

OZONIA

**OZONATION AND GRANULAR ACTIVATED CARBON FILTRATION
THE SOLUTION TO MANY PROBLEMS**

Extract from the
PROCEEDINGS
of the
FIRST AUSTRALASIAN CONFERENCE
of the
INTERNATIONAL OZONE ASSOCIATION
DOWN UNDER '96
Sydney, February 1996

OZONATION AND GRANULAR ACTIVATED CARBON FILTRATION THE SOLUTION TO MANY PROBLEMS

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Abstract

This paper explains how ozone is used in the purification of surface water to potable water both as the first treatment stage and as an intermediary stage for the reduction of organics and as a disinfectant. Taste and odour of the water are improved by the oxidation of both organic and inorganic impurities by ozone. Products resulting from algae metabolisms are shown to be easily oxidised by ozone. The oxidation mechanisms of these oxidation reactions are explained. The importance of the GAC (Granular Activated Carbon) filtration stage after ozonation for the removal of the by-products is highlighted and the complex way in which adsorption takes place is fully described.

Introduction

Ozone is the strongest oxidising agent, which is actually applied in many water treatment plants, without the disadvantages of chlorine. Mainly in Europe ozone has already displaced chlorine in almost all water treatment plants for preoxidation, main disinfection and degradation of organics. The same is happening in the paper pulp bleaching field. This tendency is on going, because ozone has many advantages in comparison with chlorine, without having the disadvantages of chlorine. These are the main reasons why ozone is so successful today.

Many different effects have to be mentioned and most of them are dependent on where the ozone is introduced and how much is applied. Two major places of introduction with different aims are realised today in water treatment processes as follows:

- Ozone as preoxidation
- Ozone as mainoxidation

For preozonation the main goals can be summarised as follows:

- Removal of soluble iron and/or manganese by oxidation
- Decoloration
- Removal of taste and odour
- Improved microflocculation
- Reduced trihalomethanes
- Decrease the trihalomethane-precursors
- Satisfy the spontaneous ozone demand
- Oxidation of inorganic substances such as cyanides, sulphides and nitrites.

For preozonation normally low doses are applied and a short reaction time in the order of 1 to 2 minutes. This is in accordance with the fast reaction taking place at this stage. Usually no or only small ozone residuals are determined in these applications.

- The main goals for a mainozonation can be summarised as follows:
- Bacterial disinfection
- Inactivation of viruses
- Oxidation of organic compounds, e.g. phenols, detergents, pesticides or other hardly biodegraded substances
- Conversion of COD to BOD
- Reduction of DOC, if a biological filtration step is installed downstream, e.g. Granular Activated Carbon (GAC), Anthracite or Slow Sand Filter
- Reducing the necessary dose for the network protection (chlorine, chlorine dioxide)
- Oxidation of complexes, such as EDTA and NTA.

A typical reaction time is in the order of 4 minutes or higher and the reaction rates are slow. To have a proper disinfection the so called c.t-value is applied.

This is achieved by maintaining an ozone residual of 0.4 mg/l during 4 minutes resulting in a c.t-value of 1.6 mg.min./l. It is known from practical experience that this would reduce the bacterial counts as follows:

- 3 decade reduction for Giardia cysts
- and a
- 4 decade reduction for Enteroviruses.

Additionally, hydrogen peroxide can be used to accelerate the removal of pesticides or other persistent organic compounds. In some cases the residual ozone is removed by the addition of hydrogen peroxide or simply by stripping with air.

Occurrence of taste and odour

The sensation of taste and odour are complementary. With the 3000 to 10 000 taste buds in the mouth, we are able to detect more readily the inorganic constituents in the water, while the sense of smell is more useful to detect organic constituents.

Taste and odour problems may occur in any potable water and are generally independent of season. Primarily these problems are associated with:

- The raw water
- The treatment method
- The distribution system
- Or any combination of these three.

The nature of the problem can be either:

- Inorganic compounds (e.g. Al, Fe, Mn, Zn, H₂S, CrO)
- Organic compounds from natural sources (e.g. algae, humic acids)
- Contamination of raw water by discharges from industry or agriculture.

Most inorganic substances exert an unpleasant taste at concentrations much lower than those required for acute toxic effects. For pesticides however the threshold taste value for detection is higher than the recommended guideline values.

Water treatment plants can convert weak odour substances into substances with a very intense odour. Example of this are amines and phenols, which will be converted to chloramines and chlorophenols by any chlorine treatment (pre- and/or post-chlorination).

Aquatic organisms have metabolic activity and can release some unpleasant substances. Two main algae species that are the origin of such substances are:

- Blue green algae (Cyanophyceae)
- Actinomycetes

The most dominant metabolites are Geosmine and Methylisoborneol (MIB), for which the structural formulas are given in Figure 1. Threshold levels for Geosmine are in the order of 10–20 ng/l giving an earthy odour.

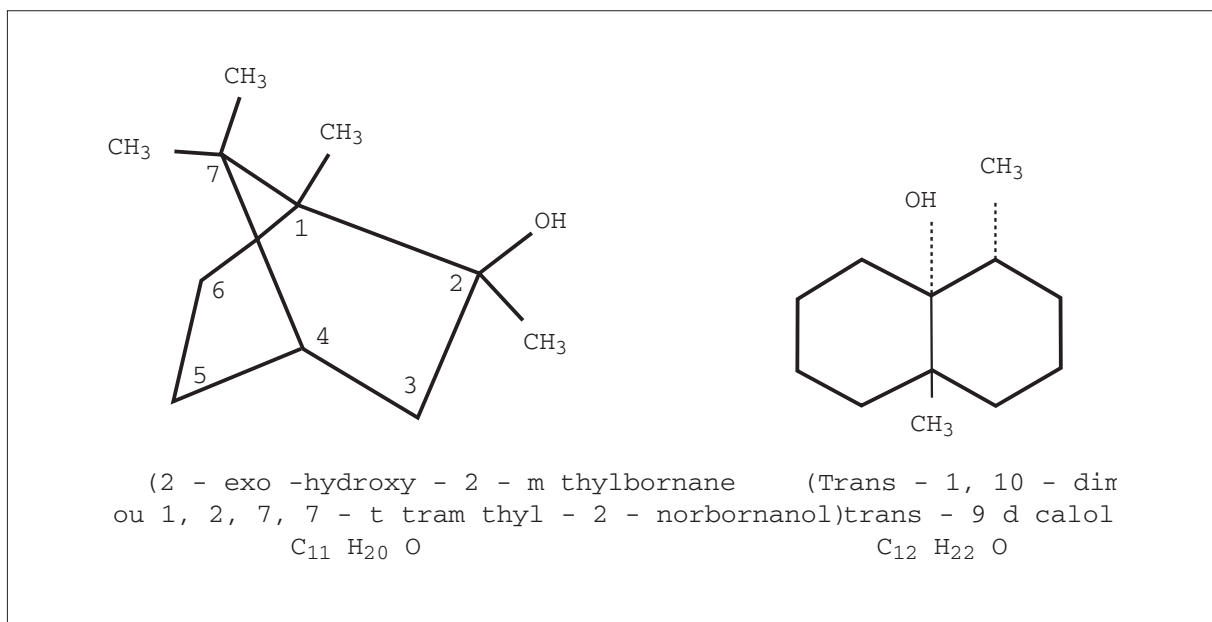


Figure 1: Molecular structures of 2-Methylisoborneol and geosmine

Further examples are the THM precursors which will be converted to THMs by the use of chlorine (prechlorination, mainchlorination or addition of chlorine at the end of the treatment process as network protection). Besides their unpleasant odour these substances are known to be carcinogenic.

Origin of odour

Algae not only synthesise their own matter but also release chemical mediators (metabolites) into the aquatic environment. High release rates of such chemicals appear especially during algae blooms or when the conditions of the nutrients are not in harmonic equilibrium.

According to the algae type the description of the odours are manifold such as:

- grassy, musty, garlic, fishy, oily, septic, bitter, spicy, cucumber, etc.

Furthermore, some of these chemicals are known to form trihalomethane precursors, which will cause taste and odour problems in drinking water treatment plants either directly or enhanced when chlorine is used for treatment purposes.

As far as taste and odour compounds are concerned they belong to a group of volatile organic compounds, with a molecular mass of up to 200 g/mole. Most of them are unknown but recently it has been

possible to identify some of the organic compounds released by the blue algae *Anabaena*.

As an example of this the plot of a gas chromatographic separation for the blue algae *Anabaena* is given in Figure 2 together with a list of 40 identified substances (see Table 1).

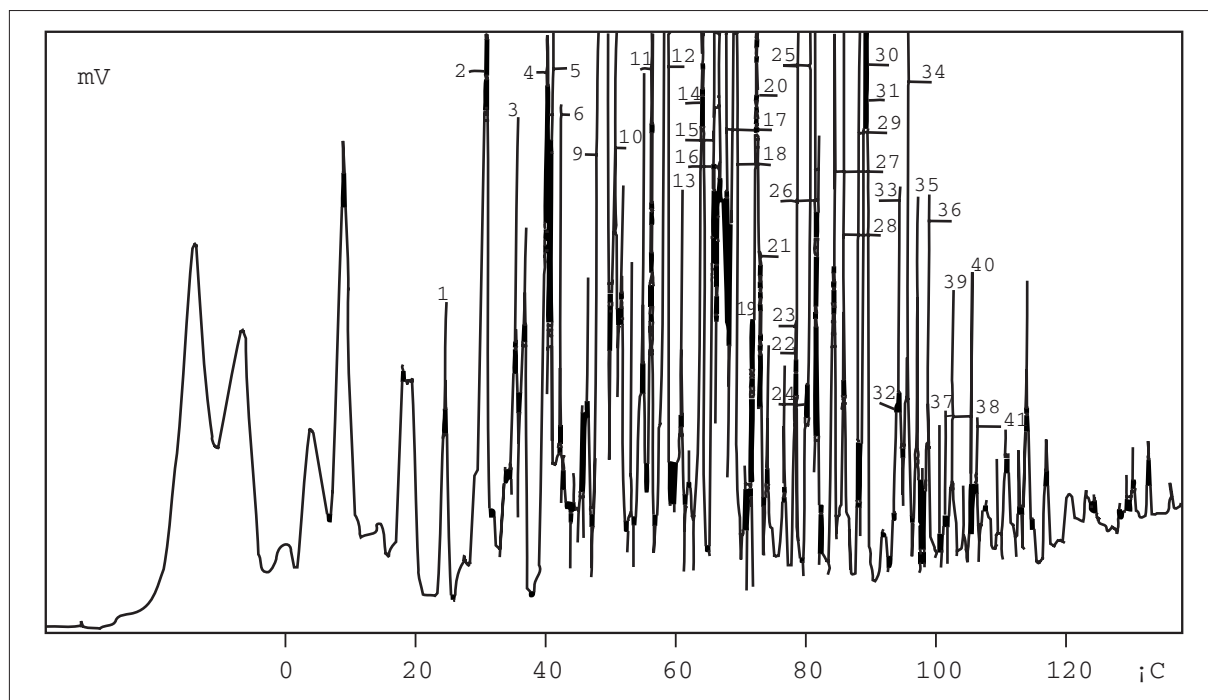


Figure 2: Separation of volatile compounds by GC from an Algae Bloom of *Anabaena* in LAke Constance (24m glass capillary, UCON 50 HB 1500, Carrier Gas H₂)

For the scope of this paper it is important to recognise that most of these compounds are either unsaturated olefins or aromatic compounds and therefore easily oxidised by ozone.

2	benzene	24	1,4 – ethylmethylbenzene
3	cis-1,2 dichloroethylene	25	1,3 – ethylmethylbenzene
4	pentanone – 3	26	limone
5	trichloroethylene	27	mesitylene
6	chloroform	28	1,2 – ethylmethylbenzene
9	tetrachlorethylene + toluene	30	pseudocumene
10	dimethyldisulfide	31,32,33&37–39	
11,12,17,18	monoterpene (isomeric)	35	C4 – benzene
14	ethylbenzene		
15	p-xylene	39	
16	m-xylene	34	hemelitene
20	o-xylene	36	indene
22	n-undecane		
23	n-propylbenzene	40	p-dichlorobenzene

Table 1: Identified compounds from *Anabaena* [3]

The applied ozone dose for the elimination of such odours is generally low, e.g. around 2 mg/l (Figure 3, curve A) as shown by the example of the River Seine water. During certain periods other organic matter appear in the raw water and the dose-effect curve is different (Figure 3, curve B). This curve corresponds to the evidence of odour compounds such as aldehydes being present.

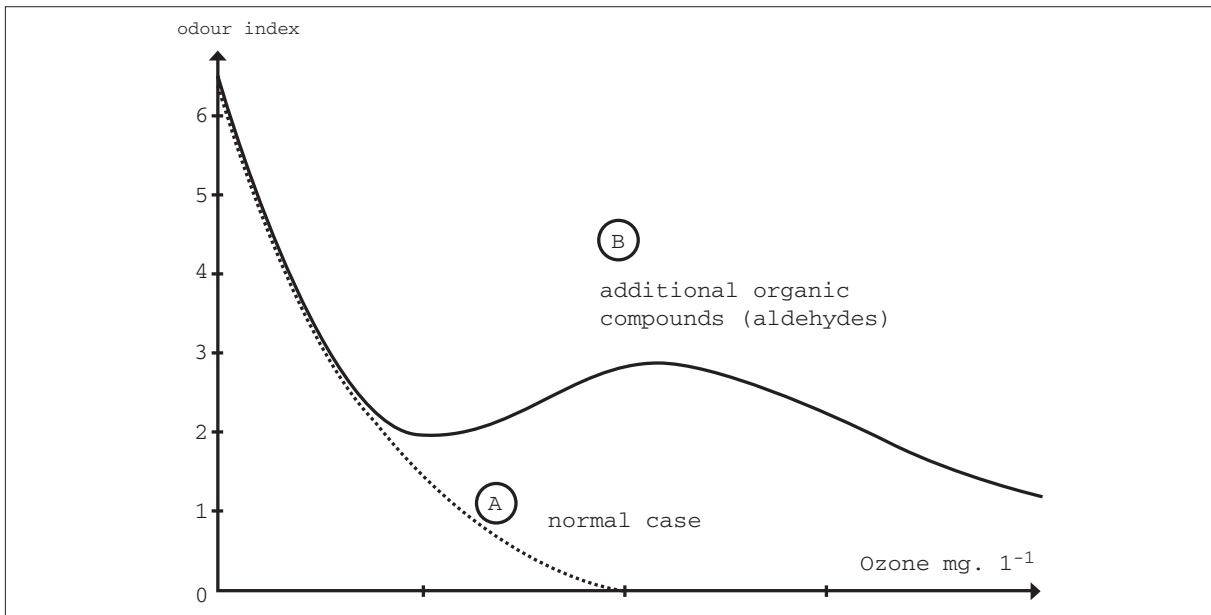


Figure 3: Influence of the ozone dose to the odour index

Oxidation of organic compounds

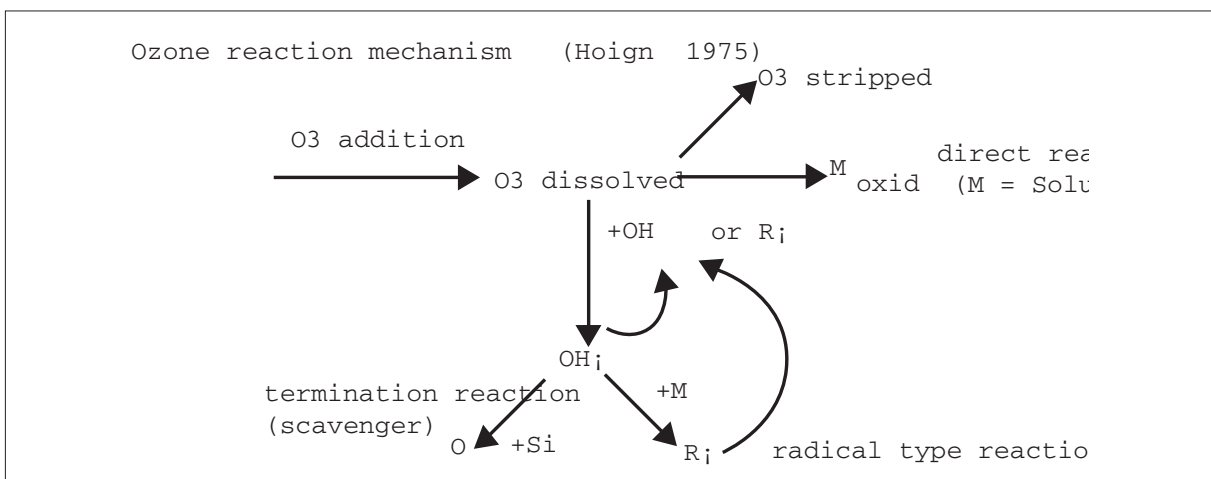
To understand the importance of the combination of ozone and GAC filtration it is necessary to explain in some words the reaction mechanism and their by-products.

The most significant reactions of ozone with organic matter are based on the cleavage of the carbon double bond, which acts as a nucleophile or a specie having excess electrons.

Ozone will always react in two different mechanisms:

- Direct reaction of ozone with organic compounds
- Reaction by free hydroxyl radicals.

This reaction model has been described by Hoigné in 1975 with the following sequences:



The consumption of ozone by direct reaction can be written as a pseudo first order reaction if the solute concentration is higher than the ozone concentration:

$$\frac{d[O_3]}{dt} = k_{O_3} [M] \cdot [O_3]_t$$

k_{O_3} : reaction rate constant (L.mole⁻¹.s⁻¹)
 M : solute concentration (mole.l⁻¹)
 O_3 : ozone concentration (mole.l⁻¹)

Depending on the chemical group of compounds a great range of reaction rate constants have been published.

Reaction rate constants of ozone and hydroxyl radicals are given in Table 2.

Compound	k, in L.mole ⁻¹ .s ⁻¹	
	O ₃	°OH
Olefins	1000 to 4.5 x 10 ⁵	10 ⁹ to 10 ¹¹
S-organics	10 to 1.6 x 10 ³	10 ⁹ to 10 ¹⁰
Phenols	10 ³	10 ⁹
N-organics	10 to 10 ²	10 ⁸ to 10 ¹⁰
Aromatics	1 to 10 ²	10 ⁸ to 10 ¹⁰
Acetylenes	50	10 ⁸ to 10 ⁹
Aldehydes	10	10 ⁹
Ketones	1	10 ⁸ to 10 ⁹
Alcohols	10 ⁻² to 1	10 ⁹ to 10 ¹⁰
Alkanes	10 ⁻²	10 ⁶ to 10 ⁹

Table 2: Reaction rate constants k of ozone and hydroxyl radicals with organic compound

It is important to notice that the direct reaction depends strongly on the chemical nature of the organic compound, whereas the radical type reaction is more or less independent. Furthermore, the reaction rate constant for the radical type reactions are a few orders of magnitude higher when compared to those of the direct reaction.

The mechanism of the cleavage of a double bond can be simplified in the following manner (Figure 4)

In this reaction chain the species of aldehydes or ketones appear twice as reaction products, the carboxylic acids only once. A further oxidation of these products will not take place easily because the reaction rate constants are low (direct reactions).

The aldehydes as well as the ketones are known to be nutrients for bacteria. It is therefore important to have a biological step after a mainozonation, as the formation of aldehydes and ketones are normally more important than after a preozonation.

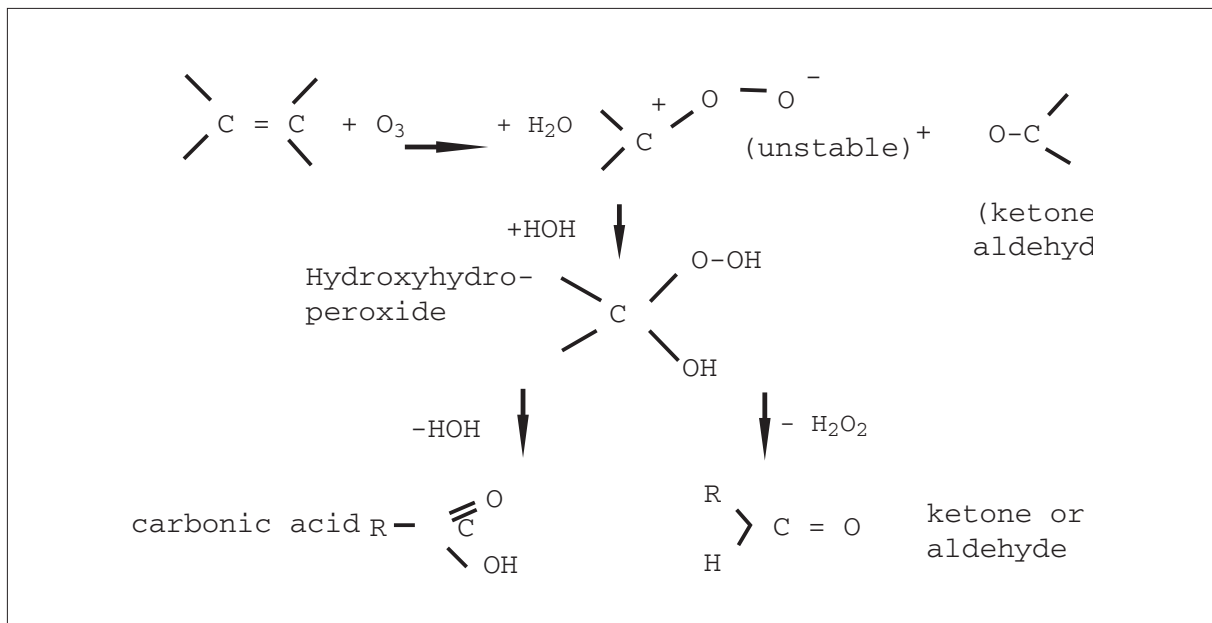


Figure 4: Direct oxidation reaction

The role of a GAC filter after ozonation in water treatment

A GAC filter after an intermediate ozonation has many purposes:

- To destroy the residual ozone in the water fed to the GAC filter – this takes place in the top few centimetres of the GAC filter
- To remove chemical compounds or ozonation by-products by adsorption
- To degrade such substances by biological activity on the surface of the GAC by bacteria.

In a GAC filter different competitive processes take place simultaneously:

- Fast adsorption
- Slow adsorption
- Biological effects and
- Biological effects enhanced by ozonation.

Between the fast and the slow adsorption there is competition. New GAC will first adsorb a lot of weakly adsorbed compounds, e.g. alcohols, ketones, aldehydes, acids, aliphatics and colloids. These compounds will then be displaced from the active carbon surface by more strongly adsorbed pollutants, e.g. aromatics, chlorinated aromatics, pesticides, chlorinated nonaromatics, and high molecular weight hydrocarbons. The displaced, weakly adsorbed material will be re-adsorbed further down in the filter. This phenomenon is called the “chromatographic effect”.

Three types of adsorption can be distinguished for a GAC filter:

- Exchange adsorption (electrical attraction of the solute by the adsorbent)
- Physical or ideal adsorption by weak van der Waals forces
- Chemisorption or chemical adsorption (chemical reaction of the adsorbate with the carbon).

In the water treatment application the primary mechanism is the physical adsorption, which is reversible followed by the chemisorption, which is generally considered as irreversible.

A GAC filter offers an excellent surface for biological activity. The rough surface provides numerous good places for attachment. Such biological activity has become evident in full-scale plants, showing that the amount of organic carbon removed is far beyond that which can be removed by adsorption alone (see Figure 5).

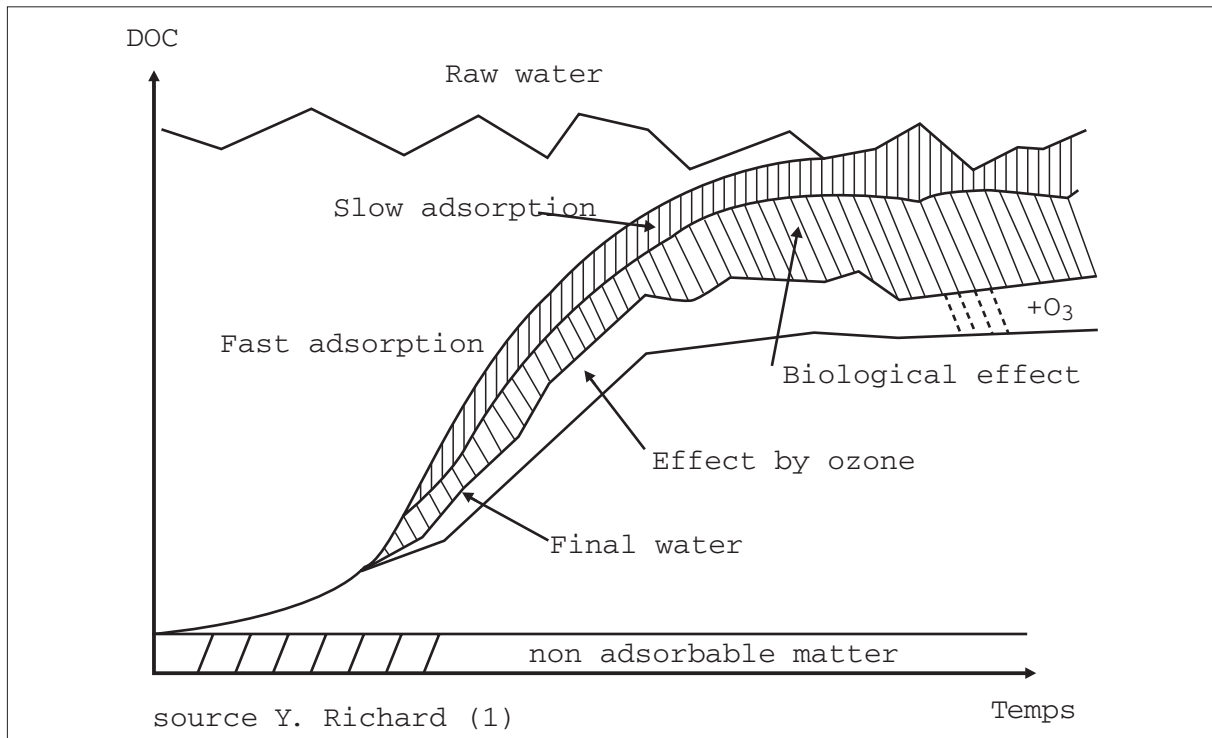


Figure 5: Elimination of organic matter

It is well established that an ozone step will produce aldehydes and ketones by oxidation of the carbon doublebonds. These products are nutrients for the bacteria which are always present in a distribution system (tolerance value in Switzerland: up to 300 per ml). If these compounds are not removed during the treatment process, they will enhance the regermination in the network system rapidly and dramatically. Complaints from the health authority will be the consequence. This situation has to be avoided and is so by the introduction of an appropriate biological treatment step, e.g. GAC filter or slow sand filter. If such biological filters are present after the main-ozonation the same organic compounds will be biodegraded on the surface of the filtermedia (Figure 6).

An additional measure to avoid a bacterial regrowth problem in the distribution network is the dosing of an oxidising agent at the end of the treatment plant, e.g. chlorine, chlorine dioxide or chloramine. If such a biological filter is not installed, the dosing of the oxidising agent has to be increased to avoid any bacterial problems in the distribution system.

With a new GAC filter rapid adsorption is dominant and nearly all organic material can be adsorbed. According to the adsorption capacity of the filter and with increasing running time, the rapid adsorption will decrease in favour of a slow adsorption. At the same time a biological activity is started and will additionally reduce the organic matter (Figure 6).

If a pre and/or main ozonation is introduced before GAC filtration a further enhancement of the biological activity takes place. A further reduction of the DOC will be achieved while a part of the by-products will be adsorbed on the GAC and/or consumed by bacteria. Such a combination improves the final

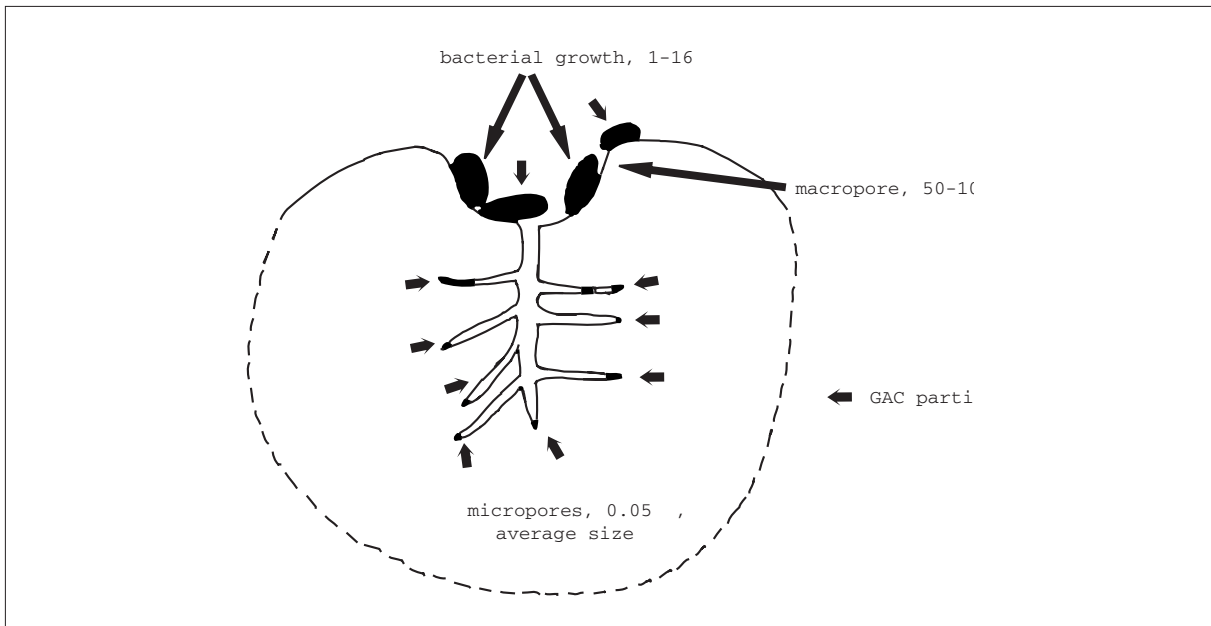


Figure 6: Schematic representation of a GAC particle showing pore size and bacterial growth

water quality [1].

Practical Experience in Water Treatment Plants

As a practical example the build-up of aldehyde has been measured at the Zurich's water supply treatment plant Lengg after the introduction of the two-stage ozonation (2).

Figure 7 shows the cumulative graphs of aldehydes after preozonation, after rapid filtration, after main-

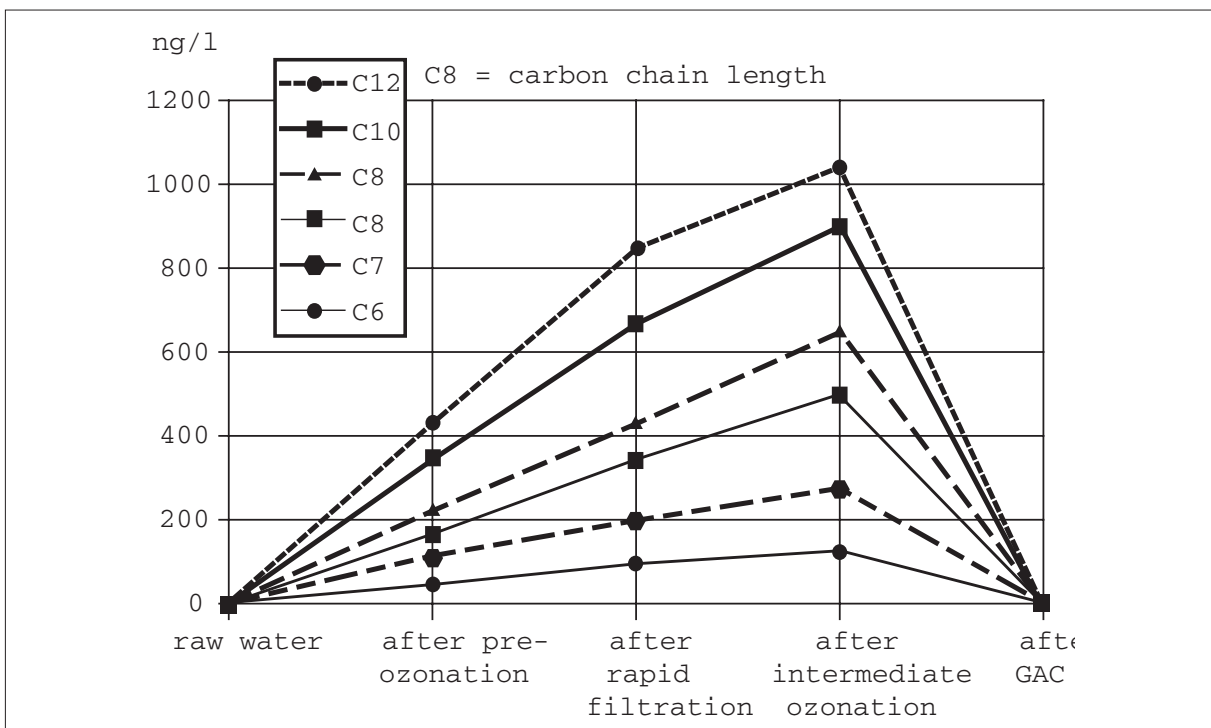


Figure 6: Schematic representation of a GAC particle showing pore size and bacterial growth

ozonation and after GAC filtration. Both ozonation steps contribute to the build-up of the aldehydes which show chain length between five and twelve C-Atoms. The formation of the aldehydes is dependent on the ozone dose. Higher doses will increase the formation more or less linearly. After the GAC filter no aldehydes can be detected even by the very sensitive analytic method of gas chromatography.

Experiences in the lake water plant Lengg at Zurich have shown the time dependence of the different effects. From these experiences it can be concluded that an operating equilibrium is reached after about 3–4 months (Figure 5). This result is valid for either new or reactivated GAC [2].

At this water treatment plant, the GAC has only been reactivated twice, the first time in 1980 and a second time in 1986. Since then no further reactivation took place with the justification that the GAC filtrate quality is stable due to biological activity.

Degrémont implemented the combination of Ozone-GAC technology in the seventies and this technology has since been introduced successfully in many water treatment plants. It is the most effective technique to eliminate organic matter. If most of the assimilable organic matter (AOC) is eliminated by the bacteria on the GAC, the addition of an oxidising agent (chlorine, chlorine dioxide or chloramine) to the final water will be minimised. The risk of new taste and odour problems will also be minimised. To keep the bacteriological quality in the distribution system within the regulations, a careful monitoring by the water company still remains necessary. From time to time a correction of the dosage will be appropriate.

Ozone dose = 2 mg/l	GAC	O3 + GAC	O3/H2O2 + GAC
elimination effect (%)	0	40	80
concentration of atrazine after treatment µg/l	1	0.6	0.2
volume of filtered water (m3) with an atrazine concentration below 0.1 µg/l per m3 GAC	18 000	35 000	105 000

Table 3: Influence of ozonation on the lifetime of a GAC filter at the WTW Mont Valérien [1]

A further example for this effect is given in Table 3 below:

The combination of ozone and GAC is an ideal and economic solution for the oxidation of organic compounds in the treatment of surface water to produce a safe potable water quality.

Conclusions

- Odour problems can arise in all types of raw waters.
- Many of these problems occur either from algae blooms or discharges from industries.
- Sometimes substances with weak odour characteristics may be transformed by chlorine to substances with strong odour (phenol ? chlorophenol, THM-precursors ? THM) by the treatment process (prechlorination).
- Newly formed THMs, or already existing THM-levels, will be partially removed by ozone/GAC filter significantly in a steady state phase.
- Ozone is an excellent chemical to eliminate odour problems. If THM precursors are present in the raw water ozone will reduce them significantly.
- The combination ozone/GAC is the most effective technique to eliminate organic matter.

- The mutagenicity of a raw water will be reduced by ozone as major oxidising agent and even improved by a downstream GAC filter.
- About one third of the DOC can be removed with the combination ozone plus GAC as a steady state result.
- Higher fraction of DOC can be successfully removed if the GAC is operated as adsorptive filter. This will definitely produce higher operating costs, either by reactivation or by complete exchange of GAC filter material.
- Especially where a GAC filter is operated as a biological active filter, a significant part of the AOC will be removed.
- The risk of bacterial regrowth in the network is therefore minimised.
- Furthermore, the lifetime of the GAC can be improved drastically and in some cases no reactivation is necessary, resulting in a substantial saving of operating cost.
- The combination ozone/GAC will minimize the addition of any oxidizing chemical to the final treated water. This will eliminate the problem of creating a new odor problem by such chemicals.

Keywords

Ozone; Activated Carbon; Taste; Odour

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