paint stores	veterinary hospitals
Algae	ethylene gas	smoke
Ammonia	formaldehyde	spa chemicals
Bacteria	fungus	stale tobacco
Car exhaust	indoor air pollution	styrene
Chemical gases	obnoxious odors	pathogens
Chemicals in pools	Paint fumes	pet odors
Chlorine	pathogens	mildew
Cleaning agents	sewage gases	mold

CONCLUSIONS

Most of the industrial waste water and drinking water exhibit variable characteristics. It becomes difficult to treat them to acceptable limits. Often complex formation is found in waste water due to the use of different chemicals. All the conventional method of treating the waste water results in partial removal of pollutants. Therefore the effluent is not safe for discharge in river stream or on land. Treatment with chlorine is an effective method but recent studies shows that it forms THM and chloramines that are carcinogenic in nature. Ozone is a good oxidant as seen from different studies. In the recent years the use of ozone has become more popular.

The oxidation potential and reactivity of ozone is exceeded only by fluorine. Ozone is capable of sterilizing all forms of bacteria and virus. The reaction with virus is so fast that it is difficult to study analytically. In the case of sewage treatment plant it causes destruction of filamentous bacterial growth and avoid bulking of sludge and foam formation. After treatment the water can be used for gardening purposes. Ozone increases the life of biological activated carbon process. Ozone is quite effective in the removal of SS and turbidity. Application of ozone in treatment of swimming pool water eliminates the pink eye problem. Industrial applications include treatment of paper mill waste water, dye unit, toxic waste water, cyanide bearing waste water, elimination of heavy metals, treatment of phenolic waste water etc. Ozone reacts with molecules responsible for colouration breaks the functional groups that have high electron density. In the treatment of cyanide waste water the cyanides are converted into cyanates and cyanates are finally converted hi carbon dioxide and nitrogen. The heavy metals are precipitated and filtered off. Ozone breaks down the phenolic waste into oxalic acid and oxygen. Unfortunately in India the practice of using ozone has not yet started. This may be due to high cost of treatment. In the near future India has to adopt the ozone technology as it is most effective method for eliminating the different water borne diseases.

REFERENCES

Applied Ozone Systems. 1999. Ozone application in air, food and water. www.appliedozone.com/applications.html 1-6.

Augugliaro, V. and Rizzuti, L. 1978. The pH dependence of the ozone absorption kinetics hi aqueous phenol solutions. *J. of Chemical Engg science.* 33 : 1441-1447.

Calvosa, L., Monteverdi, A., Rindone, B. and Riva, G. 1991. Ozone oxidation of compounds resistant to biological degradation.*/, *of Water Research.* 25(8) : 985-993.

Easton, J. K. 1967. Electrolytic decomposition of concentrated cyanide plating wastes. *J. of Water pollution control federation.* 39(10)part -1 : 1621 -1625.

Elia, V. J., Clark, C. S., McGinnis, K. T., Cody, T. E. and Kinman R. N. 1978. Ozonation in a wastewater reuse system: examination of products formed. *J. of Water Pollution Control Federation.* 50 : 1727 - 1732.

Gurol, M D. and Singer, P. C. 1982. Kinetics of Ozone Decomposition: A Dynamic Approach, *Environ. Science and Technology.* 16(7) : 377.

Hoigne, J. and Bader H. 1976. The role of Hydroxyl radical reactions in Ozonation processes in aqueous solutions. *J. of Water Research* 10 : 377-386.

Killops, S. D. 1986. Volatile ozonization products of aqueous humic material. *J. of Water Research.* 20(2) : 153-165,

Matsui, M, Hibino, T., Shibata, K. and Takase, Y.1983. Ozonation of dyes: reaction of chrysophenine G with ozone in water. *J of American dyestuff reporter.* 35-39.

Ozonetek limited. 2000. Applications and treatment of wastewater effluent. www.ozonetek.com/applv.html. 1-5.

Pelegj M. 1976. The chemistry of ozone in the treatment of water. *J. of Water research.* 10 : 361-365.

Prat, C., Vicente, M. and Espulgas, S. 1989. Ozonation of bleaching waters of the paper Industry. J. *of Water Research* 23(1) : 51-55.

Rice, R. G. and Netzer, Eds. 1982. Hand book of Ozone Technology and Applications. 1 , 2 *Butter -worth Publisher,* Boston.

Rosen, H. M. 1973. Use of ozone and oxygen in advanced wastewater treatment. *J. of Water Pollution Control Federation.* 45(12) : 2521-2536.

Sekerka, I. and Lechner, J. F. 1976. Potentiometric Determination of Low Levels of Simple and Total Cyanides. *J. of Water Research.* 10 : 479 -483.

Silter, J. T. 1974. Ozone: an alternative to chlorine? *J. of Water Pollution and Control Federation.* 46(1) : 4-6.

Stowell, J. P. and Jenson, J. N. 1991. Dechlorination of chlorendic acid with ozone. *J. of Water research.* 25(1): 83-90,

Yves, R. and Brener, L. 1995. Removal of color from drinking water with ozone. *Ozone for drinking water treatment.* Chapter 4: 49-62.