# OZONE AS A DISINFECTING AGENT IN THE REUSE OF WASTEWATER

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## Introduction

More and more countries are taking measures to reuse wastewater. This has been prompted by the ever decreasing availability of good quality raw water and the increasing cost of producing potable water. Disinfection is a major treatment step in the direct reuse of reclaimed wastewater to ensure environmental and public health protection.

"Disinfection is the destruction, inactivation or removal of those micro-organisms likely to cause subsequent infection of people. Wastewater disinfection refers to the use of a process designed specifically to reduce the numbers of viable, infectious microbial organisms in an effluent, ..." (Wright, 1997). Because of its high oxidation potential and specific lethality, ozone is the most effective disinfectant (killing bacteria, inactivating viruses and protozoa).

$O_3$ : 2.07 volt (pH = 7)
$Cl_2$ : 1.36 volt (pH = 2 - 6)
$ClO_2$ : 0.95 volt (pH = 7)

In addition to disinfection, wastewater treatment must address other factors such as lowering the COD (Chemical Oxygen Demand), and to a lesser extent sometimes the BOD (Biological Oxygen Demand), as well as making improvements in colour and odour. With ozone, oxidation of organic matter and precipitation of metals further improve the water quality and allow its reuse.

## Legislation concerning wastewater

There are four major pieces of EU legislation concerning wastewater. The Urban Wastewater Treatment Directive (1991) concerns the collection, treatment and discharge of urban wastewater and wastewater from certain industrial sectors. It calls for member states to ensure that before discharge urban wastewater entering collecting systems is subject to secondary treatment as follows:

by 31-12-00 for all discharges from agglomerations of over 15000 p.e.

by 31-12-05 " " " " " of between 10000-15000 p.e.

by 31-12-05 for discharges to fresh-water & estuaries from agglomerations of 2000-10000 p.e.

It also recommends treated wastewater to be reused whenever appropriate and that disposal routes should minimise adverse effects on the environment.

The Bathing Water Quality Directive (1975, updated 1994) and the Shellfish Waters Directives (1979, 1995), concern effluents discharged into designated bathing areas and shellfisheries and the standards that they must comply with.

## Reuse of wastewater

The treatment of wastewater for reuse depends upon the application of the re-claimed water - direct potable reuse, indirect potable reuse (e.g. groundwater that has been recharged with reclaimed water), direct nonpotable reuse, indirect nonpotable reuse, etc. - and the potential for human contact or ingestion (AWWA, 1996). It is therefore important to identify how the reclaimed wastewater will be used and in turn the standard to which it must be treated.

| | **Absorbed ozone dosage (mg/l) for nn total coliforms / 100 ml** | | |
|---|---|---|---|
| Effluent Quality | 2.2 | 70 | 200 |
| Secondary | 35 - 40 | 15 - 20 | 12 - 15 |
| Filtered Nitrified | 15 - 20 | 5 - 10 | 3 - 5 |

*Figure 1: Ozone dose to attain various levels of wastewater disinfection (Rice, 1997)*

Figure 2 shows the EPA guidelines for wastewater reuse.

| **Type of use** | **Treatment** | **Reclaimed water quality** |
|---|---|---|
| Urban uses, food crops eaten raw, recreational impoundments | Secondary, Filtration, Disinfection | pH = 6 - 9<br>10 mg/l<br>2 NTU[a]<br>no detectable faecal coli/100 ml[b]<br>1 mg/l $Cl_2$ residual[c] |
| Restricted access area irrigation, processed food crops, nonfood crops, aesthetic impoundments, construction uses, industrial cooling[d], environmental reuse | Secondary, Disinfection | pH = 6 - 9<br>30 mg/l BOD<br>30 mg/l SS<br>200 coli / 100 ml[e]<br>1 mg/l $Cl_2$ residual[c] |
| Groundwater recharge of potable aquifers by spreading | Site specific<br>Secondary & Disinfection (minimum) | Site specific<br>Meet drinking water standards after percolation through vadose zone |
| Groundwater recharge of potable aquifers by injection, augmentation of surface supplies. | includes:<br>Secondary, Filtration, Disinfection, Advanced wastewater treatment | includes:<br>pH = 6 - 8.5<br>2 NTU[a]<br>no detectable faecal coli/100 ml[b]<br>1 mg/l $Cl_2$ residual[c]<br>meet drinking water standards |

[a] Should be met prior to disinfection. Average based on 24-h. Turbidity should not exceed 5 NTU at any time
[b] Based on 7-day median value. Should not exceed 14 faecal coli / 100 ml in any sample
[c] After a minimum contact time of 30 mins
[d] Recirculating cooling towers
[e] Based on 7-day median value. Should not exceed 800 faecal coli / 100 ml in any sample

*Figure 2: US EPA guidelines for water reuse (Crook, 1999)*

Ozone's use in the treatment of municipal and industrial wastewater was thoroughly reviewed by Rice in 1997. He mentions that in the United States, the cities of Denver, CO, El Paso, TX (see Figure 3), Tampa, FL and San Diego, CA have started wastewater reuse programmes, in which ozone plays an important role as a polishing and disinfecting agent. The city of Windhoek, Namibia, which has been treating its sewage for potable reuse for many years, is planning to substitute ozonation for chlorination prior to GAC adsorption.

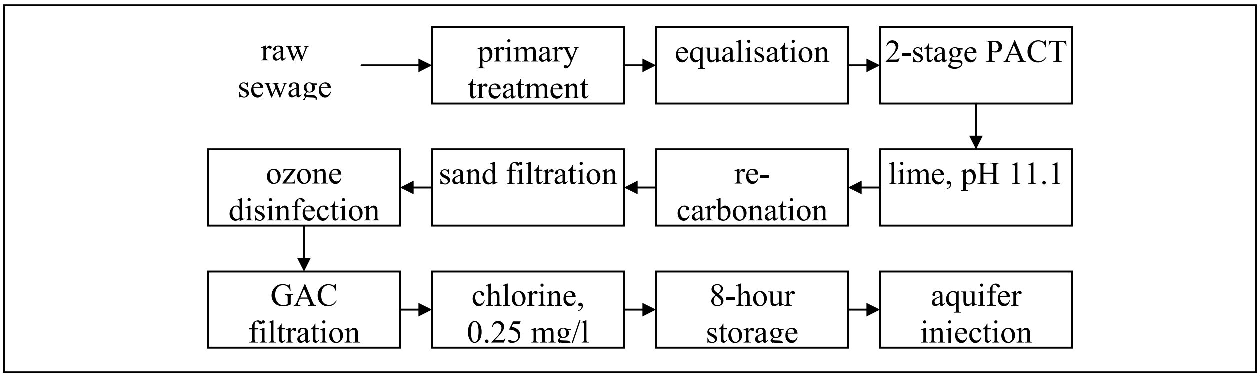


*Figure 3: Schematic of EL Paso, TX treatment process (after Rice, 1997)*

**Micro-organisms and their protection means**

Over 100 viruses excreted in human faeces have been reported in contaminated water, any of which could cause a waterborne disease. Intestinal parasites, enteric bacteria and viruses are organisms of the greatest concern for human health (EPA, 1986). Therefore, discharging wastewater without disinfection poses a direct threat to human health. Figure 4 details some of the more common micro-organisms found in wastewater with their associated disease. There is insufficient data to determine the actual health hazards, however, there is evidence that enteric pathogens can cause infections at exposure levels found in undisinfected wastewater (EPA, 1986).

| **Organism** | | **Disease Caused** |
|---|---|---|
| Bacteria | *Escherichia coli (enterotoxigenic)* | Gastroenteritis |
| | *Leptospira (spp.)* | Leptospirosis |
| | *Salmonella typhi* | Typhoid fever |
| | *Salmonella (=2,100 serotypes)* | Salmonellosis |
| | *Shigella (4 spp.)* | Shigellosis (bacillary dysentery) |
| | *Vibrio cholerae* | Cholera |
| Protozoa | *Balantidium coli* | Balantidiasis |
| | *Cryptosporidium parvum* | Cryptosporidiosis |
| | *Entamoeba histolytica* | Amebiasis (amoebic dysentery) |
| | *Giardia lamblia* | Giardiasis |
| Helminths | *Ascaris lumbricoides* | Ascariasis |
| | *T. solium* | Taeniasis |
| | *Trichuris trichiura* | Trichuriasis |
| Viruses | *Enteroviruses (72 types, e.g., polio, echo, & coxsackie viruses)* | Gastroenteritis, heart anomalies, meningitis |
| | *Hepatitis A virus* | Infectious hepatitis |
| | *Norwalk agent* | Gastroenteritis |
| | *Rotavirus* | Gastroenteritis |

*Figure 4: Infectious agents potentially present in untreated domestic wastewater, (EPA, 1999)*

The EPA (1986) defines 4 pathways by which transmission of these can occur:

- direct ingestion of untreated water
- direct ingestion of treated drinking water
- ingestion of aquatic food species infected with pathogens absorbed from contaminated waters
- invasion resulting from skin contact with contaminated water.

These micro-organisms have various methods of protection that must be over-come in order to achieve disinfection. The most common means for this are by the use of:

- chemical agents (e.g. Cl, $O_3$, $H_2O_2$, etc..)
- physical agents (e.g. heat and light)
- mechanical means (e.g. screens, filters, etc..)

| **Micro-organism** | **Description** |
|---|---|
| Bacteria | ca. 0.2 - 10 µm in length.<br>Unicellular, lacking a distinct nuclear membrane, but with an unique cell wall (complex polymers of polysaccharides & amino acids)<br>Coliform bacteria are commonly used as indicators of faecal contamination & presence of pathogenic species |
| Parasites | - protozoa ca. 2 - > 60 µm<br>Unicellular with endoplasm & protective layer of ectoplasm<br>- helminths (worms) |
| Viruses | ca. 0.01 - 0.3 µm in cross-section.<br>Nucleic acid core surrounded by an outer coat of protein |

*Figure 5: Micro-organisms*

The defences can be overcome in the following ways:

1) Diffusion
- through the protective layer and cell wall of the micro-organism
- inside the cell

2) Oxidation
- impairment or rupture of the cell wall (electron-rich outer layer such as bacteria's)
- external enzymes and polysaccharides (cysts, spores, viruses)
- of the cell material (inside the cell)

3) Coagulation
- neutralisation of the "negative" surface charge of the organism
- reduction of the electrostatic repulsion

4) UV light
- cellular proteins and nucleic acids are strongly absorptive of far UV radiation (molecular absorption of radiation)
- the photochemical changes caused by this absorption are injurious to living cells.

**Disinfection - Main parameters**

The inactivation of micro-organisms by contact time and concentration of disinfectant is well described by the Chick and Watson's model:

Ln . Nt/No = -K . Cn . t

which led to the use of the C.t concept:

Cn . t = - (Ln Nt/No)/K

- No = initial count of micro-organisms
- Nt = count of micro-organisms surviving after time t
- C = disinfectant concentration
- n = coefficient of dilution
- t = time required to achieve a given inactivation level of a micro-organism exposed under defined conditions
- K* = coefficient of lethality, specific to the micro-organism

* depends upon the "oxidation potential" & "molecular diffusivity" of the disinfectant.

| **Disinfectant** | **E-coli (vegetative bacteria)** | **Poliovirus 1** | **Entamoebia hystolityca** |
|---|---|---|---|
| $O_3$ | 2300 | 920 | 3.1 |
| $Cl_2$ (HOCl) | 120 | 4.6 | 0.23 |
| $ClO_2$ | 16 | 2.4 | -- |

*Figure 6: Specific lethality "K" (for 99% inactivation, 20°C, pH = 7)*

**Chemical agents:**

Not only does ozone have a higher electrochemical oxidation potential than other oxidants but also a superior dose-effect curve with respect to disinfection. This means that to achieve the same disinfection effect in water as other oxidants, ozone is used in smaller amounts with shorter contact times.

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

| **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 |

*Figure 7: C.t values (mg.min/l) for 99 % (2 log) inactivation of micro-organisms at 5°C.*

Being the tri-atomic form of oxygen, ozone oxidises the substances in water with nothing other than oxygen atoms.

Ozone is a powerful oxidant that destroys micro-organisms through an irreversible physico-chemical action. Ozone does not have to penetrate the body of the micro-organism to inactivate it. On the contrary, the action of ozone is instantaneous and irreversible, first on the micro-organisms' protective wall and then on the semi-permeable membrane (Finch, 1999). Such action modifies the chemical structure of the micro-organism through a coagulation effect that causes a hindrance on any exchange of product with the outside. As a result, the micro-organisms "suffocate" to death or inactivation. The protective wall and the semi-permeable membrane are composed of molecules that are very rich in electron sites (ref. Microbiology for Environmental Scientists and Engineers by Gaudy & Gaudy). This favours a very selective, and therefore efficient, action of ozone. These physico-chemical reactions present extremely rapid kinetics (the corresponding half-life time of ozone is in the order of a second).

## Physical agent: Ultra Violet (UV) light

Ultra Violet radiation is commonly used in many countries for wastewater disinfection since treatment with ozone is regarded as more expensive and complex. However, this is not necessarily a true assessment.

Unlike ozone, UV rays must penetrate the cell in order to be absorbed by the in-tra-cellular nucleic acids. These acids are the sites where the UV rays can kill or inactivate the micro-organism (EPA, 1986). In addition, UV rays do not necessarily cause irreparable damage; it has been proven that with UV there is always a non-negligible degree of reactivation. This is very important when required to reach inactivation levels of 3 log (99.9 %) or more. For certain micro-organisms such as Cryptosporidium Parvum and Giardia extremely high UV dosages are necessary.

Ozone does not propagate in straight lines but diffuses in all directions, even in-side flocs where it can reach hidden micro-organisms, whereas UV ray dispersion is negligible. It has even been demonstrated that the micro-organisms seek shelter from UV rays inside the flocs.

### Economics: ozone compared to UV

Economics are also of major importance when considering a treatment plant. An ozone installation needs only few spare parts and preventive maintenance is very simple and can be easily planned. The maintenance costs of an UV installation can be very high due to:

- loss of power of the UV lamps and therefore replacement of them, usually within one year
- frequent mechanical cleaning of the lamps (sometimes even daily)
- chemical cleaning because of inorganic scaling (sometimes weekly)
- difficulties in disposing of the spent UV lamps (mercury elimination!)

## Other beneficial impacts of ozone

Many properties of ozone, other than disinfection, are important for wastewater treatment and their dual application can improve the economics of a particular scheme. For example, using ozone for colour removal will give the additional benefits of disinfection and increased dissolved oxygen content in the effluent. Off-gases can also be recycled to earlier stages in the treatment process (Rice & Browning, 1980). Details of some further benefits of ozonation are given below.

Oxidation

Wastewaters contain a significant amount of oxidisable contaminants, giving ozone a number of applications. Generally, if an organic is resistant to oxidation by ozone it will be resistant to oxidation by other oxidants (Rice & Browning, 1980).

**Oxidation of inorganics:**

| | |
|---|---|
| *cyanides, cyanates and thiocyanates* | Gold & silver mining, electro plating, iron & steel manufacturing, in certain organic chemicals (nitriles & cyanohydrins)<br>Thiocyanate is oxidised to cyanide. Rapid oxidation of free cyanide ions and many stable metal cyanide complexes to less toxic cyanate ions |
| *ammonia and nitrites* | Sewage treatment<br>Ammonia is not readily oxidised. Nitrite ions are oxidised rapidly. |
| *sulphides, sulphites and thiosulphates* | Sulphide: tanneries, petroleum refineries, iron & steel industry, etc<br>Sulphites & thiosulphates: photoprocessing, textiles<br>Sulphide ions are oxidised to sulphite and finally sulphates |
| *cations of Mn (II), Fe (II), Hg (I), As, Al, Pb, Ni, Cr, Cu, Co, Ba, Zn & Cd* | Paint & varnish industry, photoprocessing, etc.<br>Oxidised to less soluble, higher oxidation states for removal by filtration or settling. |

**Oxidation of organics:**

| | |
|---|---|
| *phenols* | Chemicals, plastics & synthetics, petroleum refineries, iron & steel (coke) plants, soaps & detergents, photoprocessing, pulp & paper, textiles, etc.<br>Generally oxidised very easily, although complete oxidation to carbon dioxide and water may not occur. |
| *pesticides* | Agriculture, etc.<br>Some are oxidised completely, others ca. 90% and some are hardly affected. Used in combination with hydrogen peroxide hydroxyl radicals are produced that result in the effective destruction of compounds that resist ozone alone. |
| *colour and odour* | Textiles, plastics & resins, sewage, etc.<br>Generally organic macro molecules with conjugated carbon-carbon double bonds cause colour. Ozone cleaves these double bonds removing > 90% colour. Unpleasant odours can be removed by partial oxidation yielding smaller molecules. Hydrogen sulphide, phenols and trichlorphenols are also easily destroyed. |

Other oxidants, e.g. chlorine, may transform some substances with weak odour characteristics to substances with strong odour:
phenols to chlorophenols
precursors of TriHaloMethanes (THM).

Reduction of COD and BOD

During ozonation of secondary effluent the ozone carrier gas is introduced into the liquid by diffusion. This may result in a flotation process. If in the contacting chamber a skimming system (usually showers) is provided the foam containing SS (suspended solids) and the destabilised colloidal matter can be removed. Sewage ozonised in such a manner shows a considerable reduction in COD, SS, TDS (Total Dissolved Solids) and turbidity.

Ozone partially oxidises organic materials: large molecules and refractory materials are broken down into smaller biologically degradable molecules that can be removed by

- filtration over sand or activated carbon (which may in turn develop a biological activity)
- filtration with any other biological system (which is particularly efficient with a fixed bed biofilter)

## Conclusions

Ozone emerges as a very versatile solution offering the highest efficiency in the treatment of effluents. It allows the production of an effluent with no micro-organisms, no colour, no odour, low COD level and suitable for discharge into the environment, use in agriculture or return to the process. Moreover, there is a true destruction and not a displacement of the pollution.

Combined with biofiltration, ozone provides an optimised chemical and biochemical oxidation. Unlike systems that only displace pollution by producing large amounts of sludge (e.g. precipitation with salts and flocculation with polymers) or by producing a concentrate of this pollution (e.g. with membranes), ozone really eliminates the pollution and produces only a small amount of biological sludge.

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