OZONE IN WASTE WATER TREATMENT

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Contents

Summary

The combination of biological treatment with ozonation is the most important approach to apply ozone in the field of waste water processing. Beside the synergistic effects of such process combination, which lead to oxidation of recalcitrant and inhibitory compounds or intermediates by enhancement of their biodegradability, the key for raising applicability is the improvement of the ozonation efficiency. An overview about the history and progress of full scale applications is given. Beside this option other applications are described and an overview of full-scale installations is given. Landfill leachate and industrial waste water are mostly processed, while treatment of municipal waste water is of increasing interest due to several benefits such as disinfection, decolorization and removal of persistent dissolved organic carbon (DOC), EDCs or pharmaceuticals for water re-use and groundwater recharge.

1. Introduction

As an indication of technical standard and civilization waste water is handled and processed for many different reasons. All these activities have in common that contaminants have to be degraded, changed in their constitution or removed. Three main technologies are relevant for this purpose:
(a) Degradation of contaminants by biological treatment
(b) Separation of contaminants by flocculation, adsorption or membrane technique
(c) Degradation of contaminants by chemical oxidation.

Among processes, which purify waste water by means of chemical oxidation, ozone treatment has established itself steadily increasing as a powerful, effective and economic oxidation step.

The reasons for this predominance are the manifold application options and the compliance with high level environmental requirements and the reliable technical equipment.

The reuse or discharge of waste water can be limited by color, odor and by the amount of COD, AOX and/or germs. All these parameters can be significantly reduced by using ozone. According to the limiting conditions, the necessary average ozone doses are as follows:

Color ($\alpha\lambda = 436\text{nm}$)	(down to< 7/m)	5-50 gO3/m³
COD	(down to < 20 mg/l)	50-150 g O3/m³
Germs	(down to < 10 CFU/ml)	0.1-5 g O3/m³
AOX	(down to < 100 µg/l)	50-150 g O3/m³

Figure 1 gives an overview on the relation between ozone dosage and different treatment effects. For the implementation of an ozonization into existing treatment processes in every single case the premises have to be considered individually.

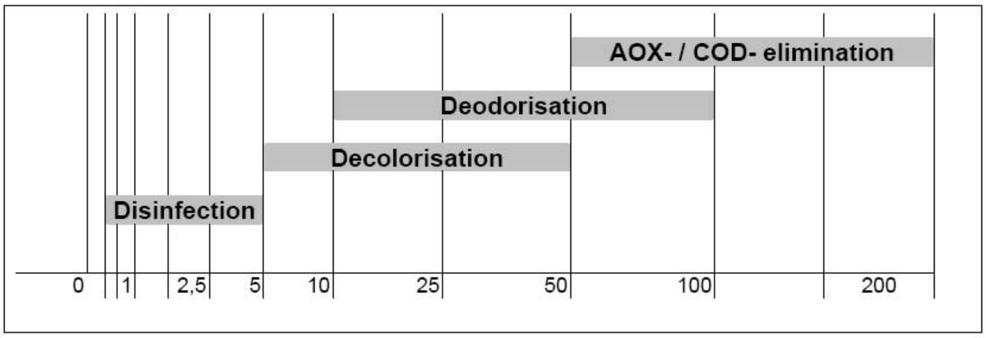


Figure 1. Spectrum of ozone activity

Figure 2 presents different options for ozone application at waste water treatment plants. Generally the following options can be specified:

- Treatment of secondary effluents
- Excess sludge treatment
- Off gas treatment

- Treatment of high polluted part streams.

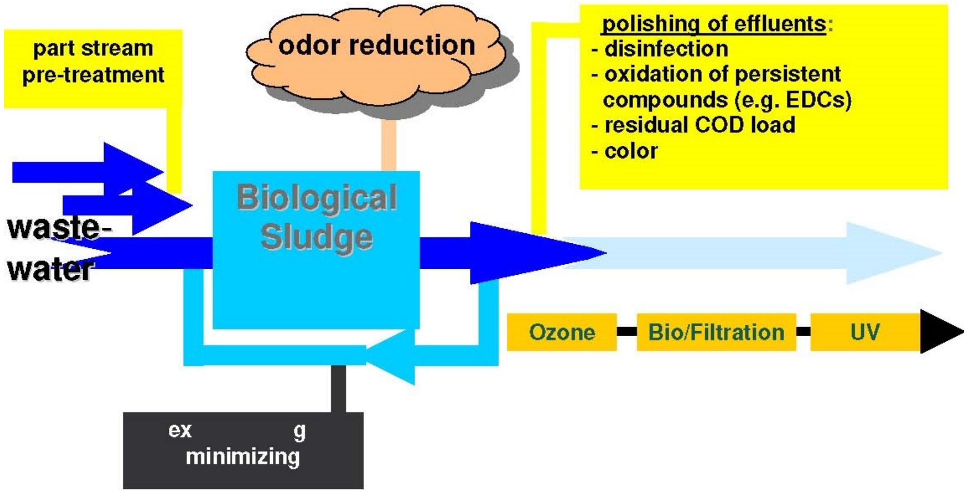


Figure 2. Ozone integration/applications at waste water treatment plants

2. Implementation of Large Scale Ozone Plants

For integration an ozone system onsite a municipal waste water treatment plant the following key points have to be considered:

- necessary ozone dose range (depends on the water matrix and the contaminants)
- calculation of the ozone demand (ozone dose * flow rate)
- components of an ozone system (ozone generator, gas supply, reaction system, off-gas handling)
- process control, online measurement.

The typical components of an ozone system are described in Figure 3.

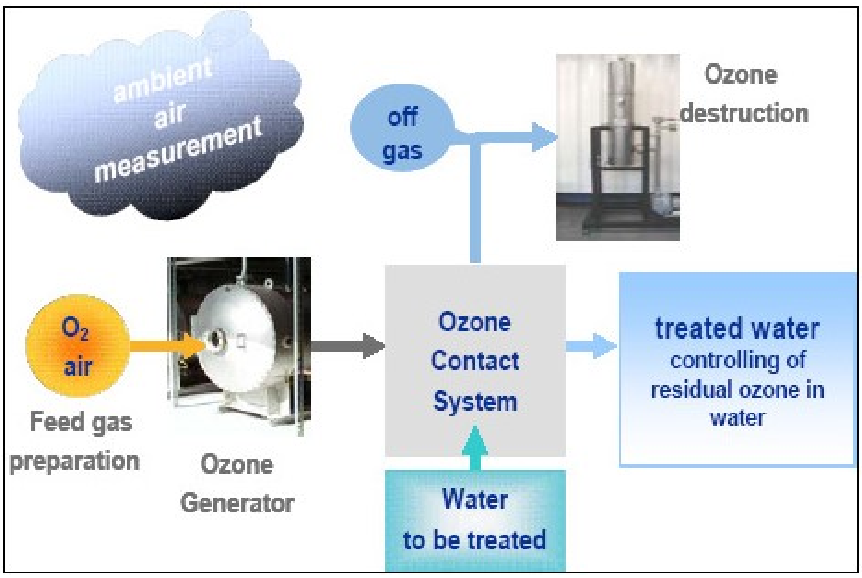


Figure 3. General layout of an ozone system

The ozone generator might be installed in a container or integrated in an existing building. The produced ozone gas can be transported through stainless steel pipes to the reaction chamber.

The feed gas for the ozone generator (either purified air or oxygen) can be supplied by a liquid oxygen tank, an air preparation unit or a PSA unit to produce oxygen onsite. The final decision for the best gas supply is depending on the availability of liquid oxygen, the cost of liquid oxygen, the energy cost and the amount of ozone to be produced.

Beside the generation of the ozone an appropriate design of the gas transfer and reaction system is important. Different gas transfer and reactor designs are known. In drinking water applications it is very common to use diffusers for the gas transfer and specific designed concrete basins as reaction chambers. This method is also used for the treatment of municipal waste water.

Beside the diffusers different type of injectors are used to mix the ozone containing gas with the water flow. Depending on water flow, required ozone dosage and the reaction kinetics various configurations are applied, e.g. side stream injection, main stream injection, plug flow pipe reactors and pressurized reaction tanks [*Roustan 2000*]. For the ozonation of secondary effluents the usage of diffusers and concrete basins could be favorable due to utilization of existing basins.

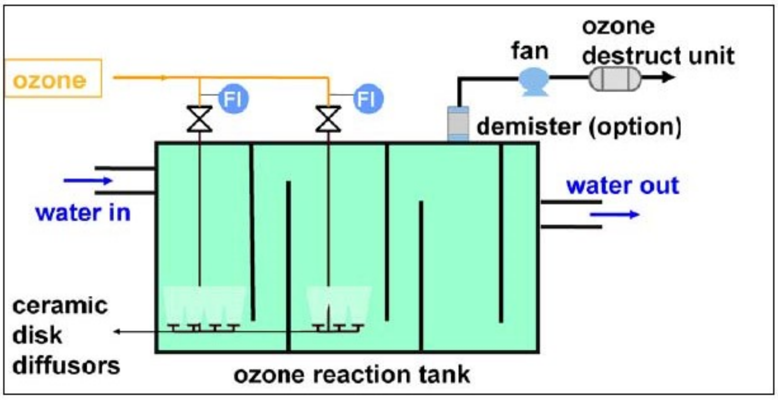


Figure 4. Layout of diffuser basins for ozone treatment

Possible online measurements for controlling the process could monitor the produced ozone mass (ozone gas concentration * feed gas flow), ozone concentration in the off-gas, dissolved ozone concentration after the reaction tank. These parameters can be measured and controlled readily. Without any difficulties the ozone plant can be operated at variable ozone dosages depending on the actual water flow rate.

3. Combined Biological Treatment and Ozonation

[*Ried, Mielcke 1999; Ried, Mielcke et. al. 2000; Ried, Mielcke, Wieland et. al. 2006*]

There are manifold ideas how to use oxidants, respectively ozone in the field of waste water processing. Nevertheless, under the aspect of technical and economic feasibility the most important approach is to combine the application of ozone with biological treatment steps.

On that way even high polluted waste waters, like landfill leachates or heavily loaded effluents from industrial production can be purified. The breakthrough of ozone applications in waste water treatment was during the beginning of the nineties. Approx. 10 combined ozone-biology applications including larger ozone systems up to 160 (4x40) kgO_3/h plants have been completed in 1992, e.g. in the textile industry for decolorization/tenside destruction and at landfill leachate treatment plants for removal of recalcitrant compounds.

At that time the post ozonation of biological pre-treated wastewater (BIO-OZONE) was used. It is interesting to note, that many of those ozone applications have started as ozone/UV based AOP processes, but by and by the UV systems were switched off due to the suitable treatment efficiency of BIO-OZONE alone.

Due to the relative high costs for production of ozone and the much lower costs for biological treatment the first application of the combination “biological pre-treatment – ozonation – biological post-treatment (BIO-OZONE-BIO)” had been installed at the end of 1992, shortly after first applications of post-ozonation [*Siemers 1995*]. In this landfill leachate BIO-OZONE-BIO application, biological post-treatment was realized by rotating disks, overgrown with biofilm.

Generally secondary effluents, containing non-further bio-degradable compounds are successfully treated by means of ozone to carry forward waste water processing. An advanced, further biological treatment step depends on the enhancement of biodegradability by the well-dosed usage of ozone. This application gains at partial-oxidation or “cracking” of intermediate dead-end compounds. The usage of the synergistic effects of this combination has led to the establishment of this very effective and economically successful procedure over the years (compare Table 2).

The next step of development for removal of recalcitrant compounds with first installation in 1995 was the BIOQUINT process, in which the ozonation is placed in a cycle loop around the second biological treatment step. This integrated ozonation process is similar to an OZONOBIO multi-step process and comes along the philosophy “*partial oxidation as low as possible and biological oxidation as high as possible*”, which enables lower ozone consumption and therefore a more cost-effective process. In order to better illustrate the relationships, Figure 5 presents a sample calculation, in which the corresponding COD degradation behavior is shown as well as the ozone mass required for the following possible combinations:
(1) biological treatment + ozonation
(2) biological treatment + ozonation + biological treatment
(3) biological treatment + ozonation + biological treatment + ozonation + biological treatment

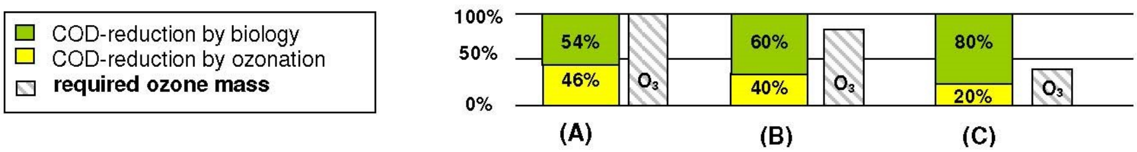
To simplify the calculation, the same initial and target concentrations are assumed for a flow rate of 1 m^3/h. Thus, it can be clearly illustrated that the ozone demand decreases from 2.375 kg ozone/h (A) to 1 kg ozone/h (C) by combining the two processing stages biological treatment and ozonation.

Obviously biologically degradable portion of the entire COD to be eliminated increases and the ozone containing portion to be degraded correspondingly decreases. This results in different ozone factors (proportional ozone demand for the elimination of 1kg COD) for the individual combinations, whereby the total COD load to be eliminated is considered taking also biological elimination into account. The requisite ozone factor decreases from 2.5 (A) to 1.1 (C). The BIOQUINT process, which combines biological filtration and ozonation in a cyclical process, showed up in practiced ozone factors lower than 1 kg ozone per kg eliminated COD. The ozone required can be reduced by more than half by using multi-step treatment schemes. The decreased ozone demand naturally has a positive effect on the investment costs for the ozone generators as well as on expenditures for oxygen and electricity [*Ried, Mielcke 1999*].

raw water 1 m3/h	COD [mg/l] (A)	COD [mg/l] (B)	COD [mg/l] (C)
supply	2,200	2,200	2,200
discharge biology I	1,100	1,100	1,100
discharge ozonation I	150	300	900
discharge biology II		150	500
discharge ozonation II			300
biology III			150

COD-reduction decomposition	2,050	2,050	2,050
COD-reduction biology (I+II+III)	1,100	1,250 (150+1100)	1,650 (150+400+1100)
COD-reduction ozonation (I+II)	950	800	400

required ozone mass (COD-reduction ozonation x 2.5)	[g/h] 2375	[g/h] 2000	[g/h] 1000



factor (ozone mass / COD-reduction with ozonation + BIO (II+III))	2.5	2.1	1.1

Figure 5. Example calculation for different combinations biological treatment + ozone

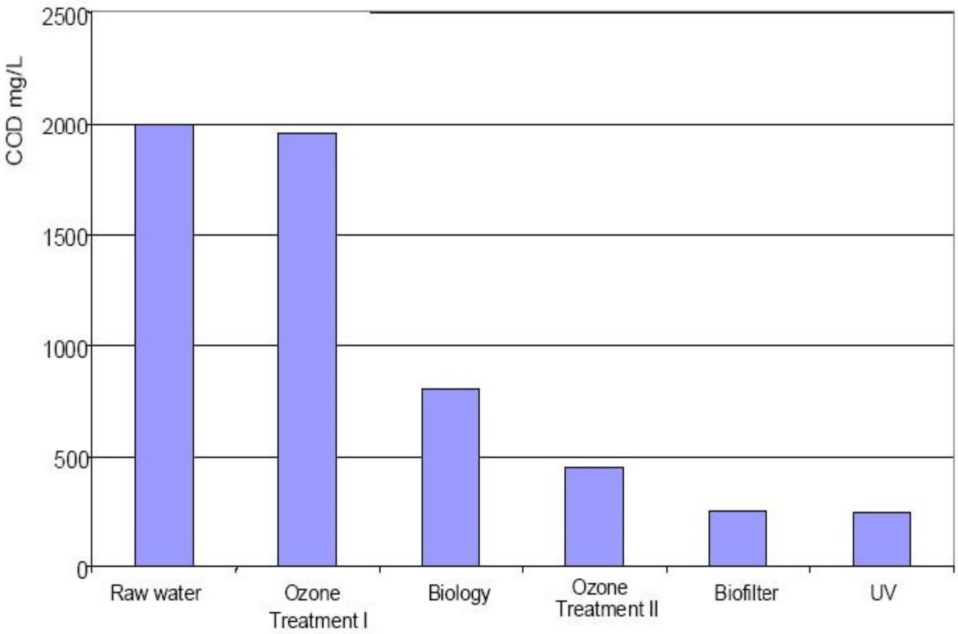
However for higher volumetric flow-rates and lower organic loading rates, e.g. in the chemical industry, the post-ozonation process BIO-OZONE seems to be more suitable due to easier operation (of different waste water characteristics based on production plan) related to the potential of less ozone consumption.

4. Industrial Waste Water Treatment

Many industrial waste water treatment plants utilize activated sludge biology as a final step of their treatment process. The biological step is able to reduce the biodegradable part of COD. The biological treatment efficiency can be disturbed by *toxic compounds* e.g. phenols in the raw water. In such cases it is recommended to use ozone in a pre-treatment step to destroy toxic compounds. For this application a typical ozone dosage is 50-100 g ozone /m³.

In the effluent of the biological step (secondary effluent) usually the remaining, not biodegradable COD can be still too high in order to meet specific limits for direct discharge or reuse purposes. At this stage it is promising to use ozone in combination with a subsequent biofiltration stage. Figure 6 gives an idea of the possible integration of ozone treatment into an existing industrial biological treatment plant.

In this theoretical example (based on practical data) the raw water COD is 2000 g/m³. By using an ozone dosage between 50 and 100 g/m³ toxic compounds can be reduced. E.g. the oxidation of phenol with ozone is very fast. Due to that a reduction of phenol is possible even with a high COD level in the raw water.



Ozone dosage	0	50-100 g/m³	0	400 -600 g/m³	0	0
effects	no	detoxification; e.g. phenol removal	biol. COD reduction;	partly COD reduction;	BOD reduction	disinfection
		odour /colour reduction	BOD reduction	cracking; decolorisation		

Figure 6. Treatment effects by using different techniques

In the effluent of the biological step the hard, not biodegradable COD might be 800 g/m³ (60% COD-reduction). For further practicable and economic treatment COD can be reduced to 400 g/m³ with an ozone dosage between 400 and 600 g/m³ (additional 50% COD-reduction).

By using a subsequent biofilter step after ozonation it is possible to reduce the COD for another 30 -40% down to 240 -280 g/m³.

The additional COD reduction in total due to ozonation and biofiltration is appr. 65 -70 %. Using UV technique subsequent to the biofiltration a final disinfection can be achieved.

4.1. Decolorization

In the huge field of industrial sewage treatment the removal of color is a single problem that can be solved quite easily by using just small amounts of ozone.

The necessary ozone dosage for color elimination dependents not only on the type of dye stuff, its concentration and the effluent concentrations, but also on the background load of COD.

For highly polluted effluents a pre-treatment to reduce the COD to a level as low as possible is therefore recommended prior to ozone oxidation, particularly to achieve low ozone consumption levels.

If the level of organic pollution of the waste water is low (*COD* = 150 -200 mg/l), high degrees of degradation of 80-90%, with reference to the colors yellow (436 nm), red (525 nm) and blue (620 nm), can be achieved with low ozone consumption levels (approximately 50 mg/l) and short reaction periods (about 10 minutes).

Colored effluents can be even reused as process water after ozone oxidation. The ozone treatment step provides additional benefits besides color reduction such as:

- disinfection
- reduction of unpleasant odors.

In March 2000 two large scale ozone systems with an ozone capacity of 13 and 7 kg/h were set in operation in order to reduce color and COD in a dye manufacturer‘s effluent. These installations followed a successful 2 month pilot plant operation performed on site in 1999.

The effluent parameters (inlet ozone plant) are: $Q = 25\,\mathrm{m^3/h}$, color = 2500 -5000 ADMI, *COD* = 250 -800 mg/l. Goal of the treatment is to reduce the color down to $ADMI < 400$.

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