OZONE IN WASTE WATER TREATMENT

BY

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Ozone Technology have since been used for the past two decades or more .It is however only now that its use in Waste water Treatment has been recognized. This delay probably could be due to the lack of confidence on ozone by consultants, prospective users etc but more because they have not had too much of references in India and around the world to convince them of its use in WWWT . However the constant pressure by regulatory bodies to look for suitable Technology to meet stringent norms have forced the Industry to consider ozone .Today after drinking water ,waste water have found maximum number of ozone users in India

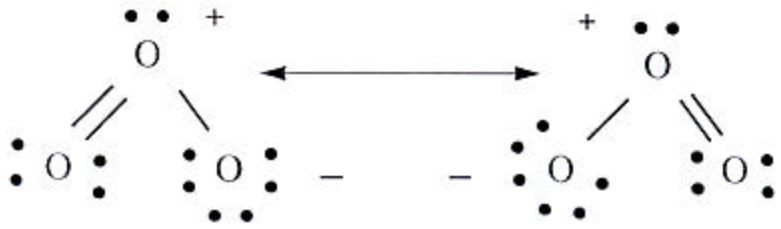
What is so special about Ozone?

OZONE IS A POWERFUL OXIDIZING AGENT :

OZONE is a very powerful oxidizing agent , only next to OH radicals . How effective ozone is ,will depend entirely on the nature of the contaminant and is directly dependant in the chemistry involved in the process. Many other oxidation agents are often used in combination with ozone to provide increased efficacy . .Agents such as peroxides, UV, and conditions of high pH assist ozone in the oxidation process.

WHY IS OZONE SO POWERFUL;

Ozone Chemistry is composed of a single bond and one double bond. The single bonds are weak and this leads t easy formation of free radicals .The double bond is as strong as the double bond of oxygen and so un reactive .Two resonance structure of ozone exists and they are inter convertible .The inter-convertabilty is so fast that at point of time ozone as seen as a blend of the two resonance structure .The strength of these two bonds ae equal



Ozone Resonance Structures

OZONE AND OXYGEN – A COMPARISON AS AN OXIDANT

As an Oxidant ozone is more powerful that Oxygen .This difference is due to the oxidation states .In water the oxidation state of the Hydrogen Atoms is +1 and that of oxygen atom is -2 (hydrogen as yielded its electron to oxygen and oxygen as acquired an electron from each hydrogen atom) The Oxidation State for oxygen atoms is usually - 2**.** However, in both ozone and molecular oxygen, the oxygen atoms each have an oxidation state of 0. Therefore, ozone and

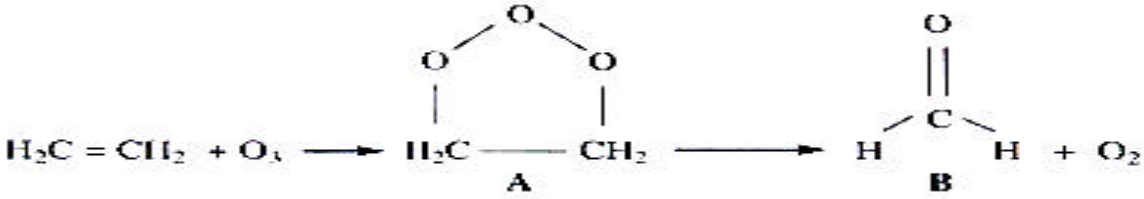
oxygen are both oxidants because they are capable of drawing electrons from a source, decreasing the Oxidation State of at least one of their oxygen atoms in the process.

OZONE is more reactive than Oxygen because ozone can readily react with substrate on its own whereas oxygen requires a catalyst such as metal ions to initiate reaction

During electrically promoted reduction of Ozone there is a release of a molecule of O2 and a formation of an oxygen atom with a -2 oxidation state .The reduction potential is 2.07V , a value greater that the reduction potentials of most other oxidants (see below)

. Reduction of Ozone

Chemically promoted ozone reduction mechanism is more complicated because of the existence of various reaction pathways .



Above is an unbalanced Reaction of Ethylene with Ozone . Here Ozone forms an intermediate compound A with two carbon oxygen links .The carbon –carbon double bond cease to exist in A .The oxygen atoms bound to Carbon have been reduced from 0 to -1 oxidation state. The reaction proceeds further to yield O2 and another compound B . Note The oxygen atom in **B** is now in the -2 state, Ethylene has been oxidized .The next step will be a complete oxidation to CO2 and H2O

The chemically promoted reduction of ozone is not as simple because of the various reaction pathways (mechanisms) that can take place. One of the more simple examples of a chemical process utilizing ozone as an oxidant is the reaction of ozone with ethylene (Figure 4). In this process, ozone reacts with ethylene to form intermediate **A** that contains two carbon-oxygen linkages. Note that the carbon-carbon double bond no longer exists in **A**. The carbon atoms have been oxidized, and the oxygen atoms bound to carbon have been reduced from 0 to -1 oxidation state. This reaction will proceed further to yield O_2 and product **B**. The oxygen atom in **B** is now in the -2 state, and the substrate (ethylene) has been oxidized and is one step closer to becoming completely oxidized (to carbon dioxide and water).

OZONE STRONG AGAINST MULTIPLE BONDS

Ozone reacts readily with compounds containing multiple bonds (such as C=C, C≡N, N=N, etc.)

But the reactions rate are slower with single bonds such as C-C, C-O, O-H etc due to the fact that easy chemical pathway are not found . But the reactions of ozone with simple oxidizable ions such as S^{2-}, to form oxy anions such as SO_3^{2-} and SO_4^{2-}. Must be noted . These are simple oxidation process that starts immediately on contact with ozone with the ion and the oxidation proceeds very rapidly .Ozone thus breaks up C-N, C-S AND C=0, C-OH etc. to CO 2, NO2, NO3 and SO4 but without contributing to the positive ions. The final byproduct of the reaction is Oxygen which is a benefit rather than a pollutant.

Aromatic rings are broken down rapidly when the links are weak and slowly when the links are strong. The reaction of Ozone on Aliphatic depends upon the length of the chain- slower the longer the chain and strength of the bonds

Ozone is a highly reactive substance that can react with many species .However most often ozone action is dependant on how it reacts with a pollutant. Though Thermodynamics may favour ozone due to its high Redox potential ,it is the kinetic factors that will determine how fast ozone will act against each pollutant . It is because of this fact that Ozone sometimes have not been very useful in certain cases of Waste water Treatment

ADVANCED OXIDATION PROCESS

Also know as AOP , these are process that use ozone in combination with peroxide , UV or reactions under high pH . Whereas Hydrogen peroxide is an oxidant, UV is not .But when used with Ozone the breakdown of organics to CO2 and H2O is facilitated. The reactions pathways are many but for easy understanding the main and most common pathway would be when Hydrogen Peroxide decomposes in the presence of ozone or UV into Hydroxyl radicals . There exist in solution a combination of ozone molecules in high oxidative state and free radical also in very high oxidative state. The combination is highly reactive as the free radicals capable of withdrawing atoms (often hydrogen) from a substrate. The role of hydrogen peroxide in AOP is thought to make the pollutant more susceptible to ozone attack and also aid in the overall oxidation

UV lights provides energy to break chemical bonds .This makes the remaining fragments more susceptible to ozone attack .UV light also converts H_2O_2 to the highly reactive hydroxyl radical and the generation of oxygen . UV lamps are thus used as ozone distructing agents as it helps convert ozone to molecular oxygen .When using UV Technology in conjunction with Ozone the location of UV is very important

High pH

High pH lead to hydroxyl radical formation through an indirect route. The hydroxyl ion reacts with ozone to form the hydrogen peroxide ion, HO_2-. HO_2- is the conjugate base of H_2O_2 and at a pH lower than 11.6 (which is the pKa of H_2O_2) will be predominantly converted to H_2O_2. Therefore, high pH catalyzes the formation of hydrogen peroxide, which is a source of hydroxyl radicals. This process is shown below.

$$HO^- + O_3 \rightarrow HO_2^- + O_2$$
$$HO_2^- + H_2O \rightarrow H_2O_2 + HO^-$$

$$O_3 + H_2O \xrightarrow{HO^- \text{ Cat}} H_2O_2 + O_2$$

OZONE IN WWWT

The Location of ozone use in WWWT will determine the goal of treatment. A simple way to explain a classical WWWT will be break up the process into:

1) Preliminary treatment consisting of process such as screening
2) Primary treatment including sedimentation
3) Secondary treatment including activated sludge treatment and secondary sedimentation
4) Tertiary treatment including discoloration, disinfection ,COD reduction etc

Ozone finds use in each of these stages of WWWT . Ozone during preliminary stage is used for detoxification .ozone at secondary stage is used for sludge reduction, and ozone during the tertiary stage is more common and used for disinfection, micro pollutant removal, COD reduction and decoloration. .The location of ozone is dependant on the goal of ozonation

In each of these cases the use of ozone has been found to be very productive .

1) Decolourisation & Deodorization
2) De toxification
3) Disinfection
4) COD/BOD reduction
5) Sludge Reduction

1) DECOLORISATION & DEODORISATION

Due to new government restrictions for the discharge of colored water and the increasing discharge costs of waste water ozone oxidation for decoloration is becoming more and more popular. The effected industries are companies producing textiles, dyes, paper or chemicals. Additional to the very successful results in decoloration, ozone brings further benefits like desinfection, improved BOD/COD-ratio, reduced AOX and reduction of odour. Waste water or recycling water can be treated in an environmentally-friendly way without any residuals or concentrates by using ozone.

The design of decoloration systems with ozone depends mainly on the color causing compounds and on the COD background load in the water. Because of the chemical structure of colors the ozone reaction takes place within a few minutes whereas the reaction for the reduction of COD can take up to several hours. But nevertheless there is a close relationship between the ozone demand for decoloration and the COD concentration. Simply expressed as higher the COD in the raw water as higher the ozone demand will usually be.

Ozone dosage: for COD < 200 mg/l = 25 – 80 g/m³ and for COD > 200 mg/l = 50 – 500 g/m³
.Ozone Retention time: varies between 5 – 30 minutes
If the raw water contains a high COD concentration a biological pretreatment is recommended prior to ozonation to reduce the COD to a level as low as possible. Based on this the ozone demand for discoloration can be reduced drastically

- Biological waste water treatment typically does not remove colorful substances sufficiently
- Reuse of colored wastewater is normally not possible (paper-, textile-, chemical-, dye-industry)
- Pollution of surface water by colored waste water is obvious so the source (WWTP) can be easily identified
- Local government restrictions are planned or in place to limit the discharge of colored waste water from industrial and municipal WWTP.

OZONE therefore is an ideal oxidation technology to remove color

Odor causing compounds that are organic in nature are easily destroyed by ozone .It is for these reasons that ozone finds immense use in Municipal drinking water plant and also in chemical industries discharging effluents that containing odorous compounds such as H2S etc.

DETOXIFICATION :

Some of the more common toxic substances that are found in Waste water (Industrial and Municipal too) are:

1) Chemicals like cyanide , phenols and phenolic compounds,nitrites
2) Pesticides and products such as Tensides (surfactants in detergents)
3) Micro pollutants such as EDC (endocrine disrupting Compounds)

We are quite aware of toxic substances such as pesticides, phenolic compounds that has been addressed by pollution Control authorities in India .However the world as woken up to a new set of compounds know as EDC .

EDCs are micro pollutants.

- Different groups of persistent micro pollutants are daily released by human activities into the water cycle
- EDC´s (Endocrine Disrupting Compounds), pharmaceuticals and personal care products are groups of emerging contaminants
- EDC´s are substances which impact hormone function in animals and humans
  -Natural or man made that disrupt growth, development, or reproduction
- Anthropogenic substances that affect the hormone balance
- A cause for great concern is the Multiplier effect
- Growing concern forced detailed Investigations into this topic all over the world (Australia, Switzerland, UK, USA,..)

Pharmaceuticals in Water: This is of very great concern all over the world. Iodinated Contrast agents such as Iopromide, Iomeprol Diatrizoate have been found is waste water **in** concentrations as high as 4.5 to 5 micro grams per ml of waste water .Other presence of antibiotics , beta blockers anti epileptics have been found in concentrations of 1-1.5 micro grams per ml.

The following substances are listed exemplarily, to demonstrate how common these compounds are (in Germany/2000): It is expected to be many more times in India

– ***17α -Ethinylestradiole***	***0,1 t/year***
– ***Doxycycline***	***8 - 16 t /year***
– ***Sulfamethoxazol***	***80 t/year***
– ***Lipid regulator***	***30 t/year***
– ***Betablocker***	***60 t/year***
– ***Ibuprofen***	***105 t/year***
– ***Paracetamol***	***500 t/year***

50% of these drugs will be secreted unchanged and goes back into the water cycle

The risk levels of these compounds in Fishes are as low as 0.0001 micro grams per ml !!! There are human evidence that these compounds cause reduced fertility, and a high tumour incidence

Some of the discussed treatments concepts for these micro pollutants are :

- Improve the existing biological system
- Evaluation of the best additional treatment step (depending on the water source, contaminant and treatment goal) such as
  - Activated Carbon
  - Oxidation Process (Ozone(UV/H2O2)
  - Membranes (Nano, RO)
  - Process combination of different steps

Independent studies conducted by RWTH Aachen, EAWAG and others identified Ozone treatment as most effective in terms of elimination rate and treatments costs
It has been found that:

- Ozone treatment achieves removal rates > 90% for most investigated compounds
- Ozone reduces the over all estrogenicity
- Relatively low doses (3 to 10 mg/L) ensure selective oxidation of contaminants
- Ozone reactions are more selective and predictable in waste water than radical reactions
- Ozone is best available technology for EDC treatment
- Ozone technology is available and reliable in large scale – practical experiences and references exist

Disinfection: Effluents of biological treatment plants for municipal sewage still contain substances that prevent a reuse: Reasons for waste water disinfection can be removal of :

- Fecal and coliform germs
- Parasites and viruses
- Biological persistant substances such as (AOX, pesticides, chlororganic substances....)
- Colour causing substances
- Unpleasant odour

These can be responsible for causing several water borne diseases.

Some of the international regulations for waste water disinfections are:

- EU Bathing Water Directive (76/160 EWG)
- WHO Guideline (2003)
- California Waste Water Reclamation Criteria (CRWC) Title 22

Low Pressure UV technology is considered one of the better Technology in waste water disinfection. But of late Ozone has been considered very seriously for the following reasons :

- Compliance with WHO or even Californian title 22 that is possible with ozone
- A small dosage of 5 g O3/m3 waste water achieves at least a 2-log reduction of coli forms, and a dosage of 15 g O3/m3 upto 3-log reduction including parasite removal
- No production of harmful by products seen with ozone
- Parallel removal of unpleasant odors has been a bonus with ozone
- Parallelly there is an extensive elimination of persistent Micro pollutants
- Removal of colored substances not possible with UV technology
- Growing increase of acceptance for water re-users

COD/BOD Reduction:

The table below gives some idea of the choice of different technologies available for waste water treatment. Mostly the Choice of a particular technology is governed by two criteria:

1) the flow of the effluent
2) The COD content

TECHNOLOGY	COD CONTENT mg/l	FLOW RATE
INCINERATION AND EVAPORATION	15000 – 100000	1M3 /hr to 10M3/hr
ANEROBIC BIOLOGICAL TREATMENT	15000 – 100000	10M3/hr to 100M3.hr
WET AIR OXIDATION	8000-50000	5M3/hr to 100M3/hr
AOP (UV /H2O2/FENTON)	1000-6000	0.5M3/HR TO 10M3/HR
AEROBIC BIOLOGICAL TREATMENTINCLUDING ACTIVATED SLUDGE/MBR/BIO FILTER	15 - 10000	10M3/HR-10000 M3/HR
OZONE	10 - 1200	1M3/HR TO 10000M3/HR
ELECTROLYTIC OZONE INCLUDING LBT UV SYSTEMS	0.1 - 0.7	0.5M3/HR TO 100M3/HR

From the above it can be seen that ozone Technology is not restricted due to the flow of the effluent .However the choice of this technology will entirely depend on the COD content. The choice of ozone will depend on the goal of the treatment.

Full Oxidation (Mineralization) :Ozonation is normally used after a classical treatment that will include a Biological treatment .The basic thumb rule to evaluate the feasibility of ozone technology will be 2-4 grams ozone per gram of COD eliminated. We can expect a COD reduction up to 40-50% if ozone is used after a good classical system. With an AOP , ozone combined with H2O2 ,the COD reduction can exceed 70%

For partial oxidation also known as cracking, mostly adopted for the improvement of BOD/COD ratio two stages of Biological treatment are recommended .The thumb rule for ozone demand will be 0.7-1.1 grams of ozone per gram of COD eliminated

SLUDGE REDUCTION

Sludge handling costs have now become one of the main operating costs (even up to 40-50% of the total costs of the waste water treatment) for waste water treatment plant operators . Especially in the textile industry, major sludge formation is due to the use of flocculants for the removal of color during primary and secondary treatment . In spite of this large usage of flocculants, color removal of certain types of dyes has not been very satisfactory. The COD reduction has also not been very consistent with classical treatment. Ozone has been tried with the main goal of sludge reduction. Large amounts of ozone are required for sludge reduction if used during primary or secondary treatment process but results have been obtained .However it is up to user to evaluate the costs associated with the use of ozone compared to the costs incurred in handling the sludge generated by conventional treatment.

Basic Principal: ozonation transforms solid waste problems to treatable liquid waste .The bacterial cell wall is attacked by ozone and lysis of cell wall occurs .Cellular contents are liberated (COD) .This liberated COD is returned to the basin where the bacteria feed on this COD. Consequently sludge is reduced ..The reduction of sludge can be as much as 40% to 45% with an ozone dose of 0.01 to 0.1gram of ozone per Kg of solids removed.

Additional properties achieved by ozonation would be elimination of foaming problems ,a positive impact on color and surfactants and a dramatic reduction in filamentous bacteria

Summary:

ozone technology in waste water treatment :

- Is a residual free treatment technology
- It is used for various applications (field proven for decades but also new emerging applications)
- OZONE is a specific tool but not a stand alone concept,
- OZONE is very effective if applied properly and in combination with especially biological treatment

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