# Wastewater - Ozone Treatment

Wastewater Treatment Processes (WWTP) are used to treat municipal as well as industrial wastewater to meet effluent standards prior to discharge in the natural environment. Wastewater discharges from industrial sources contain a wide range in levels of COD, BOD, TSS and other emerging contaminants (i.e. pharmaceuticals, aldehydes, glycol, amines, alcohols, complex proteins, etc). This includes process water from industries such as textile plants, dairies, breweries, pharmaceutical industry, paper & pulp, cosmetic, chemical and other production facilities.

The major contaminants found in wastewater are biodegradable organic compounds, volatile organic compounds, xenobiotics, metal ions, suspended solids, nutrients such as phosphorous, nitrogen, microbial pathogens and parasites. The approximate composition of organic carbon found in typical sewage wastewater are carbohydrates (11-18 %), proteins (8-10 %), free amino acids (0.5-1.5 %) fatty acids (23-25 %), dissolved organic acids (7-11 %) and other organic compounds (25-28 %). In addition, some water contaminants may be released in the surrounding air generating odours. A water contaminant becomes an odorant when it combines a high volatility with a pungent odour. Odours problems are common for wastewater treatment plants due to the abundance of the odorous contaminants. Typical examples are sulphur compounds (H2S and mercaptans), amines, ammonia and organic compounds such as skatole and indole. A top view of a complete wastewater treatment solution can be found below:

# Primary treatment

## Primary sedimentation

Sedimentation is a primary step which involves flocculants such as iron salts, aluminium, polyelectrolytes and lime for precipitation to settle solids from water by gravity. The effluent from primary treatment will typically contain considerable organic material and will have a relatively high biological oxygen demand (BOD). The average particle size range found in wastewater are found below:

| Particle size | Dissolved |
|---|---|
| **(µm)** | <0.01 |

Around 50% of the raw wastewater COD and BOD can be removed as a part of the settled solids. Settled sludge is typically treated further in the plant's sludge handling steps.

## Odour emissions from primary sedimentation

Odour emissions are quite common in this step. Since the primary sedimentation is the first step of the wastewater treatment process, the concentration of the odorous contaminants is the highest, leading to odour emissions in the surroundings. In the following steps of the treatment process, the odour emissions tend to decrease either because the contaminants are removed or because they were emitted previously.

## Ozone pre-treatment

Ozone has a complex impact on water/wastewater parameters – it reduces colour, improves taste, odour, kills bacteria, viruses, oxidize iron, manganese, cyanide, phenol, benzene, chlorophenol, atrazine, nitrobenzene and other pollutants. Ozone application shall increase the biodegradability of wastewater and the COD:BOD ratio from an industry water is shown as an example below:

| Parameters | Raw water before ozonation | Raw water after ozonation |
|---|---|---|
| **COD** | 5000 | 4500 |
| **BOD** | 200 | 2000 |

As seen in the table above the ratio of COD/BOD and biodegradability was increased 10 times due to ozonation. This is one of the potential application in treatment of complex industrial wastewaters prior to the biological process.

# Secondary treatment

This is known as biological or activated sludge process and involves the use of microorganisms to breakdown organic pollutants, total nitrogen content and phosphorus. This process involves aerobic, anoxic and anaerobic treatment through various technologies and design such as Sequential Batch Reactors (SBR), conventional treatment or Membrane Bioreactors (MBR). Aerobic treatment utilizes aerobic heterotrophic bacteria to break down BOD and ammonia-N and organic-N. This produces nitrate which can then be converted into nitrogen gas through anoxic treatment:

| Process | Reaction |
|---|---|
| Nitrification | $NH4^{+} + O2 \rightarrow NO2^{-} + 2H^{+} + H2O$<br>$NO2^{-} + O2 \rightarrow NO3^{-}$ |
| Denitrification | $NO3^{-} \rightarrow NO2^{-} \rightarrow NO \rightarrow N2O \rightarrow N2$ |

Anoxic treatment, as opposed to aerobic treatment, is characterized by an oxygen free environment, where bacteria must use oxidized nitrate for respiration. Ozone can play an important part in avoiding undesirable filamentous bacteria in the biological process. See below for more information.

Anaerobic treatment can be incorporated upstream from the aerobic and anoxic zones in order to achieve a net reduction in phosphorus.

Most of the readily biodegradable material is removed during the biological process and non-biodegradable material remains in the effluent. The net growth of biomass in the biological treatment process is removed through secondary sedimentation as Waste Activated Sludge (WAS). The remaining settled sludge is recirculated.

## Ozone Treatment of Return Activated Sludge (RAS)

MLR is an internal recirculation from aerobe to inox tanks and RAS is from secondary sedimentation to incoming flow from primary treatment.
The high water content, compressible and colloidal nature of the sludge are common characteristics found in WWTP. Filamentous bacteria are a normal part of the activated sludge microflora while excessive long filaments lead to sludge bulking and prevent flocculation. Using ozone in the RAS flows promotes the growth of floc forming bacteria and inhibit the activity of filamentous bacteria which enhanced sludge bulking and sedimentation. Low concentration of dosage of ozone can be used as an approach to promoting floc formation and inhibit the activity of filamentous bacteria and sludge bulking during process.

## Industrial Waste effluent (BOD/COD) ozone treatment

Common sludge thickening process by physical means are chemical settling, gravity settling, floatation, centrifugation, gravity belt and rotary drum. The sludge thickening process increases the portion of the liquid fraction from the sludge. These liquids have high COD and BOD values depending on the raw materials used in process industries. Typically COD range for chemical process wastewaters are between 400 – 40 000 mg/L and domestic wastewaters in the range of 100 – 450 mg/L. Generally COD above 350 mg/L range requires additional treatment and more information can be found in section 6 below. Please click here to read more about BOD and COD treatment with ozone.

# Sludge handling

## Ozone treatment of digested sludge

Anaerobic digestion is a sequence of biological processes in which microorganism breakdown biodegradable material in the absence of oxygen. During anaerobic treatment about 50 % of the organic matter in the sludge is susceptible to biodegradation into biogas, the other half of the organic material being more recalcitrant and degrading slowly. Sludge ozonation leads disintegration of complex organic substances into bio-degradable low-weight molecular compounds, which increases the biogas yield.

## Ozonation of thickened sludge permeate

Digested sludge typically contains 2-3 % total solids. This sludge requires thickening by mechanical means through a centrifuge or screw press, which leaves around 20 % dry solids. This process leaves highly concentrated waste liquid which is suitable to treat by ozonation if it cannot be reintroduced to primary treatment. For example food and beverage manufacturing facilities typically generate high strength waste streams as a by-product from their manufacturing operations.

## Ozone treatment of biogas odour

Biogas facilities often use manure and meat scraps to produce biogas. Biogas typically refers to a mixture of different gases, primarily methane and CO2, produced by the breakdown of organic compounds. In this step, sulphur-based compounds (such as H2S and mercaptans) are produced, resulting in high odour emissions due to their low odour threshold. As a solution, ozone oxidizes these compounds, significantly reducing odours with no harmful by-products. This leads to improved air quality in the surroundings as well as improved work environments.

# Tertiary treatment

The purpose of tertiary or advanced treatment is to provide a final step to raise the effluent quality or as a disinfection polishing step.

Tertiary treatment may not be needed to all wastewater treatment plants and it varies from one plant to another, depending on the type of water contamination. Some common advanced WWTP include removal of nutrients, non-biodegradable organic matter, suspended solids and toxic materials. Among other technologies commonly used methods are filtration, MBR, RO, UV and AOP. These will be covered in more detail in the following sections.

## Filtration

The most common granular media used in filtrations are sand and activated carbon. The important factors for pollutant removal include the amount of media in the column and the contact time.

| Advantages | Disadvantages |
|---|---|
| Simple to setup | Frequent clogging/filter changed |
| Broad range in pore size or surface area | Reduces the contact on the surface due to accumulation of bacteria over time |

Ozone can be used as a pre or post treatment step to filtration that break down the particles and improve the quality of water.

## Reverse Osmosis (RO) ozone permeate

RO is often used in commercial and residential water filtration. The water is moved across the membrane against the concentration gradient, from lower to higher concentration.

| Advantages | Disadvantages |
|---|---|
| Removal of both good and bad ions | Frequent clogging and chlorine concentration damages the RO system |
| Determines the taste of water | Efficiency reduces over period of time |

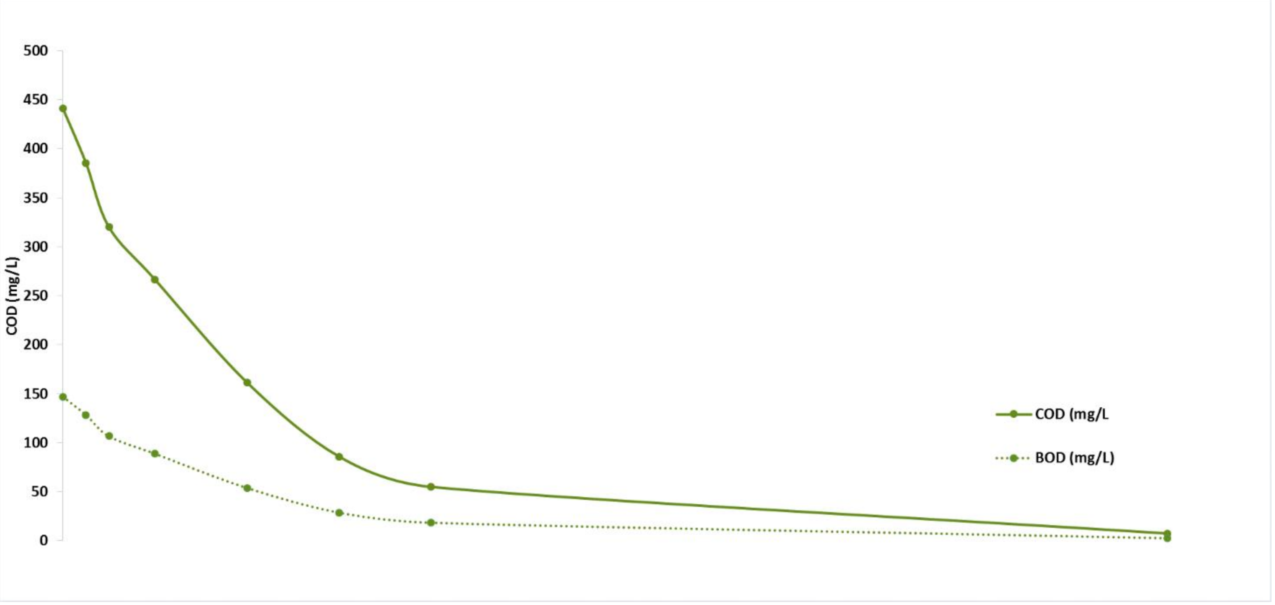
Ozone is an optimal method to disinfect or treat further the RO permeate to reclaim the water for other purposes or to comply with very high effluent regulations.

### Ozone disinfection

Disinfection of water using ozone is advantageous compared to more traditional methods, such as chlorine or UV disinfection. Ozone effectively breaks down the lipid layers in the cell membrane. Firstly, ozone is more effective at deactivating viruses and bacteria than any other disinfection treatment, while at the same time requiring very little contact time.

# Municipal wastewater treatment with ozone

The below graph is a typical example from treated wastewater using ozone as a one-step technology in reduction of COD and BOD levels at our pilot system.



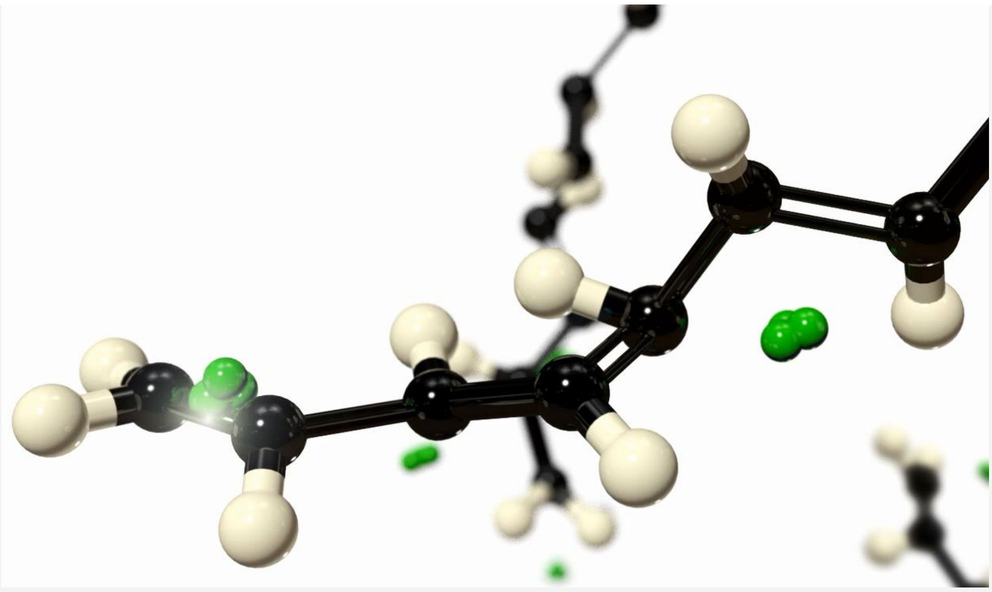

# Ozone Water Disinfection

Ozonetech offers premium disinfection technology through our in-house design and production of ozone generation systems. The ozone system can be readily installed to a side-stream of an existing water treatment system or in-line. Ozonetech also offers complete water treatment systems. Therefore we have experience in established technologies like UV-treatment and chlorination. The following text will provide some fundamentals in water disinfection to give a better understanding of the best available technology for different cases.

## Ozone advantage in water disinfection

Disinfection of water using ozone is advantageous compared to more traditional methods, such as chlorine or UV disinfection. Firstly, ozone is more effective at deactivating viruses and bacteria than any other disinfection treatment, while at the same time requiring very little contact time, thus reducing the overall treatment residence time while simultaneously leaving no chemical residues.

Due to the high oxidation potential, ozone will effectively degrade microbes and virus, causing cell membrane rupture and decomposition of essential biomolecular components in for example bacteria. As can be seen in the image below ozone can be used to oxidize hydrocarbons of cellular lipid bi-layers to kill contaminant microbes.



Hydrocarbon-ozone oxidation

There are essentially no harmful residuals from ozone use, as ozone undergoes a natural decomposition in water. Ozone treatment also prevents re-growth of micro-organisms, provided that the other processes in the disinfection process have been successful in reducing particulates in the wastewater stream. Ozone is also produced on site and does not require shipping or handling, thus removing complications like safety and environmental issues associated with chemical handling.

## Disinfection efficiency

As already stated above ozonation will enable efficient disinfection. The disinfection efficiency is commonly measured using the CT-value (concentration multiplied by time). In the image below a comparison between ozone and chlorination alternatives is shown.

Ozonation provides protection against essentially all toxic and harmful unwanted microbes. In the table below the CT-values for a range of germs are listed.

| Microorganism | Required dose, CT-value (mg/min/L) |
|---|---|
| *Bacillus* | 0.1 |
| *Clostridium botulinum* spores | 0.4 |
| *Cryptosporidium* | 7 |
| *E. coli* | 0.5 |
| *Encephalomyocarditis* virus | 0.25 |
| *Giardia* cysts | 0.5 |
| *Legionella pneumophila* | 0.1 |
| Polio virus type 1 | 0.5 |
| *Pseudomonas* | 1.5 - 2 |
| *Salmonella* | 0.1 - 0.4 |
| *Staphylococcus* | 1.5 - 2 |
| *Streptococcus* | 0.1 |

In order to compare various disinfection agents, a brief summary table is presented below for various common types of microbes typically used for benchmarking by the US EPA and WHO for disinfection efficiency among different methods.

*Benchmarking table for comparison of various disinfection agents and their efficiencies using CT-value (mg/min/L)*. Adopted from US EPA, CDC and WHO.*

| Type | Log inactivation | Ozone | Hypochlorite | Chlorine dioxide | Free chlorine | Peracetic acid (PAA) |
|---|---|---|---|---|---|---|
| *E. coli* | 2 | <0.02 | 25-30 | <1 | <0.05 | 25-30 |
| Viruses | 4 | <0.1 | <0.1 | 25-30 | 6 | Scarce studies |
| Protozoa | 3 | 1-2 | 10-20 | 15-25 | >100 | Scarce studies |

**It is important to note that the measurability of CT-values are not exact and that research reports different inactivation efficiency, but with consistent relative values. Use the table above as indication.*

Generally it can be said that spores are much more resistant. They generally show CT-values about ten to fifteen times higher than the active form. It is also important to mention that in most cases there is a disinfection "threshold". Up to this point the treatment will have a limited or low effect on the microorganisms. However above the threshold value essentially all microbes of the same species will be destroyed.

## Common water disinfection technologies

There are a variety of technologies to disinfect fluids and surfaces. Ozonetech can supply several disinfection technologies with the emphasis on environmental friendly solutions. These technologies are:

- Ozonation - Dissolving a low concentration of ozone into the water, providing rapid and efficient water disinfection.
- Ultraviolet (UV) - Irradiating the water with UV-beams.
- Chlorination - Dosing chlorine compounds to the water resulting in a residual disinfecting chemical concentration.
- Other technologies include e.g. bromine, peracetic acid, iodine, copper and silver ions, potassium permanganate, phenols, detergents, hydrogen peroxide, ultrasonication, and heat.

Every technique has its specific advantages and its own application area. In the table below some of the advantages and disadvantages are shown. Attributes for each technology are ranked from 1 (weak) to 5 (strong):

| Technology | Ozone | UV | Chlorine Dioxide | Chlorine Gas | Peracetic Acid | Hypochlorite |
|---|---|---|---|---|---|---|
| **Environmentally friendly** | 5 | 5 | 3 | 1 | 2 | 1 |
| **By-products** | 5 | 5 | 2 | 1 | 2 | 1 |
| **Efficiency** | 5 | 3 | 3 | 2 | 2 | 2 |
| **Investment** | 2 | 3 | 4 | 4 | 4 | 4 |
| **Operational costs** | 5 | 4 | 3 | 4 | 4 | 4 |
| **Fluids** | 5 | 4 | 5 | 3 | 3 | 3 |
| **Surfaces** | 5 | 5 | 1 | 1 | 1 | 1 |
| **Residual Disinfection** | 3 | 1 | 5 | 5 | 4 | 5 |
| **Handling** | 5 | 4 | 3 | 3 | 2 | 2 |
| **SCORE** | 40 | 34 | 29 | 24 | 24 | 23 |

It is difficult to make a general comparison to represent all applications and water qualities. However, as can be seen in the table above, when comparing typical water disinfection attributes ozonation stands out as an environmentally friendly, robust, compatible, and effective water disinfection treatment.

In the table below a few applications can be found.

| Technology | Applications and Industries |
|---|---|
| Ozone disinfection | Process feed and effluent water<br>Drinking water<br>Ultra-pure water<br>Surface disinfection<br>Pharmaceutical industry<br>Swimming pool<br>Legionella treatment<br>Continuous residual disinfection og e.g. piping |
| UV disinfection | Process feed and effluent water<br>Drinking water<br>Ozone destruction<br>Ultra-pure water<br>Surface disinfection<br>Swimming pool<br>Legionella treatment |
| Chlorination | Drinking water<br>Swimming pool<br>Residual disinfection of e.g. piping |

## Disinfection prerequisites

Drinking water disinfection is linked to other water purification steps. Proper disinfection can only take place when the water is sufficiently pre-treated. In many cases the disinfection process is one of the final steps in a water treatment system.

In for example drinking water treatment the disinfection step is proceeded by screening, sedimentation, flocculation, and sand filtration. At this point the water will be suitable for final disinfection.

Dissolved and insoluble particulates should be removed from water, since they may cause disinfection by-products (especially when using chlorination) and also since the particles may contain substrate (food) for pathogenic growth. Moreover, microorganisms are harder to remove from water when they are adsorbed to particles. The concentrations of undissolved particles in water should be reduced below 1 mg/l prior to disinfection. Other chemical compounds from human or natural sources also influence the performance of the disinfection treatment. The substances may react with disinfectants to disinfection by-products. This may increase the amount of required disinfectant to remove microorganisms and virus. It will also lead to difficulties in maintaining a residual concentration.

# A wide range of industries

## Pharmaceutical industry

Due their complex molecular structure, pharmaceutical residues are becoming a growing problem in biological treatment plants. Ozone treatment is a proven technology to remove these micro pollutants directly at the production facility, hospitals or municipal wastewater treatment plants.

*Examples of treatment of active substances: paracetamol, codeine, propofol, diclofenac.*

## Process industry wastewater

Whether industrial process water from the oil industry, chemical production, recycling or the textile industry, wastewater typically contain compounds which are difficult and expensive to handle in order to comply with environmental regulations. Our technology provides a cost effective solution.

*Examples of treatment of active substances and parameters: amines, alcohols, aldehydes, oil, BOD, COD, TOC*

WWW.OZONTECHNIEK.NL

info@ozontechniek.nl

NL-4854PK  Breda   0161-434183